

## Impact of a Mixed “Industrial and Domestic” Wastewater Effluent on the Southern Coastal Sediments of Sfax (Tunisia) in the Mediterranean Sea

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**ABSTRACT:** Concentrations of Zn, Cu, Cr, Cd, Pb and Fe in surface marine sediments of the southern coast of Sfax were studied in order to understand current metal contamination at the outlet of a mixed industrial and domestic wastewater effluent discharged into the seawater since 1953. We found that heavy metal concentrations (mg/kg dry weight) in surface marine sediments varied from 42 to 391 for Zn, 15 to 44 for Cu, 44 to 137 for Cr, 6 to 56 for Cd, 19 to 59 for Pb and 52344 to 54543 for Fe. The computed metal enrichment factors (EF) in the sediments showed that EF of Zn ranged from 0.49 to 9.13, EF of Cu from 0.35 to 3.04, EF of Cr from 0.3 to 3.05, EF of Cd from 0.63 to 9.37 and EF of Pb from 0.43 to 3. All heavy metals were characterized by maxima EF values greater than 1.5, indicating a considerable metallic pollution of the study area. The PCA analysis revealed two distinct groups: (i) the first group (G<sub>1</sub>) is representative of Fe selected as natural tracer and (ii) the second group (G<sub>2</sub>) is articulated around Zn, Cu, Cr, Cd and Pb. These metals which did not show any correlations with Fe of the first group imply a significantly impact of the selected wastewater effluent. The calculation of the geoaccumulation index ( $I_{geo}$ ) showed that all analyzed metals (except for Fe) can be considered as moderate to extreme pollutants. The microbial analysis of seawater samples and also of both water and sediment samples collected from the Sfax solar saltern (placed at the vicinity of the outlet of the selected effluent) showed that no indicator germs of contamination (total coliforms, faecal coliforms and faecal streptococci) were detected.

**Key words:** Sfax, Heavy metals, Marine sediments, Enrichment factor, PCA,  $I_{geo}$ , GIS, 16S rRNA gene sequence

### INTRODUCTION

Marine sediments result from accumulated autochthonous organic compounds that derived from biological productivity and continental materials supplied through Aeolian and alluvial process (Libes, 1992; Emelyanov, 2001). In oxygenated environments, physical, chemical, and biological processes in the water column and even at the sediment-water interface can destroy a large fraction of these particles before their final remineralization (Calvert and Pedersen, 1993). Sediments in the coastal zone are normally dominated by terrigenous particles due to the important supply of continental material. With the rapid industrialization and economic development in coastal regions, organic and inorganic pollutants are continuing to be introduced

to estuarine and coastal environment through rivers, runoff and land-based point sources. Sediment contamination by heavy metals poses one of the worst environmental problems in marine ecosystems, acting as sinks and sources of contaminants in aquatic systems (Adams *et al.*, 1992; Rowlatt and Lovell, 1994; Mucha *et al.*, 2003; Nasrabadi *et al.*, 2010; Uba *et al.*, 2009).

Due to their environmental persistence and biogeochemical recycling and ecological risks, heavy metals are of particular concern worldwide (Liu *et al.*, 2003; González-Mačias *et al.*, 2006). Marine sediments have often been regarded as the ultimate reservoir for heavy metals in the coastal environment (Sin *et al.*, 2001; Hkepd, 2005; Santos *et al.*, 2005). However, if

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the equilibrium between marine sediments and the overlying water body is broken, marine sediments would transfer most pollutants into seawater (Valdés *et al.*, 2005). As metal concentrations in marine sediments increase, more heavy metals will return to water bodies via chemical and biological processes (Sin *et al.*, 2001).

The spatial distribution of heavy metals in marine sediments is of major importance in clarifying the pollution history of aquatic systems (Rubio *et al.*, 2001; Birch *et al.*, 2001; Liu *et al.*, 2003). Furthermore, such distribution in marine sediments is impacted by natural and anthropogenic factors including parent rock weathering, industrial wastewater, transportation, agriculture and climate (Morillo *et al.*, 2004; El Nemr *et al.*, 2006; Luo *et al.*, 2006). It is essential to distinguish between natural and human impacts on heavy metals in marine sediments. Sediment analyses play an important role in assessments of pollution status of marine environment.

Our attention was focalized on the coastline of Sfax, which is located in the southeast of Tunisia on the Mediterranean Sea. Sfax is a heavily industrialized city. Since the 1950<sup>th</sup>, the growing manufacturing industries, the population expansion and the rapid urban development have resulted in industrial and municipal wastewater and heavy metal pollution that have seriously contaminated much of Sfax's marine sediments (Illou, 1999; Gargouri *et al.*, 2006; Mkawar *et al.*, 2007; Gargouri *et al.*, 2010; Ghannem *et al.*, 2010). In order to control the current levels of pollution or restore habitats, effective measures were used such as banning leaded fuel or regulating sewage disposal. Nevertheless, heavy metals, already present in the marine sediments of coastal areas and typhoon shelters, would still pose a potential ecological risk to marine organisms and human health (Wong *et al.*, 2000).

The purpose of this study is to investigate first, the microbial contamination of seawater and sediments in the southern coast of Sfax (Tunisia), downstream a mixed "industrial and domestic" wastewater effluent and second, the current distribution concentrations of zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb) and iron (Fe) in the surface marine sediments. Such effluent is drained through a channel to the sea since 1952 and it is one of the most important effluents discharging into the coast of urban Sfax.

## MATERIALS & METHODS

In June 2005, measurements of flow rate, pH, COD and BOD<sub>5</sub>, selected heavy metals (Zn, Cu, Cr, Cd, Pb and Fe), total bacteria as well as faecal coliform and faecal streptococci were undertaken in the mixed

"industrial and domestic" wastewater effluent. The wastewater flow rate was measured through the channel (Fig. 1) by a TOLEI flow-meter, model TK-105. The pH measurement was made with an HORIBA pH-meter. COD was undertaken according to JIS K0102.20 (JIS, 1995). BOD<sub>5</sub> was measured using a respirometric method described in French standard NF T90-103, 1975 (AFNOR, 1990). The BOD-meter used was a Sanyo. Bacteria isolation from seawater samples (B1) and also from solar saltern water and sediment samples (B3) was performed in medium prepared using the seawater enriched with 5 g/L yeast extract (Difco) and 10 g/L tryptone (Difco). Bacterial identification was determined by sequencing 16S rRNA gene as described by Baati *et al.* (2010). Total coliforms, faecal coliforms and faecal streptococci were counted respectively on liquid media: BLBVB (lactose brilliant green bile) (24 at 48h at 30°C), DCL (Desoxycholate-Citrate-Lactose) (24-48h at 44.5°C) and ROTHE (24-48h at 37°C). The MPN (Most Probable Number) procedures were performed by using a series of four decimal dilutions per sample, with five tubes for each dilution. One gram of wet sediment and 30 ml of water collected from a pond of Sfax solar saltern were used for DNA extraction and clone libraries construction as described by Baati *et al.* (2008). The 16S rRNA gene sequences were compared to those of the GenBank and EMBL databases by advanced BLAST searches from the National Center for Biotechnology Information (NCBI).

21 surface sediment samples were also collected from the southern coast of Sfax, downstream the mixed "industrial and domestic" wastewater effluent. Sampling was performed in nearly spacing sites (500 m) through three radials (Fig. 1). Sampling sites were located by a Global Positioning System (GPS) technology and samples were collected with an Ekman bucket. The top 5 cm of the sediment was removed with an acid-washed spatula to prevent contamination. After collection, samples were immediately placed in polyethylene bags, refrigerated, and transported to the laboratory (ASTM, 2001). Samples were oven-dried at 60 °C for 4 days, lightly ground in an agate mortar for homogenization, sieved to pass <63 µm (metals are most often associated with small grains) (Morillo *et al.*, 2004). The dry samples were digested with HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HCl according to US EPA method 3050B (US EPA, 1999) and the digestate made up to volume with Milli-Q deionized (DI) water (18 MΩ). Afterwards, the digests were analyzed for the amount of Zn, Cu, Cr, Cd, Pb and Fe by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in triplicate (US EPA, 1996). The instrument is equipped with a cross flow nebulizer and a glass spray chamber. The detection limits (mg/L) were 0.007 for Zn, 0.004 for Cu, 0.006 for

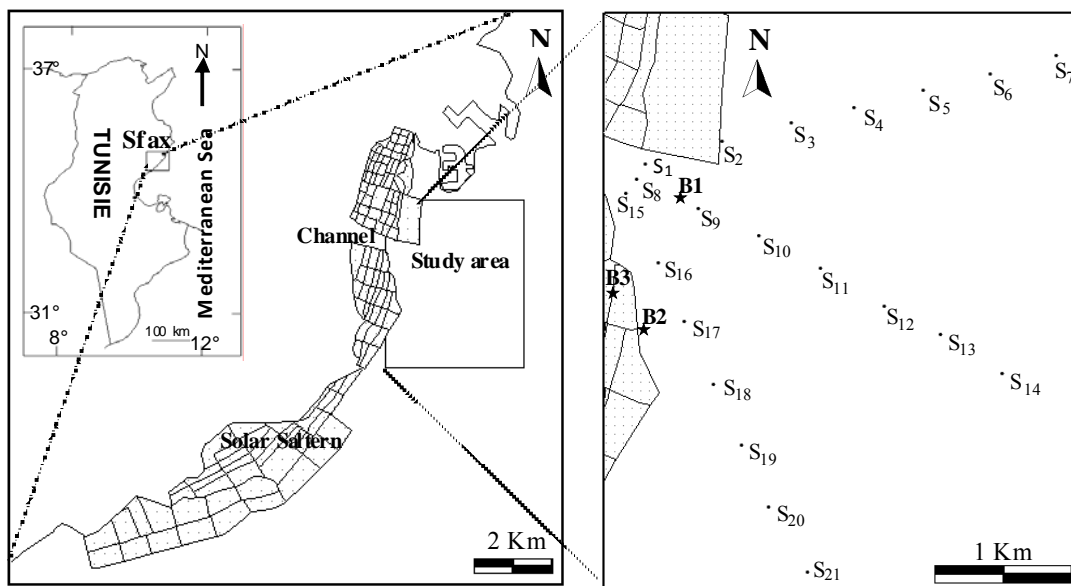


Fig. 1. Location of stations in the southern coast of Sfax

Cr, 0.007 for Cd, 0.035 for Pb and 0.013 for Fe. Analytical procedures are described in details (Pekey *et al.*, 2004). Data reported in this study are calculated on dry weight basis.

**RESULTS & DISCUSSION**

The study area is located downstream a mixed “industrial and domestic” wastewater effluent on the southern coastal sediments of Sfax, latitude 34°43’N, longitude 10°46’E (Fig. 1). The selected effluent is a mixture of an industrial wastewater drained outside the phosphate treatment factory SIAPE since 1952 and a treated domestic wastewater drained from the wastewater treatment plant of Sfax city which has been operational since 1983. This mixed effluent drained through a three-kilometer long channel and disposed of in the sea. It is one of the most important effluents in urban Sfax, which flows into the sea. Its daily average

volume accounted for about 85% of the rejected total flow to the coast of urban Sfax (Illou, 1999). The principal physical and chemical characteristics of the effluent are presented in Table 1.

The pH value of the selected effluent, equal to 3, is significantly influenced by the quality of the industrial effluent which has a pH of 2 (the pH of domestic wastewater is equal to 8.3). This acidic pH of the wastewater effluent favours then the dissolution of the heavy metals. This condition reinforces the mobility of the ionic form of these metals in seawater and also in interstitial water. The concentrations of the majority of all analyzed heavy metals (except for Pb and Cu) are characterized by high values exceeding far Tunisian standards. The mineral and organic loads (in terms of DCO and DBO<sub>5</sub>) are also characterized by high values exceeding 10 and 37 folds their respective

Table 1. Physical and chemical characteristics of the “industrial and domestic” wastewater effluent

	Flow rate	pH	COD	BOD <sub>5</sub>	Fe	Zn	Cu	Cr	Cd	Pb
	m <sup>3</sup> /day		kgO <sub>2</sub> /day	kgO <sub>2</sub> /day			Kg/day			
Selected effluent	1730	3	1470.5	1903	6.57	12.46	0.52	21.11	1.97	0.17
Tunisian Standards		6.5-	156	52	1.0	10.0	1.50	2.0	0.005	0.50
		8.5								

standards loads. These huge quantities of mineral and organic effluent contaminants disposed of in the seawater since the 1950<sup>th</sup> are considered as deemed to be serious pollutants because of their toxicity, persistence and non-degradability in the environment. Bacteriological analysis of the domestic wastewater effluent (before mixing with industrial effluent), were  $9.7 \times 10^5$  bacteria mL/L with a presence of total coliform ( $4.6 \times 10^3$  bacteria per 100 ml) and faecal coliform ( $1.4 \times 10^2$  bacteria per 100 ml) and faecal streptococcus ( $2.1 \times 10^3$  bacteria per 100 ml). After connecting with industrial wastewater, the mixed “industrial and domestic” wastewater effluent is acidic and no significant bacterial growth was observed on plate count agar medium with a pH value of 7.2. At the outlet of the mixed effluent (B1), only a very low bacterial concentration (less than 30 bacteria per ml) was present in seawater. The bacteria isolated were affiliated to the genera: *Bacillus licheniformis* (AY842871), *Staphylococcus* sp LMG 19417 (AJ276810), *Staphylococcus* sp. J33 (AB167056), *Halomonas* sp. WP38 (AJ551113), *Halomonas* sp. WP31 (AJ551108) and *Halomonas venusta* GSP4 (AY553064) while total coliform as well as faecal flora were absent. However, Maalej et al. (2003) have reported the presence of *Aeromonas* and faecal coliforms in seawater samples (B2), close to the coastline, 1 km far from the outlet of the mixed “industrial and domestic” wastewater effluent.

In order to reveal a microbiological contamination of Sfax solar saltern (designed for NaCl production by seawater evaporation) placed at the vicinity of the outlet of the above effluent, a culture independent molecular approach was used. Two samples (water and sediment) from the pond (B3) were chosen near to the seawater contaminated zone (B2) (Fig. 1) were analyzed by amplification and sequencing of 16S rRNA gene clones. The result presented in Table 2 showed that *Bacteria* domain clones were represented exclusively by *Proteobacteria* (*Alpha* and *Gamma*) and *Bacteroidetes*. *Archaea* domain clones were closely related to the *Halobacteriales* order (phylum *Euryarchaeota* class *Halobacteria*). Indeed, indicator germs of contamination (total coliforms, faecal coliforms and faecal streptococci) are not detected. The flora retrieved in the Sfax solar saltern pond is adapted to the hostile ecological condition. Other germ cannot develop in such ecosystem. Therefore, the effluent rejected in the seawater doesn't affect the saline microbiology and the quality of salt produced.

The main objectives are to assess the heavy metal status of surface marine sediment samples, and prepare distribution maps of concentrations and enrichment factors of the selected heavy metals using the geographic information system (GIS) approach coupled

with analytical approaches based on Principal Component Analysis (PCA) and Geoaccumulation Index ( $I_{geo}$ ). We focussed our attention first of all on the behaviour of the heavy metals (Zn, Cu, Cr, Cd, Pb and Fe) in the surface marine sediments (a second study is now in progress related to the behaviour of metals in the solar saltern). We found that heavy metal concentrations (mg/kg dry weight) in surface marine sediments varied from 42 to 391 for Zn, 15 to 44 for Cu, 44 to 137 for Cr, 6 to 56 from Cd, 19 to 59 for Pb and 52344 to 54543 for Fe (Table 3). Median metal concentrations in the study area decrease in the order Fe>Zn>Cr>Pb>Cu>Cd. We compared the metal concentrations from our study with those of previous studies in the coast of Sfax and other regions and found that : (i) Cu, Cr and Pb concentrations are comparable to those found in several Mediterranean regions (Northern coast of Sfax, Golf of Tunis, Bay of Alger and Izmir Bay “Turkey”) and other regions throughout the world such as Bremen Harbor “Germany”, Boston Harbor “USA”, New York Harbor “USA” and Western Xiamen Bay (China) (Table 4). However, these metal concentrations are significantly lower than those found in Golden Horn Estuary “Turkey”, (ii) Zn concentrations are characterized by maxima values largely exceeding those registered in the above selected regions (except for Golden Horn Estuary “Turkey”) and (iii) Cd concentrations are distinguished from all selected regions by their higher maxima values. We also compared our metal concentrations against American marine Sediment Quality Standards, SQS, (WDOE, 1995) and Chinese Marine Sediment Quality Standards (GB 18668-2002) (Zhang *et al.*, 2007) (Table 5). GB 18668-2002 has three standard criteria for marine sediments. The primary sediment standard criteria, which is the most strict, is applied to protecting habitats for marine life including natural, rare and endangered species as well as places for human recreation and sports. The secondary standard criteria are applied to regulating general industrial use and coastal tourism; and the tertiary standard criteria are for defining harbors and special use for ocean exploration. Referring to SQS, only Cd and Zn values appeared to be very high. However, referring to GB 18668-2002, only Pb concentrations in sediments of the study area meet the primary standard criteria (Table 5). Cu and Cr concentrations meet the secondary standard criteria. However, Cd and Zn concentrations exceed largely the GB 18668-2002 standard criteria values.

In order to assess the impact of the mixed “industrial and domestic” wastewater effluent related to the abundance of heavy metals in the study area, the computation of Enrichment Factor (EF) is required.

**Table 2. Affiliations of the bacterial and archaeal 16S rRNA gene sequences obtained from B3 pond**

No. of clones	Microorganism or clone with highest 16S rRNA sequence similarity	
	Taxon and accession number	% similarity
<b>Water sample from B3 pond</b>		
<b>Bacteria domain</b>		
<i>Alpha-Proteobacteria</i>		
1	<i>Roseovarius tolerans</i> (Y11551)	96.90
2	Uncultured <i>Rhodobacteriaceae</i> (AF513928)	97.95-98.91
<i>Gamma-Proteobacteria</i>		
17	Uncultured <i>gamma Proteobacterium</i> (AF452606)	96.00-96.53
4	Uncultured <i>Ectothiorhodospiraceae</i> (AF513947)	97.00-97.65
<i>Bacteroidetes</i>		
1	<i>Psychroflexus torquis</i> (AY167318)	96.87
6	Benzene mineralizing consortium (AF029041)	92.00
10	Uncultured <i>Flavobacterium</i> sp (AJ487527)	96.08
4	Uncultured bacterium EKH0-12 (AF142895)	97.31-97.53
3	<i>Flavobacteriaceae</i> bacterium (AY319330)	92.13-92.98
<b>Archaea domain</b>		
28	Halophilic archeon PalaeaII (AJ276863)	91.00-92.00
8	Haloarcheon CSW4 (AY498649)	94.00
<b>Sediment sample from B3 pond</b>		
<b>Bacteria domain</b>		
<i>Bacteroidetes</i>		
21	Halophilic eubacterium EHB (AJ133744)	98.39
12	Halophilic bacterium EHB-5 (AJ242997)	99.42
2	Halophilic bacterium EHB-4 (AJ242996)	98.17
8	<i>Salinibacter ruber</i> (AF323502)	98.17
5	Uncultured <i>Salinibacter</i> (EF459723)	96.26
<b>Archaea domain</b>		
1	<i>Halonubrum orientale</i> (AM235786)	99.11
1	<i>Halobacterium</i> sp. 7Sb5 (AY987829)	96.90
2	<i>Halonubrum</i> sp (AM268115)	97.04
6	<i>Halonubrum</i> sp. C35 (DQ373061)	99.31
1	Haloarcheon CSW2 (AY498650)	98.45
2	Halophilic archeon Naxos II (AJ400624)	99.33
3	<i>Halobacteriaceae</i> archaeon L (AY647219)	92.60
1	Uncultured haloarcheon (EF533953)	93.46
16	Uncultured <i>Euryarchaeote</i> (EU585947)	95.17
2	Uncultured archaeon (DQ432517)	95.86

**Table 3. Medians, standard deviations and ranges of heavy metals in surface marine sediments at the outlet of the selected wastewater effluent**

	Median	SD	Range
Zn	97	76	42-391
Cu	19	8	15-44
Cr	70	30	44-137
Cd	8	11	6-56
Pb	29	15	19-59
Fe	52443	1008	52344-54543

**Table 4. Trace element concentrations (mg/kg dry weight) from various sources**

	Zn	Cu	Cr	Cd	Pb	Reference
Our study	42-391	15-44	44-137	6-56	19-59	This study
Background values	39	13	41	5.5	18	Serbaji (2000)
Northern coast of Sfax	39-117	13-29	41-82	5.5-7	18-88	Gargouri et al. (2010) Ghanem et al. (2010)
Golf of Tunis	226	79	-	7	112	Added et al. (2003)
Bay of Alger	256	79	63	1.1	93	Boudjellal et al. (1992)
Izmir Bay (Turkey)	99-260	32-70	208-308	0.22-0.42	36-62	Rivail Da.Silva et al. (1996)
Izmir Harbor (Turkey)	182	182	108	6.2	97	Filibeli and Yilmaz (1995)
Golden Horn Estuary (Turkey)	551-9943	337-4432	275-551	-	141-797	Ergin et al. (1991)
Bremen Harbor (Germany)	182	87	108	6.2	97	Hamer and Karius (2002)
Boston Harbor (USA)	118	67	131	-	86	Bothner et al. (1998)
New York Harbor (USA)	188-244	105-131	175	1-2	109-136	US EPA et al. (1999)
Western Xiamen Bay (China)	139-144	30-44	75	0.2-0.7	50-77.2	Chen et al. (1987;1992) Zhang et al. (2007)

**Table 5. Trace element concentrations (mg/kg dry weight) compared to marine Sediment Quality Standards (SQS and GB 18668-2002)**

	Zn	Cu	Cr	Cd	Pb	Reference	
Our study	42-391	15-44	44-137	6-56	19-59	This study	
American marine Sediment Quality Standards, SQS	90-260	390	260	5.1	450	(WDOE, 1995)	
Chinese Marine Sediment Quality Standards (GB 18668-2002)	Sediment primary standard criteria	150	35	80	0.5	60	(Zhang et al., 2007)
	Sediment secondary standard criteria	350	100	150	1.5	130	

Commonly, geochemical normalisation of the heavy metals data to conservative elements such as Al or Fe is employed in order to identify anomalous metal concentration. Al concentration was not analyzed in the studied sediments. Instead, Fe can be used as a crustal reference (Feng *et al.*, 1998; Schiff and Weisberg, 1999; Mucha *et al.*, 2003). In this work, Fe concentrations analyzed in the surface marine sediment samples varied from 52344 to 54543 mg/kg dry weight. They exceeded by 0.6 to 4.5 % background values (52000 mg/kg dry weight) and could testify a slight

influence of the mixed “industrial and domestic” wastewater effluent. When compared to those found in numerous works using Fe as a crustal reference, these proportions appeared however, relatively low (Garcia and Prego, 2003; Zhang *et al.*, 2007; Gargouri *et al.*, 2010; Gannem *et al.*, 2010). Fe is then chosen to calculate enrichment factors. According to Ergin *et al.* (1991), EF is defined by the following equation (1):

$$EF = \frac{(C_x/C_{Fe})_{sample}}{(C_x/C_{Fe})_{background}} \quad (1)$$

Where  $(C_x/C_{Fe})_{sample}$  is the ratio of concentration of the element being tested ( $C_x$ ) to that of Fe ( $C_{Fe}$ ) in the sediment sample and  $(C_x/C_{Fe})_{background}$  is the same ratio in unpolluted reference baseline. If an EF value lies between 0.5 and 1.5 (i.e.,  $0.5 \leq EF \leq 1.5$ ), it suggests that the trace metals may entirely originate from crustal materials (Zhang and Liu, 2002). However, if a value of EF is greater than 1.5, it means that a significant portion of trace metal is derived from non-crustal materials. Instead, the trace metals are provided by other sources, such as point and non-point pollution sources and biota (Klerks and Levinton, 1989; Zhang and Liu, 2002).

According to Serbaji (2000), the metal background values (mg/kg dry weight) adopted in this work (Table 3) are fixed to 39 for Zn, 13 for Cu, 41 for Cr, 5.5 for Cd, 18 for Pb, and 52000 for Fe. Based on these background values, the computed metal enrichment factors in the sediments (Table 6) showed that the EF of Zn ranges from 0.49 to 9.13, EF of Cu from 0.35 to 3.04, EF of Cr from 0.3 to 3.05, EF of Cd from 0.63 to 9.37 and EF of Pb from 0.43 to 3. It appears that the studied sediments are significantly enriched with metals. In fact, all the analyzed metals present maxima EF values greater than 1.5, indicating a considerable metallic pollution of the study area. The distribution patterns of Zn, Cu, Cr, Cd, and Pb concentrations and their EF depicted through the interpolation of elemental data by using Arc View GIS 3.2 showed similar spatial repartitions (Figs 2 and 3). Maxima values are located at the outlet of the wastewater effluent. Their significant extension through the sites (S1 to S3, S8 to S12 and S15 to S16) is probably influenced by the coastal hydrodynamic conditions. The maxima concentrations of all analyzed heavy metals (except for Fe) were characterized by their high values exceeding more than twice background values. These maxima were shown in zones characterized by muddy facies enriched with organic matter (TOC varying between 5 and 8 %) (Illou, 1999). The spatial

distributions of all the studied metals which were shown to be very different from the distribution of Fe concentrations (chosen as a natural tracer) (Fig. 4) highlighted the significant impact of the selected man-made wastewater effluent.

In order to refine the results obtained by the enrichment factors, the concentrations of the studied heavy metals were analyzed by a Principal Component Analysis (PCA). This analytical method is a multivariable statistical technique that can simplify large data sets and allow to reduce the number of variables to a smaller set of orthogonal factors of easier interpretation by displaying the correlations existing among the original variable (Ashley and Baker, 1999).

PCA applied to all data (elementary concentrations), using the ITCF statistical software package (STATIT-CF, 1987), resulted essentially in three principal components. A varimax rotation with Kaiser Normalisation was used for all data sets of the studied sites. The threshold of significance considered for  $p < 0.05$  is equal to 0.42 after a test of student ( $n=21$ ). The significant correlations between selected parameters (variables) and the components represent approximately 96% of the total variance. The first, second and third PCs explained 63%, 18% and 15% of the total variance respectively. The projection over the (1x2) factorial plane (presenting 81% of inertia) of all selected variables shows two distinct data groups (Fig. 5).

- The first group ( $G_1$ ), which is positively displayed over axis 2, is representative of Fe (selected as natural tracer). It is representative of the natural component;
- The second group ( $G_2$ ), which is positively displayed over axis 1, is articulated around Zn, Cu, Cr, Cd and Pb. They present among each other highly to averagely significant positive correlation coefficients. These metals which did not show any correlations with Fe of the first group imply the impact of man-made sources.

**Table 6. Metal enrichment factors with respect to background level in surface marine sediments downstream the wastewater effluent**

	Median	SD	Range
Zn	1.32	1.78	0.49-9.13
Cu	0.61	0.58	0.35-3.04
Cr	1.35	0.68	0.3-3.05
Cd	0.68	1.89	0.63-9.37
Pb	0.94	0.76	0.43-3

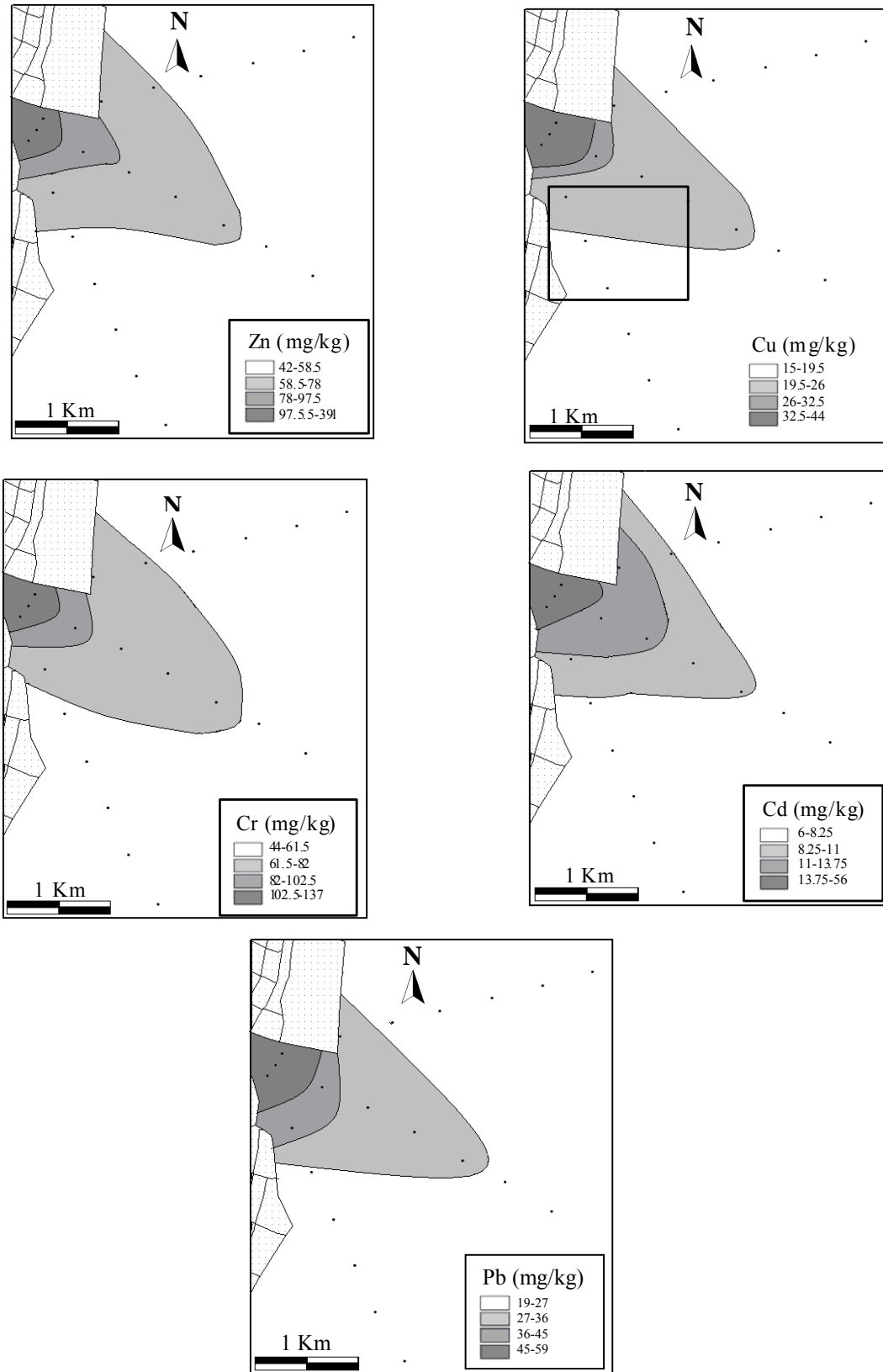


Fig. 2. Distribution maps of Zn, Cu, Cr, Cd and Pb concentrations in surface marine sediments



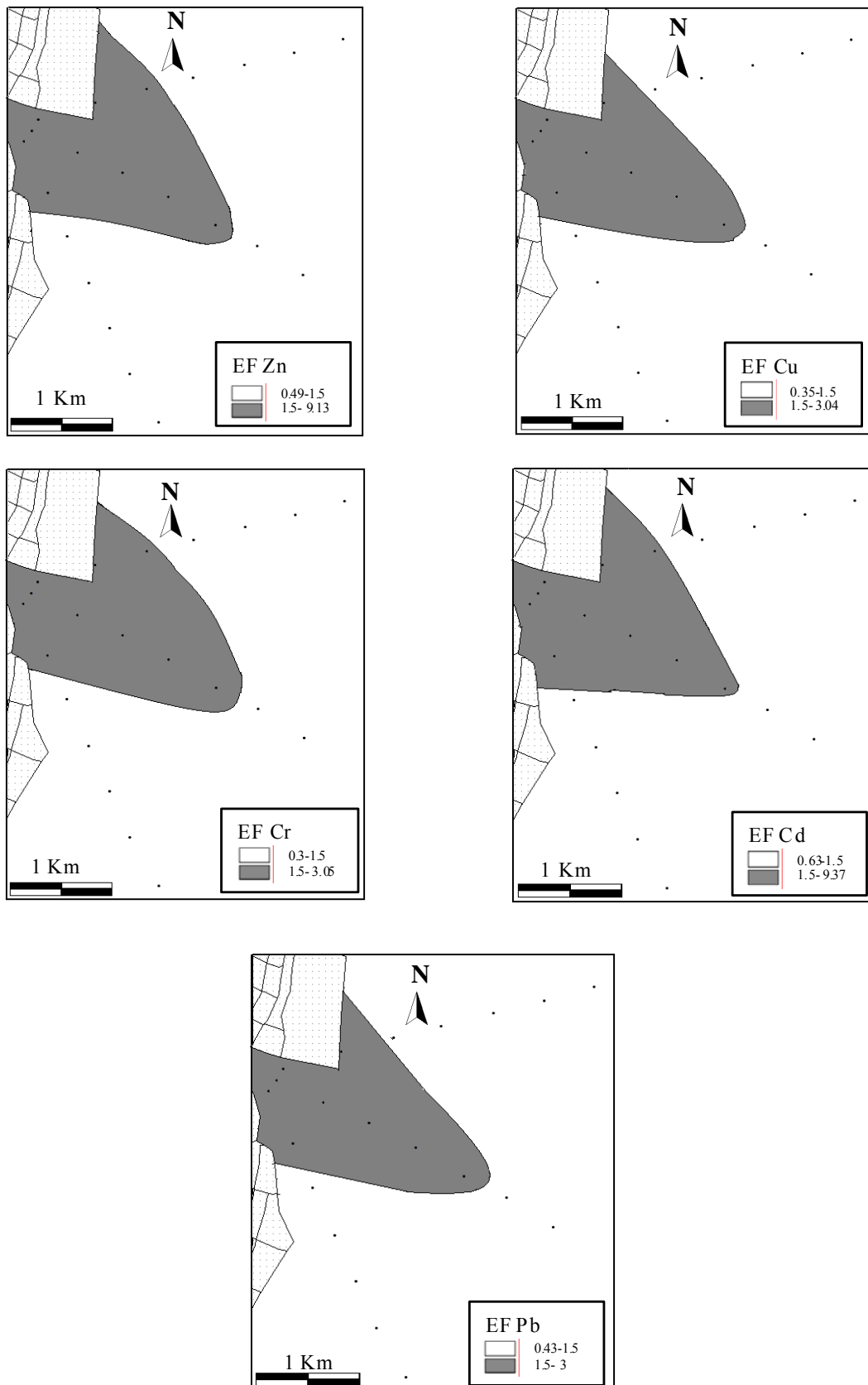
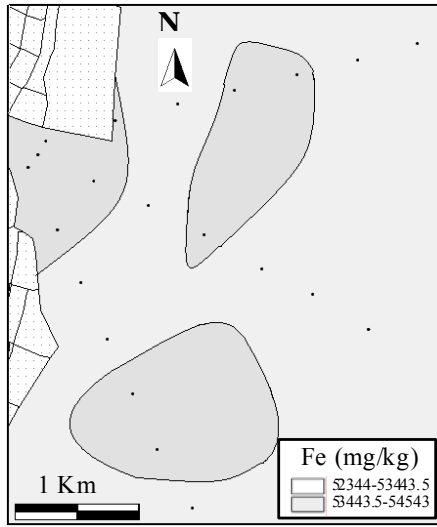
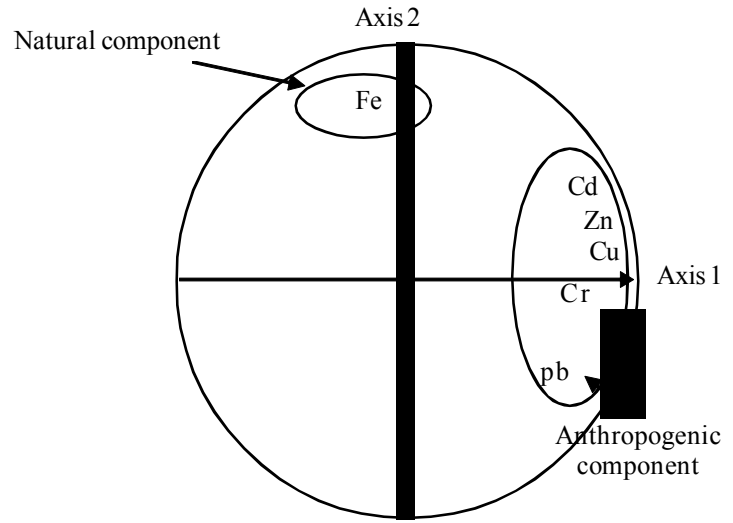


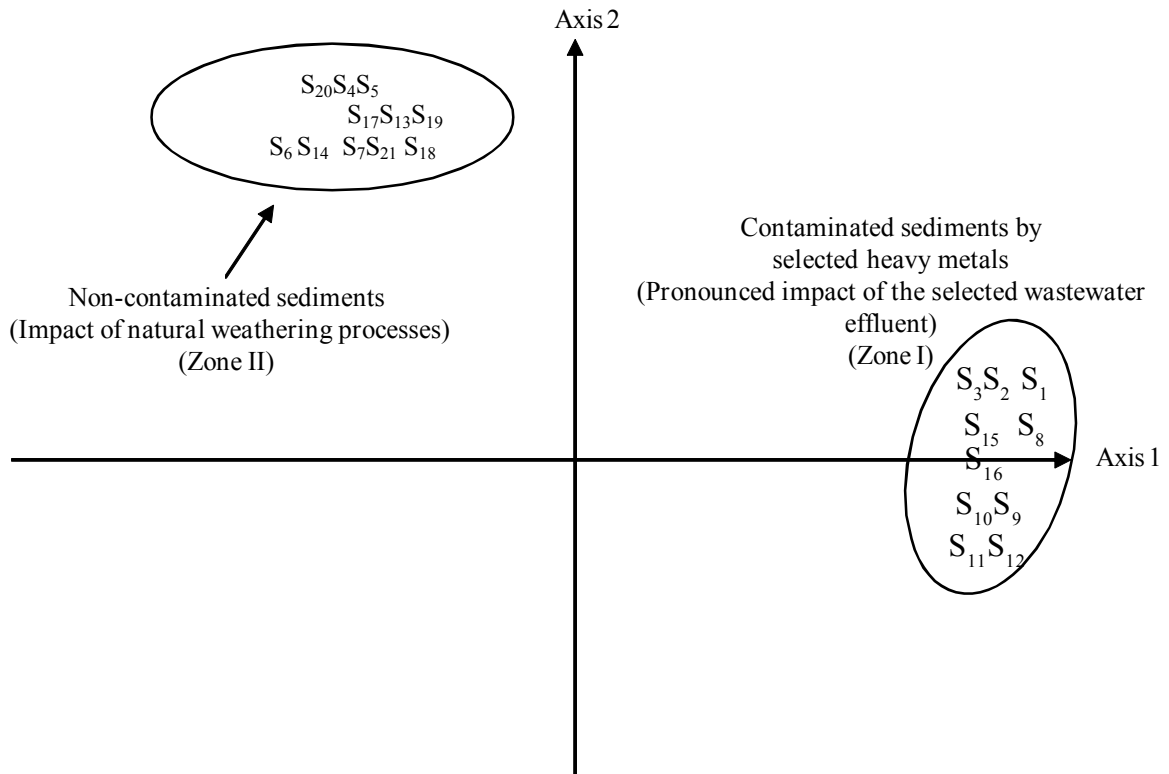
Fig. 3. Distribution maps of enrichment factors of Zn, Cu, Cr, Cd and Pb in surface marine sediments



**Fig. 4. Distribution map of Fe concentrations in surface marine sediments**



**Fig. 5. Projection of variables (metal concentrations) in the 1x2 factorial plane**



**Fig. 6. Projection of individuals (studied sites) in the 1x2 factorial plane**

**Table 7. Geoaccumulation index ( $I_{geo}$ ) values of heavy metals in the surface marine sediments downstream the wastewater effluent**

$I_{geo}$ value	Class	Quality of sediment	Metal	$I_{geo}$ range	Quality of sediment
≤0	0	Unpolluted	Zn	-1.55 to 2.59	From unpolluted to strongly polluted
0-1	1	From unpolluted to moderately polluted	Cu	-2.12 to 1.02	From unpolluted to moderately polluted
1-2	2	Moderately polluted	Cr	-2.22 to 1.10	From unpolluted to moderately polluted
2-3	3	From moderately to strongly polluted	Cd	-1.16 to 0.84	From unpolluted to moderately polluted
3-4	4	Strongly polluted	Pb	-1.73 to 0.97	From unpolluted to moderately polluted
4-5	5	From strongly to extremely polluted	Fe	-0.62 to -0.52	Unpolluted
>5	6	Extremely polluted			

The projection, over the (1x2) factorial plane of the selected variables and individuals leads to the division of the study area into two sub-zones (Fig. 6). The sub-zones are delineated by regrouping sites, statistically correlated on the factorial plane (1x2). It seems that the zone I represented by the sites (S1 to S3, S8 to S12 and S15 to S16) is significantly influenced by the metal contamination. It corresponds to the area which is menaced by the discharges of the mixed “industrial and domestic” wastewater effluent. The zone II represented by Fe covering the rest of studied sites retraces the impact of natural weathering processes. Another criterion to evaluate the heavy metal pollution is the geoaccumulation index ( $I_{geo}$ ). It was originally defined by Müller (1981) in order to determine the degree of metal-contamination in sediments, by comparing current concentrations with pre-industrial levels and can be calculated by the following equation (2):

$$I_{geo} = \text{Log}_2\left(\frac{C_n}{1.5B_n}\right) \quad (2)$$

Where  $C_n$  is the measured concentration of the examined metal (n) in the sediment and  $B_n$  is the background concentration of the metal (n). 1.5 is the background matrix correction factor due to lithogenic effects. According to the Müller scale (1981), the calculation of the geoaccumulation index related to the studied samples showed different values (Table 7). All analyzed metals (except for Fe) can be considered as

moderate to extreme pollutants. First, Zn is characterized by higher levels close to 2.5. Second, Cu and Cr are characterized by higher levels slightly exceeding 1. Third, Pb, and Cd are distinguished by their higher levels not exceeding 1.

The results show that the metal contamination found in the southern coast of Sfax by simple examination (comparison with other results and standards) can be more correctly evaluated if complementary approaches based on Enrichment factors (EF), Principal Component Analysis (PCA) and Geoaccumulation index ( $I_{geo}$ ) were used.

### CONCLUSION

A geographic information system (GIS) approach coupled with analytical approaches based on Enrichment factors (EF), Principal Component Analysis (PCA) and Geoaccumulation index ( $I_{geo}$ ) was applied to investigate the spatial distribution patterns of heavy metals at the outlet of a mixed « industrial and domestic » wastewater effluent discharging into the southern coast of urban Sfax since 1952. The concentrations of the majority of all analyzed heavy metals in this wastewater effluent are characterized by high values exceeding far Tunisian standards. The mineral and organic loads (in terms of DCO and  $\text{DBO}_5$ ) are also characterized by their high values exceeding 10 and 37 folds the respective standards loads. In the surface marine sediments, the heavy metal

concentrations (mg/kg dry weight) varied from 42 to 391 for Zn, 15 to 44 for Cu, 44 to 137 for Cr, 6 to 56 from Cd, 19 to 59 for Pb and 52344 to 54543 for Fe. Metal concentrations were compared to previous data reported in the literature, the American marine sediment quality standards (SQS) and the Chinese Marine Sediment Quality Standards (GB 18668-2002) to assess the pollution status of the sediments. Referring to SQS, only Cd and Zn values appeared to be very high. However, when we referred to GB 18668-2002, only Pb concentrations in sediments of the study area meet the primary standard criteria. Cu and Cr concentrations meet the secondary standard criteria. However, Cd and Zn concentrations exceed largely the GB 18668-2002 standard criteria values. PCA analysis, metal enrichment factors (EF) and geoaccumulation index (Igeo) confirm the certain extent of metal contamination of surface marine sediments at the outlet of the selected wastewater effluent. All analyzed metals (except for Fe) can be considered as moderate to strong pollutants.

Consequently, if the microbial contamination is not significant downstream the wastewater effluent, the metal contamination of surface marine sediments is however, disquieting. It may possibly be extended if significant effective strategies of management are not adopted.

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