Scientific Research Publishing

Journal of Materials Science and Chemical Engineering, 2023, 11, 13-28
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Distribution of 26 Metals in the Waters of the Aquatic Ecosystems of the Cotonou Channel and Lake Nokoué, Benin

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How to cite this paper: Karim, A.Y.A., Gbaguidi, A.N.M., Saizonou, K.M.V.M., Dovonon, L.F., Laly, G., Moussa, A.K.A., Azokpota, E., Seby, F., Donard, O. and Soclo, H.H. (2023) Distribution of 26 Metals in the Waters of the Aquatic Ecosystems of the Cotonou Channel and Lake Nokoué, Benin. *Journal of Materials Science and Chemical Engineering*, **11**, 13-28.
https://doi.org/10.4236/msce.2023.112002

Received: January 24, 2023
Accepted: February 25, 2023
Published: February 28, 2023

Abstract

Metallic elements have various origins: natural and anthropogenic sources as geochemical, marine and atmospheric sources resulting from the fallout of pollutants emitted or dust raised and which are transported by water and air currents. Thus marine, brackish and fresh continental waters may have high metal concentrations. In addition, some essential metals can become toxic above certain concentration values in aquatic environments. The aquatic ecosystems of Cotonou channel and lake Nokoué receive the pollutants charges from the town cities of Cotonou, Abomey-Calavi and town hall of So Ava. The aim of this study is to analyze waters from Eighteen (18) stations identified in the two ecosystems (nine by ecosystem). The concentrations of magnesium (Mg), calcium (Ca), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), beryllium (Be), aluminum (Al), strontium (Sr), molybdenum (Mo), silver (Ag), tin (Sn), barium (Ba), platinum (Pt), mercury (Hg), thallium (Tl), lead (Pb), thorium (Th) and uranium (U) were measured after acid digestion of the water samples using the inductively coupled plasma source mass spectrometer (ICP-MS). The results of the analyses indicate an unequal distribution of metals in the different ecosystems. However, atypical concentrations were observed at some stations of the lake and the channel.

Magnesium, calcium and manganese have very high values in Lake Nokoué respectively at Ganvié market station GAN_M (2990 ± 105 mg/L), Ganvié center, station GAN_C (4991 ± 177 mg/L) and Lake middle station MLak4 (10662 ± 17.03 µg/L). On the other hand, iron, aluminum and strontium have very high concentrations in the Cotonou Channel respectively at Agbato station AGB (5236 ± 103 and 8289 ± 519 µg/L) and at the estuary station EST (6118 ± 68 µg/L). The concentrations were compared to wells and cborehole waters in sixth neighborhood of Cotonou. We have used statistical analyzers such as MANOVA which have made it possible to classify the waters and metals in the ecosystems studied compared to groundwater and Well water waters. We use hierarchical clustering on principal components to identify similarities between stations based on metal concentration with R software packages "FactoMineR" and "factoextra". In general, we can conclude that most of the metals have an anthropogenic source except strontium and major elements (Ca and Mg) which could respectively provide from marine waters and geochemical sources.

Keywords

Metals, Water, MANOVA, R Software Packages, Nokoué Lake, Cotonou Channel

1. Introduction

Metals are elements characterized by common properties such as the property of malleability, they are good conductor of heat and electricity, hard, ductile, high tensile strength. The use of metals by human is very important. But in ecosystems, some metals have essential functions for the survival of living aquatic organisms. Some ones else are grouped among trace elements which are essential and have well-determined physiological functions in reasonable concentrations, while others are toxic and have no use for living aquatic organisms. Metals are elements of the earth's crust that can be transported in aquatic ecosystems where they are distributed between the water column, sediments and living matter. But human activities are the most important sources of these elements in surface waters. Some of the metals are essential for living organisms and humans, while others have no specific physiological function: This is the case for toxic metals such as lead (Pb), mercury (Hg), cadmium (Cd), Aluminum (Al), etc. [1]. These have effects on the central and peripheral nervous system. Despite the fact that some metals are essential at low concentration for living organisms, such as: 1) trace elements (Cu, Zn, Fe, Mn, Co, Mo, Cr and Se) and 2) major elements (Ca, Mg, Na); at higher concentrations, they could induce toxic effects disrupting the growth, metabolism or reproduction of organisms with consequences for the entire food chain, including in humans [2]. Other metals have isotopes that can be radioactive sources and emit ionizing radiation that can harm human health. We can cite ^{212}Pb, ^{232}Th, ^{137}Cs, ^{40}K, ^{228}Am and ^{241}Am [3]. Thus knowledge of the distribution of the 26 metals in surface waters is of definite interest not only for preventing ecotoxicological effects but also for considering measures to limit the increase of these contaminants in the various systems [1]. The aim of this study is to analyze waters from eighteen (18) stations identified in the two ecosystems (nine by ecosystem).

2. Material and Methods

2.1. Characteristics of the Study Area

Lake Nokoué and the Chenal de Cotonou are located in the southern part of Benin under the influence of the cities of Cotonou, Abomey-Calavi, Porto-Novo, lakeside villages and continental contributions from the northern part of the country [4]. It is indeed the main receptacle for lacustrine discharges of effluents contaminated by metal residues from anthropogenic activities [5] [6]. Following a rapid increase in cottage industry and urbanization in recent years, this area is characterized by a galloping population. **Figure 1** represents the study area composed of Lake Nokoué, the Channal of Cotonou and the city of Cotonou, in particular the 6th district. **Table 1** and **Table 2** present the sampling points identified on the lake and the channel.

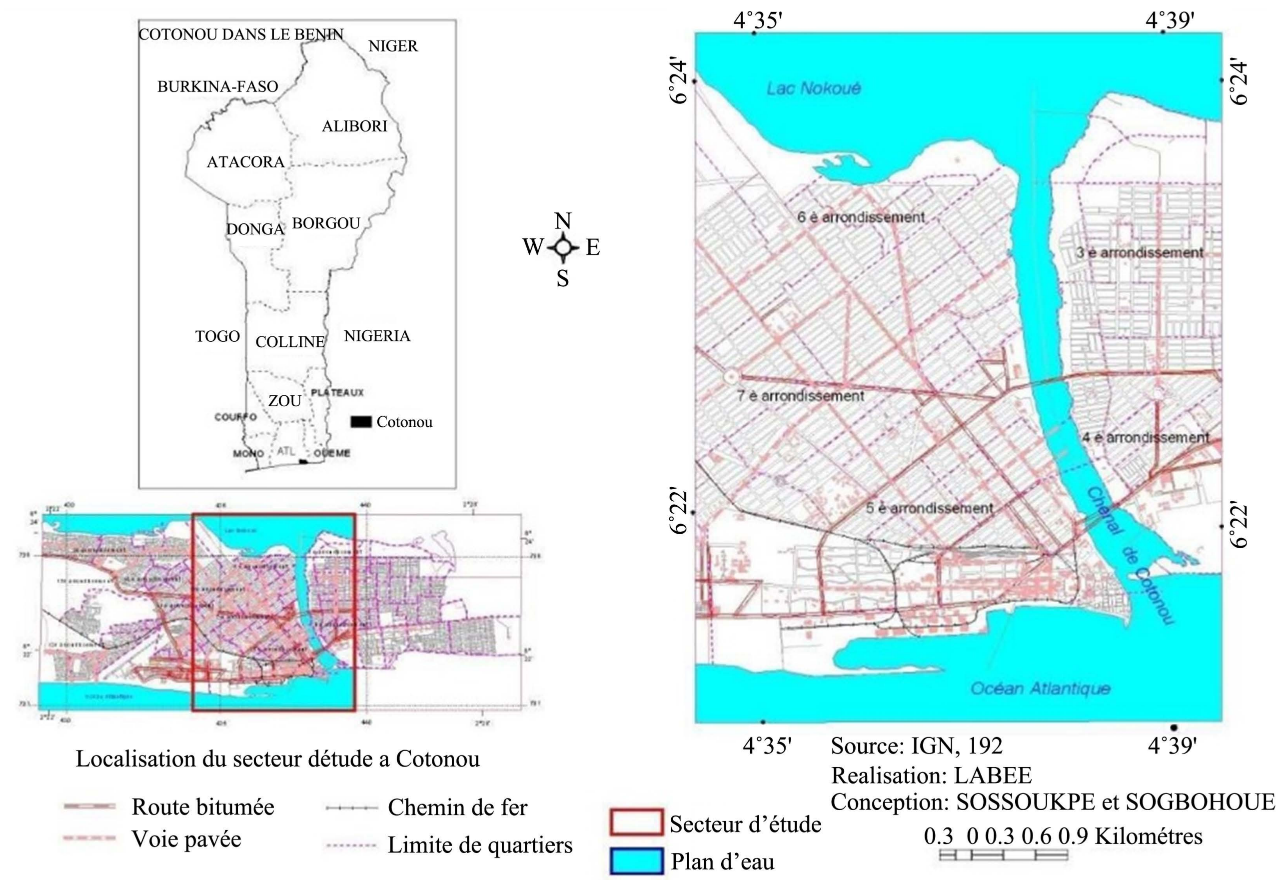

Figure 1. Study area.

Table 1. Description of the positioning of points and activities of the Cotonou channel.

No.	Symbol	Site name	Location & Description	X (UTM)	Y (UTM)
1	AGB	Agbato	West Shore	437,680	706,737
2	DJI	Djidje	West Shore	437,510	705,292
3	HIN	hinde	West Shore	-	-
4	DAN3	Dantokpa West	East shore	437,579	704,821
5	DAN2	Dantokpa Median	Median	437,731	704,869
6	DAN1	East Dantokpa	West	437,822	704,952
7	GBO1	Gbogbanou West	East shore	437,779	703,708
8	GBO2	East Gbogbanou	West Shore	-	-
9	EST	Estuary	West Shore	438,249	702,609

NB. The missing coordinates are very close to the others, but these stations were sampled because of the observations we had made.

Table 2. Description of the positioning of the points and activities of lake Nokoué.

No.	Symbol	Site name	Location & Description	X (UTM)	Y (UTM)
1	CAL	Calavi	North	429,660	712,747
2	GAN_M	Ganvie Market	North East (Lacustrine)	432,421	714,401
3	GAN_C	Ganvie center	North East (Lacustrine)	432,683	714,946
4	SOA	Soava	North (Lacustrine)	432,480	715,781
5	MLak1	Middle Lak1	Center (low activities)	433,408	714,029
6	MLak2	Middle MLak2	Center (low activities)	434,268	712,038
7	MLak3	Middle MLak3	Center (Fishing, accadja)	435,585	708,273
8	MLak4	Middle MLak4	Center (Fishing, accadja)	-	-
9	JES	Jesuko	South EAST (stilts)	437,061	706,809

NB. The missing coordinates are very close to the others, but these stations were sampled because of the observations we had made.

2.2. Metal Analysis by ICP-MS

The water samples were taken in the two ecosystems at 9 stations for the Chenal de Cotonou and Lake Nokoué. In order to deepen a better understanding of the high levels of metallic contaminants observed in certain areas during previous studies (Youssao *et al.* 2011a and b) [5] [7], we have brought closer points, particularly in the middle of Lake Nokoué (ML 1 to 4) and in the Dantokpa market area (DAN 1 and 2; GBo 1 and 2) on the Cotonou channel. The water samples were taken from the surface after rinsing with medium water and stored properly (Youssao *et al.*, 2018) [8]. Water samples were extracted by hot acid digestion [8] [9] [10]. To do this, 2 ml of ultra-pure HNO_3 and 1 ml of hydrogen peroxide were added to 2 ml of juice samples in a Teflon container, closed loosely to let the vapors escape. The entire system was placed in a programmable oven with two temperature levels (45˚ and 90˚). This characteristic of DigiPrep made it possible to gradually bring the samples to 45˚C for 20 min, then maintain it at this temperature for 40 min, then gradually bring it to 90˚C for 30 min and finally maintain it at this temperature level for 160 min. MRC certified water standards are digested under the same conditions; which allowed us to obtain good recovery rates for the 21 chemical elements recorded with recovery rates between 80% and 105% maximum except for zinc and cadmium with SRM SLRS-5 which respectively give 224.9% and 138.3%.

2.3. Metal Analysis by ICP-MS

We have used hierarchical clustering on principal components to identify similarities between stations based on metal concentration with R software packages "FactoMineR" and "factoextra". The method is indicated for multiple continuous variables to reduce the dimension of the data into few continuous variables containing the most important information in the data before performing the cluster analysis [11] [12]. Based on the principal component analysis, we reduced metals to three linearly uncorrelated variables that explains 84% of the variance in the metal data. And then, we identified three groups of metals: 1) macro elements (Mg and Ca), 2) micro-elements associated with the second cluster (Mn, Fe, Ni, Cu and Zn) and 3) trace elements (Mo, V, Co, Cr). We use multivariate analysis of variance (MANOVA) with the test of Pillai to identify whether there is significant difference between the four ecosystems (Lake Nokoue, channel of Cotonou, the Well water and the drilling) regarding to their concentration in each metal. We use pairwise comparison test of Games_Howell in the case that any significant difference is detected at α value set to 0.05. The test is based on Welch's degrees of freedom correction and uses Tukey's studentized range distribution for computing the p-values. Since the micro and trace elements contain more than two metals, we have chosen two uncorrelated metals among them to perform the Manova as the result for a metal can be extrapolated to its correlated metal.

3. Results and Discussion

3.1. Variations of Major, Minor and Trace Elements in the Two Areas

The results of the analyzes indicate an unequal distribution of metals in the different ecosystems. However, analysis of the following tables (Table 3 and Table 4) shows atypical concentrations at certain points in the lake and the channel. Magnesium, calcium and manganese have very high maximum values in Lake Nokoué respectively at Ganvié market station GAN M (2990 ± 105 mg/L), Ganvié center, station GAN C (4991 ± 177 mg/L) and ML4 station (10662 ± 17.03 µg/L). On the other hand, iron, aluminum and strontium have very high concentrations in the Cotonou Channel respectively at Agbato station AGB (5236 ± 103

Table 3. Concentrations of major elements (Mg and Ca in mg/L), minor and trace elements (in µg/L) in the waters of the Cotonou channel.

	AGB	*DJI*	*HI*	*DAN1*	*DAN2*	*DAN3*	*GBO1*	*GBO2*	*IS*
Mg*	34.9 ± 1.0	96.6 ± 3.3	67.6 ± 1.8	239 ± 9	94.8 ± 3.5	157 ± 4	329 ± 14	269 ± 12	974 ± 58
Ca*	18.3 ± 0.7	32.3 ± 1.0	73.4 ± 2.0	81.7 ± 0.6	33.3 ± 1.2	54.7 ± 1.0	108 ± 5	88.5 ± 3.8	303 ± 14
V	10.1 ± 0.4	9.73 ± 0.23	5.30 ± 0.20	9.30 ± 0.20	8.65 ± 0.02	8.70 ± 0.20	7.32 ± 0.24	10.1 ± 0.5	15.4 ± 0.6
Cr	8.23 ± 0.18	5.80 ± 0.02	2.33 ± 0.01	2.78 ± 0.07	4.22 ± 0.19	1.72 ± 0.03	<LOQ	4.23 ± 0.24	1.24 ± 0.03
Mn	76.4 ± 2.4	56.7 ± 1.8	125 ± 3	58.4 ± 0.6	41.8 ± 1.0	58.9 ± 0.6	13.9 ± 0.5	51.0 ± 1.8	24.1 ± 1.1
Fe	5236 ± 103	3696 ± 65	1097 ± 21	2074 ± 24	3296 ± 57	2885 ± 14	208 ± 8	2058 ± 60	591 ± 14
Co	1.45 ± 0.12	0.98 ± 0.06	0.52 ± 0.01	0.64 ± 0.05	0.87 ± 0.05	0.89 ± 0.02	0.14 ± 0.02	0.61 ± 0.01	0.20 ± 0.01
Ni	<LOQ	<LOQ	<LOQ	4.09 ± 0.07	<LOQ	5.49 ± 0.09	<LOQ	<LOQ	<LOQ
Cu	<LOQ	<LOQ	<LOQ	8.96 ± 0.22	<LOQ	6.29 ± 0.19	<LOQ	<LOQ	<LOQ
Zn	<LOQ	<LOQ	6.68 ± 0.26	35.8 ± 0.4	<LOQ	18.3 ± 0.6	<LOQ	<LOQ	<LOQ
As	1.11 ± 0.25	3.41 ± 0.44	4.62 ± 0.34	4.91 ± 0.51	2.74 ± 0.47	8.83 ± 0.45	2.42 ± 0.15	2.40 ± 0.32	5.81 ± 0.74
Se	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.29 ± 0.68
Cd	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Be	0.23 ± 0.01	0.23 ± 0.03	<LOQ	<LOQ	0.20 ± 0.01	<LOQ	<LOQ	0.13 ± 0.01	<LOQ
Al	8289 ± 519	6587 ± 273	292 ± 15	3947 ± 88	5715 ± 239	5710 ± 197	240 ± 12	3838 ± 165	582 ± 28
Sr	249 ± 1	627 ± 3	601 ± 6	1449 ± 18	617 ± 6	965 ± 6	2112 ± 11	1709 ± 15	6118 ± 68
Mo	1.40 ± 0.06	1.92 ± 0.02	1.79 ± 0.06	5.39 ± 0.01	1.69 ± 0.02	3.09 ± 0.11	3.77 ± 0.06	3.26 ± 0.02	11.1 ± 0.1
Ag	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sn	<LOQ	3.52 ± 0.10	<LOQ	<LOQ	3.28 ± 0.03	<LOQ	5.47 ± 0.04	<LOQ	5.42 ± 0.05
Ba	41.7 ± 0.5	40.8 ± 0.1	43.7 ± 0.3	36.2 ± 0.4	40.2 ± 0.4	42.0 ± 0.7	28.0 ± 0.3	32.1 ± 0.3	14.7 ± 0.1
Pt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hg	<LOQ	<LOQ	<LOQ	6.66 ± 0.06	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	0.088 ± <LQ5	0.083 ± <0.009	0.042 ± 0.014	0.17 ± 0.01	0.075 ± <0.008	<LOQ	0.042 ± <0.009	0.057 ± <0.002	0.061 ± 0.015
Pb	1.77 ± 0.03	1.26 ± 0.02	0.56 ± 0.01	1.01 ± 0.03	1.28 ± 0.02	1.34 ± 0.02	0.30 ± 0.01	0.93 ± 0.01	0.56 ± 0.02
Th	0.78 ± 0.02	<LOQ	0.65 ± 0.01	<LOQ	<LOQ	<LOQ	0.65 ± 0.05	0.70 ± 0.04	<LOQ
U	0.42 ± 0.01	0.48 ± 0.01	0.25 ± 0.01	0.78 ± 0.02	0.45 ± 0.01	0.61 ± 0.01	0.92 ± 0.01	0.88 ± 0.01	2.67 ± 0.04

<LOQ: below the limit of quantification.

Table 4. Concentrations of major elements (Mg and Ca in mg/L), minor and trace elements (in µg/L) in the waters of lake Nokoué.

	CAL	GAN_M	GAN_C	SOA	MLak1	MLak2	MLak3	MLak4	JES
Mg*	50.5 ± 1.8	2990 ± 105	2879 ± 101	2878 ± 91	11.3 ± 0.2	32.3 ± 1.0	126 ± 4	166 ± 6	240 ± 10
Ca*	17.5 ± 0.5	4585 ± 148	4991 ± 177	4568 ± 122	10.5 ± 0.1	15.9 ± 0.5	42.3 ± 1.7	148 ± 6	79.5 ± 2.5

Continued

V	8.21 ± 0.25	2.29 ± 0.03	2.25 ± 0.09	2.03 ± 0.10	4.19 ± 0.11	5.59 ± 0.16	4.81 ± 0.27	0.92 ± 0.05	6.08 ± 0.21
Ca	3.58 ± 0.10	0.93 ± 0.03	0.67 ± 0.05	0.75 ± 0.01	<LOQ	2.09 ± 0.05	<LOQ	4.91 ± 0.08	<LOQ
Mn	242 ± 5	119 ± 4	104 ± 3	145 ± 3	101 ± 1	58.2 ± 1.6	132 ± 3	10662 ± 17.03	128 ± 4
Fe	4440 ± 100	2443 ± 79	2678 ± 49	2929 ± 88	1861 ± 26	1653 ± 24	231 ± 4	1712 ± 33	199 ± 10
Co	1.05 ± 0.02	0.64 ± 0.02	0.73 ± 0.02	0.97 ± 0.03	0.58 ± 0.04	0.55 ± 0.04	0.22 ± 0.02	6.66 ± 0.06	0.18 ± 0.01
Ni	<LOQ	<LOQ	<LOQ	<LOQ	6.97 ± 0.07	<LOQ	<LOQ	125 ± 2	<LOQ
Cu	<LOQ	<LOQ	<LOQ	<LOQ	11.9 ± 0.4	<LOQ	<LOQ	422 ± 9	<LOQ
Zn	21.4 ± 0.7	<LOQ	<LOQ	<LOQ	10.5 ± 0.4	<LOQ	<LOQ	633 ± 12	<LOQ
As	1.65 ± 0.15	2.44 ± 0.19	1.83 ± 0.16	<LOQ	4.40 ± 0.20	<LOQ	1.53 ± 0.37	1.83 ± 0.15	1.66 ± 0.23
Se	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
As	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Be	0.16 ± 0.02	<LOQ	<LOQ	0.074 ± 0.016	<LOQ	0.11 ± 0.01	<LOQ	0.084 ± 0.012	<LOQ
Al	4813 ± 202	1161 ± 37	1218 ± 53	1162 ± 52	1756 ± 27	2768 ± 121	218 ± 10	215 ± 11	223 ± 11
Sr	249 ± 2	57.1 ± 0.8	57.6 ± 0.7	58.2 ± 0.3	130 ± 2	225 ± 1	795 ± 7	597 ± 1	1530 ± 17
Mo	1.48 ± 0.04	0.91 ± 0.02	0.71 ± 0.03	1.77 ± 0.05	1.17 ± 0.02	27.2 ± 0.1	1.87 ± 0.05	16.2 ± 0.2	2.71 ± 0.01
Ag	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sn	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6.00 ± 0.33	12.7 ± 0.2	<LOQ
Ba	48.1 ± 0.7	49.1 ± 0.1	52.0 ± 0.5	54.1 ± 0.6	42.0 ± 0.2	23.3 ± 0.2	30.8 ± 0.2	184 ± 4	41.5 ± 0.3
Pt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Hg	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.51 ± 0.01	<LOQ
Tl	0.060 ± <0.007	0.053 ± 0.009	0.049 ± 0.005	0.048 ± 0.008	<LOQ	0.055 ± 0.003	0.044 ± 0.014	4.02 ± 0.04	0.042 ± <0.007
Pb	2.43 ± 0.09	0.76 ± 0.02	0.45 ± 0.01	0.44 ± 0.03	1.10 ± 0.04	0.94 ± 0.03	1.57 ± 0.03	3.22 ± 0.05	0.24 ± 0.01
Th	0.83 ± 0.03	<LOQ	<LOQ	0.61 ± 0.06	<LOQ	0.62 ± 0.03	0.67 ± 0.01	1.31 ± 0.05	0.60 ± 0.02
U	0.28 ± 0.01	0.075 ± 0.003	0.082 ± <0.007	0.075 ± 0.005	0.19 ± 0.02	0.35 ± 0.01	0.41 ± 0.01	0.043 ± 0.006	0.61 ± 0.01

<LOQ: below the limit of quantification.

and 8289 ± 519 µg/L) and at the estuary station EST (6118 ± 68 µg/L). In general, we can conclude that these metals have an anthropogenic source except strontium which could come from marine waters. Particular on the site of Agbato, this atypical value of aluminum exceeds more than 25 times that of the WHO (2017) [13] which is 200 µg/L. This site must be particularly followed with regard to this toxic metal.

Water from traditional wells was sampled in the 6th district of Cotonou in the area bordering the Chenal de Cotonou and Lake Nokoué. The results of this work have been published [14].

Table 5 indicate that the concentrations of metallic elements in surface waters are generally higher than those of well and borehole waters except for magnesium and calcium which are respectively more abundant in well waters (7950 mg/L and 2.73 µg/L) and drilling (2.82 µg/L Pb). These two chemical elements could have a source related to the geochemical background.

The characterization of groundwater and surface water and the search for trace elements in these resources have been the concerns of many researchers in recent years [15] [16].

Table 5. Comparison of concentrations in the Cotonou channel, lake Nokoué and wells.

Elts	*Channel*			*Lake*			*Well*			*Drilling*
	Min	*Max*	*Avg*	*Min*	*Max*	*Avg*	*Min*	*Max*	*Avg*	*F*
Mg*	34.90	974.00	251.32	11.30	2990.00	1041.46	11.1	7950	3765.69	808.00
Ca*	18.30	303.00	88.13	10.50	4991.00	1606.41	25.00	1090	917.77	9382.00
V	5.30	15.40	9.40	0.92	8.21	4.04	0.85	17.8	10.04	0.85
Ca	<LOQ	8.23	3.39	<LOQ	4.91	1.44	<LOQ	5.54	1.90	0.00
Mn	13.90	125.00	56.24	58.20	10662.00	1299.02	<LOQ	98.6	37.51	5.49
Fe	208.00	5236.00	2349.00	199.00	4440.00	2016.22	<LOQ	2711	512.05	0.00
Co	0.14	1.45	0.70	0.18	6.66	1.29	0.15	0.76	0.35	0.20
Ni	<LOQ	5.49	1.06	<LOQ	125.00	14.66	<LOQ	<LOQ	<LOQ	0.00
Cu	<LOQ	8.96	1.69	<LOQ	422.00	48.21	<LOQ	8.03	1.15	8.03
Zn	<LOQ	35.80	6.75	<LOQ	633.00	73.88	<LOQ	82.8	21.89	76.10
As	1.11	8.83	4.03	<LOQ	4.40	1.70	<LOQ	4.51	2.92	0.00
Se	<LOQ	8.29	0.92	<LOQ	<LOQ	0.00	<LOQ	<LOQ	<LOQ	0.00
Cd	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00	<LOQ	<LOQ	<LOQ	0.00
Be	<LOQ	0.23	0.09	<LOQ	0.16	0.05	<LOQ	0.17	0.03	0.17
Al	240.00	8289.00	3911.11	215.00	4813.00	1503.78	<LOQ	5008	507.18	13.90
Sr	249.00	6118.00	1605.22	57.10	1530.00	410.99	16.3	601	290.94	16.30
Mo	1.40	11.10	3.71	0.71	27.20	6.00	0.21	11.3	5.25	0.21
Ag	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00	<LOQ	<LOQ	<LOQ	0.00
Sn	<LOQ	5.47	1.97	<LOQ	12.70	2.08	<LOQ	4.81	0.44	0.00
Ba	14.70	43.70	35.49	23.30	184.00	58.32	10.00	134.00	41.23	15.40
Pt	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.00	<LOQ	<LOQ	<LOQ	0.00
Hg	<LOQ	6.66	0.74	<LOQ	0.51	0.06	<LOQ	<LOQ	<LOQ	0.00
Tl	<LOQ	0.17	0.07	<LOQ	4.02	0.49	<LOQ	0.11	0.06	0.04
Pb	0.30	1.77	1.00	0.24	3.22	1.24	<LOQ	2.73	0.77	2.82
Th	<LOQ	0.78	0.31	<LOQ	1.31	0.52	<LOQ	0.84	0.59	0.54
U	0.25	2.67	0.83	0.04	0.61	0.24	0.05	3.18	0.72	0.17

Moreover, these waters are also contaminated by metals such as aluminum and iron. These two metallic elements presented an atypical observation in the well waters sampled [14] [17], but these concentrations are lower than those obtained in surface waters respectively at Agbato station AGB (5236 ± 103 and 8289 ± 519 µg/L). These compounds produce very unpleasant effects on the aesthetic level, such as stains on clothing, sanitary appliances and household appliances, but do not necessarily have an impact on health. Even if the consequences linked to the consumption of water containing a high level of aluminum have not yet been fully proven on human health and living aquatic organisms, it is advisable to monitor this element closely in drinking water. Drink and in ecosystems [14]. Dovonou (2014) [15] had recorded the total iron concentration of 0.5 mg/L and 40% of his samples have total iron contents exceeding 0.3 mgl/L in the Godomey wells. These values are lower than those recorded in surface waters. The toxic effects of this element appear only in case of absorption of very large quantities. If the diet is rich in calcium, the bioavailability of other absorbed minerals may be disturbed.

Magnesium concentrations ranging from 5 to 10 meq/L (6 to 12 mg/dL) can alter heart rhythm. Skeletal muscle paralysis, reduced lung capacity, coma and death may occur at magnesium concentrations of 15 meq/L (18 mg/dL) in plasma.

Dissolved manganese can form blackish particles in water and cause similar colored stains on appliances. High concentrations of dissolved iron in the wellbore can lead to the growth of iron bacteria. These bacteria can coat the inside of the casing or any other submerged part of the plumbing in the well and can cause problems.

The health effects of silver are: digestive disorders, gum line and bluish-gray discoloration of the skin. This dyschromia predominates on the face and uncovered parts, as well as on the nails (Rodier *et al.*, 1984) [18].

Aluminum causes Alzheimer's disease and parkinsonian syndromes as well as slight cerebral atrophy [19]. Acute aluminum poisoning can cause lip and mouth ulceration [20].

3.2. Comparative Study of Ecosystems and Water Sources (Wells and Boreholes)

3.2.1. Statistical Analyzes of the Results of Waters Analyzes

We can distinguish three main groupings of samples in the dendrogram below:

- The first group (in blue) is that of sites polluted by market or urban waste. Remember that the only lake site represented in this group is the Calavi pier.
- The second group is that under lacustrine influence. Indeed, the populations settled in the lake reject all kinds of polluting loads, including human faeces. The control borehole was found in this group.
- The third group includes sites with latrines on stilts, all sites in the middle of the lake including heavy fishing activities. The three quartiles are there, indicating that the majority (more than 75% of the values) are concerned.

The station name in **Figure 2** consists of 1) prefix L for Lake Nokoué or C for channel Cotonou, 2) the station location and when applied 3) the station specific number. For example C_DAN3 is the third station on the channel of Cotonou located in Dantokpa.

The following three clusters are obtained (**Table 6**).

3.2.2. Statistical Analyzes of the Results of Waters Analyzes

Three clusters emerged from the analysis based on the similarities between stations. The first group is made up of Forage, L_GAN_C, L_SOA and L_GAN_M. This cluster is characterized by a high concentration of Ca and low concentration of V. Indeed, the mean values of the concentration of Ca variable in cluster 1 are 5881.5 mg/kg which is more than its overall mean (1296.47 mg/kg) across all clusters. For the V the mean in the cluster 1 (1.86) is less than its overall mean (6.41) across all clusters. The second cluster consists of the station of L_ML4, Q3, Q2, C_GBO2, C_DAN1, L_ML1, L_ML2, C_EST, Q1, C_HIN, L_ML3, C_

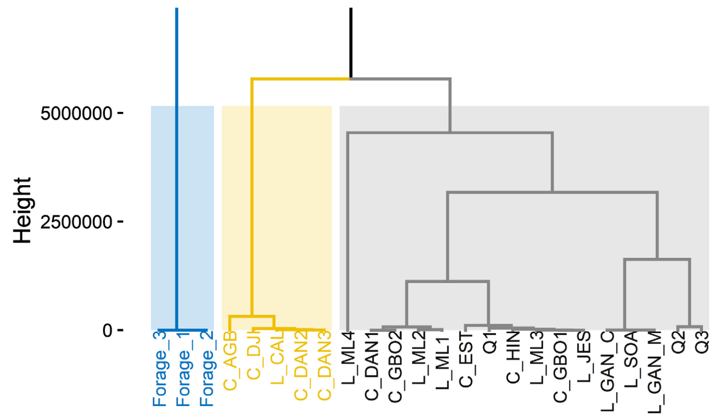

Figure 2. Dendrogram of hierarchical clustering on principal component.

Table 6. Quantitative variables describing the most each cluster.

Cluster	*Metal*	*Mean in category*	*Overall mean*	*sd in category*	*Overall sd*	*p. value*
Cluster 1	Ca	5881.5	1129.63	2028.1	2401.93	0
	V	1.86	6.94	0.59	3.84	0
Cluster 2	Be	0.01	0.06	0.02	0.08	0.01
	Al	373.14	2225.15	483.44	2499.82	0
	Fe	632.81	1805.28	646.99	1499.34	0
Cluster 3	Al	5208.38	2225.15	1638.59	2499.82	0
	Fe	3167.25	1805.28	1172.29	1499.34	0
	Ca	4.08	2.23	1.99	2.18	0
	Be	0.13	0.06	0.09	0.08	0
	Mg	121.76	1111.54	85.62	1695.93	0.04

and L_JES. And is associated with low value of Al, Be and Fe (Table 6). The third cluster is composed of stations of C_AGB, C_DJI, L_CAL, C_DAN2 and C_DAN3. These stations are characterized by high value of Fe, Al, Cr, Be and low value of Mg.

Table 7 represents the average concentrations in the different waters. Surface waters have the highest concentrations of metals. Aluminum (3911.11 ± 2968.18 μg/L), arsenic (4.03 ± 2.32 μg/L), berilyum (0.09 ± 0.11 μg/L), chromium (3.39 ± 2.53 μg/L), iron (2349 ± 1609.95 μg/L), mercury (0.74 ± 2.22 μg/L), selenium (0.92 ± 2.76 μg/L), strontium (1605.22 ± 179 μg/L) and uranium (0.83 ± 0.73 μg/L) the channel with the highest average values. While barium (58.32 ± 48.19 μg/L), cobalt (1.29 ± 2.04 μg/L), copper (48.21 ± 140.23 μg/L), manganese (1299.02 ± 3511.47 μg/L), molybdenum (6.00 ± 9.33 μg/L), nickel (14.66

Table 7. Descriptive statistic of the concentration of metals.

Variable	*Channel*	*Lake*	*Well Water*	*Drilling Water*
Al	3911.11 ± 2968.18	1503.78 ± 1495.13	68.47 ± 58.55	13.92 ± 0.03
As	4.03 ± 2.32	1.7 ± 1.31	3.48 ± 0.76	0.00 ± 0.00
Ba	35.49 ± 9.35	58.32 ± 48.19	28.23 ± 9.07	15.4 ± 0
Be	0.09 ± 0.11	0.05 ± 0.06	0.00 ± 0.00	0.17 ± 0.00
Ca	88.13 ± 85.83	1606.41 ± 2334.65	73.01 ± 21.95	9382 ± 0.00
Co	0.7 ± 0.41	1.29 ± 2.04	0.34 ± 0.13	0.17 ± 0.06
Ca	3.39 ± 2.53	1.44 ± 1.75	1.84 ± 1.63	0.00 ± 0.00
Cu	1.69 ± 3.43	48.21 ± 140.23	0.00 ± 0.00	8.06 ± 0.06
Fe	2349 ± 1609.95	2016.22 ± 1325.98	143.03 ± 151.57	0.00 ± 0.00
Hg	0.74 ± 2.22	0.06 ± 0.17	0.00 ± 0.00	0.00 ± 0.00
Mg	251.32 ± 288.68	1041.46 ± 1407.78	4003.59 ± 2726.43	802.33 ± 8.96
Mn	56.24 ± 32.03	1299.02 ± 3511.47	38.03 ± 29.8	5.49 ± 0.00
Mo	3.71 ± 3.05	6.00 ± 9.33	5.62 ± 1.77	0.21 ± 0.00
Ni	1.06 ± 2.14	14.66 ± 41.44	0.00 ± 0.00	0.00 ± 0.00
Pb	1.00 ± 0.47	1.24 ± 1	0.3 ± 0.16	2.82 ± 0.00
Se	0.92 ± 2.76	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Sn	1.97 ± 2.44	2.08 ± 4.45	0.00 ± 0.00	0.00 ± 0.00
Sr	1605.22 ± 179	410.99 ± 493.54	307.17 ± 122.46	16.3 ± 0.00
Th	0.31 ± 0.37	0.52 ± 0.44	0.63 ± 0.07	0.54 ± 0.00
Tl	0.07 ± 0.05	0.49 ± 1.33	0.06 ± 0.01	0.04 ± 0.00
U	0.83 ± 0.73	0.24 ± 0.19	0.38 ± 0.19	0.17 ± 0.00
V	9.4 ± 2.72	4.04 ± 2.36	10.31 ± 3.07	0.86 ± 0.01
Zn	6.75 ± 12.5	73.88 ± 209.8 0	8.6 ± 14.9	76.08 ± 0.07

± 41.44 µg/L), tin (2.08 ± 4.45 µg/L), and thallium (0.49 ± 1.33 µg/L) are more abundant in Lake Nokoué. As for magnesium (4003.59 ± 2726.43 mg/L), horium (0.63 ± 0.07 µg/L) and vanadium (10.31 ± 3.07 µg/L), they are in highest concentrations in well water in the 6th district of Cotonou. Finally, the water from the reference borehole is richer in calcium (9382 ± 0.00 mg/L), lead (2.82 ± 0.00 µg/L) and zinc (76.08 ± 0.07 µg/L). The concentrations of tin (1.97 ± 2.44 µg/L) and vanadium (9.4 ± 2.72 µg/L) in the waters of the channel have values close to the highest values obtained respectively in the lake and well water. On the other hand, the average concentration of zinc (73.88 ± 209.80 µg/L) obtained in the lake is close to the highest value obtained in the drilling water.

Water contamination has been studied by several researchers in Benin and around the world [21]. But metals have been the subject of recent studies with regard to their toxic nature [14] [19] [20]

3.3. Multivariate Analyses Results

3.3.1. Macroelements

The comparison of the different zones shows the highest concentrations of major elements in the lake, but atypical values are highlighted in tank waters for magnesium (**Figure 3** and **Table 8**).

3.3.2. Microelements (Fe and Mn)

Mn concentrations are strongly correlated with Ni, Cu and Zn. Then we use Mn and Fe for the Manova test (**Figure 4**).

The concentrations of iron and manganese are shown on the graph in **Figure 4** and the significance in **Table 9**. These results show a significantly higher iron concentration in surface water (lake and channel) than in groundwater.

Table 8. Pairwise comparison of Ca and Mg.

Metal	Group 1	Group 2	P. Adj	P. Adj. Signif
Ca	Channel	Well water	0.961	NS
Ca	Channel	Drilling	5.16E−14	****
Ca	Channel	Lake	0.282	NS
Ca	Well water	Drilling	1.86E−13	****
Ca	Well water	Lake	0.274	NS
Ca	Drilling water	Lake	3.98E−05	****
Mg	Channel	Well water	0.319	NS
Mg	Channel	Drilling	0.002	**
Mg	Channel	Lake	0.403	NS
Mg	Well water	Drilling	0.397	NS
Mg	Well water	Lake	0.442	NS
Mg	Drilling water	Lake	0.955	NS

NS: Not Significant.

3.3.3. Trace Elements

There is no evidence correlation between the elements. We choose Cr and V for the Manova test (Figure 5).

The elements present in the groundwater of the sixth arrondissement of Cotonou have concentrations lower than the standard values and hide disparities that should be underlined. Indeed, Mn, Zn, Pb and Th have a more elongated distribution towards high values with atypical observations for lead at Vossa and Djadjo (control well) and for Th at TOWETA [14]. This result can be generalized to surface waters (Figure 5).

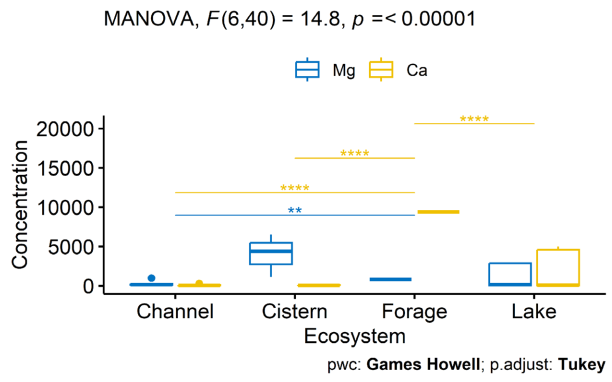

Figure 3. Pairwise comparison of Ca and Mg.

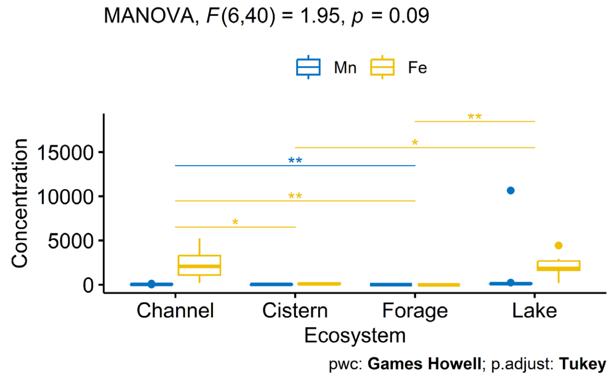

Figure 4. Comparison of concentrations of minor elements (Mn, Fe).

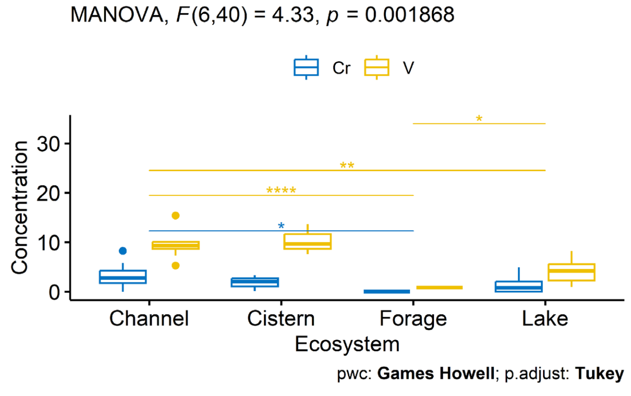

Figure 5. Comparison of concentrations of minor elements (Mn, Fe).

Table 9. Pairwise comparison of Fe and Mn.

Metals	Group 1	Group 2	P. Adj	P. Adj. Signif
Fe	Channel	Well water	0.014	*
Fe	Channel	Drilling water	0.01	**
Fe	Channel	Lake	0.963	NS
Fe	Well water	Drilling water	0.515	NS
Fe	Well water	Lake	0.012	*
Fe	Drilling water	Lake	0.008	**
Mn	Channel	Well water	0.807	NS
Mn	Channel	Drilling water	0.006	**
Mn	Channel	Lake	0.721	NS
Mn	Well water	Drilling water	0.436	NS
Mn	Well water	Lake	0.712	NS
Mn	Drilling water	Lake	0.697	NS

NS: Not Significant.

4. Conclusion

Metals are unevenly distributed in the waters of the Cotonou Channel and Lake Nokoué ecosystems. The major elements such as Ca and Mg have an essentially geochemical origin, but also anthropogenic. This is confirmed by the values recorded on the Ganivié market (GAN_M). On the other hand, heavy metals generally come from anthropogenic activities. This is the case of lead, which would be released particularly at Lake Nokoué (MLak4) by fishing communities, and mercury, which would come from hospital sources in the lagoon maternity area. The monitoring of trace elements must be reinforced especially at the level of GAN_M and MLak4.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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