

FIRST VERTICAL EXPLORATION OF ORGANOMETALLIC CONTAMINATION OF SEDIMENT AT THE FISHING PORT OF SAFI (WEST OF MOROCCO)

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Abstract

This work investigates the level of metallic trace elements (MTEs) and organic matter (OM) vertical contamination in the sediments of the Safi fishing port (Atlantic coast of Morocco). The choice of the site, never dredged since its construction and operation, constitutes a first scientific study on a national scale. Two sampling campaigns were carried out on 40 cm deep columns of sediment. The particle size profile of the sediment was studied and the organic matter and MTEs (Cd, Cu and Zn) contents were quantified. The results showed a homogeneous sediment profile over the entire depth with a dominance of medium and fine fractions. The average contents of MTEs revealed a significant state of contamination as well as a non-uniform distribution along the column. The recorded values are several times higher than the standards established by the legislation in force for the dredging operation. In addition, the eco-toxicological risk at the port, estimated through the calculation of various pollution and ecological risk indices, seems obvious. The correlations between MTEs and OM pointed out to probably similar origin for Cd and Zn, which is different from that of Cu. On the other hand, these analyses conclude that these metals are likely to bind to ligands other than OM. In addition, and according to the HCA analysis, the high organometallic concentrations recorded the sediment column could possibly be the result of four episodes of contamination emanating from human activities inherent in the activity of the entire port since its creation. The sediments of the fishing port therefore constitute a real threat to the marine environment, as various pollutants are likely to be released during a potentially future dredging operation.

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1. Introduction

Sediments from marine ports constitute a privileged compartment for the storage and release of inorganic (metallic trace elements) and organic (hydrocarbons, PAHs, PCBs, etc.) pollutants [1]. At very high concentrations, these elements can cause direct toxic effects on living organisms in marine ecosystems [2] and indirect toxic effects via transport of these elements along the food chain, which represents a real hazard for the environment and human health [3, 4]. The level of MTEs contamination in port sediments as well as the risks associated with them depend on several factors mainly the sediment cover, the particle size properties of this sediment, the hydrodynamic characteristics prevailing in the site and the nature of the sediment, as well as the intensity of human and industrial activities in ports [5-8]. Fishing ports, as highly anthropized ecosystems, are proper places where pollution, in various forms, can reach high and threatening levels. In this context, we evaluated, for the first time, the degree of pollution of the fishing port sediments with high anthropogenic incidence, located on the Moroccan Atlantic coast (Safi, West Morocco). In fact, the port is known for its commercial and mineral activities, in particular phosphate products [9]. The effluents flow directly into the harbor basins. Consequently, the accumulation of sediment deposits hinders shipping routes and necessitates dredging operations, which dump the dredged materials/sediments in the deep marine environment without any prior treatment. These operations pose a large number of environmental problems (organic, biological and metallic pollution), which constitute a threat for fishery resources in general and for benthic species in a specific way [4]. The objective of this work is to assess the time-based pattern of metal contamination in the sediment of the fishing port of Safi. This analysis focused on three trace elements; cadmium, considered a highly toxic element, copper and zinc, known to be toxic when their doses exceed thresholds physiologically tolerable by organisms. We also undertook an analysis of the organic matter contents in this sediment never dredged. Then, we discussed the potential ecological risks associated with MTEs and identified the contamination episodes at through the sediment column of the fishing basin.

2. Materials and methods

2.1 Study site

The port of Safi is located on the Atlantic coast ($32^{\circ}18'N$ - $9^{\circ}15'W$) (Figure 1). It is placed at the end of a bay dominated by high cliffs offering shelter to ships against north-northwest winds (NNW) and west (W) and southwest (SW) storms [10]. The port of the city of Safi is probably the oldest port in Morocco [9].

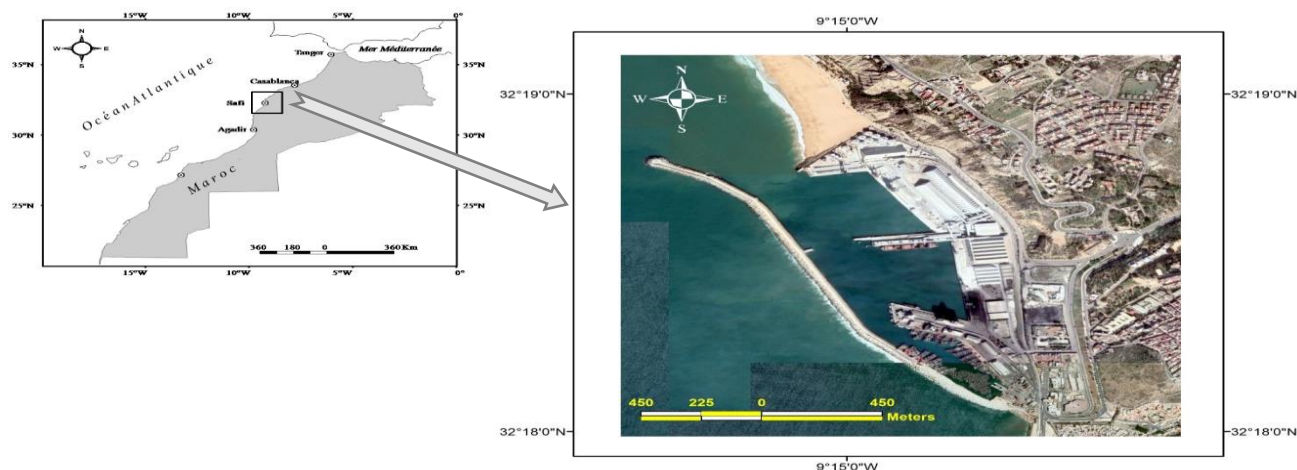


Figure 1. Location of study sites.

Its infrastructure shows three basins of which basin I is reserved for fishing, basin II is reserved for trade, and basin III is mainly reserved for mineral trading [11]. After the development of the chemical industries in Safi, this port is ranked fifth at the national level among the commercial ports and a 3rd among the fishing ports. In this regard, it is counted among the greatest sardine ports in the world [12]

2.2. Water circulation in the port of Safi

The port of Safi is a semi-diurnal tide port. Figure 2 shows that the main inflow of seawater in the port is through a single entrance located at north-west (NW) of the port. The water circulates into Basins III, then towards Basin II, and finally arrive at Basin I, from west to east and vice versa.

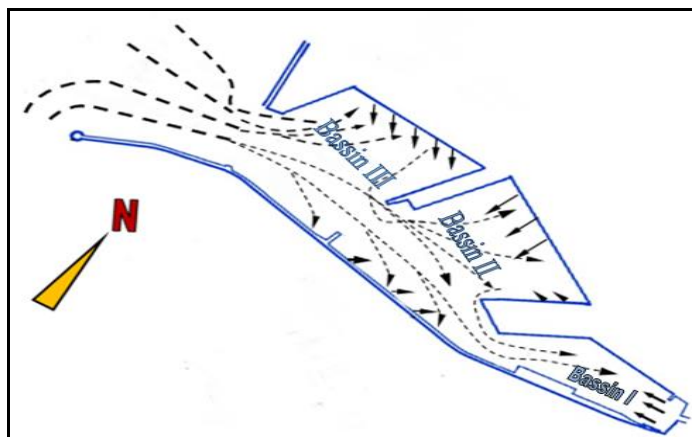


Figure 2. Water circulation in the basins of the port of Safi [13].

2.3. Sampling

The fishing port of Safi is a class 3 (6500T / year) [10], which recommends a sediment sampling every 3 years at a single station. We took two sediment samples (column 40 cm depth and 3 cm in diameter) per campaign. The first campaign was carried out on March 21, 2017 at 10:30 a.m. and the second on April 19, 2017 at 11 a.m., both at low tide. Port sediments are eroded by boat propellers as well as by hydrodynamic erosion [7, 14, 15]. The study of the bathymetry of the fishing basin allowed us to choose a shallow station (< 1m) (S) discovered at low tide (Figure 3) [11].

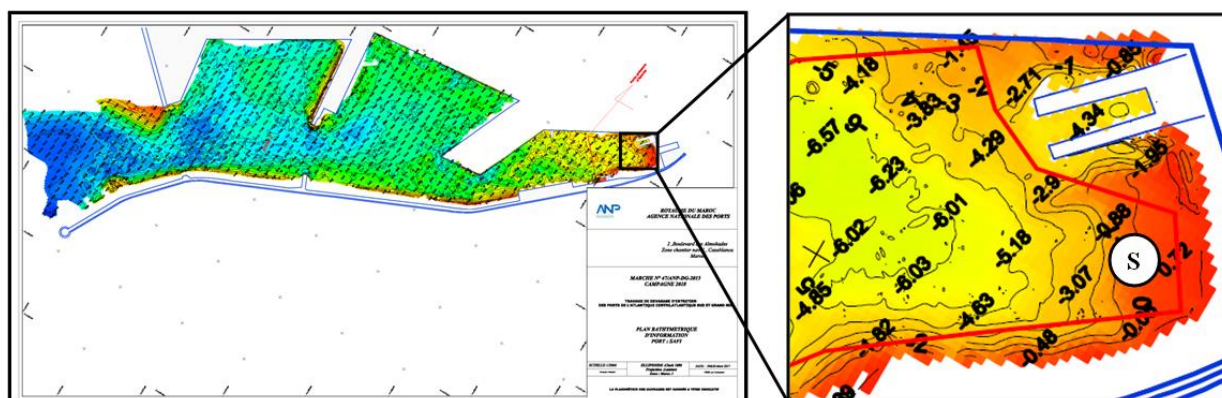


Figure 3. Bathymetry of the SAFI port and location of the study station (S) [11].

2.3.1. Method of sediment sampling

We have adopted the hand corer method. It was made using a PVC tube of 3 cm in diameter and 40 cm in height, driven in with a sledgehammer, and then we had to dig around the core to extract the sediment. Once removed, the cores or carrots were cut into eight slices of 5 cm each, and then frozen at -20°C.

2.3.2. Granulometric (particle size) study of the sediment

Granulometry is statistical distribution analysis of the particle size classes in a sample. The sieving was done according to the AFNOR method [16]. The series of sieves used ranges from 2mm to 50 µm. The residual of the last sieve was also collected. The sieving time is limited to 150 min.

2.3.3. Choice of particle size fraction for sediment analyses

We opted for the fraction <2mm, used by European standards (N1, N2) [17] and in some other studies [18, 19].

2.3.4 Marine sediment quality grid

The assessment of marine sediments was made based on French regulations relating to marine and estuarine sediments. The reference system used is based on the decree of June 14, 2000 [17] and that of August 9, 2006 GEODE standards. Two reference levels have been provisionally defined (Table 1):

- A first level (N1) comprising the values below which dumping would be authorized without any particular treatment;
- A second level (N2) corresponding to the levels above which dumping would be liable to be prohibited, provided that the other methods of eliminating dredged material are less damaging to the environment.

Table 1. Threshold values of the studied metals (mg / kg) according to GEODE standards [17]

GEODE standards	N1	N2
Cd	1.2	2.4
Cu	45	90
Zn	276	552

2.4. Determination of organic matter

The organic matter (OM) content is determined by calcination in a muffle oven (SELECTA). A portion of sediment (20-25 g) of each stratum was dried in an oven at 105 °C for 24 hours, and then weighed on a precision balance (220g / 0.1 mg). The samples are then calcinated in an oven at 550 °C for 6 hours. Once cooled in a desiccator, a new weighing took place to determine the rate of organic matter, which is equivalent to the difference in mass before and after calcination (ash) [20].

2.5. Determination of MTEs

The determination of MTEs levels was made on 0.5 g of ash for each stratum according to the protocol adopted by [4]. The MTEs were assessed using the Aurora TRACE AII200 air-acetylene flame atomic absorption spectrometer (FAAS). The validity of the analytical methods was verified by internal control using standard samples.

2.6. Marine sediment quality assessment

Pollution indices related to the environmental quality of the sediments made it possible to carry out a complementary approach combining the values of each analyzed pollutant. This is the case of the contamination factor (FC), the

geo-contamination index (I_{geo}), and the ecological risk (ER), with indices that give synthetic values such as the pollution load index (PLI). In addition, the ecological risk index (ERI) integrates all the pollutants in a representative formula and thus give a more global indication of the contamination level in the sediment and the anthropogenic impact on the marine environment.

For lack of data related to the local geochemical background, we used the reference values proposed by [21] for the calculation of the pollution indices.

✓ The contamination factor:

$$CF = C_{\text{Metal}} / C_{\text{Background}} \text{ [22]}$$

Where, C_{Metal} is the concentration of metal measured in the sample, and $C_{\text{Background}}$ is the reference concentration of the metal in marine sediments.

✓ Geo-accumulation index (I_{geo})

I_{geo} allows to assess the level of contamination by a metal in the environment compared with the geochemical background. I_{geo} is expressed as follow:

$$I_{\text{geo}} = \log_2 C_m / (B_n \times 1.5) \text{ [23]}$$

Where, C_m : Concentration of the element measured in the sample, and B_n : Concentration of the element in the geochemical background.

✓ The pollution load index (PLI): It provides a global indication (involves all the studied pollutants) of the anthropogenic impact on the marine environment.

$$PLI = (CF^1 \times CF^2 \times CF^3 \times \dots \times CF^n)^{1/n} \text{ [24]}$$

✓ Ecological Risk Factor: The E_r^i assesses the probability that negative ecological effects may occur as a result of exposure to one or more stressors.

$$E_r^i = T_r^i \times CF^i \text{ [22, 25]}$$

Where, T_r^i is the toxicity factor assigned for each metallic trace element (Zn=1, Cu=5, and Cd=30) according to [22], CF^i is the contamination factor of each element.

✓ The potential ecological risk index (ERI) is a diagnostic tool for predicting the level of environmental safety from contamination. It represents the sum of all E_r^i values and used to express the potential ecological risk for a given aquatic system.

$$ERI = \sum E_r^i$$

Each index assesses the quality of the sample according to the scores and classes established by: [24, 26, 27].

2.7. Statistical analyzes

The particle size profile of the sediment for each stratum was determined by calculating the particle size distribution and plotted using Microsoft Excel software. The variability of MTEs contents per depth was represented graphically.

The tests of simple linear correlations based on Pearson coefficient was calculated to find out the link between MTEs in different strata and MTEs and the organic matter. Significant correlations were retained at the level of $p < 0.05$. Statistical processing was performed using PAST software version 4.02 (<http://folk.uio.no/ohammer/past/>).

We also adopted a principal component analysis (PCA) and an ascending hierarchical classification analysis (CHA) to seek the distribution of the studied parameters in the sediments and possibly identify the origin of contaminants, as well as the probable episodes of contamination.

3. Results and discussion

3.1. Particle size distribution of the sediment

All the strata have a uni-modal curve (Figure 4) which reflects perfect homogeneity of the port's sediments along its profile. The medium (0.4-0.25 mm) and fine (0.2-0.1 mm) fractions of sand are dominated (40-50% each). Grainy and very grainy fractions (0.8-1mm and 1-1.6 mm) as well as very fine fractions (0.08-0.05 mm) of sand, silt, and clay (less than 0.05 mm), known to be more favorable to the fixation of MTEs, remain very low <1%. This may suggest that the sedimentation dynamics in the fishing basin, especially at our study station, do not vary greatly over time and that the study column is entirely representative of the sedimentation phenomena that have taken place in the past. The location of the fishing basin and the direction of the currents (Figure 2) suggest that only the medium to fine sand fraction reaches the fishing port while the grainy fractions undergo a preliminary settling process at the dikes. The source of the sedimentary fractions being purely marine explains the virtual absence of clay and silt. For a possible dredging, the dominant fractions would be favorable to settling down to the bottom.

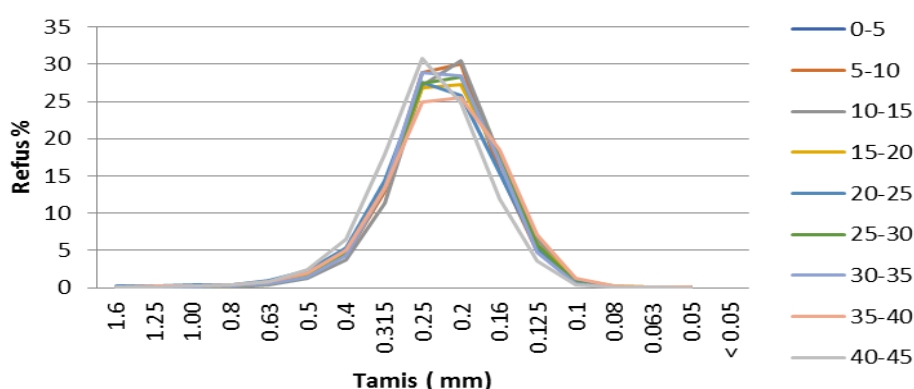


Figure 4. Particles size distribution curve of the sediment of different strata.

3.2. Classification of sediment according to GEODE standards

The comparison of the MTEs contents at the level of all the sediment strata (Table 2) compared to the GEODE standards shows an enrichment in the following order:

- Cd with a maximum value of 32.2 mg / kg dry sediment: 13 x N2 (GEODE),
- Cu with a maximum value of 411.82 mg / kg dry sediment: 4 x N2 and,
- Zn with a maximum value of 1864.8 mg / kg dry sediment: 3 x N2.

These values would be related to the hydrodynamic process, in particular sea currents including upwelling, which are, very frequent in this Atlantic region [28]. Likewise, they would also be influenced by the dredging activity of basins II and III, suspending the MTEs from contaminated sediments and transported by tidal currents to basin I. According to GEODE standards, the sediment of the fishing port of Safi would be prohibited from dumping at sea unless the conditions of the dumping site are favorable allowing the dilution of the contamination load. These average values greatly exceed the Cu, Zn, and Cd contents recorded in the surface port sediments of the entire French coast between 1986 and 1988 (24 mg / kg for Cu, 155 mg / kg for Zn, and 0.60 mg / kg for Cd). It exceeds as well as the sediments collected between 1989 and 1995 at the Loire-Atlantique ports (27 mg / kg Cu, 150 mg / kg Zn, 0.32 mg / kg Cd) [18].

3.3. Organic matter content

[29] qualify soils as highly loaded with OM when their contents exceed 10%. For the sediment of the port of Safi, we actually note high OM values at the level of the majority of the strata. These levels seem to be attributed to the specific

discharges of the fishing port (organic waste, hydrocarbons). The variation in OM contents between the strata could be attributed to the diversification of the port's activities over time and to the variation in the biodegradability of the water. Organic matter in view of its heterogeneity (fish waste, household waste from feluccas, hydrocarbons, etc.).

Table 2. Average Cd, Cu, Zn and OM content in different strata of the sedimentary column in the port of Safi

Depth (cm)	Code Strata	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	MO %
0-5	St1	162.22±0.15	387.00±1.02	16.90±0.05	5.23±0.52
5-10	St2	257.20±0.08	506.90±0.890	17.50±0.12	15.40±0.12
10-15	St3	411.82±0.54	74.00±0.05	27.10±0.54	7.67±0.98
15-20	St4	383.85±0.12	1361.40±1.56	30.30±0.36	9.94±0.10
20-25	St5	84.48±0.65	1041.00±1.98	29.30±0.58	17.73±0.11
25-30	St6	191.71±0.78	788.00±0.96	28.70±0.02	10.56±0.87
30-35	St7	62.00±0.02	1536.90±1.25	30.50±0.56	15.53±0.58
35-40	St8	181.13±0.36	1864.80±1.89	32.20±0.67	13.22±0.16

3.4. Vertical distribution of MTEs in the sediment column

In the sediment core, Zn and Cd show increasing concentrations with depth, while the distribution of Cu concentrations appears to follow the opposite path. It varies according to the strata with the maximum located between 5-20 cm, and then drops in the deeper layers. The sedimentary profiles of the core strata (Figure 5) revealed the occurrence of aggravated multi-contamination episodes in the port via the presence of contamination peaks in the 5-20 cm strata.

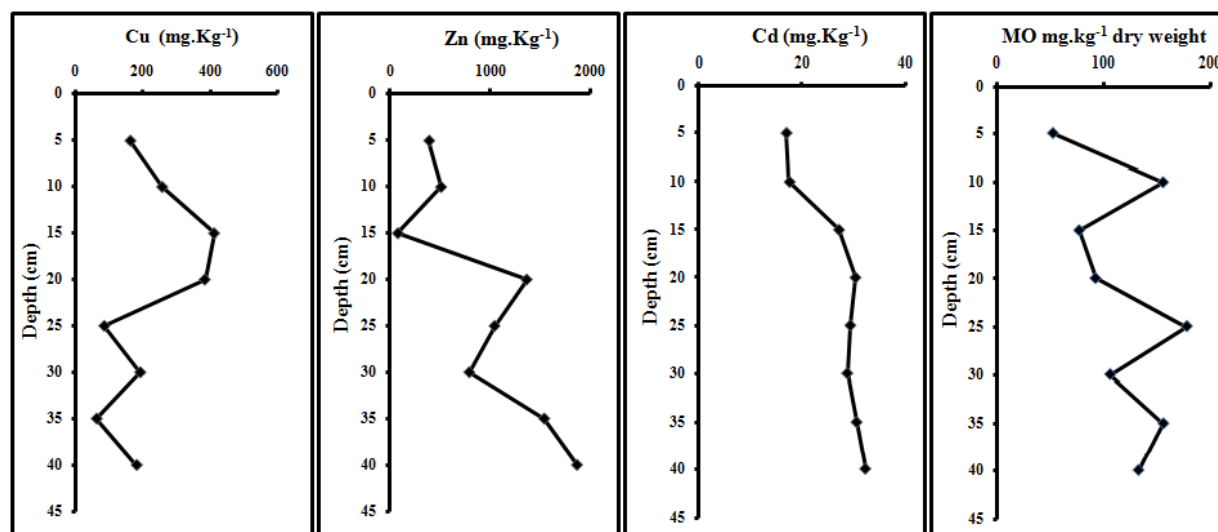


Figure 5. Profiles of the vertical distribution of MTEs and OM in the sediment column of the fishing port of Safi.

This could be linked to past activities at the port, such as the development of port infrastructure, the dredging of trade and mineral basins, the use of antifouling (source of Cu) and the periods of sedimentation corresponding to the strata 5-20 cm were probably the most active. Literature data [30-33] show a classification of MTEs according to their adsorption potential, in the following order: Pb>Zn>Cd>Cu. In soils, Zn and Cd are the most mobile MTEs compared to Pb and Cu. In even slightly acidic soils, Zn can migrate relatively easily to deeper layers although a significant

fraction of the metal remains associated with natural organic matter and mineral compounds. In an anoxic environment, Zn precipitates quantitatively in the form of sulphide (ZnS) [7]. According to [34], Cd is present in all rocks but more abundant in sediments rich in carbon, sulphides and phosphates. The chalcophiles properties of Cd favor its association with Zn and Hg and to a lesser extent with Pb and Cu [35]. The presence of carbon from organic matter or from biocenosis shells as well as phosphorus and sulfur, gypsum, and barite overlooked during imports/exports activities could justify such results. In addition, due to the fact that has a particular affinity for sulphides where it often associated with iron [36], it is above all the most common active ingredient in antifouling paints. Cu is considered to be one of the least mobile MTEs in hypergenesis processes, except under extreme acidity conditions [37], hence its concentration at the surface of the sediment.

3.5. Correlation between MTEs and OM

The correlation analysis was carried out to explore the possible relationships between the contents of MTEs on the one hand and between these contents and those inherent in organic matter on the other hand (Table 3). Pearson's coefficients show positive correlations between Cd and Zn, Zn and MO, Cd and MO. It show also a negative correlation between Cu and Cd, Zn and MO, and Cu and MO. Cd and Zn have strong correlations indicating common sources, probably phosphate and similar behavior during transformation or migration [38]. The low correlation values between Cd, Zn, and OM suggest the possibility of adsorption of these metals on other ligands such as phosphorus, carbonate and sulfur. The negative correlation between Cu and MO assumes preferential adsorption at the sulfur level.

Table 3. Matrix of correlations between the pollutant contents (MTEs) and MO (the values indicate the Pearson correlation coefficient)

	Cu	Zn	Cd
Zn	-0,40		
Cd	-0,05	0,68	
MO	-0,54	0,46	0,30

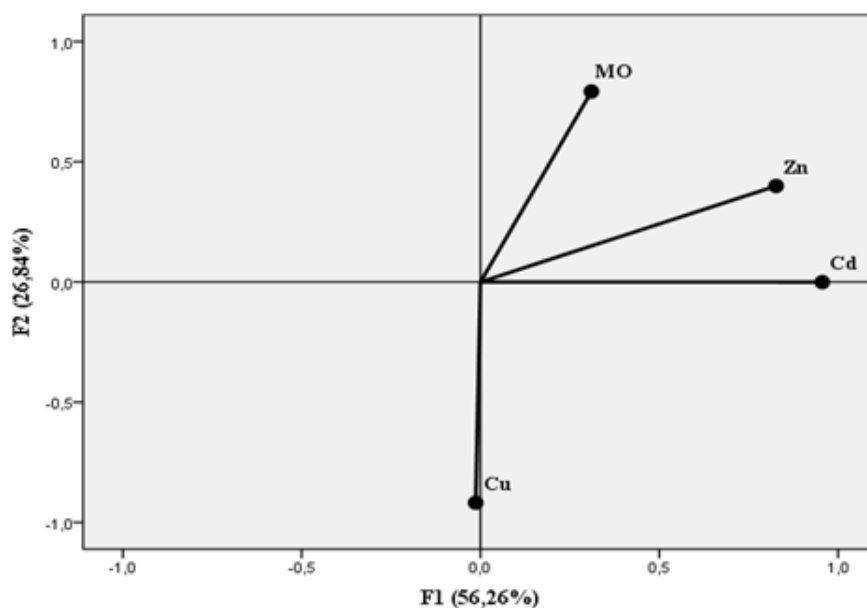


Figure 6. Correlations of MTEs and OM with the two PCA factors (F1 and F2).

In order to search for the distribution of MTEs and organic matter at the level of the different strata, a multivariate analysis of the PCA type was adopted (Figure 6). The result of this analysis shows that the percentage of inertia explained by the first two axes is 56.26% and 26.83% for the first and the second axis respectively. The first factor is negatively correlated with Cu and positively with Cd, Zn, and organic matter. Since these two groups exhibit different correlations suggests they have different sources. The result of the PCA confirms the correlations highlighted by the Pearson method.

The ascending hierarchical analysis based on Ward's method [39] and Euclidean distance allowed us to define three clusters (Figure 7a).

- The first cluster includes strata St1, St2 and St3 characterized mainly by the lowest Zn, Cd and OM concentrations and the highest Cu contents.
- The second cluster contains the St4 and St5 strata characterized by average Zn, Cd and OM concentrations and high Cu contents.
- The third cluster includes strata St4, St7 and St8, the Cd, Zn and MO contents of which are high compared to Cu.

The strata of the same class generally present similar contents of MTEs and OM and suggests the same origins of contamination and possibly the same conditions of sedimentation of the detrital particles forming these strata. Such a classification seems to be the result of four episodes of contamination at our study site (Figure 7b): the first represented by the superficial layers: 0-15 cm, the second episode represented by the stratum: 15-20 cm, the third episode represented by the 20-30 cm stratum and the fourth episode represented by the 30-40cm stratum. Similar events occurred in strata 4 and 7-8 probably due to dredging from basins II and III.

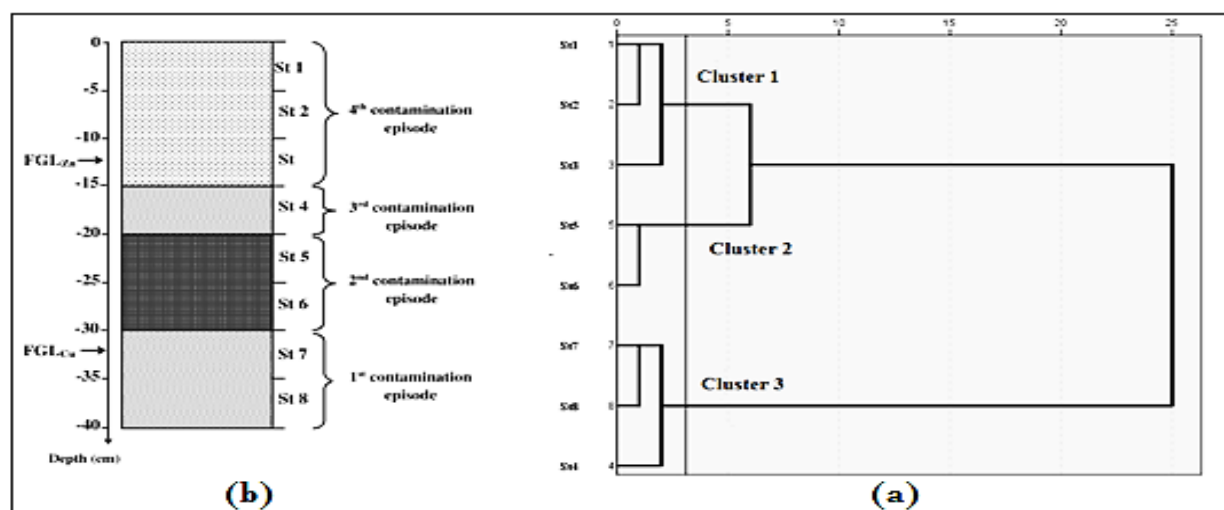


Figure 7. Classification dendrogram of the sediment column layers obtained with the CHA method (a) and representation of organometallic contamination episodes (b). St: stratum, FGL: local geochemical background.

3.6. Assessment of sediments contamination according to pollution indices

It should be noted that the GEODE thresholds are a legislative standard serving as a reference for administrative procedure purpose associated with dredging but does not prejudice a possible toxicity of the sediment or even its real contamination [7], hence the interest of studying the contamination indices (Table 4).

The contamination factor of Cu shows irregular variations in the intensity of contamination depending on the strata. These variations would be related to the variation in the activities of the fishing port due to the use of antifouling. For

Zn, the contamination is considerable at the level of the upper layers (0-10 cm), to very high for the lower layers (15-40cm). The 10-15 cm layer remains uncontaminated. Zinc would be trapped mainly in the lower strata. Whereas for Cd, all strata show very high CFs of several orders of magnitude from the surface to the bottom. This shows the permanent pollution over time by Cd and its entrapment by the sediments. All the strata have pollution load indices (PLI) greater than 1 and vary between 9 and 23, thus confirming a real anthropogenic contribution of the three metals. According to the geo-contamination index: Most strata are moderately contaminated with copper compared to the geochemical background, which shows that anthropogenic inputs at this level are moderate. With the exception of the 20-25 cm layer, which seems uncontaminated, the 30-35 layer whose I_{geo} is negative suggests that the local geochemical background of Cu would probably be around 62 mg / kg of dry sediment compared to the values found by [21]: 45 mg / kg. The Zn contamination increases with depth; however, the 10-15 cm layer shows negative I_{geo} suggesting that the local geochemical background would be around 74 mg / kg dry sediment compared to the value of [21] (95 mg / kg dry). Concerning Cd, the I_{geo} are at the level of all class 6 strata and therefore extremely contaminated, thus showing the strong anthropogenic contribution of cadmium compared to the geochemical background (0.3 mg / kg dry according to [21]). A more in-depth exploration could have given us an idea of the local geochemical background of cadmium

The three metals present very high ecological risks exceeding by several orders of magnitude the maximum value ($ER > 320$). All the strata present very high risks exceeding 3 to 7 times the maximum level of risk taking into account the simultaneous presence of the 3 studied metals ($IRE > 600$).

3.7. Assessment of the overall contamination of the sediment column

To assess the contamination of the entire column, we suggested that the average indices (Table 4) could give us an idea of the sediment reworked during the dredging operation. Thus, the sediment is considerably contaminated with copper.

Table 4. Assessment of pollution along the sediment column of Safi's fishing port as well as the average of the indices in different strata

Strata (cm)	CF			I_{geo}			ER			PLI	ERI
	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd		
0-5	3.60	4.073	56.33	1.26	1.44	5.23	811.10	387.00	507.00	9.38	1705.10
5-10	5.71	5.33	58.33	1.92	1.83	5.28	1286.00	506.90	525.00	12.11	2317.90
10-15	9.15	0.77	90.33	2.60	-0.94	5.91	2059.10	74.00	813.00	8.63	2946.10
15-20	8.53	14.33	101.00	2.50	3.25	6.07	1919.25	1361.4	909.00	23.11	4189.65
20-25	1.87	10.95	97.66	0.32	2.86	6.02	422.40	1041.00	879.00	12.61	2342.40
25-30	4.26	8.29	95.66	1.50	2.46	5.99	958.58	788.00	861.00	15.00	2607.58
30-35	1.37	16.17	101.66	-0.12	3.43	6.08	310.00	1536.90	915.00	13.13	2761.90
35-40	4.02	19.62	107.33	1.42	3.70	6.16	905.66	1864.80	966.00	20.39	3736.46
Mean	4.81	9.94	88.53	1.42	2.25	5.84	1084.01	945.00	796.87	14.29	2825.88

For Zn and Cd the contamination factor is very high. The reworked sediment would have a value of 14.29 as PLI showing a strong anthropogenic contamination by the three MTEs. Likewise for the I_{geo} , the sediment is class 2 moderately contaminated with Cu, class 3 for Zn (moderately to highly contaminated). While Cd, the sediment is class 6 (extremely contaminated). The ecological risk for the considered sediment disturbed by dredging is in the following decreasing order: $Cu > Zn > Cd$. Thus, the ecological risk index of the reworked sediment has a value of 2825.88, therefore 4.7 times higher risk to the environment. Such an inversion would be related to the physicochemical behavior of MTEs with respect to ligands: MO, phosphorus, sulfur, carbonates. The copper is probably less well trapped by the sediment and therefore more bioavailable.

4. Conclusion

At the end of this prospective and preventive of ecological risks study of the sediment in the fishing port of Safi, never dredged before, we have shown that the contamination is mainly of endogenous origin emanating from the activities of the trade, mineral, and fishing basins. The particle size study showed that the sediment is homogeneous in the integrity of its profile and suggests a low hydrodynamic activity in the fishing basin. As for the MTEs contents over the entire column of the studied sediment, the concentrations exceeding by several orders of magnitude the threshold value N2 of the GEODE standards. In addition, the concentrations of Zn and Cd increase towards the sedimentary bottom while they remain irregular for Cu. All the pollution indices in fact corroborate these high levels and reflect a consequent metallic pollution of the sediment for the three analyzed metals at the level of the different strata. Concerning the average of the strata simulated with the sediment reworked during a possible dredging, the calculation of the ecological risk inherent in each MTE reveals a radical inversion of $Cu > Zn > Cd$ succession with respect to its order of enrichment. The copper would probably be less well trapped by the sediment and therefore more bioavailable. We also believe that we have found local geochemical background values for Cu and Zn relative to the geochemical background. However, the situation appears to be more alarming for Cd given its high concentration throughout the sediment. Statistical correlations between MTEs have shown a common origin for Zn and Cd which both probably originate from exported crude phosphate. However, most of the Cu comes from antifouling paints. According to the ascending hierarchical analysis, the contamination profile of the strata shows the existence of 4 episodes of contamination. The most significant episodes are located in strata 4, 7 and 8, and would probably be concomitant with dredging operations. The results of this work constitute a starting point and reference data for future more in-depth research on the values of the local geochemical background and their monitoring over time, as well as on the establishment of processes aimed at treating, ex situ, the polluted sediments of the port with a view to their recovery.

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