Original Research Article

Ecological risk link to trace metals levels in surface sediments from Fresco Lagoon, Côte d’Ivoire, Southern Africa.

ABSTRACT

To examine spatial variations and understand current metal contamination due to urbanization, fisheries and agricultural activities developed around Fresco City (Côte d’Ivoire), the concentrations of five selected trace metals (Pb, As, Mn, Zn and Fe) and organic matter content were determined in surface sediments samples collected from ten (10) stations, from June 2019 to March 2020. Trace metals concentrations were determined using an ICP-OES Instrument and organic matter content was determined by the mass loss on ignition. The sediment pollution assessment and ecological risk were done using the Geoaccumulation Index (Igeo), Enrichment Factor (EF), Degree of Contamination (DC), Pollution Load Index (PLI), and sediment quality guidelines. The results indicated that organic matter contents ranged from 5.28 to 28.31% and that trace metal concentrations (in $mg.kg^{-1}$ dry weight) observed in surface sediments varied from 3.68 to 38.2 for Pb, 0.98 to 19.1 for As, 19.79 to 325 for Mn, 13.78 to 461.18 for Zn, and 1269.21 to 59862.37 for Fe. Based on Igeo values, the sediments of Fresco Lagoon can be treated as unpolluted to moderately polluted with As, but unpolluted with Zn, Pb, Mn, Fe. The Enrichment factors of Pb, Zn, As, Mn and Fe were: 64.22±52.32, 107.04±111.88, 227.29±203.06, 10.25±8.76, and 52.04±47.44 respectively, suggesting that the source of those metals was more likely to be anthropogenic. The falling trend of enrichment factors is as follows: As > Zn > Pb > Fe > Mn. Moreover, the PLI values (PLI>1) showed higher values at the stations closed to the urban area, due to the influence of direct external sources such as agricultural runoff, and other anthropogenic inputs. This study showed that, based on the comparison with the sediment quality guidelines, the concentrations of As, Pb and Zn would not be toxic to sediment-dwelling organisms.

Keywords: Trace metals, Geoaccumulation index, Enrichment factor, contamination, Fresco Lagoon, Côte d’Ivoire (West Africa).

1. INTRODUCTION

Waters and sediments pollution by trace metals has become a major concern worldwide. Rivers and their tributaries constitute the major water resources for many local communities in the world. They are valuable resources used for bathing, drinking, fishing, farming, recreation, transportation, and power generation. However, the quality of waters and sediments respect to trace metals is threatened by increasing anthropogenic activities. High concentrations in trace metals such as arsenic, lead, cadmium, copper, and zinc, have been reported in waters and sediments from many estuaries, rivers and streams [**1-3**] due to agriculture and urbanization. In agricultural practices, the use of pesticides, fertilizers, and manures are the main sources of metals in river basins **[4]**. Trace metals are one type of pollutant released into the environment, leading to an increase in metal contamination. When trace metals are released into the environment, they can be dispersed by the wind and deposited in soil and water bodies, accumulated in sediments **[5**]. Metal contamination can lead to adverse effects on both ecosystems and human health **[6]**. Indeed, trace metals can enter the food chain and accumulate in the human body, sometimes at harmful levels **[7]**. The most common trace elements found in the environment are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb), zinc (Zn), and mercury (Hg) **[7]**. Moreover, because of the absorption and sedimentation of suspended matters, several trace metals get deposited in sediments; however, with the environment physicochemical properties changes, they are released into the water column again and cause pollution **[8-10]**. Compared to waters and organisms, sediments usually contain more trace metals and can provide accurate detection results **[6; 11]**. Indeed, sediments act as adsorptive sink for trace metals since they can scavenge some elements, thus, in aquatic ecosystems, trace metals concentrations found in sediment are higher than those observed in the water column. Then, metals concentrations in sediments is an important environmental indicator. Therefore, sediment is an appropriate matrix for trace metals contamination assessment in the aquatic environment **[12-13]**. The sources of trace metals in the countries are various, but notably include landfill, mining, tanning, textile and several cottage industries **[14]**. The distinction between the sources of trace metal contamination in many coastal environments poses a challenge to researchers due to the availability of metals from both anthropogenic and natural sources **[15]**. The present study was undertaken in Fresco Lagoon, which has wetland extended between 5° 03' and 5° 11' North latitude and between 5° 29' and 5° 44' West longitude and located in a rural environment. This lagoon is subject to anthropic pressure, in relation with various activities practised on the banks. The objective of the present study was therefore to determine the trace elements concentrations in the sediment on one hand, and on the other hand, to identify their main sources of contamination. This study will allow an updating of data, an understanding on origin and the extent of contamination of these trace metals through their spatial distribution in aquatic environment of the Fresco Lagoon.

2. MATERIAL AND METHODS

2.1. Study area

Fresco Lagoon extends from East to West over a length of about 6 km and a width between 2 and 4 km with an average depth of 4 m and an estimated area between 17 km^2 and $29km^2$ **[16-17]**. The Fresco Lagoon has a humid equatorial climate and is characterised by a succession of four seasons with unequal durations: a long rainy season from April to July, a short dry season from August to September, a short rainy season (also named flood season) from October to November and a long dry season from December to March. Fresco Lagoon communicates with the Atlantic Ocean through a non-permanent shallow channel and is diluted with waters from the Bolo and Niouniourou Rivers and by seawater, the effects of which disturb the lagoon waters chemical quality. On the banks of Fresco Lagoon, is located Fresco City, a small rural agglomeration with only 101,298 inhabitants **[18]** and a non-existent industrial activity. The dominant activity remains the agriculture with large industrial plantations of rubber trees, oil palms, coffee, cocoa, etc. **[19]**. In addition, the size and depth of Fresco Lagoon do not allow any maritime traffic. Only a few pirogues equipped with outboards navigate on the Fresco Lagoon. Sediment samples were collected at ten (10) stations distributed as follows: one (1) in each of the Bolo and Niouniourou rivers and the other eight (8) stations are located in the lagoon water body (Figure 1). The geographical coordinates are presented in **Table 1**.

Table 1. Geographical coordinates of the sampling stations

N°	Station	Latitude	Longitude
1	Bolo	5°06'46''N	5°33'58''W
2	Niouniourou	5°06'25''N	5°33'32''W
3	Bolo - Niouniourou	5°06'15''N	5°33'47''W
4	Embouchure	5°04'54''N	5°34'30''W
5	Dadjidje	5°06'09''N	5°34'57''W
6	Entrée Falaise	5°06'07''N	5°35'16''W
7	Vron	5°05'26''N	5°36'47''W
8	Dabien	5°06'14''N	5°36'37''W
9	Ex Zakareko	5°06'29''N	5°36'00''W
10	Nouveau Zakareko	5°06'40''N	5°35'05''W

2.2. Sampling and pre-treatment

Forty (40) surface sediment samples (0-5 cm depth) were collected from June 2019 to March 2020 for the ten selected stations throughout the main four seasons (**Fig. 1**). Sediment samples were collected using a sediment grab, packed into plastic bags labelled and stored in a cool box containing ice packs at (4°C).

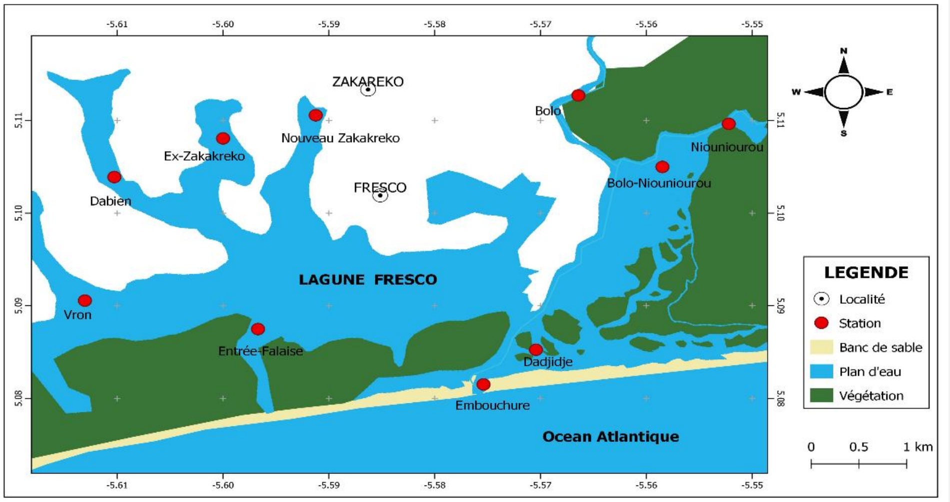

Fig.1. Geographical locations of sampling stations.

Sediment samples were transported to the Lab according to the reference methods for marine pollution studies **[20]**. In the laboratory, the sediment samples were oven dried at 60°C for 24 hours. Then, sub-samples of the previous dried sediment were used for the determination of the organic matter contents. For the determination of trace metals concentrations, each dry sediment sample was pre-screened on a 2 mm mesh sieve to remove shells, branches and leaves debris. Sub-samples of dry sediment were ground in an agate mortar and sieved to 63µm to obtain the fine fraction (fraction < 63µm), which was used for the chemical analyses. Prior the analyses, the samples were stored in polyethylene bags with plastic tape around the closure to protect them from moisture and then stored in a dark and cool (+20°C) area.

2.3. Analytical procedures

For the determination of organic matter content in sediment samples, the standard method detailed by Heiri et al. **[21]** was applied in the present study. It consists of calcining the organic material in an oven at 550°C for 4 hours. The procedure is as follows: 0.25 g of dry sediment sample prepared for testing is weighed into a quartz capsule, placed in an oven and calcined at 550°C for 4 hours. Then, the capsule is removed and left to cool. The weight difference is used to determine the organic matter content by loss on ignition. Regarding trace metal analysis, dry sediment samples (0.3g) was placed in a Teflon tube underwent hot mineralisation, using 1 mL of aqua regia (HNO_3: HCl; 1:3, v/v) and 6 mL of concentrated HF (48% of purity). Heating is done at 120°C in a water bath for 2 hours 30 minutes. After cooling in ambient air, the residues are taken up in a solution of boric acid H_3BO_3 (2.70 g in 20 mL of bi-distilled water) for the neutralisation of the hydrofluoric acid and the final volume is reduced to 50 mL. The resulting solution was left to stand overnight before analysis. The concentrations of the trace metals (Pb, Zn, As, Mn, Fe) were then determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES 720-ES Varian).

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2.4. Assessment of sediment contamination

The pollution indices are useful tools which can be applied for sediment contamination assessment. The used indices for the present study are presented as follows:

2.4.1. Enrichment factor (EF)

Enrichment factor (EF) is a useful tool in determining the degree of anthropogenic trace element pollution in aquatic environment **[22]**. The EF is computed using the relationship below:

$$EF = (C_{Metal} / C_{Al})_{sample} / (C_{Metal} / C_{Al})_{background} \qquad (1)$$

where, $(C_{Metal} / C_{Al})_{sample}$ is the ratio of concentration of trace metal (C_{Metal}) to that of aluminium (C_{Al}) in the sediment sample, and $(C_{Metal} / C_{Al})_{background}$ is the same reference ratio in the background sample. The background values of the metals in this study were taken from the baseline values adopted the upper continental crust (UCC) **[23]**. The EF values were interpreted as suggested by **[22]**, where: EF < 1 indicates no enrichment; < 3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and > 50 is extremely severe enrichment.

2.4.2. Index of geoaccumulation (Igeo)

The index of geoaccumulation (Igeo) is defined by the following equation:

$$Igeo = \log_2 (C_n / 1.5 \times B_n)$$

where, C_n is concentration of the examined element 'n' in the surface sediments; B_n is geochemical background concentration of element 'n'. Factor 1.5 is the background matrix correction factor due to lithospheric effects. **[24]** proposed the following classes for increasing Igeo values: Class 0 (practically uncontaminated): Igeo ≤ 0; Class 1 (uncontaminated to moderately contaminated): 0 < Igeo < 1; Class 2 (moderately contaminated): 1 < Igeo < 2; Class 3 (moderately to strongly contaminated): 2 < Igeo < 3;

Class 4 (strongly contaminated): 3 < Igeo < 4; Class 5 (strongly to extremely contaminated): 4 < Igeo < 5; Class 6 (extremely contaminated): 5 ≥ Igeo.

2.4.3. Contamination Factor (CF) and Degree of Contamination (DC)

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value **[25-26]**:

$$CF_i = C_{metal\ (i)} / C_{background\ (i)}$$

where, $C_{metal(i)}$ is the concentration of metal (i) in the sediment sample and $C_{background(i)}$ is the background value of the metal (i). CF values were interpreted as suggested by **[26]**, where: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination. The Degree of contamination (DC) was defined as the sum of all contamination factors.

2.4.4. Pollution Load Lndex (PLI)

The PLI represents the number of times by which the metal content in the sediment exceeds the average natural background concentration, and gives a summative indication of the overall level of trace metal toxicity in a particular sample. For the entire sampling site, it is defined as the nth root of the product of the n CF **[27]**:

$$\text{PLI} = (\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \ldots \times \mathrm{CF}_n)^{1/n}$$

Where, CF_1, CF_2, CF_n are contamination factors of the sediment sample with respect to element 1, 2, and n, respectively; n is the number of metals investigated. When a value of PLI < 1 denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI >1 indicates deterioration of site quality **[27]**.

2.5. Ecological risk assessment by sediment quality guidelines (SQGs)

The assessment can be achieved through a comparison of measured trace metal concentrations in sediment samples with the consensus-based threshold effect concentration (TEC) and Probable Effect Concentration (PEC) values of the sediment quality guidelines (SQGs). The toxicity to organisms living in the sediment of all metals in sediments was evaluated by determining the mean quotient PEC (m-PECQ). Sediment samples are predicted to be not toxic if the m-PECq is below 0.5. In contrast, sediment samples are predicted to be toxic **[28]**.

2.6. Statistical Analysis

Means, standard deviations, and graphical representations were determined and drew with Microsoft Excel 2010. The spatial variability of the different parameters was investigated by analysis of variance (ANOVA) at P < 0.05. The correlation matrix, Principal Component Analysis (PCA) and the one-way ANOVA test were performed using Statistica 2005 (version 7.1).

3. RESULTS AND DISCUSSION

3.1. Sediment types and organic matter contents

The spatial variations of organic matter contents in sediments collected from Fresco Lagoon at the different stations are represented in Table 2. The mean values of organic matter levels ranged from 5.28 % (Embouchure) to 28.31% (Ex Zakareko) with a mean of 18.40±8.55%

(Table 2). The organic matter levels showed a significant difference between the selected stations ($p < 0.05$). The highest organic matter values were recorded at Niouniourou, Entrée-Falaise, Vron, Dabien, Ex Zakareko, and Nouveau Zakareko while the lowest ones were observed at stations Embouchure and Dadjidje. The organic matter levels showed that the sediments of the Fresco lagoon were highly loaded with organic matter, especially those collected in the stations close to the urban area of Fresco. The highest average value recorded at station Niouniourou could be explained by the Niouniourou River draining large quantities of organic matter of continental origin that is deposited in the surface sediments and, on the other hand, by the strong presence of plant organic matter due to a forested area crossed by this river. As for the average values recorded at stations Entrée-Falaise, Vron, Dabien, Ex Zakareko, and Nouveau Zakareko, which are close to the urban area of Fresco, they could be explained by a zone where the water is poorly renewed above the sediment and by hypoxic conditions of the bottom waters. Consequently, organic matter that is no longer oxidised accumulates in the sediments and sulphides appear through the reduction of sulphates. These high levels of organic matter could therefore be attributed to domestic and agricultural wastewater discharges from the Fresco agglomerations. The low levels of organic matter recorded at stations Embouchure and Dadjidje could be due to the influence of marine waters. Indeed, the marine waters could have a dilution or degradation effect on the polluting masses, which causes a strong decrease in the intensity of pollution by organic matter in the sediments of the stations close to the marine waters.

Table 2. Sediment types and organic matter content (%) in surface sediments collected from Fresco Lagoon.

Station	sediment types	Organic matter
Bolo	Sand	13.11
Niouniourou	Mud	22.55
Bolo-Niouniourou	Sandy-muddy	12.14
Embouchure	Sand	5.28
Dadjidje	Sand	5.68
Entrée-Falaise	Mud	25.08
Vron	Mud	25.13
Dabien	Mud	24.38
Ex Zakareko	Mud	28.31
Nouveau Zakareko	Mud	22.33
Mean	-	18.40
Standard deviation	-	8.55

3.2. Trace elements distribution in surface sediments

The spatial distribution of total concentrations of trace metals in sediments collected from Fresco Lagoon is represented in **Table 3**.

Lead: The concentrations ranged from 3.68 mg/kg (Embouchure) to 38.2 mg/kg (Ex Zakareko) with a mean of 23.055±14.832 mg/kg (**Fig. 2**). The observed mean value was higher than that of the Upper Continental Crust (UCC).

Zinc: Concentrations values observed for Zn ranged from 13.78 mg/kg (Bolo) to 461.18 mg/kg (Niouniourou) with an average value of 119.31±130.04 mg/kg (**Fig. 3**). The mean value recorded was higher than that of the UCC. The one-way analysis of variance showed significant differences ($P < 0.05$) between the stations.

Arsenic: The observed concentrations of As ranged from 0.98 mg/kg (Niouniourou) to 19.1 mg/kg (Vron) with an average value of 8.80±7.34 mg/kg (**Fig. 4**). The mean value recorded was higher than that of the UCC. According to the one-way analysis of variance, there was no significant difference ($P > 0.05$) between the different stations.

Manganese: the mean values of manganese concentrations ranged from 19.79 mg/kg (Bolo) to 325 mg/kg (Bolo-Niouniourou) with a mean of 130.76±105.21 mg/kg (**Fig. 5**). At all stations, the average values recorded were low and below that of the UCC.

Iron: the mean values of iron concentrations ranged from 1269.21mg/kg (Bolo) to 59862.37 mg/kg (Vron) with a mean of 32731.29±25148.35 mg/kg (**Fig. 6)**. The mean value recorded was higher than that of the UCC. The one-way analysis of variance revealed a significant difference ($P < 0.05$) between the stations.

Table 3. Spatial distribution of total concentrations of trace metals in surface sediments (in mg/kg).

Station	**Pb**	**Zn**	**As**	**Mn**	**Fe**
Bolo	6.61	13.78	1.58	19.79	1269.21
Niouniourou	9.53	461.18	0.98	96.94	4893.24
Bolo-Niouniourou	30	58.29	2.94	325	17171.84
Embouchure	3.68	17.71	7.84	69.6125	10121.12
Dadjidje	4.63	19.29	1.01	71.59	13104.22
Entrée-Falaise	35.9	124.74	6.24	291	59106.09
Vron	33.2	126.68	19.1	165	59862.37
Dabien	36.5	122.46	15.3	54.235	51536.07
Ex Zakareko	38.2	126.00	15.3	46.48	55546.27
Nouveau Zakareko	32.3	122.93	17.7	168	54702.49
Mean	23.055	119.31	8.80	130.76	32731.29
Standard deviation	14.832	130.04	7.34	105.21	25148.35
UCC	17	52	2	527	30890

UCC: Upper Continental Crust

The comparison of the average concentrations of trace metals (Pb, Zn, As, Mn, Fe) obtained in the surface sediment samples showed that iron is the most abundant element in the sediments. The quantitative distribution of the average contents follows the following order of abundance: Fe > Mn > Zn > Pb > As. Our results indicate that, with the exception of manganese, the concentrations of trace metals (lead, zinc, arsenic, iron) were highest in the sediments close to urban areas (Entrée-Falaise, Vron, Dabien, Ex Zakareko and Nouveau Zakareko), which are rich in organic matter and made up of mud. It has been shown that metals are mainly bound to the organic and clay phase of the sediments **[29]**. Furthermore, the concentrations of trace metals observed in the present study were higher than those recorded in the same lagoon by **[19]**. This could be explained by the leaching of agricultural soils containing pesticides and located on the banks. In addition, economic activities linked to lagoon transport, tourism, and a galloping demography and accelerated urbanisation could be the source of significant domestic discharges which could contribute to increasing the levels of trace metal elements. **[30]** observed in the Altata-Ensenada del Pabellon costal lagoon system (South East Gulf of California) that there is a direct relationship between the enrichment of the sediments in Cr, Cu, Mn and Pb and the concentrations of effluents drained from intensive agricultural areas.

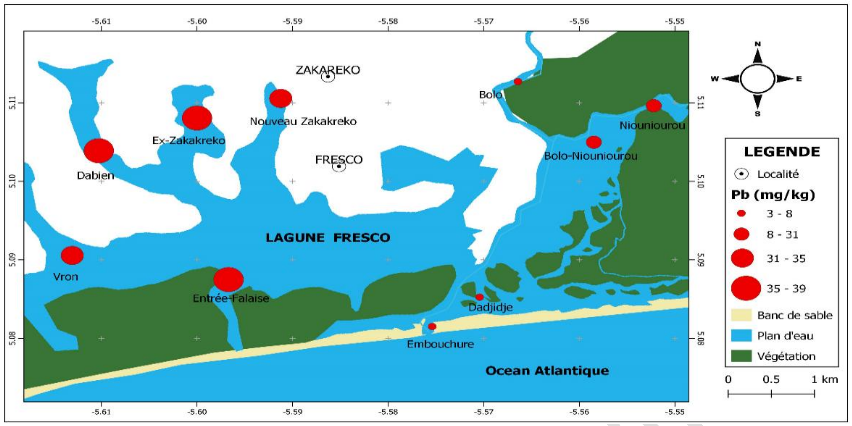

Fig. 2. Spatial distribution of lead concentrations in surface sediments of Fresco lagoon.

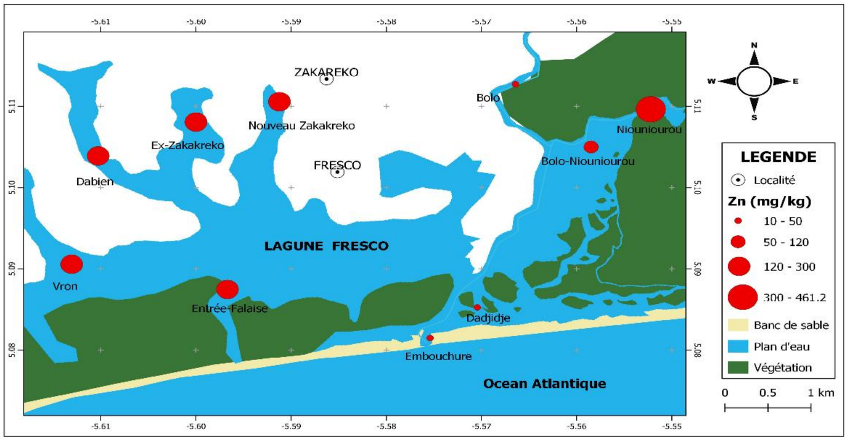

Fig. 3. Spatial distribution of zinc concentrations in surface sediments of Fresco lagoon.

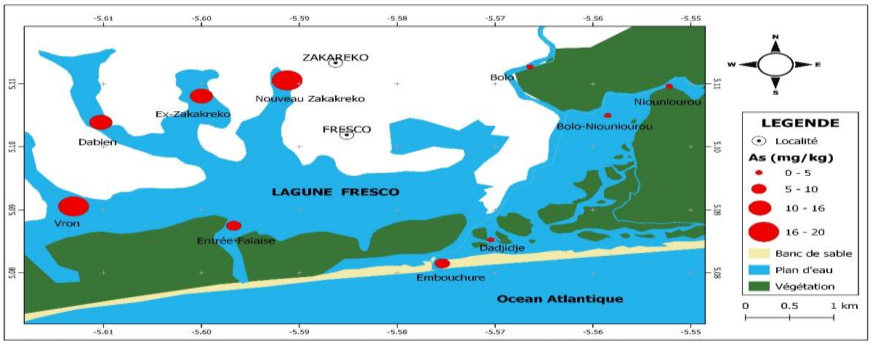

Fig. 4. Spatial distribution of arsenic in surface sediments of Fresco lagoon.

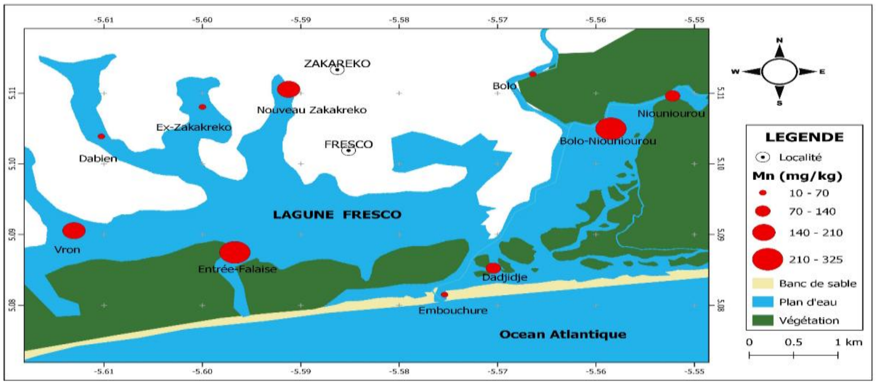

Fig. 5. Spatial distribution of manganese in surface sediments of Fresco lagoon.

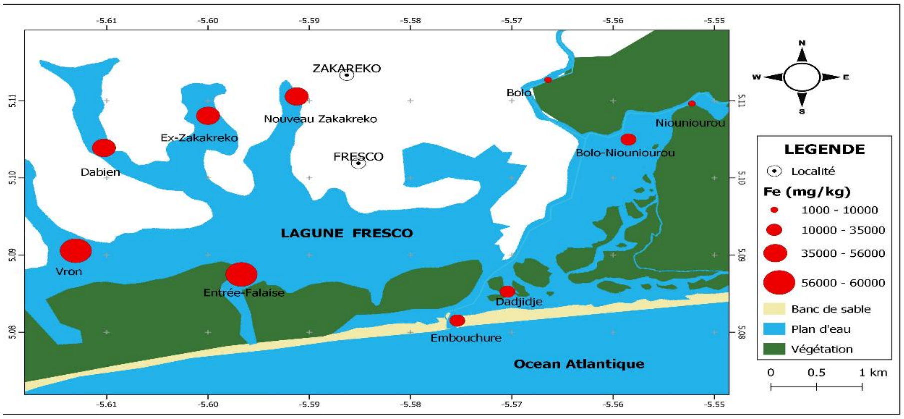

Fig. 6. Spatial distribution of iron concentrations in surface sediments of Fresco lagoon.

3.3. Relationships between trace elements and organic matter contents in surface sediments

In order to establish relationships between metals and to verify the similarity of the sources of metallic trace elements in the sediments, a correlation matrix was carried out (**Table 4**). Significant correlations have been observed between lead and arsenic, between lead and iron, and between iron and arsenic. The strong correlations observed between lead and arsenic (R^2 = 0.70), then between lead and iron (R^2 = 0.89), and finally between arsenic and iron (R^2 = 0.84) indicate that these elements (Pb, As, Fe) could come from anthropogenic sources. In addition, strong correlations were observed between organic matter and the elements lead (R^2 = 0.79) and iron (R^2 = 0.76), which means that organic matter could therefore control the fate of these elements by the formation of more or less stable complexes. Under these conditions, the lead and iron concentrations would depend on the levels of organic matter contained in the sediments. On the other hand, zinc shows negative correlations with arsenic (R^2 = - 0.06) and iron (R^2 = - 0.01) and weak correlations with lead, manganese, and organic matter. This could mean that zinc would come from reverse processes that brought this element into circulation. The presence of zinc in the sediments could be due to the wastewater brought into the lagoon environment by the Niouniourou river, to the runoff from household waste from the town of Fresco and to the leaching of agricultural soils containing pesticides (fungicides containing zinc) and some farm manure. Manganese does not show any significant correlation with other metallic elements and with organic matter, indicating that this element has a lithological source.

Table 4. Correlation coefficients trace elements and organic matter.

	Pb	Zn	As	Mn	Fe	Organic matter
Pb	1.00					
Zn	0.05	1.00				
As	**0.70**	-0.06	1.00			
Mn	0.45	0.01	-0.05	1.00		
Fe	**0.89**	-0.01	**0.84**	0.28	1.00	
Organic matter	**0.79**	0.51	0.61	0.12	**0.76**	1.00

Values in bold are significant (p <0.05)

3.4. Sources of trace elements in sediments by Principal Component Analysis (PCA)

Principal component analysis (PCA) reveals three main components that express approximately 95.03% of the total variance in the data set. **Table 5** presents the variables, their correlations with the axes as well as the eigenvalues of the three components and their contribution to the total cumulative variance.

- The main component (F1) represents 56.62% of the total variance. It shows negative correlations with lead (R^2 = - 0.95), arsenic (R^2 = - 0.82), iron (R^2 = - 0.96) and organic matter (R^2 = - 0.879) (**Table 5**). These negative correlations explain the inverse processes that cause the presence of these elements in the sediments. These trace metals could have an anthropic origin linked to domestic waste and leaching from agricultural soils containing fertilisers and pesticides. Organic matter from domestic discharges and continental waters could have a trapping effect on trace elements in sediments. The highest organic matter levels and concentrations of lead, arsenic, and iron were recorded at stations Vron, Dabien, Ex Zakareko and Nouveau Zakareko. Therefore, the factor F1 is the anthropogenic origin of metals in sediments.

The main component (F2) represents 77.12% of the total variance. It shows a strong correlation with zinc (R^2 = 0.96) (**Table 5**). The highest concentration of zinc was recorded at station Niouniourou. This metal could come not only from anthropogenic activities related to the use of fertilisers in agricultural activities in the catchment area, but also from wastewater discharged into the Niouniourou River. Indeed, zinc and lead are recognised as indicators of anthropogenic inputs. Therefore, the F2 factor is a factor of anthropogenic origin of metals in sediments.

The main component (F3) represents 95.03% of the total variance. It shows a strong negative correlation with manganese (R^2 = -0.91) (**Table 5**). The negative correlation between the F3 factor and manganese indicates an inverse process behind the presence of this element in the sediments. Manganese is generally related to the geochemical nature of the sediments. Therefore, the F3 factor is the natural origin factor for metals in sediments.

Table 5. Distribution of the eigenvalue, the total variance and the correlation between the sediment variables with the axes.

Variables	F1	F2	F3
Pb	-0.95	-0.14	-0.16
Zn	-0.18	0.96	-0.15
As	-0.82	-0.20	0.43
Mn	-0.32	-0.21	-0.91
Fe	-0.96	-0.19	0.07
O.M	-0.88	0.42	0.06
Eigenvalue	3.40	1.23	1.07
% Total variance	56.62	20.50	17.91
% Total cumulative variance	56.62	77.12	95.03

3.5. Assessment of sediment contamination

The mean values of EF and Igeo for the different trace metals are presented in **Table 6**. Taking into account the uncertainties, an EF between 0.5 and 2 is considered to be in the range of natural variability, while above 2 it indicates anthropogenic enrichment **[31]**. The analysis of the mean values of the EF shows values above 2 indicating anthropogenic enrichment for trace metals in all stations. A significant enrichment was observed for manganese, while this enrichment was extreme for lead, zinc, arsenic, and iron. The overall order of sediment enrichment is: As > Zn > Pb > Fe > Mn. The Igeo showed negative mean values for lead (-0.61±1.32), zinc (-0.11±1.62), manganese (-3.05±1.26) and iron -1.25±1.90), which means that the sediments are classified as "not contaminated" with lead, zinc, manganese and iron. Arsenic showed a mean value (0.83±1.72) between 0 and 1, which means that the sediments are classified as "not contaminated to moderately contaminated" with arsenic. In addition, the accumulation of trace metals in the sediments was observed in the following order: As > Zn > Pb > Fe > Mn. Overall, EF and Igeo showed the same decreasing order of contamination by the metals.

Table 6. Mean values of Enrichment factor and Index of Geoaccumulation (Igeo).

	Pb	**Zn**	**As**	**Mn**	**Fe**
Present study	Mean ±Sd	Mean ±Sd	Mean ±Sd	Mean ±Sd	Mean ±Sd
EF	64.22±52.32	107.04±111.88	227.29±203.06	10.25±8.76	52.04±47.44
Igeo	-0.61±1.32	-0.11±1.62	0.83±1.72	-3.05±1.26	-1.25±1.90

Sd: Standard deviation

The spatial distributions of contamination factor (CF), degree of contamination (DC) and pollution load index (PLI) of trace metals in the sediments are presented in **Table 7**. The results obtained show an absence of manganese contamination at all stations (CF<1). However, very high metallic contamination (CF > 6) was observed for arsenic at the Vron (CF = 9.55), Dabien (CF = 7.65), Ex Zakareko (CF = 7.65) and Nouveau Zakareko (CF = 8.85) stations, and for zinc at the Niouniourou station (CF = 8.87) (**Table 7**). In addition, low polymetallic contamination (DC< 6) in lead, zinc, arsenic, manganese and iron was observed at the Bolo, Bolo-Niouniourou, Embouchure, and Dadjidjé stations while moderate polymetallic contamination (6 ≤ DC < 12) was observed at the Niouniourou and Entrée falaise stations (**Table 7**). The Vron, Dabien, Ex Zakareko, and Nouveau Zakareko stations showed high levels of polymetallic contamination (12≤ DC < 24), accounting for considerable polymetallic contamination (**Table 7**). The pollution load index values were less than or equal to 1 (PLI ≤ 1) at the Bolo, Niouniourou, Bolo-Niouniourou, Embouchure and Dadjidje stations (**Table 7**), indicating that the sediments at these stations do not show any appreciable

anthropogenic effect. On the other hand, the pollution load index of the stations Entrée falaise, Vron, Dabien, Ex Zakareko and Nouveau Zakareko were higher than 1 (PLI > 1) (**Table 7**), indicating that the sediments of these stations have a high pollution load.
The evaluation of the contamination indices revealed sediment pollution (PLI =1.10±0.68 > 1). Arsenic was the most enriched element (EF = 227.29±203.06) due to its significant trapping by organic matter. This contamination is explained by a rural environment marked by phenomena such as fishing practices by poisoning, the use of pesticides and phytosanitary products in the treatment of cash crops (cocoa, rubber, etc.) and by urbanisation of the banks. Furthermore, the stations close to the urban area were the most affected by polymetallic contamination due to the weak hydrodynamic conditions of the water and the domestic and agricultural discharges from the study area. On the other hand, the stations close to the marine area were the least affected by polymetallic contamination, due to the dilution of the pollutants by the marine waters.

Table 7. Spatial distributions of CF, DC and PLI of trace metals in the surface sediments.

Station	CF					DC	PLI
	Pb	Zn	As	Mn	Fe		
Bolo	0.39	0.26	0.79	0.04	0.04	1.52	0.16
Niouniourou	0.56	8.87	0.49	0.18	0.16	10.27	0.59
Bolo-Niouniourou	1.76	1.12	1.47	0.62	0.55	5.53	1.00
Embouchure	0.22	0.34	3.92	0.13	0.33	4.94	0.42
Dadjidje	0.27	0.37	0.51	0.13	0.42	1.71	0.31
Entrée-Falaise	2.11	2.40	3.12	0.55	1.91	10.10	1.76
Vron	1.95	2.44	9.55	0.31	1.94	16.19	1.94
Dabien	2.15	2.35	7.65	0.10	1.67	13.92	1.46
Ex Zakareko	2.25	2.42	7.65	0.09	1.80	14.21	1.46
Nouveau Zakareko	1.90	2.36	8.85	0.32	1.77	15.20	1.86
Mean	1.36	2.29	4.40	0.25	1.06	9.36	1.10
Standard deviation	0.87	2.50	3.67	0.20	0.81	5.58	0.68

3.6. Ecological risk assessment

Sediment quality guidelines (SQGs) were applied to qualitatively assess ecological risks caused by Pb, Zn and As concentrations to the benthic organisms. The **Table 8** shows the comparison of metal concentrations in the sediments against the TEC (Threshold effect concentration) and PEC (Probable effect concentration) guide values. Sediment samples with concentrations below the TEC concentrations have a percentage of 92.5%; 77.5%; 87.5% for lead, zinc and arsenic respectively (**Table 8**). Those with concentrations above the PEC concentrations have a percentage of 0%; 7.5% and 0% for lead, zinc and arsenic respectively (**Table 8**). These results indicate that the sediments are considered non-toxic to burrowing and benthic organisms for lead, zinc and arsenic. The evaluation of the ecotoxicological quality of the sediments by calculating the average PEC quotient (m-PEC-q) revealed that the average value of the average PEC quotient remains below 0.5, which classifies the sediments of the Fresco lagoon as being of good quality and non-toxic for burrowing organisms (m-PEC-q = 0.23 < 0.5). Therefore, the eco-toxicological risk remains low.

Table 8. Comparison of trace metal concentrations in the sediments against the TEC and PEC guide values.

	Pb	Zn	As
*TEC (mg/kg)	35.8	121	9.79
**PEC (mg/kg)	128	459	33
Mean values for the present study (mg/kg)	23.05	119.31	8.80
% < TEC	92.5	77.5	87.5
% > PEC	0	7.5	0

*TEC: *Threshold Effect Concentration*; **PEC: *Probable Effect Concentration*

4. CONCLUSION

The purpose of this study was to assess levels of lead, zinc, arsenic, manganese, and iron in sediment samples from Fresco Lagoon. The results indicated that, all metal concentrations in the sediments except for manganese were higher than those in the Upper Continental Crust due to anthropogenic activities. The falling trend of trace metals is Fe > Mn > Zn > Pb > As with respective average concentrations of 32731.29±25148.35 > 130.76±105.21 > 119.31±130.04 > 23.055±14.832 > 8.80±7.34 mg/kg. The principal component analysis and trace metal correlation matrix indicated that the sediment pollution was dominated by anthropogenic contamination and that trace metals were associated with organic matter and mainly with mud content coming from domestic and agricultural discharges. The metal Enrichment Factor (EF) and Geoaccumulation Index (Igeo) of arsenic showed that the sediments were classified as "not contaminated to moderately contaminated" with arsenic, whereas lead, zinc, manganese and iron were generally unpolluted. Moreover, the PLI and degree of contamination values showed higher values (PLI >1) at stations close to urban area, due to the influence of direct external sources like agricultural runoff, and other anthropogenic inputs. The ecological risk assessment for lead, zinc and arsenic indicated these metals posed to low risk to the aquatic ecosystem. A decontamination of the Fresco lagoon would therefore be necessary to avoid any risk caused by the diffusion of metals in the water column following a change in the physicochemical condition of the environment.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

REFERENCES

1. Chakraborty P, Ramteke D, Chakraborty S, Nath, BN. Changes in metal contamination levels in estuarine sediments around India–an assessment. Mar Pollut. Bull. 2014; 78:15–25. http://dx.doi.org/10.1016/j.marpolbul.2013.09.044.

2. Alves RS, Sampaio CF, Nadal M, Schuhmacher M, Domingo JL, Segura-Muñoz S. Metal concentrations in surface water and sediments from Pardo River, Brazil: human health risks. Environ Res. 2014; 133:149–155. http://dx.doi.org/10.1016/j.envres.2014.05.012.

3. Abidi M, Yahyaoui A, Ben Amor R, Chouba L, Gueddari M. Evaluation of heavy metal pollution risk in surface sediment of the South Lagoon of Tunis by a sequential extraction procedure. Sci. Mar. 2022; 86(1): e028. https://doi.org/10.3989/scimar.05172.028.

4. Windham-Myers L, Fleck JA, Ackerman JT, Marvin-DiPasquale M, Stricker CA, Heime WA, Bachand PAM, Eagles-Smith CA, Gill G, Stephenson M, Alpers CN. Mercury cycling in agricultural and managed wetlands: a synthesis of methylmercury production, hydrologic export, and bioaccumulation from an integrated field study. Sci. Total Environ. 2014; 484 :221–231. http://dx.doi.org/10.1016/j.scitotenv.2014.01.033.

5. Skorbi.owicz E, Rogowska W, Skorbi.owicz M, Ofman P. Spatial Variability of Metals in Coastal Sediments of E.ckie Lake (Poland). Minerals; 2022; 12, 173. https://doi.org/10.3390/min12020173

6. Liang X, Song J, Duan L, Yuan H, Li X, Li N, Qu B, Wang Q, Xing J. Source identification and risk assessment based on fractionation of heavy metals in surface sediments of Jiaozhou Bay, China. Marine Pollution Bulletin; 2018; 128: 548–556. https://doi.org/10.1016/j.marpolbul.2018.02.008.

7. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton D J. Heavy metals toxicity and the environment. Mol. Clin. Environ. Toxicol. 2012; 101: 133–164. DOI: 10.1007/978-3-7643-8340-4_6.

8. Guan Q, Wang L, Pan B, Guan W, Sun X, Cai A. Distribution features and controls of heavy metals in surface sediments from the riverbed of the Ningxia-Inner Mongolian reaches, Yellow River, China. Chemosphere; 2016; 144: 29 - 42. http://dx.doi.org/10.1016/j.chemosphere.2015.08.036.

9. Xie M, Alsina MA, Yuen J, Packman AI, Gaillard JF. Effects of resuspension on the mobility and chemical speciation of zinc in contaminated sediments. J. Hazard Mater. 2019; 364, 300–308. https://doi.org/10.1016/j.jhazmat.2018.10.043.

10. Tuo AD, Trokourey A, Yobou B. Spatial and Seasonal Trends of Trace Metals Diffusive Fluxes in Ebrié Lagoon, Côte d'Ivoire. Ijsrm. Human; 2020; Vol. 16 (1): 148-161.

11. Varol M. Environmental, ecological and health risks of trace metals in sediments of a large reservoir on the Euphrates River (Turkey). Environmental Research; 2020; 187, 109664. https://doi.org/10.1016/j.envres.2020.109664

12. Nishitha, D., Amrish, V.N., Arun, K., Warrier A. K., Udayashankar K. B., 2022. Study of trace metal contamination and ecological risk assessment in the sediments of a tropical river

estuary, Southwestern India. Environ Monit Assess. 2022 ; 194, 94. https://doi.org/10.1007/s10661-021-09728-1.

13. Anandkumar A, Nagarajan R, Gounder ES, Prabakaran K. Seasonal variation and mobility of trace metals in the beach sediments of NW Borneo. Chemosphere; 2022; 287,132069. https://doi.org/10.1016/j.chemosphere. 2021; 132069.

14. Sajimol S, Roy PD, Lakshumanan C, Nagarajan R. Evaluation of metals and trace elements in sediments of Kanyakumari beach (southernmost India) and their possible impact on coastal aquifers. Mar. Pollut. Bull. 2021; 169, 112527. https://doi.org/ 10.1016/j.marpolbul.2021.112527.

15. Takarina N. Geochemical fractionation of toxic trace heavy metals (Cr, Cu, Pb, and Zn) from the estuarine sediments of 5 river mouths at Jakarta Bay, Indonesia. Journal of Coastal Development; 2011; 13(2), 92–102.

16. Sankaré Y, Avit J-B, Egnankou W, Saenger P. Etude floristique des mangroves des milieux margino-littoraux de Côte d'Ivoire. Bulletin Jardins Botaniques Nationaux Belge; 1999; 67: 335 - 360. French.

17. Egnankou WM, Sankaré Y, CONARAMS-CI. Fiche descriptive sur les zones humides Ramsar (FDR), Fresco (Côte d'Ivoire). 2004. French

18. Institut National de la Statistique (INS). Répertoire des localités, région du Gbôklè. Récensement général de la population et de l'habitat. 2014 ; 27p. French.

19. Issola Y, Kouassi AM, Dongui BK, Adingra AA, Biemi J. Concentration en métaux lourds des sédiments d'une lagune côtière tropicale : lagune de Fresco (Côte d'Ivoire). Journal of Applied Biosciences. 2009; 18: 1009 – 1018. French.

20. Lalah JO, Ochieng EZ, and Wandiga SO. Sources of Heavy Metal Input into Winam Gulf, Kenya, Bull. Environ. Contam. Toxicol. 2008; 81, 277-284. DOI 10.1007/s00128-008-9452-3.

21. Heiri O, Lotter AF & Lemcke G. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolimnology. 2001; 25: 101–110. https://doi.org/10.1023/A:1008119611481.

22. Sakan SM, Djordjevic DS, Manojlovic DD, Polic PS. Assessment of heavy metal pollutants accumulation in the Tisza River sediments. J. Environ. Manag. 2009; 90, 3382–3390.

23. Wedepohl KH. The composition of the continental crust. Geochimica et cosmochimica Acta; 1995; 59(7), 1217-1232.

24. Müller G. Die Schwermetallbelstung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chemiker-Zeitung; 1981; 105, 157–164. National Research Council, 2000. The Toxicological Effects of Methylmercury. National Academy Press, Washington, DC.

25. Hakanson L. An Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach. Water Research; 1980; 14, 975-1001. http://dx.doi.org/10.1016/0043-1354(80)90143-8.

26. Syakti AD, Demelas C, Hidayati NV, Rakasiwi G, Vassalo L, Kumar N and Doumenq P. Heavy Metal Concentrations in Natural and Human-Impacted Sediments of Segara Anakan Lagoon, Indonesia. Environmental Monitoring and Assessment; 2015; 187, 1-15. http://dx.doi.org/10.1007/s10661-014-4079-9.

27. Tomlinson DL, Wilson JG, Harris CR and Jeffrey DW. Problems in the Assessment of Heavy-Metal Levels in Estuaries and the Formation of a Pollution Index. Helgoländer Meeresuntersuchungen, 1980; 33, 566-575. http://dx.doi.org/10.1007/BF02414780.

28. Macdonald DD, Ingersoll CG, Berger TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 2000; 39, 20.

29. Li X, Shen Z, Wai OW, Li YS. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. Mar. Poll. Bull. 2001; 42: 215-223. https://doi.org/10.1016/S0025-326X(00)00145-4.

30. Green-Ruiz C, and Paez-Osuna F. Heavy metal distribution in surface sediments from a subtropical coastal lagoon system associated with an agricultural basin. Bull. Environ. Contam. 2003;71: 52-59. DOI: 10.1007/s00128-003-0130-1.

31. Hernandez L, Probst A, Probst JL, Ulrich E. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Science of the Total Environment ; 2003 ; 312, 195–219.

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My Overall Evaluation

RAIMI Morufu Olalekan (Review Comment 11/05/2022)

Accepted with moderate revisions

This paper presents a study on **"Ecological risk link to trace metals levels in surface sediments from Fresco Lagoon, Côte d'Ivoire, Southern Africa".** This research aims to create a space to generate dialogue important in shaping and responding to trace metals levels in surface sediments about the drive in addressing its Ecological risk impact. The paper contains original and interesting information, which would attract civic-minded Scientist who are concerned with more than just advancing their careers. They want to make the world a better place, as much of the assessment are useful to the readers in the world at large. The results of this paper bring some useful information. The topic of this paper falls within the scope of the **International Research Journal of Pure and Applied Chemistry.** The contribution of this paper sounds good; the contents are well performed. **I would like to suggest the acceptance of this paper after moderate revision**. This is an engaging article that purposefully question our knowledge of the subject. Author write clear novelty related to topic Some detailed comments and suggestions are given as follows.

- The article title is appropriate.
- The abstract accurately reflects the content **but** Abstract should lay out five key points:
  Rationale (1-2 sentences) - why was the research needed?
  Objective (1 sentence)- what were you trying to provide to meet that need?
  Method(s) (up to 3 sentences) - briefly summarize what and which parameters were measured.
  Results (up to 4-5 sentences)- what did you find? Please add some data to demonstrate the findings.
  Conclusions/Recommendations (1 sentence) - so what should be done with or in response to your findings?
- Keywords is appropriate.
- The purpose or purported significance of the article is explicitly stated.
- The research study methods are explained clearly.
- The justification of the study is missing.
- There are few grammatical and spelling mistakes. Please double check you text and correct them all.
- Author Methodology provide context to the research. The author research methodology is presented sufficiently for better understanding. Methodologies used in the manuscript is describe clearly.
- All figures and tables are necessary and place appropriate.
- Novelty of the work is established.
- Separate Discussion section from Results. Rather than combining both together. This section must consist of following components: Describe the major findings of your study in the opening sentence. Correlation of your results with previous literature is essential. So, discuss your own results before relating them to the results of other published work. Then correlate your work with at least 7-8 recent publications either in support or in contradiction for justification of results.
- Use your distribution map to expand reader understanding why each of these variables matter and its implication.
- The conclusions is accurate and supported by the content.
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- **Significant Statement:** Please write the significance statement as follows: "This study discovered the ---- that can be beneficial for ---- and last sentence of this statement could be as: this study will help the researchers to uncover the critical areas of ---- that many researchers were not able to explore. Thus, a new theory on ----- may be arrived at"

This suggestion would strengthen the study further and when addressed will improve the manuscript.

Best regards,
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