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Heavy Metal Contamination and Ecological Risk Assessment of Overlying Water and Sediments of Nkozoa Lake (Southern Cameroon)

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Authors' contributions

This work was carried out in collaboration among all authors. Authors NTSD and EBAZ designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors TKB and WKSA managed the analyses of the study. Authors EJ and BP managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Examination of heavy metals (Cr, Cu, Zn, Pb, Hg, Cd and Ni) in overlying water and sediments was conducted in Lake Nkozoa, in a peripheral area of Yaoundé characterized by a high population density and rapid economic development in Cameroon. Sediment samples were collected at the entrance and near the center of the lake, using a raft and polyvinyl chloride (PVC) pipes. They were subjected to water quality parameters, heavy metals comparisons and calculations of pollution indices and ecological risks followed by statistical analysis in order to identify and estimate the sources of metal contamination in overlying water and sediments of the Nkozoa Lake. The

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physico-chemical parameters of water show that the pH (5 < pH < 6), total dissolved solids (TDS~130 g/L) and conductivity (EC~194.8 µs/cm) are below the recommendations of the WHO. The average heavy metal concentrations in sediments, except Cd, are lower than the upper continental crust (UCC) and several environmental contamination monitoring parameters, such as threshold effect level (TEL), probable effect level (PEL), and severe effect level (SEL). The sediment samples show a low heavy metal contamination degree (class 0) and low potential ecological risk (PER) level, except for Cd and Hg which have high contamination degree (class 1 to 6) and moderate PER. Matrix correlation shows that some parameters like pH, EC, Cr and TDS, Cu, Hg in water have perfect positive correlations (r = 1.00) suggesting common sources of contamination. Cluster analyses coupled with matrix data for sediments revealed that Cd is the most contaminant elements derived from anthropogenic sources.

Keywords: Nkozoa lake; overlying water; sediments; heavy metals; contamination; ecological risk.

1. INTRODUCTION

Environmental pollution by heavy metals has been a hotly debated topic over the last two decades. The issue of heavy metal pollution in sediments and in the water of lakes and rivers has received much more attention from many environmental researchers. As a result of industrial development and the increasing use of its by-products, every day a large amount of industrial waste is dumped into low-lying areas and water bodies as lakes without adequate treatment. It is assumed that the balance between metals in sediments and freshwater is disturbed [1-4], and would contribute to increase water contamination which can produce health effects [2].

Generally, sediments provide useful information on the state of environmental and even geochemical pollution [5,6]. Depending on environmental conditions and hydrodynamic features, metallic trace elements, especially heavy metals, tend to adsorb from the water column onto the surfaces of fine particles and generally move with the sediment, and can affect benthic, pelagic and even planktonic organisms and, to some extent, the food chain if toxic levels are reached, thus posing a health risk [7-9].

According to Filgueiras et al. [10], less than 1% of pollutants are dissolved in water while more than 99% are stored in sediments throughout the hydrological cycle. Consequently, sediment represents one of the ultimate sinks for heavy metals released into the aquatic environment [11,12]. But, heavy metals, presented here as contaminants, are not necessarily bound to sediment, but may also be released into the water column through various remobilization processes. Thus, in water bodies, sediment can be both a vector and a potential source of pollutants [13,14]. Lake water is used as household and irrigation water for agriculture and fish farming. It is also important in maintaining soil fertility, transportation, development of forest resources and wildlife conservation [5]. However, most of the lakes in urban areas of developing and underdeveloped countries are at the end of their lifespan and also places of accumulation of pollutants due to industrial and domestic effluents that are discharged into them [15-18]. There is therefore a need for a water quality monitoring program for rivers and lakes in highly urbanized areas to protect human health and preserve water resources [19,20].

Through the aim of creating employment opportunities, eradicating poverty, and promoting rapid economic growth, the Government of Cameroon has decided to put in place a development policy that aims to improve the living conditions of its people by 2035. Due to a very cheap local labour force and somewhat relaxed environmental and tariff regulations, foreign and local investors are strongly attracted to create manufacturing units for exportable products including textiles, dyeing, plastics, metal fabrication, semiconductor products, foam tanning and so on. Every day, huge amounts of metals from industries are discharged without proper treatment into watersheds and lakes. A case in point is the Nkozoa artificial Lake located at the entrance of Yaoundé (capital of Cameroon). Effluents generated by industries, dwellings upstream of Lake Nkozoa are discharged into its watershed and then carried into the lake, causing great concern for the aquatic environment. In addition, local farmers frequently use water from the Nkozoa Lake and rivers, supplying this lake for irrigation and fishing. However, no detailed study has been carried out so far in this area, in particular on the ecological risk assessment of heavy metal contamination. Therefore, the purpose of this study is to investigate the physico-chemical properties (i.e., pH, TDS (total dissolved solids) and electrical conductivity (EC)) of water, as well as the contents of heavy metals (Cr, Cu, Zn, Pb, Hg, Cd and Ni) in sediment and water from the Nkozoa Lake, to generate the water quality and the metal distributions and concentrations in the studied lake on the one hand, and to assess the degree of contamination and potential ecological risk in the study area on the other hand. It is important to understand the status of heavy metal contamination in Lake Nkozoa in order to provide a baseline for waste control and management for local authorities and residents.

2. MATERIALS AND METHODS

2.1 Study Area

The area of investigation for this study is an artificial lake created three decades ago. Lake Nkozoa, as it is known, is located at the northern entrance of Yaoundé, the political capital of Cameroon (Fig. 1a). It is situated between latitudes 3°57'41" and 3°57'57" N and longitudes 11°32'09" and 11°32'32" (Fig. 1b). The area is rich in industrial establishments such as textiles, dyeing and clothing. Upstream of this lake, agriculture is strongly practiced. Effluent from these structures is discharged into the shallows that flow into the lake. During the dry season, agricultural, household and industrial effluents are deposited on the crests of watersheds and river banks, while during the rainy season, the land overflows and the toxic constituents of the effluents are washed away from nearby villages and other water bodies including the river that feeds Nkozoa Lake (Fig.1c).

The study area is characterized by a four-season equatorial climate (2 rainy and 2 dried seasons); with a cumulative annual precipitation of 1498 mm and an average annual temperature of 24°C. The vegetation is typical of the Guinean-Congolese type with Atlantic forest Biafran to Caesalpiniaceae. The South Cameroonian plateau is the geomorphological unit to which the study area belongs. It has an average altitude of 700 m where the upper altitudes are made up of high peaks reaching up to 1200 m and the lowlands drained by the watercourses of the Foulou sub-catchment area. These climatic and geomorphological conditions are at the origin of the formation of ferralitic soils on the interfluves and hydromorphic soils in the marshy lowlands.

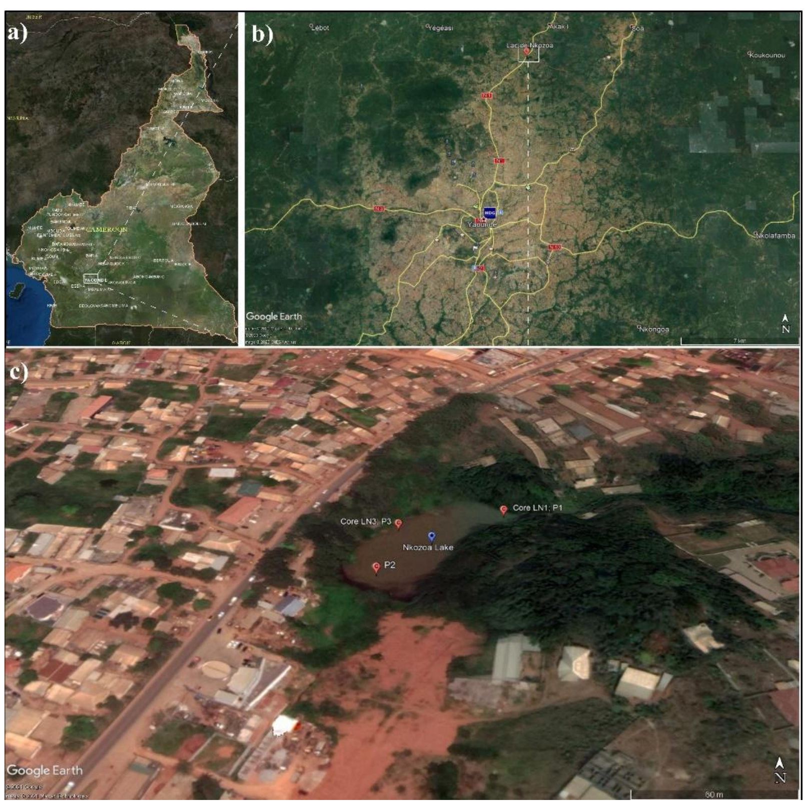


Fig. 1. Investigated area and sampling location: a) location of the study area in Cameroon; b) location of Nkozoa Lake in Yaoundé and c) sampling location of water and sediments

Geologically, the study area is located in the Yaoundé Group whose lithological nature is essentially composed of granulite, migmatite and schists. These rocks are organized into two main lithological entities more or less migmatized: (a) a meta-bearing unit consisting essentially of pyriclasites, pyroxenites and talcschists (b) a metasedimentary unit consisting essentially of garnet and kyanite gneiss, garnet and plagioclase gneiss and garnet micaschists in which are intercalated levels of calcium silicate rocks and in places quartzites and talcschists [21]. The study area is located in this metasedimentary unit.

2.2 Sampling

Two sediment cores (LN and LA) were collected using PVC pipes in a wood raft inside the Nkozoa Lake. The sampling procedure is similar to that described by many authors [e.g., 22,23]. For each of the two cores selected for this study, sampling was done every 10 cm. Thus, seven samples were taken from the core LN (LN1 to LN7) located near the entrance of the lake and six samples from the core LA (LA1 to LA6) taken near the center of the lake. The thirteen sediment samples taken from the cores were air dried and then dried again in an oven at 40°C for 24 hours at the Laboratory of Geosciences of Superficial Formations and Applications (GSFA) of the University of Yaoundé I (Cameroon) before being crushed in a Fritsch electric pulverizer. The resulting powders (θ < 80 μm) were submitted to heavy metal analysis at the Laboratories of the Botswana International University of Sciences and Technology (BIUST) in Botswana.

Water samples from Nkozoa Lake were collected at three predetermined locations (at the entrance, middle and outlet of the lake; Fig. 1b) during the short rainy season. Water samples were collected in pre-cleaned plastic bottles following filtering through Whatman filter paper No. 541 and stored in a 4°C refrigerator with the addition of 2 mg/l HNO3 prior to laboratory analysis [24].

2.3 Analytical Procedures

A quantity of 1 g of each dried sediment sample was taken from a clean Pyrex test tube and digested with 1 ml of $HClO_4$ diluted to 70%, 4 ml of HNO_3 concentration at 150°C in an oil bath. The solution was diluted with deionized water and quantitatively filtered (Whatman No. 541) into a 50 ml volumetric flask. A blank and a standard reference material were digested in the same way for quality control and accuracy verification. The determination of heavy metals (Cr, Cu, Zn, Pb, Hg, Cd and Ni) in all sediment samples was performed by an Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MPAES) at BIUST. All samples were collected and analysed in triplicate and the average results were used to represent the data. The statistical software, xlstat 20.0 and Microsoft Excel 2016, were used for hierarchical cluster analysis, and for a correlation matrix of heavy metals in water and sediment.

Measurements were made for physico-chemical parameters for water samples in the field, including pH, electrical conductivity (EC), and total dissolved solids (TDS), using the HI 9811-5 portable pH meter, which was calibrated before and during the campaign. Alkalinity was determined using a Hach field titration kit within 8 h after sample collection, in which a volume of 0.16 NH_2SO_4 was added dropwise to the sample while continuously stirring with a pH meter to reach the final titration (pH □ 4.5). The method for sampling water in this lake is described in detail by Mimba et al. [25]. All samples were collected in new 50-ml polyethylene bottles, previously washed, rinsed separately with distilled and collected water. Trace element (Cr, Cu, Zn, Pb, Hg, Cd and Ni) concentrations were determined in water samples by inductively coupled plasma mass spectrometry (ICP–MS) with certified reference materials (JA–3, JB–3, JG–3) and blanks were simultaneously analyzed to check for analytical precision and accuracy in Japan Geological Survey, Japan. The detection limit varies between 0.01 and 3 ppm.

2.4 Assessment of Contamination

2.4.1 Geo-accumulation index (Igeo)

An essential criterion for assessing the intensity of metal pollution is the geo-accumulation index [26]. This empirical index compares a given concentration against a value considered as geochemical background.

$$\mathrm{Igeo} = \mathrm{Log2}\ (\mathrm{Cn}/1.5\mathrm{Bn})$$

Where Igeo = geo-accumulation index; log2 = logarithm to base 2; n = element of interest; C = measured sample concentration; B = geochemical background; 1.5 = geochemical background exaggeration factor, which is designed to account for natural fluctuations in geochemical background. In addition, Muller [26] defined a scale of values with six classes depending on the intensity of the pollution. This scale stipulates that: Igeo < 0 (class 0), no contamination; 0-1 (1), no to slight contamination; 1-2 (2), moderate contamination; 2-3 (3), moderate to heavy contamination; 3-4 (4), heavy contamination; 4-5 (5), heavy to extreme contamination and Igeo > 5 (6) indicates extreme contamination.

2.4.2 Contamination Factor (CF) and Pollution Load Index (PLI)

The Contamination Factor (CF) was used to express the level of contamination by each metal in the sediment. It is expressed as:

$$\mathrm{CF} = \left(\frac{\mathrm{C_{metal}}}{\mathrm{C_{background}}}\right)$$

Where Cmetal is the concentration of the element in the sediment sample and Cbackground is the geochemical background value of the element by Taylor and McLennan [27]. Due to the absence of geochemical background for Yaoundé sediments continental crustal values of Taylor and McLennan [27] were considered as representative of the geochemical background. CF values were interpreted as suggested by Hakanson [28], where: CF < 1 indicates low contamination; 1 ≤ CF <3 is moderate contamination; 3 ≤ CF < 6 is significant contamination; and CF > 6 is very high contamination. The assessment of the degree of contamination was also carried out using the Pollution Load Index (PLI). The latter has been widely used to assess the level of contamination and pollution in lake sediments. A PLI value greater than 1 indicates progressive deterioration of sediment quality [29]. The equation used to calculate PLI was developed by Tomlinson et al. [29].

$$\mathrm{PLI} = \sqrt[n]{(\mathrm{CF1} \times \mathrm{CF2} \times \mathrm{CF3} \times \ldots \ldots \times \mathrm{CFn}}$$

Where CF is the contamination factor, and n the number of elements analyzed. The relationships between the elements analyzed were tested on the basis of the Pearson's coefficient with a statistical significance set at $p < 0.05$.

2.5 Ecological Risk Assessment

The ecological risk assessment was conducted for the potential ecological risk (PER) such as potential ecological risk index (RI) and potential ecological risk factor (Er). The potential ecological risk index (RI) for heavy metals is known as the sum of the risk factors and was developed for six toxic metals using the equations of Hakanson [28] and Zhu et al. [30].

$$\mathrm{RI} = \textstyle\sum_1^n \mathrm{Er} \text{ and } \mathrm{Er} = \mathrm{Tr} \times \mathrm{CF}$$

where Er is the unique index of the ecological risk factor, and n is the quantity of the heavy metal class, Tr = toxic response factor suggested by Hakanson [28] for seven metals: Cr (5), Cd (30), Cu (5), Pb (5), Ni (5), Zn (1) and Hg (40). The Er and RI express the potential ecological risk factor for each metal and for several metals, respectively. The following expressions were used for the potential ecological risk factor: Er < 40, low potential ecological risk; 40 ≤ Er < 80, moderate potential ecological risk; 80 ≤ Er < 160, significant potential ecological risk; 160 ≤ Er < 320, high potential ecological risk; and Er ≥320, very high ecological risk. In addition, the potential ecological risk index is: RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, significant ecological risk; and RI > 600, very high ecological risk [28].

3. RESULTS AND DISCUSSION

The results presented and discussed in this study take into account the physico-chemical parameters, variations and the degree of contamination by heavy metals (Cr, Cu, Zn, Pb, Hg, Cd and Ni) in water and sediment samples taken from Lake Nkozoa in Yaoundé, Cameroon.

3.1 Assessment of Contamination

The physico-chemical parameters including pH, EC and TDS of Lake Nkozoa are presented in Table 1. The values found reveal that the pH is acidic at all three sampling points in Lake Nkozoa (5 < pH < 6; Fig. 2). This would be due, on the one hand, to the alteration of silicic rocks such as quartzites and gneiss found in the Yaoundé zone and also to the weak hydrolysis leading to the formation of illite in this area [16], and on the other hand, the presence of garages, households and hairdressing salons around the lake and its sub-basin by the dumping of products such as vehicle batteries, wicks for hairdressing, toxic products and household waste. The pH (between 6.5 and 8.5) is below the recommendations of the World Health Organization (WHO). It is also lower than those found in Bini and Dang Lakes in northern Cameroon [31], and those in the municipal lake of Yaoundé at around 15 km of Lake Nkozoa [32;

Table 1]. The acid values of the water of this lake are lower than those of a healthy lake (pH~6.5), which could cause significant changes in the planktonic community such as the appearance of mosses and less useful planktonic species and the progressive loss of certain species like certain fish, fry, tadpoles are likely.

Conductivity measurement is a good assessment of the degree of contamination of water where each ion acts by its specific concentration and conductivity. The recorded values show small variations. They fluctuate between 190.4 µs/cm at P1 and 198.3 µs/cm at P3 (Fig. 2; Table 1) in the waters of Lake Nkozoa indicating leaching of the surrounding metamorphic rocks and runoff of domestic and semi-industrial residues.

The salinity of the water at our sampling points ranges from 124 g/L measured at the lake entrance to 145 g/L reported towards the centre of the lake. The TDS value is 124 g/L at the outlet of the lake (Fig. 2; Table 1). This situation of high salinity of the water is not exclusively related to the wastewater discharges from the locality of Nkozoa but also to the geological nature of the land crossed by the lake's watershed.

3.2 Heavy Metal Contents

3.2.1 Heavy metals in water

The heavy metal concentrations in the waters of Lake Nkozoa are shown in Table 1. It appears that the values (in mg/L) of heavy metals in these waters vary as follows: Cu (~ 5.463) > Ni (~ 1.470) > Hg (~ 0.492) > Cr (~ 0.346) > Cd (~ 0.047) > Pb (~ 0.018) > Zn (~ 0.006). On the one hand, concentrations of all metals, except Zn and Cr, are above the WHO recommended values (3 mg/L and 0.05 mg/L respectively) for drinking water [33]. On the other hand, low concentrations of Zn (0.006 mg/L) and Cr (0.346) were observed in all sampling points, exceeding the environmental quality standard in 100% of the points. On the whole, these values are slightly higher than those found in several lakes around the world, including Lake Tuskegee in the USA [34]; Lake Nokoue in Benin [35]; Lakes Bini and Dang in North Cameroon [31] and in the municipal lake of Yaoundé near Lake Nkozoa [32]. This difference between the data for Lake Nkozoa and the other lakes (Table 1) could be related to the proximity of small trades and mostly households near the lake. These results indicate that contamination in metals, except Zn, has become a major environmental problem in and around Lake Nkozoa. The main source of heavy metals in the waters of the lake under investigation is the discharge of waste streams from various industrial processes, such as metallurgical alloys, ceramics, metal plating, photography, pigment mills, and textile printing and hair treatment industries [5]. Agriculture and farming carried out in the watershed of Lake Nkozoa may also contribute to increasing the concentration of metals in the lake water. These features show that water of Lake Nkozoa are of poor quality for domestic use and aquatic life according to the above-mentioned standards.

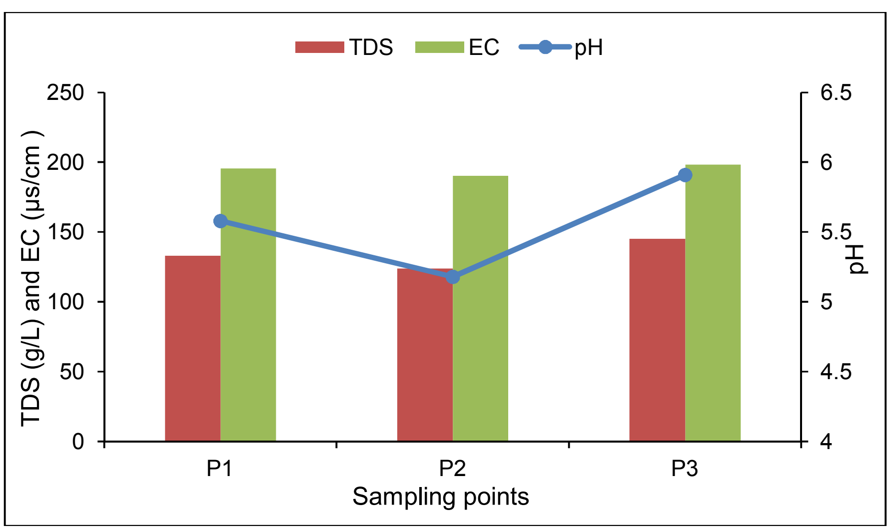


Fig. 2. Variations in the contents of physico-chemical parameters

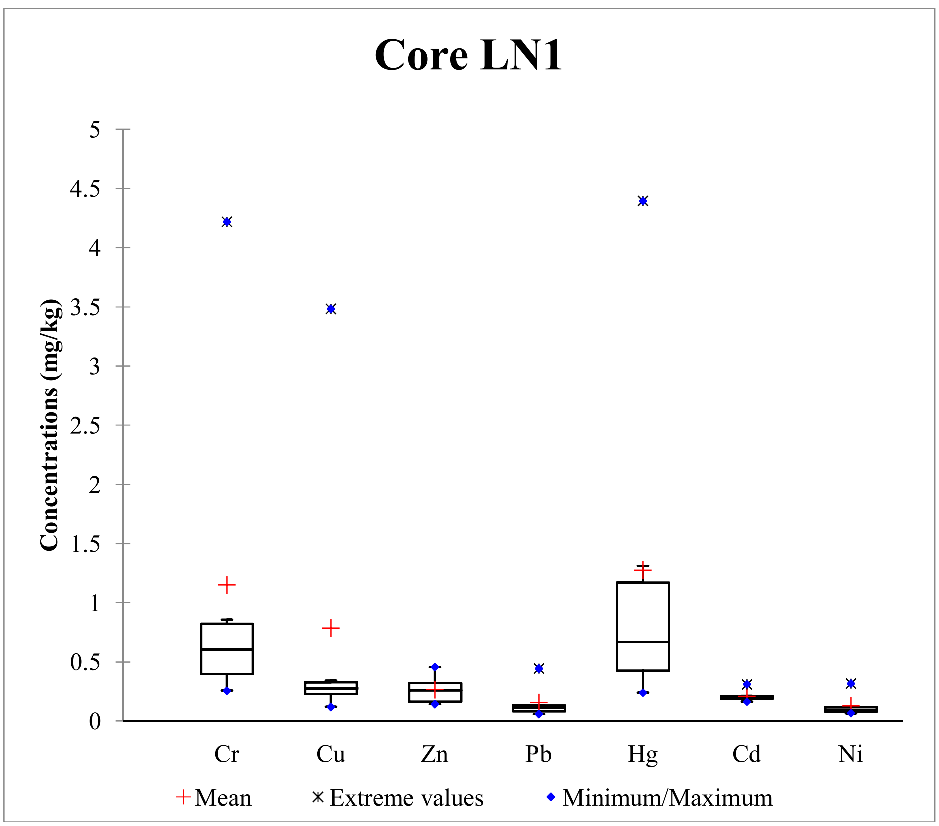
Table 1. Heavy metal concentrations, physicochemical parameters of Nkozoa Lake water samples (mg/L) and comparison with values taken from other lakes around the world

	pH	TDS	EC	Cr	Cu	Zn	Pb	Hg	Cd	Ni
P1	5.58	133	195.6	0.356	5.264	0.018	0.041	0.430	0.009	1.468
P2	5.18	124	190.4	0.313	4.954	0.004	0.029	0.303	0.029	1.683
P3	5.91	145	198.3	0.378	5.972	0.008	0.007	0.681	0.064	1.257
Mean Nkoazoa Lake (present study)	5.56	134.00	194.77	0.35	5.40	0.01	0.03	0.47	0.03	1.47
WHO [33]	-	-	-	2	0.05	3	0.01	0.006	0.003	0.07
Tuskegee Lake, USA [34]	7.24	-	185.2	0.0021	0.0012	0.0057	0.0007	-	0.00001	0.0066
Nokoue Lake, Benin [35]	-	-	-	-	0.2	-	0.08	-	<0.01	-
Municipal Lake, Cameroon [32]	7.22	-	304	-	0.008	0.012	0.016	-	0.007	0.006
Bini Lake, Cameroon [31]	7.74	-	-	0.00001	-	0.00001	0.00002	-	0.00003	0.00001
Dang Lake, Cameroon [31]	7.6	-	-	0.00002	-	0.00004	0.00002	-	0.00004	0.00002

Table 2. Heavy metal concentrations (mg/kg) in Nkozoa Lake sediment samples

	Cr	Cu	Zn	Pb	Hg	Cd	Ni
LN1-1	4.219	3.483	0.456	0.444	4.395	0.211	0.317
LN1-2	0.256	0.255	0.146	0.060	0.24	0.31	0.078
LN1-3	0.501	0.220	0.217	0.100	0.592	0.197	0.084
LN1-4	0.362	0.119	0.144	0.074	0.369	0.195	0.066
LN1-5	0.708	0.341	0.303	0.130	0.744	0.163	0.122
LN1-6	0.856	0.296	0.327	0.133	1.311	0.186	0.099
LN3-1	0.267	0.356	0.142	0.088	0.172	0.193	0.140
LN3-2	0.687	0.439	0.380	0.159	0.776	0.318	0.100
LN3-3	0.440	0.325	0.366	0.141	0.726	0.245	0.126
LN3-4	0.881	0.289	0.238	0.215	0.724	0.256	0.074
LN3-5	0.738	0.230	0.351	0.252	3.33	0.145	0.111
LN3-6	1.042	0.331	0.505	0.392	2.366	0.154	0.147
LN3-7	0.53	0.170	0.225	0.326	3.132	9.384	0.088
Min.	0.256	0.119	0.142	0.060	0.172	0.145	0.066
Max.	4.219	3.483	0.505	0.444	4.395	9.384	0.317
Avg.	0.884	0.527	0.292	0.193	1.452	0.920	0.119
Guidelines for metals contamination in sediment*							
TEL	37.3	35.7	123	35	0.174	0.596	18
PEL	70	197	315	91.3	0.486	3.53	36
SEL	110	110	820	250	2	10	75

** MacDonald et al. (2000)*



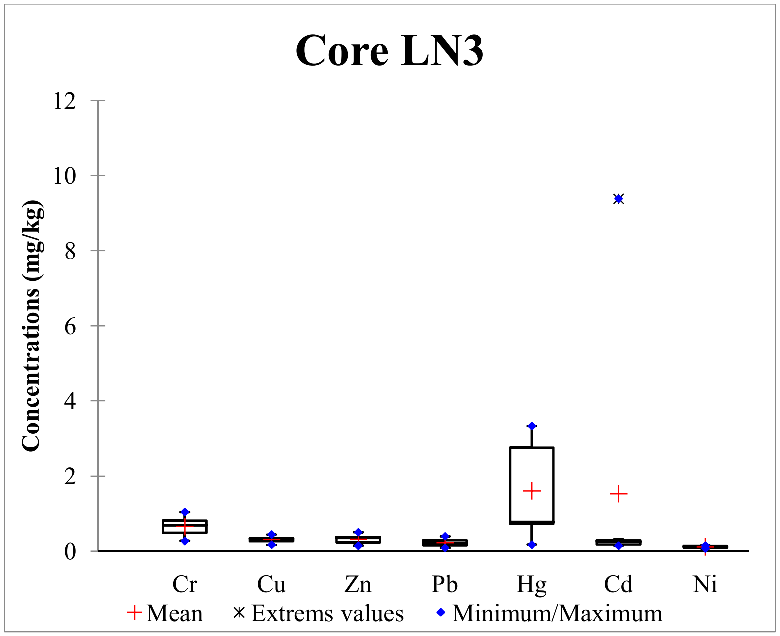


Fig. 3. Concentrations of heavy metals in sediments of the Nkozoa Lake (mg/kg)

3.2.2 Heavy metals in sediments

The average concentrations (mg/kg) of heavy metals vary in the following order: Hg (~ 1.275) >Cr (~ 1.150) > Cu (~ 0.786) > Zn (~ 0.266) >Cd (~ 0.210) > Pb (~ 0.157) > Ni (~ 0.128) in the core LN1 located near the entrance of the lake and Hg (~ 1.604) > Cd (~ 1.528) > Cr (~ 0.655) > Zn (~ 0.315) > Cu (~ 0.306) > Pb (~ 0.225) > Ni (~ 0.112) in the core LN3 from the centre of the lake (Fig. 3). Mean Hg concentrations are the highest heavy metal contents in lake sediments of the two cores (Table 2). Average Cr and Cu concentrations are higher in the sediments of the core near the lake entrance (LN1). Average Cd concentrations are higher in the sediments of the LN3 core located in the centre of the lake. There was no apparent spatial variability in the mean Pb and Ni concentrations, which appear very low in all the samples. Heavy metal concentrations are below the upper continental crust (UCC) and several environmental contamination monitoring parameters, such as threshold effect level (TEL), probable effect level (PEL), and severe effect lever (SEL). The increase in metal content in these sediments implies that a substantial increase in anthropogenic metal loading has occurred in this lake, as suggested by Sondi et al. [36]. This comparison shows that sediments of Lake Nkozoa impact in water quality and aquatic life according to the TEL, PEL and SEL standards.

3.3 Assessment of Sediments Contamination

The geo-accumulation index of heavy metals in sediments of Nkozoa Lake showed that the sediments were not polluted (Table 3; Fig. 4), they fall into class 0. Among the heavy metals, only cadmium shows slight contamination. Thus, 7.7% Cd show unpolluted sediment from class 0; the majority of the Cd pollution in the sediments of Nkozoa Lake; 69.2% is from class 1, comprised between 0 and 1, and representing no to slight contamination; 15.4% of this element represent moderate contamination (class 2), their range values are between 1 and 2; only one sample representing 7.7% has Igeo > 5 (class 6) and indicates extreme contamination of sediments. This high Cd enrichment could be explained by anthropogenic activities such as agriculture through the use of chemical inputs, cars and motorcycles washing, effluents from households and finally atmospheric deposits from fuel combustion related to road traffic.

The contamination factor (CF) and pollution load index (PLI) are applied to assess the conservation status of an environment and monitor its condition [37,38]. Table 3 and Fig. 5 show the variation of CF and PLI of sediments in Lake Nkozoa. In general, all elements have low contamination degree in both cores and at all levels except for Cd which has considerable levels of contamination. The highest value of CF was estimated at 7.7% of the general Cd contamination rate and it is located at the top of the core from the centre of the lake. The Cd would therefore have a very high contamination degree (CF > 6) in this part of the core. The previous percentage in these sediments has a significant degree of contamination (3 < CF < 6) for this element. In 76.9% of the sediments of Nkozoa Lake, the Cd ranges between 1 and 3, with a moderate contamination degree. Consequently, the high degree of contamination in Cd showed that multiple sources contributed significantly to the contaminant loadings in Lake Nkozoa. These sources included semi-industrial inputs, such as palm oil manufacturers, food manufacturers that are located along the stream that feeds the lake, household discharges, agriculture, and livestock. The contamination factor (CF) also indicates that the entire concentration of metals is influenced by anthropogenic inputs, especially highly toxic elements such as Cd, and sometimes Hg which is enriched at high levels in the sediments.

The PLI values in this study are very low overall. They are below unity except for the top of the core taken around the centre of the lake. These sediments would therefore be considered unpolluted (Table 3). Only a single sample representing less than 8% of the total collected could be considered polluted. The sediments were slightly contaminated with these metals due to the influence of discrete external sources such as agricultural runoff and other anthropogenic inputs mentioned above.

3.4 Assessment of Ecological Risk

Potential ecological risk (PER) represents the sensitivity of the biological community to a given substance and illustrates the risk caused by contamination [39]. The calculated PER indices for an individual element (Er) are shown and the complete PERs (RI) are shown in Table 3 and Figure 6. In Nkozoa Lake, almost all elements had low PERs, except Cd and Hg. Therefore, the Er values of the most part < 40 with the exception of one sampling point in Cd which presents a high potential ecological risk factor (Er = 281.52) and some points in Hg which present at 7.7%, a moderate potential ecological risk factor and at 30.8%, a significant potential ecological risk factor (80 < Er < 160), the rest presenting a low potential ecological risk factor. As shown in Table 5, some sediment samples from the studied lake have a high PER. This may be due to the development of the semi-industrial sector and urbanization in the peri-urban area of Nkozoa, and the RI distribution graphs could be useful in identifying the area mostly in need of attention.

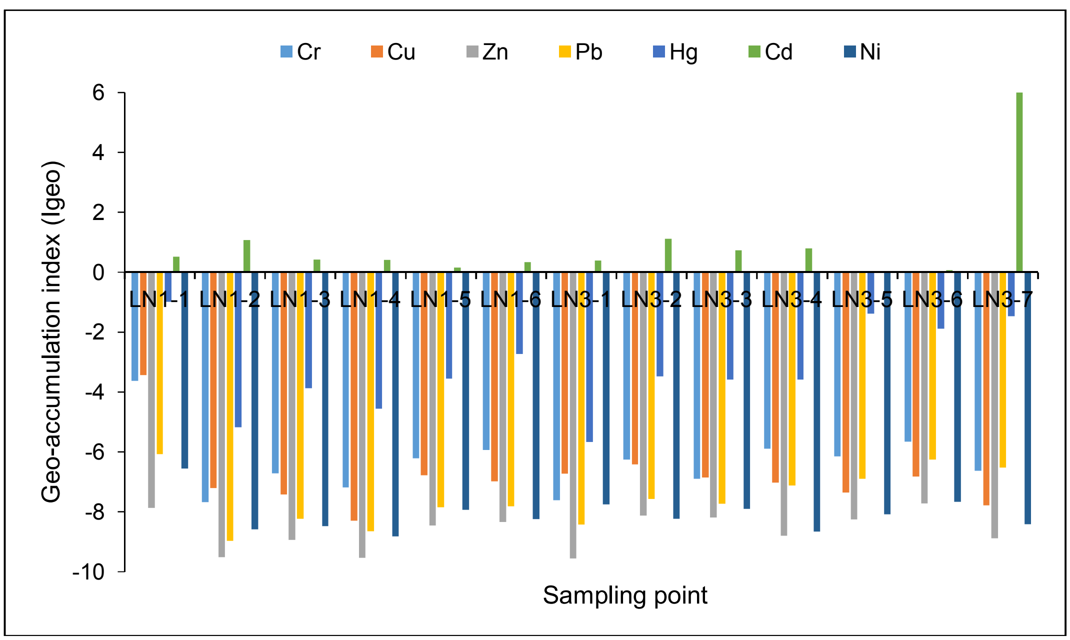


Fig. 4. Geo-accumulation index of selected metals in sediments from Nkozoa Lake

Table 3. Calculations of geo-accumulation index (I-geo); contamination factor (CF); pollution load index (PLI); potential ecological risk factor (Er) and potential ecological risk index (RI) of metals in Nkozoa Lake sediments

			I-geo					
Metals	**Cr**	**Cu**	**Zn**	**Pb**	**Hg**	**Cd**	**Ni**	
LN1-1	-3.637	-3.428	-7.868	-6.079	-0.985	0.524	-6.565	
LN1-2	-7.678	-7.200	-9.514	-8.974	-5.180	1.076	-8.586	
LN1-3	-6.712	-7.413	-8.936	-8.232	-3.876	0.425	-8.478	
LN1-4	-7.181	-8.301	-9.535	-8.654	-4.559	0.408	-8.827	
LN1-5	-6.212	-6.782	-8.458	-7.848	-3.548	0.153	-7.938	
LN1-6	-5.939	-6.986	-8.346	-7.822	-2.730	0.336	-8.237	
LN3-1	-7.618	-6.719	-9.554	-8.420	-5.661	0.391	-7.749	
LN3-2	-6.255	-6.416	-8.133	-7.564	-3.486	1.115	-8.226	
LN3-3	-6.898	-6.850	-8.186	-7.729	-3.583	0.736	-7.894	
LN3-4	-5.897	-7.019	-8.803	-7.125	-3.587	0.798	-8.666	
LN3-5	-6.152	-7.352	-8.246	-6.895	-1.385	-0.025	-8.085	
LN3-6	-5.655	-6.822	-7.721	-6.257	-1.879	0.065	-7.670	
LN3-7	-6.630	-7.789	-8.884	-6.523	-1.474	5.996	-8.412	
				CF&PLI				
Metals	**Cr**	**Cu**	**Zn**	**Pb**	**Hg**	**Cd**	**Ni**	**PLI**
LN1-1	0.121	0.139	0.006	0.022	0.758	2.157	0.016	0.460
LN1-2	0.007	0.010	0.002	0.003	0.041	3.163	0.004	0.462
LN1-3	0.014	0.009	0.003	0.005	0.102	2.013	0.004	0.307
LN1-4	0.010	0.005	0.002	0.004	0.064	1.991	0.003	0.297
LN1-5	0.020	0.014	0.004	0.007	0.128	1.667	0.006	0.264
LN1-6	0.024	0.012	0.005	0.007	0.226	1.894	0.005	0.310
LN3-1	0.008	0.014	0.002	0.004	0.030	1.966	0.007	0.290
LN3-2	0.020	0.018	0.005	0.008	0.134	3.249	0.005	0.491
LN3-3	0.013	0.013	0.005	0.007	0.125	2.499	0.006	0.381
LN3-4	0.025	0.012	0.003	0.011	0.125	2.608	0.004	0.398
LN3-5	0.021	0.009	0.005	0.013	0.574	1.474	0.006	0.300
LN3-6	0.030	0.013	0.007	0.020	0.408	1.569	0.007	0.293
LN3-7	0.015	0.007	0.003	0.016	0.540	95.755	0.004	13.763
				Er&RI				
Metals	**Cr**	**Cu**	**Zn**	**Pb**	**Hg**	**Cd**	**Ni**	**RI**
LN1-1	21.095	17.415	0.456	2.219	175.800	6.342	1.585	224.912
LN1-2	1.282	1.276	0.146	0.298	9.600	9.300	0.390	22.291
LN1-3	2.504	1.101	0.217	0.499	23.696	5.919	0.421	34.357
LN1-4	1.809	0.595	0.144	0.372	14.768	5.853	0.330	23.870
LN1-5	3.542	1.704	0.303	0.651	29.756	4.902	0.612	41.469
LN1-6	4.279	1.479	0.327	0.663	52.440	5.568	0.497	65.254
LN3-1	1.337	1.780	0.142	0.438	6.880	5.781	0.698	17.055
LN3-2	3.436	2.196	0.380	0.793	31.052	9.552	0.501	47.909
LN3-3	2.201	1.625	0.366	0.707	29.032	7.347	0.631	41.908
LN3-4	4.406	1.446	0.238	1.075	28.964	7.668	0.369	44.165
LN3-5	3.692	1.148	0.351	1.261	133.200	4.335	0.553	144.538
LN3-6	5.210	1.657	0.505	1.961	94.632	4.614	0.737	109.315
LN3-7	2.650	0.848	0.225	1.631	125.280	281.520	0.441	412.595

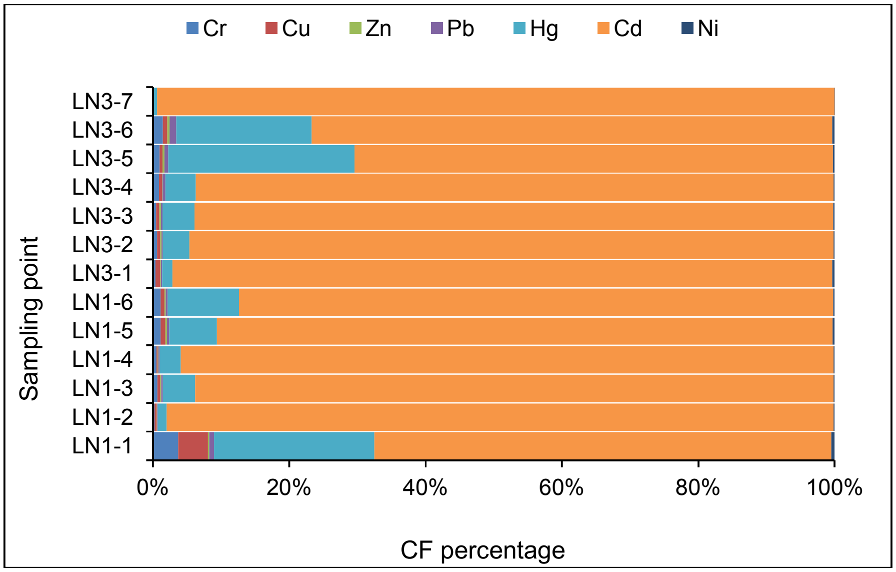


Fig. 5. Contamination factor (CF) and pollution load index (PLI) of heavy metals in the Nkozoa Lake sediments

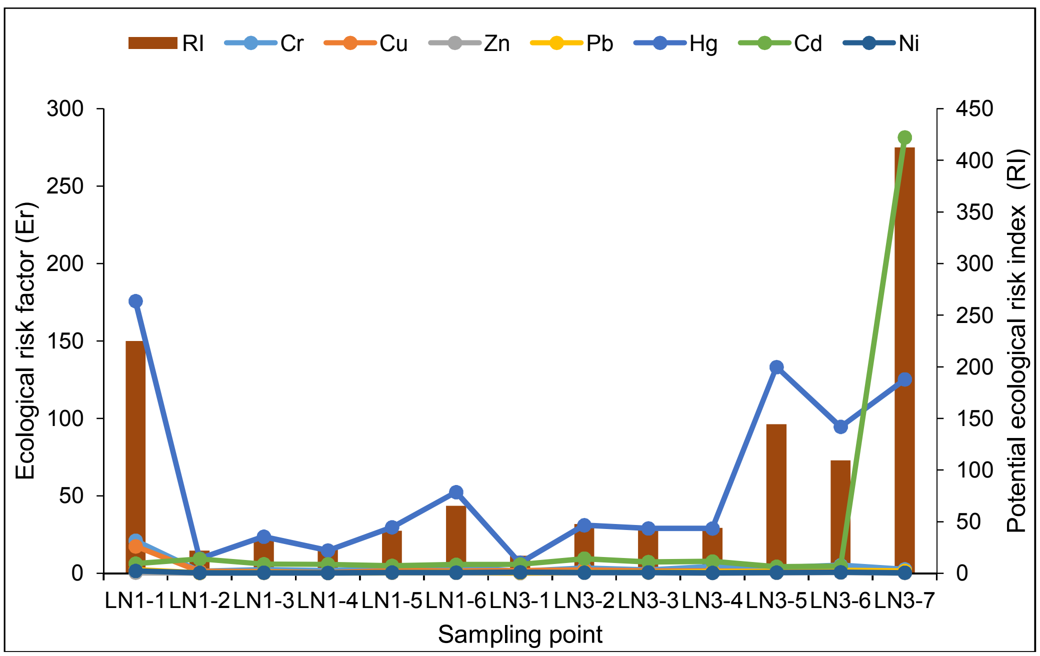


Fig. 6. Ecological risk factor (Er) and ecological risk index (RI) of heavy metals in sediments from the Nkozoa Lake

According to the classification, the risk associated with Cd and Hg in the sediments of Nkozoa Lake (RI < 300) shows a low to moderate potential ecological risk index, which corroborates the results of the Igeo, CF, PLI and Er indices. Contaminants in sediments can enter the food chain, particularly if the contaminants are in bioavailable forms. Cadmium and Hg can accumulate in relatively large amounts in plants with no apparent effects, which could cause human health problems [22,40]. It is therefore important to continue to carefully monitor heavy metal contaminants, particularly Cd, in lake sediments in Nkozoa.

3.5 Statistical Analysis

Variable relationships can provide information on the sources of heavy metals and chemical parameters [41]; therefore, Pearson's correlation coefficients for heavy metals and chemical parameters were analyzed (Table 4). The Pearson's correlation coefficient analysis amongst the chemical parameters of water and heavy metals for water and sediment samples was performed and presented in Tables 1 and 2. In water samples (Table 4), pH showed a perfect positive correlation with EC, Cr and each other (r = 1.00). Similarly, TDS, Cu showed a perfect positive correlation with Hg (r ~ 1.00), suggesting a common source of Cu and Hg. TDS and pH showed significant positive correlations with all metals except Pb and Ni. Likewise, a close relationship was also observed in water samples between Hg and all metals except Pb and Ni, whereas a perfect negative correlation (r = -1) was observed between Pb and Cd and between TDS and Ni. A significant to strong negative correlation (r = -0.69 to -0.98) was also found between Ni and other parameters and some metals (e.g., Cr, Cu, Hg and Cd). Correlation coefficients (r) between the physicochemical properties and different heavy metal concentrations in water samples (Table 4) suggested that the concentrations of metals are not linked to Ni and Pb contamination, but can be very close to Cr, Cu and Hg productions.

In sediment samples (Table 5), significant to strong positive correlations ($p > 0.05$) between all elements with each other except Cd (r = 0.46 to 0.97) were observed. The matrix data for the studied sediments revealed that Cd was lowly positively and negatively correlated with other parameters (ranging from r = -0.11 to 0.36), suggesting a different source of these metals and that Cd contamination in sediments is not directly linked to other metals.

Table 4. Pearson correlation matrix of heavy metals and water quality parameters of water samples

Variables	pH	TDS	EC	Cr	Cu	Zn	Pb	Hg	Cd	Ni
pH	1									
TDS	0.96	1								
EC	1.00	0.97	1							
Cr	1.00	0.96	1.00	1						
Cu	0.91	0.99	0.92	0.92	1					
Zn	0.47	0.20	0.45	0.45	0.06	1				
Pb	-0.47	-0.70	-0.49	-0.49	-0.80	0.56	1			
Hg	0.92	0.99	0.93	0.93	1.00	0.09	-0.77	1		
Cd	0.46	0.69	0.48	0.47	0.79	-0.57	-1.00	0.76	1	
Ni	-0.98	-1.00	-0.98	-0.98	-0.97	-0.28	0.64	-0.98	-0.63	1

Values in bold are different from 0 at significance level alpha=0.05

Table 5. Pearson correlation matrix of heavy metals of sediment samples

Variables	Cr	Cu	Zn	Pb	Hg	Cd	Ni
Cr	1						
Cu	0.97	1					
Zn	0.57	0.46	1				
Pb	0.71	0.60	0.71	1			
Hg	0.71	0.62	0.60	0.90	1		
Cd	-0.11	-0.12	-0.17	0.31	0.36	1	
Ni	0.92	0.94	0.59	0.66	0.65	-0.15	1

Values in bold are different from 0 at significance level alpha=0.05

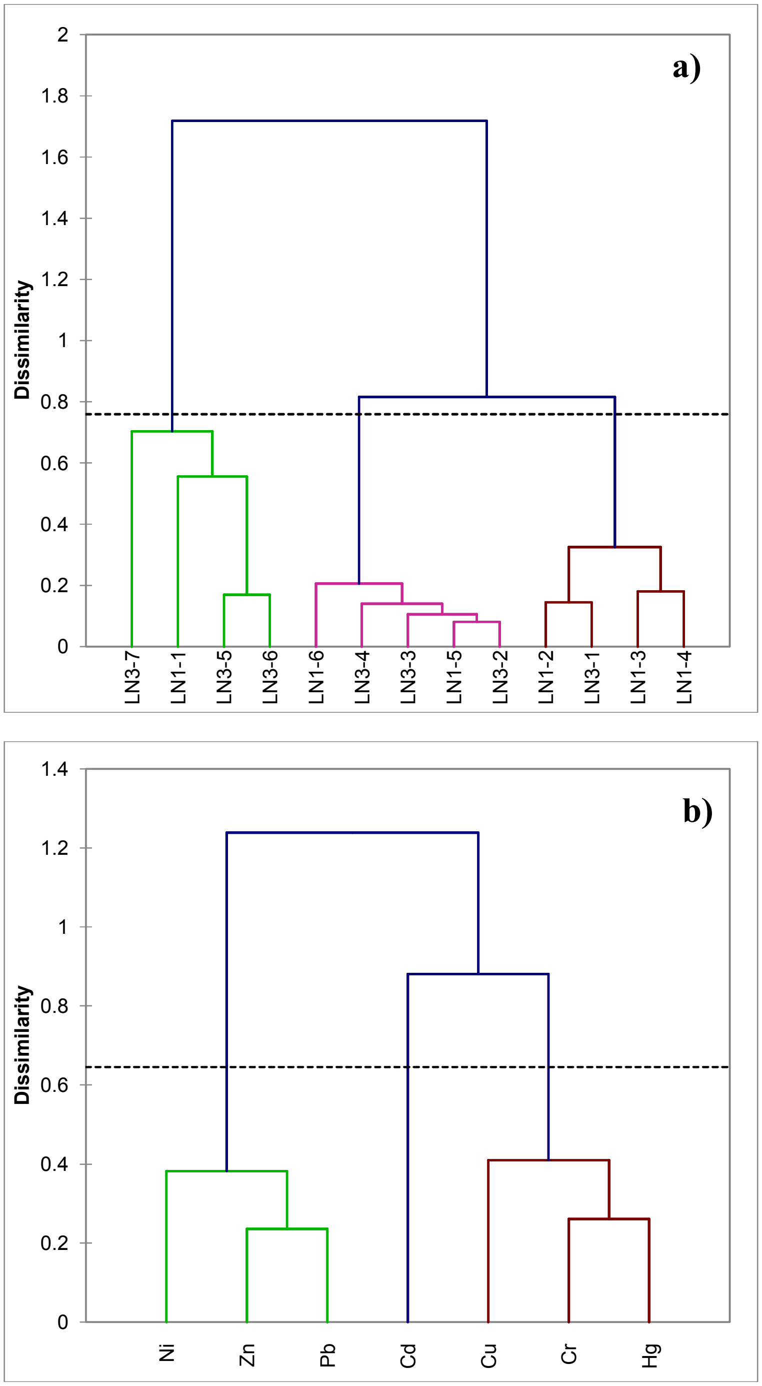


Fig. 7. Dendrogram clustering: a) sediment sampling locations and b) analyzed parameters in sediment samples from the Nkozoa Lake

A cluster analysis was performed on heavy metals of sediment from Nkozoa Lake using between-groups linkage method with Pearson correlation [42]. Cluster analysis was used to group the similar sampling sites (spatial variability) and to identify source of heavy metal contamination [43,44]. Hierarchical agglomerative was performed on the normalized data set using Ward's method with Euclidean distances as a measure of similarity. In order to identify relationships between the analyzed parameters and their possible sources, cluster analyses resulted in two dendrograms (Fig. 7) where the thirteen samples from two cores from Lake Nkozoa were grouped into two statistically significant clusters. In the first dendogram (Fig. 7a) focussed on spacial similarity, two statistically significant clusters at (Dlink/Dmax) > 0.76 are grouped. Cluster 1 consists of four samples (LN1-1, LN3-7, LN3-6 and LN3-5) principally samples from the top of the center of the cores, cluster 2 is made up of the samples from the middle of the cores (LN1-6, LN1-5, LN3-2, LN3-3 and LN3-4) and cluster 3 consists of four basal samples especially from the core located at the entrance of the lake (LN1-4, LN1-2, LN3-3 and LN3-1). The cluster classifications vary with significance level because the samples in these clusters had similar characteristic features and anthropogenic/natural background source types. Cluster 1 corresponds to the highest contaminated samples and cluster 3 corresponds to the lowest contaminated samples. Similarly, cluster analysis was performed to identify the relationships among the analyzed parameters and their possible sources [45,46]. Cluster analysis rendered a dendrogram (Fig. 7b) where all seven parameters were grouped into three statistically significant clusters at (Dlink/Dmax) > 0.65. Cluster 1 includes Ni, Pb and Zn, which in the previous section were identified as non-pollutants, cluster 2 contains Cd, the most contaminant elements from the studied metals. This element was lowly positively and negatively correlated with other parameters (Table 5). Cadmium mainly derives from anthropogenic sources (agriculture, washing of cars and motorcycles, effluents from households and road traffic). Cluster 3, which contains Cu, Cr and Hg, is derived from lithogenic sources, also confirmed by their strong positive correlations (Table 5) and their small variabilities along the cores (Table 2).

4. CONCLUSION

The purpose of this study was to assess levels of physico-chemical parameters of water (TDS, EC and pH) and seven metals (Cr, Cu, Zn, Pb, Hg, Cd and Ni) in both surface water and sediment samples from the Nkozoa Lake. The following conclusions can be drawn:

1- The results obtained from physico-chemical parameters of water show that the pH, EC and TDS measured during the study period are below the recommendations of the WHO. The acid values of the water of this lake are lower than those of a healthy lake.

2- Mean concentrations of the seven heavy metals in water samples are lower than the WHO (2017) recommended guideline for drinking water except Zn. The main source of heavy metals in the water appears to be the discharge of waste streams from various semi-industrial processes, agriculture and farming carried out in the watershed of Lake Nkozoa.

3- The average heavy metal concentrations in sediments are lower than the TEL, PEL, SEL and UCC with exception of Cd. The sediment samples show a low degree of contamination by heavy metals and low PER level, except for Cd and Hg sometimes which has high contamination degree and moderate PER. These contaminants can accumulate in relatively large amounts in plants with no apparent effects, which could cause human health problems.

4- Matrix correlation showed that some parameters like pH, EC and Cr on the one hand and, TDS, Cu and Hg in water on the second hand, have common sources. The statistical analysis also shows that the concentrations of metals were not linked to Ni and Pb contamination, but can be very close to Cr, Cu and Hg productions. The matrix data for studied sediments revealed that Cd contamination could not be directly linked to other metals.

5- The cluster classifications for sediment samples varied with significance level and are group into similar characteristic features and anthropogenic/natural background source types from contaminated to uncontaminated samples. It also shows that Cd is the most contaminant element from the studied metals and derived from anthropogenic sources. However, Cu, Cr and Hg are derived from lithogenic sources while the other elements appear as natural.

6- Due legal measures such as the control of wastes should be taken to reduce the anthropogenic discharges in the Nkozoa Lake; the constant collection of household waste and other activities by the existing sanitation company or the creation of a new structure to deal with it; otherwise, future high levels of contamination will greatly influence the population and will invite socio-economic disaster. Moreover, a regular monitoring program of the heavy metals is recommended to protect this lake and also reduce environmental risks.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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