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Ikram Naifar*, Fernando Pereira**, Raja Zmemla *, Moncef Bouaziz*, Boubaker Elleuch*, Daniel GARCIA**

*National School of Engineers of Sfax, Laboratory of Environmental Engineering and Ecotechnology, 1173-3038, Tunisia
ikramnaifar@hotmail.com

**École Nationale Supérieure des Mines de Saint-Étienne, Centre SPIN and UMR 5600, 158 cours Fauriel, 42023 Saint-Etienne /France.

Abstract: In order to investigate the current distribution of metal concentrations in surface marine sediments of the southern coast of Sfax (Tunisia), thirty-nine samples were collected in the vicinity of a mixed industrial and domestic wastewater effluent discharge. In comparison with the threshold effect level and probable effect level, the majority of metals had high ecological and biological risks. Enrichment factor and geoaccumulation Index showed that the majority of sediments are unpolluted by As, Ni and Pb, moderately polluted by Cr and Cu and moderately to strongly polluted by P, Y, Zn. Besides, all sites are extremely polluted by Cd. Principal component analysis indicates that As, Cu and Ni were mainly from lithogenic sources, whereas Cd, Cr, F, P, Pb, Y and Zn were mainly derived from anthropogenic source. Findings of this research can be used as suitable reference for future studies and environmental management plans in the region.

Keywords: Heavy metals, Marine sediments, Spatial distribution, Pollution assessment, Gabes Gulf.

Introduction

Integrated management of coastal areas takes into account all environmental parameters that may affect its development. In this context, Tunisian coastal areas (southern Mediterranean Sea) are the focus of many studies including Sfax area (Gulf of Gabes GG) which is considered as the second principal pole of economic activities. Due to the numerous industrial activities, the southern coast of Sfax, became one of the most damaged Mediterranean coasts inducing significant degradations of the environment (ecosystem, quality of life, local population ...).

Marine environment can be considered as one of the most fragile areas, and as a result, the extension of urban activities on the south-eastern Tunisian coasts increased marine pollution, especially in Sfax coasts. This city is one of the most industrialized cities. The main operating industries, such as the phosphate treatment factory (Tunisian Chemical Group (GCT)/SIAPE) and the lead secondary melting industries are collectively generating many liquid and solid wastes. Those are usually loaded with both mineral and organic pollutants that are released within the littoral zone without treatment (Bouzid et al., 1993; Azri et al., 2007; Azri et al., 2008).

Due to their toxicity, non biodegradability and accumulative behaviors, heavy metals are considered as dangerous environmental pollutants that need to be monitored with care (Billah et al., 2017; Pekey, 2006; Yu et al., 2008). These elements play a role in many biological and geochemical cycles due to their presence in both solid and dissolved form. Marine coastal sediments are usually dominated by terrigenous particles and shell debris; they are considered as a reservoir where an important range of pollutants such as heavy metals can be stored (Pekey, 2006; Santos et al., 2005; Sin et al., 2001).

Heavy metals have a rapid and efficient tendency to be associated with solid sediments when dropped in solution to the natural environment through different mechanism: adsorption or incorporation into a biogenic material or precipitation (Szefer et al., 1996; Cho et al., 1999). Heavy metals in sediments casue various deletrious effects to both benthic and aquatic biota as they can be released into the overlying water via biological and chemical processes (Ip et al., 2007). Their distribution and accumulation are influenced by many factors, including sediment texture, mineralogical composition and hydrodynamic conditions.

Most of recent studies aiming at the assessment of marine environment quality in GG revealed an enrichment of surface sediments with a wide range of pollutants especially in heavy metals, showing a potential degradation of sediments quality (Serbaji et al., 2000; Ayadi et al., 2014;Gargouri et al., 2011; Ghannem et al., 2011; Houda et al., 2011; El Zrelli et al., 2015; Rabaaoui et al., 2015). It also resulted in the appearance of red tides (Hamza and el Abed, 1994), the disappearance of some marine species (El Kateb et al., 2016), unbalance in different local benthic communities (Rabaoui et al., 2015) and malformations in different benthic foraminifera species (Ayadi et al., 2016). However, none of the studies in the southern coast of Sfax have reported the distributional patterns of heavy metals according to the granulometric and mineralogical characteristics of the surface marine sediments.

In this context, metals like As, Cd, Cr, Ni, Mn, Sr, V, Zn... are often used for marine contamination monitoring and assessment due to their dependence on anthropogenic activities (Caccia et al., 2003; Burton et al., 2004). The evaluation of their distribution in surface marine sediment is useful to assess the pollution status of the studied area. For this purpose, we investigated the current metals distribution and concentrations in coastal sediments of Sfax to evaluate its environmental status after more than 65 years of industrialization and to update the relevant data for an effective environmental management in the region.

2

We analyzed many geochemical and some physical parameters, such as pH, heavy metals, fluoride and granulometry in both waters and coastal sediments. Then, the distribution maps of concentrations were estabished using a geographic information system (GIS) approach coupled with geostatistical and multivariate statistical techniques to identify covariations among them and to discuss their significance and potential source.

Materials and methods

Study area

The studied area covers the southern coastal line of Sfax to the northern edge of the Gabes Gulf (south-east of Tunisia). It is characterized by a semi-arid Mediterranean climate influenced mainly by a mild and gentle topography. This coast experiences a semidiurnal and low tide with an amplitude approximately 1.4 m during spring tides and 0.3 m during neap tides. The wave currents precede towards the N-NW and those of ebb towards the S-SE (Amari, 1984).

Sfax region contains large flat plains characterized by soils rich in limestone, siliciclastic sediments, and gypsum (Watson, 1985; Mtimet, 1999). From a sedimentological viewpoint, surface sediments are dominated by slightly gravelly, sandy mud and poorly sorted, muddy sand. This coastline is subjected to an increasing pressure due to the development of several industrial activities that generate industrial and domestic wastewaters. These effluents are drained to the sea causing deleterious effects to waters, marine sediments and the whole natural ecosystem (Illou, 1999; Ghannem et al., 2011; Gargouri et al., 2011).

Our study area, is located downstream a mixed industrial and domestic wastewater effluent on the southern coast of Sfax (latitude 34°43'N and longitude 10°46'E) transported through a three kilometers long channel. Its outlet is connected directly to the sea (Fig. 1). This channel drains together an acidic industrial effluent originated from the phosphate treatment factory since 1952 and the wastewater generated by the Wastewater Treatment Plant (WWTP) of Sfax City since 1983. This effluent also contains phosphogypsum particles; It causes a severe contamination of marine waters and sediments by heavy metals (Illou, 1999; Gargouri et al., 2011), fluoride and phosphorus (Ayadi et al., 2015) and hydrocarbons (Fourati et al., 2017; Aloulou et al., 2010; Serbaji et al., 2000). These pollutants pose a potential ecological risk to marine organisms and human health (Wong et al., 2000).

Samples and analysis

Thirty nine surface marine sediments were sampled, in March 2016, from the southern coast of Sfax receiving the mixed industrial and domestic effluents. Sampling was performed in spaced sites (from 150 to 250 m) through different radials covering an area approximately of 4.3 km^2. Location was recorded using a Global Positioning System (GPS) technology (Fig. 1). Eleven samples were collected from the upper shoreface where water depth does not exceed 0.3 m. For other stations, the depth of water varied from 0.5 to 2m. At each sampling station, the upper 0–10 cm layer of surface sediment was collected using a Van Veen grab sampler. Immediately after their collection, samples were transported to the laboratory and stored in polyethylene bags at 4°C for subsequent analysis.

Samples were oven dried at 60°C for five days and lightly ground to reduce aggregates, then sieved to <63 µm to be used later in the chemical analysis. Grain size plays a significant role in the determination of heavy metals concentrations in sediments. Fine-grained sediments tend to have relatively high metal contents (Horowitz, 1991; Tam

and Wong, 2000; Morillo et al., 2004) because of their high specific surface (Horowitz, 1987). pH was measured for both of marine waters (pH$_L$) and sediments (pH$_S$) using a pH meter (INOLAB WTW 720). The granulometric analysis was performed on the bulk sample sieved below 1 mm using the laser analyzer (Masteriser 2000).

Chemical analysis was performed on the particle size fraction of <63 μm. About 1g of calcinated sediments was dissolved with Aqua Regia (3:1 HNO$_3$: HCl). The concentrations of Al, Ca, Fe, Mn, P, Zn and Y were measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Jobin Yvon 138 Ultrace). As, Cr, Cu, Cd, Ni and Pb concentrations were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7800). Data reported in this study are recalculated on a dry weight basis.

Fluoride concentrations were determined by dissolving 1 g of marine sediment samples in 3 ml of 6 M HCl and diluted to 100 ml with deionized water. Then, an aliquot of the extract was used for the determination of fluoride by selective electrode method (perfectION™) (Abu Hilal, 1985).

A subset of the collected fine-grained fractions (<63 μm) was analyzed by X- rays Diffraction (XRD) to assess the mineralogy of the marine material, and to compare their content with the solids collected in the bedload of the wastewater channel.

Enrichment Factor EF

In order to assess the impact of the anthropogenic activities through the abundance of trace metals, enrichment factor (EF) was calculated using the following equation (Ergin et al., 1991; Choi et al., 2008; Garcia et al., 2008):

$$EF = \frac{(C/_{Al})S}{(C/_{Al})B} \tag{1}$$

Where (C∕Al)$_S$ is the metal to reference ratio in the samples of interest and (C∕Al)$_B$ is the same ratio for the used background reference (earth crust or unpolluted reference baseline). To minimize the influence of grain size and mineral composition on elemental concentrations and to identify possibly anomalous metal concentrations, heavy metal concentrations were generally normalized by conservative elements, such as Al, Fe and Sc (Aloupi and Angelidis, 2001; Amin et al., 2009). In this study, we selected Al as the commonly used normalizer element (Zhang and Liu, 2002). The choice of background values plays an important role in the assessment of pollution status. The average shale value (Turekian and Wedepohl, 1961) or the average crustal abundance data (Taylor and McLennan, 1985) can be used as background metal values. However, the use of these data for a specific area may give misleading results. The regional background values might be more appropriate (Gao et al., 1998; Xu et al., 2016). Moreover, in the case of partially digested samples, it seems more appropriate to use a sample processed with the same analytical protocol as a reference. In this study, a sample of marine sediment (S$_T$), 8 kilometers apart from the study area, was employed as the reference for the background values (Table 2).

According to Zhang and Liu (2002), an EF value of less than 1.5 suggests a geogenic origin of the studied metal (may be entirely from crustal materials or natural weathering processes). A high EF (> 1.5) means a significant input of trace metal derived from non-crustal materials. Instead, they are provided by an anthropogenic source. Sutherland (2000) used a five categories ranking system to assess the degree of contamination : EF <2: deficient to minimal

4

contamination; 2<EF<5: moderate contamination; 5<EF<20: significant contamination; 20<EF<40: very high contamination and EF >40: extremely high contamination.

Geoaccumulation Index Igeo

According to Muller (1979), the geoaccumulation index (Igeo) may contribute to the estimation of the degree of pollution by heavy metals. The equation (2) that describes Igeo is as follows:

$$Igeo = \log2 \frac{Cx}{K \times Bx} \tag{2}$$

Where C_x and B_x are concentrations of metal (x) in the sediment and in the background, respectively. To eliminate the effect of possible lithological variations in sediments that can affect background data, a correction factor (K =1.5) was used accordingly. Based on Igeo values, sediments can be classified into seven levels as follows: <0: unpolluted; 0-1: unpolluted to moderately polluted; 1-2: moderately polluted; 2-3: moderately to strongly polluted; 3-4: strongly polluted; 4-5: strongly to extremely polluted; >5 extremely polluted (Muller, 1979).

Geostatistical and statistical analysis

In environmental investigations and pollution mapping, geographic information system (GIS) has been widely applied (Xu et al., 2016). The Inverse Distance Weighted (IDW) technique is the selected interpolation method as the best normalizer to picture the spatial distribution of metals. Continuous surfaces are predicted through a linear combination of the available data and greater weighting values; they are assigned to those closer to the interpolated point (Zhou, 2007; Li and Heap, 2008; Xie et al., 2011). Statistic results of IDW interpolation showed a good agreement between measured and predicted lines with an acceptable mean error and Root Mean Square (<0.05). Distribution maps were performed using ArcGIS 10.4.

In this paper, correlation coefficients were calculated, and principal component analysis PCA was performed to examine the relationship between metals, fluoride and < 63μm fraction. These calculations were carried using the version 13.0 of SPSS software.

Most multivariate statistical methods require variables to conform to the normal distribution. Thus, the normality of the distribution of each variable was checked by analyzing kurtosis and skewness statistical tests before multivariate statistical analysis (Papatheodorou et al., 2006; Zhou et al., 2006). The original data demonstrated that most of the variables were heavily skewed, with kurtosis values much higher than zero (p < 0.05), ranging from −1.089 to 32.464 and skewness ranging from −2.397 to 5.677; This may indicate that distributions were far from normal with 95% confidence. To remove the effect of magnitude differences between variables, an additive logarithmic transformation log(1+X) of the raw values is required (Frontalini, 2007). This may further contribute to data normalization and increase of the importance of smaller values. After log transformation, kurtosis and skewness values ranged from −1.615 to 5.796 and from −0.575 to 1.93, respectively.

PCA (Varimax rotation mode) is also an effective method to understand the relationships between elements (Reid and Spencer, 2009; Gu et al., 2012) via a multivariate technique used to analyze data tables and extract important information for later representation as a set of new orthogonal variables: Principal components PCs. In this case, PCA is

used to clarify the relationship between heavy metals. Before applying this method, it is compulsory to examine the adequacy of sampling data examination through the Kaiser-Meyer-Olkin (KMO) test.

Further classification was performed via the hierarchical cluster analysis (HCA), using centroid clustering methods and squared Euclidean distance for similarity measurement, was applied to better understand the spatial distribution pattern in each cluster.

Results and discussion

Physical and geochemical results

Particle size Median value D_{50} is defined as the value where half of the population resides above this point. It was calculated as a handy tool to understand the overall sediment size. Our results indicated medium-sized sand (D_{50} between 500 and 250 μm) for samples near the discharge channel (Distance ≈ 250 m). However, when distance reached 500 m or more from the pollution source sands become fine to very fine for the majority with D_{50} between 250 and 100 μm.

pH_L and pH_S of the study area ranged between 3.37- 8.06 and 7.4 - 8.84, respectively. The pH of the acidic effluent drained from the phosphate treatment plant is 2.73, while the pH of domestic wastewater is 8.3. In addition, its chemical properties are characterized by high values exceeding 10 to 37 times the standard loads of wastewater discharge into the marine environment (Table1). Acidic pH in the effluent favored the dissolution of heavy metals in the surrounding areas, leading to higher mobility of these metal cations in seawater and also in interstitial water. In addition, spatial distribution showed a great variation of pH values according to the distance from the discharge channel.

X-ray diffactograms indicate that quartz, apatite, calcium sulfate (i.e., phosphogypsum), fluorite and barite are present in the bedload of the wastewater channel downstream the phosphate treatment plant. All these minerals are also found in the phosphogypsum stockpiles of the plant: quartz and apatite are unreacted minerals while phosphogypsum, fluorite, barite and a chukrovite-like phase ($Ca_4[FSO_4SiF_6AlF_6],12H_2O$) are likely secondary minerals of the production process (Papageorgiou et al., 2015). The sediment located in the mouth of the wastewater channel contains quartz, fluorite and apatite, but neither gypsum nor calcite were detected by XRD. Quartz and calcite are ubiquitous in all the other marine samples. They are often associated with feldspars (microcline and sodic plagioclase) which are very common detrital minerals in the sand mode, and less frequently with some clay minerals (illite and/or kaolinite). In marine sediments, XRD patterns also indicate the presence of halite, which may represent evaporated seawater.

Satellite pictures proved the presence of mouth bars at the outlet of the wastewater channel, and it is thus likely that the channel delivers solids to the sea as bedload and suspended load, in addition to dissolved species. XRD data suggest that Fluorite is transported to the sea, while solid phosphogypsum is dissolved in seawater at the channel mouth. Moreover, the lack of marine calcite at the channel mouth suggests that it is readily dissolved, or converted to Fluorite, by the acidic and fluoride rich wastewater. Many other pollutants are not abundant enough for their host to be identified by XRD. Hence, we rely on their spatial distributions to assess their importance and to discuss their origins.

Spatial distributions of the studied metals in surface sediments are given in Fig. 2. The proportion of fine particles varies as a function of the distance to the shoreline, with a marked dissymmetry on both sides of the discharge channel (more fine particles to the North and coarser material to the South). On the contrary, pH_L and many metal concentrations varied strongly and directly about the distance from the discharge channel. Physical and chemical

parameters of both metals and background values are summarized in Table 2. It was found that major and trace metals concentrations in sediments (in mg/kg dry weight) were found as follows: Al (2487 - 21393), As (1.90 - 10.30), Ni (4 – 60), Ca (12657.2 – 137772.6), Cd (0.55 - 24.52), Cu (11.10 - 359), F (65 - 29000), Mn (44 – 106), P (367 - 15110), Pb (3.68 - 39.70), Cr (21.90 - 381), Y (4.40 - 946) and Zn (29.90 - 375). The abundance decreasing sequence of those elements was found to be as follows: Ca>Al>Fe>P>F>Y>Zn>Cr>Mn>Cu>Ni>Pb>Cd>As.

According to Fig.2, the highest values of As, Cd, Cr, Cu, Ni, Pb, Y and Zn concentrations were observed in the channel mouth samples (S0 and S38), in sediments near (less than 300 m) the discharge channel (S9, S12, S16, S20, S26, S27, S35, S36 and S37) and for samples located on the coastline up to a distance of 1300 m from the wastewater outlet (S1, S2, S3, S4, S29, S30, S31 and S32). Their significant extension through these sites may be influenced by the coastal hydrodynamic conditions. For these sediments, concentrations of Cr, Cu, Ni and Zn are higher than the current regional background and other values revealed in previous studies for the same area (Table 3). Compared to these different studies carried between 2000 et 2010 in the southern coast of Sfax, concentrations of Cu, Cr, Ni and Zn in the surface marine sediments found in our study are much higher. The increasing values may be caused by the development of phosphate treatement activities or by the accumulation of pollutants in sediments as they represent an important reservoir for metals.

These metals also showed higher values when compared to some published studies, in Tunisia and all over the world, and Sediment Quality Guidelines SQGs. Threshold effects level (TEL) and probable effects level (PEL) are also two widely used guidelines for bio-toxic sediments risks. Below TEL, concentrations of metals in sediments have a rare biological effect. However, PEL is a level above it, concentrations of metals cause important biological risks (Macdonald, 1996). In the case of our study, for the majority of analyzed sediments concentrations in Cd, Cu, Cr, Zn and Ni far exceed PEL level especially for Cd. Thus, high ecological and biological risks are expected in this coast.

As, Cd and Y in all the analyzed samples far exceed values in other studies carried out in coastal areas in Sfax. By far, the highest amounts are recorded in S0 and S38, at the wastewater outlet, and all sediments in the coastline. Although it exceeds normal levels, concentrations in Cd still lower than those recorded from the coast of Gabes, due to the high amount of discharged phosphogypsum into the sea (El Zrelli et al., 2015; Ayadi et al., 2014). In contrast, for all surface sediments, Al, Fe and Pb (except S0 and S12) were found to be low and in agreement with natural levels.

Ca and Mn showed very high concentrations far exceeding the reference used to calculate the EF and the Igeo for all samples in the study area. This is due to the important amount of these pollutants rejected by the phosphate treatment plant. These latter findings are confirmed by the spatial distributions of F and P (Fig.3), the leading elements discharged by the GCT (Darmoul et al., 1980; Zrelli et al., 2017), contributing to a clear degradation pattern of the marine water and sediment quality in areas including this factory.

Enrichment and pollution assessment

Based on a regional background (S_T), enrichment factor (EF) was used as an index to assess the status of environmental contamination. According to Fig. 4a, the EF values of As, Ni and Pb are between 047-5.37, 0.77-6.19 and 0.59-5.12 , respectively. Those of Cd, Cr, Cu, P, Y and Zn range from 2.10-115.38, 0.99-13.10, 1.10-29.61, 0.69-45.03, 0.52-15.30 and 1.12-14.06, respectively. The average EF for As (1.81) in the study area is below 2, while those for Cd (56.44), Cr (3.81), Cu (6.13), Ni (2.17), P (9.06), Pb (2.45), Y (4.04) and Zn (6.51) exceed 2. Consequently, metals can be classified as follows : weak to moderate enrichment in As, Ni and Pb with a significant enrichment in Ni

and Pb for some samples (S0); a moderate enrichment in Y for 82.05% of samples (significant enrichment for S0, S35, S36, S37, and S38) and Cr for 74.36% of samples (significant enrichment for S0, S35, S36, S37, S38); a significant enrichment in Zn for more than 80% of analyzed sediments; from moderate to very strong enrichment in P (S38 is extremely contaminated in P); For Cu, 80% of samples are moderately to significantly contaminated while S5, S20, S27, S31, S35, S37 and S38 are weakly enriched. For Cd , 92.31% of samples are extremly contaminated. Their EF in Cd far exceed the value of 40 especially for S4, S12 and S38 where EF attended 100. This confirms the very high amount of Cd rejected by the phosphate treatment plant (GCT) in the discharge channel. In conclusion, S0, S35, S36, S37 and S38 are the most enriched samples for the majority of pollutant due to their proximity to the pollution source and to the low hydrodynamic activity in this area.

In the same way, Igeo ranged from -1.03 to 1.42 (average -0.01) for As, 1.40 to 6.90 (average 4.77) for Cd, -0.37 to 3.77 (average 0.88) for Cr, 0.08 to 5.12 (average 1.34) for Cu, -1.14 to 2.78 (average 0.09) for Ni, 0.14 to 5.53 (average 1.81) for P, -0.94 to 2.51(average 0.30) for Pb, 0.83 to 4.28 (average 2.31) for Y and 0.35 to 4.01 (average 1.75) for Zn (Fig. 4b). For As, Ni and Pb, Igeo values show that the marine sediments in our study area can be classified as unpolluted to moderately polluted in these metals. Cr and Cu display a moderate pollution. For P, Y and Zn, the calculated Igeo indicates that sediments range from moderately to strongly polluted. In terms of Cd, the majority of marine sediments (64.11%) can be classified from strongly to extremely polluted, confirming the EF results. An exception is always made for the sediments located in the surrounding area to the effluent outlet (S0, S35, S36, S37, and S38). The calculated Igeo indicates that these samples are strongly polluted in Cu and Zn and extremely polluted in P and Y. Based on the mean values of Igeo, sediments were enriched with metals in the following sequence : Cd > Y > P > Zn> Cu > Cr > Pb > Ni > As.

Results of EF and Igeo are in concordance with the spatial distribution maps where the nearest samples to the pollution source are qualified as the most polluted and enriched in all the heavy metals, except As, Ni and Cu where their EF and Igeo are below 2 and 1, respectively.

Statistical analysis

In order to establish relationships among metals and to discuss their source in the southern coastal area of Sfax, a correlation matrix was created for heavy metals, major elements and F.fine. Generally speaking, the strong correlation between metallic contaminants is already evident in the distribution maps (Figs. 2 and 3). In addition, granulometry and carbonate content are important controlling factors of adsorption and trace metals abundance. The main types of mineral particles to which metals can be adsorbed are silicates (silica, quartz and feldspar), aluminosilicate clays (kaolinite, smectite, illite...), carbonate (calcite, dolomite...), phosphate (apatite), Fe-Mn oxides/hydroxides and sulphate (Honeyman et Santschi, 1988).

According to Table 4, Pearson correlation matrix reveals a strong relationship between heavy metals. The very significant positive correlation could indicate that these elements in sediment share common anthropogenic sources (Garcia et al.2008) and may underwent analogous pathways and geochemical process (Wang et al., 2012; Zhuang and Gao, 2014). Medium correlations exist between Al, Fe and mud content (fractions <63µm) with r= 0.400 and r= 0.373, respectively. This suggests that these metals may be moderately associated with silt/clay-sized constituents of the surface sediments. Mn correlates moderately with Fe (r=0.402), indicating that those lithogenic elements are bound to the fine-grained sediments.

In the marine surface sediments, the very high correlation between P and the analyzed heavy metals like Zn (r= 0.975), Y (r=0.901), Cr (r=0.804), Cd (r=0.979), Pb (r=0.796) and Ca (r=0.864) not only indicates that these elements are derived from the same anthropogenic source but also some of them could be hosted in phosphate (dissolved or released by the dissolution of phosphogypsum in the channel).

A very high correlation is revealed between Zn, Y, Cr, Cd and Pb, indicating that these elements share a common anthropogenic origin (i.e., industrial and WWTP effluent). Ni highly correlates with As (r=0.715) and Cu (r=0.908). It is probably due to common influential factors. Frequently, heavy metals are associated with the calcite. In particular, Cd and Pb have a strong affinity to calcite (Zachara et al., 1991; Van Proosdij et Reddy, 1997). These two elements showed a significant correlation with Ca (r= 0.746 and r= 0.834). Ca was also strongly correlated with metals like P, Cr, Y and Zn, which indicates that there is a probability that these metals are getting co-precipitated with $CaCO_3$ (Nirmala et al., 2016), except sediments located around the channel mouth where calcite is dissolved under low pH. This is confirmed by the absence of calcite in XRD analysis for S0 and S38.

In the case of our study, adsorption does not seem to be the main fixing mechanism because under a pH 8.5, positive surface charge of calcite does not allow cationic adsorption (Van Proosdij et Reddy, 1997). A significant correlation between Al and Zn, Y, Cr, Cd and Pb may indicate that these elements can be also associated with aluminosilicate minerals (Pereira et al., 2017). High concentrations in all metals for S26 (300 m distant from the pollution source) may be due in part to the presence of microcline ($KalSi_3O_8$) and kaolinite ($Al_2Si_2O_5$) as shown in XRD diffractograms. Although their distance from the discharge channel outlet , S3, S4, S5, S6, S8, S9 and S10 showed moderate concentrations in Zn, Ni, Pb and especially in Cu. These sediments are located in the northern part of the study area where the depositional energy is low. The existence of very small amounts of microcline in these samples could be responsible in part for fixing some elements.

In addition to heavy metals, the wastewater effluent transport very high concentrations of fluoride (≈3500 mg/l). For the majority of samples, surface marine sediments also showed high concentrations of fluoride. XRD analysis revealed the abundance of Fluorite (CaF_2) in the channel and the nearing sediments (S18, S35, S36, S37 and S38). This indicates that Fluorite could be transported as a solid phase from the phosphate treatment plant. In addition, neither calcite nor gypsum exist in S38 which means that the majority of extracted CaO may be derived from Fluorite as a result of the reaction between waters rich in fluoride and carbonate precipitated by their major source: shells.

In order to elucidate the potential sources of heavy metals in the surface marine sediments of the southern coast of Sfax, we performed factor analysis on heavy metals based on principal component method with a varimax rotation. For the present study, KMO was equal to 0.795 (close to 1) which means that PCA is useful.

PCA applied to all data (elementary concentrations and F.fine) resulted essentially in three principal components (PC). A significant correlation between the studied variables and three extracted components is obtained with approximately a total variance of 85.13%. According to Table 5, the first group (G1) of metals represented by Ca, Cd, Cr, F, P, Pb, Y and Zn showed a correlation (exceeding 0.700) with PC1 with 59.24% of the total variance. The second group (G2) is positively displayed over PC2 with 13.94% of the total variance and articulated around Fe, Al and F.fine. The third group(G3) is positively correlated with PC3 (11.94% of the total variance) and presented by Ni, Cu and As. PC3 also showed a moderate correlation with PC2 and PC1. According to Fig. 5, the loading plot of the three components, confirmed the three obtained groups: G1: Ca, Cd, Cr, F, P, Pb, Y and Zn originated from anthropogenic resources, confirming the results of calculated EF and Igeo. The main source of these elements seemed to be the phosphate treatment factory by generating important amounts of impurities due to the presence of phosphogypsum and

phosphate particles transported in the fluoride-rich wastewater to the sea ; G2: in this group, Al and Fe are considered as natural components. Their concentrations are in concordance with natural values. Spatial distribution patterns of these metals are almost identical in all the studied area; G3: As, Cu and Ni may be influenced by both natural and anthropogenic sources. The high concentrations of As and Cu in local sites, especially in the northern part of the study area, may be related to the muddy sediments with low organic matter contents.

Hierarchical cluster analysis (HCA) has identified three distinct clusters (I, II, III) based on metal concentration distributions (Fig.6). Cluster I is associated with samples S0, S35, S36, S37 and S38, the nearest sediments to the pollution source. They are characterized by the highest concentrations of pollutants . Cluster II, with a lower hierarchical order, associate with samples with medium distance from pollution source (S12 and S20) and coastline samples (S3, S5, 29 and S30). This group is characterized by lower concentrations than Cluster I. Finally, Cluster III groups sediment with the lowest contamination level. This is consistent with EF and Igeo measurements.

Conclusions

This study has been undertaken to assess the contamination level of the costal area to the southern edge of sfax city. Our results indicated high metals concentrations in the surface marine sediments of the southern coast of Sfax, far exceeding natural values. Spatial distribution of those metals shows different patterns with higher concentrations near the coastline. It was also found that this part of the coast is a favorable environment for the accumulation of some pollutants because of its proximity to pollution sources, a mixed «industrial and domestic» wastewater effluent and variable depositional energy. Tidal currents played key role in sediment particles and heavy metals distribution.

Hydrodynamic condition and fine particle (silt and clay) distribution show that the study area can be subdivided into two dissymmetry zones: a north characterized by a low depositional energy that facilitated fine particles and pollutant accumulation and a south characterized by longshore currents where sediments are dominated by coarse-grained particles (sand).

EF, Igeo and PCA analysis, are different methods used for pollution assessment. It appears that Al and Fe derived from natural sources. However, the strong enrichment recorded for Cu, P, Y and Zn and the extreme enrichment in Cd confirms that these metals predominately have an anthropogenic source. The comparison of EF and Igeo with previous studies elaborated in 2005 and 2010 for the nearby areas showed that the enrichment in pollutants and the pollution degree are increasing year by year. Also, metals pollution affected all the samples but values of elements concentrations, EF and Igeo decreased with increasing distance from the source. These results were confirmed by HCA.

Multivariate analysis PCA helped to conclude that majority of metals are related to the anthropogenic sources. Results show no correlation between these elements and Silt/clay minerals (except few samples in the northern part of the study area) and Fe-Mn oxides which suggest that pollution is mainly derived from similar sources (GCT effluent) in solid phases transported by the mixed channel to the sea, or in secondary solid (but unidentified) phases formed where the acidic wastewater is neutralized at the channel outlet.

When compared to previous data reported in the literature, concentrations of the majority of analyzed metals were higher than their background values, metal concentrations in earth crust and those of Interim Sediment quality guidelines (SQGs).The concordance between the WWTP discharge analyzed parameters and Tunisian standards for industrial discharge in the maritime field led to deduce that industrial discharges, mainly from GCT, are predominantly responsible for the marine waters and sediment degradation in the northern coast of Gabes Gulf.

As severe pollution impacts on the southern coast of Sfax, several hectares of azoic areas are created. In addition, the north-south direction of water currents seems to extend the influence and to increase the transfer of hazardous pollutants toward the southern areas, to be accumulated by marine species and integrated into food chains and to end in humans. This situation is leading to serious health risks if significant effective strategies of management are not adopted. It is important to know that the coastal ecosystems of the northern part of gulf of Gabes are able to establish their auto-remediation once the discharge of this effluent into the sea is stopped or properly treated.

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Table 1 Physical and chemical characteristics for the industrial and domestic wastewater effluent (ppm)

	pH	F	Fe	Zn	Cd	Cu	Pb	Reference
Phosphate treatement plant effluent	1,9	1245	16	18	3,1	0,3	0,2	
WWTP effluent	7,6	5,3	2,2	1,9	<0,05	0,5	0,3	Serbaji et al. (2000)
Mixed wastewater effluent	2,8	252	3,8	7,2	1,1	0,3	0,1	
Tunisian standards	6,5-8,5	5	1	10	0,01	1,5	0,5	NT106.02

Table 2 Ranges (Min, Max), Average and Standard Deviations of Geochemical parameters in surface marine sediments from the southern coast of Sfax and regional background values

	Min	Max	Average	SD	Background values S_T (This study)
D50	80.44	495.40	232.11	118.30	-
F.fine	0	6.31	1.46	1.46	-
PH_L	2.23	8,06	6.97	1.53	-
PH_S	7.40	8.65	8.06	0.30	-
Al (mg kg^{-1})	2 487	21 393	7 289	4 513	7 285
As (mg kg^{-1})	1.,90	10.30	4.17	1.87	2.58
Ca (mg kg^{-1})	12 657.2	137 772.6	42 011.62	29 584.29	18 461
Cd (mg kg^{-1})	0.55	24.52	8.14	6.95	0.14
Cr (mg kg^{-1})	21.90	381	77,22	90.88	18.90
Cu (mg kg^{-1})	11.10	359	37	56	7.00
F (mg kg^{-1})	65	29 000	1 446	4 965	-
Fe (mg kg^{-1})	1 837	15 740	4 339	2 602	4 911
Mn (mg kg^{-1})	44	106	73	11.84	50
Ni (mg kg^{-1})	4	60	11.08	9.27	5.87
P (mg kg^{-1})	367	15 110	2 456	3 819	222
Pb (mg kg^{-1})	3.68	39.70	10.71	8.70	4.68
Zn (mg kg^{-1})	29.90	375	104.90	89.51	15.70
Y (mg kg^{-1})	4.40	946	147.68	156.31	36.80

Table 3 Comparison of heavy metal concentrations in sediments of the southern coast of Sfax with other published values from the Gulf of Gabes and other selected areas and SQGs

Locations	Metals concentrations (mg/kg dw)							References
	Cd	Cu	Pb	Cr	Zn	Ni	Fe	
Analysis method: Aqua regia								
This study	0.55 - 24.52	11.1 - 359	3.68 - 39.7	21.87 - 381	29.9 - 375	4.00 - 59.9	1837 - 15740	Present study
Aegean Sea	0.14 - 0.74	2.96 - 8.92	2.23 - 13.68	7.33 - 29.10	29.42 - 72.39	-	-	Tunca et al. (2017)
Persian Golf	-	1.90 - 304.83	0.97 - 14.48	5.70 - 52.40	5.10 - 123.60	5.40 - 80.0	-	Delshab et al. (2016)
Coast of Gabes	0.11 - 950	0.59 - 5.8	3.8 - 13.9	9 - 69.3	5.2 - 7165	-	-	El Zrelli et al. (2015)
Coast of Cameroon	0.01-0.21	1.0-64	1.14-21	5.13-328	7.9-212	1.59-457	3473.9-136762	Ngeve et al. (2015)
Gulf of Gabes	0 -1225	1.5 - 58.7	0 - 10.2	3 - 120	6.75 - 10.1	-	-	Ayadi et al. (2014)
Southern coast of Sfax	6.0 - 56	15 - 44	19 - 59	44 - 137	42 -391		52344 - 54543	Houda B et al. (2011)
Coast of Sfax	5.5 - 7	13 -29	18 - 88	41 - 82	39 - 117	7 - 5.5	41011-50163	Gargouri et al. (2011)
Southern coast of Sfax	3.21-5.87	2.25-2.28	1.75-3.04	11.4-15.6	19.7-23.8	1.62-2.87	-	Aloulou et al. (2010)
Sfax-Kerkenah shelf	35.9	38.4	125	196	2077	348	8835	Ghannem et al. (2010)
Coast of Sfax	5.5	13	18	41	39	7	52000	Serbaji (2000)
Analysis method: Total digestion								
Sancti Petri estuary, Spain	0.08 - 0.4	12.9 - 90.82	9.8 - 70.6	-	31.70 - 162	4.6 - 58.5	-	Bhuiyan et al. (2018)
TEL* (threshhold effect level)	0.68	18.7	30.2	52.3	124	15.9	-	Macdonald et al. (1996)
PEL* (probable effect level)	4.21	108	112	160	271	42.8	-	

*American Sediment Quality Guidelines

Table 4 Pearson correlation matrix of studied elements in the southern coastal area of Sfax

|	F.fine	Al	Fe	Ca	Mn	F	P	Zn	Y	Cr	Ni	Cu	As	Cd	Pb
F.fine	1														
Al	**0,400**	1													
Fe	**0,373**	**0,843**	1												
Ca	-0,049	**0,402**	-0,060	1											
Mn	0,261	0,308	**0,475**	-0,201	1										
F	-0,152	0,215	0,018	**0,364**	0,007	1									
P	-0,072	**0,499**	0,046	**0,975**	-0,183	**0,451**	1								
Zn	0,004	**0,583**	0,159	**0,858**	-0,009	**0,548**	**0,901**	1							
Y	-0,087	**0,455**	0,081	**0,729**	-0,020	**0,872**	**0,804**	**0,869**	1						
Cr	-0,055	**0,541**	0,101	**0,964**	-0,156	0,287	**0,979**	**0,865**	**0,697**	1					
Ni	-0,100	**0,457**	0,330	0,371	0,245	**0,879**	0,469	**0,626**	**0,825**	0,366	1				
Cu	-0,177	0,177	0,046	0,277	0,162	**0,940**	0,349	0,481	**0,789**	0,204	**0,908**	1			
As	-0,074	**0,611**	**0,459**	0,516	-0,048	**0,561**	**0,583**	**0,629**	**0,649**	**0,558**	**0,715**	0,553	1		
Cd	0,030	**0,517**	0,087	**0,746**	-0,093	**0,418**	**0,796**	**0,916**	**0,763**	**0,773**	0,485	0,334	0,496	1	
Pb	-0,018	**0,545**	0,183	**0,834**	0,092	**0,593**	**0,864**	**0,940**	**0,854**	**0,815**	0,696	0,546	0,663	0,828	1

*Correlation is Bold number: correlation is significant at the 0.01 level (two-tailed)

**Table 5** Factor loading and accumulated variance of metals

|	PC1	PC2	PC3
F.fine	-0,044	**0,669**	-0,547
F	**0,738**	0,067	0,215
Al	0,507	**0,83**	0,127
Fe	0,089	**0,937**	0,206
Ca	**0,921**	-0,065	0,031
As	0,444	0,255	**0,569**
Cd	**0,916**	0,021	0,067
Cr	**0,891**	0,301	0,175
Cu	0,062	-0,108	**0,883**
Ni	0,355	0,411	**0,785**
P	**0,961**	0,224	0,094
Pb	**0,831**	0,268	0,381
Zn	**0,899**	0,262	0,249
Y	**0,923**	0,178	0,253
% of Variance	49,25	18,45	17,43
% of Cumulative variance	49,25	67.706	85,13
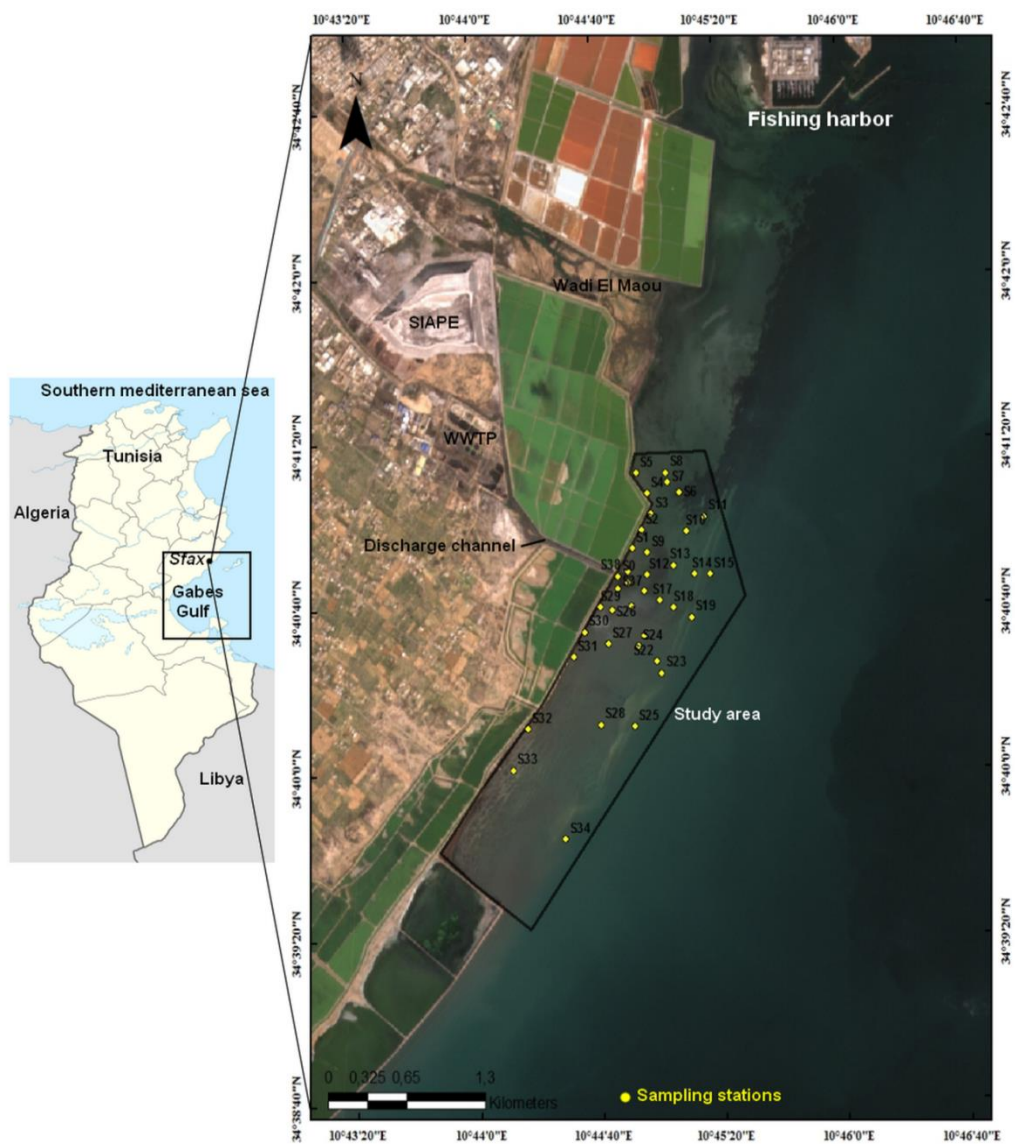
Fig.1 Location of sampling stations in the southern coastal area of Sfax (North of Gabes Gulf).
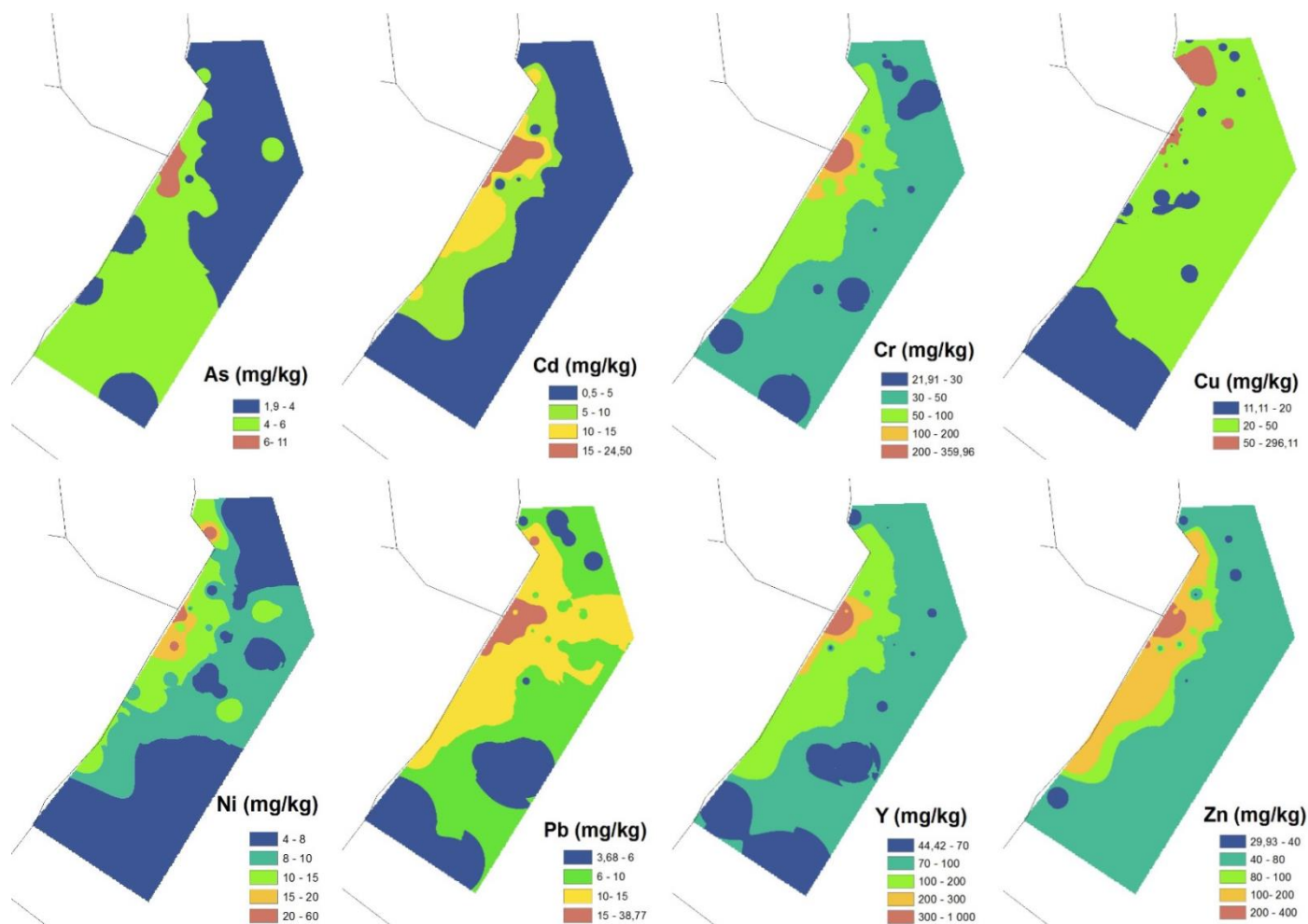
Fig. 2 Distribution maps of heavy metals concentrations in surface marine sediments of the Southern coastal area of Sfax.
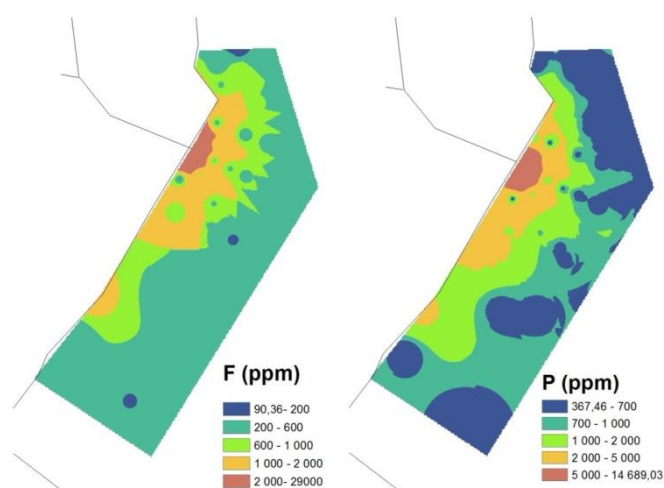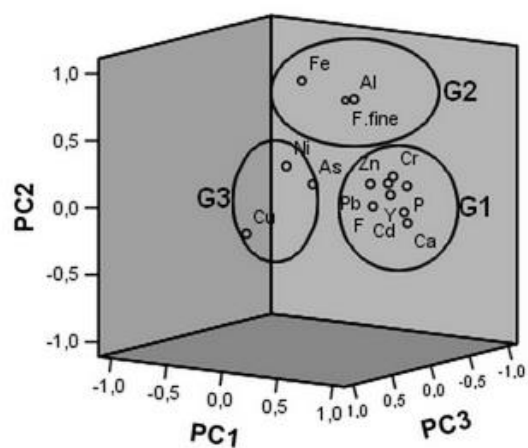
Fig. 3 Distribution maps of Fluorine and Phosphorus concentrations in surface marine sediments of the Southern coastal area of Sfax.
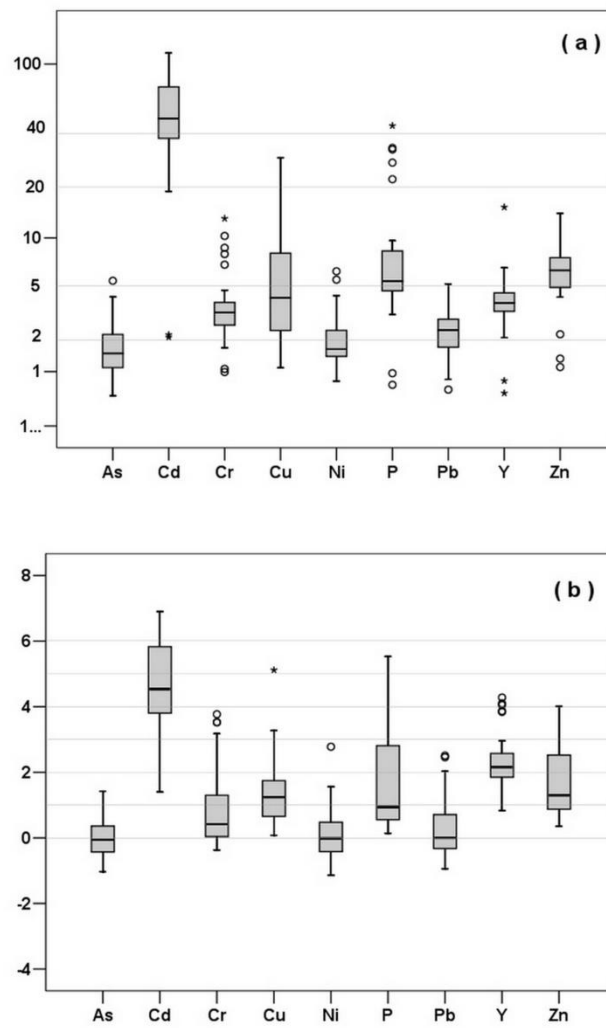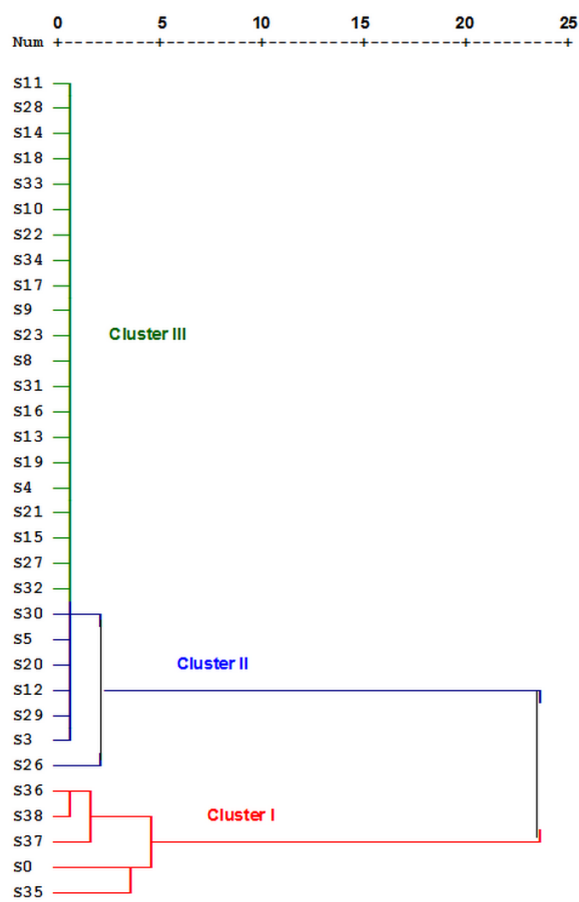
Fig.4 Box-and-whisker plots for enrichment factors (a) and geoaccumulation index(b) of heavy metals in the surface sediments.

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

Fig.6 Hierarchical cluster analysis for sampling stations based on metals concentrations