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Distribution and assessment of trace metal contamination in the surface sediments of the Meliane River and the Coast of the Gulf of Tunis (Tunisia, Mediterranean Sea)

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ABSTRACT

The Meliane River, the second longest and most important river in Tunisia, is one of the major rivers that flow into the Gulf of Tunis. However, it is known by its significant discharges of urban and industrial activities that have seriously affected the quality of the aquatic ecosystem. The highest amounts of Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), Chromium (Cr) and Manganese (Mn) in the surface sediments of the Meliane River indicate that the downstream part is the most polluted area. The chemical speciation shows that the majority of the trace metals are bound to a reducible fraction (Zn, Mn, Cr and Ni) and the Pb and Cu are bound to the oxidizable fraction. The Cd is linked to the exchangeable fraction, which indicates its high mobility and toxicity. Both the contamination and enrichment factors values of some trace metals are elevated in the downstream part of the Meliane River. The percentage of the risk assessment code in Cd is 59.8%, which presents a very high environmental risk. Therefore, the spatial distribution of trace elements in the surface sediments is characterized by its high concentration of metals in the downstream part of the Meliane River. These concentrations decrease as a function of change in the physicochemical parameters from the freshwater-saltwater mixing zone to marine stations.

KEYWORDS

Trace metals; surface sediments; chemical speciation; river pollution; anthropogenic sources

Q1 Introduction

Trace metals are persistent, toxic and non-biodegradable elements. They constitute a serious pollutant for any aquatic system (Pekey 2006; Joy et al., 2019). The major sources of trace elements are natural due to the erosion of geological materials and anthropogenic caused by domestic, industrial and agricultural activities (Dawson et al., 1998; Demirak et al., 2006; Sakan et al., 2013; Leung et al., 2017; Çağlar et al., 2019; Köse et al., 2019). Besides, in recent years, the rapid urbanization and industrialization have affected the transport of the trace metals in the aquatic environment (Lusher and Ramsden, 2000; Tzimopoulos et al., 2005; Chetty et al., 2019). The contamination of river water and surface sediments by trace metal is becoming the main quality problem in rapidly-developing cities as maintenance of water and sediment quality as well as hygienic structure do not grow with

population and urbanization (Ahmad et al., 2010; Bhuyan et al., 2019). Thus, the aquatic ecosystem can be affected by contamination with trace metals in the sediments and, therefore, bioassimilation and bioaccumulation of pollutants in the biota threaten both the human health and the ecosystem (Raghunath et al., 1999; Li et al., 2004; Ip et al., 2007; Dou et al., 2013). In fact, the huge amount of trace metals released into rivers may be greatly accrued in water, sediment and biota (McGeer et al., 2000; Jones et al., 2001; Almeida et al., 2002; Xu et al., 2004; Yi et al., 2011). The coastal environments are also exposed to this type of pollution. Tunisia coastline represents about 2.5% of the total of Mediterranean coastline (Ennouri et al., 2010). The Gulf of Tunis coastline opens to the central Mediterranean and plays an utmost important economic role to the country. It is densely populated (2.5 million people) and

characterized by the presence of massive economic and industrial activities (Ennouri et al., 2010). Moreover, due to intensive anthropogenic activities, the Meliane River has become a major source of pollution with trace metals in the Gulf of Tunis coast, which forced the state to prohibit swimming in the coastline between Rades and Hammam-lif. This area, centered by the Meliane River discharging significant amounts of sediment, has a major importance in the capital of Tunis. It has been affected by the problem of urbanization and continuous development of industrial and agricultural sectors. Thus, huge amounts of pollutants released from different types of water discharges makes Meliane River subject to significant pollution risks and threatens the quality of water and sediment flowing from its upstream to its downstream, and transported to the sea. Due to the natural processes and the anthropogenic interventions, the coastline sediment balance is very sensitive to any environmental change (Zaaboub et al., 2014a; Brahim et al., 2015). Several previous studies (Zaaboub et al., 2014b; Ben Amor et al., 2019) have investigated the trace metals in the surface sediments of the Gulf of Tunis without focusing on the potential sources of these elements. In this work, in addition to the assessment of trace metals in marine sediments, we are interested to their inputs by Meliane River from the watershed to the sea. This study can help establish background values for the contaminants studied that can be useful in establishing new pollution events and potentially help identify point sources of contamination. In fact, geochemistry knowledge about the trace metals transported from the river to the sea is limited due to the fact that geochemical characteristics and the spatial distribution on the riverine were infrequently reported (Liu et al., 2019). Indeed, the concentrations of trace metals in the surface sediments of the Meliane River were rarely studied.

The main objectives of this study were (1) to quantify and evaluate the spatial distribution of trace metals in surface sediments of Meliane River and marine stations; (2) to assess the degree of contamination and toxicity of trace metals in each fraction of surface sediments and (3) to estimate the degree of the menaces of the trace metals using the pollution indicators and risk assessments.

The amount of Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), Chromium (Cr) and Manganese (Mn) were determined by the total amount of trace metals and sequential chemical extraction. The statistical analysis and the measurement of different contamination indexes were carried out.

Study area

The Meliane River is located in northern Tunisia between 36° and 36°45' north latitude and 9°30' and 10°15' east longitude (Figure 1). It covers a distance of 150 km. The study area begins from the downstream of the Bir M'Cherga Dam, located near the Zaghouan region, 47 km from southwest of Tunis, to 35 km from its exit in the Gulf of Tunis (Ayadi and Bargaoui, 1998). At the Bir M'Cherga Dam, it drains a catchment of 1442 km² and extends for 100 km in length, and between 8 and 35 km width (Ayadi and Bargaoui, 1998). The coastline of the Rades - Hammam lif, is about 10 Km of length and 5 km of width; centered by the Meliane River, Rades city in the North and Hammam lif city in the South. In the Gulf of Tunis, the distribution of sediment is managed by the circulation of water in the Mediterranean and the local wind-induced currents and waves as well as by the contributions from rivers and streams (Brahim et al., 2015). The direction axis of the Gulf of Tunis is NE-SW (Rais, 1999). The main swell directions in the Gulf of Tunis are those from the NNE to NE direction, with a North-South coastal drift (El Arrim, 1996). The Gulf of Tunis area is characterized by Oligo-Miocene geological origin which consists of a series of clayey sandstones (Ben Ayed et al., 1983; Brahim et al., 2015), with Pliocene hills made up of a series of green clays (M'âamri, 1998; Brahim et al., 2015) and Quaternary plains containing a rich gray sand layer, an alluvium formed by sandy clays, sands and gravels (Jouirou, 1982; Brahim et al., 2015).

After the construction of the dams of El Kbir in 1920, Bir M'Cherga in 1971 and Lahma in 2002, the sediments input into the Gulf of Tunis decreased from 3.3 10⁶ to 2.2 10⁶ tons/year (Sliti, 1990; El Arrim, 1996; Saïdi et al., 2013). This reduction affects the solid and liquid inputs to the Gulf of Tunis containing the discharged polluted waters (Added et al., 2003; Khadhar et al., 2018; Kabouchi et al., 2020).

The Meliane River is the focal point of different human activities. It is strongly affected by the urban agglomeration as well as by the concentration of the industrial and agriculture activities. It is also considered as the exit point of the wastes of the industrial zones (e.g., electronic and mechanic industries, chemical manufacturing plants), food factories (e.g., cake factory, tomato-canning factories), municipal wastes (e.g., slaughterhouse, sewage treatment plants) and pharmaceutical society. According to the National Office of Assessment (ONAS) (2008), the wastewater discharged into the Meliane River represents 59,840 m³/d from the urban discharges, and about

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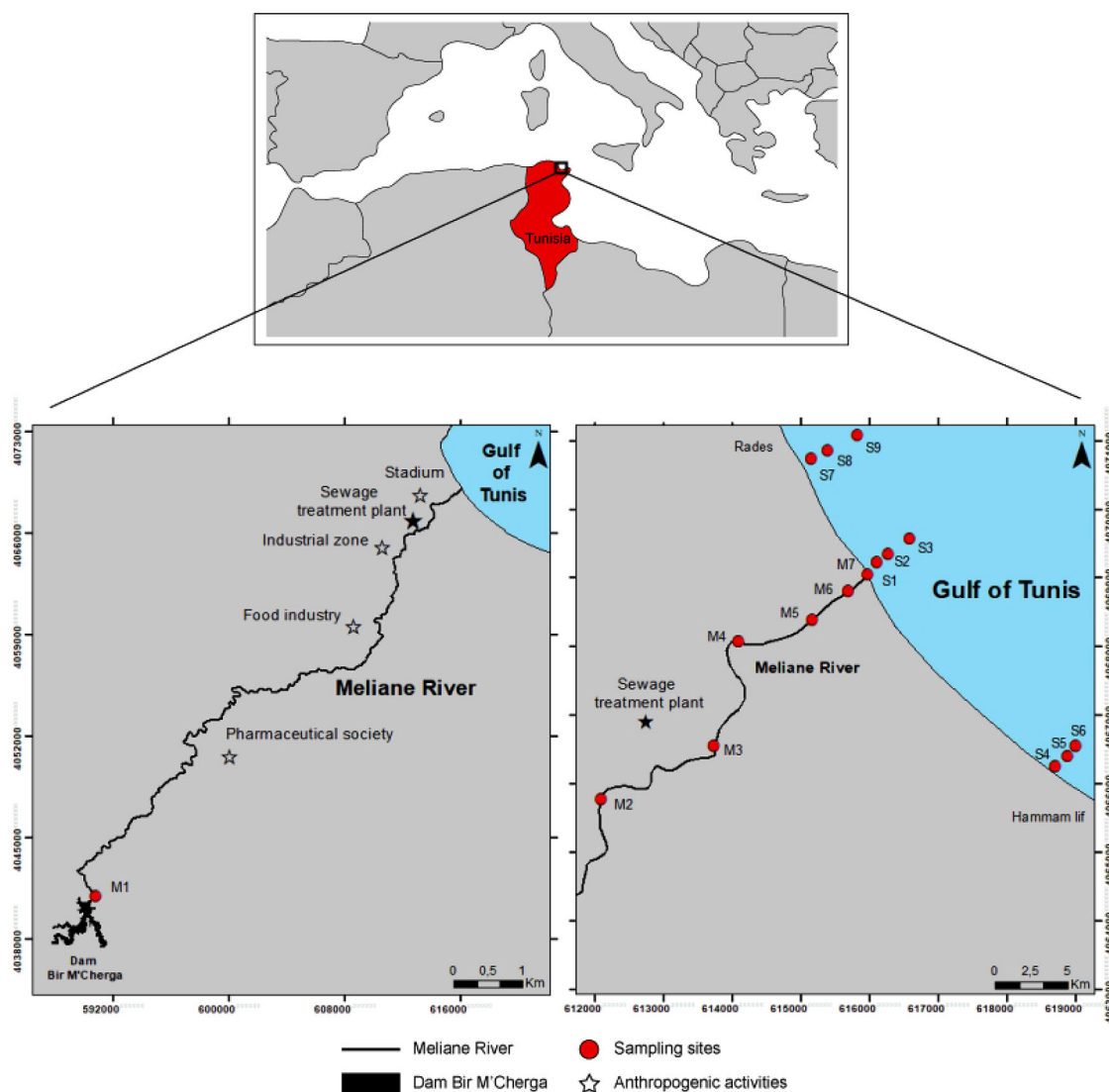


Figure 1. Study area and samples sites in the Meliane River and marine stations on the Gulf of Tunis.

382 m³/d of untreated water from the industrial discharges (ONAS, 2008). Domestic wastes come essentially from the Rades sewage treatment plant, which flows directly into the Gulf of Tunis. In addition, this area is considered as a container for several agricultural wastes, along with urban disposals of the Meliane sewage treatment plant, Mornag sewage treatment plant and the gravel station of Ben Arous (Agence nationale de Protection de l'Environnement [ANPE], 2014; Khabouchi et al., 2020). Thereby, the Meliane River crosses densely populated area and affected by several types of industries and its sediments certainly act as an important sink for trace metals, which releases directly and permanently into the Gulf of Tunis, as well as the effluents of waste treatment plant of "Sud Meliane" and some treated or non-treated industrial discharges (Ben Charrada, 1997; Ayari and afli, 2008). The Rades - Hammam lif

coastline is known, since 1994, by a high nutrient concentration and turbidity caused by the flows of the Meliane River (Souissi et al., 2000; Yahia et al., 2004; Ben Lamine et al., 2012).

Materials and methods

The distribution of sampling localization is shown in Figure 1. In this study, sixteen samples of surface sediment were collected. Seven surface sediment samples were collected from the upstream to the downstream of the Meliane River. They were collected at the upstream of the Meliane River, before the sewage treatment plant, and at the downstream part of the watercourse. The rest were collected from the marine stations of the Gulf of Tunis coast along three radials. Those radials, with depths of 3, 5 and 7 meters, were

taken from the front part of the Meliane River, at Rades in the north, and Hammam-lif in the south.

The Meliane River samples were harvested using a stainless-steel shovel; while the marine surface sediments were harvested using a Van Veen grab. The sediments were immediately placed in polyethylene plastic bags and stored at -4°C . In the laboratory, the samples were lyophilized. Then, they were homogenized and sieved. A granulometric analysis was carried out for 20 minutes on a series of AFNOR-type sieves using a RoTap Sieve Shaker. The total organic matter was determined by the method of ignition weight loss and 1 g of surface sediments was incinerated at 450°C for 5 hours. In order to ensure the quality control of the results (Table 1), a sediment reference sample (Sed IAEA, 405) was utilized in each series of the analyses. Subsequently, the analysis of the total contents of Cd, Cu, Pb, Zn, Ni, Cr, Mn and Al and chemical speciation by sequential extraction of surface sediments samples were performed.

Total amounts of Cd, Cu, Pb, Zn, Ni, Cr and Mn were determined using the microwave dissolution technique. The digestion of surface sediments was specified using 0.25 g of sample put in Teflon reactors and mixed with 5 ml of nitric acid and 2 ml of hydrofluoric acid. After mineralization in the microwave (Milestone ETHOS), 0.8 g of boric acid was added. The dissolved samples were diluted with ultrapure water up to 50 ml. The Al was determined by adding 1 g of sample, with a mixture of hydrofluoric and perchloric acid (2/3–1/3), and using a triacid attack. This mixture was heated until almost total evaporation. Then, it was recovered by adding 5% nitric acid and heated again till boiling. After cooling, the volume of the solution was adjusted.

The sequential extraction (Tessier et al., 1979) is a method which consists in extracting five fractions: the “exchangeable” fraction, the “carbonate-bound” fraction, the “reducible or Fe/Mn oxide-bound” fraction, the “oxidizable or organic matter-bound and sulfide” fraction, and the “residual” fraction. Its different steps are described below:

- Extracting exchangeable fraction (F1) 1 g of sediment with magnesium chloride.
- Extracting carbonate-bound (F2) fraction using Sodium acetate.
- Extracting reducible fraction (F3) with Hydroxylammonium chloride in acid acetic.
- Extracting oxidizable fraction (F4) with Nitric acid, Hydrogen peroxide and then Ammonium acetate.
- Extracting residual fraction (F5) using Nitric and Perchloric acids.

Table 1. Results of standard sediment reference material IAEA-405.

Metal ($\mu\text{g.g}^{-1}$)	IAEA 405	This study
Cd	0.68–0.78	0.75
Cu	46–48.9	49.79
Pb	72.6–77	74.36
Zn	272–286	282.21
Ni	31.1–33.9	33.65
Cr	80–88	78.86
Mn	484–506	504.68
Al	72,700–83,100	85825

Each sample was shaken in a shaking incubator. The extractions were afterwards conducted in 50 ml polyethylene tubes. The phase-separation sediment-solution was obtained by centrifugation for 20 minutes at 5000 t/mn.

Statistical analysis

The relationships between the total trace metals were tested using the XLSTAT (2019) software applying the correlation matrix, the principal component analysis (PCA) and the relation between elements and samples. A statistical treatment was applied on all the elements and samples.

Assessment of sediment contamination

The classifications of pollution indicators and risk assessments are explained in Tables 2 and 3.

The contamination factor (CF) was measured according to Hakanson (1980) using the following formula:

$$CF = \frac{C_m}{C_B}$$

where C_m and C_B are the concentrations of the element in the sediment sample and background, respectively.

The M1 station is situated near the downstream of the Bir M'Cherga Dam used for water drinking, fishery and irrigation. In this study, we used the M1 of the Meliane River as uncontaminated station.

To estimate the sources of metals and to assess the impact of anthropogenic activities, a formula of the enrichment factor (EF) (Hilton et al., 1985; Sutherland, 2000; Cukrov et al., 2011; Ahmedat et al., 2018) was measured according to the following equation:

$$EF = \frac{\left(\frac{C_m}{C_{Al}}\right)S}{\left(\frac{C_m}{C_{Al}}\right)B}$$

where the Aluminum (Al) is considered as a natural element of reference; $(C_m/C_{Al})S$ denotes the ratio between the concentration of the element “m” and that of Al in the sediment sample and $(C_m/C_{Al})B$

Table 2. Classification of contamination factor (CF), enrichment factor (EF), and ecological risk (RI and MRI).

Contamination factor (CF)	Enrichment factor (EF)	Ecological risk assessment (RI and MRI)
CF < 1, low contamination		RI – MRI < 150 low ecological risk
1 < CF < 3, moderate contamination	EF < 2: deficiency to low enrichment 2 < EF < 5: moderate enrichment	150 < RI – MRI < 300, moderate ecological risk
3 < CF < 6, considerable contamination	5 < EF < 20: significant enrichment 20 < EF < 40: very high enrichment	300 < RI – MRI < 600, high ecological risk
6 > CF, very high contamination	EF > 40: extremely high enrichment	RI – MRI ≥ 600, significantly high ecological risk

Table 3. Classifications of individual contamination factor (ICF), global contamination factors (GCF), risk assessment code (RAC) and modified risk assessment code (mRAC).

ICF and GCF		RAC and mRAC	
ICF < 0	Low risk	< 1	No risk
GCF < 6		1% < RAC < 10%	Low risk
1 < ICF < 3	Moderate	11% < RAC < 30%	Medium risk
6 < GCF < 12			
3 < ICF < 6	Considerable	31% < RAC < 50%	High risk
12 < GCF < 24			
ICF > 6	High contamination	RAC > 50%	Very high risk
GCF > 24			

designates the ratio between the concentration of the element “m” and that of Al in the background.

According to Hakanson (1980), the potential ecological risk index was calculated as follows:

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times CF^i$$

where E_r^i is the potential ecological risk index of an individual element, T_r^i corresponds to the toxicity coefficient for the metal “i” and CF^i refers to the contamination factor of each element (Soliman et al., 2015; Zhang et al., 2016, 2018).

A modified ecological risk index (MRI) using the enrichment factor (EF) was suggested by Brady et al. (2015); Gargouri et al. (2018), as follows:

$$MRI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times EF^i$$

The individual contamination factor (ICF) and the global contamination factor (GCF) were calculated according to Ikem et al. (2003); Chen et al. (2013). The ICF was obtained by dividing of the exchangeable, the carbonates, the reducible and the organic applying the residual fraction. The GCF was determined by summing the ICF of all trace elements for each sample. The ICF and GCF were calculated as follows:

$$ICF_m = \frac{C_{non-residual}}{C_{residual}}$$

$$GCF = \sum_{i=1}^n CF_i$$

The risk assessment code (RAC) was computed using the percentage of exchangeable metals and

carbonate bound in the sediments (Perin et al., 1985; Jain, 2004; Ghrefat and Yusuf, 2006; Chen et al., 2013). The RAC was used to assess the bioavailability and the mobility of metals. The applied equation is written below:

$$RAC = \frac{F1 + F2}{C_t} \times 100$$

where F1 and F2 are the concentrations of the metal in exchangeable and carbonate-bound fractions, respectively and C_t is the total concentration of the metal.

A modified risk assessment code (mRAC) was measured using the following equation (Saeedi and Jamshidi-Zanjani, 2015):

$$mRAC = \frac{\sum_{i=1}^n T_i RAC_i}{\sum_{i=1}^n Tri}$$

where RAC is the percentage of each metal in the exchangeable and carbonate-bound fractions, Tri represents toxicity coefficient of metal according to Hakanson (1980), and n is the number of metals (Saeedi et al., 2015).

Results and discussion

Grain-size distribution

The grain-size distribution was determined using the GRADISTAT program. The distribution pattern of the sand, silt and clay fractions showed a significant variation characterized by the dominance of the sand fraction (Figure 2). The Meliane River had the highest percentage of sand with an average content of 98.6%. This percentage ranged from 96.38% to 99.99%

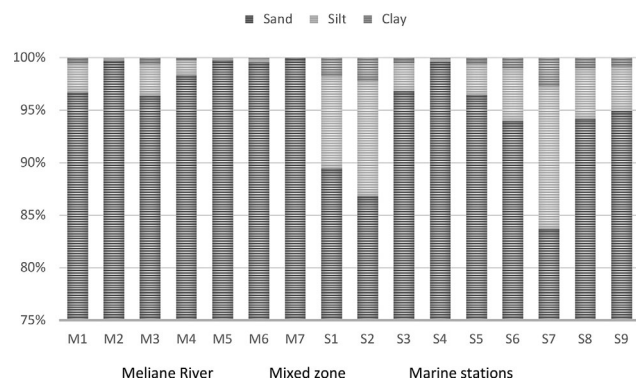


Figure 2. Distribution of grain size (%) in the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

recorded in the stations near the sewage treatment plant (M3) and the mouth of the Meliane River (M7), respectively. In marine sediments, the sandy fraction varied between 83.68% and 99.57%. The highest percentage was recorded in the Hammam-lif city in the south (S4) and the lowest in stations of the Rades (S7) in the north.

Organic matter

The percentages of organic matter range from 1.15% to 29.9%, in the Meliane River, and varied between 1.8% and 11.9% in the marine stations (Figure 3). In Meliane River, the highest recorded percentage was at the downstream part and the lowest in the mixed zone of the Meliane River. In the marine stations of the Gulf of Tunis coast, the highest percentages were located in front of the Meliane River and the lowest value was obtained in the Hammam-lif city. This variation is related to discharges of sewage treatment plant located near the Meliane River.

This variation results from the discharges of sewage treatment plant located near the Meliane River and the physicochemical parameters changes observed in the area extending from the salt-freshwater mixed region to the marine stations.

Total trace metals

Trace metal concentrations of surface sediments are listed in Table 4. In the Meliane River, the total concentrations of trace metals in the surface sediments ranged from $0.26 \mu\text{g g}^{-1}$ to $0.97 \mu\text{g g}^{-1}$ for Cd, from $2.16 \mu\text{g g}^{-1}$ to $205.7 \mu\text{g g}^{-1}$ for Cu, from 5.26 to $31.12 \mu\text{g g}^{-1}$ for Pb, from $29.25 \mu\text{g g}^{-1}$ to $317.93 \mu\text{g g}^{-1}$ for Zn, from $32.83 \mu\text{g g}^{-1}$ to $50.27 \mu\text{g g}^{-1}$ for Ni, from $29 \mu\text{g g}^{-1}$ to $78.97 \mu\text{g g}^{-1}$ for Cr, and from $120.4 \mu\text{g g}^{-1}$ to $1203.51 \mu\text{g g}^{-1}$ for Mn.

The spatial distribution of trace metals in the surface sediment of the Meliane River (Figure 4) shows that, from upstream to downstream (M1 to M7), the highest concentrations of Cd, Cu, Pb, Zn and Cr were recorded in the downstream part after the sewage treatment plant (station M5). However, for Ni and Mn, the highest recorded values were in the upstream (station M1) near the dam of Bir M'Cherga. Except Cd and Mn, the lowest concentration of Cu, Pb, Zn, Ni and Cr were observed in the mouth of the Meliane River (station M7).

The spatial distribution of trace metals in surface sediments at marine stations of the Gulf of Tunis between Rades and Hammam-lif cities is shown in (Figure 4). Concentrations of trace metals in these sediments vary between $0.22 \mu\text{g g}^{-1}$ and $0.55 \mu\text{g g}^{-1}$ for Cd, between $1.55 \mu\text{g g}^{-1}$ and $12.28 \mu\text{g g}^{-1}$ for Cu, between 4.9 and $11.85 \mu\text{g g}^{-1}$ for Pb, between $35.56 \mu\text{g g}^{-1}$ and $99.89 \mu\text{g g}^{-1}$ for Zn, between $30.11 \mu\text{g g}^{-1}$ and $43.68 \mu\text{g g}^{-1}$ for Ni, between $30.14 \mu\text{g g}^{-1}$ and $52.24 \mu\text{g g}^{-1}$ for Cr, and between $128.54 \mu\text{g g}^{-1}$ and $228.7 \mu\text{g g}^{-1}$ for Mn. The highest concentrations of Pb, Zn, Ni, Cr and Mn were obtained in the stations in front of the Meliane River. The highest concentrations of Cd and Cu were seen in the marine stations of the Rades city in the north. Besides, a relatively high concentration was observed at stations in front of the Meliane River and the lowest concentrations were generally provided at the Hammam-lif in the south.

The spatial distribution of the total trace metals, in surface sediments, is characterized by trace metals with significant concentrations in the Meliane River due to its discharges and the decrease in the marine stations of the Gulf of Tunis between Rades and Hammam-lif cities. The distribution of trace metals in the surface sediments is related to the transport of an important content of sediments and wastewater discharged by the Meliane River and the north-south shoreline drifts in the Gulf of Tunis.

Pollution indicators

The contamination factor (CF) values ranged from 0.58 to 2.55 for Cd; from 0.03 to 4.37 for Cu; from 0.81 to 5.12 for Pb; from 0.36 to 3.87 for Zn; from 0.6 to 0.87 for Ni; from 0.55 to 1.50 for Cr, and from 0.1 to 0.24 for Mn. According to the classification of Hakanson (1980), the CF values of Cu, Ni and Mn indicate a low contamination ($\text{CF} < 1$) in all stations, except for Cu in the downstream part zone (station M5). The CF of Cd was moderate in the Meliane

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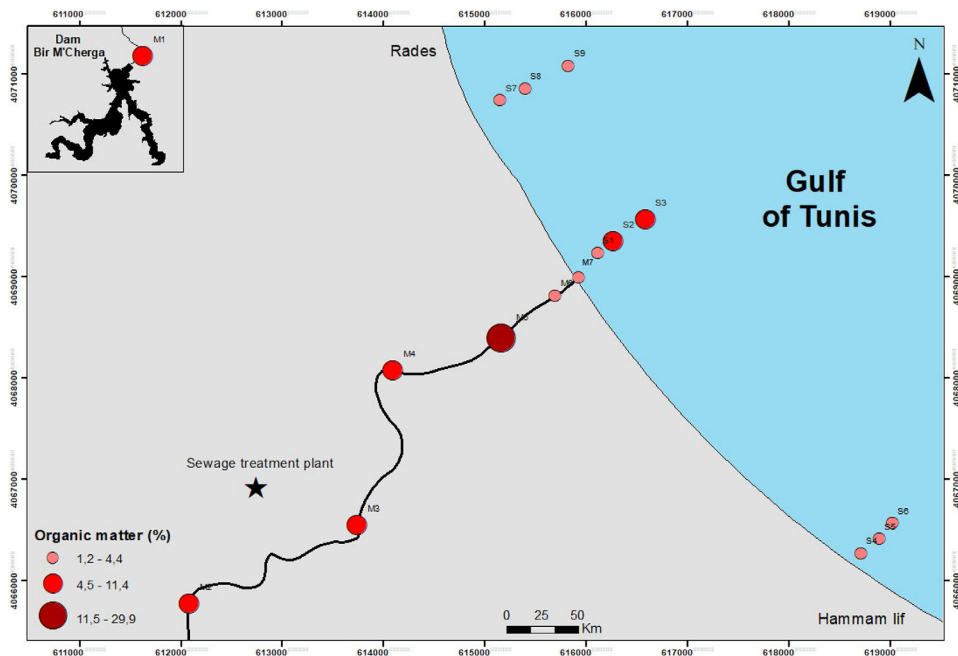


Figure 3. Spatial distribution of organic matter in the Meliane River and marine stations of the Gulf of Tunis.

Table 4. Trace metals concentrations ($\mu\text{g g}^{-1}$) in the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Stations	Cd	Cu	Pb	Zn	Ni	Cr	Mn
M1	0.38	47.04	6.08	82.17	50.27	52.72	1203.51
M2	0.49	37.92	16.12	191.28	34.92	63.73	187.29
M3	0.42	20.05	19.46	111.61	33.88	43.54	228.66
M4	0.26	18.84	8.46	69.71	33.39	41.35	287.85
M5	0.97	205.70	31.12	317.93	37.59	78.97	196.13
M6	0.91	3.81	7.83	211.90	34.17	32.08	120.40
M7	0.83	2.16	5.26	29.25	32.83	29.00	124.10
S1	0.36	2.24	10.63	61.40	30.11	44.77	149.08
S2	0.33	2.62	7.92	62.67	43.68	48.80	188.70
S3	0.52	3.78	11.85	99.89	30.94	59.24	228.17
S4	0.22	1.55	5.02	35.56	31.84	30.14	161.10
S5	0.24	2.22	4.90	46.95	35.39	30.34	159.17
S6	0.25	2.53	5.75	56.99	35.98	52.89	180.30
S7	0.55	1.99	6.68	77.97	33.30	44.95	151.11
S8	0.37	12.28	6.62	46.87	34.78	36.71	128.54
S9	0.43	2.27	6.61	57.92	35.07	41.93	137.46

River site and low in the marine stations, except at S3, S7 and S9. The CF values of Pb and Zn showed considerable contamination in the Meliane River and a moderate contamination in the marine stations. Moreover, the CF for Cr was low in the Meliane River and marine stations, except M1, M5 and S3 which were moderate (Figure 5).

The enrichment factor (EF) values varied from 1.09 to 83.53 for Cd; from 0.13 to 6.11 for Cu; from 1 to 33 for Pb; from 1 to 44.52 for Zn; from 0.84 to 24.92 for Ni; from 1.24 to 20.99 for Cr; and from 0.19 to 3.93 for Mn. The EF values indicated a low enrichment ($\text{EF} < 2$) of Mn and Cu for the majority of the stations in the study area, except M5 of Cu and M7 of Mn which were moderate. The EF values of Pb, Ni

and Cr were identified to be low-to-moderate for marine stations. But, in the sites upstream of the Meliane River, these metals had significant EF values. The EF values of Cd and Zn were low-to-moderate, in the upstream, and extremely high in the downstream. For marine stations, they were identified to be moderate-to-significant (Table 5). The results of RI varied from 28.96 to 134.72 (Table 4). The RI values show a low risk in the Meliane River as well as the marine stations. The modified ecological risk index (MRI) values oscillated between 5.58 and 2858.34. In the Meliane River, the upstream MRI values were low, while MRI values indicated a very high risk in the downstream part and the mixed zone. In fact, at the marine stations, the MRI was moderate.

Statistical analysis

The positive correlations between Cd ($r=0.70$), Cu ($r=0.79$), Pb ($r=0.82$) and Cr ($r=0.66$) with Zn may indicate similar and/or a common origin (Table 7).

Principal component analysis (PCA) was applied for 16 stations and 7 parameters (Figure 6). PCA allowed the discrimination of two axes (F1 and F2), which accumulate 80.01% of the total variance. In the variable space, F1, defined by a positive charge of the contents of Cd, Cu, Pb, Zn, and Cr, represents the axis of 52.84% of the variance. The F1 axis presents the origin of pollution. The F2, characterized by

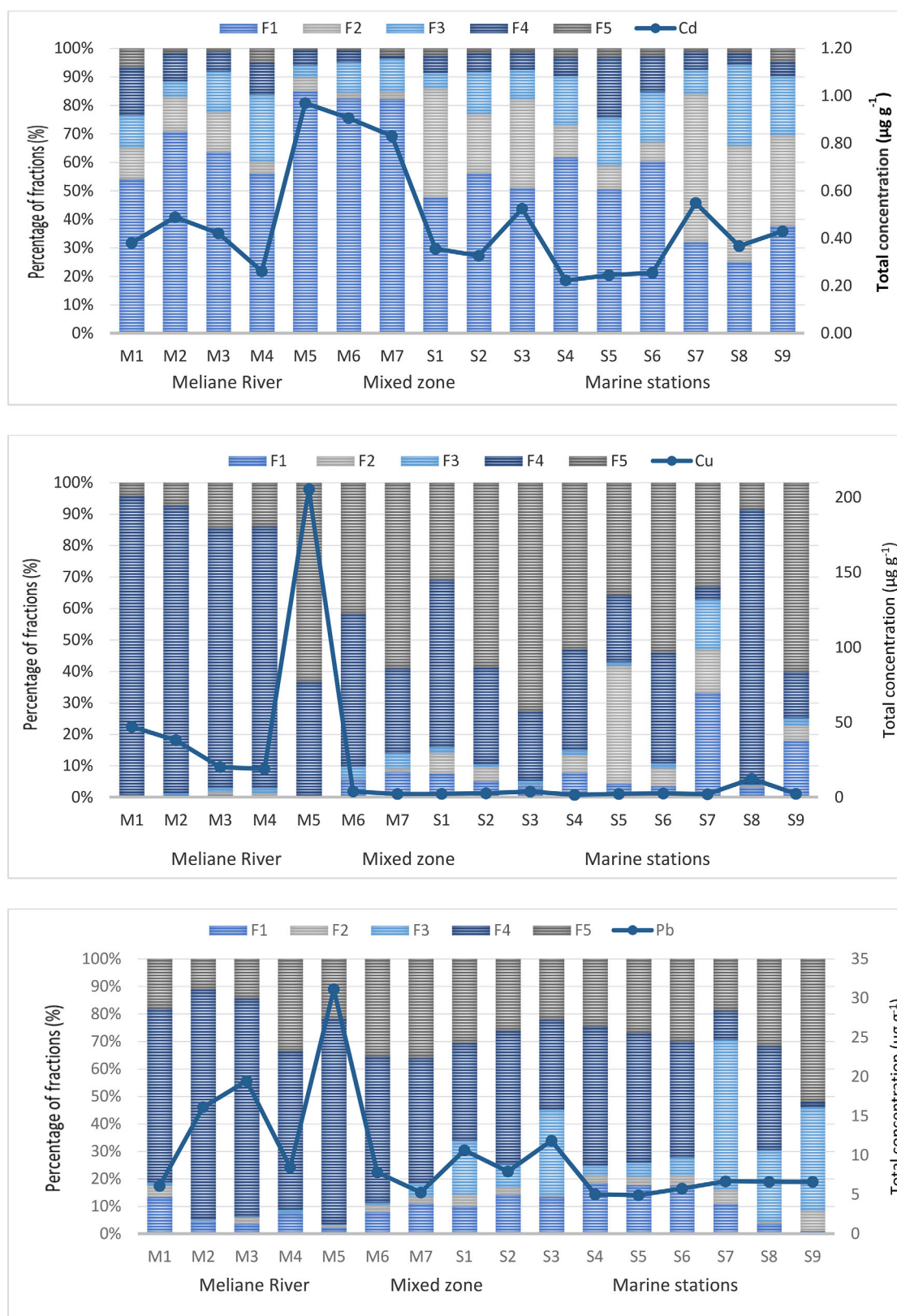


Figure 4. Distribution of trace metals in total concentrations ($\mu\text{g g}^{-1}$) and chemical fractions (%) in the surface sediments (Cd, Cu, Pb, Zn, Ni, Cr and Mn) of the Meliane River and marine stations of the Gulf of Tunis.

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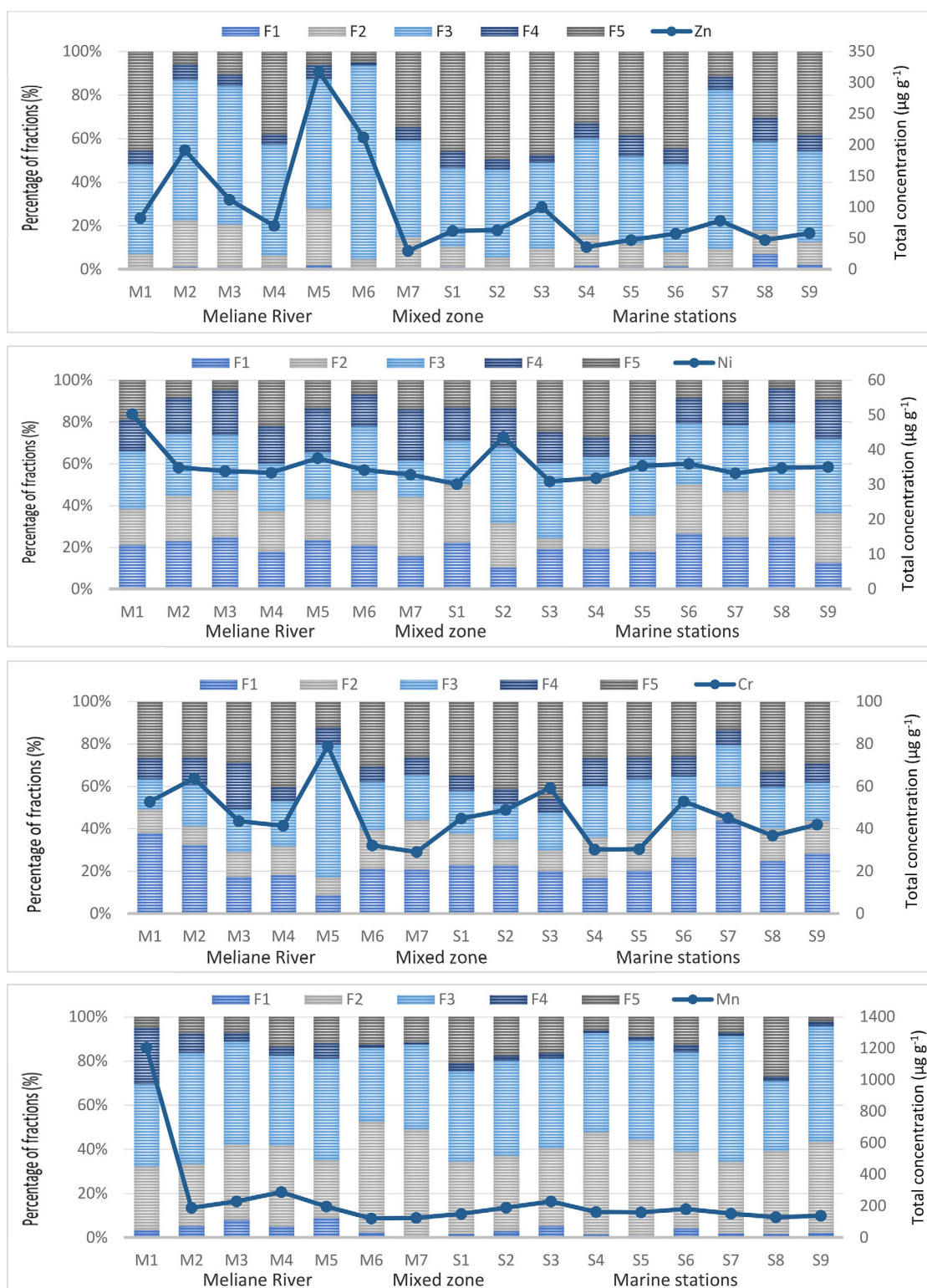


Figure 4. Continued.

positive contributions of Ni and Mn, shows the axis of 27.17% of the variance

The corresponding analysis (Figure 7) depicts the relations between the stations and the different

parameters used in order to clarify this link. The loading plot of two factors shows the presence of three groups resulting from the quality and nature of water; river and marine stations and wastewater discharge.

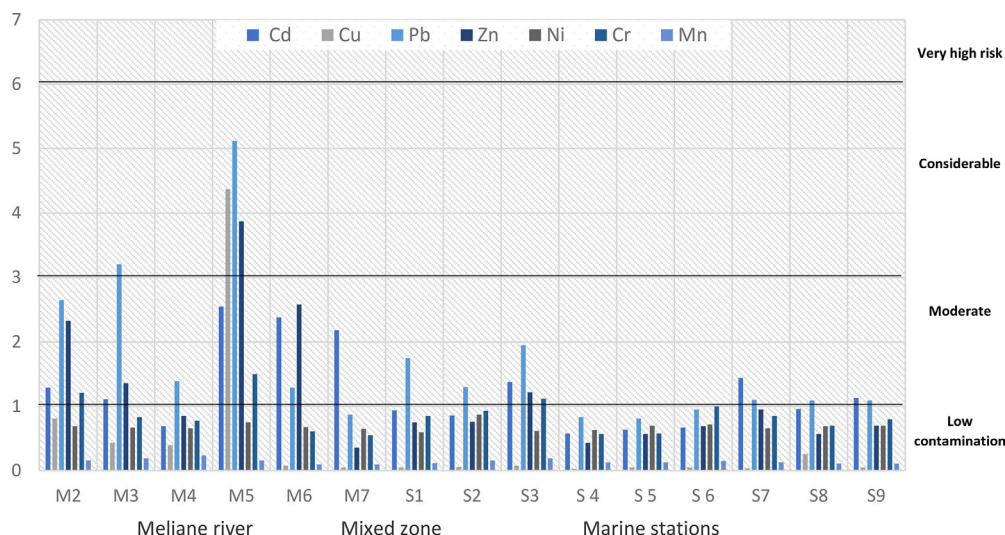


Figure 5. Contamination factor (CF) of the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Table 5. Enrichment factors (EF) of the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Stations	Cd	Cu	Pb	Zn	Ni	Cr	Mn
M2	1.55	0.97	3.19	2.80	0.84	1.46	0.19
M3	1.75	0.67	5.04	2.14	1.06	1.30	0.30
M4	1.09	0.64	2.21	1.35	1.05	1.24	0.38
M5	3.57	6.11	7.16	5.41	1.05	2.09	0.23
M6	41.15	1.40	22.22	44.52	11.73	10.51	1.73
M7	83.35	1.75	33.00	13.58	24.92	20.99	3.93
S1	5.10	0.26	9.53	4.07	3.26	4.63	0.67
S2	2.59	0.17	3.92	2.30	2.62	2.79	0.47
S3	2.30	0.13	3.25	2.03	1.03	1.88	0.32
S4	6.09	0.34	8.60	4.51	6.60	5.95	1.39
S5	4.97	0.36	6.22	4.41	5.43	4.44	1.02
S6	2.62	0.21	3.70	2.71	2.80	3.93	0.59
S7	5.95	0.17	4.53	3.91	2.73	3.51	0.52
S8	7.39	2.00	8.33	4.37	5.30	5.33	0.82
S9	5.86	0.25	5.64	3.66	3.62	4.13	0.59

Table 6. Potential ecological risk (RI), and modified potential ecological risk (MRI) in the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Stations	RI	MRI
M2	64.22	77.34
M3	57.92	91.27
M4	35.52	56.35
M5	134.72	188.37
M6	85.65	1478.42
M7	74.91	2858.34
S1	42.64	232.34
S2	39.67	119.43
S3	58.28	97.33
S4	26.71	278.15
S5	28.96	223.55
S6	31.50	123.27
S7	55.10	227.11
S8	41.22	315.61
S9	45.48	235.92

This discrimination of station groups is essentially reflected in the following observations:

- The first group (the GI group) includes the stations located upstream (M1), taken at the exit of Bir M 'Cherga Dam. It involves Ni and Mn.

Table 7. Correlations matrix of elements in the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Elements	Cd	Cu	Pb	Zn	Ni	Cr	Mn
Cd	1						
Cu	0.52	1					
Pb	0.49	0.84	1				
Zn	0.70	0.79	0.82	1			
Ni	-0.08	0.26	-0.03	0.08	1		
Cr	0.26	0.73	0.75	0.66	0.27	1	
Mn	-0.15	0.16	-0.08	-0.03	0.78	0.21	1

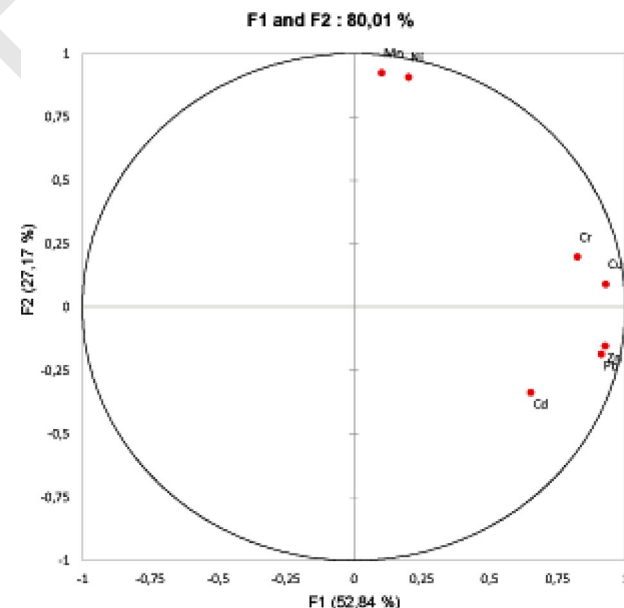


Figure 6. Loading of the parameters on the principal component axis.

- The second group (the GII group) is composed of the M5 station with Cd, Cu, Pb, Zn, and Cr. This group presents the relation between the most contaminated station (M5) in the Meliane River and these elements (Cd, Cu, Pb, Zn). The source of

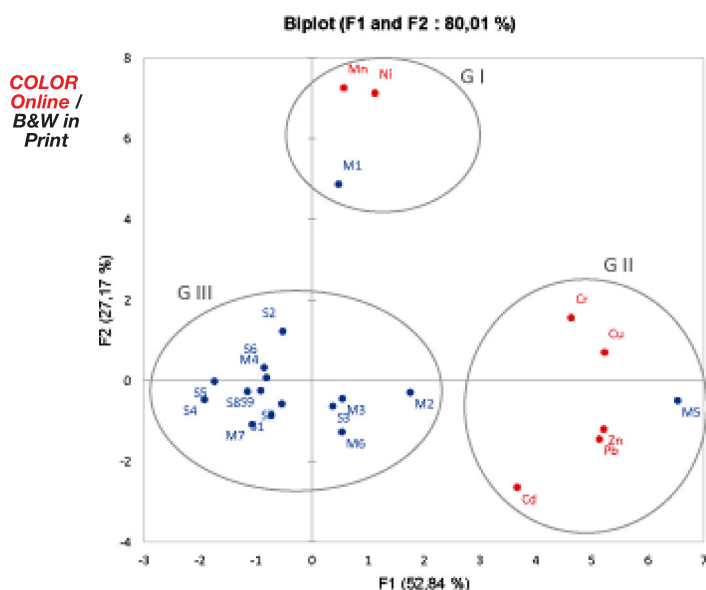


Figure 7. Loading of elements and stations on the principal component axis.

these metals is the domestic and industrial wastewater discharged into the Meliane River.

- The third group includes river stations that are not affected by the discharges into Meliane River and the marine stations of the Gulf of Tunis between Rades and Hammam-lif cities.

Chemical speciation

The use of sequential extraction techniques may provide very useful information regarding the chemical nature or potential mobility and bioavailability of a particular element, which can consequently offer a more realistic estimate of the actual environmental impact (Abdullah et al., 2019). Determining the total concentration of metals is arguably the most fundamental way to assess the quality of sediments; but for further understanding the potential mobility, bioavailability and toxicity of metals in sediments. The fractionation of metals makes it possible to assess the bioavailability and toxicity of metals.

The distribution of trace metals in different fractions of sediments is shown in Figure 4. Cd was present in the highest percentage in the exchangeable fraction, with an average of 57.22%. Zn, Ni and Mn were observed in the highest percentages in the reducible fraction, with average proportions of 50.54%, 27.20% and 43.33%, respectively. Cu and Pb dominated the oxidizable fraction, with average proportions of 47.77% and 47.84%, respectively. Cr was present in the residual fraction with a percentage of 29.26%.

Cadmium

The chemical speciation showed that Cd was mainly bound to the exchangeable fraction with percentages ranging from 54.11% to 84.92% in the Meliane River. However, in marine stations of the Gulf of Tunis between Rades and Hammam-lif cities, this percentage varied between 24.99% and 61.77%. It explains the fact that the Meliane River could be the main source of Cd. The high percentage of Cd bound to the exchangeable fraction lead to a potential environmental and ecological risks in the aquatic ecosystem.

The trace metals linked to the exchangeable fraction can easily migrate to the aqueous phase and have high bioavailability and toxicity (Li, 2007; Lin et al., 2014; Wang et al., 2015; Ben Amor et al., 2019). The average of abundance of Cd in the different fractions is as follows: exchangeable > carbonate-bound > reducible > oxidizable > residual.

Copper

The chemical speciation performed on the surface sediments of the Meliane River shows that Cu is bound to the oxidizable fraction with percentage ranging from 27.01% to 95.01%. The relative affinity of copper to the fraction bound to the oxidizable is due, in part, to the fact that copper compounds are stable (Stumm and Morgan, 1970; Smith and Martell, 1976; Rais, 1999). However, in the marine stations, chemical speciation shows that Cu is related to the residual fraction with percentages ranging from 8.43% to 72.57%. The dominance of these two fractions (oxidizable/residual) depends on many factors such as the organic matter content in the sediment and its degree of oxidation, the Cu anthropic contribution and the influence of the detritus (Rais, 1999). The average of the different fractions of Cu is in the order of: oxidizable > residual > exchangeable > carbonate-bound > reducible.

Lead

The chemical speciation of Pb demonstrates the abundance of this metal in the oxidizable fraction with percentages ranging from 46.67% to 83.55%, in the Meliane River, and from 2.02% to 50.75% in the marine stations. Lead is generally linked to organic matter and clay (Helali et al., 2016). The distribution of Pb to the oxidizable phase in the Meliane River increases slightly in the downstream. However, in the Gulf of Tunis between Rades and Hammam-lif cities, the percentage of the oxidizable raises from the north to the south. The oxidizable fraction is characterized by a low mobility and liberates a little quantity of trace

Table 8. Individual (ICF), and global contamination factors (GCF) in the surface sediments of the Meliane River and marine stations of the Gulf of Tunis.

Stations	ICF							GCF
	Cd	Cu	Pb	Zn	Ni	Cr	Mn	
M1	13.99	21.80	4.52	1.20	4.23	2.76	19.43	67.93
M2	59.32	12.57	7.95	15.80	10.94	2.77	12.25	121.61
M3	76.70	5.94	5.95	8.30	20.46	2.47	12.93	132.73
M4	19.53	6.18	1.99	1.63	3.55	1.47	6.42	40.78
M5	143.22	0.58	3.58	15.32	6.40	7.16	7.29	183.54
M6	124.71	1.40	1.81	18.64	13.73	2.26	6.90	169.46
M7	36.08	0.70	1.78	1.86	6.17	2.79	7.53	56.91
S1	37.49	2.24	2.27	1.18	6.74	1.87	3.74	55.52
S2	55.01	0.70	2.83	1.03	6.40	1.42	4.72	72.12
S3	67.85	0.38	3.52	1.10	3.01	1.18	5.12	82.15
S4	33.20	0.89	3.09	2.03	2.67	2.75	15.38	60.01
S5	32.58	1.79	2.75	1.62	2.80	2.84	9.91	54.30
S6	34.86	0.85	2.36	1.25	10.83	2.87	6.90	59.91
S7	77.00	2.03	4.30	7.70	8.37	6.48	13.08	118.95
S8	56.16	10.86	2.17	2.27	24.07	2.03	2.69	100.25
S9	20.59	0.66	0.93	1.62	9.59	2.40	43.53	79.32

metals into the environment (Filgueiras AV, 2002; Okbah et al., 2020). On the average, the abundance of Pb associated with different fractions was in the order of: oxidizable > residual > reducible > exchangeable > carbonate-bound.

Zinc

The chemical speciation performed on the surface sediments reveals that Zn is bound to the reducible fraction. The proportions of Zn in the reducible fraction range from 41.22% to 89%, in the Meliane River, and from 36.14% to 72.92% in the Gulf of Tunis between Rades and Hammam lif cities. There is also a significant proportion related to the residual fraction with percentages ranging from 5.09% to 45.51%, in the Meliane River, and from 11.49% to 49.36% in the marine stations. The average of the different fractions of Zn was in the order of: reducible > residual > carbonate-bound > oxidizable > exchangeable.

Nickel

The chemical speciation of Ni shows the abundance of this metal in the reducible fraction. It presents a percentage ranging from 17.6% to 30.55%, in the Meliane River, and varies between 8.54% and 36.36% in the marine stations. The distribution of Ni in both river and marine stations demonstrates an approximate percentage of fractions linked to reducible, carbonate-bound and exchangeable fractions with an average of 27.2%, 22.17% and 20.34%, respectively. The order of abundance of Ni is as follows: reducible > carbonate-bound > exchangeable > oxidizable > residual.

Chromium

The chemical speciation shows that Cr is bound to the residual fraction with percentages ranging from 12.26% to 40.41%, in the Meliane River, and from 13.37% to 45.96% at the marine stations. In general, the residual fraction is a non-mobilizable phase. It is considered as geochemical background value of the elements in the sediment (Tessier et al., 1979; Li et al., 2020). The residual fraction is made essentially of detrital silicate minerals, refractory organic matter and resistant sulfides (Tessier et al., 1979). The order of the average of abundance of Cr in the different fractions is: residual > exchangeable > reducible > carbonate-bound > oxidizable.

Manganese

The chemical speciation demonstrates the abundance of Mn first to the reducible fraction in first degree and second to carbonate-bound. The percentages of the reducible fraction range between 33.72% to 50.28%, in the Meliane River, and from 31.86% to 56.95% in the marine stations. For the carbonate-bound, the percentages range from 26.33% to 50.23% and from 32.47% to 46.37% in the Meliane River and marine stations, respectively. The average of the different fractions of Mn was in the order of: reducible > carbonate-bound > residual > oxidizable > exchangeable.

The chemical speciation used to know the proportions of trace metals in each fraction of surface sediments proves that Cd, Cu, Pb, Zn, Ni and Mn are associated to the non-residual fraction and only the Cr is bound to the residual fraction. The sources of trace metals in the surface sediments can be related to the anthropogenic origin from the industrial and domestic wastewater, which can be insufficiently treated, the surrounding farmland and the geological background. The anthropogenic contributions have exceeded natural inputs in the increases of trace metals accumulation in the environment, especially in developed areas with high population density and industrial activities (Wang et al., 2012; Hu et al., 2018; Huang et al., 2019).

Pollution indicators

The individual contamination factor (ICF) values show a high risk for Cd at all stations (Table 8). The ICF values of Ni and Mn are high in the Meliane River and in most marine stations. The Cr values were moderately affected by metallic trace elements ($1 < \text{ICF} < 3$) in most of the studied samples. The ICF values of Pb and Zn indicate moderate risks in

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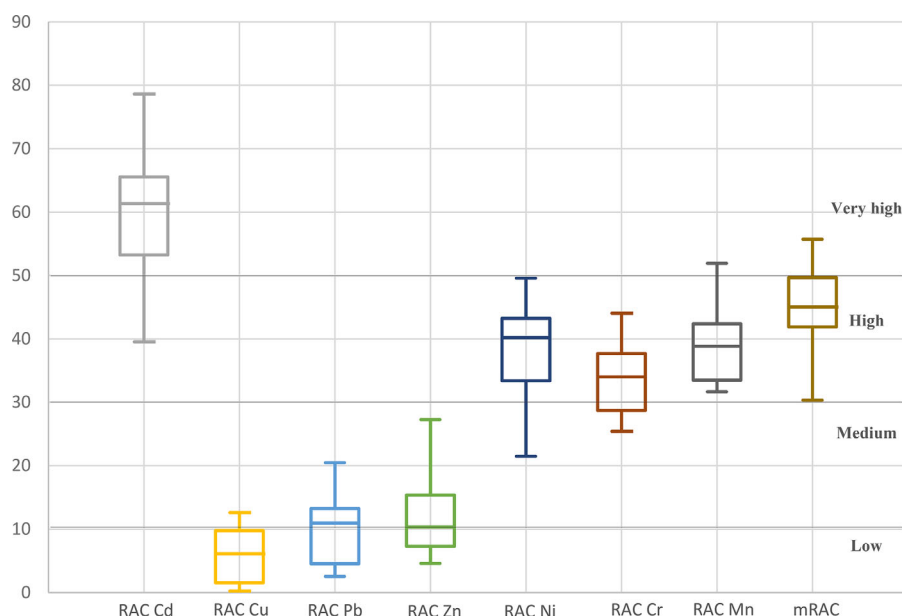


Figure 8. Box-plots of RAC and mRAC measured in the Meliane River and marine stations of the Gulf of Tunis.

the majority of stations; and oscillate from low to high contamination of Cu. The global contamination factor (GCF) values expose a high risk for all samples ($GCF > 24$) from the Meliane River to the marine stations.

The box plot (Figure 8) of the risk assessment code (RAC) values demonstrates that the percentages of Cu, Pb and Zn range from low risk to medium risk with percentages from 0.2 to 43%, for Cu, from 2.5 to 20.4%, for Pb, and from 4.6 to 27.3% for Zn. The RAC values of Ni, Cr and Mn show minimum percentages of 21.5%, 13.8% and 31.7%, respectively, and maximum percentages of 49.6%, 51.4% and 51.9%, respectively. The risk is therefore medium to high. The average percentage of Cadmium is 59.8%. Thus, this element presents a very high environmental risk. The modified risk assessment code (mRAC) values range between 30.3% and 55.7% (Figure 8). They oscillate from a high to very high potential adverse effect. Discharges caused by coastal activities and urban wastes are adsorbed, to easily release the bound fractions, such as the exchangeable and carbonate-bound fractions (Saeedi and Jamshidi-Zanjani, 2015; Soliman et al., 2018).

Conclusion

The distribution and the evaluation of metals in the surface sediments of the Meliane River and the marine stations of the Gulf of Tunis were assessed, in this work, using several tools and approaches (distribution of some trace metals Cd, Pb, Zn, Ni, Cr and Cu, sequential extraction, numerous indices and statistical

approaches). The study of the variation in the total concentrations of the surface sediments of Cd, Cu, Pb, Zn, Ni and Cr showed that the highest values were recorded in the downstream part of the Meliane River. The chemical speciation revealed that most of the Cd was bound to the exchangeable fraction, indicating its high bioavailability and toxicity. Zn, Ni and Cr were mainly bound to the reducible fraction, while Cu and Pb were mostly associated with the oxidizable fraction, and Cr was related to the residual fraction. The distribution of the trace metals in the total concentrations of surface sediments was characterized by elements with high total contents values in the Meliane River. Obviously, it decreased in the marine stations. The high values of trace metals in River, which decrease in marine stations, resulted from the changes in the physicochemical parameters. This change started from the salt-freshwater mixed zone to the marine stations of the Gulf of Tunis. Pollution indicators and risk assessment indices were efficiently applied to evaluate the quality of surface sediments. The contamination and enrichment factors showed high values in the downstream part. The concentrations with trace metals in the surface sediments proved that the Meliane River is the main source of pollution in the Gulf of Tunis, essentially between the Rades and Hammam lif coast where the swimming is prohibited. The Meliane River drained different types of pollutants linked to the anthropogenic inputs. In addition to the different types of treated and untreated discharges, there is a solid waste discharge located in the river. Thus, we may conclude that the Meliane River is very susceptible and defenseless. There is a

need to control the treatment of wastewater discharged in this river since contamination by discharges caused problems in the Gulf of Tunis between Rades and Hammam lif cities. Obviously, the Gulf of Tunis is a semi-enclosed area, which starts showing some signs of degradations.

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