EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology 2022, 23(5), 84–90
https://doi.org/10.12912/27197050/151641
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Received: 2022.06.20
Accepted: 2022.07.16
Published: 2022.08.01

Assessment of Heavy Metals Pollution in the Marine Sediments of the Lévrier Bay (Nouadhibou, Mauritania)

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ABSTRACT

Geochemical study of twenty-seven marine sediments of the Levrier Bay used eleven heavy metals to display descriptive statistics and to assess the environmental impact of this industrial area. The analysis of eleven heavy metals (Pb, Zn, Cu, Ni, V, Cr, Co, Hg, Cd, As and Mo), major and other trace elements, were performed by ICP-MS. Pollution load Index (PLI) show low degree of contamination. Geochemical Index (Igeo) and enrichment Factor (EF) have been used to assess the environment quality at varied sites in sediments. Results display moderate concentrations for the most of elements excepted the As and Hg which often are upon the amount measured in the UCC baseline. The local presence Hg and As, limited to some sites of the area, allow to conclude that the sediments of the Lévrier Bay didn't suffer from the human activities in the area.

Keywords: heavy metals, pollution assessment sediments, Nouadhibou, Mauritania.

INTRODUCTION

The development of human activities and urbanization are all factors that can harm the environment and public health. Especially in industrial surface soils and coastlines where waste discharges, untreated sewage and other anthropogenic activities caused a significant deterioration of water and sediment quality by the addition of new chemical elements particularly heavy metals (Chuan et al., 1996; Steinmann and Stille, 1997; Sheppard et al., 2000). This may influence fish at sea and therefore indirectly human bodies. Thereby, geochemistry of metallic trace elements is a real tool for descriptive statistics and assessing the environmental pollution of different reservoirs; water, sediment and soil. Heavy metals in industrial surface soils and marine sediments may come from bedrock and constitute a lithogenic contribution. Since soils exposed to anthropogenic activities may accumulate large quantities of trace elements, it is necessary to evaluate the content of traces elements added to the native elemental contents in soils without human influence composition of soils. According to Tack et al. (1997) and Reimann & Garrett (2005); the "natural background" contents are those derived solely from natural processes.

The geochemical study of heavy metals can provide information on the spatial distribution of these elements in the three reservoirs (soils, water, sediments), as well as on the concentrations of these elements which can constitute good indicators of the anthropogenic or natural origin of these elements.

On the other hand, heavy metals in industrial marine sediment may come from various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion (e.g. Chon et al., 1995; Wong and Mak, 1997; Martin et al., 1998). Increased amounts of heavy metals in industrial soil were related to the intensity of human activities and traffic volume (Zheng et al., 2002).

The study of heavy metals added to sediments is also important since these metalscan give information on contamination source in another geochemical reservoir of the ecosystem. Then,analysis of marine sediment is a powerful approach not onlyfor studying the distribution of contaminants in an aquaticsystem, but also for reconstructing historical inputs of thesecontaminants, improving management strategies and evaluatingthe effectiveness of recent pollution control measures (Lara-Martín et al., 2015)

METHODOLOGY

Study area

The Levrier Bay is an area rich in industrial and fishing activities. It houses four ports around which are concentrated more than 60 industrial companies working in the fishing sector, mainly in the fishmeal and fish oil industry, in addition to the mines. The Levrier Bayis one of the most fish-rich areas in the world. From an ecological point of view, it encompasses two remarkable sites, the Cap Blanc satellite reserve and the Etoile Bay. This area is at the origin of the development of the city of Nouadhibou; economic capital and second largest city of Mauritania (Figure 1). Due to its contribution to socio-economic development (job creation, assessment of fishery products, etc.), industrial activity in the area is the source of several direct discharges of wastewater into the bay's waters and the surrounding soil. This could have a negative impact on the environment and public health. This work proposes to carry out an environmental assessment of the sediments of the Lévrier Bayon the basis of eleven metallic trace elements (Pb, Zn, Ni, Co, Cr, V, Hg, Cu, Mo, As, Cd) and to study source (s) and the spatial distribution of the latter throughout this marine sediments area. This study can be considered the first attempt to evaluate the heavy metals pollution in marine sediments of Lévrier Bay by using pollution load index, Enrichment factor and geoaccumulation index.

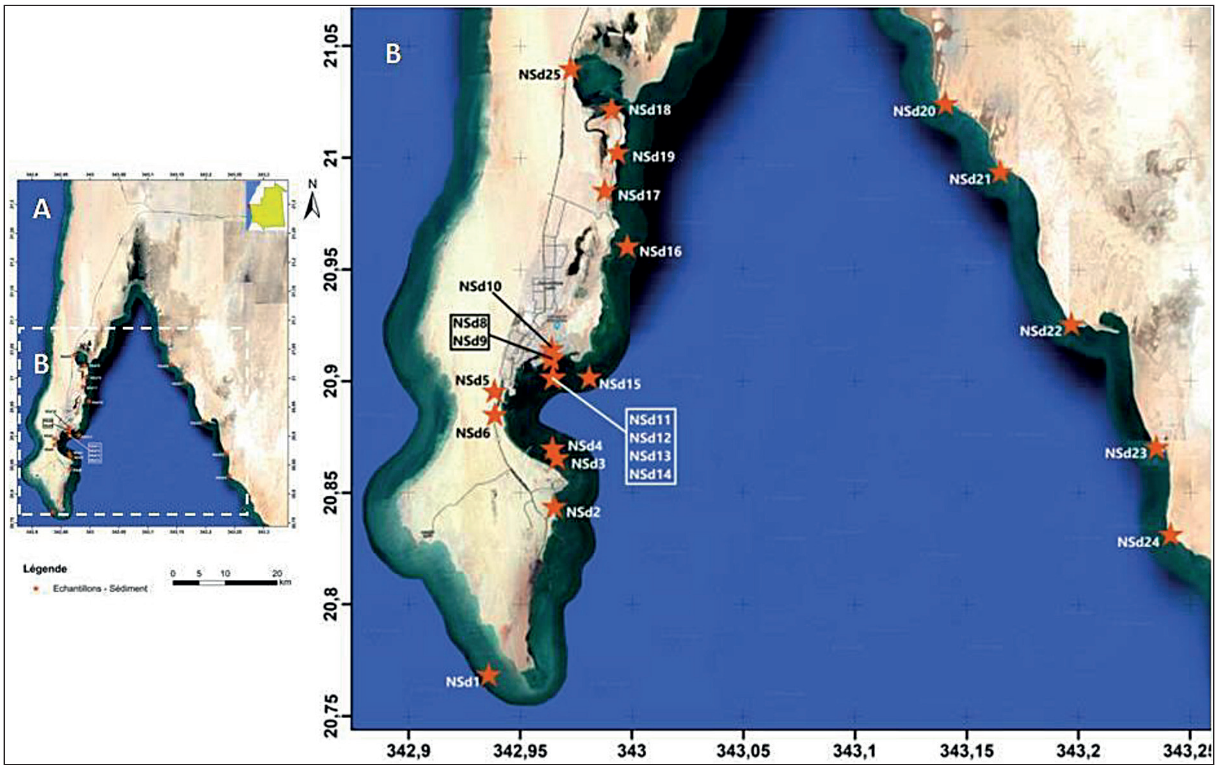

Figure 1. Location of studied area and sediments samples points

Sampling method

The first campaign was carried out during the winter season corresponding to the month of December 2019. The geographical position of the sampled points was determined using a GPS, but also using the existing geographic and geological cartography. Sampling points are referenced by a letter and a number.

The experimental study was carried out on marine sediments from the coast of the Levrier Bay. The sampling sites chosen are located along the coastline between Cap Blanc and the Etoile Bay, around the town of Nouadhibou and on the other side of the Greyhound bay (Figure 1).

The choice of these sites was based on the presence or absence of a source of domestic and industrial pollution. Depending on the site, these sediments are of a different nature (muddy, clayey, sandy, etc.).

Twenty-four (24) sediment samples were collected. About 1 kg of wet sediment was collected per point sampled, using a 40 cm long PVC tube, in opaque glass bottles and transported to the laboratory at room temperature. The washing of the collection tools and the preparation of the sediment samples are cleaned and prior to the collection of each grab sample or compound. Rinse the sampling tool with distilled water to remove major residue and clean surfaces with brush, distilled water.

The sediments are dried at 105 °C for 48 hours to remove their moisture. After drying, the sediments were ventilated to air and sieved. The samples were then sent for analysis for major and trace elements.

Geochemical processing

Chemical analysis was performed at ALS laboratory in Dublin. The analytical method used to evaluate the marine sediment geochemistry is the super Trace Lowest DL AR by ICP-MS. The Super Trace method combines an aqua regia digestion with ICP-MS instrumentation utilizing collision/reaction cell technologies to provide ultra-low detection limits. Instrumentation has been optimized for long-term ICP-MS signal stability, in particular for samples with high Ca content. The extremely low detection limits are particularly useful for exploration in sediments, and the methods can also be performed on the clay fraction of soils. (Clay size fraction separation is available using ALS method SCR-CLAY.) This method is not appropriate for mineralized samples. ME-MS41L – for the ALS standard aqua regia digestion a prepared sample (nominal 0.5g) is digested with 75% aqua regia (3:1 ratio of $HCl:HNO_3$) in a graphite heating block.

HEAVY METAL ASSESSMENT IN SEDIMENTS

Pollution index and integrated pollution index

To assess the environmental quality of the soil, the pollution index (PI) and the integrated pollution index (IPI) of Chen et al. (2005) are used. "PI = Concentration of X analyzed heavy metal/ Concentration of X heavy metal in the background, When IPI = Mean value of metal's IP".

Geo-accumulation Index (GI)

The geo-accumulation index (I*geo*) can also be used to assess the possible environmental impact on soils by heavy metal elements (Muller, 1969).

$$\text{Igeo} = \text{Log}\,(\text{Cn}/1.5 * \text{Bn}) \quad (1)$$

where: Cn corresponds to the concentration of a given heavy metal element and Bn corresponds to the concentration of the same heavy metal element in the upper continental crust (Taylor and McLennan, 1995). The constant value 1.5 permits to analyze fluctuations in the content of a given substance due to lithogenic variations.

Enrichment factor

The Enrichment factor (EF) can be used to evaluate the anthropogenic impact of heavy metals in the environment (Franco-Uria et al., 2009) and also to distinguish anthropogenic and natural sources. The EF is calculated according to the following formula of Selvaraj et al., (2004):

$$\text{EF} = (C_M/C_{Rb})_{sample} \,/ (C_M/C_{Rb})_{background} \quad (2)$$

where: $(C_M/C_{Rb})_{sample}$ corresponds to the ratio of concentration of heavy metal CM to that of rubidium C_{Rb} and $(C_M/C_{Rb})_{background}$ corresponds to the same ratio but in the background (Upper continental crust).

EF value of 1 suggests a natural source for a given heavy metal (Zhang and Liu, 2002). When the EF value is >1.5 this implies an anthropogenic source.

RESULTS AND DISCUSSION

Heavy metals concentrations in marine sediments samples

Concentrations of 11 heavy metals in the sediments of the "Lévrier Bay" are presented in Table 1. The concentrations range of Pb, Zn, Cu, Ni, V, Cr, Co, Hg, Cd, As and Mo are respectively 0.52–30.2, 1.50–225, 0.80–29.8, 0.59–8.51, 1.00–9.30, 8.53–26.20, 0.23–1.49, 0.01–0.06, 0.02–0.78, 0.16–2.14, 0.16–0.19, with mean value of 5.08, 19.02, 5.55, 2.15, 3.23, 13.03, 0.49, 0.02, 0.16, 1.01 and 0.33. Mean of heavy metals concentrations decrease according the following order Zn> Cr> Cu > Pb >V>Ni>As>Co>Mo>Cd>Hg. Cr and Zn have the largest median values when Hg and Mo have the lowest median values. Compared to the Upper Crust corresponding background values (Taylor and Mc Lennon, 1985), concentrations ofsome heavy metals (Ni, V, Cr, Mo) have values very lowerwhen others (Pb, Zn, Cu, As) display values slightly higher (Pb, NSD10-NSD12, NSD18; Zn, NSD18; Cu, NSD11, NSD18, NSD9) (Figure 2).

Compared to the background values, some sites display higher concentrations in some heavy metals. Thereby, Pb in NS8, Cu-Ni in NS27, Cd in NS3, Mo in NS24, As in NS24 and Hg in many sites NS1, NS15, NS16, NS18, NS20, NS3 and NS4. Hgremains the heavy metal the most overriding area.

Determination of the coefficient of variation (CV) allows to distinguish two groups of heavy metals, one group with CV>0.5 (Pb, Zn, Cu, Hg, Cd, Ni, V, Co, Mo,) and that with CV<0.5 (As, Cr). According to Han et al. (2006) and Guo et al. (2012), the first group where heavy metals have high CV value (>0.5) may be dominated by anthropogenic sources, when the second group where heavy metals have low CV value (<0.5) it may be matched to a natural source. Regardless of their anthropogenic or natural origin, concentrations of heavy metal don't seem to affect the quality of the marine sediment of the industrial area of the "Lévrier Bay".

Also, in a study aimed at establishing the reference situation of the marine environment in the Nouadhibou region (MEDD, DCE, 2018), the levels of heavy metals analyzed (mercury, cadmium, copper, lead and zinc) in the sediments are relatively low, and shows contents of 0.006 mg/kg, 0.04 mg/kg, 0.25 mg/kg, 0.42 mg/kg and 0.665 mg/kg, respectively. The establishment of the reference situation of the marine environment at the mineral port of Nouadhibou by SNIM in 2010 for the construction of a new loading dock shows levels ranging from 0.2 to 0.6 mg/kg of Cadmium, 1 at 6 mg/kg of copper, 5 to 7 mg/kg of lead, 6 to 20 mg/kg of zinc, 6 to 30 of chromium, 2 mg/kg of cobalt and 2 to 123 mg/kg of nickel. For mercury, it was not detected.

Heavy metal pollution assessments in marine sediments samples

Calculated PIs means relatively to the UCC background of Taylor and Mc Lennon (1985) exhibit lower values for Zn, Ni, V, Cr, Co, Hg, As, Mo elements (PI<1) (Table 1) whilst the Pb, Cu and Cd (1<PI<3) displaying mid-level PIs.The PIs values are all under 1, except the Cd with a value

Table 1. Descriptive statistics of heavy metals in the sediments of the "Lévrier Bay

Limit detection		Mean	Min	Max	Median	SD	VC	Skewness	PImax	PImin	Mean	UCC Mean
Pb	0.005	5.08	0.52	30.20	1.49	7.94	1.56	2.18	1.78	0.03	0.30	20.00
Zn	0.1	19.02	1.50	225.00	3.90	44.82	2.36	4.38	4.33	0.03	0.37	71.00
Cu	0.01	5.55	0.80	29.80	1.98	7.38	1.33	2.24	2.08	0.06	0.39	25.00
Ni	0.04	2.15	0.59	8.51	1.65	1.61	0.75	2.86	0.46	0.03	0.12	20.00
V	0.1	3.23	1.00	9.30	2.55	1.84	0.57	1.75	0.18	0.02	0.06	60.00
Cr	0.01	13.03	8.53	26.20	11.20	5.02	0.39	1.86	0.75	0.24	0.37	35.00
Co	0.001	0.49	0.23	1.49	0.46	0.28	0.56	2.11	0.13	0.02	0.04	10.00
Hg		0.02	0.01	0.06	0.02	0.01	0.53	1.25	0.97	0.17	0.41	0.06
Cd	0.001	0.16	0.02	0.78	0.13	0.14	0.88	3.40	7.78	0.15	1.64	98.00
As	0.01	1.01	0.16	2.14	0.90	0.43	0.42	0.73	0.87	0,08	0,51	1,50
Mo	0.01	0.33	0.16	1.19	0.24	0.23	0.71	2.79	0.85	0.11	0.23	1.50

n = 27

Table 2. *Igeo* values of studied heavy metal elements in marine sediment samples

Parameter	Pb	Zn	Cu	Ni	V	Cr	Co	Hg	Cd	As	Mo
Igeomin	-1.69	-1.72	-1.42	-1.67	-1.90	-0.79	-1.88	-0.95	-1.00	-1.27	-1.12
Igeomax	0.07	0.46	0.15	-0.52	-0.93	-0.30	-1.07	-0.19	0.71	-0.15	-0.25
Median	-1.23	-1.30	-1.03	-1.23	-1.50	-0.67	-1.58	-0.61	-0.05	-0.52	-0.94

between 1 and 2. The PI value of Cd ranged from 1.64 to 7.78 with a mean value of 0.15 (Table 1). Together, PPs and IPIs (<1) allow to conclude that there is no obvious pollution of the marine sediment in the industrial area of the "Lévrier Bay").

I*geo* values of eleven studied heavy metal elements (Table 2) are very low (I*geo*<<0) and allow to classify studied marine sediment as having an uncontaminated level. This may be clearly demonstrated in Figure 2 where the majority of the heavy metal's values are below level zero, indicating that the anthropogenic impact in the studied marine sediment are insignificant. The As, Hg, Cd and Zn concentrations slightly enriched in marine sediment and to a lesser extent Pb, Mo and Cr. The highest contamination site is NS8 for Pb; NS24 for Cu; NS27 for Cr; NS15, NS18, NS20, NS3, NS4 for Hg; and NS3 for Cd; NS24 for Mo and As.

The enrichment factor is calculated to assess the extent of the enrichment and/or depletion of heavy metals in the marine sediment of the "Levrier Bay" (Table 3). Heavy metal concentrations are normalized to the upper continental crust of Taylor and Mc Lennan (1985). Results summarized in Figure 2 are all less than 1 then are depleted relatively to the upper continental crust; indication that the studied marine sediment is not affected by anthropic sources.

Table 3. Calculated enrichment factor of heavy metals in studied sediment

Factor	Min	Max	Mean
EFPb	0.03	1.50	0.28
EFZn	0.02	3.19	0.30
EFCu	0.03	1.21	0.26
EFNi	0.00	0.01	0.00
EFNi	0.01	0.28	0.04
EFV	0.03	1.73	0.15
EFCr	0.12	0.50	0.20
EFCo	0.02	0.99	0.09
EFHg	0.18	1.04	0.46
EFCd	0.00	0.01	0.00
EFAs	0.11	1.47	0.71
EFMo	0.11	1.03	0.26

Correlation coefficient analysis

According to correlation matrix in Table 4, three groups of interrelationships can be distinguished; the first group with a strong positive correlation includes Zn, Cu; Ni, Pb and V; supporting their common natural origin. The second group with a low negative relationship contains Cr, V and Co. The third group (Cd, As, Mo) displays middle correlation. Hg doesn't correlate with any element.

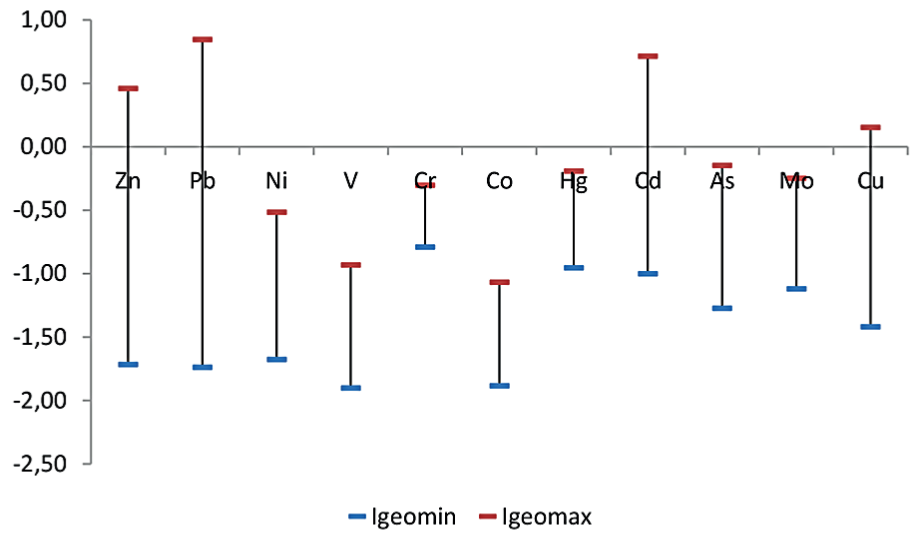

Figure 2. *Igeo* values of studied heavy metal elements in marine sediment samples

Table 4. Correlation matrix of heavy metals

Metal	Pb	Zn	Cu	Ni	V	Cr	Co	Hg	Cd	As	Mo
Pb	1										
Zn	0.81	1.00									
Cu	0.86	0.86	1.00								
Ni	0.62	0.85	0.73	1.00							
V	0.06	0.18	0.11	0.25	1.00						
Cr	0.41	0.56	0.53	0.78	-0.04	1.00					
Co	0.58	0.77	0.67	0.86	0.57	0.69	1.00				
Hg	0.63	0.62	0.57	0.50	-0.10	0.41	0.37	1.00			
Cd	0.77	0.94	0.80	0.78	0.35	0.39	0.73	0.58	1.00		
As	0.27	0.49	0.27	0.57	0.46	0.22	0.54	0.19	0.60	1.00	
Mo	0.64	0.81	0.72	0.90	0.09	0.73	0.79	0.51	0.70	0.50	1.00

CONCLUSIONS

The present work studies the distribution of heavy metal concentrations in marine sediments in the industrial area of the Levrier Bay. It aims also to assess the pollution of these elements on the two compartments by using geo-accumulation index and enrichment factor. Most results show that in the marine sediments concentrations of eleven heavy metals (Pb, Zn, Cu, Ni, V, Cr, Co, Hg, Cd, As and Mo) display values lower compared to the mean amount of UCC and the baseline sample. The geoaccumulation index and the enrichment factor values revealed that the studied sediments are slightly polluted respectively by Cd, Mo, Hg and Pb, Zn, Cu, Cd. Normalized enrichment factor values for eleven elements to the average of the UCC shows that concentrations of Pb, Zn, Cu, Cr, Hg, Cd and As from are lower in the sediment. The geochemical survey indicates natural origin for the most of heavy metals.

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