



Article Spatial Distribution and Contamination Level Assessment of Marine Sediment of the Safi Bay (Moroccan Atlantic Coast)

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Abstract: This study assesses the spatial distribution and contamination level of heavy metals in Safi Bay surface sediments. In this order, 28 surface sediment samples were retrieved from the study area and analyzed using the x-fluorescence method. To assess the contamination of the examined sediment, we used geo-ecological indices such as contamination factor (CF), degree of contamination (DC), geo accumulation index, and pollution load index (PLI). The results show that only Pb and Cd present moderate and considerable contamination in some sampling sites, while other elements (Cr, Cu, Zn, and Ni) indicate no contamination and low contamination by these elements. The inhomogeneous distribution of metal concentrations along the bay suggests different heavy metal sources. Given the ecological and socioeconomic importance of the study area, there is a need for a further analysis of both sediments and biological samples for a better understanding of the contamination levels and origin of metals, in addition to the sustainability of Safi Bay.

Keywords: heavy metals; sediment; spatial distribution; environmental indices; Safi Bay; Morocco

1. Introduction

Heavy metals are common environmental pollutants in marine and coastal ecosystems because of their toxicity, non-biodegradability in sediments, and their bio-accumulative nature [1–8]. Once these pollutants reach aquatic environments from both natural processes and/or anthropogenic activities, they may damage marine organisms or can be accumulated in sediments via chemical adsorption and or physical precipitation [9–12], causing biodiversity loss [13,14]. In aquatic ecosystems, heavy metals do not remain for long in the water column but are precipitated and deposited in sediments as a final receptor [15]. Sediments represent an essential ecological component and play an important role in pollutant storage and distribution, which reflects actual system quality [7,16–19]. Accordingly, marine sediments can be used as an indicator of pollutants [20]. The growth of human activities around coastal cities, mainly industrial activities in response to the development of socioeconomic sectors, has resulted in human overpopulation and pollution level increase, affecting water resources, sediment, and marine organisms [8,11,21,22]. Indeed, coastal sediments have been found to be polluted by wastewater effluent issued from domestic and industrial activities [17,22-24], where several studies indicated that coastal sediment is an important tool for analyzing pollution levels by heavy metals [11,17,22,25–34]. According to statistical analysis, about 85% of heavy metals are accumulated in superficial



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). sediments [11,22,35,36]. In this order, the study of the pollution level in a coastal environment, which provides various ecosystem services of environmental, socioeconomic, cultural, and recreational value [37], imposes analyzing sediment as an essential ecological component of the coastal environment.

The Bay of Safi is located on the Moroccan Atlantic coast, where multiple human activities are concentrated, including industrial activities, agriculture, and fishing, among others. Thus, the Bay of Safi is subjected to pollutants released from the growth of industrial activities along this littoral zone. Indeed, Kouali et al. and Rafiq et al. [38,39] have identified the intertidal area in Safi as a hotspot of metal contamination. However, few studies have been carried out to analyze the pollution level in this coastal zone despite its socioeconomic and ecological interests. Thus, this ongoing study is the first investigation of the degree of heavy metal pollution in the marine sediment of Safi Bay.

The main aims of this study are to:

- Analyze and quantify the pollution level by heavy metals in Safi Bay sediment using various environmental indices, including contamination factor (CF), degree of contamination (Cd), index of geo accumulation (Igeo), and pollution load index (PLI).
- Calculate the potential ecological risk of metals detected in the Safi Bay sediment.
- Establish the spatial distribution of heavy metals in Safi Bay.
- Attempt to define the possible origin of the heavy metals in this coastal environment to allow for the adequate and efficient management of Safi Bay for sustainable socioeconomic and environmental development.

2. Materials and Methods

2.1. Study Area

The Safi Bay is located on the Moroccan Atlantic coast $(32^{\circ}18' \text{ N}-9^{\circ}15' \text{ W})$ along a coastal line that extends about 5 km from the tip of the cliff of Sidi Bouzid in the north to Jorf Ammouni in the south (Figure 1). The study region includes the city beach with an NW-SE orientation and the sharp cliff south of the port with an N-S direction [40]. Safi Bay is a triangular bay which has experienced strong population growth and economic development in the last decade. It is characterized by chemical (phosphates) and parachemical industries (cement, brickworks, plateries) and the agro-industry, especially the fish canneries related to the fishing sector.

At the bottom of this bay, a port with industrial and mineral vocations has been established and is one of the main commercial ports in Morocco. This port has a general traffic of about 5 million tons, a major part of which is destined for mining exports. It is composed of three units (fishing port, commercial port, and ore carrier port). The commercial port has traffic of cereals, gypsum, barite, potash, manganese, fertilizers, and preserves, and the mineral port has traffic of phosphates, sulfur, and phosphoric acid; these industrial, urban, and port activities can constitute sources of heavy metals in this bay.

In Safi Bay, the slope of the continental shelf varies according to the depth, where it reaches 4% between the zero line and the isobath -10 m. The bottoms from -10 m to -25 m have only a slope between 2.5% and 1%. A vast plateau develops from -25 m to -30 m and gradually flares until it reaches a width of 2.5 km. The wave direction is dominant from NW to NNW [40], with the most frequent waves reaching 0.5 to 1.5 m [41]. The distribution of sediments at the bay is controlled by this swell, and an estimated transit of 250,000 m³/year is generated [42].



Figure 1. Study area and sampling locations, (S1, ..., S38 are the sampling sites codes).

2.2. Sampling

The superficial sediments of the bay are composed of mostly bioclastic material, with significant biogenic sedimentation favored by the development of bedrock on which fixed organisms are abundant. In contrast, terrigenous detrital inputs are of little importance, while quartz grains and lutites are present only in sheltered coastal areas [43,44]. The main sedimentary inputs in the Bay of Safi come from the erosion of the north coast (cliffs) and are then transited by a north–south littoral drift [40–42]. This sediment distribution is controlled by natural (waves, currents) and anthropogenic (geomorphological modification by port developments) factors.

Twenty-eight sediment samples were retrieved in August 2019 on radials perpendicular to the coastline at different depths, with the water depth ranging from 3.5 m to 31.8 m (Figure 1 and Table 1). All samples were collected with a Van Veen grab, preserved in sealed polyethylene bags, and marked for particle size distribution determination, while only the fine fraction of the samples (sediment <63 μ m) was considered for chemical composition

analysis. These samples were dried at 50° in an oven and then sieved through 63 μ m mesh size, crushed using the grinder, and placed in a new polyethylene bag.

Table 1. Sampling stations, depth (m), sand (%), mud (%), carbonate content, and textural class of each sample.

| Stations | Latitude | Longitude | Depth (m) | Sand (%) | Mud (%) | %CaCO ₃ | Textural Class |
|----------|----------------|---------------|-----------|----------|---------|--------------------|---------------------|
| S1 | 32°19′48.30″ N | 9°17′17.10″ W | 18.4 | 97.39 | 2.61 | 72.34 | Sand |
| S2 | 32°19′21.05″ N | 9°16′7.33″ W | 6.5 | 98.79 | 1.21 | 82.13 | Sand |
| S3 | 32°19′22.04″ N | 9°16′45.43″ W | 23.2 | 82.16 | 17.84 | 62.98 | Slightly muddy sand |
| S4 | 32°19′21.54″ N | 9°17′17.67″ W | 30.08 | 97.16 | 2.84 | 78.30 | Sand |
| S5 | 32°18′45.88″ N | 9°17′10.03″ W | 29.3 | 95.15 | 4.85 | 72.77 | Sand |
| S6 | 32°18′49.35″ N | 9°16′37.21″ W | 25.5 | 92.02 | 7.98 | 71.06 | Slightly muddy sand |
| S7 | 32°18′50.34″ N | 9°16′11.42″ W | 21.9 | 84.64 | 15.36 | 74.47 | Slightly muddy sand |
| S8 | 32°18′50.83″ N | 9°15′42.71″ W | 17.05 | 96.86 | 3.14 | 79.57 | Sand |
| S9 | 32°18′52.32″ N | 9°15′23.37″ W | 15.2 | 98.55 | 1.45 | 82.13 | Sand |
| S10 | 32°18′53.31″ N | 9°15′4.03″ W | 3.5 | 98.86 | 1.14 | 82.55 | Sand |
| S12 | 32°18′17.65″ N | 9°15′28.64″ W | 13.76 | 98.41 | 1.59 | 79.57 | Sand |
| S13 | 32°18′18.64″ N | 9°16′6.73″ W | 23.5 | 95.88 | 4.12 | 79.57 | Sand |
| S15 | 32°17′43.48″ N | 9°16′12.58″ W | 26.5 | 94.25 | 5.75 | 77.45 | Sand |
| S16 | 32°17′42.49″ N | 9°15′41.53″ W | 25.8 | 95.41 | 4.59 | 77.87 | Sand |
| S17 | 32°17′42.99″ N | 9°15′14.00″ W | 21.4 | 96.98 | 3.02 | 76.17 | Sand |
| S18 | 32°17′43.97″ N | 9°14′51.73″ W | 12.5 | 96.94 | 3.06 | 69.36 | Sand |
| S19 | 32°17′43.97″ N | 9°16′40.12″ W | 28.2 | 96.46 | 3.54 | 82.55 | Sand |
| S20 | 32°17′42.48″ N | 9°17′2.39″ W | 29.74 | 93.72 | 6.28 | 65.53 | Slightly muddy sand |
| S21 | 32°17′6.83″ N | 9°16′45.97″ W | 30.6 | 96.26 | 3.74 | 79.57 | Sand |
| S22 | 32°17′7.33″ N | 9°16′13.75″ W | 28.4 | 93.85 | 6.15 | 73.62 | Slightly muddy sand |
| S23 | 32°17′6.84″ N | 9°15′46.21″ W | 26.8 | 67.57 | 32.43 | 52.34 | Muddy sand |
| S28 | 32°16′30.19″ N | 9°15′48.56″ W | 24.8 | 98.30 | 1.70 | 77.45 | Sand |
| S29 | 32°16′30.68″ N | 9°16′13.74″ W | 26.5 | 87.41 | 12.59 | 37.02 | Slightly muddy sand |
| S30 | 32°16′31.67″ N | 9°16′43.62″ W | 29.2 | 90.79 | 9.21 | 41.28 | Slightly muddy sand |
| S32 | 32°15′49.57″ N | 9°16′31.31″ W | 26.3 | 97.35 | 2.65 | 80.00 | Sand |
| S33 | 32°15′48.59″ N | 9°16′2.03″ W | 22.5 | 99.02 | 0.98 | 77.45 | Sand |
| S34 | 32°15′18.87″ N | 9°15′59.69″ W | 11.22 | 96.96 | 3.04 | 72.34 | Sand |
| S38 | 32°15′19.34″ N | 9°17′15.84″ W | 31.8 | 97.82 | 2.18 | 77.02 | Sand |

2.3. Heavy Metals Determination

Samples were prepared and analyzed at the Marine Geosciences and Soil Science Laboratory (LGMSS) to determine sediment texture and carbonate content using Bernard calcimetry (Table 1). The grain distribution of each sample was measured using a dry setting on a series of AFNOR standard sieves, and the granulometric parameters were calculated after classification according to [45].

For chemical analysis, only the fine fraction of samples $<63 \mu m$ was analyzed, where 1 g of each sample was weighed, placed in a bag, and sent for analysis to the ICP-AES laboratory of the Centre National de Recherche Scientifique et Technique de Rabat (CNRST).

The first step of metals analysis consists of removing all organic matter from sediment, so approximately 1 g of dried samples and 10 mL of concentrated HNO₃ were placed together in a plastic digestion tube using a microwave digestion system. Then, a mixture of HNO₃-HFHCl was added to the sediment sample and heated to a temperature of 100–110 °C to obtain a transparent solution [46]. A total of 50 mL of demineralized water was added to the resulting solution and stored at room temperature for the subsequent analysis of heavy metals. The elements Cu, Zn, Cr, Ni, Pb, and Cd were determined, in the

Division of Technical Support Units for Scientific Research (UATRS) in the National Center for Scientific and Technical Research of Rabat (CNRST), using Jobin Yvon's ICP AES model Ultima 2 unit and controlled with 7.4 ICP-Expert Sequential software.

2.4. Statistical Analyses

ArcGis 10.8 software (Esri Co., Ltd., Redlands, CA, USA) was used to draw distribution maps of metal concentrations in surface sediments. All statistical analyses of the data (mean, minimum, maximum, Pearson correlation matrix, and contamination indices) were determined using XLSTAT statistical software 2019. Metal sources were analyzed using primary component analysis (PCA) and Pearson correlation analysis. The PCA was employed to examine both natural and man-made sources of potential pollution [47].

2.5. Assessment of the Environmental Pollution Degree

The environmental indices employed in this study have been widely used in studies related to pollution level assessment and quantification in coastal sediments [18,34,48–50]. Some authors have adopted many calculation methods [51–55], whose proposed pollution impact ranges to convert the measured concentrations of heavy metals in soil and sediment into a comprehensive description of pollution levels based on the intensity increase. Thus, in the present study, we used heavy metals pollution indices such as CF, DC, PLI, Igeo, and the potential ecological risk index (E_r^i and RI) to assess the pollution degree of Safi Bay sediments.

2.5.1. Contamination Factor (CF)

The contamination factor is an environmental indicator used to monitor and track the pollution level by heavy metals, where it allows for the assessment of the contamination degree by each metal in each sediment sample. CF values were obtained by dividing the concentration of each metal in the sediment by the baseline or background value (Equation (1)) [52].

$$CF = \frac{C_{sample}}{C_{background}}$$
(1)

where C_{sample} is the concentration of metal measured in the studied samples, and $C_{background}$ designates the metal concentration of the reference material or the background value. The authors in [52] defined four categories for sediment quality based on the CF calculated value ranging from low contamination (CF < 1), moderate contamination (1 \leq CF < 3), considerable contamination (3 \leq CF < 6), to very high contamination (CF \geq 6).

2.5.2. Degree of Contamination (DC)

The degree of contamination (DC) is an index that can be derived from CF values and defined as the sum of all individual metal contamination factors [52]. It is calculated as follows (Equation (2)):

$$DC = \sum_{i=1}^{9} Ci f$$
(2)

As the utilized components for this index are not always possible to analyze, Abrahim et al. (2008) [56] proposed an alternative method. The modified equation proposed to calculate the degree of contamination is given below (Equation (3)):

$$mCd = \sum_{i=1}^{9} Ci f$$
(3)

Regarding the classification and description of the modified contamination degree of sediments, the following terminology was adopted (Table 2):

| Classification | Description |
|----------------|--|
| 0 < mCd < 1.5 | Nil-very low degree of contamination |
| 1.5 < mCd < 2 | Low degree of contamination |
| 2 < mCd < 4 | Moderate degree of contamination |
| 4 < mCd < 8 | High degree of contamination |
| 8 < mCd < 16 | Very high degree of contamination |
| 16 < mCd < 32 | Extremely high degree of contamination |
| $mCd \ge 32$ | Ultra-high degree of contamination |

Table 2. Description of the modified contamination degree classification.

2.5.3. Pollution Load Index (PLI)

The PLI is used as an indicator of contamination level by heavy metals for each sampling point [57,58]. The PLI is calculated through the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$
(4)

where "n" is the number of determined metals, and CF designates the contamination factor. The contamination can be estimated as follows:

PLI < 1, no metal pollution; PLI > 1, polluted condition.

2.5.4. Geo-Accumulation Index (Igeo)

The Igeo was used to assess the metal pollution in the sediment of Safi Bay. The following equation is used to calculate the Igeo for each metal in each sample [51]:

Igeo =
$$\log 2\left(\frac{Cn}{1.5 Bn}\right)$$
 (5)

where Cn is the measured concentration of the heavy metal (n) in the investigated sediments, and Bn is the background value; here, we used the average abundance value of the upper continental crust (UCC) of a given metal. Also, 1.5 is the background matrix correction factor due to lithogenic effects [59–63]. The classification of sediment pollution level depends on the value of the Igeo, where 7 classes have been defined in Table 3.

Table 3. Geo-accumulation index classes and designation.

| Igeo Value | Igeo Class | Designation of Sediment Quality | | | | | |
|------------|------------|---|--|--|--|--|--|
| >5 | 6 | Extremely contaminated | | | | | |
| 4–5 | 5 | Strongly to extremely contaminated | | | | | |
| 3–4 | 4 | Strongly contaminated | | | | | |
| 2–3 | 3 | Moderately to strongly contaminated | | | | | |
| 1–2 | 2 | Moderately contaminated | | | | | |
| 0-1 | 1 | Uncontaminated to moderately contaminated | | | | | |
| <0 | 0 | Uncontaminated | | | | | |
| | | | | | | | |

2.5.5. Potential Ecological Risk Index (E_r^i and RI)

The potential ecological risk factor E_r^i and the potential ecological risk index (RI) were proposed by [52]. Those indices were widely used to evaluate the potential ecological risk associated with heavy metals in aquatic sediments [6,64–68].

 E_r^i is calculated using the following equation [52]:

$$C_f^i = C^i / C_n^i \tag{6}$$

$$E_r^i = T_r^i \times C_f^i \tag{7}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{8}$$

where E_r^i is the potential ecological risk factor of each heavy metal, and T_r^i is the toxic response factor for heavy metal *i*. The toxic response factor for Cu, Zn, Cr, Ni, Pb, Cd, and V is 5, 1, 2, 5, 5, 30, and 2, respectively [52,69,70], C_f^i is the contamination factor of heavy metal *i*, and C^i is the measured concentration of heavy metal *i* in the sediment. The E_r^i and RI values were deduced as follows [7,10,22,71,72]:

2.5.6. Sediment Quality Guidelines (SQGs)

Several authors [11–13,33,34] have assessed the impact of metals on the toxicity of aquatic organisms using sediment quality guidelines (SQGs). The threshold effect level (TEL) and probable effect level (PEL) were used in this study to assess the potential biotic influence of metals contained in sediment samples.

3. Results and Discussions

3.1. Spatial Distribution of Sediment Grain Size and CaCO₃ Content

The spatial distribution of sediment grain size and $CaCO_3$ content are shown in Figure 2. The collected samples are almost sandy except for S23, S7, and S3, which show a relatively important fine fraction of 32.42%. The sand fraction oscillates between 99% and 67.85%. The CaCO₃ content ranged from 37 to 82.5%, while its spatial distribution shows a similar trend as sand fraction, reflecting a significant correlation between sand and CaCO₃ content. The lowest values of CaCO₃ were recorded in the stations with a significant portion of mud, mainly S29, S30, and S23.



Figure 2. Spatial distribution map of sand, mud, and CaCO₃.

3.2. Assessment of the Surface Sediment Contamination by Heavy Metals

Twenty-eight sediment samples retrieved from Safi Bay have been analyzed for Cu, Zn, Cr, Ni, Pb, and Cd concentration determination. The concentrations fluctuate from one sampling point to another, probably reflecting different origins. The metals concentrations varied over the following ranges: Cd (0.305–0.801 mg/kg); Cr (0.305–120.983 mg/kg); Cu (1.740–12.715 mg/kg); Ni (1.573–81.319 mg/kg); Pb (16.575–63.381 mg/kg); and Zn

(14.266–127.719 mg/kg). The highest concentrations were recorded in the following stations: S15 (Ni), S17 (Zn), S23 (Cr et Pb), and S29 (Cd et Pb). Industrial and domestic discharges into the ocean are the possible origin of the highest values detected in these sediment samples as they are collected near the city. In addition, these domestic and industrial discharges flow directly into the ocean as the treatment plant is still an ongoing project. The lowest values were registered in the samples retrieved from the north part of the bay, distant from the city and related anthropogenic discharges. Noting also that natural factors such as the granulometric composition of the sediment, seawater dilution levels, and the hydrodynamic conditions that characterize the sampling sites can also affect the distribution of heavy metals in Safi Bay [73]. Noting that stations S23 and S29 indicate significant content fine fractions compared to other sites, explaining the highest recorded concentrations. It is well known that fine fractions accumulate pollutants more than coarser fractions because of their high specific surface area, whereas the presence of important pollutant concentrations in coarser fractions can be explained most likely by the coating phenomena. Organic matter coating on mineral particles may enhance the capacity of dissolved pollutants adsorption [74,75]. Moderate concentrations were found in the following stations, S5, S6, S7, S8, S9, and S10, located near the entrance of loading and unloading vessels for chemical and mining products in Safi port. Figure 3 displays the spatial distribution of heavy metals in Safi Bay, suggesting that the highest concentrations of heavy metals are associated mainly with human activities and port activities, which is in good accordance with the findings of [67], as the lowest concentrations were recorded in the north part far from the Safi port and anthropogenic discharges.

The average concentrations of heavy metals of all sampling stations for each metal Zn = 36.546 mg/kg, Pb = 33.972 mg/kg, Cr = 11.343 mg/kg, Ni = 10.395 mg/kg, Cu = 3.850 mg/kg, Cd = 0.395 mg/kg were compared to the average concentrations found in sediments from similar ecosystems in the world and to upper continental crust (UCC) values Table 4. The heavy metal concentrations of this study were almost less high than those reported in Dakhla Bay, except for Ni and Zn [76]. Cu, Zn, and Pb show low concentrations compared to almost all the coastal ecosystems listed in Table 5. The heavy metal concentrations were indeed compared to the sediment quality guideline values, including the threshold effect level (TEL) used to show the concentrations below, where no effect of metal content was detected in sediment on aquatic organisms and the toxic effect threshold (TET) utilized to indicate the heavy metal concentrations, above which substantial effects are likely to occur [77]. Heavy metal concentrations in Safi Bay sediments are less significant than the TELs values in Table 4; therefore, they do/did not present a toxicity risk to marine organisms living in these sediments.

| Tal | ole | 4. | The | E_r^{ι} | and | RI | value | es c | lassi | ficat | tion |
|-----|-----|----|-----|---------------|-----|----|-------|------|-------|-------|------|
|-----|-----|----|-----|---------------|-----|----|-------|------|-------|-------|------|

| E ⁱ _r Value | Risk Intensity | RI Value | Risk Intensity |
|-----------------------------------|-----------------------------|----------------------------|------------------------------|
| <40 | Low ecological risk | <150 | Low ecological risk |
| $40 < E_r^i \le 80$ | Moderate ecological risk | $150 \leq \text{RI} < 300$ | Moderate ecological risk |
| $80 < E_r^i \le 160$ | Appreciable ecological risk | $300 \le \text{RI} < 600$ | Considerable ecological risk |
| $160 < E_r^i \le 320$ | High ecological risk | RI > 600 | Very high ecological risk |
| $E_r^i > 320$ | Serious ecological risk | | |



Figure 3. The spatial distribution map of Cd (mg/kg), Cr (mg/kg), Zn (mg/kg), Ni (mg/kg), Pb (mg/kg), and Cu (mg/kg) determined in the fine fractions of sediment samples.

| Table 5. Comparison table of the heavy metal concentrations measured in Safi Bay surface sediment |
|---|
| and other similar marine ecosystems. (ND: not determined). |

| Teadland | | | D (| | | | |
|----------------------------|-------------|--------|------------|--------|-----------|----------|---------------|
| Locations | Cd | Cr | Cu | Ni | Pb | Zn | Keferences |
| Safi Bay, Morocco | 0.395 | 11.343 | 3.850 | 10.395 | 33.972 | 36.546 | Present study |
| Dakhla Bay, Morocco | 0.4 | 108 | 17.3 | 5.8 | 71.3 | 20.8 | [76] |
| Bohai Bay, China | 0.04 - 0.84 | ND | 7.20-44.0 | ND | 5.90-97.0 | 56.3-309 | [78] |
| Bay of Bengal, India | 19.8 | 109.45 | 76.45 | 27.984 | 49.629 | 78.76 | [8] |
| Zhelin Bay, China | 0.063 | 23.07 | 7.95 | 7.5 | 35.69 | 74.95 | [79] |
| Laizhou Bay, China | 0.19 | 32.69 | 10.99 | 17.38 | 13.37 | 50.63 | [11] |
| Tahaddart Estuary, Morocco | 0.16 | 91.83 | 57.1 | 34.92 | 25.55 | 73.73 | [66] |

| Locations | | Ν | Ietal Concent | rations (mg/k | g) | | - D (|
|---|-----------|-----------|---------------|---------------|------------|------------|------------|
| Locations | Cd | Cr | Cu | Ni | Pb | Zn | Keferences |
| Oualidia Lagoon, Morocco | 0.66 | 102.4 | 17.7 | 15.73 | 10.1 | 75.8 | [18] |
| Nador Lagoon, Morocco | 1.6 | 71.6 | 150.8 | 45.2 | 135 | 554.9 | [10] |
| OumEr Bia estuary, Morocco | 0.36 | 9.5 | 19.6 | ND | 28 | 138 | [80] |
| The fishing port of Safi, Morocco | 1.2–2.4 | ND | 45-90 | ND | ND | 276–552 | [67] |
| Bay of Biscay, Spain | 0.08-0.11 | 2.13-6.16 | 11.8–21.76 | 4.17-15.12 | 6.88–26.23 | 28.8-66.79 | [81] |
| Upper Continental Crust | 0.09 | 35 | 25 | 20 | 20 | 71 | [82] |
| The suspended sediment of World Rivers | 1.55 | 133 | 75.9 | 74.5 | 61.1 | 208 | [83] |
| TEL | 0.6 | 37.3 | 35.7 | 18 | 35 | 123 | [84] |
| TET | 3 | 100 | 86 | 61 | 170 | 540 | [84] |

Table 5. Cont.

3.3. Correlation among Metals

The Pearson correlation among the heavy metals results is shown in Table 5. The results indicate no significant correlation among heavy metals measured in Safi Bay sediment, suggesting a different origin of these metals in the bay in good accordance with their inhomogeneous distribution along the bay. Only Cu shows a highly significant correlation with Pb (p < 0.01), while Cu, Cr, and Zn indicate significant correlations (p < 0.05), which is in good accordance with Kouali et al.'s (2022) [38] findings. These significant correlations among Cu, Cr, and Zn may signify similar chemical properties, a similar degree of contamination, or derived from the same sources [85,86].

As shown in Table 6, a positive and significant correlation between Cr, Cu, and Pb with mud reveals the affinity of these metals to fine elements. The correlation matrix shows a negative and significant correlation observed for Cr, Cu, Pb, and Zn with $CaCO_3$ and sand, except for Cr and $CaCO_3$ (non-significant negative value), indicating that these metals are not associated with $CaCO_3$.

| Variables | Cd (mg/kg) | Cr (mg/kg) | Cu (mg/kg) | Ni (mg/kg) | Pb (mg/kg) | Zn (mg/kg) | Sand (%) | Mud (%) | %CaCO ₃ |
|--------------------|---------------|---------------|---------------|---------------|---------------|---------------|-------------|------------|--------------------|
| Cd (mg/kg) | 1.00 | | | | | | | | |
| Cr (mg/kg) | -0.07 | 1.00 | | | | | | | |
| Cu (mg/kg) | 0.27 | 0.62 * | 1.00 | | | | | | |
| Ni (mg/kg) | 0.05 | -0.02 | 0.12 | 1.00 | | | | | |
| Pb (mg/kg) | 0.44 | 0.32 | 0.83 ** | 0.08 | 1.00 | | | | |
| Zn (mg/kg) | 0.34 | 0.45 | 0.68 ** | 0.25 | 0.53 * | 1.00 | | | |
| Sand (%) | -0.18 | -0.71 ** | -0.82 ** | -0.09 | -0.70 ** | -0.50 | 1.00 | | |
| Mud (%) | 0.18 | 0.71 ** | 0.82 ** | 0.09 | 0.70 ** | 0.50 | -1.00 | 1.00 | |
| %CaCO ₃ | -0.35 | -0.26 | -0.78 ** | -0.05 | -0.81 ** | -0.48 | 0.63 * | -0.63 * | 1.00 |

Table 6. Pearson correlation matrix of studied heavy metals, sand, mud, and CaCO₃ in Safi Bay.

Significant correlation marked (** p < 0.01) and (* p < 0.05).

The Dendrogamme (Figure 4) based on Ward's method [87] shows three different clusters: Cluster 1 (sand and CaCO₃), Cluster 2 (Pb and Zn), and Cluster 3 (Cr, Ni, Cd, Cu, and mud).



Figure 4. Dendrogram produced with the classification ascendant hierarchy (CAH) representing all variables.

3.4. Assessment of Heavy Metal Contamination

The results of the calculated indices CF, DC, mCd, and PLI for the sediment collected from Safi Bay are shown in Table 6. Except for S17 and S29, which show considerable contamination by Cd, almost all the stations display low to moderate contamination by Cd CF > 3. The contamination factor for Pb indicates considerable contamination in stations S3, S7, S8, S18, S23, S29, S30, and S38, suggesting an anthropogenic origin, while moderate contamination was recorded in the other sampling sites. Other investigated heavy metals show low contamination, suggesting that Cd and Pb mainly contaminate the study area, which is in good accordance with [38], where the Cd exhibited moderate contamination of coastal sediment from Jorf Lihoudi in Safi. Both cadmium and lead indicated a strong positive correlation and considerable contamination, reflecting similar sources into the sediment bay. In addition, the inhomogeneous distribution of contamination levels along the bay reflects different origins of heavy metals, such as domestic, industrial, and ship effluent. Industrialand port-activities-related waste are reported as the main activities having heavy impacts on the bay environment [88]. The management of this ecosystem is a major concern as 70% of the released waste is thrown into the bay without pre-treatment [88]. In addition, the navigation activities may have potential impacts on this ecosystem environment by causing physical modifications of seabed substrate and habitats [89]. Ships were first identified as a major source of metal pollution in the 1970's, particularly copper [90].

A considerable degree of contamination was recorded in S23 and S29, while the other stations indicate low and moderate contamination in good accordance with the CF values.

The PLI values calculated for each station are shown in Table 7 and Figure 5. Almost all studied stations indicate no pollution by heavy metals, where the PLI values are inferior

to 1. These results may be explained by the strong dilution and dispersion of heavy metal concentrations in seawater because of the strong agitation. The authors in [67] reported high PLI values for sediment retrieved inside the Safi harbor where the sediment grain size is finer, allowing for the accumulation of heavy metals. In contrast, almost all investigated samples were sandy with a high CaCO₃ content, suggesting that those factors are not controlling the distribution and accumulation of the heavy metals in Safi Bay sediments. Thus, further investigation of sediments mainly from the harbor area is needed to provide a clearer picture of the pollution levels and sources.

Table 7. Metal contamination factors (CFs), degree of contamination (DC), modified degree of contamination (mCd), and pollution load indices (PLIs) for sediments of all sites studied in Safi Bay.

| | | Co | ontaminat | ion Facto | r (Cf) | | Degree of | Modified Degree of | |
|-------|------|------|-----------|-----------|--------|------|--------------------|---------------------|------|
| Sites | Cd | Cr | Cu | Ni | Pb | Zn | Contamination (DC) | Contamination (mCd) | PLI |
| S1 | 2.53 | 0.00 | 0.05 | 0.14 | 2.70 | 0.29 | 5.72 | 0.95 | 0.19 |
| S2 | 1.78 | 0.00 | 0.04 | 0.09 | 1.33 | 0.24 | 3.49 | 0.58 | 0.14 |
| S3 | 1.62 | 0.21 | 0.09 | 0.08 | 3.73 | 0.51 | 6.23 | 1.04 | 0.41 |
| S4 | 1.68 | 0.00 | 0.05 | 0.06 | 2.25 | 0.25 | 4.29 | 0.72 | 0.15 |
| S5 | 2.49 | 0.27 | 0.07 | 0.22 | 2.26 | 0.36 | 5.66 | 0.94 | 0.45 |
| S6 | 1.69 | 0.19 | 0.07 | 0.06 | 2.52 | 0.48 | 5.01 | 0.84 | 0.35 |
| S7 | 2.90 | 0.00 | 0.07 | 0.16 | 3.32 | 0.51 | 6.97 | 1.16 | 0.25 |
| S8 | 2.81 | 0.00 | 0.07 | 0.16 | 3.42 | 0.34 | 6.81 | 1.13 | 0.23 |
| S9 | 1.97 | 0.09 | 0.04 | 0.02 | 2.83 | 0.29 | 5.24 | 0.87 | 0.22 |
| S10 | 1.74 | 0.00 | 0.03 | 0.04 | 1.91 | 0.20 | 3.93 | 0.65 | 0.12 |
| S12 | 1.86 | 0.00 | 0.05 | 0.04 | 2.30 | 0.30 | 4.56 | 0.76 | 0.15 |
| S13 | 1.55 | 0.61 | 0.05 | 0.13 | 1.81 | 0.39 | 4.54 | 0.76 | 0.40 |
| S15 | 1.67 | 0.00 | 0.06 | 1.08 | 2.39 | 0.75 | 5.95 | 0.99 | 0.30 |
| S16 | 1.54 | 0.09 | 0.05 | 0.12 | 1.78 | 0.56 | 4.13 | 0.69 | 0.30 |
| S17 | 3.04 | 0.16 | 0.07 | 0.15 | 2.58 | 1.82 | 7.83 | 1.30 | 0.54 |
| S18 | 1.63 | 0.00 | 0.14 | 0.19 | 3.74 | 0.93 | 6.62 | 1.10 | 0.28 |
| S19 | 1.76 | 0.04 | 0.04 | 0.05 | 1.60 | 0.26 | 3.75 | 0.63 | 0.20 |
| S20 | 1.61 | 0.00 | 0.07 | 0.09 | 2.73 | 0.44 | 4.94 | 0.82 | 0.18 |
| S21 | 1.61 | 0.00 | 0.06 | 0.05 | 1.74 | 0.33 | 3.79 | 0.63 | 0.14 |
| S22 | 1.64 | 0.24 | 0.07 | 0.07 | 2.08 | 0.53 | 4.62 | 0.77 | 0.36 |
| S23 | 1.93 | 1.21 | 0.23 | 0.15 | 5.07 | 1.43 | 10.01 | 1.67 | 0.92 |
| S28 | 1.98 | 0.00 | 0.04 | 0.03 | 2.57 | 0.33 | 4.95 | 0.83 | 0.14 |
| S29 | 4.01 | 0.01 | 0.15 | 0.17 | 4.89 | 0.85 | 10.08 | 1.68 | 0.36 |
| S30 | 1.65 | 0.00 | 0.11 | 0.16 | 4.28 | 0.86 | 7.07 | 1.18 | 0.27 |
| S32 | 1.87 | 0.00 | 0.04 | 0.12 | 2.88 | 0.40 | 5.31 | 0.88 | 0.19 |
| S33 | 1.59 | 0.00 | 0.04 | 0.07 | 1.89 | 0.31 | 3.91 | 0.65 | 0.14 |
| S34 | 1.53 | 0.00 | 0.05 | 0.07 | 2.42 | 0.35 | 4.42 | 0.74 | 0.15 |
| S38 | 1.70 | 0.00 | 0.05 | 0.08 | 3.08 | 0.29 | 5.20 | 0.87 | 0.16 |
| Mean | 1.97 | 0.11 | 0.07 | 0.14 | 2.72 | 0.52 | 5.54 | 0.92 | 0.27 |
| Min | 1.53 | 0.00 | 0.03 | 0.02 | 1.33 | 0.20 | 3.49 | 0.58 | 0.12 |
| Max | 4.01 | 1.21 | 0.23 | 1.08 | 5.07 | 1.82 | 10.08 | 1.68 | 0.92 |

Bold values represent significant contamination.



Figure 5. Spatial distribution map of CF, CD, and PLI.

The geo-accumulation index (Igeo)-calculated values for the investigated sediment are shown in Table 8. Almost all sampling sites show no pollution by Cr, Cu, Ni, and Zn. Only Cd and Pb show values that fluctuate between 0 and 2, indicating weak and moderate pollution, which is in good accordance with other calculated indices.

| Citor | | G | eo-Accumulat | ion Index (Ige | eo) | |
|-------|------|-------|--------------|----------------|-------|-------|
| Siles | Cd | Cr | Cu | Ni | Pb | Zn |
| S1 | 0.75 | -8.80 | -4.85 | -3.40 | 0.85 | -2.37 |
| S2 | 0.25 | -8.72 | -5.27 | -4.02 | -0.18 | -2.62 |
| S3 | 0.11 | -2.86 | -4.04 | -4.23 | 1.31 | -1.56 |
| S4 | 0.16 | -8.81 | -4.94 | -4.64 | 0.59 | -2.56 |
| S5 | 0.73 | -2.50 | -4.50 | -2.76 | 0.59 | -2.05 |
| S6 | 0.17 | -2.95 | -4.35 | -4.68 | 0.75 | -1.65 |
| S7 | 0.95 | -8.60 | -4.42 | -3.19 | 1.15 | -1.55 |
| S8 | 0.90 | -8.65 | -4.39 | -3.21 | 1.19 | -2.12 |
| S9 | 0.39 | -4.08 | -5.25 | -6.16 | 0.92 | -2.36 |
| S10 | 0.21 | -8.75 | -5.57 | -5.25 | 0.35 | -2.88 |
| S12 | 0.31 | -8.66 | -4.89 | -5.08 | 0.61 | -2.30 |
| S13 | 0.04 | -1.29 | -4.89 | -3.53 | 0.27 | -1.95 |
| S15 | 0.15 | -8.82 | -4.56 | -0.47 | 0.67 | -1.00 |
| S16 | 0.04 | -4.12 | -4.90 | -3.66 | 0.25 | -1.43 |
| S17 | 1.02 | -3.19 | -4.38 | -3.32 | 0.78 | 0.28 |
| S18 | 0.12 | -8.85 | -3.46 | -2.96 | 1.32 | -0.69 |
| S19 | 0.23 | -5.09 | -5.29 | -4.80 | 0.09 | -2.52 |
| S20 | 0.10 | -8.86 | -4.36 | -4.13 | 0.86 | -1.77 |
| S21 | 0.10 | -8.86 | -4.75 | -5.05 | 0.22 | -2.17 |
| S22 | 0.12 | -2.64 | -4.45 | -4.43 | 0.47 | -1.51 |
| S23 | 0.36 | -0.31 | -2.70 | -3.31 | 1.76 | -0.07 |
| S28 | 0.40 | -8.57 | -5.24 | -5.57 | 0.77 | -2.18 |
| S29 | 1.42 | -8.13 | -3.32 | -3.10 | 1.71 | -0.82 |
| S30 | 0.13 | -8.83 | -3.76 | -3.19 | 1.51 | -0.80 |
| S32 | 0.31 | -8.65 | -5.09 | -3.62 | 0.94 | -1.92 |
| S33 | 0.08 | -8.88 | -5.11 | -4.38 | 0.34 | -2.29 |
| S34 | 0.02 | -8.94 | -4.83 | -4.48 | 0.69 | -2.12 |
| S38 | 0.18 | -8.79 | -5.02 | -4.20 | 1.04 | -2.37 |
| Mean | 0.35 | -6.65 | -4.59 | -3.96 | 0.78 | -1.76 |
| Max | 1.42 | -0.31 | -2.70 | -0.47 | 1.76 | 0.28 |
| Min | 0.02 | -8.94 | -5.57 | -6.16 | -0.18 | -2.88 |

Table 8. Geo-accumulation index (Igeo) for metals in Safi Bay.

Bold values represent significant contamination.

The ecological risk index E_r^i was used to assess the risk associated with heavy metal pollution in Safi Bay. The results of E_r^i calculation are presented in Table 9. The values of E_r^i ranged from 30.50 to 80.10 for Cd, with an average of 39.49; from 0.01 to 2.69 for Cr, with an average of 0.25; from 0.19 to 1.41 for Cu, with an average of 0.43; from 0.12 to 5.98 for Ni, with an average of 0.76; from 4.14 to 15.85 for Pb, with an average of 8.49; and from 0.18 to 1.34 for Zn, with an average of 0.38. The ecological risk index E_r^i of the investigated heavy metals was less than 40, reflecting a low ecological risk.

| | | | Ecological Ri | sk Factor (E_r^i) | | | DI | |
|---------------|-------|------|---------------|-----------------------|-------|------|-------|----------|
| Sites | Cd | Cr | Cu | Ni | Pb | Zn | - KI | KI Grade |
| S1 | 50.60 | 0.01 | 0.32 | 0.78 | 8.44 | 0.21 | 60.36 | Low |
| S2 | 35.60 | 0.01 | 0.24 | 0.51 | 4.14 | 0.18 | 40.68 | Low |
| S3 | 32.30 | 0.46 | 0.56 | 0.44 | 11.64 | 0.38 | 45.77 | Low |
| S4 | 33.50 | 0.01 | 0.30 | 0.33 | 7.04 | 0.19 | 41.36 | Low |
| S5 | 49.80 | 0.59 | 0.41 | 1.22 | 7.05 | 0.27 | 59.33 | Low |
| S6 | 33.70 | 0.43 | 0.45 | 0.32 | 7.88 | 0.35 | 43.14 | Low |
| S7 | 57.90 | 0.01 | 0.43 | 0.91 | 10.38 | 0.38 | 70.00 | Low |
| S8 | 56.10 | 0.01 | 0.44 | 0.89 | 10.70 | 0.25 | 68.39 | Low |
| S9 | 39.30 | 0.20 | 0.24 | 0.12 | 8.85 | 0.22 | 48.92 | Low |
| S10 | 34.80 | 0.01 | 0.19 | 0.22 | 5.96 | 0.15 | 41.33 | Low |
| S12 | 37.10 | 0.01 | 0.31 | 0.25 | 7.18 | 0.22 | 45.07 | Low |
| S13 | 30.90 | 1.36 | 0.31 | 0.71 | 5.67 | 0.29 | 39.24 | Low |
| S15 | 33.30 | 0.01 | 0.39 | 5.98 | 7.46 | 0.55 | 47.69 | Low |
| S16 | 30.80 | 0.19 | 0.31 | 0.66 | 5.57 | 0.41 | 37.94 | Low |
| S17 | 60.80 | 0.36 | 0.44 | 0.83 | 8.06 | 1.34 | 71.83 | Low |
| S18 | 32.50 | 0.01 | 0.83 | 1.06 | 11.67 | 0.68 | 46.76 | Low |
| S19 | 35.10 | 0.10 | 0.23 | 0.30 | 5.00 | 0.19 | 40.93 | Low |
| S20 | 32.20 | 0.01 | 0.45 | 0.47 | 8.52 | 0.32 | 41.97 | Low |
| S21 | 32.20 | 0.01 | 0.34 | 0.25 | 5.44 | 0.25 | 38.48 | Low |
| S22 | 32.70 | 0.53 | 0.42 | 0.39 | 6.50 | 0.39 | 40.93 | Low |
| S23 | 38.50 | 2.69 | 1.41 | 0.84 | 15.85 | 1.05 | 60.33 | Low |
| S28 | 39.60 | 0.01 | 0.24 | 0.17 | 8.02 | 0.24 | 48.29 | Low |
| S29 | 80.10 | 0.01 | 0.92 | 0.96 | 15.29 | 0.62 | 97.91 | Low |
| S30 | 32.90 | 0.01 | 0.68 | 0.91 | 13.38 | 0.64 | 48.51 | Low |
| S32 | 37.30 | 0.01 | 0.27 | 0.67 | 9.00 | 0.29 | 47.54 | Low |
| S33 | 31.80 | 0.01 | 0.26 | 0.40 | 5.92 | 0.23 | 38.61 | Low |
| S34 | 30.50 | 0.01 | 0.32 | 0.37 | 7.57 | 0.25 | 39.03 | Low |
| S38 | 33.90 | 0.01 | 0.28 | 0.45 | 9.63 | 0.21 | 44.48 | Low |
| Mean | 39.49 | 0.25 | 0.43 | 0.76 | 8.49 | 0.38 | 49.81 | Low |
| E_r^i grade | Low | Low | Low | Low | Low | Low | Low | |

Table 9. Potential ecological risk factors (E_r^i) and potential ecological risk index (RI) for studied metals in Safi Bay.

4. Conclusions

This study analyzed the spatial distribution of Cr, Zn, Cu, Ni, and Pb in Safi Bay sediments. The results showed an inhomogenous distribution of heavy metals along the bay, suggesting different sources of these metals. However, the concentrations of heavy metals were more elevated in the sampling sites located near the city and the Safi Port, while lower concentrations were recorded in the northern part of Safi City where human activities are less intense.

The use of environmental indices, including CF, DC, mCd, PLI, and E_r^i , allowed for the gathering of an understanding of the pollution levels of the bay sediments. The results revealed that the Safi Bay sediment is mainly contaminated by Cd and Pb according to the CF and DC factors. The PLI values were almost >1, suggesting that Safi Bay is an unpolluted area. However, the obtained results imply that there should be a further investigation of the bay sediments, mainly the sediment cores, which would allow for a better understanding of the pollution history in the study area to be obtained. Factors such as the hydrodynamic conditions, currents, waves, and resuspension/deposition characterizing the study area need to be analyzed to obtain a better understanding of the pollutant spatial distribution and their concentration fluctuations sources.

This study is the first investigation of the contamination of Safi Bay sediments by heavy metals. Thus, the present work provides a database for future investigations of the bay's environmental quality, mainly its ecological and socioeconomic interests, contributing towards developing conservation and protection projects for the sustainable use of its related ecosystem services.

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