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Spatial distribution and assessment of surface Soils contamination by heavy metals of an industrial area: The Lévrier Bay (Nouadhibou, Mauritania)

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ABSTRACT

Geochemical study of seventeen surface soils of the Lévrier 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 (0 – 25cm) soils. 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 soils of the Lévrier Bay didn't suffer from the human activities in the area.

Key words : *Heavy metals, Pollution assessment, Soils, 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 (e.g., Chuan *et al.*, 1996; 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 and 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.

Materials and Methods

Study area

The Lévrier 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 Lévrier 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. 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. These activities send heavy metals into surrounding soil and consequently could have a negative impact on the environment and public health. There is also a lack of data concerning the behaviour and speciation of major and trace elements (Rb, Ba, Ga, Li, U, Y, Th and Zr) included some Rare Earth Elements (La, Ce).

This work proposes to establish the spatial distribution of major and trace elements in the Lévrier Bay soil, and to carry out an environmental assessment of this soil on the basis of eleven metallic trace elements (Pb, Zn, Ni, Co, Cr, V, Hg, Cu, Mo, As, Cd).

This study can be considered the first attempt to evaluate the heavy metals pollution in the soil of Lévrier Bay by using pollution load index, enrichment factor and geo accumulation index.

Sampling techniques

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.

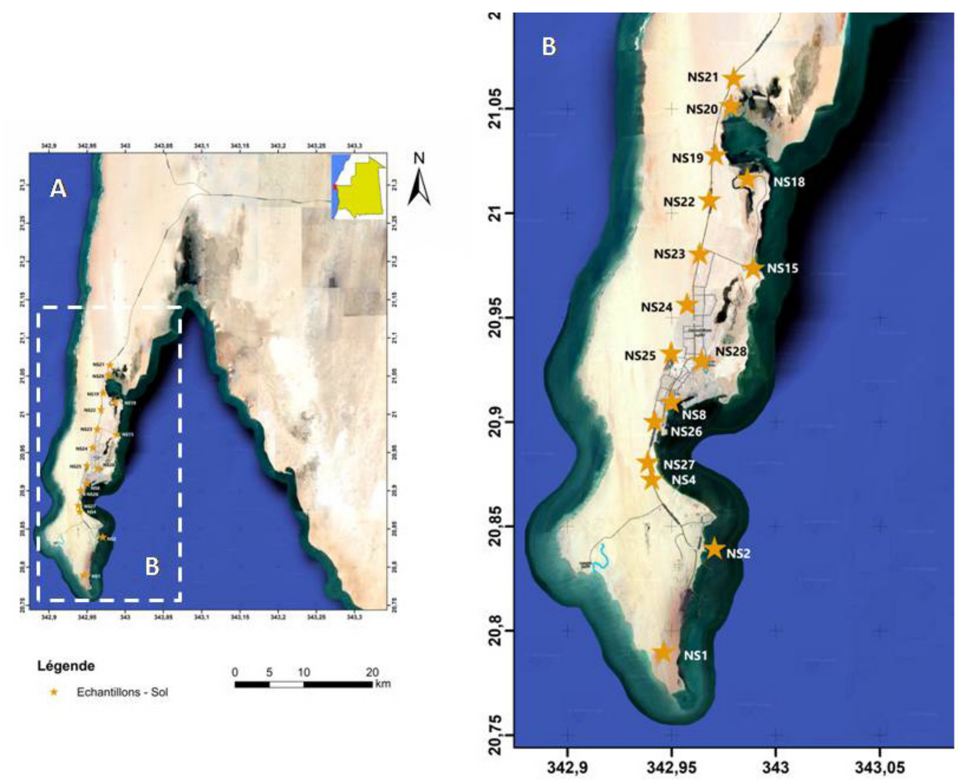

Fig. 1. Location of studied sediments samples

Seventeen (17) soil samples were taken around the town of Nouadhibou between Cap Blanc and Etoile Bay. The geographical location of certain polluting sources motivated the choice of the location of the sampled points.

A PVC tube and an auger were used for soil sampling; the tube method consists of taking a sample by pushing a tube into the ground from the surface. Once pushed in as far as possible, the tube comes out and the soil sample is collected. The length of the tube, like that of the auger, is 30 cm. Samples are stored and handled properly. Only the first 15-20 centimeters of the soil were taken from each site and stored in bags at room temperature.

The analysis was carried out on the so-called "fine earth" part (diameter less than 2 mm) of the soil dried in the open air.

Geochemical processing

Chemical analysis was performed at ALS laboratory in Dublin. The analytical method used to evaluate the soil and 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 soils or 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 soils

Pollution Index (PI) and Integrated Pollution Index (IPI)

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).

I*geo* = Log (Cn/1.5*Bn)

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 (EF)

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):

$$EF= (C_M/C_{Rb})_{sample} / (C_M/C_{Rb})_{background}$$

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.

Geological context

The study area (Lévrier Bay) is located in the Senegalese-Mauritanian coastal basin which developed during the Permo-Triassic along the Atlantic Sea. Indeed, the region is mainly covered withmarine, lacustrine and fluvial sediments of Quaternary age. To the east, terrestrial Neogene sediments as well as Mesozoic formations (e.g., Liger, 1980; Ritz and Bellion, 1990) may outcrop. Further east, about 100km, is the Reguibat ridge which includes the oldest rocks of the Mauritania (amphibolites, gneiss, granites etc.).

Results and Discussion

Characterization of soils samples

The granulometric observation of the studied soils indicates the predominance of the sandy fraction. In fact, the soil in the study area has a typically sandy texture. These are classified into three types of soils: sandstone soils on the coast (Cap Blanc sandstone), sand dunes on the coast and alluvium soils (Etoile Bay). The soils in despair are salty soils. The soils, developed on sands, are characterized by a textural profile with a slight increase in depth of the clay fraction and a dominance of sands along the profile.

For all solids developed on white blanks and alluvium, the structure is generally clustered on the surface.

The rate of organic matter is very low. On an average sample of these soils, the OM content is very low 0.05 **j—**. Organic Carbon varies between 0.01 to 0.08 ppm.

Limestone contents are low. The organic matter contents of the surface horizons of the profiles studied are very low.

Distribution of major and traces elements in the soils

Major and traces elements data in the soils are given in Table 1. Mean value of TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O are respectively 0.03%, 0.60%, 1.05%, 0.29%, 13.37%, 0.39% and 0.20%, CaO and Ba have the highest median values when the Ti, K and S have the lowest median values (Table 1). Compared to the mean of the UCC background and the baseline, amounts of CaO are higher. All other chemical elements have lower concentrations; Ti, Mg, K, La and Ce. The Mn content is the largest.

Heavy metals concentrations in soils

Concentrations of 11 heavy metals in the soilsof the "Lévrier Bay" are presented in Table 1. Table 2 gives the descriptive statistics (mean, range, SD, VC.) of heavy metals. The concentrations range of Pb, Zn, Cu, Ni, V, Cr, Co, Hg, Cd, As and Mo are respectively 0.57-13.25, 2.2-30.1, 1.79-12.5, 1.26-4.84, 2.40-12.10, 7.16-19.50, 0.35-1.68, 0.007-0.10, 0.034-1.30, 0.81-2.76, 0.16-0.55, with mean value of 3.52, 11.15, 3.85, 2.609, 6.11, 11.39, 0.89, 0.028, 0.19, 1.31 and 0.26. Mean of heavy metals concentrations decreases according the following order Cr>Zn> V>Cu>Pb>Ni>As>Co>Mo>Cd>Hg.Cr, V and Zn have the largest median values and Hg has the lowest median value. Compared to the Upper Crust corresponding background values (Taylor and McLennon, 1985), concentrations of the heaviest metals (Pb, Zn, Cu, Ni, V, Cr, Mo) have values very lower when others (As, Hg, Cd) display values slightly higher (Hg, NS1; Cd, NS3; As, NS24).

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, As) and that with CV<0.5 (Ni, V, Cr, Co, As, Mo). 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 soil of the industrial area of the Lévrier Bay.

Heavy metal pollution assessment in soils

Calculated PIs means relatively to the UCC background of Taylor and McLennon(1985) exhibit lower values for all elements (PI<1) (Table 2b) apart from the Hg and Cd (1<PI<3) which display mid-

Table 1. Descriptive statistics (mean, range, SD, VC.) of heavy metals in the soils of the "Lévrier Bay"

Heavy metals	Mean	Max	Min	SD	VC	Median	Skewness	PImean	PIMin	PIMax	UCC/Tay Mean
Pb	3.52	13.25	0.57	3.37	0.96	2.35	1.03	0.18	0.03	0.66	20.00
Zn	11.16	30.10	2.20	9.66	0.87	6.30	4.80	0.16	0.03	0.42	71.00
Cu	3.86	12.50	1.79	2.85	0.74	2.76	2.00	0.15	0.07	0.50	25.00
Ni	2.61	4.84	1.26	1.07	0.41	2.53	2.26	0.13	0.06	0.24	20.00
V	6.11	12.10	2.40	2.81	0.46	6.40	6.40	0.10	0.04	0.20	60.00
Cr	11.40	19.50	7.16	3.28	0.29	10.95	9.87	0.33	0.20	0.56	35.00
Co	0.90	1.68	0.36	0.37	0.41	0.89	0.89	0.09	0.04	0.17	10.00
Hg	0.03	0.10	0.01	0.02	0.84	0.02	0.01	0.47	0.12	1.72	0.06
Cd	0.20	1.30	0.03	0.29	1.47	0.14	0.14	0.06	0.00	1.00	98.00
As	1.32	2.76	0.81	0.46	0.35	1.20	0.95	0.54	0.00	1.84	1.50
Mo	0.27	0.55	0.16	0.11	0.42	0.25	0.20	0.24	0.00	1.00	1.50

This study (n=17)

level PIs.

Together, IPs and IPIs (<1) allow to conclude that there is no obvious pollution of the soil in the industrial area of the Lévrier Bay. The PI value of Hg ranged from 0.12 to 1.74 with a mean value of 0.47. The PI value of Cd ranged from 0.00to 1 with a mean value of 0.06 (Table 2). ThePI of the whole analyzed heavy metals has a value of 0.46 (Table 1).

Based on the *Igeo* values, seven classes of the geo-accumulation are distinguished. In the whole, *Igeo* values of eleven studied heavy metal elements are very low (*Igeo*<<0) and allow to classify studied soils 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 soil are insignificant. The Cd concentrations slightly exceeds level zero and to a lesser extent Hg and Mo. The highest contamination site is NS1 for Hg and NS18 for Cd.

The enrichment factor is calculated to assess the extent of the enrichment and/or depletion of heavy metals in the soil of the Lévrier Bay. Heavy metal

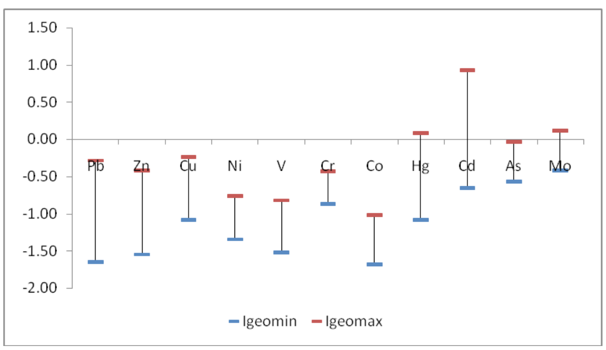

Fig. 2. Igeo values in the soils of the studied heavy metal elements

concentrations are normalized to the upper continental crust of Taylor and Mc Lennan (1985). Results summarized in Table 2 are all less than 1 then are depleted relatively to the upper continental crust; indication that the studied soil is not affected by anthropic sources.

Correlation coefficient analysis

Several authors have emphasized that using of correlation coefficient can give indication about the interrelationship among various heavy metals (Caspari *et al.*, 2006; Li *et al.*, 2008). Such interrelationships can also indicate the origin of such metals (Riba *et al.*, 2002; Youngming *et al.*, 2006). According to correlation matrix in Table 2, two groups of interrelationships can be distinguished; the first group with a strong positive correlation includes Zn, Cu; Ni, Co, Pb and V; supporting their common natural origin. The second group with a low negative relationship contains Cr, Cd, As and Mo. Hg doesn't correlate with any element.

Correlation coefficient analysis

According to correlation matrix in Table 2, 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.

Conclusion

The present work studies the distribution of heavy metal concentrations in soils in the industrial area of the Lévrier Bay. It aims also to assess the pollution

Table 2. Correlation matrix of heavy metals

	Pb	Zn	Cu	Ni	V	Cr	Co	Hg	Cd	As	Mo
Pb	1										
Zn	0.83	1.00									
Cu	0.68	0.88	1.00								
Ni	0.47	0.78	0.79	1.00							
V	0.33	0.49	0.34	0.59	1.00						
Cr	0.04	0.21	0.27	0.64	0.32	1.00					
Co	0.42	0.67	0.60	0.85	0.90	0.53	1.00				
Hg	-0.14	-0.16	-0.21	0.02	0.21	0.11	0.12	1.00			
Cd	0.13	0.39	0.08	0.20	0.27	-0.02	0.25	0.02	1.00		
As	0.39	0.68	0.89	0.77	0.33	0.42	0.55	-0.03	0.01	1.00	
Mo	0.28	0.57	0.78	0.80	0.22	0.71	0.55	-0.20	-0.04	0.83	1

of these elements on the samecompartment by using geo-accumulation index (I*geo*) and enrichment factor (EF). Most results show:

- In the surface soils, 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 (*Igeo*) and the enrichment factor (EF) values revealed that the studied soils are slightly polluted respectively by Cd, Mo, Hg, Pb, Zn, Cu, Cd.
- Normalized enrichment factor values for eleven elements to the average of the UCC shows that concentrations of Cd, Cu and As are higher in the soil.
- The geochemical survey indicates natural origin for the most of heavy metals.

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