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Quantification of the Few Parameters and Metallic Elements in the Quaternary Sediments of "Baie Du Repos" and their Interrelation

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ABSTRACT

Mauritania is a fishing country. However, the Mauritanian coast is increasingly exposed to environmental issues mainly due to anthropogenic activities such as the mining, gas, oil, and fishing industries, as well as new agricultural practices that unreasonably use inputs. Environmental monitoring of the Mauritanian coast faces several challenges; thus, improving the fisheries sector begins with enhancing the state of marine ecosystems and implementing environmental monitoring adapted to climatic conditions and local needs. This study aims to evaluate the quality of the sediments of the "Baie du Repos" in the town of Nouadhibou, Mauritania, through the study of organic matter and the quantification of trace metallic elements in the Quaternary sediments of the Bay. Six samples deemed representative of this Bay were taken and transported to the laboratory. The physicochemical analysis of these samples shows that the superficial horizons of 30 cm depth have overall organic matter contents higher than the average threshold value proposed by the literature for 4 out of 6 of the points studied. The contents recorded for the different metallic trace elements indicate that point 1 is the most exposed to contamination, with the highest concentrations of cadmium, lead, copper, iron, and zinc. The ACP (Principal Component Analysis) showed that the metallic trace elements Pb, Cu, Fe, Cd, and Zn are closely related and evolve positively in the same direction. Additionally, it was found that the points studied are divided into three groups: Group 1 contains only point 1, which is the most exposed to contamination by these toxic elements (Pb, Cu, Zn, Fe, and Cd). Group 2 contains points 3, 5, and 6, which are moderately contaminated by metallic elements with a significant dominance of organic matter (OM). Finally, Group 3 is the least contaminated, with a very high content of organic matter (OM).

INTRODUCTION

Seawater is considered an essential resource for life and, therefore, deserves preservation and particular attention, as it is exposed to various sources of anthropogenic contamination. Indeed, human activities have significantly impacted the marine ecosystem (Tornero & Hanke 2016). This includes acid mine drainage, fallout from atmospheric pollutants, gas and oil exploration activities, and effluent from industrial discharges, agriculture, and fisheries. The harmful effects caused by these organic and inorganic contaminants are consistently reported in the scientific literature and continue to be the subject of research (Nriagu & Pacyna 1988, Shirahata et al. 1980).

The physicochemical and metallic quality of the marine environment plays a crucial role in determining its biological quality and degree of contamination (Cebu & Orale 2017, Echapare et al. 2019). In this context, the "Baie du Repos" in Nouadhibou is exposed to discharges from the fishing and mining industries, which significantly contribute to the physicochemical and metallic contamination of the bay's waters.

This study aims to evaluate the degree of contamination in the "Baie du Repos." It proposes an analytical investigation to determine the content of metallic trace elements and organic carbon, as well as their correlation. The study focuses on metallic trace elements such as Cd, Pb, Zn, Cu, Al, Fe, and organic matter in the Quaternary sediments of the "Baie du Repos." To achieve this, six samples deemed representative of the bay were collected using a specialized sample collector. These samples were analyzed at the Chemistry Laboratory of the National Office for Health

Inspection of Fisheries and Aquaculture Products (ONISPA) in Nouadhibou, Mauritania.

MATERIALS AND METHODS

Sampling

Six samples considered representative of the “Baie du Repos” (Nouadhibou, Mauritania) were taken for this study. A portable GPS was used to determine the in-situ geographic coordinates of the sampling points. These Universal Transverse Mercator (UTM) coordinates were used with Google Earth Pro and ArcGIS 10.2.2 to produce a geographic map and perform spatial geo-referencing (Fig. 1). The sediment samples were taken from superficial horizons approximately 30 cm deep using a sediment grab, with each 500 g glass tube filled to the top. Fig. 1 shows the spatial location of the samples taken. All samples were conditioned in situ and then transported to the laboratory for analysis.

However, to avoid any contamination, the sample tubes were washed carefully with a solution of 1:1 HCl and 1:1 HNO3 and stored at 4°C in the refrigerator until their use (Abdallah & Adel 2015, Abdallah 2007, ASTM 1991)

Chemical Analysis

Each sample was analyzed in duplicate. The surface layer of the sediment, potentially oxidized by oxygen, was removed. Part of the sample was freeze-dried to analyze trace metal elements, while another part was air-dried. The dried sediment clods were then broken up using a plastic mortar and pestle, and the sediments were sieved to 2 mm to measure the organic matter.

Organic carbon (C_{org}) was determined according to the protocol of Walkley and Black (Centre d’expertise en analyse environnementale du Québec et ministère de l’agriculture et QUÉBEC 2003) to deduce the level of organic matter (OM). Metallic trace elements (MTE) (Cu, Fe, Zn, Pb, Al, and Cd) were determined after acid mineralization by atomic absorption spectrophotometry (ISO 15586 2003).

The analysis was carried out at the Chemistry Laboratory of the National Office of Sanitary Inspection of Fishing and Aquaculture Products (ONISPA) in Mauritania, in collaboration with the Laboratory of Marine Geosciences and Soil Sciences of the Faculty of Sciences at Chouaib Doukkali University (Morocco).

The analysis results were statistically processed using Xlstat software. Descriptive statistical analysis, linear regression, and principal component analysis (PCA) were performed to better describe the characteristics of the sediments in the studied Bay. The correlation between metallic elements and organic matter was also assessed using the Pearson method (Ling et al. 2023).

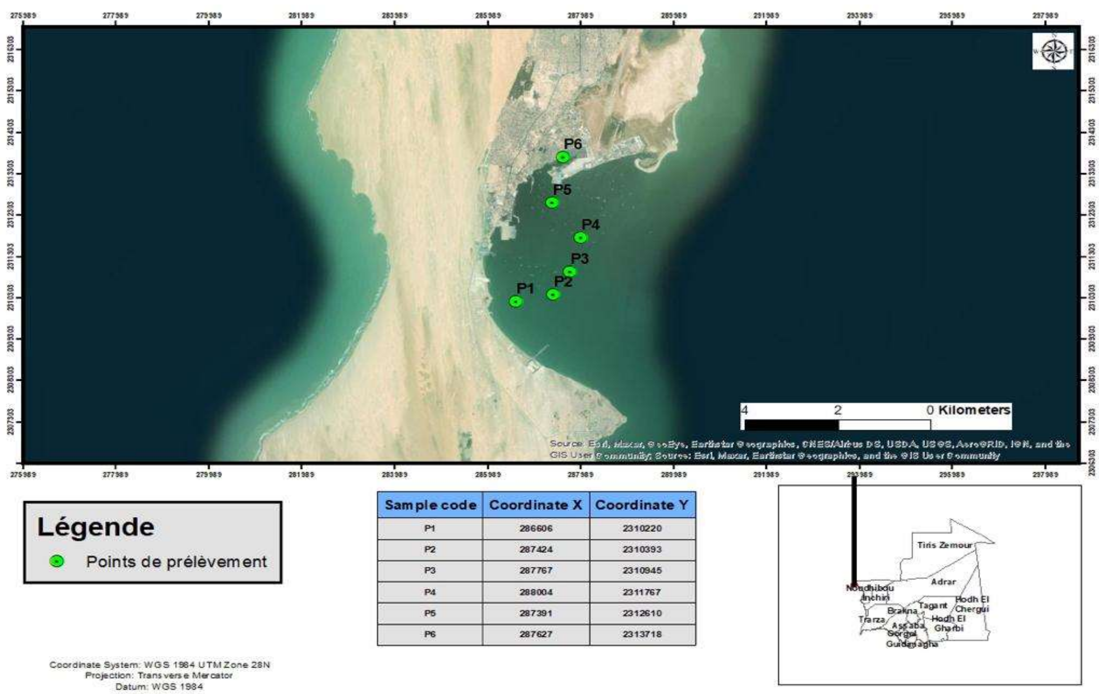

Fig. 1: Geographic location of the study area and sample location (sat image from Google Earth Pro).

Table 1: Content of metallic elements and organic matter.

Samples code	CO in %			OM in %			Cd in mg.kg^{-1}			Pb in mg.kg^{-1}		
	Trial 1	Test 2	Average	Trial 1	Test 2	Average	Trial 1	Test 2	Average	Trial 1	Test 2	Average
P1	5,274	5,178	5,226	9,093	8,927	9,010	0.922	0.905	0.914	17,545	18,785	18,165
P2	0.036	0.038	0.037	0.062	0.066	0.064	0.834	0.840	0.837	2,649	2,567	2,608
P3	4,629	4,611	4,620	7,980	7,949	7,964	0.089	0.093	0.091	0.635	0.629	0.632
P4	0.906	0.909	0.907	1,562	1,567	1,565	0.337	0.326	0.331	2,889	2,833	2,861
P5	6,010	6,080	6,045	10,361	10,482	10,421	0.143	0.150	0.146	0.681	0.722	0.702
P6	7,050	7,090	7,070	12,155	12,223	12,189	0.425	0.431	0.428	3,108	2,981	3,045
Samples code	Cu in mg.kg^{-1}			Fe in mg.kg^{-1}			Zn in mg.kg^{-1}			Al in mg.kg^{-1}		
	Trial 1	Test 2	Average	Trial 1	Test 2	Average	Trial 1	Test 2	Average	Trial 1	Test 2	Average
P1	1,964	1,989	1,976	21207,386	22289,519	21748,453	2800.15	2791.36	2795,754	5574,802	5667,649	5621,225
P2	0.593	0.582	0.587	14928,624	14593,489	14761.056	990.81	991.40	991,106	6854,563	7008,354	6931,459
P3	0.210	0.206	0.208	2496,887	2357,139	2427.013	48.56	47.62	48,086	4871.016	4945,839	4908,428
P4	0.198	0.200	0.199	13351,792	12949,629	13150.711	282.48	280.66	281,571	5746,640	5505,935	5626,287
P5	0.126	0.130	0.128	3399.079	3297,534	3348,306	133.13	134.14	133,635	6318,815	6238,190	6278.503
P6	0.314	0.314	0.314	12578.980	12811.009	12694.995	406.72	406.31	406,514	4997,512	4992,545	4995.029

RESULTS AND DISCUSSION

The results, presented in Table 1, show the concentrations obtained for the samples taken from six points considered representative of the Bay.

Organic Materials

The results presented in Table 1 show that the percentages of the parameters and metal concentrations vary slightly at different points. Notably, 4 out of 6 of the sediment samples have organic matter (OM) contents greater than 2% (Fig. 2). The high levels of OM in the Bay are primarily due to discharges from the fishing industries (Bouyer & Dabin 1963).

The Metallic Trace Elements Cd, Pb and Cu

For cadmium, the highest values were obtained in the sediments of points 1 and 2, which are respectively of the order of 0.914 mg.kg^{-1} and 0.837 mg.kg^{-1}, while the lowest concentrations, which were identified are 0.146 mg.kg^{-1} and 0.091 mg.kg^{-1}, respectively for points 3 and 5. Generally, there does not seem to be a significant difference between the six points sampled. For lead, the sediments have high levels, particularly in point 1 (18.165 mg.kg^{-1}), which is notable in the histogram as shown in Fig. 3. This is essentially due to the presence of factories and thermal centers in the vicinity of point 1. These factories dispose of their industrial waste directly into the Bay. Regarding copper, its content in the sediments is higher in point 1 (1.9764 mg.kg^{-1}) than in the other points, 0.587; 0.314; 0.208; 0.199, and 0.128 mg.kg^{-1}, respectively, for points 2, 6, 3, 4 and 5 (Ouaty et al. 2022, Wang et al. 2022).

Contents of Metallic Elements Fe, Zn and Al

For the three metallic elements Fe, Zn, and Al, we see that their maximum concentrations are identified at point 1. These contents are 21748, 453, 2795.754, and 5621.225 mg.kg^{-1}, respectively, which denotes the effect of these factories on the environment of Rest Bay, especially at points 1 and 2 (Fig. 4). This proves the presence of iron and aluminum in the marine environment at very high concentrations (Abdallah & Adel 2015, Armstrong-Altrin et al. 2015, Lopes-Rocha et al. 2017).

This heterogeneity in the distribution of these parameters is primarily due to the locations of the points, with those closest to the shore being more exposed to contamination.

The results found in the sediments of Rest Bay (Table 2) were compared with results from several bays located on different continents to evaluate the results found in the sediments of Rest Bay (Table 3). The concentrations of

Pb and Cu were observed to be lower than all the comparison results. However, the average Cd content recorded in 'Baie du Repos' is lower than all comparison concentrations except for Beibu Bay in China. For Zn, the comparison shows that 4 out of 6 concentrations are lower than the average Zn value obtained in the sediments of the bay studied, while 2 out of 6 are higher.

Fig. 5 illustrates the significant correlation curves observed in the correlation matrix, highlighting significant correlations between zinc and the following elements: cadmium (Cd), copper (Cu), iron (Fe), and lead (Pb). Additionally, significant correlations are observed between iron (Fe) and cadmium (Cd), as well as between copper (Cu) and lead (Pb). Therefore, the correlation curves indicate that 4 out of the 6 elements studied exhibit significant correlations with zinc.

Correlation Between Metallic Elements and Organic Matter

Principal component analysis (PCA) established a correlation between several elements studied in the sediments from the Bay, with a correlation coefficient of R = 0.80 at the 5% significance level. This provides a better understanding of the possible results and sources affecting the studied system (Alves et al. 2018, Garcia et al. 2023, Tripathi & Singal 2019) (Table 4).

According to the correlation matrix, we can make the following observations: Zinc is well correlated with all metallic

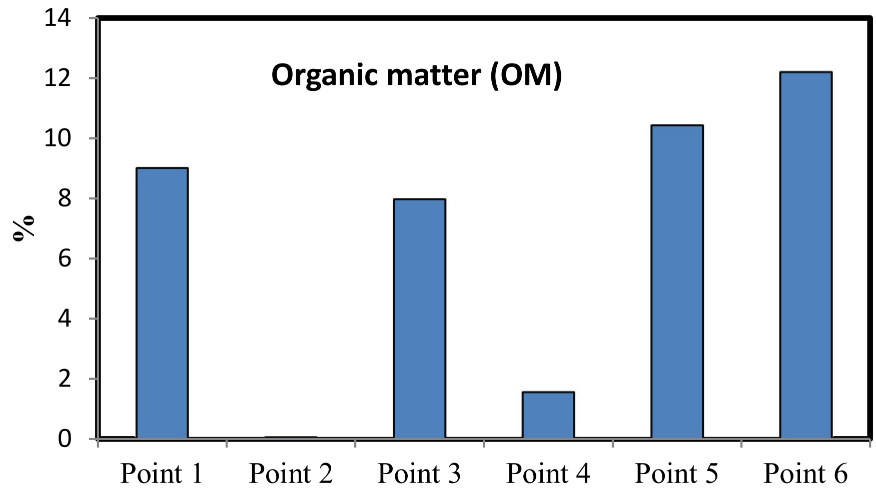

Fig. 2: Percentage of organic matter.

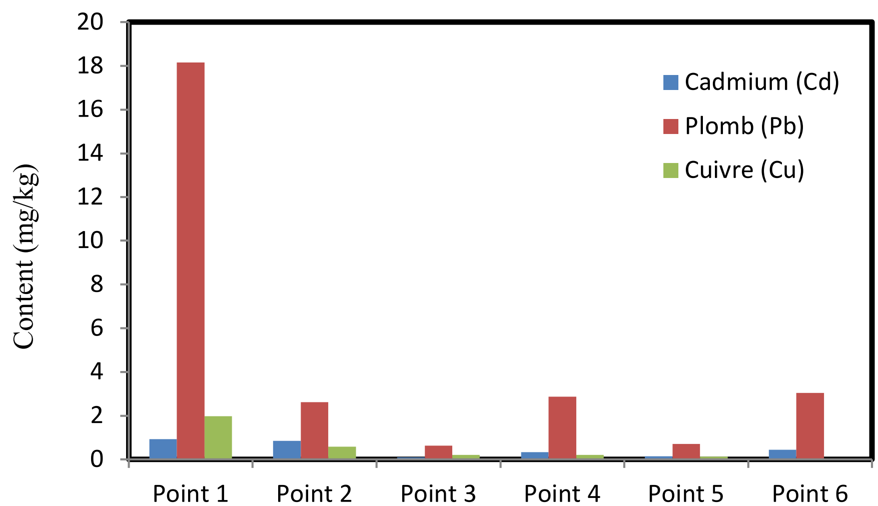

Fig. 3: Content of trace metal elements.

elements except aluminum. This could be explained by the fact that zinc likely shares the same source as cadmium (Cd), copper (Cu), iron (Fe), and lead (Pb). On the other hand, aluminum (Al) shows a very low correlation with all the elements.

As for cadmium (Cd), the correlation matrix indicates that it is strongly correlated with iron and moderately correlated with zinc (Zn), copper (Cu), and lead (Pb). Conversely, it is only slightly correlated with aluminum (Al). The latter elements are considered lithological (natural) elements, unlike the others, which originate from contaminating industrial sources.

Principal Component Analysis (PCA)

For a relevant graphical visualization of the correlations and to ensure access to all interactions between the variables, a PCA was performed. Fig. 6 displays the observations in a new coordinate system, with component 1 as the abscissa and component 2 as the ordinate. The PCA results reveal groupings, oppositions, and directional trends. The F1 axis accounts for 56.42% of the variance and contrasts MO with aluminum (Al). Meanwhile, the other metallic trace elements Cu and Zn are closely linked, evolving positively in the same direction and differentiating along the F1 axis.

Axes F1 and F2, therefore, present, respectively, 56.42% and 32.47% affinity between the elements studied from different points. The variables Pb, Cu, Zn, Fe, and Cd are well represented and positively correlated in the correlation circle and approach the axis F1 of positive coordinate. The aluminum variable Al is very close to the axis F2.

Fig. 7 illustrates the distribution of the different points studied in relation to the PCA axes. The points are divided into three groups: Group 1 contains only point 1, which is the most exposed to contamination by toxic elements (Pb, Cu, Zn, Fe, and Cd). Group 2 includes points 3, 5, and 6 and is characterized by moderate contamination with a significant presence of organic matter (OM). Finally, Group 3 is the least contaminated but has a very high content of organic matter (OM). The results reveal a slight correlation between organic matter and these metallic trace elements (Elmokhtar et al. 2021, Tiquio et al. 2017).

CONCLUSION

The values of the parameters obtained in 'Baie du Repos'

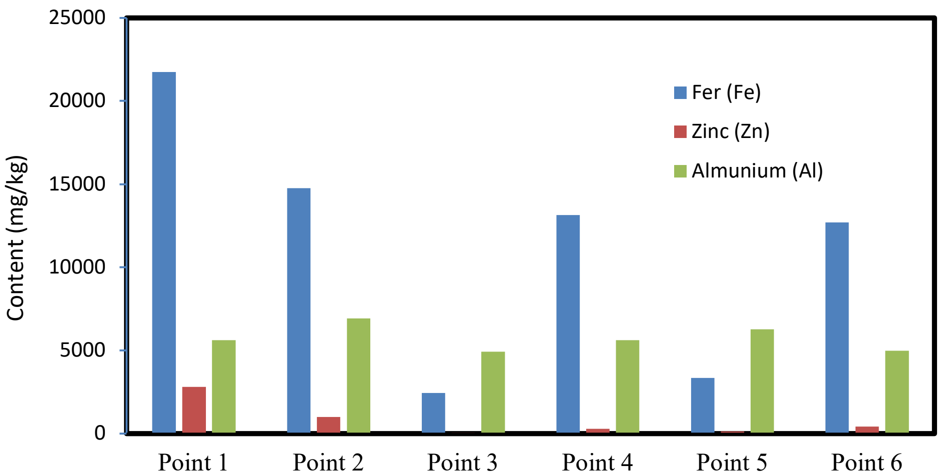

Fig. 4: Content of metallic elements.

Table 2: Descriptive statistics.

Statistical	Cd in mg.kg^{-1}	Pb in mg.kg^{-1}	Cu in mg.kg^{-1}	Fe in mg.kg^{-1}	Zn in mg.kg^{-1}	Al in mg.kg^{-1}	CO in %	MO in %
Minimum	0.091	0.632	0.128	2427.013	48,086	4908,428	0.037	0.064
Maximum	0.914	18,165	1,976	21748,453	2795,754	6931,459	7,070	12,189
Average	**0.458**	**4,669**	**0.569**	**11355.089**	**776,111**	**5726,822**	**3,984**	**6,869**
Standard deviation (n)	0.317	6,115	0.646	6689.063	952,991	704,988	2,607	4,493
Asymmetry (Pearson)	0.356	1,685	1,597	-0.030	1,430	0.463	-0.474	-0.474
Flattening (Pearson)	-1.476	1,021	0.820	-1.145	0.469	-1.020	-1,398	-1,398

Table 3: Comparison of heavy metal concentrations in "Baie du Repos" with values from other studies ($mg.kg^{-1}$).

Continent	Region	CD	Pb	Cu	Zn	Year	References
Africa	Eastern harbor (Egypt)	0.79	82.50	53.44	1588.59	2007	(Abdallah 2007)
Africa	Western Harbor (Egypt)	8.09	53.59	-	305.38	2007	(Abdallah et al. 2007)
Europe	Thermaikos Gulf (Greece)	-	77.0	80.1	184.1	2009	(Christophoridis et al. 2009)
Asia	Coastal Bohai Bay (China)	-	34.7	38.5	131.1	2012	(Gao & Chen 2012)
Asia	Beibu Bay (China)	0.16	27.99	58.26	67.28	2013	(Dou et al. 2013)
Africa	AbuQir Bay (Egypt)	17.21	56.05	12.07	8532	2014	(Abdallah & Mohamed 2015)
Africa	Baie du Repos (Mauritania)	**0.458**	**4,669**	**0.569**	**776,111**	**2022**	**Current study**

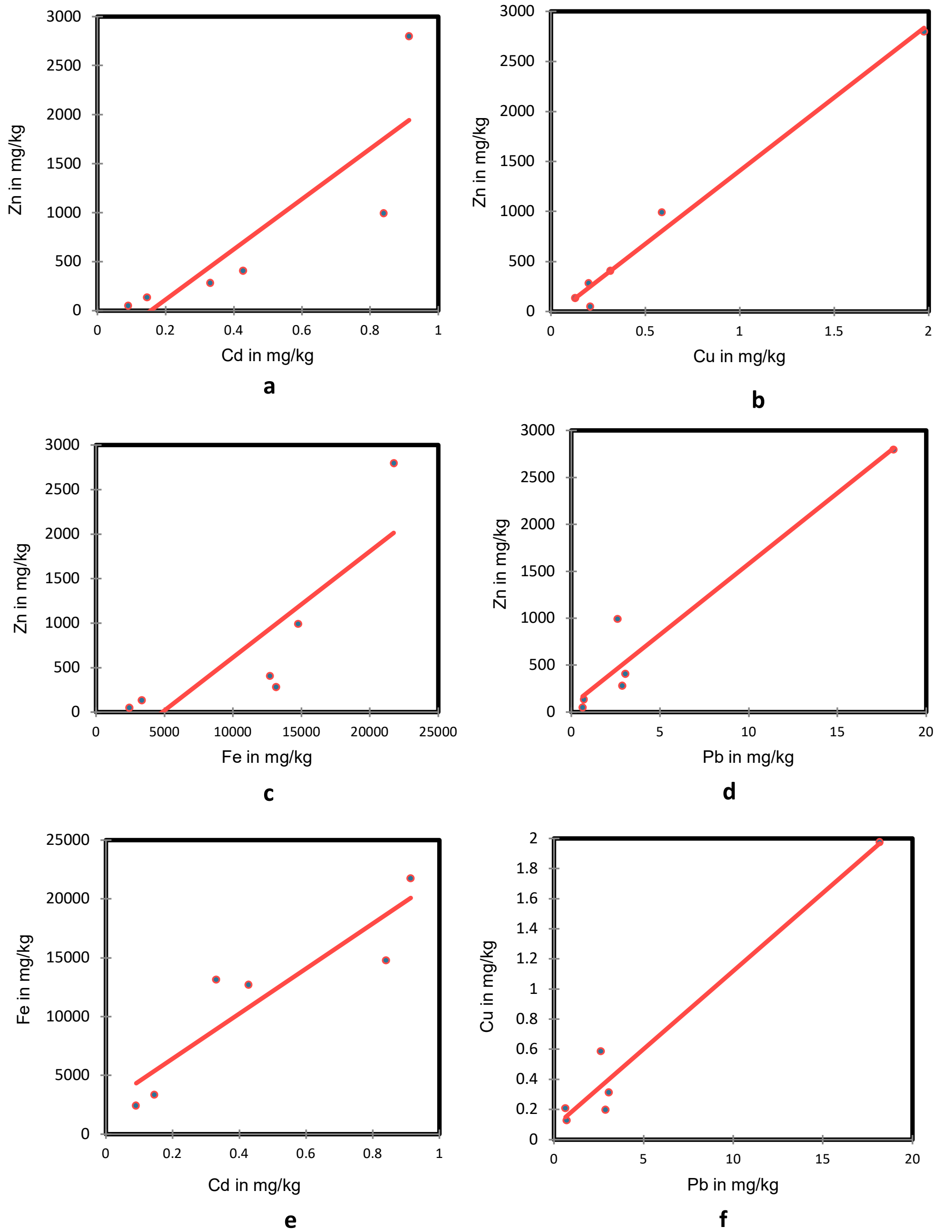

Fig. 5: Curves of significant correlations observed in the correlation matrix.

for the six points covered by this study allow us to make the following observations: significant levels of organic matter were found at the different sampled points. Additionally, observations were made regarding the metallic elements.

For cadmium, the highest value was obtained in the sediments of point 1, which is of the order of 0.914 $mg.kg^{-1}$. However, for lead, the sediments studied have high levels, particularly in point 1 (18.165 $mg.kg^{-1}$). And also, it is the same for copper, which is of the order of 1.9764 $mg.kg^{-1}$ in point 1. As for the two metallic elements, Iron and Zinc, we also see that their maximum concentrations have been identified in point 1. These contents are respectively 21748, 453, and 2795.754 $mg.kg^{-1}$. On the other hand, the highest Aluminum content was identified in point 2.

The results show that point 1 is the most exposed to sources of pollution. In contrast, point 3 contains the lowest levels of metallic elements, likely due to its geographical position, which benefits from natural aeration. This factor is more significant here than at other points, leading to continuous dilution of the metallic elements' concentrations. According to the correlation matrix, all elements except aluminum are well correlated with zinc. Aluminum (Al), however, shows a very low correlation with all other elements due to its natural (lithological) origin. For cadmium (Cd), the correlation matrix indicates a strong correlation with

Table 4: Correlation matrix of physicochemical parameters of the sediments studied.

Variables	Cd in $mg.kg^{-1}$	Pb $mg.kg^{-1}$	Cu in $mg.kg^{-1}$	Fe in $mg.kg^{-1}$	Zn in $mg.kg^{-1}$	Al in $mg.kg^{-1}$	CO in %	MO in %
Cd in $mg.kg^{-1}$	**1**							
Pb in $mg.kg^{-1}$	0.719	**1**						
Cu in $mg.kg^{-1}$	0.792	**0.980**	**1**	**1**				
Fe in $mg.kg^{-1}$	**0.908**	0.797	0.788					
Zn in $mg.kg^{-1}$	0.852	0.967	0.993	0.836	1			
Al in $mg.kg^{-1}$	0.429	-0.055	0.055	0.167	0.151	**1**		
CO in %	-0.307	0.154	0.088	-0.230	0.017	-0.564	**1**	
MO in %	-0.306	0.154	0.088	-0.230	0.017	-0.564	**1,000**	**1**

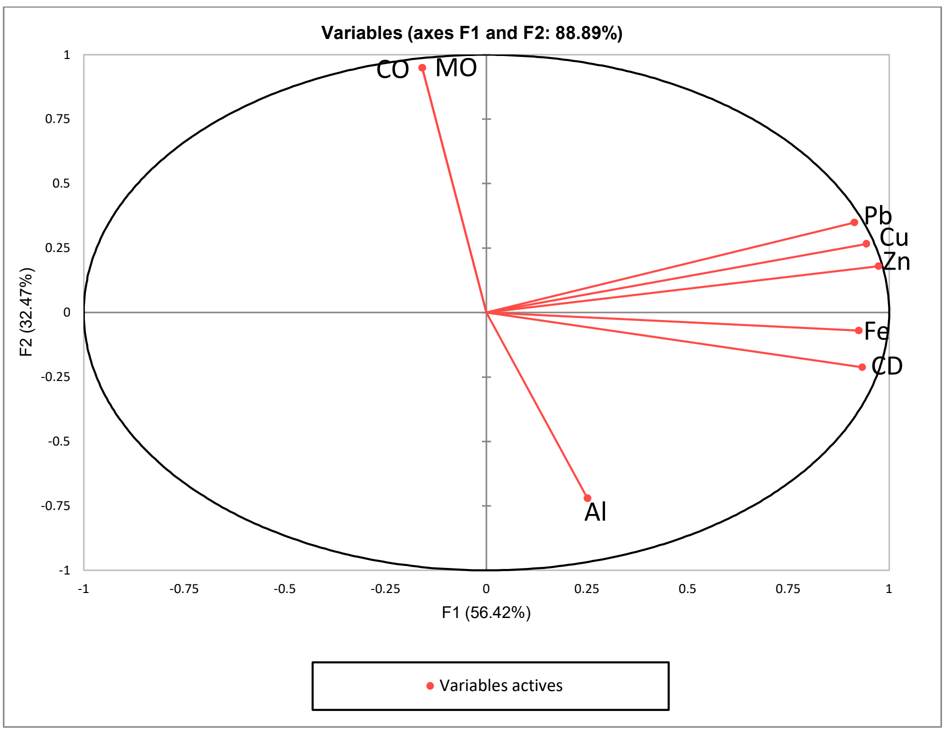

Fig. 6: Analysis of the principal components of the physicochemical variables of the sediments.

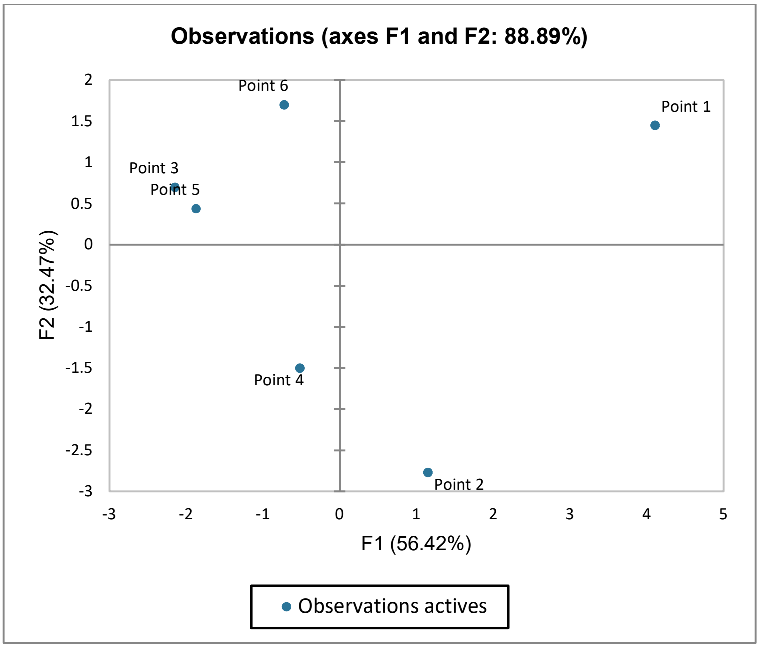

Fig. 7: Plots of scores based on mean values for each principal component analysis (PCA).

iron and a moderate correlation with copper (Cu), lead (Pb), and zinc (Zn).

To enhance this investigation, it should be complemented by a study focusing on the hydrochemical characteristics of the Bay to determine both the degree of anthropogenic activity and the main constraints affecting the ecosystem of "Baie du Repos."

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