Research Article

Bioavailability and Assessment of Metal Contamination in Surface Sediments of Rades-Hamam Lif Coast, around Meliane River (Gulf of Tunis, Tunisia, Mediterranean Sea)

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The total concentration and the speciation of heavy metals (Pb, Cd, Cu, Zn, Ni, and Cr) in surface sediments of Rades-Hamam Lif coast were determined, with particular focus on the effect that urban and industrial waste in the Meliane river has on the estuary and coastal surface sediments of the Rades-Hamam Lif coast, off the Mediterranean Sea. Several geochemical indices were applied to assess the risk of contamination and the environmental risks of heavy metals on surface sediments. The total concentrations of these heavy metals are influenced by runoff, industrial, and urban wastewater. The Cd, Pb, Zn, and Ni are affected by anthropogenic sources, especially at the mouth of the Meliane river. The sequential extraction of Cd was presented dominantly in the exchangeable fraction and thus the high potential bioavailability. In contrast, Cr and Cu were mostly bound to the residual fraction indicating their low toxicity and bioavailability. The order of migration and transformation sequence was Cd > Pb > Ni > Zn > Cr > Cu, and the degree of pollution was Cd > Pb > Ni > Zn > Cr > Cu.

1. Introduction

Coastal sediments are generally exposed to heavy metal pollution from urban and industrial activities, especially in river mouth [1, 2]. Trace metals in marine sediments may have natural and anthropogenic sources such as sewage discharges and urban and industrial effluents [3, 4]. With high geochemical availability, heavy metals easily migrate among waters, suspended matter, and sediments through many geochemical reactions between the water-sediment interface [5, 6]. Therefore, the use of sequential extract allows having more detail about origin, behavior, bioavailability, and the degree of toxicity of trace metal [7, 8]. Further, contamination due to heavy metals leads to severe environmental problems, which has been proven [9, 10]. As a sink and source, sediments represent the reservoir of bioavailable and play an important role in the geochemical cycle [11]. In addition, several geochemical indexes can be used to evaluate the anthropogenic

impact of heavy metals in sediments, such as geoaccumulation index, contamination factor, and pollution load index [12]. On the other hand, heavy metal contamination in a marine coastal environment is associated with pollution sources in estuaries and adjacent rivers. Metals are mainly transported to the marine environment by rivers across estuaries. In general, the main source of anthropogenic metals in coastal areas is of terrestrial origin, i.e., mining, industrial, as well as urban development, and other human practices near rivers [13, 14].

Tunisia has about 1300 km of coastline on the Mediterranean Sea, which is of important environmental, economic, and touristic value. Some of the Tunisian coastal areas of the Mediterranean Sea (in particular, in front of the large cities) receive different types of pollution sources, such as the Rades-Hamam Lif coast, a part of a Gulf of Tunis, which is under the pressure of a rapidly growing population due to a major industrial concentration and plenty of touristic and port activity.

The Meliane river, located in the eastern shore of the Gulf of Tunis, characterized by an intensive industrial and urban activity in its watershed appears to be a good subject for study especially with all the discharges that the Meliane river sends to the Tunis bay. The Rades-Hamam Lif coast (Gulf of Tunis) has experienced, since the past few years, major environmental problems due to urban and industrial discharge on the Meliane river, which has led the Tunisian authorities to close this coast for summer visitors.

The main objectives of this study were to (1) quantify and explain the spatial distribution of chemical fractions of metal (Pb, Cu, Cr, Zn, Ni, and Cd) in surface sediments of the Rades-Hamam Lif coast and (2) assess the degree of heavy metal pollution using different contamination indices (geoaccumulation index, contamination factor, pollution load index, and biological assessment of surface sediments).

2. Materials and Methods

2.1. Study Area. The Meliane river, with its delta located on the eastern shore of the Gulf of Tunis, is the second longest river in Tunisia after Medjerda River (Figure 1), with a catchment area of 2283 km², an about water flow of 17 m³s⁻¹ and can reach 200 m³s⁻¹ in the flood period. A sediment flow varies from 20 to 400 T per year [15]. The Meliane river flows through many cities, such as Bir Mchergua, Fouchana, Al Khlydia, Naasaan, and Rades Meliane and finally in floods into the Tunis bay at the Rades-Hamam Lif coast. The Meliane river passes through densely populated and industry-affected areas, and its sediments certainly act as an important sink for the anthropogenic contribution of heavy metals. Consequently, the Rades-Hamam Lif coast extends to 10 km length centered on the mouth of the Meliane river (Figure 1), may be considered as a focal point in where industrial (chemical manufacturing, metal processing, and electronic and mechanic industries), agricultural, and municipal waste can be observed. Indeed, the human activity has produced considerable amounts of residues in waste dumps around the Meliane river (Figure 2). These industrial and domestic wastes are rejected; they will first accumulate in animal and plant tissues to be deposited in the end in the seabed [16]. This study concern the Rades-Hamam Lif coast, a part of the Gulf of Tunis, which occupies a central position because it is influenced by the hydrological regime of the Mediterranean Sea, which is fed by the waters of the Atlantic, especially in the western part.

Since the Gulf of Tunis is a semienclosed basin, the movement of water essentially controls the sediment distribution, where a large fraction of fine sediments is transported by the main Mediterranean currents to settle in the central zone of the Gulf. Those coarse sediments are found along the west coast of the gulf. This coastal transport is particularly under the action of waves and swell [17]. The direction of its axis (NE-SW) makes that the main swells which intervene in the littoral dynamics are of direction NE and E. These swells induce a shoreline drift, usually N-S along the west coast of the Gulf of Tunis. The swells of the north and those of the SE act only locally and in a relatively

rare way. The swells of the north are responsible for the E-W coastal drift between Soliman and Rades, and those of the SE cause an S-N drift to the south [2, 16, 17]. This hydrodynamic inversion between the northern and the southern part of the Gulf indicates that the mixture influence is limited at the coast and that the central zone of the gulf seems to be a sink of the contaminants from Mejerda and Meliane rivers.

2.2. Sampling and Sample Processing. Surface sediment samples were collected from 21 stations along the coastal area of Rades-Hamam Lif around the mouth of Meliane river, through six profiles to the beach (Figure 1) in which the depth varied between -0.5 and -10 m. Among these samples, two river samples were also taken: station 21 taken in the Meliane river after discharges from the treatment plant and station 20 taken at the mouth of the river where the sweet and salty ones mix perfectly. Samples from each station were collected using the Peterson grab. The first 5 cm of the surface sediment was taken with acid-washed spatula to avoid any contamination. Once recovered, the samples were stored in polyethylene bags and held at a temperature of 4°C until laboratory analysis.

For the determination of the total trace metals, the surface samples were digested by adding to 1 g of sediment a mixture of three concentrated solutions: 15 mL of HClO₂, 15 mL HF, and 20 mL HNO₃. The resulting solutions were analyzed for Ni, Pb, Cu, Cr, Cd, and Zn by atomic absorption spectrometry (Thermo Scientific, ICE 3,000 series). The procedure used for trace metals analysis was checked for accuracy using the IAEA-405 certified reference material (Table 1), obtaining good occurrence (12.5%). The certified values and the average standard deviations obtained from five replicates of one sample were typical.

The sequential extraction procedures were applied in order to identify metal distribution in five sediment fractions: the exchangeable fraction (F1), bound to carbonates (F2), the reducible fraction (F3) (oxides Fe/Mn), oxidizable (F4) (organic matter and sulfides), and the residual fraction (F5) (remaining, nonsilicate bound metals) fractions of heavy metals in sediments [18]. The sequential extraction procedures are resumed in Table 2.

Grain size analysis of the surface sediment samples was performed using a series of eight sieves ranging from 1000 μ m to 20 μ m for 20 mn using RoTap Sieve Shaker [19]. For total carbon analysis, 1 g of sediment samples was homogenized and crushed, then decarbonated with 1 M HCl solution and dried at 60°C. TOC was measured with a PerkinElmer PE 2400 CHN.

2.3. Pollutants Indicators. In order to evaluate the state of contamination of the surface sediments of the Rades-Hamam Lif coast by heavy metals, various indices can be calculated. Different authors have used these indices [2, 3, 8, 10, 11, 18, 20], but the choice of the reference value varies from author to author. In this study, three indices were chosen: the contamination factor (Cf), the geoaccumulation index (Igeo), and the pollution load index

FIGURE 1: Location map of surface sediment samples along the Rades-Hamam Lif coast around the mouth of the Meliane river.

(PLI). The different formulas and classes of calculated contamination indices are reported in Table 3.

In this study, to avoid overestimating or underestimating Igeo values, it was necessary to define the values of a local

geochemical background specific to the Rades-Hamam Lif coast for each studied metal. For this, the five lowest concentrations were measured for each ETM for the totality of the results was averred [24].

FIGURE 2: Location of several industries along the Meliane river.

TABLE 1: Accuracy of heavy metal analysis (%).

Elements	IEAE 405	This study	RSD (%)
Pb	72.6–77.0	76.8	2.9
Cd	0.68–0.78	0.9	6.4
Zn	272–286	287.5	2.5
Cu	46.5–48.9	41.1	2.51
Cr	80–88	88.0	4.76
Ni	31.1–33.9	34.4	4.3

TABLE 2: Heavy metals sequential procedures.

Fractions	Methods
F1: exchangeable fraction	Exchangeable fraction from sediment sample with MgCl_2 solutions
F2: metals bound to carbonates	The metals bound to carbonates were extracted with a NaOAc solution from the residue of the previous fraction
F3: Fe/Mn oxides fraction (reducible fraction)	The metals bound to this fraction were extracted from the residue of the previous fraction with NH_2OH , HCl , and HOAc solutions
F4: organic matter and/or sulfide fraction (oxidizable fraction)	Metals bound to this fraction were extracted from the residue of stage (2) with HNO_3 , H_2O_2 , and NH_4OAc solutions
F5: residual fraction	Metals were extracted by digestion of the remaining residue of the previous stages by HF and HClO_4

2.4. Statistical Analysis. The data obtained by the chemical analysis of the Rades-Hamam Lif surface sediments were analyzed using principal component (PCA) techniques (XLSAT 2013) in order to establish the relationship between the different variables and identify the most common sources of pollution.

TABLE 3: Pollutants indicators: sediment quality indexes.

Sediment quality index	
Contamination factor: $C_f = C_{\text{heavy metal}}/C_{\text{background}}$ [21]	
$C_f < 1$, low factor	
If:	$1 \leq C_f < 3$, moderate factor
	$3 \leq C_f < 6$, considerable factor
	$C_f \geq 6$, very high factor
Geoaccumulation index: $I_{\text{geo}} = \log_2 (C_n/1.5 B_n)$ [22]	
$I_{\text{geo}} \leq 0$, uncontaminated	
$0 < I_{\text{geo}} \leq 1$, uncontaminated to moderately contaminated	
$1 < I_{\text{geo}} \leq 2$, moderately contaminated	
If:	$2 < I_{\text{geo}} \leq 3$, moderately to strongly contaminated
	$3 < I_{\text{geo}} \leq 4$, strongly contaminated
	$4 < I_{\text{geo}} \leq 5$, strongly to extremely contaminated
$I_{\text{geo}} > 5$, extremely contaminated	
Pollution load index: $PLI = (C_{f1} * C_{f2} * C_{f3} \dots)^{1/n}$ [23]	
If:	$PLI \leq 1$, no pollution
	$PLI > 1$, pollution

3. Results and Discussion

3.1. General Characteristics of Sediments. Grain size distribution and TOC concentration were determined to obtain the general characteristics of the surface sediment samples from the Rades-Hamam Lif coast. The studied surface sediments were characterized by heterogeneous concentration of TOC. That constituted 0.75–3.02% of the dry weight the sediment (Table 4).

The lowest TOC contents were recorded at the south of the study area. The variation in TOC contents among the sediments was important. In fact, the highest TOC contents were mainly found at the estuaries stations 19, 20, and 21 at the mouth of the Meliane river.

The sediment texture was characterized mainly by silt and clay in the area surrounding the Meliane river with a small fraction of sand. This suggests that the finest sediments have been transported by fluvial inputs. South of the study area, toward the city of Hamam Lif, there is reversal of the trend. In fact, the sediments are rather sandy with a small amount of clay and silt. This suggests that these coarsest sediments can originate not only from terrigenous inputs but also from offshore.

3.2. Total Trace Metals. Total trace metals composition of surface sediments of the Rades-Hamam Lif coast is shown in Table 4. Metal concentrations showed significant differences between the sampled sites. The average metal levels are in the following order: $Zn > Pb > Ni > Cr > Cu > Cd$.

Ranges of heavy metals in sediments are 16.14–107.02 $\mu\text{g/g}$ for Pb with an average of 39.17 $\mu\text{g/g}$, 1.53–19.55 $\mu\text{g/g}$ for Cu with an average of 10.66 $\mu\text{g/g}$, 0.25–1.37 $\mu\text{g/g}$ for Cd with an average of 0.43 $\mu\text{g/g}$, 15.55–55.44 $\mu\text{g/g}$ for Cr with an average value of 29.44 $\mu\text{g/g}$, 27.34–450.68 $\mu\text{g/g}$ for Zn with an average of 70.62 $\mu\text{g/g}$, and 13.98–50.88 $\mu\text{g/g}$ for Ni with an average of 24.05 $\mu\text{g/g}$.

All surface sediments collected exceed the upper continental crust (UCC) for Pb and Cd [25]. Only sediments collected in the mouth of the Meliane river exceed the UCC for Zn and Ni [25].

Concerning spatial distribution, all of Pb, Cd, Zn, Cr, Ni, and Cu showed a significant decrease in concentrations with increasing distance from the coast. The higher value is recorded in station 20, at the mouth of the Meliane river. This behavior may suggest a seawater role in metal concentration after drifting of beach sediment away.

The values of Zn and Pb in Rades-Hamam Lif coastal sediments were significantly higher than those recorded in coastal sediments of Rosetta coast beach (Egypt), the north of Morocco, Mediterranean Spain coast. On the other hand, the values of the lead recorded opposite the Meliane river are higher than those recorded at the north of this coast in front of the Mejerda River despite the proximity of this river to lead and zinc mines. The total zinc concentration in the sediments of Rades-Hamam Lif is lower than those recorded at the mouth of the Mejerda River [26]. In contrast, Cr, Cd, Ni, and Cu values were less than those recorded in the same location (Table 5).

In general, the average values of Cd, Zn, and Pb are much higher than background shale [27] and continental crust and from other coastal areas (Table 5). Generally, the concentration of these elements was all higher in the estuary of the Meliane river and lower in the offshore. The same distributions may indicate the same sources.

3.3. Pollutants Indicators. In this study, the background value was calculated from five of the lowest values measured for each element [24]. The geoaccumulation index of Zn varied from 2.79 to 4.01 and between 2.43 and 3.25 for Pb. Similarly, the I_{geo} for Cu varied from 0.61 to 1.47. I_{geo} values of Cr ranged from 2.28 to 2.83 and that of nickel oscillated from 2.26 to 2.76. Finally, I_{geo} for Cd varied between 0.31 and 0.35.

The calculated results for I_{geo} indicate that the surface sediments could be considered “moderately to strongly contaminated” for Pb, Cr, Cd, and Ni. The geoaccumulation index for Zn showed that all samples were strongly contaminated. The I_{geo} values for copper indicated that all samples were uncontaminated except the river station (Table 6).

The C_f of lead varied from 0.64 to 4.26 and from 0.74 to 9.13 for Cu. The C_f values of cadmium are between 0.81 and 4.43. For Cr, the C_f oscillated between 0.81 and 2.97. The calculated values of the contamination factor of Zn varied from 0.79 to 13.16. Finally, the C_f values varied between 0.82 and 2.99 for Ni. According to the classification adopted by Hankanson [21], the contamination factor (C_f) values for surface sediments of the Rades-Hamam Lif coast were found to be moderate for Pb, Cu, Cd, Cr, Ni, and Zn in all sites except those collected in front of the mouth of Meliane river. In fact, for these stations, the contamination factor is “considerable” for Ni, Pb, and Cd and “very high” for Zn and Cu. Only the C_f of Cr is low in the station in front of Meliane river.

The PLI values oscillated between 1.02 and 2.51. According to Tomlinson classification [22], the calculated PLI values in all sites were >1 . All surface sediments collected in the Rades-Hamam Lif coast around the Meliane river can

TABLE 4: Textural parameters and total heavy metals for surface sediments of the Rades-Hamam Lif coast.

	Station	Silt (%)	Clay (%)	Sand (%)	TOC (%)	Cd ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)
Marine samples	1	21.5	14.49	64.01	0.76	0.38	4.08	35.07	39.33	22.91	34.93
	2	27.43	10.46	62.11	0.75	0.40	3.82	16.14	39.23	23.02	18.74
	3	33.09	7.72	59.19	0.96	0.37	1.53	43.30	100.70	55.44	39.11
	4	19.33	12.22	68.45	1.02	0.58	7.11	27.10	67.73	47.97	25.86
	5	32.29	20.39	47.32	1.04	0.34	7.86	28.60	58.09	50.74	26.75
	6	29.19	24.99	45.82	1.21	0.38	9.77	43.52	78.95	55.14	31.78
	7	23.08	9.77	67.15	1.23	0.36	128.82	50.40	41.74	25.34	17.85
	8	27.22	10.33	62.45	1.34	0.36	3.42	24.69	48.32	27.30	19.65
	9	28.3	1.69	70.01	1.52	0.32	2.86	26.23	50.87	28.13	20.95
	10	15.45	19.32	65.23	1.76	0.47	2.40	44.99	34.42	22.35	18.34
	11	27.1	9.89	63.01	1.69	0.42	3.49	54.69	70.16	34.99	25.43
	12	23.69	16.75	59.56	1.75	0.36	5.65	37.57	60.75	26.61	21.79
	13	23.89	22.88	53.23	2.02	0.35	2.51	55.14	46.86	26.98	18.70
	14	32.25	18.5	49.25	1.85	0.39	3.45	32.77	43.78	25.00	23.83
	15	36.24	14.74	49.02	1.99	0.38	3.80	28.62	39.29	23.54	21.06
	16	24.15	18.6	57.25	2.14	0.33	2.40	33.70	35.92	21.05	15.98
	17	19.88	20.58	59.54	2.56	0.35	2.43	29.66	57.88	22.78	22.88
	18	35.23	29.58	35.19	2.51	1.37	4.07	27.55	56.77	29.64	20.93
	19	31.04	36.77	32.19	2.78	0.25	1.87	38.39	450.68	15.55	15.66
	20	29.96	36.83	33.21	2.96	0.27	2.98	37.43	34.22	18.24	13.98
River samples	21	45.92	20.88	33.22	3.02	0.65	19.55	107.02	27.34	15.55	50.88

TABLE 5: Comparison between heavy metals in the studied sediments and other worldwide localities.

Locations	Cd	Cu	Zn	Cr	Pb	Ni	Reference
Rades-Hamam Lif Coast	0.25–1.37	1.53–19.55	27.34–450.68	15.55–55.44	16.14–107.2	13.98–50.88	Present study
Rosetta coast beach	21–37	7.6–42.7	53–388	0.10–0.29	214–476	114–894	El Sorogy et al. [14]
North Morocco	0.1–0.3	2.8–29.11	63.7–115.3	88.4–161	35.4–447.8	34.2–79.9	Omar et al. [28]
Spain	0.003–0.28	4.4–29.2	22.3–103.2	31.8–394.7	7.7–30.4	0.1–11.6	Diaz de Alba et al. [29]
Mouth of Mejerda River (Gulf of Tunis)	—	62	209	—	25	72	Zaaboub et al. [26]
UCC: crust average	0.2	32	127	71	16	49	Martin and whitefield [25]
Background shale	0.3	45	95	90	20	68	Turkian and Wedpohl [27]
Background continental crust	0.2	55	70	100	12.5	75	Taylor [30]

TABLE 6: Geoaccumulation index (Igeo), contamination factor (C_f), and pollution load index (PLI) values in surface sediments from the Rades-Hamam Lif coast.

Stations	C_f (Cd)	C_f (Cu)	C_f (Cr)	C_f (Zn)	C_f (Pb)	C_f (Ni)	Igeo (Cd)	Igeo (Cr)	Igeo (Ni)	Igeo (Pb)	Igeo (Cu)	Igeo (Zn)	PLI
1	1.2	1.9	1.2	1.1	1.3	2.0	0.31	2.4	2.5	2.7	0.8	2.9	1.4
2	1.2	1.7	1.2	1.1	0.6	1.1	0.3	2.4	2.3	2.4	0.8	2.9	1.1
3	1.2	0.7	2.9	2.9	1.7	2.3	0.31	2.8	2.6	2.8	0.6	3.3	1.7
4	1.9	3.3	2.5	1.9	1.0	1.5	0.32	2.7	2.4	2.6	1.0	3.1	1.9
5	1.0	3.6	2.7	1.6	1.1	1.5	0.31	2.7	2.4	2.6	1.1	3.1	1.7
6	1.2	4.5	2.9	2.3	1.7	1.8	0.31	2.8	2.5	2.8	1.2	3.2	2.2
7	1.1	60.2	1.3	1.2	2.0	1.0	0.31	2.4	2.3	2.9	2.2	2.9	2.5
8	1.1	1.5	1.4	1.4	0.9	1.1	0.31	2.5	2.3	2.6	0.8	3.0	1.2
9	1.0	1.3	1.5	1.4	1.0	1.2	0.31	2.5	2.3	2.6	0.7	3.0	1.2
10	1.5	1.1	1.2	1.0	1.7	1.0	0.32	2.4	2.3	2.8	0.7	2.8	1.2
11	1.3	1.6	1.8	2.0	2.1	1.4	0.31	2.6	2.4	2.9	0.8	3.2	1.7
12	1.1	2.6	1.4	1.7	1.4	1.2	0.31	2.5	2.3	2.8	1.0	3.1	1.5
13	1.1	1.1	1.4	1.3	2.1	1.1	0.31	2.5	2.3	2.9	0.7	3.0	1.3
14	1.2	1.6	1.3	1.2	1.3	1.4	0.31	2.4	2.4	2.7	0.8	3.0	1.3
15	1.2	1.7	1.2	1.1	1.1	1.2	0.31	2.4	2.3	2.6	0.8	2.9	1.2
16	1.0	1.1	1.1	1.0	1.3	0.9	0.31	2.4	2.2	2.7	0.7	2.9	1.1
17	1.1	1.1	1.2	1.6	1.1	1.3	0.31	2.4	2.4	2.6	0.7	3.1	1.2
18	4.4	1.9	1.5	1.6	1.0	1.2	0.35	2.5	2.3	2.6	0.8	3.1	1.7
19	0.8	0.8	0.8	13.1	1.5	0.9	0.31	2.2	2.2	2.8	0.6	4.0	1.4
20	0.8	1.3	0.9	0.9	1.4	0.8	0.31	2.3	2.2	2.7	0.7	2.8	1.0
21	2.1	9.1	0.8	0.7	4.2	2.9	0.32	2.2	2.7	3.2	1.4	2.7	2.3

be classified as "Polluted." The high value of PLI characterizes samples taken in front of Meliane river, indicating that the sediments of this area are strongly polluted by the examined heavy metals, especially Zn, Pb, and Cu.

The different pollution indices (Cf, PLI, and Igeo) show that the area around the mouth of the Meliane river is the most polluted zone. However, a downward trend has been observed from the coast to the open sea as a function of littoral drift. This is probably due to the continued discharge of urban wastewater as well as industrial discharges at the Meliane river. These discharges are then transported to the Rades-Hamam Lif coast. On the other hand, the piers of Rades channel limited the extension in the north in favor to the south of the study area.

3.4. Statistical Analysis. A principal component analysis (PCA) was also performed to identify the relationships between variables (Table 7). Granulometry and organic matter content are among the two main factors that could influence the geochemical behavior of heavy metals in sediments [31]. The significantly positive correlation of Pb ($r = 0.63$; $n = 21$), of Ni ($r = 0.67$; $n = 21$) with Cd, and of Cr ($r = 0.46$; $n = 21$), Cu ($r = 0.63$; $n = 21$) with Zn, and of Cu ($r = 0.48$; $n = 21$), Cr ($r = 0.72$; $n = 21$) with Pb could indicate a similar origin of these elements. Generally, the elements that have high correlation in sediments can have the same origins, similar behaviors during the different phases of transformation between the dissolved and particulate phases [3, 31]. Therefore, Pb, Cd, Cr, Cu, Ni, and Zn may have a common source which is most probably the urban and the industrial wastewater discharged into the Meliane river. However, no significant correlation was observed between TOC and the total heavy metals concentration indicating that are not bound to organic matter.

3.5. Sequential Extraction. Determining the total concentration of metals is probably the most fundamental way to assess sediment quality; but for further understanding of potential mobility, bioavailability and toxicity of metals in sediments, metal fractionation, acid volatile sulfur (AVS), and simultaneously extracted metal (SEM) can investigate the bioavailability and the toxicity of metals [32]. In Tunisia, few studies have been conducted on monosulfide in sediments. For example, the AVS contents in surface sediments of Tunis Gulf varied from 3.43 to 9.55 $\mu\text{mol/g}$ according to Rais [31], ranged from 1 to 7 $\mu\text{mol/g}$ according to Hellali et al. [2], from 9 to 84 according to Oueslati [33], and from 3.11 to 127.9 $\mu\text{mol/g}$ according to Zaaboub et al. [34]. This AVS fraction represents the concentration of different chemical forms of metals associated with sulfur in sediment; it plays a key role in the distribution of these elements, especially in anoxic environments.

However, sequential extraction remains the most common method. Therefore, the sequential extraction procedure was performed to obtain information about the strength and ways of metal associating with sediments [10, 32].

The concentration of trace elements is usually controlled by a variety of physical and chemical factors [26, 35] such as

granulometry, composition, oxidation/reduction reaction, and adsorption/desorption processes. Clay minerals, Fe and Mn oxides, and organic matter are among the major constituents of sediments. These particles have a large surface area that allows them to adsorb metal cations in water and to release equivalent amounts of other cations; this is the cationic exchange phenomenon [25, 31]. The sorption phenomena are reversible, so metal elements "sorbed" on the sediment are therefore bioavailable and potentially toxic. This toxicity in natural environments is dependent on the changes of the physicochemical parameters such as salinity, pH, and Eh [36, 37, 38].

In this study, the distribution of different fractions of heavy metals in sediments of the Rades-Hamam Lif coast is shown in Figure 3 and presented as percentages of the sum of all fractions.

The metals in F1 fraction are considered to be the weakest bound metals in sediments and can be defined as "the exchangeable fraction" which can migrate to the aqueous phases and therefore become the most movable fraction. The heavy metals bound to this fraction are sensitive to any environmental changes [32, 39]. They are easy to migrate and change and have high bioavailability and toxicity [10, 32, 39]. The heavy metals bound to the exchangeable fraction are the most bioavailable metals and represent a high risk for the environment. Except for Cu and Zn at all sites, the proportions of metals in the exchangeable fraction (F1) were relatively high, especially for Cd. The mean proportion of copper in the acid-soluble fraction was the lowest among the studied metals, and its values were only 3.68%, indicating its low mobility. On the other hand, the contents of Cd in F1 fraction were largely higher than the other Cd fractions. In fact, the highest percentage of Cd in this fraction, reaching 86% in all sites, was observed with an average of 49.43%, indicating its very high mobility. The high proportion of Cd in this fraction may be due to the fact that it is an element of mainly anthropogenic origin and mostly enters the aquatic environment through the discharges of industrial and urban effluents. The mean proportion of Ni and Pb in exchangeable fraction (F1) was 24.88% and 35.11%, respectively, indicating that they had some degree of mobility and can represent a risk to the environment.

For Cr, though its mean proportion in the acid-soluble fraction was 16.44%, it presented a clear spatial variation from the north to the south of the study area, with a range of 9.6% and 21.56%. On average, the percentage of Zn in the acid-soluble fraction from different sampling sites was fairly constant, with ranges varying from 1.36 to 6.95% and 12.84% for the station 21 located in the mouth of the Meliane river (Figure 3). The order of abundance of trace metals in the exchangeable fraction is as follows: $\text{Cd} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cu} > \text{Zn}$.

This sequence should reflect the relative concentrations of the metallic elements in the water since the trace metals linked to the exchangeable fraction are electrostatically adsorbed and, therefore, they are weakly bound and can therefore be released by cation exchange at near neutral pH [32].

The metal bound to carbonates varies significantly from one element to another. Indeed, the Cu content in the F2 fraction varies from 0.02 to 3.82% with an average of 1.08%.

TABLE 7: Pearson coefficient for Ni, Zn, Cr, Cd, Cu, Pb, sand, clay, silt, and TOC for surface sediments of the Rades-Hamam Lif coast.

Variables	Ni ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Sand (%)	Silt (%)	Clay (%)	TOC (%)
Ni ($\mu\text{g/g}$)	1	-0.09	0.29	0.67	-0.1	0.15	-0.03	0.3	-0.19	-0.38
Zn ($\mu\text{g/g}$)		1	0.46	0.1	0.63	0.41	-0.24	0.11	0.24	0.04
Cr ($\mu\text{g/g}$)			1	0.63	0.65	0.72	-0.04	0.14	-0.05	-0.31
Cd ($\mu\text{g/g}$)				1	0.14	0.62	-0.32	0.51	0.05	0.03
Cu ($\mu\text{g/g}$)					1	0.48	0.03	-0.05	-0.01	-0.11
Pb ($\mu\text{g/g}$)						1	-0.44	0.3	0.38	0.24
Sand (%)							1	-0.7	-0.84	-0.7
Silt (%)								1	0.2	0.36
Clay (%)									1	0.68
TOC (%)										1

The highest values characterize the sediments collected at the mouth of the Meliane river. Overall, the average proportions of Pb, Zn, and Cr are relatively low, and they are of the order of 8.02%, 4.82%, and 6.28%, respectively. Ni values related to the carbonate fraction vary from 3.14% to 34.72% with an average of 11.97%. The highest value characterizes the station sampled at the mouth of the Meliane river. Cadmium (Cd) bounds to carbonate fraction with the highest proportions ranging from 12.6 to 56.31% with an average of 45.85%. The lowest proportion (12.6%) bound to carbonates corresponds to the highest percentage of cadmium in the exchangeable fraction (86.46%). The most labile fraction (exchangeable fraction and carbonate-related fraction) is greater than 95.29% for Cd, which confirms the bioavailability and mobility of this element. The order of abundance of trace metals bounded to carbonates fraction is as follows: Cd >>> Ni > Pb > Cr > Zn >> Cu.

The F3 fraction is the part of the heavy metals represented by Fe/Mn oxide or hydroxide precipitation. Metals bound to Fe/Mn oxides would be released under reductive conditions and, therefore, are unstable under anaerobic condition [39, 40]. The reducible fraction was the most abundant fraction for Ni in all sites (except stations 3, 4, and 5). The proportion of Ni in Fe/Mn oxide or hydroxide fraction was much higher than that of other metals in this fraction. 41.77% of Ni was measured in this fraction with the range of 35.68–66.37%. The percentage of Cd, Cu, Zn, Pb, and Cr in Fe/Mn oxide fraction was low to moderate, with the mean values of 0.91%, 4.41%, 20.28%, 22.23%, and 24.11%, respectively.

The percentages of cadmium and copper in the reducible fraction are the lowest and the average values being, respectively, 0.91% and 4.41%, suggesting the order of abundance of heavy metals in the oxide and hydroxide fraction of Fe and Mn as follows: Ni >> Cr > Pb > Zn >>> Cu >> Cd.

In the oxidizable fraction (F4), heavy metals tend either to associate with reactive groups of organic matter or to generate water-insoluble materials with sulfur ions, that is why it is difficult to release under normal and moderate reduction or weak oxidizing environment [10]. The mean percentage of metals in this fraction of surface sediments was 39.24% for Zn, 27.46% for Cu, 17.24% for Pb, 2.32% for Cd, 16.38 % for Cr, and 4.49% for Ni. Zinc is essentially bound to organic matter (40%), and it is of limited toxicity.

The results showed that the most chrome and copper in all the sediments were strongly retained in the residual fraction (F5). Their average percentage in this fraction was

64.42% and 43.09%, respectively. A high proportion of this fraction was also observed for Ni and Zn in some sites. These facts suggested that these metals are strongly associated with the aluminosilicates lattice of minerals [10, 32, 41, 42]. This trend indicates that metals bound to the residual fraction have relatively low mobility, bioavailability, and toxicity [10, 32, 42, 43]. Therefore, the order of heavy metal migration in the Rades-Hamam Lif coast surface sediments was Cd > Pb > Ni > Zn > Cr > Cu.

The heavy metals bound to the exchangeable and carbonate fraction are the most moveable fraction, followed by reducible and oxidizable fractions, which are easier to be released into the water column and are considered to have high bioavailability and toxicity. The sum of these four fractions is called the extractable fraction [9, 40, 44]. On the contrary, the residual fraction is bound with mineral lattice and can only be released during the weathering process [10]. Indeed, the exchangeable fraction and the carbonate fraction are more mobile and dangerous than other fractions. Even if the percentage in this fraction is small, the pollution is considerably important. However, the residual fraction presents in the inert phase, which is less dangerous to public health. The reducible and oxidizable fractions are easily available under oxidation-reduction conditions [10–12].

In order to be able to explain the risk posed by sediment to organisms, it is essential to know the bioavailable fraction of contaminants [22, 37]. It is represented by the nonresidual fraction, that is to say all the exchangeable fractions, carbonated, bound to Fe/Mn oxyhydroxides and the fraction bound to organic matter [10, 22]. These fractions are considered potentially toxic according to the conditions of the environment and present a potential risk for living organisms [18]. Indeed, the released trace metals may have a higher toxicity.

According to Cai et al. [10], the extractable fraction (exchangeable, carbonates, Fe/Mn oxides, and organic matter) is considered essentially bound to human-made pollution. Therefore, the ratio of extractable to residual fraction may indicate the degree of heavy metal pollution in sediments: a high percentage of the extractable fraction indicates greater anthropogenic heavy metal pollution, according to the same authors. In Rades-Hamam Lif coast around the mouth of the Meliane river, the percent of extractable fractions of Pb, Cu, Cd, Cr, Zn, and Ni was 74.59%, 35.57%, 98.54%, 56.90%, 64.69%, and 71.16%, respectively, so the polluted sequence was Cd > Pb > Ni > Zn > Cr > Cu,

FIGURE 3: Chemical speciation of Pb, Zn, Cu, Cd, Cr, and Ni (in %).

same as the order of heavy metal migration. The application of the latest ratio allows to calculate the biological assessment index (P), and P is the ratio of extractable to the residual phases, that is, $P = (F1 + F2 + F3)/F4$. The P value was carried out to better reflect the activities of heavy metals in the Rades-Hamam Lif coast and to better understand the

role of the Meliane river discharges into the sea (Table 8). According to Li [39], a value of P lower than 1 represents no pollution, 1-2 slight pollution, 2-3 moderate pollution, and higher than 3 heavy pollution. Table 7 shows the statistical values of heavy metal P values in the surface sediments of the Rades-Hamam Lif coast. All the river stations, located in the

TABLE 8: Biological assessment index values P calculated for heavy metals in Rades-Hamam Lif surface sediments.

	Range	Average
Pb	0.59–10.57	4.72
Cu	0.006–12.06	1.13
Cd	27.72–513.72	113.14
Cr	0.44–3.11	1.55
Zn	0.63–7.92	2.43
Ni	0.96–7.65	3.02

mouth of the Meliane river (stations 19, 20, and 21), showed a high value of P especially for Cd, Zn, and Pb, indicating heavy pollution due to urban and industrial discharges in the river. In the rest of the study area, chrome and copper showed no pollution and Zn and Ni show slight to moderate pollution. Heavy pollution was detected at all sites for Cd and Pb.

4. Conclusion

Different useful tools, indices, and approaches such as chemometric indices, sequential extraction, and multivariate statistical analysis have been carried out for the evaluation of sediments contamination of the Rades-Hamam Lif coast.

The total concentrations of Cd, Cr, Cu, Zn, Pb, and Ni showed significant spatial variation. The highest concentrations of heavy metals were recorded at the mouth of the Meliane river, and they tend to decrease with increasing distance from the coast. The total concentration of trace metals was influenced by runoff, industrial wastewater, and wastewater discharged into the Meliane river. Cd, Pb, Cr, and Ni were mainly bound to an exchangeable fraction with a very high percentage for Cd indicating its high mobility and toxicity. Ni was bound to Fe/Mn oxide, suggesting that this element is difficult to release in the environment. Zn is bound to oxidizable fraction. The Cr and Cu in all sediment samples were strongly retained in the residual fraction. The north-south shoreline drift appears to extend the influence and to increase the transfer of hazardous pollutants toward the southern and offshore areas, to be accumulated by marine species and integrated into food chains and to end in humans. This study suggests that the surface sediments of the Rades-Hamam Lif coast are polluted by high concentrations of several pollutants due essentially to several industrial and urban discharges in the Meliane river which is mainly close to the coast. The state of contamination of the sediments of the Rades-Hamam Lif coast requires the concern of competent authorities.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors wish to confirm that there are no known conflicts of interest associated with this publication.

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