Original Research

Spatial Distribution and Source Identification of Heavy Metals in Surface Waters of Three Coastal Areas of Tunisia

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Abstract

The concentrations of selected dissolved trace elements (Ni 446-919 µg L^{-1}, Pb 383-1015, Fe 195-739, Cu 217-318, Cr 156-336, Zn 9-236, Mn 0-187, Co 0-310, and Cd 26-77) were assessed in the surface water of 30 stations belonging to three coastal areas along the Gulf of Gabes, i.e., the southern (stations 1-10) and northern (stations 11-20) coastal areas of Sfax and the Ghannouch area (stations 21-30) during October and November 2014. Results showed that dissolved metals in surface waters, which were analyzed by means of flame atomic absorption spectrophotometry, followed the concentration levels (Pb>Ni>Fe>Cu>Cr>Co>Mn>Cd>Zn) on the southern and (Ni>Pb>Fe>Cu>Cr>Zn>Mn>Co>Cd) on the northern coasts of Sfax, and (Ni> Fe>Pb>Cu>Cr>Zn>Co>Cd>Mn) in the Ghannouch area. In the southern and the northern coasts of Sfax, all analyzed metals were detected in 100% of sampled stations except Co, which was revealed in 90 and 80% of stations, respectively. However, in the Ghannouch area all analyzed metals were detected in 100% of sampled stations except Mn, which was revealed in 70% of stations. These trace elements, except for Fe and Mn, exceeded the safety limit of the USEPA water quality criteria for the protection of aquatic fauna and flora survival and their uses. The Sfax and Ghannouch coastal areas should be considered relatively polluted with metals (Zn, Ni, Pb, Co, Cr, Cd, and Cu). The elevated metal contents were attributed to anthropogenic waste inputs around the study area. The main sources of Ni and Co loading in the seawater were the SIAPE phosphoric acid and fertilizer plant and a waste water treatment plant located close to station 1. Whereas the fishing harbor of Sfax, which is situated on the southern coast (station 9), is the second source of high amounts of Cd, Mn, Cr, and Pb. This situation has led to serious human health risks and chronic toxicity caused by their potential bioaccumulation in some aquatic fauna such as shrimp, fish, crab, shellfish, mollusk, and cephalopoda.

Keywords: trace element, anthropogenic impacts, safety limit, southern and northern coasts of Sfax, Ghannouch area

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Introduction

Growing concern over the potential contamination of marine coastal ecosystems has gained momentum in recent years and become a priority issue [1-3]. Heavy metals in ecosystems have received extensive attention because they are toxic and non-biodegradable regarding their bioaccumulation in the environment, and easy to accumulate and magnify in organisms [4-10]. They are categorized as potentially toxic (e.g., Cd, Cr, Co, Pb, and Ni) and essential (e.g., Cu, Zn, and Fe) [11-14]. Among other contaminants, heavy metals in seawater have received particular attention as a way of assessing the impact of human activities on the marine environment [3, 11, 15-16]. Concentrations of heavy metals in aquatic ecosystems have increased considerably due to the inputs of industrial waste, sewage runoff, and agriculture discharge [17-18]. Anthropogenic activities and urban effluents are known to be significant sources of the metals, resulting in the deterioration of water quality with a long-term implication for human health and ecosystems [19-20]. They are common pollutants that have severely deteriorated the aquatic ecosystems in different parts of the world [21-23]. Even at low concentrations, toxic metals can be very harmful to human health when ingested over a long period. Essential metals can also produce toxic effects with excessive intake [24-26]. In other words, heavy metal pollution may likely go hand in hand with rapid economic development [5, 27].

Over the last decades, several studies have been carried out both in the eastern [28-29] and western Mediterranean regions [30-31]. However, there is still a lack of information regarding the North African regions skirting the southern part of the Mediterranean. Tunisia, being one of these regions, could have sustained the simultaneous effect of transfrontier pollution and urban activities concentrated in its main coastal cities. In fact, Tunisia has a marine space spreading over than more 7 million hectares and including important characteristic ecosystems such as the *Posidonia meadows* and the coralligenous constructions. This area has been subjected to increasing pressure linked to the development of several activities on the coast and in the sea. The Gulf of Gabes (southwestern Mediterranean) is one of the most vulnerable aquatic ecosystems, contributing about 65% of national fish production in Tunisia [32-33], fauna biodiversity [34-38] and a wide distribution of *Posidonia Oceanica*, an endemic species representing a good nursery for fish eggs and larvae [39]. However, due to the increase of urbanization, industry, overfishing, tourism, and the discharge of huge amounts of phosphogypsum and other pollutants, the Gulf of Gabes has been reported to be densely polluted [40]. Sfax city (Tunisia), located on the southeastern Mediterranean Sea, is one of the main harbors of this gulf, and is an important industrial center whose pollution level is in contrast to nearby Kerkennah Island.

In 2009 the northern coast of Sfax was restored by cleaning a zone of 400 ha, removing 4.3 million m³ of polluted soil, including 1.7 million m³ of phosphogypsum,

an industrial by-product of phosphoric acid produced from natural phosphate rock through the wet process [41]. This area was recently restored through the Taparura Project, which was aimed at remediating this part of Sfax city. The project included the rehabilitation of a former industrial site, cleaning-up beaches, and restoring the area [42]. Indeed, this zone was strongly polluted by the phosphogypsum wastes from the NPK phosphoric acid industry, situated near the commercial harbor. NPK was closed in 1992 and the Taparura Project allowed for the burial of the phosphogypsum wastes and the rehabilitation of the area between the commercial harbor and the zone of Sidi Mansour. On the northern coast, there are also the mouth of the rainwater draining channel ("PK4"), which crosses the city from southwest to northeast, and the outlet of the Wadi Ezzit, which receives untreated domestic and industrial effluents. However, the southern coast, which was not yet been restored, is under a great environmental pollution and harbors many anthropogenic and industrial activities. Although there have been a number of investigations on the impacts of pollutants such as hydrocarbons and nutrients (e.g., phosphate, nitrate, ammonium), total polyphenolic compounds and phosphogypsum wastes in the Sfax coast (e.g., [40, 43, 44]), the human and ecological risk from pollutants, namely heavy metals, have not yet been investigated in the gulf of Gabes. Indeed, the coastal zone of Sfax has been subjected to some investigations on trace metals in sediments [45] or in some seafood such as annular sea bream fish (*Diplodus annularis*), cow bream (*Sarpa salpa*), and cuttlefish (*Sepia officinalis*) [46], and in the marine bivalve *Ruditapes decussatus* [47-48], but data on the spatial distribution of dissolved trace metals in the surface seawater are scarce or absent.

To sum up, the purposes of this study are to:
1. Quantify and explain the spatial distribution and fractionations of nine metals (Zn, Ni, Pb, Co, Fe, Cr, Cd, Cu, and Mn) in the surface water of 30 stations in the Sfax northern and southern coasts and Ghannouch area during October and November 2014 (Gulf of Gabes, Tunisia).
2. Explore the contamination degree and potential ecological risks.
3. Identify potential sources of contamination to these three marine coastal ecosystems by heavy metals.

This evaluation will help develop effective coastal management guidelines and strategies for better management of coastal activities.

Material and Methods

Study Area

The Gulf of Gabes (Eastern Mediterranean Sea, between 35°N and 33°N, Tunisia) is endowed with rich aquatic resources contributing to about 65% of the national fish production in Tunisia [32]. Sampling was carried during October and November 2014 in three

coastal areas: the Southern (hereafter called SC; stations 1-10) and northern (hereafter called NC; stations 11-20) coasts of Sfax and the Ghannouch area (hereafter called GA; stations 21-30) in the Gulf of Gabes. Ten sampling stations were chosen for each area, taking into account the pollution gradient (Fig. 1).

Sampling

Sampling was performed on board the vessel "Taparura" between 10:30 and 15:30 (18 and 23 October 2014), and 08:30 and 12:30 (13 November 2014) around high tide and under conditions of calm sea and sunny weather (18 and 23 October, 13 November 2014).

Seawater samples were collected at ~0.1-m depth using 4-l Nalgene polycarbonate bottles. The bottles were opened below the water surface to avoid sampling of the surface microlayer. They were extensively washed with 1 M hydrochloric acid (HCl) and Milli-Q water before use to prevent the contamination of the bottles, rinsed three times with the respective sample before filling, and placed in cold and dark conditions after collection.

Analysis

Trace metals, i.e., cadmium (Cd), cobalt (Co), chrome (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), manganese (Mn), and zinc (Zn) were analyzed by means of flame atomic absorption spectrophotometry (AAS) (Perkin Elmer A-Analyst 200 instrument copyright @ 2007, version 6 model). Some characteristics of the metal trace analysis, e.g., absorption wavelength λ (nm) were detected using UV radiation. Etalon concentration for each metal, detection limit ranges and certified standard are given in Table 1. Seawater samples were filtered under vacuum filtration with a 0.2 μm porosity filter and underwent acid attack. The blank used to analyze the different heavy metals was composed of 100 ml of water and 2 or 3 drops of HCl.

Data Processing and Statistical Analysis

We applied geographic information systems (GIS) tools using ArcGIS 10.2 software to make contour plots. Kriging was the method used to build maps relative to spatial distribution for all dataset parameters.
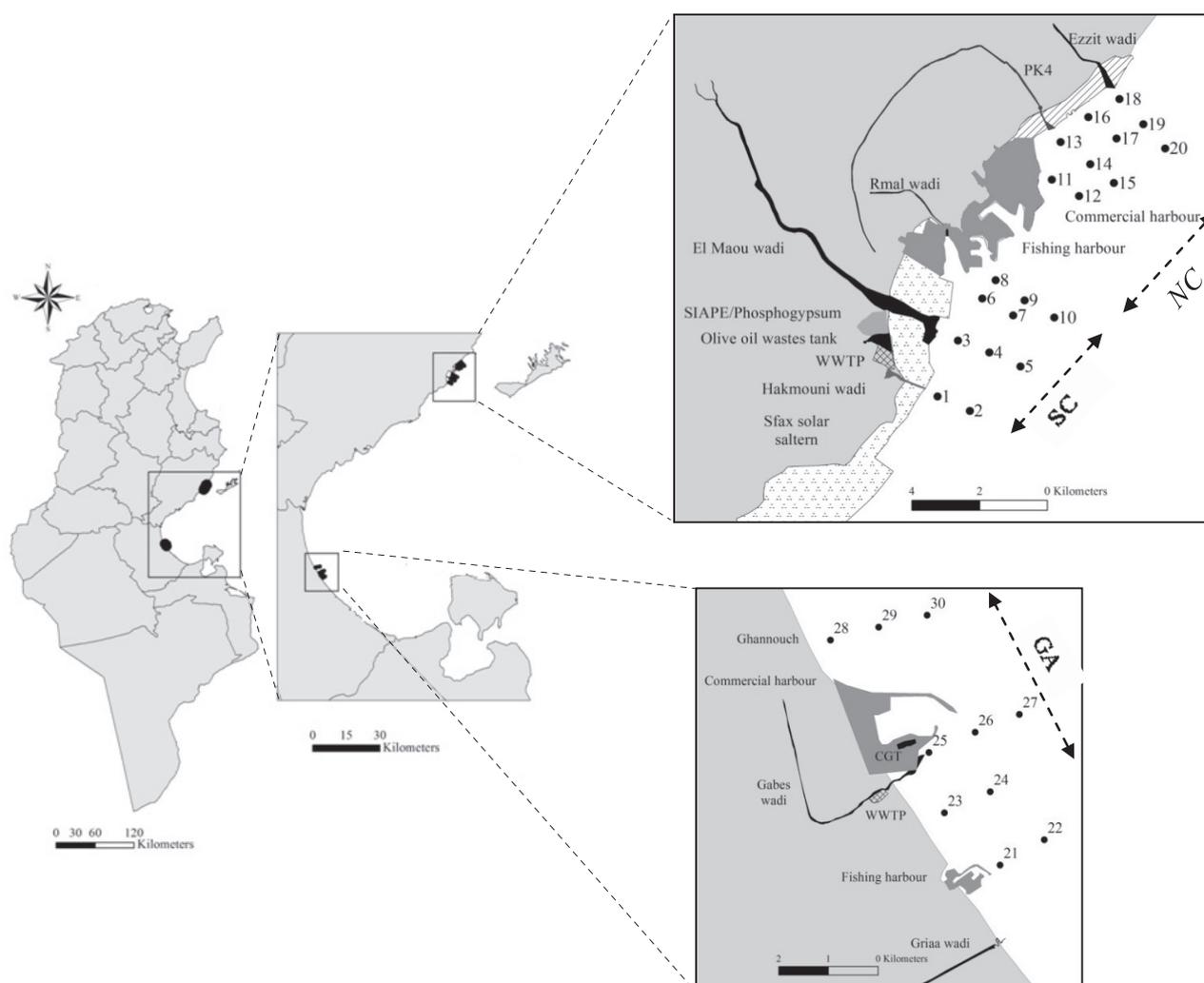

Fig. 1. Location of the studied stations in the southern (stations 1-10) and northern (stations 11-20) coastal areas of Sfax and the Ghannouch area (stations 21-30) sampled during autumn (October-November 2014).

Table 1. Some characteristics of the metal trace analysis, such as UV wavelength absorption λ (nm), etalon concentration, limit of detection, and standard certified for some trace metals (ND: Non Defined).

Trace metal Levels	Absorbance : λ (nm)	Etalon concentration (mg l⁻¹)			Limit of detection (mg l⁻¹)	Standard certified for some metal trace
Zn	213.86	1	3	5	0.012	ND
Ni	232.00	1	5	10	0.07	ND
Pb	283.31	1	3	5	0.085	Lead AA standard 1,000 ± 5 µg ml⁻¹ in 2 % HNO₃
Co	240.73	1	3	5	0.075	ND
Cu	324.75	1	5	10	0.035	ND
Fe	248.33	1	5	10	0.08	Iron AA standard 1,000 ± 5 µg ml⁻¹ in 2 % Hcl
Cr	357.81	0.5	1	1.5	0.05	Chromium standard 1,000 ± 5 µg ml⁻¹ in 2 % Hcl
Cd	228.80	1	3	5	0.012	ND

Risk Assessment

The Metal Pollution Index (MPI) represents the composite influence of all metals on water quality [49]. It represents the sum of the ratio between the concentration of analyzed metals and their corresponding maximum allowable concentrations (MAC) as used by [50] for Zn, Ni, Pb, Cr, Cd, and Cu, and by [51] for Co, Mn, and Fe.

$$MPI = \sum_{i=1}^{n} \frac{c_i}{(MAC)i}$$

…where the concentration of 'iᵗʰ' metal; MAC = Maximum allowable concentrations. Water quality is categorized into six different classes depending on the degree of anthropogenic input of metals during various periods of sampling [52]. An MPI of < 0.3 is very poor (Class I), 0.3-1.0 poor (Class II), 1.0-2.0 slightly affected (Class III), and 2.0-4.0 moderately affected (Class IV), 4.0-6.0 strongly affected (Class V), and an MPI > 6.0 is seriously affected (Class VI) [11, 49].

Results and Discussion

Spatial Distribution of Dissolved Trace Metals in Surface Waters of Three Coastal Areas along the Gulf of Gabes

The spatial distribution of heavy metal concentrations in the sampled water is presented in Table 2 and Fig. 2. Trace metal concentrations in water samples was measured in the order Ni>Pb>Fe>Cu>Cr>Zn>Mn>Co>Cd (Table 2 and Fig. 2). All these estimated trace elements exceeded the permissible limit of the USEPA water quality criteria except Fe and Mn [50, 51]. Ni, Pb, and Fe contributed 68% of the total trace metals measured while the others did not exceed 32%. Ni represented 26% and varied from 446 (station 5, SC) to 919 µg. l⁻¹ (station 1, SC), with an average of 705±102 µg l⁻¹ (Table 2 and

Fig. 2). Pb represented 23% and varied from 383 (station 22, GA) to 1,015 µg l⁻¹ (station 9, SC), with an average of about 623±180 µg l⁻¹ (Table 2 and Fig. 2). Fe averaged 505±135 µg l⁻¹, varying from 195 (station 5, SC) to 739 µg l⁻¹ (station 15, NC). Mn and Co were detected in 90% of samples, whereas Ni, Pb, Fe, Cu, Cr, Zn, and Cd were detected in 100% of the samples. 45% of the highest trace metal concentrations, i.e., Pb, Mn, Cd, and Cr were measured at station 9 situated close to the fishing harbor in SC (Fig. 2). The most important concentrations of Ni and Co were observed in station 1, situated close to the phosphoric acid and fertilizer plant, the WWTP, and Hakmouni wadi of SC. These sources are responsible for loading the seawater with chemically polluted wastes, notably Ni and Co (Fig. 2).

Most trace metals displayed significant differences between NC, SC, and GA, i.e., Pb, Fe, Cu, and Zn (ANOVA, p<0.0001), Co and Mn (ANOVA, p<0.001), and Ni (ANOVA, p<0.05) (p>0.01), except for Cd and Cr (ANOVA, p<0.05). The near-shore coastal environments are the most marine ecosystems vulnerable to metal pollution due to intense activities of coastal inhabitants – most notably urbanization and industrialization [11]. The trace metals analyzed in surface water exhibited the following decreasing order: (Pb>Ni>Fe>Cu>Cr>Co>Mn>Cd>Zn) on the SC, (Ni>Pb>Fe>Cu>Cr>Zn>Mn>Co>Cd), on the NC, and (Ni> Fe>Pb>Cu>Cr>Zn>Co>Cd>Mn) in GA.

A close look at the results showed mean concentrations of metals in surface water. In this study, metals such as Zn (9-236 µg l⁻¹), Ni (446-919 µg l⁻¹), Pb (383-1015 µg l⁻¹), Co (0-310 µg l⁻¹), Cr (156-336 µg l⁻¹), Cd (26-77 µg l⁻¹), and Cu (217-318 µg l⁻¹) are among toxic chemicals that exceeded the safety limit of the USEPA water quality criteria. However, Fe (195-739 µg l⁻¹) and Mn (0-187 µg l⁻¹) elements were within the allowed limits [50-51]. The same result was found in surface sediments from the Sfax-Kerkennah coastal zone (Tunisia) [53]. In fact, all analyzed metals (except for Fe and Mn) can be considered as moderate to extreme pollutants, especially in Sfax Bay. Fe and Mn in the city of Sfax were derived from natural sources [53]. Industrial activity, shipyard

Table 2. Mean values and standard deviation (SD) of some trace element levels at stations sampled in the northern and southern coastal areas of Sfax and the Ghannouch area during autumn (October-November 2014). In the last column, results of one-way ANOVA. F values: between-groups mean square/within-groups mean square; asterisks denote significant differences between the southern and northern coasts: $*p < 0.05$; $**p < 0.001$; $***p < 0.0001$. (BLD: Below the Detection Limit).

| Trace metal Levels	OF (%)	RA (%)	Safety limit ($\mu g\ l^{-1}$)		Southern coastal area			Northern coastal area			Ghannouch area			Stations with min value	Stations with max value	F (values)
			Spanos (2014)	USEPA (1999)	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD			
Nickel (*Ni*) ($\mu g\ l^{-1}$)	100	26	273.55	74	446	919	657±131	577	780	679±61	687	861	779 ± 55	5	1	5.290 (0.012)*
Lead (*Pb*) ($\mu g\ l^{-1}$)	100	23	362.11	210	569	1,015	765±140	389	961	638±174	383	567	467 ± 69	22	9	12.211 (0.000)***
Iron (*Fe*) ($\mu g\ l^{-1}$)	100	19	416.46	---	195	522	356±98	501	739	618±84	485	644	541 ± 48	5	15	28.422 (< 0.0001)***
Copper (*Cu*) ($\mu g\ l^{-1}$)	100	10	190.11	4.8	217	263	244±13	242	318	283±24	245	314	291 ± 23	5	19	14.014 (< 0.0001)***
Zinc (*Zn*) ($\mu g\ l^{-1}$)	100	4	256.87	90	9	85	44±23	52	156	100±29	141	236	183 ± 29	5	28	65.176 (< 0.0001)***
Cobalt (*Co*) ($\mu g\ l^{-1}$)	90	4	133.47	---	0	310	112±89	0	125	60±47	103	181	151 ± 30	4, 15, 18	1	5.626 (0.009)**
Manganese (*Mn*) ($\mu g\ l^{-1}$)	90	3	191.3	---	37	187	110±54	11	139	80±39	0	100	43 ± 36	22-24	9	5.819 (0.008)**
Cadmium (*Cd*) ($\mu g\ l^{-1}$)	100	2	87.21	42	29	77	51±14	26	53	44±10	37	51	44 ± 4	17	9	1.779 (0.188)
Chrome (*Cr*) ($\mu g\ l^{-1}$)	100	9	161.96	50	157	336	248±58	165	305	222±48	193	298	235 ± 32	5	9	0.758 (0.478)
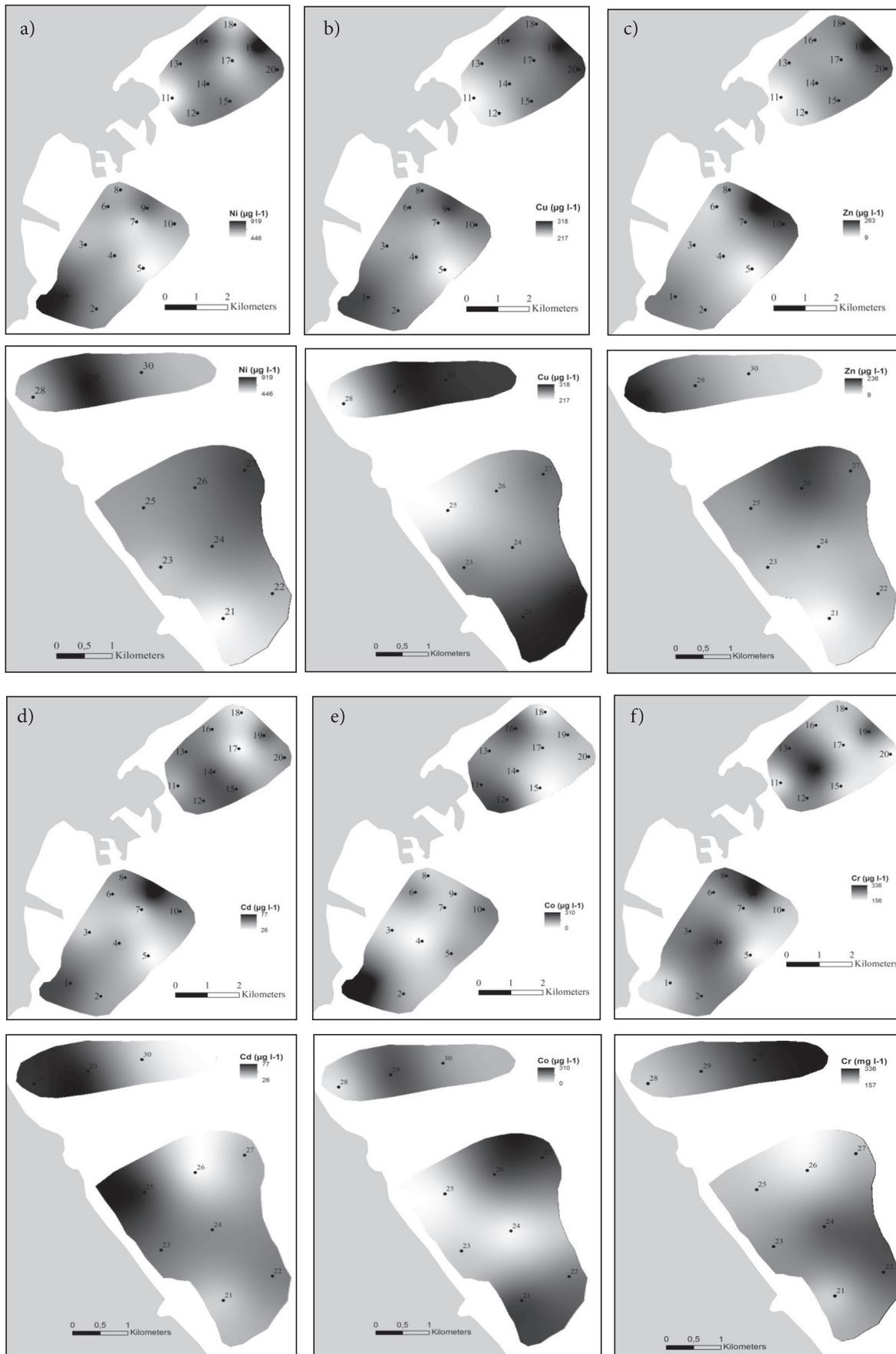
Fig. 2. Spatial variation Iron of trace metals, i.e., nickel (Ni) a), copper (Cu) b), zinc (Zn) c), cadmium (Cd) d), cobalt (Co) e), chrome (Cr) f), lead (Pb) g), manganese (Mn) h), and iron (Fe) i) at stations sampled in the northern and southern coastal areas of Sfax and the Ghannouch area during autumn (October-November 2014).
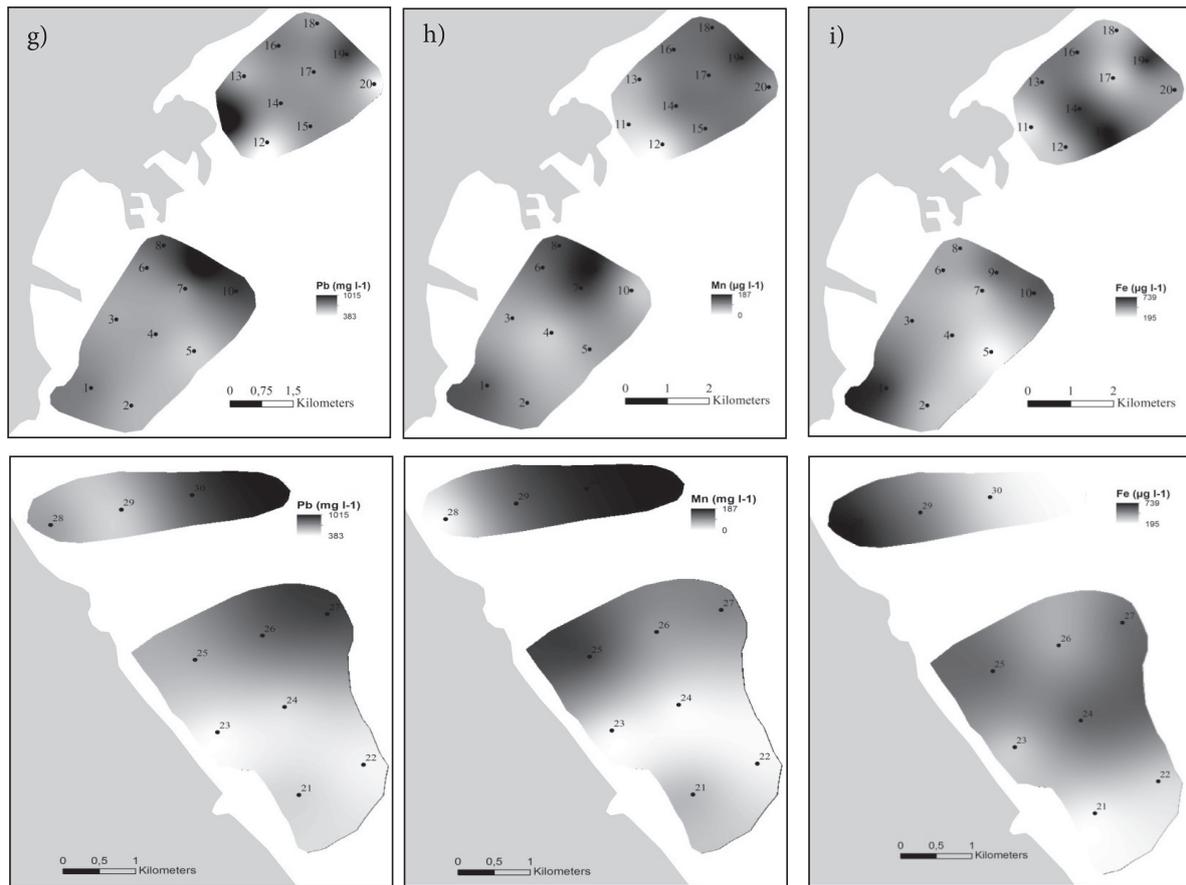
Fig. 2. Continued.

and shipping activity in coastal marine ecosystems have a negative impact on water quality, because heavy metals from water can be poisonous to organisms and can lead to a decrease in the productivity in marine fisheries, marine culture, and biodiversity [54]. This was the case of SC, in which the high rate of dissolved heavy metals in water could also accumulate in sediments and fish [55].

The only study concerning the heavy metal levels in Gulf of Gabes seawater was conducted in SC [56]. They showed that heavy metal concentrations decreased in the order Fe>Ni>Zn>Cu>Pb>Cd. Compared to our results, the highest contents of the different metals analyzed in this study were relatively lower Cd (0.21 µg l^{-1}), Cu (4.34 µg l^{-1}), Fe (30.74 µg l^{-1}), Ni (10.21 µg l^{-1}), Pb (3.43 µg l^{-1}), and Zn (5.78 µg l^{-1}) [56]. These differences of concentrations were due to the fact that seawater samples were collected in front of the different sources of pollution. The mean concentrations of metals in surface waters in this study were lower than for other Mediterranean polluted areas as reported by Abdallah (2008) [57] from El-Mex Bay along the Alexandria coast (Egypt, Mediterranean Sea). The dissolved trace metals analyzed followed the order Zn>Pb>Co>Cu>Cr>Cd. They reached 33.6± 12.7 mg l^{-1} for Zn, 14.19±7.5 mg l^{-1} for Pb, 14.15± 5.5 for Co mg l^{-1}, 4.29±0.46 for Cu mg l^{-1}, 47.58±14.3 mg l^{-1} for Fe, 3.68±1.7 mg l^{-1} for Cr, and 3.1 ±2.1 for Cd mg l^{-1}.

In other Mediterranean regions such as Lake Manzala, Egypt, the mean concentration of the measured metals in water was found to be in the order: Zn (0.311 mg l^{-1}) > Cu (0.055 mg l^{-1}) > Pb (0.022 mg l^{-1}) > Cd (0.020 mg l^{-1}) [14], which are lower than the concentrations in the present study. In other Tunisian regions such as the lagoon of Boughrara, heavy metals were measured in the following order: Cu>Al>Pb>Cd>Cr>Hg, with concentrations of 7,080±400, 368±690, 173±230, 260±230, 180±20, and 110±650 µg l^{-1} as measured in 2008 [58]. These results obtained from Boughrara Lagoon showed that some trace elements (i.e., Cu and Cd) were relatively higher than in the SC, which represented 273±28 and 46±10 µg l^{-1}, respectively. However, Cr (234±46 µg l^{-1}) and Pb (623±179 µg l^{-1}) were most important in our study than in Boughrara Lagoon. The elevated concentration of trace metals such as Cr and Pb is explained by industrial waste, sewage, and mainly harbor pollution [58]. The various heavy metals in seawater are sited in other marine regions, which become toxic if present in excessive quantities and pose a potential threat to the ecosystem [58].

The level of metal pollution in water samples was assessed through the metal pollution index. The estimated pollution evaluation indices for the assessed metals exhibited a variation among the three studied Gulf of Gabes areas as per the dissolved metal load in the marine water. GA (9.31) showed higher MPI values than NC (8.89) and SC (8.05), implying relatively high
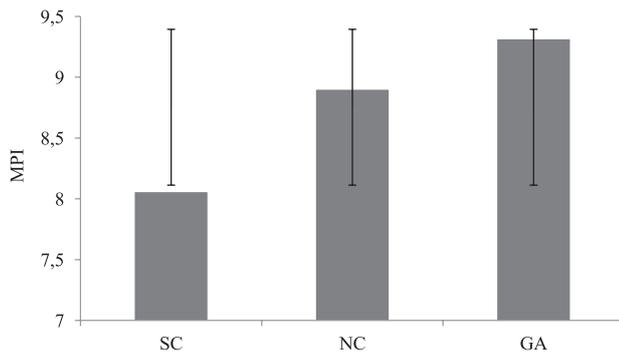
Fig. 3. Bar chart showing Metal Pollution Index (MPI) values in the three studied areas at stations sampled in the northern and southern coastal areas of Sfax and the Ghannouch area during autumn (October-November 2014).

concentrations of metals during this period. It is inferred from the indices calculated for the entire study period that MPI>6.0 represents seriously affected stations (Class VI) (Fig. 3). The MPI showed that Sfax and Ghannouch coastal areas were seriously affected (MPI of > 6.0, Class VI) by the trace metal pollutants [11, 49].

Origin of Trace Element Loading in Surface Waters in Three Gulf of Gabes Coastal Areas

During the last decade, the coastal environment of the Gulf of Gabes experienced intense development in industry, urbanization, and aquaculture. Several metals are known to be discharged frequently through industrial and domestic effluents along the coast. The present study was carried out to determine heavy metal distribution in coastal waters. The sampling of coastal water was carried out during October and November 2014. The enrichment in the concentration of heavy metals in the samples taken close to the coastal areas, indicating that higher concentra-
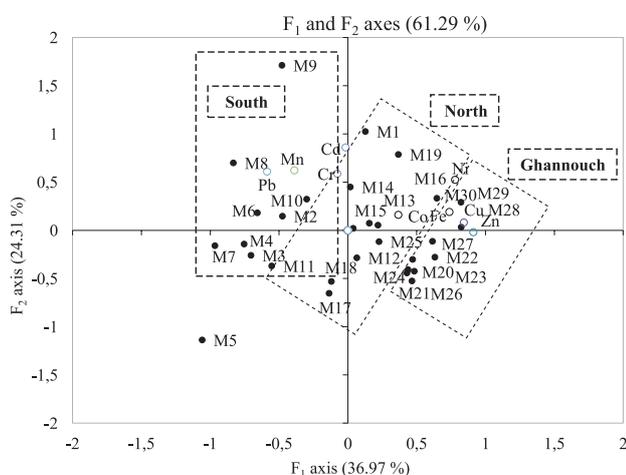

Fig. 4. Canonical correspondence analysis (CCA) (Axis I and II) on mean values of several trace metals in stations sampled in the northern and southern coastal areas of Sfax and the Ghannouch area sampled during autumn (October-November 2014).

tions were due to the anthropogenic activities in the coastal area. The canonical correspondence analysis (CCA) on the studied trace metals explained 61.29% for the F_1 and F_2 axes (Fig. 4). The F_1 axis (36.97%) selected negatively SC stations (2-10) with Pb, Mn, Cd, and Cr, which were high in station 9 situated close to the fishing harbor of SC. The F_1 axis selected positively GA stations (21-30) with Zn. The high concentration was recorded in station 28, which was near the commercial harbor. NC stations (11-20) with station 1 belonging to SC did not show a regular pattern. Some stations were selected positively and others negatively with a high concentration of Ni, Co, and Fe (Fig. 4). The CCA analysis confirms our results that the phosphoric acid and fertilizer plant, the WWTP, and the Hakmouni wadi (located in front of station 1) are responsible for loading the seawater with chemically polluted compounds – notably Ni and Co. Meanwhile, the fishing harbor of Sfax is the second source of trace metal pollution in SC (primarily Cd, Mn, Cr, and Pb) (located in front of station 9). Station 28 was near the commercial harbor and belonged to GA with a high concentration of Zn. The Gabes region in southeastern Tunisia, is a polluted area where such a situation is expected to contribute to the transfer of heavy metals from the marine to the bordering terrestrial ecosystems [59]. This area is nowadays considered as a pollution hotspot mainly due to the operation of the Gabes-Ghannouch factory complex of phosphate treatment for acid and fertilizer production since the early 1970s [60]. With the absence of scavenging processes and treatment plants for industrial wastes, persistent toxic elements and heavy metals find their way into the sea. Alarmingly, 10,000 to 12,000 tons of phosphogypsum, containing heavy metals (mainly Cd, Pb, Zn, Cu, and Cr), are released in the sea of GA per day [59-61]. Previous studies have shown high levels of heavy metals in the coastal sediments close to the industrial complexes [61-62]. Particularly high concentrations were recorded in the site where the effluents are released: Cd>100 µg l^{-1}, Pb 10-12 µg l^{-1}, Zn>1,000 µg l^{-1}, Cu 50-60 µg l^{-1}, and Cr 100-120 µg l^{-1} [59, 61].

The most important Ni and Co concentrations were observed in station 1, situated close to the phosphoric acid and fertilizer plant. Indeed, the phosphogypsum stock enriches the seawater with dehydrated calcium sulfate and heavy metals like cadmium, zinc, chromium, copper, cobalt, nickel, and lead [41, 55]. Phosphate industry in the city of Sfax (production of crude phosphate, phosphoric acid, and fertilizer), urban agglomerations, and industrial zone [63] can release high amounts of heavy elements such as Ni and Co.

The second source of trace metal pollution is the fishing harbor in the SC (primarily Cd, Mn, Cr, and Pb). The spatial distribution of Cr, Cd, Ni, Zn, Cu, and Pb concentrations in surface sediments from the coastal zone permit the identification of a highly contaminated zone in the vicinity of Sfax harbor [53]. These factors, combined with very shallow water, do not allow sufficient mixing with ''clean'' sediment to dilute terrigenous polluted loads. All analyzed metals (except for Fe and Mn) can be

considered as moderate to extreme pollutants, especially along the Sfax coast [53]. In general, the present study showed that metal pollution has decreased in most of the studied sites along the Tunisian coast, although in Bizerta Channel, the fishing harbor of Gabes, and at Menzel Jemil, some contamination was still evident in 2011 [63]. In the southern region of the Gulf of Gabes, Cd concentrations were highest among the studied sites. In this area, the major factor behind this metallic pollution by heavy metals is phosphogypsum wastes, as shown in several previous works [61, 64-67]. Indeed, high amounts of phosphogypsum are discharged by the phosphate industry in the Gulf of Gabes, quantified at 11,250 tons per day and stretching along large surfaces in the open sea with deleterious effects on biota [60, 64-65, 68]. These discharges contain various metals, including Cd (39.8 mg kg^{-1}), Zn (315 mg kg^{-1}), Cu (5.9 mg kg^{-1}), Ni (15.4 mg kg^{-1}), Fe (58.4 mg kg^{-1}), and others like Hg, Mo, Co, and F [69]. According to Kharroubi et al. (2012) [66], the amounts of metals found in the flux of the principal effluents from the industrial pole of Gabes are estimated at 300 kg day^{1} for Cd, 200 for Cu, 3,500 for Zn, 50 for Pb, 250 for Mn, and 9,330 for Fe.

Industrial pollution in Tunisian waters is partly caused by the major industries and first of all by the natural phosphates processing industry. The chemical complex of Sfax and Gabes is thus responsible for pollution with massive ocean dumping of millions of tons of highly acidic phosphogypsum waste water, and heavy metals (e.g., cadmium). However, highly polluting tanneries located near the coast are responsible for organic matter, sulphides, and Cr as the main trace element load and paper industry (mercury) [70]. In comparison, the concentration of Fe (22,000 µg l^{-1}), Zn (21,100 µg l^{-1}), Cd (370 µg l^{-1}), and Pb (210 µg l^{-1}) in the waste water from SIAPE [70] were lower than those detected in our sampling area, except for Pb (383-1,015 µg l^{-1}). This showed that Pb did not only emanate from the SIAPE facility but also from other sources of pollution.

Based on this research, land-based activities, sewage disposal from vessels, and residential areas close to harbors are the main sources of metal pollution in the Gulf of Gabes. The high level of Pb in the fishing harbor of the SC could be attributed to the spill of leaded petrol from fishing boats and dust, which holds a huge amount of lead from the combustion of petrol [71-72]. The same source of metal pollution was found in the fishing harbor of the Gulf of Chabahar [72] and along the Jeddah Red Sea Coast [71]. Indeed, Pb is used in a number of industrial applications and has been used as an anti-knocking additive in gasoline and is deposited following combustion [73]. In terms of anthropogenic activities, SC harbors 600 fishing boats (i.e., trawlers, sardine boats, tuna boats, and small artisanal boats) [63]. Furthermore, our results showed that the high concentration in Zn was revealed in GA in station 28 close to commercial harbor. Zn contamination could be related to phosphogypsum residues generated by the phosphate industry. Indeed, high Zn concentrations in sediments were reported in the outer fishing harbor of

Gabes, with values reaching 1,200 µg g^{-1} dw in July 2010 [61, 63] and 7,165 µg g^{-1} dw during September 2013 in Chatt Essalem, close to the fishing harbor [63, 67]. The major sources of Zn are domestic and municipal wastes, followed by dumping and atmospheric deposition [74-76]. These trace elements were measured in the lixiviate water near the phosphogypsum dump site by Zairi and Rouis (1999) [77], and revealed the following important concentrations, i.e., 35.6 mg l^{-1} for Zn, 0.53 mg l^{-1} for Hg, and 2.03 mg l^{-1} for Ni.

The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgical operations involving zinc and the use of commercial products containing zinc [78]. Domestic waste, shipyard, automotive, and industrial effluent are the sources of Zn to the aquatic environment. Besides, household wastes, including powder and liquid laundry detergents, shampoos, toilet tissue and other cleaning products, may also contribute to the zinc load in the aquatic environment [79]. Nickel is a naturally occurring element widely used in many industrial applications for the shipbuilding, automobile, electrical, oil, food, and chemical industries [80]. The major sources of Ni in the ocean are domestic wastewater effluents (boating activities) and metal smelters, which later accumulate in the biota – particularly in the phytoplankton or other aquatic plants [81]. Pb can be introduced into the aquatic environment through soil erosion, as atmospheric dust, by oil combustion, domestic and industrial landfills, and precipitation [82]. Lead is ubiquitous in the aquatic ecosystem and it is bioaccumulative. It is present as an inorganic or organic element [83]. The toxicity of lead depends on fish age, pH, and water hardness [84]. Many toxic heavy metals such as Hg, Ni, and Pb influence water quality due to their chromic toxicity and persistence, and the potential to be bioaccumulated in many aquatic organisms such as shrimp, fish, crab, shellfish, mollusks, and cephalopoda [58, 85-90]. This result confirms our findings that the most important concentration of heavy metals was recorded in stations 1 and 2, which were situated in front of the fishing harbor (transect 1). The occurrence frequency of these two stations is characterized by maximum values of the different analyzed heavy metals (about 80%). These stations were also sampled in 2011, showing that Zn, Pb, and Ni were the most common metals, representing 21.79±2.96, 2.39±0.92, and 2.25±0.82 mg l^{-1}, respectively [91]. It seemed that the pollution level in SC has risen between 2011 and 2013 by the increasing heavy metals pollution discharge into seawater. During the present study, the measurement of these metals in stations 1 and 2 revealed 137.68-98.04 mg l^{-1} for Zn, 3.774-0.951 mg l^{-1} for Pb, and 18.549-1.739 mg l^{-1} for Ni. We infer that the fishing activities in the SC seawater contributed to high organic loads of pollution characterized by important heavy metal contents exceeding the permissible limit [50-51]. The increase of the heavy metal contents also involves Cd, which showed in this study the lowest mean value concentration (5.1±5.5 µg l^{-1}) compared to previous

works carried out in 2005 (0.61±0.02 μg l^{-1}) [92]. These waste waters are discharged into the sea and the pollution greatly affects the ecological balance of this zone, plus the yields of fish and seafood toward biological accumulation [93]. Moreover, Fe is usually present in extremely low concentrations in oceanic surface waters and is one of the elements that limit phytoplankton growth [94].

Conclusions

The study of heavy metal distribution in coastal waters is an important component in understanding the distribution levels as well as assessing the cause of anthropogenic influences on the marine ecosystem. Results show that the commercial harbor of GA, the SIAPE manufactory in Sfax (production of phosphate, phosphoric acid, and fertilizer), and the fishing harbor of the SC were contaminated, respectively, by high amounts of Zn, Ni-Co, and Cd, and Mn, Cr, and Pb were the main sources of heavy metals pollution in the Gulf of Gabes. The results revealed that the fishing port is subject to allochthonous pollution input, which exerts a strong influence on the concentration of heavy metals in the seawater of the SC. The heavy metal levels recorded in this study, which exceeded the permissible limits (Zn, Ni, Pb, Co, Cr, Cd, and Cu; except the Fe and Mn elements), altered the marine structure and functioning of this polluted ecosystem. This situation leads to serious human health risks caused by their potential bioaccumulation in some seafood in the SC. For this reason, this study proves the need for effective treatment and management measures for industrial effluents and other anthropogenic discharges into the SC waters so as to reduce the impact of heavy metal pollution.

Some heavy metals such as Zn, Ni, Pb, Co, Cr, Cd, and Cu analyzed in the present study are required as a chemical marker under a future project of monitoring programs, management, and restoration in SC for reliable estimates of water quality. The use of these biomarkers is recognized as an important approach for the assessment of pollution, as chemical analysis of environmental samples alone provide evidence of impacts of contaminants in the studied biota. Moreover, additional anthropogenic inputs of heavy metals in the Gulf of Gabes might be critical not only to vulnerable and fragile ecosystems, but also to human health.

Acknowledgements

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