

# Assessment of contaminated sediment by phosphate fertilizer industrial waste using pollution indices and statistical techniques in the Gulf of Gabes (Tunisia)

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**Abstract** On July 2010, 26 surface sediments of the Gulf of Gabes, Tunisia were sampled at depth ranging from 0.5 to 10 m. These specimens were analyzed to determine Al, Cd, Cr, Cu, Pb, Zn, F, P, and N concentrations and total organic carbon contents. The distribution map shows that the high amounts of pollutants are principally located between the commercial harbor and the fishing harbor of Gabes. Measurements of heavy metal contents were carried out using (absorption atomic spectrometer), where the enrichment factor (EF), the geoaccumulation index ( $I_{geo}$ ), and the contamination index (CI) are determined. The EF values of all metals were  $>1.5$ , corroborate anthropogenic impact on the metal levels in this studied area. However, the  $I_{geo}$  and CI values of Cd and Zn elements indicated that sediments collected from sites at the vicinity of the commercial harbor are very contaminated, although for Pb, Cr, and Cu elements these indices indicated that the same sediments are uncontaminated. Statistical analyses (principal component analysis/factor analysis and matrix correlation) show that heavy metals, fluoride, and phosphorus are resulting from the same anthropogenic source.

**Keywords** Heavy metals · Fluoride · Phosphorus · Marine pollution · Gulf of Gabes (Tunisia)

## Introduction

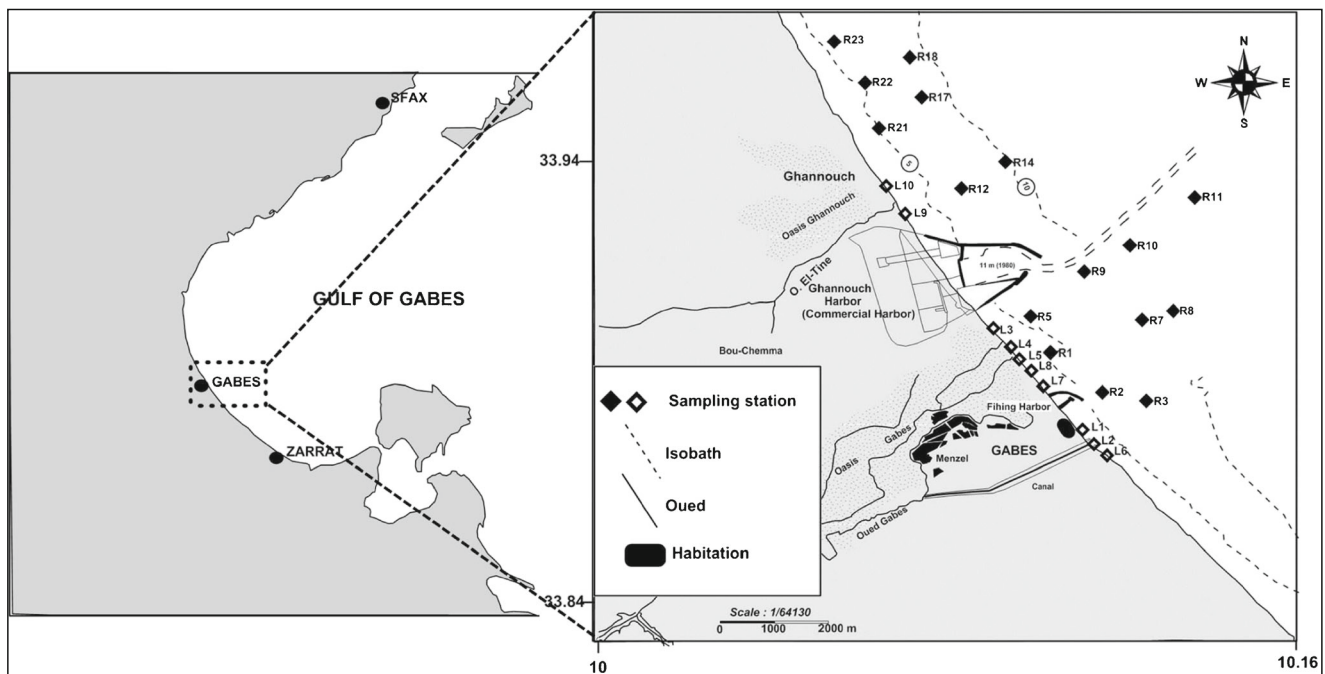
The Gulf of Gabes is located in the eastern coast of Tunisia. This zone extends from the tip of Rass Kaboudia to Tunisian–Libyan borders (about 200 km). The climate of this region is characterized by temperate, humid, and hot Mediterranean air coming from the east part, beside the subtropical, dry, and hot with Saharan dust coming from the south-west part (Essersi et al. 2010). In addition, this studied area is commonly distinguished by low sandy coasts and shallow depth with a gentle slope and by the presence of three main kinds of ocean currents such as coastal currents of low amplitude, tidal currents, and surface currents, which are determined by wind patterns (Bel Hassen et al. 2009; Hattour et al. 2010). The tide in this region is semi-diurnal; the tidal range is greatest in the southern Gulf and decreases at the edges and its amplitude is the highest in the Mediterranean Sea, which get to 1.7 m (Sammari et al. 2006).

The Gulf of Gabes is recognized by a high marine productivity. According to Bradai et al. (1995), this area is considered as one of the most important zone for fishing in Tunisia. But, since 1972, this Gulf is usually influenced by industrial wastes. Especially, those of the “Chemical Group Ghannouch-Gabes” located near the commercial port at 3 km north of the Gabes city. The major type of products is the manufacture of phosphoric acid and phosphate fertilizers. The industrial unit deposits their waste in the environment: anhydrite and anhydrite sulfuric are released into the atmosphere, water from production unit of sulfuric acid, wash water coming from production unit of phosphoric acid, and fertilizers and phosphogypsum from the production unit of phosphoric acid (Béjaoui et al. 2004). These effluents are acidic and contain high amounts of fluoride and phosphate, in addition to variable contents of heavy metals as cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), and lead (Pb) (Gouidera et al. 2009; Garrett et al. 2011).

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**Fig. 1** Location map of the Gulf of Gabes and studied area

Phosphorus and fluoride are essential nutrient in marine ecosystem but the enrichment by both elements may cause diverse problems on biota and human health (Paytan and Mclaughlin 2007; Ramachandran et al. 2012; Fekri and Kasmaei 2013). Heavy metals are considered as environmental pollutants, because of their toxicity, persistence, no biodegradable properties, and accumulative behaviors (Pekey 2006; Yu et al. 2008; Attia et al. 2012), which are transported and stored in marine sediments (Pekey 2006; Parizanganeh et al. 2007; Yu et al. 2008; Erdoğan 2009; Ben Garali et al. 2010; Varol 2011). So the evaluation of pollutants distribution in surface sediment is useful to determination of the degree of pollution in marine environment (Buccolieri et al. 2006).

The aim of this present work is (1) to evaluate the level of pollution in the sediment sample from the coast line Ghannouch-Gabes, most polluted part of the Gulf of Gabes, Tunisia; (2) to discover the degree of heavy metal pollution using contamination indices; (3) to determine relationship among heavy metals, fluoride, and phosphorus; and (4) to define their origin using multivariate statistical techniques.

## Materials and methods

### Samples and sampling

Sediment samples were collected on July 2010 from 26 sites from two zones. Ten samples from the coastal shelf of the study area (zone I indicated zone L), which the depth did not

**Table 1** General features of the sediment samples

Station	pH water	Salinity (g/l)	pH sediment
Reference point	8	37	7
L1	7	38	9.35
L2	7	37.9	9.34
L3	5	36.9	6.25
L4	5	37.3	6.88
L5	6	36.8	7.65
L6	7	36.2	9.3
L7	6	33.9	8.45
L8	5	36.8	8.32
L9	7.5	37.8	9.17
L10	8	37.2	9.1
R1	8.07	38.2	7.73
R2	8.06	37.9	8.51
R3	8.18	38	7.84
R5	8.16	38	6.9
R7	8.2	37.8	8.05
R8	8.22	38	8.29
R9	8.14	37.9	7.5
R10	8.17	37.8	7.9
R11	8.22	37.8	8.13
R12	8.06	40.8	7.78
R14	7.92	40.9	8.61
R17	8.15	40.7	8.06
R18	8.19	40.7	8.35
R21	8.09	40.9	8.15
R22	8.06	40.9	8.15
R23	8.16	40.8	8.12

exceed 0.5 m. Those sites are divided into three parts; the first part (P1) located between the Chemical Group of Ghannouch (33°55'12, 48" N; 10°05'49, 08" E) and the fishing harbor of Gabes (33°53'38, 83" N; 10°00'7'04, 80" E), the second part (P2) situated north of the chemical group, and the third part (P3) is to the south of the fishing harbor. However, 16 stations were sampled from the zone II located around the commercial port of Ghannouch and the fishing harbor of Gabes, using a Peterson grab sampler (denomated R). The depth of stations "R" is ranged between 5 and 12 m (Fig. 1). In this region, magnoliophyte recovery is very low (Zaouali 1993) and foreshore is described as wide up to 1,000 m where the sediment is very muddy (Amorri et al. 2011). Only the top 2 cm of the surface sediment were taken, sealed in clean polyethylene bags, and stored at 4 °C until analyses in laboratory.

### Chemical analysis

Measurements in situ of pH sediments, salinity, and pH of marine water were determined using a glass electrode WTW pH 720. But, sampled sediments were dried at 60 °C in an

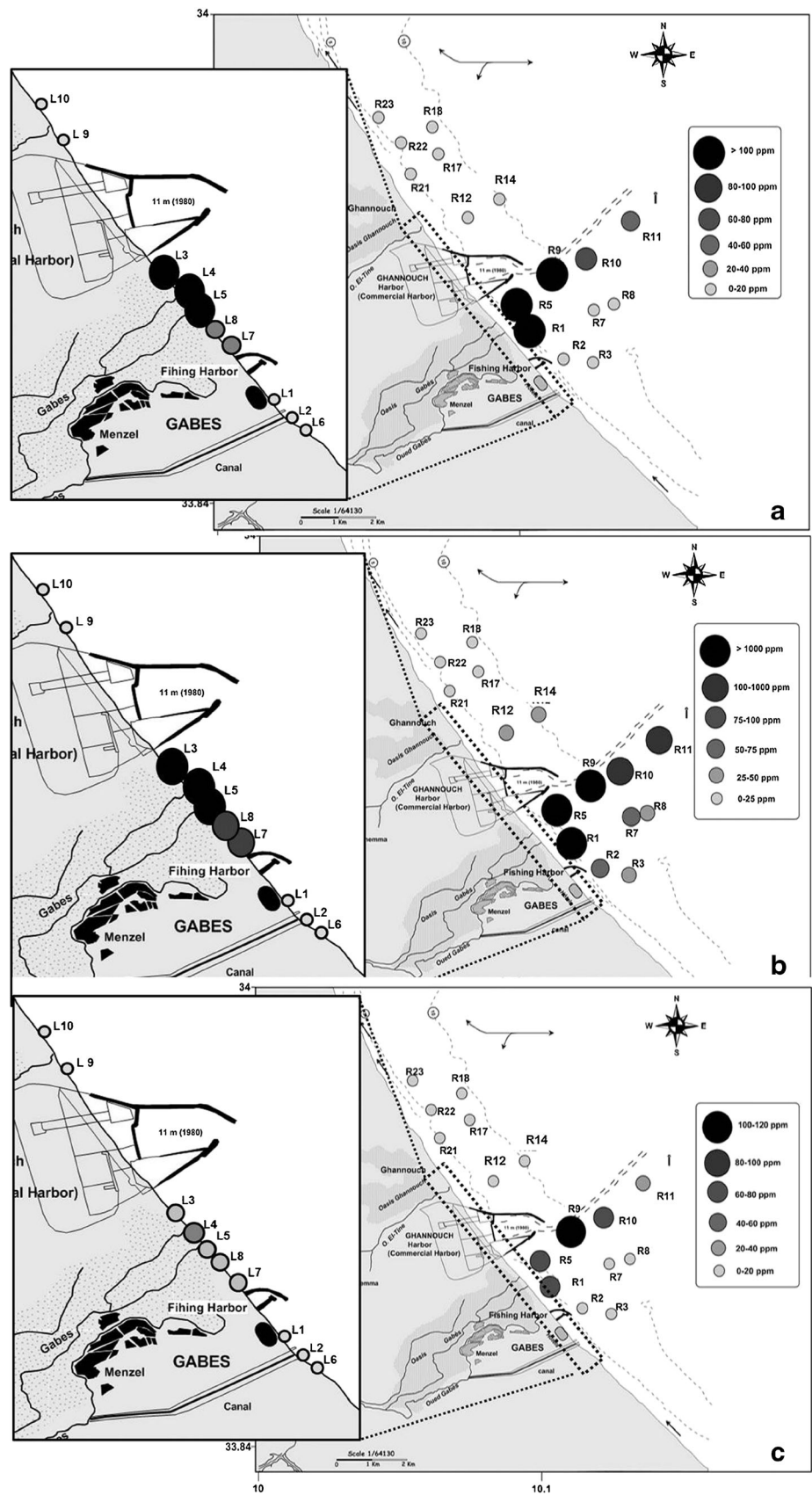
oven and pass through a 63- $\mu$ m sieve in laboratory. For heavy metal and phosphorus contents determinations: 1 g of each sample was digested with HNO<sub>3</sub> (65 %): HCl (37 %). Pb, Zn, Cd, Cu, Cr, and Al concentrations were measured using an absorption atomic spectrometer (Thermo Scientific, ICE 3000 series) and the detection limits (mg/l) were 0.005 for Cd, 0.05 for Cr, 0.022 for Cu, 0.05 for Pb, 0.008 for Zn, and 0.013 for Al. However, phosphorus content was carried out using by spectrometer (Hitachi U-2000), with a wavelength of 880 nm following the NFT90.023.

The total organic carbon (TOC) content in sediment was determined by measurements of the amount of dichromate which did not interact with the sample using titration process (Centre d'Expertise en Analyse Environnementale du Québec CEAEQ 2006). For the fluoride determination: (0.5–1)g of sediment sample was dissolved in 3 ml of 6 M HCl and diluted to 100 ml with deionized water and an aliquot of the extract was used for the determination of fluoride by the specific ion electrode method (Abu Hilal 1985). The content of total nitrogen was determined by mineralization of sediment sample by sulfuric acid, followed by a titration with HCl 0.01 M (NFT90.110).

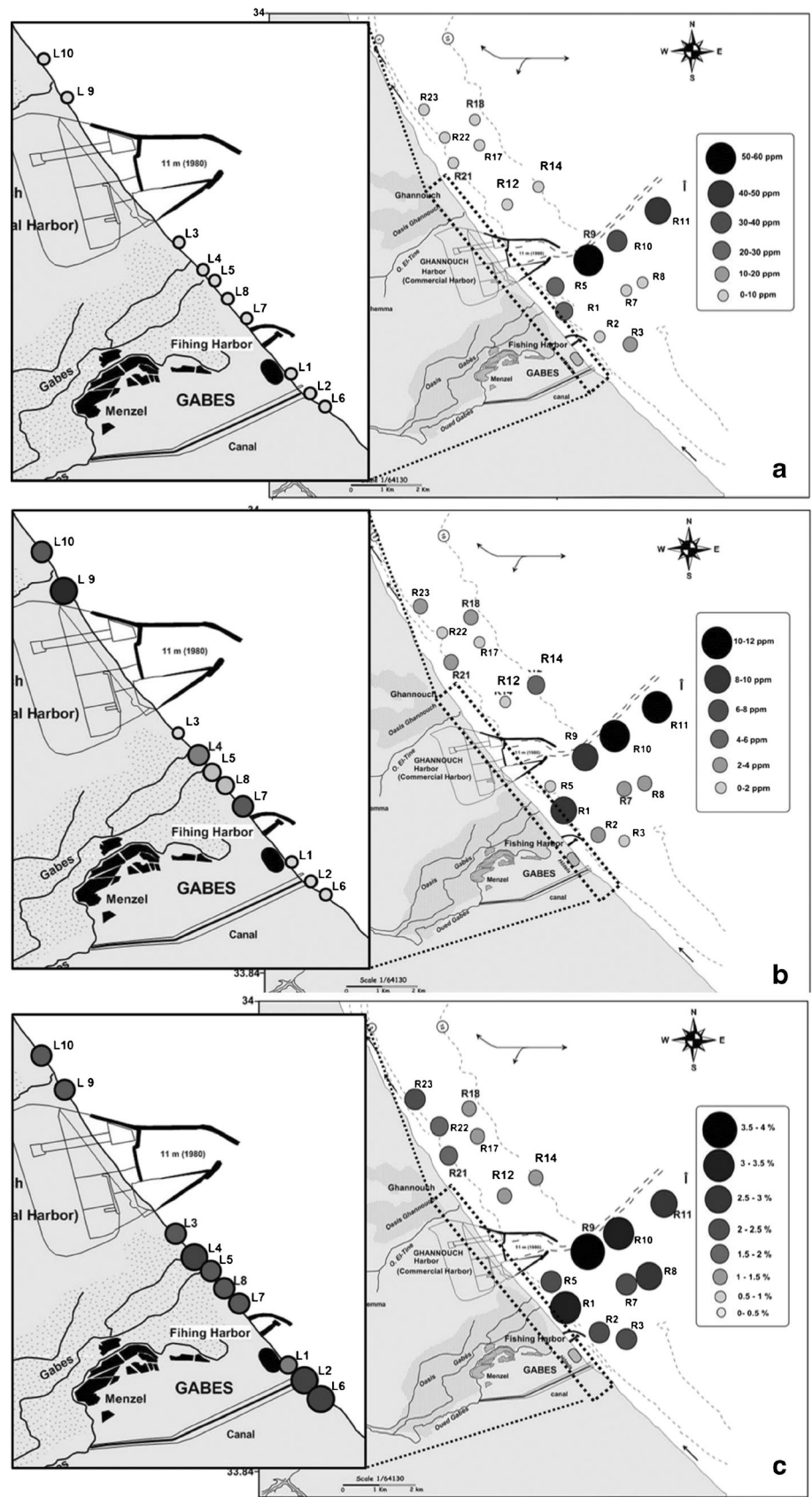
**Table 2** Pollutants concentration in surface sediment of the study area

Stations	Pb (ppm)	Zn (ppm)	Cr (ppm)	Cu (ppm)	Cd (ppm)	F (%)	P (ppm)	N (%)	TOC (%)	pH sediment
L1	ND	8.5	3	2	ND	0.02	229.5	0.0491	1.95	9.35
L2	ND	6.75	3.5	2	ND	0.023	173.4	0.0315	2.05	9.34
L3	2	10,175	35.25	6.75	1,225	5	1,495	0.0589	2.3	6.25
L4	4.75	5,725	45	6.5	825	4	1,418.75	0.03	2.7	6.88
L5	2.25	3,675	30.5	8	550	2.6	2,010	0.0556	2.25	7.65
L6	ND	7.5	4	1.5	ND	0.045	2.025	0.036	2.25	9.3
L7	6.5	375	37.75	6.75	54	3	1,562.5	0.036	2.4	8.45
L8	3.5	365	31.5	7.5	56	2.9	3,450	0.0294	2.35	8.32
L9	9.5	14	4.75	7	ND	0.2	83.25	0.0245	2.35	9.17
L10	7	10	3.75	3.5	ND	0.112	2.25	0.0315	2.3	9.1
R1	8	4,925	70	28.75	700	7.2	12,575	0.1225	3.5	7.73
R2	3.25	50	17.75	5.5	3.5	0.5	2,562.5	0.063	2.3	8.51
R3	2	34.5	13.75	10.25	2	0.3	2,922.5	0.0875	2.2	7.84
R5	ND	5,075	65	20.5	725	6.5	12,725	0.14	2	6.9
R7	3.5	50	15	4.5	3.5	0.23	6,345	0.091	2.5	8.05
R8	2.25	30	12.5	4	2	0.16	616.75	0.0805	2.85	8.29
R9	10	1,200	120	58.75	167.5	6.8	25,100	0.273	4	7.5
R10	10.25	625	75	39	60	3	5,625	0.273	3	7.9
R11	11	475	37.5	41.5	45	2.6	5,650	0.248	2.6	8.13
R12	4.75	45	10.75	5.75	4	0.232	860	0.063	1.5	7.78
R14	1.25	31.25	8.25	5.25	2.75	0.152	976.25	0.0595	1.5	8.61
R17	ND	9	5	3.75	ND	0.11	300	0.042	1.5	8.06
R18	2.5	7.75	4.5	3.75	ND	0.12	240	0.0525	1.5	8.35
R21	2.5	21.25	6	5.75	1.25	0.144	660.5	0.091	2	8.15
R22	2	11.5	4.25	3.25	0.5	0.096	415	0.091	1.65	8.15
R23	3	17.5	5.75	4	1.25	0.112	448.25	0.091	2.15	8.12

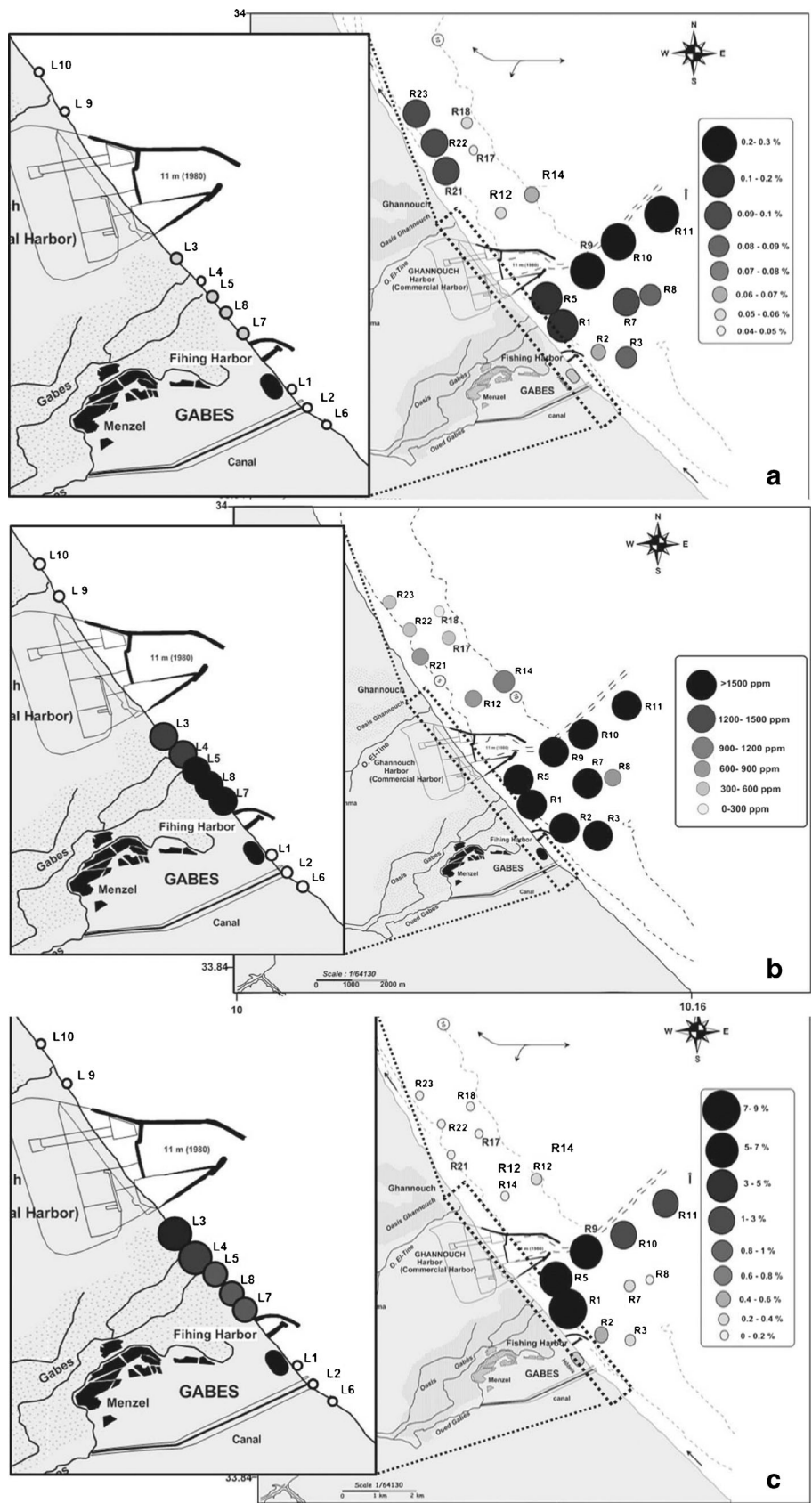
**Fig. 2** Concentrations of **a** Cd, **b** Zn, and **c** Cr in superficial sediment of study area



**Fig. 3** Concentrations of **a** Cu, **b** Pb, and **c** TOC concentrations superficial sediment of study area



**Fig. 4** Concentrations of **a** N, **b** P, and **c** F concentrations superficial sediment of study area



**Table 3** Pollutants concentration in surface sediment of the reference point

Site	Cr (ppm)	Cu (ppm)	Cd (ppm)	Zn (ppm)	Pb (ppm)	P (ppm)	F (%)	N (%)	TOC (%)
Reference point (Zarrat)	2.45	3.25	ND	4.125	ND	52.375	0.02	0.01	0.672

**Assessment index**

According to Gabelle (2006), the discussion and the interpretation of the raw values of heavy metals and the contamination are in fact not easy. Thus, in order to establish further accuracy for the contamination of the sediment, three factors are used to evaluate the degree of heavy metal contamination sediments of the Gulf of Gabes.

**Enrichment factor**

Enrichment factor (EF) presents state of natural or anthropogenic enrichments of sediment by heavy metals, which is calculated as follows (Choi et al. 2008; Garcia et al. 2008):

$$EF = \frac{\frac{[X]}{[Al]_{sediment}}}{\frac{[X]}{[Al]_{Earth's crust}}} \quad (1)$$

Where,  $X/Al$  is the ratio of the concentration of element  $X$  to  $Al$  in both contaminated and uncontaminated sediment. The EF value of 1 indicates predominant natural origin of the element in the sediment. The EF above 1.5 indicates enrichment of natural processes (e.g., biota contribution) or anthropogenic influences.

**Geoaccumulation index**

According to Muller (1979), the geoaccumulation index ( $I_{geo}$ ) highlights the assessment of sediment pollution by heavy

metals. This index is a comparison between currents levels and geochemical background and can be calculated by the following equation presented by Ahdy and Khaled (2009), Chakravarty and Patgiri (2009), Varol (2011), and Emam and Saad-Eldin 2013:

$$I_{geo} = \log_2 \left( \frac{[C_n]}{1.5[B_n]} \right) \quad (2)$$

Where  $C_n$  is the measured concentration of the metal ( $n$ ) in the sediment and  $B_n$  is the geochemical background concentration of metal ( $n$ ).

**Contamination index**

The contamination index (CI) is the ratio obtained by dividing the concentration of each metal in the sediment by background value (concentration in uncontaminated sediment) (Gabelle 2006)

$$CI = \frac{[C]^{heavy\ metals}}{[C]^{background}} \quad (3)$$

To this index is associated a scale of contamination, which will allow determining the state of contamination of the sediment:  $CI < 3$ : slightly contaminated site;  $3 < CI < 9$ : moderately contaminated site;  $CI > 9$ : highly to very highly contaminated site.

**Statistical analysis**

The obtained data of chemical analysis of the Gulf of Gabes surface sediments was performed using principal component

**Table 4** Heavy metal concentrations in sediment samples from the Gulf of Gabes and other selected areas from the literature

Locations	Metals concentrations (mg/kg)					References
	Cd	Cr	Cu	Pb	Zn	
Gulf of Gabes	ND–1225	3–120	1.5–58.75	ND–10.25	6.75–10,175	Present study
Frensh Harbor Level 1*	1.2	90	45	100	276	Frensh Decree of 14 June 2000
Frensh Harbor Level 2**	2.4	180	90	200	552	
Coast of Sfâx (1)	0–5.88	1.25–18.39	1.09–5.77	1.38–19.51	3.80–26.02	Aloulou et al. 2011
Coast of Sfâx (2)	5.5–7	41–82	13–29	18–88	39–117	Gargouri et al. 2011
West Egyptian coast	0.52–0.92	16.24–34.16	26.52–33.33	20.67–35.62	26.26–112.07	Ahdy and Khaled 2009
Izmir Bay		404–1,563	66–150	82–203	23–1,031	Guven and Akinci 2008
Quanzhou Bay	0.28–0.89	51.1–121.7	24.8–119.7	34.3–100.9	105.5–241.9	Yu et al. 2008

\*[M] < level 1: normal concentration, the potential impact of sediment is negligible; level 1 < [M] < level 2: alert level, the potential impact of sediment is to consider; \*\*[M] > level 2: pollution level, the potential impact of sediment is high

analysis/factor analysis (PCA/FA) technique. This statistical analysis was applied to experimental data standardized through  $z$ -scale transformation to avoid misclassification due to wide differences in data dimensionality. The Kaiser–Meyer–Olkin (KMO) Bartlett's sphericity tests were performed to examine the suitability of the data for PCA/FA. KMO is a measure of sampling adequacy that indicates the proportion of variance that is common, i.e., variance that may be caused by underlying factors (Varol 2011). A high value (close to 1) generally indicates that principal component/factor analysis was useful for the present study where KMO = 0.65. Relationships among the considered variables were tested using Spearman correlation with statistical significance set at  $p < 0.05$ . PCA/FA analyses were performed using SPSS® for Windows Release 16.

Correspondence analysis (CA) was performed also on registered data, which studying the association between two or more qualitative variables. This analysis is based on a raw data matrix of counts, classified by  $n$  rows (objects) and  $p$  columns (variables). The CA analyses were performed using XLSTAT 2013 for Windows.

## Results and discussions

Salinity, pH of the water, and the pH of sediment were given in Table 1. The salinity ranged between 33.9 and 40.9 g/l. In the zone I, the pH of water values are lower than those of zone II, but salinity showed a significant decrease, especially L3, L4, L5, L7, and L8 studied stations. The variation of salinity and pH may be related to industrial releases of the chemical compounds. These discharges are characterized by an acidic pH (between 2.75 and 6.25) and a salinity of up to 22 g/l (Darmoul et al. 1980). The concentration of metals in the sediments showed significant differences among the sampled locations. Ranges of heavy metals in sediments are 0–11 ppm for Pb, 6.75–10,175 ppm for Zn, 3–120 ppm for Cr, 1.5–58 ppm for Cu, 0–1,225 ppm for Cd, and 855–8,956 ppm for Al (Table 2).

The highest concentration of Zn, Cd, Cr, and Cu are found at sites L3, L4, L5, L7, and L8 located between the Commercial Harbor and the Fish Harbor of Gabes. However, L9 and L10 showed a high Pb and Cu concentration (Figs. 2 and 3). For the zone II, the high amount of metals is detected at R1, R5, R9, R10, and R11. Cd and Zn concentrations showed the same form (Fig. 2), an accumulation of these metals between the commercial harbor and the fishing port, and then the concentration gradually decreased. The maximum value of the concentration of Cr and Cu elements (Figs. 2 and 3) is located at point R9 (120 and 58 ppm, respectively). Finally, the distribution of lead showed two areas of maximum concentration; the first next to the fishing port and the second at the radial R9–R11, and two areas of minimum content located

**Table 5** P and N concentrations in sediment samples from the Gulf of Gabes and other selected areas from the literature

Locations	Elements		References
	P (ppm)	N (%)	
Gulf of Gabes	2–12,725	0.02–0.27	Present study
Eastern Adriatic coastal	201–768		Matijevic et al., 2008b
Abu-QirBay	980–10,100		El Gohary et al., 2012
French coast		0.35	INEIR 2010
Tanger Bay		0.218	El Hatimi et al., 2002

on both sides of the commercial harbor (Fig. 3). The averages calculated for each element followed the order: Zn > Al > Cd > Cr > Cu > Pb in zone I and Al > Zn > Cd > Cr > Cu > Pb in zone II.

The total organic carbon content of the sediments of the study area varies between 1.5 and 4 %. The spatial distribution of TOC showed a slight similarity between stations in the littoral zone. The highest concentration is distinguished on the south of the chemical complex which the maximum level is detected at point R9 (4 %; Fig. 3). The spatial distribution of nitrogen showed a similar variation between stations located on the coastline, although concentrations not exceeding 0.06 %. Superficial sediments on the south of zone II were rich in total nitrogen compared to north part whose contents varied between 0.042 and 0.091 % (Fig. 4). Both elements phosphorus and fluoride showed a high accumulation in superficial sediment between the commercial harbor and the fishing harbor of Gabes. Those elements tended to decrease with increasing distance (Fig. 4). The stations L8 and R9 had the highest phosphorus content with 3,450 and 25,000 ppm, respectively, while high accumulation of fluoride was detected at station L3 (5 %) and at R1 (7.2 %). The accumulation of pollutants in the area between the commercial harbor of Ghannouch and the fishing harbor of Gabes can be explained by the presence of the drainage channel of the chemical group in this zone. In addition, both harbors have acted as barriers and transformed the area into a confined zone. Thus, this

**Table 6** Muller's classification for the Geoaccumulation Index (Ahdy and Khaled 2009)

$I_{geo}$ value	Class	Quality of sediment
$\leq 0$	0	Unpolluted
0–1	1	From unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	From moderately polluted to strongly polluted
3–4	4	Strongly polluted
4–5	5	From strongly polluted to extremely polluted
$\geq 6$	6	Extremely polluted



configuration has limited the dispersion of those pollutants into the sea.

To assess the level of pollution in the study area compared to other regions in the Gulf of Gabes, a reference point was chosen at the Zarrat area (60 km south of the city of Gabes). Table 3 showed that the levels of chromium, cadmium, zinc, and lead were lower than their equivalent in the studied area. Fluoride, phosphorus, and copper had also lower content comparing to the contents of this elements of the study area excepting L1, L2, and L6 for Cu; L10 for Pt; and L1 and L2 for F.

The comparison of heavy metal concentrations with the reference levels of marine and estuarine sediments laid down by the French Decree of 14 June 2000 (Aloulou 2010) (Table 4) showed that: (1) concentrations of Pb, Cr, and Cu elements are lower than level 1 of the French Decree, the potential impact of sediment is slight, excepting of the point R9, which Cr and Cu elements an alert level for. (2) Zn and Cd showed a level of pollution at points (R1, R5, R9, R10, and R11) near the Ghannouch Chemical Group. Away to the

depth, the concentrations of these metals indicate an alert level and become a normal level at the points farther away, where the potential impact of sediment is minor.

Pollutant concentrations were compared with the values presented in previous study determined in sediment from the adjacent coast of Sfax (Tunisia) and of other country presenting various levels of contamination (Aloulou et al. 2011; Gargouri et al. 2011; Ahdy and Khaled 2009; Guven and Akinci 2008; Yu et al. 2008). For heavy metal contents, the following observations were made: (1) the values of Cd and Zn concentrations in this study were, respectively, of about 1,300 and 400 higher than others compared areas (Coast of Sfax (Tunisia), West Egyptian coast, Izmir Bay (Turkey) Quanzhou Bay (China)); (2) concentrations found for Pb was lower than values of those polluted areas; (3) the concentrations of Cr and Cu were higher than concentrations found in coast of Sfax and west Egyptian coast, which are considered as polluted zones. Izmir Bay and Quanzhou Bay showed higher values of Cr and Cu than that of the study area (Table 4).

**Table 7** Geoaccumulation index, enrichment factor, and contamination index of heavy metals values in sediment from the Gulf of Gabes

Sites	Pb			Zn			Cr			Cu			Cd		
	<i>I<sub>geo</sub></i>	EF	CI	<i>I<sub>geo</sub></i>	EF	CI	<i>I<sub>geo</sub></i>	EF	CI	<i>I<sub>geo</sub></i>	EF	CI	<i>I<sub>geo</sub></i>	EF	CI
L1	0	0	0	-2.95	5.47	0.11	-4.36	1.65	0.03	-3.43	3.66	0.08	0	0	0
L2	0	0	0	-3.22	6.18	0.09	-4.18	2.74	0.04	-3.43	5.2	0.08	0	0	0
L3	-2.9	5.27	0.11	5.33	6,430	143	-1.47	19	0.42	-2	12.11	0.27	10.66	610,725	13,611
L4	-1.96	12.07	0.27	4.66	3,485	80	-1.19	23.43	0.54	-2.05	11.23	0.26	10.2	396,197	9,166
L5	-2.84	9.66	0.13	4.14	3,780	51	-1.64	26.84	0.36	-1.8	23.37	0.32	9.73	446,400	6,111
L6	0	0	0	-3.1	6.1	0.1	-4.02	2.78	0.04	-3.76	3.46	0.06	0	0	0
L7	-1.6	21.3	0.38	1.47	294	5.28	-1.39	25.35	0.45	-2	15.05	0.27	7.01	33,447	600
L8	-2.32	9.18	0.2	1.44	229	5.14	-1.6	16.92	0.37	-1.88	13.38	0.3	7.05	27,753	622
L9	-1.15	23.65	0.55	-2.37	8.34	0.19	-3.82	2.42	0.05	-1.96	11.85	0.28	0	0	0
L10	-1.51	23.91	0.41	-2.76	8.17	0.14	-4.1	2.62	0.04	-2.77	8.13	0.14	0	0	0
R1	-1.67	5.78	0.47	5.53	860	69.36	-0.83	10.63	0.84	-0.38	14.56	1.15	12.34	106,366	7,777
R2	-2.97	12.08	0.19	-1.09	44.86	0.7	-2.81	13.85	0.21	-2.76	14.31	0.22	4.69	2,732	38.89
R3	-3.67	4.66	0.11	-1.62	19.41	0.48	-3.17	6.73	0.16	-1.87	16.72	0.41	3.88	978	22.22
R5	0	0	0	5.57	1,080	71.47	-0.93	12.03	0.78	-0.87	12.65	0.82	12.39	134,234	8,055
R7	-2.86	10.61	0.2	-1.09	36.6	0.7	-3.05	9.55	0.18	-3.05	9.55	0.18	4.69	2,229	38.89
R8	-3.5	8.14	0.13	-1.82	26.22	0.42	-3.31	9.5	0.15	-3.22	10.13	0.16	3.88	1,520	22.22
R9	-1.35	5.87	0.58	3.49	170	16.9	-0.05	14.79	1.44	0.64	24.14	2.35	10.27	20,648	1,861
R10	-1.31	5.44	0.6	2.55	80.21	8.8	-0.73	8.37	0.9	0.05	14.51	1.56	8.79	6,699	666
R11	-1.21	7.13	0.64	2.15	74.35	6.69	-1.73	5.1	0.45	0.14	18.83	1.66	8.38	6,128	500
R12	-2.42	17.03	0.27	-1.24	38.94	0.63	-3.53	8.09	0.12	-2.7	14.43	0.23	4.88	3,012	44.44
R14	-4.35	5.08	0.07	-1.76	30.67	0.44	-3.91	7.045	0.09	-2.83	14.94	0.21	4.34	2,348	30.55
R17	0	0	0	-3.56	5.11	0.12	-4.63	2.47	0.06	-3.32	6.18	0.15	0	0	0
R18	-3.35	7.34	0.14	-3.78	5.49	0.1	-4.79	2.77	0.05	-3.32	7.71	0.15	0	0	0
R21	-3.35	7.3	0.14	-2.32	14.98	0.29	-4.37	3.68	0.07	-2.7	11.75	0.23	3.21	766	13.89
R22	2	8.78	0.11	-3.21	12.19	0.16	-4.87	3.92	0.05	-3.52	9.99	0.13	1.88	461	5.56
R23	-3.08	16.7	0.17	-2.6	23.52	0.24	-4.43	6.72	0.06	-3.22	15.59	0.16	3.21	1,461	13.89

**Table 8** Spearman's rho correlation matrix of studied pollutants in the Gulf of Gabes

	Pb	Zn	Cr	Cu	Cd	F	P	N	TOC	pH
Pb	1									
Zn	0.443'	1								
Cr	0.487'	0.926"	1							
Cu	0.601"	0.818"	0.851"	1						
Cd	0.37	0.980"	0.924"	0.768"	1					
F	0.129	0.519"	0.538"	0.383	0.534"	1				
P	0.392'	0.830"	0.905"	0.810"	0.818"	0.395'	1			
N	-0.368	-0.373	-0.462	-0.493	-0.386	-0.532	-0.278	1		
TOC	0.524"	0.532"	0.624"	0.615"	0.526"	0.432'	0.531"	-0.464	1	
pH	-0.191	-0.834	-0.788	-0.666	-0.847	-0.447	-0.707	0.161	-0.296	1

The phosphorus concentrations are higher than average concentrations found in diverse sediment samples along the eastern Adriatic coastal area (Matijevic et al. 2008b) and the coastal zone of Abu-Qir bay, Egypt (El Gohary et al. 2012). However, nitrogen concentrations are lower than mean concentration calculated in sediment from French coast (INEIR 2010) and the bay of Tanger, Morocco (El Hatimi et al. 2002) (Table 5). Unfortunately, information concerning fluoride content in Mediterranean sediment area was insufficient.

#### Assessment of heavy metal pollution

In this study, the EF value were  $>1.5$  in the sediment of the Gulf of Gabes, except of Pb at points R5 and R17 and Cd at points R17 and R18, suggesting anthropogenic impact on the metals levels. The highest EF values were found at zone I, especially for Cd and Zn, due to its proximity to the discharge source (Table 7). According to the Muller scale (Table 6), the calculated results of  $I_{geo}$  values indicated that Cd and Zn can be considered as from extremely polluted to moderately polluted zones except that of L10, L9, L1, L2, and L6 stations, which showed unpolluted sediment. Unpolluted situation was recorded for Pb for all stations ( $I_{geo} < 0$ ). Cr and Cu showed unpolluted sediment ( $I_{geo} < 0$ ) except for stations R9, R10, and R11, which indicated moderate pollution level (Table 7). Basing on the mean values of  $I_{geo}$ , sediments were enriched for metals in the following order:  $Cd > Zn > Pb > Cu > Cr$ . Maximum values of CI for Zn are noted for sediment of L3, L4, L5, R1, R5, and R9 stations, but moderate contaminations was recorded at L7, L8, R10, and R11 stations. All stations in the present study recorded low contamination factor for Cr, Cu, and Pb. Zone I indicated high contamination factor of Cd at L3, L4, L5, L8, and L7 stations. While at zone II, the high contamination factor was recorded for Cd at all station except station R22 which exhibited moderate contamination for this metal R17 and R18 stations, which showed low contamination factor (Table 7).

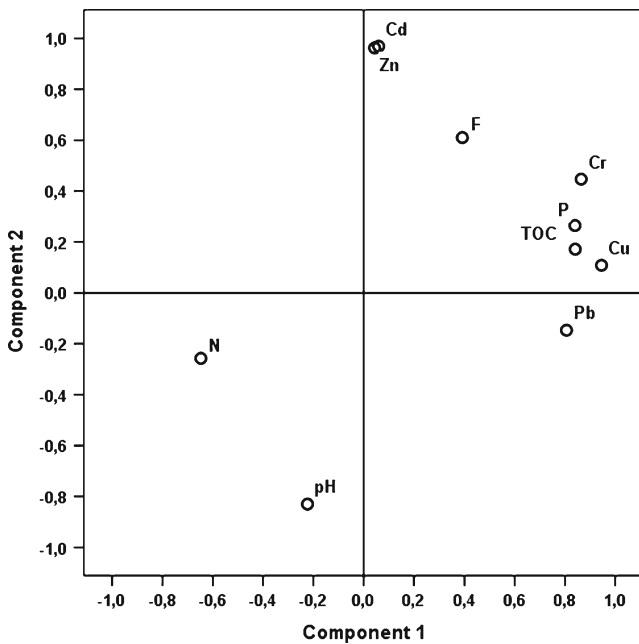
Despite low values detected in some stations, sediment samples showed anthropogenic enrichment of metals. However, this enrichment is not similar between both sampled stations and metals. Pb, Cr, and Cu did not reach the threshold of contamination according to CI and  $I_{geo}$ . Zn and Cd showed high contamination values of those indexes at stations close to sources of pollution. As Zn and Cd contents in sediment samples, values of CI and  $I_{geo}$  decreased with increasing distance.

#### Statistical analysis

In order to establish relationships among metals and to determine the source of metals in the Gulf of Gabes, a correlation matrix was calculated for heavy metals in the sediments. According to the values of Spearman's rho correlation coefficients, a significant positive correlation determined among the metals studied (Table 8).

**Table 9** Loadings of experimental variables (10) on significant principal components for the Gulf of Gabes data set

	PC 1	PC 2
Pb	0.806	-0.147
Zn	0.044	0.962
Cr	0.864	0.447
Cu	0.945	0.109
Cd	0.059	0.969
F	0.392	0.61
P	0.84	0.265
N	-0.647	-0.258
TOC	0.847	0.171
pH	-0.223	-0.83
Eigenvalue	5.342	2.314
% Total variance	53.416	23.14
Cumulative % variance	53.416	76.557



**Fig. 5** Loading plots of the two components obtained with PCA for the data set

The significantly positive correlation of Cu ( $r=0.768$ ), Cr ( $r=0.924$ ), and Zn ( $r=0.980$ ) with Cd; of Pb ( $r=0.601$ ), Zn ( $r=0.818$ ), and Cr ( $r=0.851$ ) with Cu; and of Pb ( $r=0.487$ ) and Zn ( $r=0.926$ ) with Cr could indicate the same or similar source input. In addition, significant correlations among most of these heavy metals are observed, which suggesting that these heavy metals were associated with each other (Garcia et al. 2008).

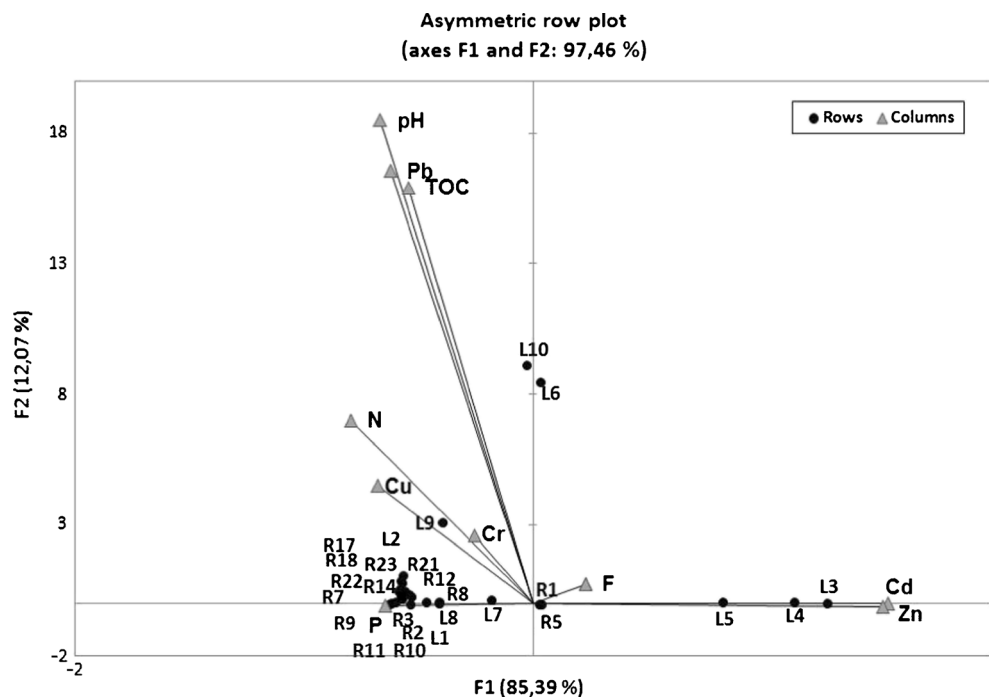
A second correlation matrix (Table 8) was calculated for all pollutants studied in order to establish relationships among them. In this study, the pH of the sediment and the total nitrogen showed negative correlation with other pollutants. This indicated its insignificant effect in the adsorption of these pollutants in the marine sediments of the study area.

Fluoride showed significant correlation with heavy metals, especially Zn ( $r=0.519$ ), Cd ( $r=0.534$ ), and Cr ( $r=0.538$ ) and with TOC ( $r=0.432$ ). Phosphorus was highly correlated with Cu ( $r=0.810$ ), Cd ( $r=0.818$ ), Zn ( $r=0.830$ ), Cr ( $r=0.905$ ), and with total organic carbon ( $r=0.531$ ). Finally, total organic carbon showed a significant correlation with all metals especially Cu ( $r=0.615$ ) and Cr ( $r=0.624$ ). Positive correlations between fluoride, phosphorus, total organic carbon, and heavy metals can also be an indicator for the same source input.

Principal component analysis is an effective method to evaluate results obtained from sediment samples and to identify the factor influencing each one. In this case, PCA (VARIMAX rotation method) identified two components for all sites that explained about 77.53 % of the total variance in the sediment quality data set (Table 9). The first PC accounted for 52.71 % of the total variance, it correlated with Cu, Cr, Pb, TOC, and P elements. The second PC accounting for 20.81 % of the total variance was correlated with Zn, Cd, and fluoride. Figure 5 presented the loadings plots of the two components. The correlation are considered significant when component coefficients are greater than 0.70.

Component 1 had a strong positive loading ( $>0.70$ ) on Cr, Cu, P, and TOC contents. This component is characterized by high loading of the total organic carbon, which can be

**Fig. 6** Loading plots of the two factors obtained with correspondence analysis



explained by the significance role of organic carbon to the binding of certain pollutants. Component 2, which accounted for 20.81 % of the total variance, had strong positive loadings on Cd and Zn. Both of components represents anthropogenic source. The loading plots (Fig. 5) of the two components showed negative correlation of nitrogen and sediment pH. This can indicated that pollutant adsorption on marine sediment cannot depend on pH and nitrogen.

Correspondence analysis (CA) was applied to all sampling stations (26) and studied variables (10), in order to show relations between stations and pollutants. This analysis identified two principal factors (F1 and F2) that explained 97.45 % of the total inertia of observations.

The loading plot (Fig. 6) of the two factors showed the presence of four different groups:

- The first group included stations L3, L4, and L5, at which the dominance of Cd and Zn are determined.
- The second group included stations R1 and R5 and is dominated by fluoride.
- Station L9, constituting the third group, characterized by the presence of Cr and Cu.
- Finally, the last group included stations L1, L2, L7, L8, R2, R3, R7, R8, R9, R10, R11, R12, R14, R17, R18, R21, R22, and R23 stations. These sites are dominated by phosphorus.

This plot also showed that L6 and L10 stations are independent of all pollutants, indicating their non-contamination. The pH of sediment, Pb, and TOC contents are not linked with any station. This proved that adsorption of pollutants (except of Pb) in the sediments were independent of pH and TOC.

Statistical tool revealed a problem: although the principal component analysis indicated the same source input of pollutants, correspondence analysis has linked each pollutant at different stations, posing a question about the modality dispersion of these pollutants in sediments.

## Conclusion

The coast of Ghannouch-Gabès, Gulf of Gabès, Tunisia, is known to be polluted by high concentrations of several pollutants. The evaluation of sediment pollution in this coastline was made by different tools and methods. The highest concentrations of heavy metals, fluoride, and total phosphorus was found principally in the stations located between the commercial harbor and the fishing harbor of Gabès. The average calculations for heavy metals respectively: Zn > Al > Cd > Cr > Cu > Pb in zone I and Al > Zn > Cd > Cr > Cu > Pb in zone II. The results of geoaccumulation index ( $I_{geo}$ ), enrichment factor (EF), and contamination index (CI) prove

that concentrations of pollutants tend to decrease with increasing depth.

Multivariate analysis (PCA/FA) identified two components. Both of these components (F1 and F2), which are noted with Cd, Zn, Cr, Cu, P, and TOC content, are related to the anthropogenic sources. A significant positive correlation is observed among Zn, Cd, Cr, Cu, Pb, TOC, F, and P, indicating that these pollutants were derived from similar sources and moving together.

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