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ASSESSMENT OF THE IMPACT OF INDUSTRIAL DEVELOPMENT AT THE COAST OF LÉVRIER BAY THROUGH THE SPATIO-TEMPORAL STUDY OF METALLIC CONTAMINANTS (CD, PB, CU, ZN AND HG) IN SURFACE SEDIMENTS

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ABSTRACT:
Lévrier Bay is located at the northern Atlantic Mauritanian coast, between 19 ° 20'N and 20 ° 40'N and between the coast and 17 ° 20W in the vicinity of Cap Blanc peninsula. This work aims at contributing to the assessment the impact of industrial development in the Lévrier Bay through the study of the toxicity and the spatio-temporal distribution of trace metals (Cd, Pb, Cu, Zn and Hg) in surface sediments, during the four hydrological seasons. The trace metal concentrations of the sediments are generally heterogeneous and vary according to the metal analyzed and the sampling site according to the order Zn> Cu>Pb> Cd>Hg. In fact, the present work shows higher average concentrations of metals studied in surface sediments than those found for the same metallic elements in previous recent studies at Lévrier Bay, which may be due to anthropogenic pressure in these areas. , especially since the different sites of the Bay are deprived of any sanitation system. In addition, the levels of these metals in the sediments of Lévrier Bay are below the international standards recommended for the toxicity assessment of sediments.

Key-words: *Sediment, Trace metals, Industries, Seasons, Lévrier Bay*

1. INTRODUCTION

The fisheries sector is one of the pillars of Mauritania's economy and the main activities related to this sector are located in the Lévrier Bay. The Lévrier Bay is located at the northern Atlantic Mauritanian coast, between 19 ° 20'N and 20 ° 40'N and between the coast and 17 ° 20W in the vicinity of Cap Blanc peninsula. (Fig.1).In addition, this area includes two natural sites of great ecological importance, notably the Cap Blanc satellite reserve, classified as World Heritage (recognized for its role in protecting the last viable colony of Mediterranean monk seals) and the Baie de l'Etoile, site recognized by IUCN and candidate to be classified Marine Protected Area (IUCN, 2008). This area is characterized by four hydrological seasons. They have been identified in the context of studies carried out in Mauritanian marine waters (Dubrovin et al.1991; Wagne et al.2011; Wagne et al.2013), namely, the cold season (January to May) and the hot season (August to October). These are interspersed by two inter-seasons, hot-cold (from June to July) and cold- hot (from November to December).

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The Lévrier bay is under heavy human pressure because of the economic activities. Indeed, the installation of fishing companies such as fishmeal and fish oil factories which represent 32 factories in more than 70 establishments for processing fishery products intended for human consumption (WebgateEU2019). These pressures are, among other things, at the origin of several types of industrial discharges at sea, such as 2,388 active canoes (IMROP 2019), the presence of four main ports (fishing, trade, mineral and petroleum), in addition to domestic discharges are all potential sources of chemical pollution (Dartige and OuldDedah1996;Belin and Le Gal2005). These various urban and industrial wastes are directly dumped into the marine environment in the absence of any sanitation system. In addition, Zamel et al. 2010 have shown that 75,632 m3 of wastewater are discharged daily into the bay, including 3 m3 of oily water and 51,755 tons of solid discharge which constitute a major source of pollution, harmful to the bay environment. In the aquatic and coastal environment, numerous studies have shown that trace metals are used to reveal the level of anthropogenic influence, because they are persistent, toxic and have a tendency to bioaccumulate that which constitutes a risk for biotas and ecosystems (USEPA 2002; Memet 2011; Diop et al. 2012; Liang et al.2013).

In Mauritania, numerous studies on the state of contamination of the Atlantic coasts of Nouadhibou (Lévrier Bay) by trace metals in biological tissues have been carried out, notably in bivalve filter molluscs (Sidoumouet al.1992; Dardige2006; Wagneet al.2013; M'Hamada et al.2014; Legraa et al.2019). For the first time a study using the sediment matrix over two seasons only (cold season and hot season) during 32 months from January 2013 to October 2016 (Legraa et al.2019) has been conducted. For the sake of contributing to the evaluation of the impact of industrial development at the level of the Lévrier Bay, the present study was conducted, to assess the toxicity and the spatio-temporal distribution during the four hydrological seasons in the surface sediment matrix. To give a better visibility of the space-time distribution, we will compare our results with those found by authors cited above.

2. MATERIALS AND METHODS

2.1. Sampling

Depending on the nature of the industrial activities, eight sites (discharge points) were chosen according to the nature of the discharges from the source of pollution, at the Lévrier Bay (**Fig. 1**). The different sampling sites were subject to seasonal monitoring and the characteristics of the sampled sites are as follows:

- Bountiya (hereafter BONT): area of agglomeration of fishmeal and fish oil production factories, which generate several types of discharges such as: waste water, organic matter, solid discharges and cooling water, etc.
- Port Artisanal (hereafter EPBR): home port and landing of canoes and coastal vessels intended for artisanal fishing generating the main discharges which may contain oils, fuel, detergents, waste water (untreated) and solid waste.
- Centrale électrique [fr] (Powerplant, hereafter CE): main thermal power station, which supplies electricity to the Nouadhibou city including the discharge of hot and contaminated water.
- Port minéralier [fr] (Mineral port, hereafter PM): main port for loading iron ore.
- SNIM 1 (Port minéralier = Mineral port): tidal balancing area near the mining port
- SNIM2 (Port minéralier = Mineral port): tidal balancing area near the mining port further offshore.
- Cap Blanc coast (hereafter CBC): witness sites (absence of industries).
- Cap Blanc large (hereafter CBL): the tip of Cap Blanc, which is a tidal balancing area.

We carried out 3 sampling sat each site and per hydrological season during the period from June 2016 to December 2017. The offshore sediment sampling was carried out on board of a research boat (Amrigue), using an Eckman type grab whose jaws close automatically, thus collecting the substrate (sediment), over an area of 1,225 m². In the coastal area, the sediments were collected on a canoe board, using an Eckman type grab over an area of 0,225 m^2, however, at the sampling sites located on the coast (intertidal area), surface sediments were collected using a PVC cover with 66 mm in diameter and 50 cm in length over a depth of 5 cm.

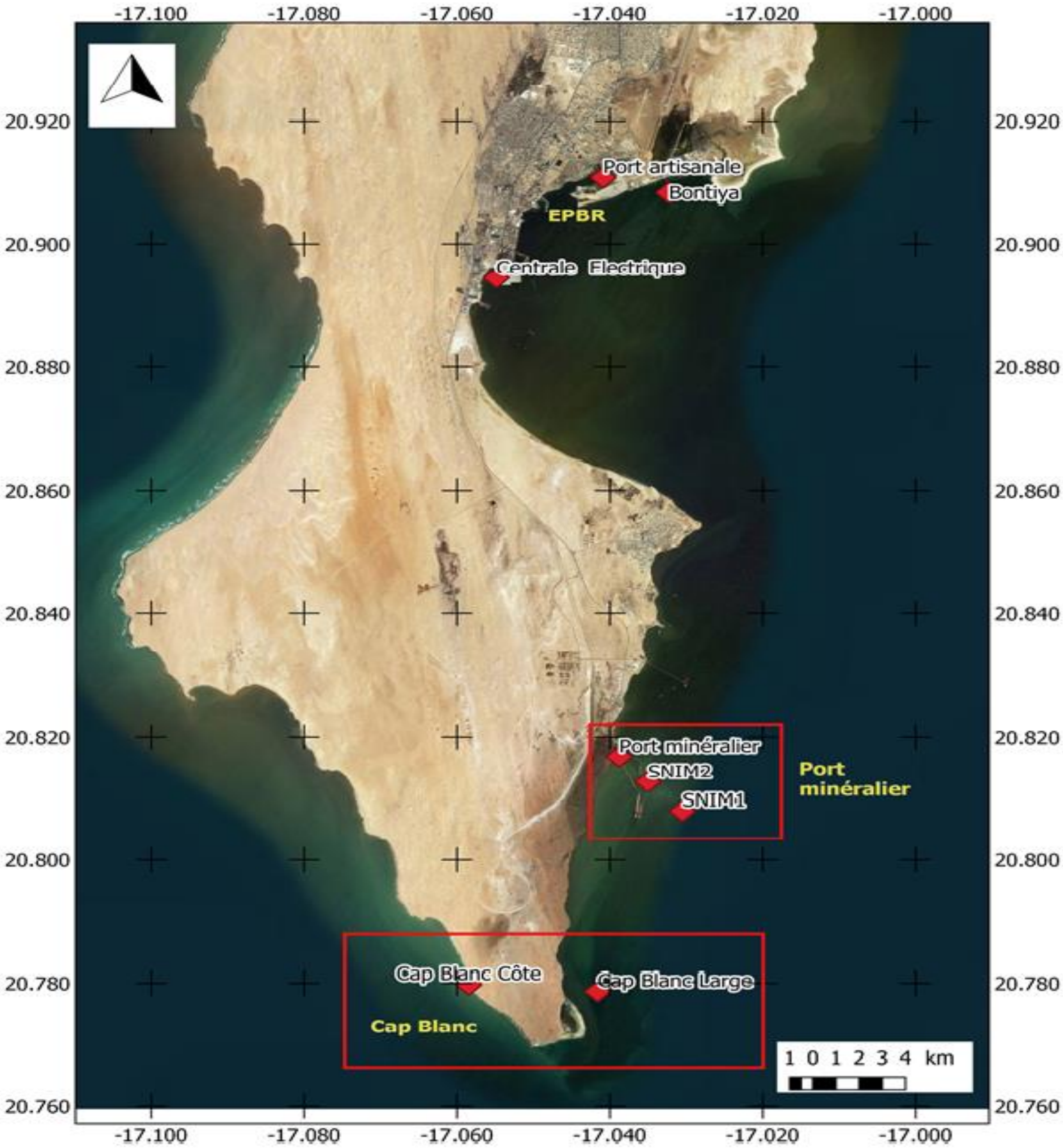

Fig.1. Location of the study area and sampling sites.

2.2. Sample preparation and analytical procedure

Samples of 0.5 g were digested by duplicate, then, were placed in microwave closed-vessels with a mixture (6:2) of ultra-pure nitric acid 67% and hydrogen peroxide 30% at room temperature for one hour and then extracted by microwave. Digestion conditions applied in the microwave system were as follows: 3 min at 250 W, 5 min at 650 W, 22 min at 500 W, 5 min at 0 W and vent. The digested samples were diluted to 50 mL with deionized water (Milli-Q quality).

The analysis of Pb, Zn, Cu and Cd were conducted using an atomic absorption spectrometer with furnace graphite (LOD of 0.046 for Pb and 0.004 µg·g-1 for other elements), according to the ISO 15586:2003. Hg was analyzed using Direct Mercury Analyzer (LOD=0.003µg/g), according to the method “MA.207–Hg 2.0, (Centre d’expertise en analyse environnementale du Québec).

The potential presence of trace metals in the chemicals that were used during the digestion was determined. Blanks were run simultaneously in each batch analysis to authenticate the analytical quality. All of the glassware and plastics were soaked overnight in 10% (v/v) nitric acid, rinsed with distilled and deionized water and dried before being used. The potential presence of trace metals in the chemicals that were used during the digestion was determined. Blanks were run simultaneously in each batch analysis to authenticate the analytical quality. All of the glassware and plastics were soaked overnight in 10% (v/v) nitric acid, rinsed with distilled and deionized water and dried before being used.

Samples were mineralized by nitric acid (67%) mixed with hydrogen peroxide (30%) and then the extraction was carried out using an Anton- Paar microwave model Multiwave-3000.

Atomic Absorption Spectrometer (AAS, Perkin Elmer AAnalyst 800) and Direct Hg Analyzer (DMA-80, Millstone) equipment was used to analyze the trace metals. The certified standard reference material for sediment samples (BCR 146R) was used, it shows recoveries varied from 93% to 113% of certified values (**Table** 1).

Table 1.

Measured and certified values of metal concentrations (mg/kg).

	Cd	**Pb**	**Cu**	**Zn**	**Hg**
n	4	4	4	4	4
Measured value	18	569,7	966,7	2839,3	7,6
certificate value	18 ± 0.5	609±14	838±16	3060±60	93
Recovery (%)	102	94	116	93	90,5

2.4. Statistical analysis

All data were imported and statistically processed in the SPAD software (version. 5) and Excel 2016. The trace metal concentrations in the sediments were compared at the different sites in the study area and during the hydrological seasons (Spatio-temporal distribution). The study of variations of intra-site and inter-site, trace metals as well as the correlations study between trace metals (PCA) were carried out.

3. RESULTS AND DISCUSSION

The results obtained relate to the variations in trace metals concentrations (Cd, Pb, Cu, Zn and Hg) in the surface sediments of the sampling sites exposed to different industrial and urban discharges and then the results found are presented in **Table 2**.

Cadmium (Cd) variations were found for the lowest value at 0.00 mg / kg at the CE, while the largest value (0.58 mg / kg) was recorded at the CBL offshore. In addition, the average minimum and maximum concentrations recorded for Cd are respectively: (0.04 ± 0.014 mg / kg and 0.265 ± 0.078 mg / kg) at CE and EPBR. The important significant variations of Cd concentrations (0.04 to 0.58 mg / kg; 0.07 to 0.42 mg / kg; 0.03 to 0.39 mg / kg and 0.14 to 0.38 mg / kg) by site are recorded, respectively, at CBL, EPBR, PM and BONT. While the lowest variations of Cd concentrations (0.00 to 0.07 mg / kg and SNIM1 0.08 to 0.2 mg / kg) were found in the CE site, we note nevertheless the absence of variation of the Cd concentration values at the SNIM2.

Table 2.

Concentrations of trace metals (mean ± Standard deviation: mg/kg) in sediments for the studied sites.

Sites	Cd	Pb	Cu	Zn	Hg
EPBR	0,265±0,078	5,7±2,924	11,284±4,903	47,245±16,835	0,008
CE	0,04±0,014	2,125±0,880	4,434±1,028	9,185±1,939	0
BONT	0,225±0,053	1,017±0,393	3,337±1,319	15,445±6,906	0,001
PM	0,142±0,084	1,722±0,719	11±3,214	5,137±2,072	0
CBC	0,11±0,054	0,555±0,306	6,505±4,760	5,105±0,995	0
SNIM1	0,137±0,030	1,135±0,401	4,862±1,180	15,035±4,131	0
CBL	0,202±0,126	0,647±0,294	4,317±3,400	5,85±1,774	0
SNIM2	0,147±0,012	0,637±0,126	2,775±0,745	8,397±3,869	0

According to Bowen (1966) the concentration in natural seawater is around 0.1µg/l and comes mainly from petrochemical or metallurgical industrial activities (Odin1995). Our results for Cd contain a maximum average concentration (0.265 ± 0.07 mg/kg), these results are very close to those in the sediments of Dakar coast (0.270 mg / kg) reported by Diop et al. 2014. But the maximum average value Cd concentration (0,130±0,070) found by Legraa et al. (2019) at Etoile bay which is part of the Lévrier bay, could lead us to say that the Cd comes from a source of pollution such as the deposit of industrial and anthropogenic discharges and the current discharge in the EPBR.

Although other sources of the Cd are not excluded, such as the permanent presence of upwelling in the Cap Blanc area, the results found by (Kaimoussi et al.2000) in the coastal marine sediments of the Atlantic coast of the region of EL Jadida in Morocco (0.75 mg/kg) and those reported by (Belabed et al.2013) in the sediments of the Gulf of Annaba in Algeria displayed Cadmium contents (0.02 to 2.2 mg/kg).

The lowest Pb concentration was found at the CE (0.00 mg/kg), while at the EPBR the Pb displayed its highest value (12.11 mg/kg). Yet the mean minimum and maximum Pb concentrations (0.555 ± 0.306 mg/kg to 5.7 ± 2.924 mg/kg) are recorded respectively at the CBL and at EPBR. The highest concentrations of Pb (0.00 to 12.11 mg/kg; 0.00 to 4.11 mg/kg and 0.00 to 3.10 mg/kg) are respectively recorded at (EPBR, CE and PM), while the lowest concentration (0.00 to 0.82 mg/kg) were found at SNIM2. The high concentrations of Pb can be mainly due to the port activity through the wide use of lead in fishermen's nets and the high fuel consumption by motor boats as well as the nature of the hull paints of the different boats. Lead concentrations in sediments are not high compared to the threshold for unpolluted sediments which is 30 mg/Kg (OSPAR, 1997).

The lowest Copper (Cu) concentration (0.09 mg/kg) was found at CBL, while the highest most concentration (24.40 mg/kg) was recorded at the EPBR. In addition, the average concentrations of Cu (2.775 ± 0.745 mg/kg and 11.284 ± 4.903 mg/kg) were recorded respectively at SNIM2 and the EPBR site. The significant variations in Cu concentrations (3.52 to 24.40 mg/kg; 0.80 to 20.74 mg/kg; 3.70 to 19.15 mg/kg; 1.03 to 6.70 mg/kg and 2.74 to 6.99 mg kg) were recorded respectively at EPBR, CBC, PM, CE, BONT and SNIM1. The average concentration of Cu (11.284 ± 4.903 and 11 ± 3.214 mg/kg) were respectively recorded at EPBR and PM, indeed, Cu is considered like an urban pollutant (Pichardetal. 2005), then, these high concentrations can be explained by a high contribution of industrial discharges and urban domestic waste from Nouadhibou city without any sanitation system.

The variations in Zinc (Zn) found for the lowest values at 0.00 mg/kg at the BONT site and SNIM2, while the most important value at 77.2 mg/kg was recorded at the EPBR level. In addition, the average concentrations Minimum and Maximum recorded for Zinc are respectively 5.105 ± 0.995 mg/kg in the two sites (CBC and SNIM2) and 47.245 ± 16.835 mg/kg in the EPBR. Although, the average maximum metal concentrations of Zn at BONT and EPBR do not exceed the guideline values of surface sediments toxicity, they remain higher than those at (CE, PM, SNIM and CB) sites, which can be explained by the pressure due to artisanal canoes and coastal boats at EPBR area and the regrouping of fishmeal and fish oil production factories in the BONT area. In fact, these two zones are deprived of any drainage system, in addition to the weak currentology in the Lévrier bay.

The high concentration of Zn was recorded at EPBR while the lowest concentration was fond at BONT and SNIM2. In addition, the minimum and maximum average Zn concentrations (4.72 to 77.2 mg/kg; 00.0 to 30.20 mg/kg; 2.87 to 21, 30 mg/kg; 0.00 to 16.30 mg/kg; 4.72 to 13.2 mg/kg; 0.52 to 10.6 mg/kg) were recorded respectively at the EPBR, BONT, SNIM2, EC and PM.

In the present study, all mercury (Hg) concentrations are below the detection limit (<0.0058) for all sites and during all seasons with the exception of EPBR and BONT during the cold season and the inter hot cold season. The maximum value was recorded at EPBR (0.03 mg/kg), however this value remains below the standard of 0.5 mg/kg set by the OSPAR convention (1997) for sediments contaminated by Hg. Lead, coper and Zinc levels in Lévrier Bay are the highest in Mauritania coast. The increase of trace metals concentration in levier Bay environment is caused by the demographic and industry development in Nouadhibou city, which is became a free zone and it known a proliferation of fish industry (**Table 3**).

Table 3.

Comparison of the results of this study with other results from the littoral zone of Mauritania (mg/kg).

Site	Cd	Pb	Cu	Zn	Hg	Coordinates	References
EPBR	0,265±0,078	5,7±2,924	11,284±4,903	47,245±16,83	0,008± 00	20° 54' 38.8"N. 17° 02'27.1"W	Present study
CE	0,04±0,014	2,125±0,880	4,434±1,028	9,185±1,939	0	20° 53’ 40.0"N. 17° 03'17.4"W	
BONT	0,225±0,053	1,017±0,393	3,337±1,319	15,445±6,906	0,001± 00	20° 54' 30.1"N. 17° 01'56.2"W	
PM	0,142±0,084	1,722±0,719	11±3,214	5,137±2,072	0	20° 49' 00.5"N. 17° 02'19.6"W	
CBC	0,11±0,054	0,555±0,306	6,505±4,760	5,105±0,995	0	20° 46' 47.2"N. 17° 03'30.4"W	
SNIM1	0,137±0,030	1,135±0,401	4,862±1,180	15,035±4,131	0	20° 48' 28.8"N. 17° 01'49.8"W	
CBL	0,202±0,126	0,647±0,294	4,317±3,400	5,85±1,774	0	20 46. 722 N. 17 02.496W	
SNIM2	0,147±0,012	0,637±0,126	2,775±0,745	8,397±3,869		20° 48' 45.5"N. 17° 02'06.0"W	
COMECA	0,090±0,018	1,671±0,534	0,084±0,003	1.349±0,011	0,016 ±0,002	20° 50’ 24.7’’ N. 17° 02’ 03.6’’ W	Legraa & al,2019
Etoile Bay	0,130±0,070	1,000±0,400	0,590±0,007	1,283±0,04	0,017 ±0,002	21° 02’ 19.2’’ N. 17° 01’ 36.8’’ W	
Cap Blanc	0,076±0,021	0,251±0,111	0,573±0.083	1,900±0,620	0,020 ±0,002	20° 46' 47.58" N. 17° 03' 30.24" W	
IMROP	0,082±0,012	0,805±0,028	0,352±0,008	1.219±0.424	0,019 ±0,002	20° 51’ 26.2’’ N. 17° 01’ 52.0’’ W	
Iwik	2,03±0,32	0,40±0,09	nd	nd	0,02 ±0,002	19° 53’ 02.7’’ N, 16° 17’ 32.8’’ W	S.Bilal, Thesis 2014
Mamghar	1,96±0,36	0,33±0.6	nd	nd	0,02 ±0,002	19° 52’ 03.3’’ N, 16° 17’ 43.2’’ W	

Comparing the concentrations of Cd (0.04 to 0.265 mg/kg) recorded in the present work with those found (0.076 to 0.130 mg/kg) by Legraa et al. (2019), we found that the cadmium level in Lévrier Bay are increased in recent years. Meanwhile, the cadmium level in Lévrier Bay is less than in Iwik and Mamghar (2.03 and 1.96 respectively. Bilal 2014) at Banc d'Arguin region. The important variation of cadmium level could be linked to the permanent presence of upwelling in this area. However, mercury concentration in Lévrier Bay was low in ours samples. The considerable variation between ours finding and others previous studies. in Mauritania coast (Legraa et al. 2019; Bilal 2014) can probably be linked to the sampling points that differ in this study compared to previous works.

3.1. Relationship between the trace metals

Figure 2 shows a relatively high positive correlation between Zn and Pb and moderate correlation between zinc, lead and copper, then these correlations indicate a possible common source of the elements from industrial and/or urban activities as well as comparable behavior in the sediment. The percentage of the eigenvalues relative to the variables Zn, Cu and Pb are well projected on Axis1, because it 66.25% of information. However, Cd is well represented on Axis 2 and constitutes 18,12% of information; the source of which can be attributed to other origins.

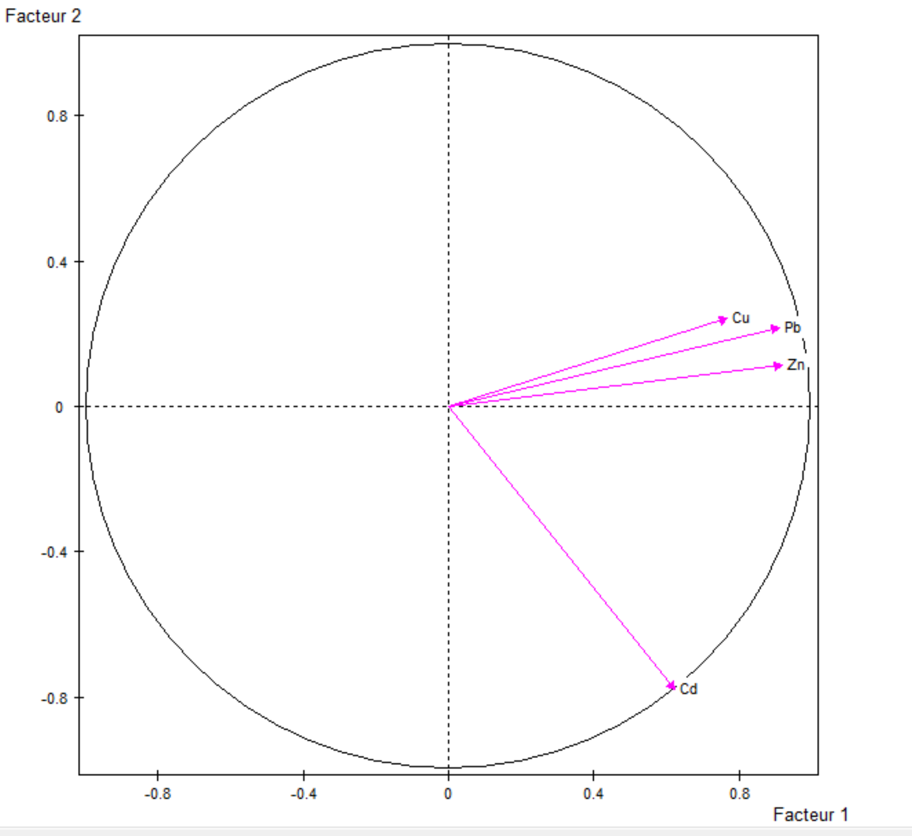

Fig. 2. PCA between the variables (trace metals: Zn, Pb, Cu and Cd) in the surface sediments of the Lévrier Bay

3. 2. Seasonal variations

The ANOVA test showed the absence of significant (P > 0, 5) seasonal variations in the metallic elements analyzed in the sediments at all the sites studied (**Table 4**).

Table 4.

ANOVA analysis of variance of the elements studied (ZN, Pb, Cu et Cd)

Metal	Cd	Pb	Cu	Zn
P. value seasons	0,219	0,076	0,217	0,123

Although the ANOVA applied between metallic elements, sites and seasons did not give rise to a significant season effect because this statistical analysis used the cumulative average concentrations; nevertheless, in all the sites studied, zinc displayed in hot season its highest contents of all the elements analyzed and its lowest values in cold season (**Fig. 3**). For the other elements, the highest values were also encountered in the hot season and the lowest values of the metals analyzed were recorded in the cold season for all studied sites, with the exception of Cd, which had its highest content in the cold –hot season. The high concentrations of Zn observed at PM during the cold season may be due to intensive ore shipping activities during this period.

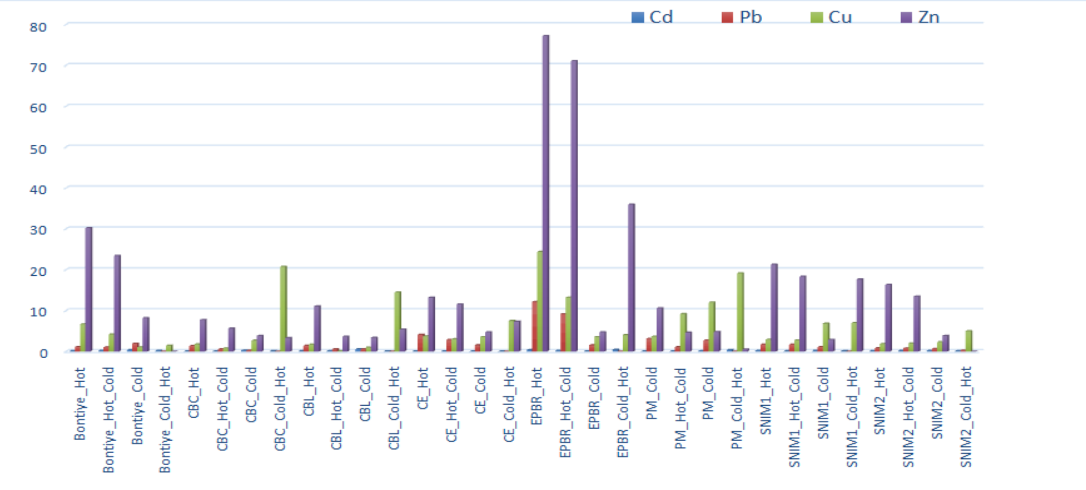

Fig. 3. Variations in trace metals by site and by season.

3.3. Comparison with previous studies carried out on the Mauritanian coast

For comparison, the concentrations found for Pb, Cu and Zn in the sampling sites of the present study remain higher than those found by other authors in previous studies carried out on the Mauritanian coast for the same elements (Legraa et al, 2019 ; Bilal, 2014).This may be due to the absence of industries and infrastructures at the sites sampled in previous studies, unlike those in this work, the sediments of which were collected in areas close to industries that could be sources of elements cited. Moreover, the concentrations of Cd recorded in the present work are similar to those found in the works carried out on the Mauritanian coast, with the exception of certain high contents of this element encountered in Iwik and Mamghar (Banc d'Arguin), which could be linked to the permanent presence of upwelling in this area.

3.4. Comparison with international standards

Spain and France are among the various countries' signatories to the Oslo Convention for the Guide values proposed for trace metals (Alzieu et al. 1999). Environment Canada (CCME, 1999), whose ELP is the concentration above which harmful effects are expected to occur frequently and the ISOGS is a quality guideline value. The comparison between the average concentrations of trace metals in this study and those proposed by the international standards relating to the toxicity of metals in surface sediments showed that all the values recorded for trace metals in all the sites of the present work are less than those recommended by these standards (**Table 5**).

Table 5.
Comparison of the average concentration values of the present study with theproposed guideline values for trace metals (mg / kg) in certain countrieswhich are signatories to the Oslo Convention. (Alzieu et al. 1999) and with international standards

	Standard				Present study							
	Spain	France	Canada environment (CCME, 1999)									
			PEL	ISOGS	EPBR	CE	BONT	PM	CBC	SNIM1	CBL	SNIM2
Cd	1 to 5	0,2-2,4	4,2	0,7	0,265±0,078	0,04±0,014	0,225±0,053	0,142±0,084	0,11±0,054	0,137±0,030	0,202±0,126	0,147±0,012
Pb	120-600	20-40	112	30,2	5,7±2,924	2,125±0,880	1,017±0,393	1,722±0,719	0,555±0,306	1,135±0,401	0,647±0,294	0,637±0,126
Cu	100-400	26-36	108	18,7	11,284±4,903	4,434±1,028	3,337±1,319	11±3,214	6,505±4,760	4,862±1,180	4,317±3,400	2,775±0,745
Zn	500-3000	140-200	271	124	47,245±16,835	9,185±1,939	15,445±6,906	5,137±2,072	5,105±0,995	15,035±4,131	5,85±1,774	8,397±3,869

4. CONCLUSION

The five metals (Zn, Cu, Pb, Cd and Hg) were detected in our samples and their concentrations in sediment were generally heterogeneous and vary according to the metal analyzed and the sampling site, where Zn showed the high value recorded among all metallic elements, according to the order Zn > Cu >Pb> Cd >Hg.

The metallic elements analyzed displayed significant seasonal variations for certain studied sites; however, the use of ANOVA did not show any seasonal effect.

Indeed, the present work shows high average concentrations of the metals studied in the surface sediments than those found for the same metallic elements in recent previous studies at the Lévrier Bay, which due to the absence of important sources in metals at the sampled sites in previous work.

Furthermore, the average concentrations of the metals studied in this work are all below the average values of the international standard guideline relating to the toxicity of surface sediments. However, the high concentrations of metals at the EPBR and BONT sites compared to those found for the same elements at the other sampling sites could be explained, on the one hand, by the increased presence of artisanal canoes and coastal vessels at EPBR level (home port), and by the presence of all fishmeal and fish oil production plants at BONT on the other hand, which discharges may be the source having contributed to the elevation of the trace metals at these two spaces.

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