Anthropogenic Contributions to Heavy Metal Distributions in the Surface and Sub-surface Sediments of the Northern Coast of Sfax, Tunisia

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ABSTRACT: Eight selected heavy metals (Cu, Zn, Pb, Cd, Cr, Mn, Fe and Al) in surface and sub-surface sediments in the northern coast of Sfax (Tunisia) were studied in order to assess the sediment quality and to highlight the anthropogenic contributions to heavy metal distributions in the two study sediment levels. Multiple chemometric approaches based on Geographic Information System (GIS), Enrichment factors (EFs), geoaccumulation index (I_{geo}) and Principal Component Analysis (ACP) were applied. Enrichment factors (EFs) and principal component analysis (PCA) revealed two distinct groups of metals. The first group attributed to Mn, Fe and Al that were derived from natural sources, and the second group contained Cu, Zn, Pb, Cd and Cr mainly originated from man-made sources. The contribution rates of these later in terms of the sediment's enrichment exceed 98%. The geoaccumulation index (I_{geo}) values explained that only Zn, Pb, Cd and Cr can be considered as moderate to extreme pollutants both in surface and sub-surface sediments.

Key words: Sfax coast, Tunisia, Heavy metals, Sediments, Chemometric methods

INTRODUCTION

Man-made activities are responsible for a major decline of the world's biological diversity, and the problem is so critical that combined human impacts could have accelerated present extinction rates to 1000-10,000 times the natural rate (Lovejoy, 1997). In the oceans, the risk to marine life comes in various forms, such as overexploitation and harvesting, dumping of waste, pollution, alien species, land reclamation, dredging and global climate change (Beatley, 1991; National Research Council, 1995; Irish, K.E. and Norse, E.A.,1996. Ormond *et al.,* 1997; Tickel, 1997; Snelgrove, 1999). Marine sediments result from accumulated autochthonous organic and mineral compounds derived from biological productivity and continental materials supplied through aeolian and alluvial processes (Libes, 1992; Emelyanov, 2001).

Sediments in coastal zones are normally dominated by terrigenous particles due to the important supply of continental material. However, coastal sediments in urban and industrial areas are mainly menaced by several man-made discharges enriched with organic matter, nutriments and heavy metals. Such areas are characterized by high accumulation rates. These rates together with hypoxic bottom environment favour the preservation of biogenic debris within the sediments. This situation combines with the bottom environment's hydrodynamic conditions, the sedimentary composition (mineral and organic matter content) and grain size, to control the behavior of many chemical substances, including heavy metals (Lallier-Verges and Albe´ric, 1990; Murray and Kuivila, 1990; Dean *et al.,* 1997; Keil and Cowie, 1999).

Heavy metals are introduced in aquatic environments by atmospheric deposition, weathering and erosion of the geological matrix or through anthropogenic sources (Molisani *et al.,* 1999; Yu *et al.,* 2011; Young Do and Park, 2011; Houda *et al.,* 2011; Ajibola and Lapido, 2011). In these environments, sediments act as an important reservoir for metals (Montouris *et al.,* 2002; Nasrabadi *et al.,* 2010; Alimohammad Kalhori *et al.,* 2012). Because of their

toxicity, persistence and potential to bioaccumulate, trace elements are among the most serious pollutants within the natural environment and can be a serious threat to ecosystems at a global scale (Tam and Wong, 2000; Ghaderi *et al.,* 2012; Haruna *et al.,* 2011). Trace elements introduced into aquatic environments are distributed among water-soluble species, colloids, and suspended and sedimentary solid phases (Filgueiras *et al.,* 2004) which are ultimately adsorbed and incorporated into sediments. Sediments are considered as a compartment with a large capacity for pollutants (Salomons and Stigliani, 1995) and therefore represent the most concentrated physical pool of trace metals (Pourang, 1996). Organic matter in coastal sediments having a strong binding capacity for metal cations, is capable of adsorbing and retaining a significant amount of atmospherically deposited trace elements (Perkins *et al.,* 2000) as well as sequestering large quantities of environmental contaminants (Dinges, 1982; Gray *et al.,* 2000) via various physical, chemical, and biological processes. Trace elements in sediments pose a serious threat to the native plants and animals (Perkins *et al.,* 2000).

The purpose of this study is to assess the heavy metal status of the surface and sub-surface sediments from the northern coast of Sfax (Tunisia) and prepare distribution maps of concentrations and enrichment factors of copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), chromium (Cr), iron (Fe) and Aluminium (Al) using GIS approach coupled with chemometric methods.

MATERIALS & METHODS

In 2006, 33 top 1-5 cm surface and 45-50 cm sub-surface sediment samples were collected from the northern coast of Sfax. Sampling was performed in nearly spacing sites (100 m) through three radials perpendicular to the coastline (Fig. 1). Sampling sites were located by a Global Positioning System (GPS) technology and samples were collected through 33 sites. Sediment samples were removed with an acid washed spatula to prevent contamination. Immediately after collection, samples were placed in polyethylene bags, refrigerated, and transported to the laboratory (ASTM, 2001). Samples were dried in an oven at 60 °C for 4 days, lightly ground in an agate mortar for homogenization, sieved to pass <63 ìm (metals are most often associated with small grains) (Morillo *et al.,* 2004). The dry samples were digested with HNO_3–H_2O_2–HCl according to US EPA method 3050B (US EPA, 1999) and the digestate made up to volume with Milli-Q deionized (DI) water (18 MÙ). Afterwards, the digests were analyzed for the amount of Cu, Zn, Pb, Cd, Cr, Mn, Fe and Al by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in triplicate (US EPA,

1996 US EPA, 1996. SW-846 reference methodology: Method 6010B. Inductively Coupled Plasma-Atomic Emission Spectrometry, Washington, DC.US EPA, 1996). The instrument is equipped with a cross flow nebulizer and a glass spray chamber. The detection limits (mg/l) were 0.004 for Cu, 0.007 for Zn, 0.035 for Pb, 0.007 for Cd, 0.006 for Cr, 0.0002 for Mn, 0.013 for Fe and 0.0003 for Al. Analytical procedures are described in details (Pekey *et al.,* 2004). Data reported in this study are calculated as dry weight.

RESULTS & DISCUSSION

Medians, standard deviations, and ranges of Cu, Zn, Pb, Cd, Cr, Mn, Fe and Al concentrations in studied surface and sub-surface sediments are summarized in Table 1. Their horizontal distribution patterns depicted through the interpolation of elemental data by using Arc View GIS 3.2 showed different spatial repartitions (Figs 2 and 3). All maxima values are located at the proximity of the coastline downstream two principal anthropogenic effluents (Oued Ezzit and PK4) and also at the proximity of the phosphogypsium deposit resulting from old processing plants of NPK ''phosphates''. Their significant extension with water depth is probably influenced by the coastal hydrodynamic conditions. At both surface and sub-surface sediments, maximum concentrations were shown in zones characterized by muddy facies enriched with organic matter (TOC varying between 5 and 8 % in superficial sediments and between 1 and 3 % in sub-surface sediments) (Illou, 1999 and Serbaji, 2000). The nearly superposition of surface and sub-surface maxima concentrations of Cu, Zn, Pb, Cd, Cr could testify the importance of their mobility until the surface. The computed enrichment rates of heavy metals (by equation 1) in selected surface and sub-surface sediments showed that the surface area is more enriched in terms Cu, Zn, Pb, Cd, Cr (Fig. 4). In such area, these metals are characterized by higher rates varied between 30 and 80%.

$$T(\%) = \frac{C(X)^{\text{surface area}} - C(X)^{\text{sub-surface area}}}{C(X)^{\text{surface area}}} \times 100$$

(1) (Yaboue 1991)

Where:

$T(\%)$: Enrichment rate of sediments for surface area with respect to that of sub-surface area, fixed as a reference;

$C(X)^{\text{surface area}}$: Concentration of a selected heavy metal (X) in the sediment sampled in the surface area;
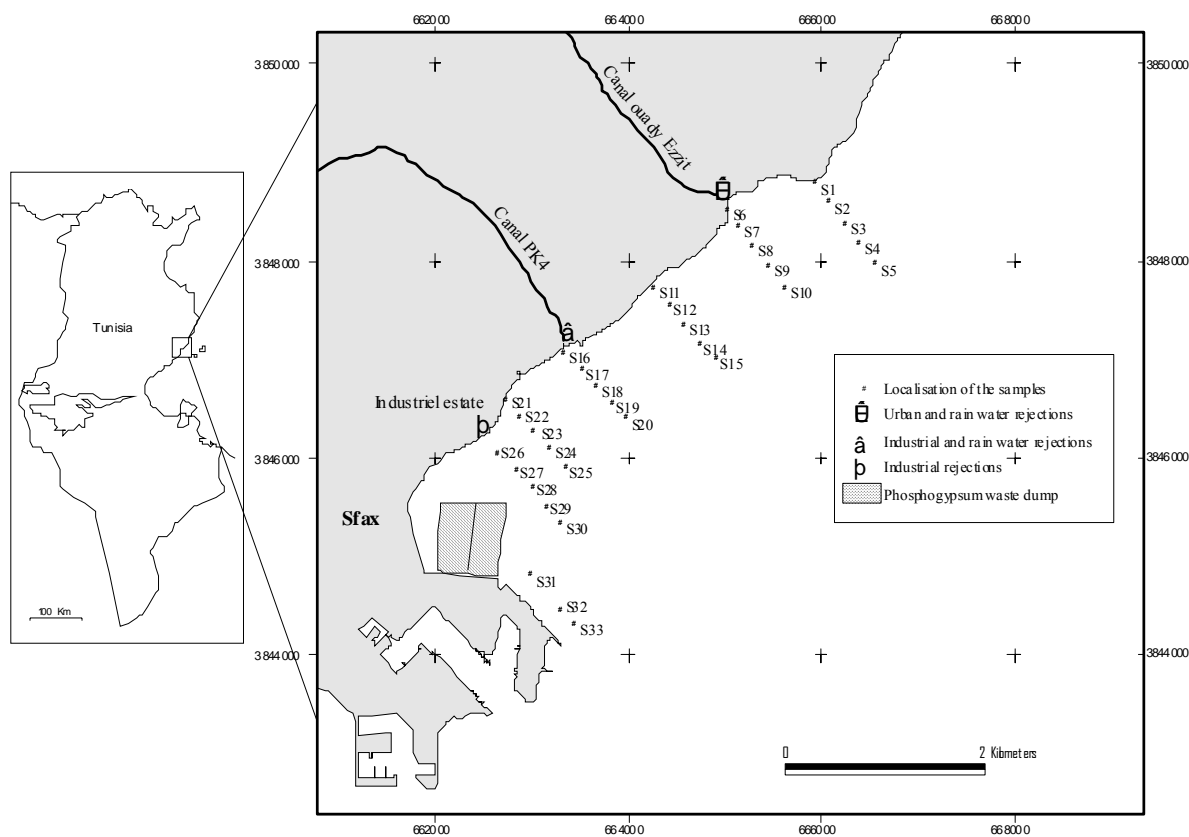
Fig. 1. Location of stations in the northern coast of Sfax

Table 1. Medians, standard deviations and ranges of heavy metals (in mg/kg dry weight) in surface and sub-surface marine sediments from northern coast of Sfax

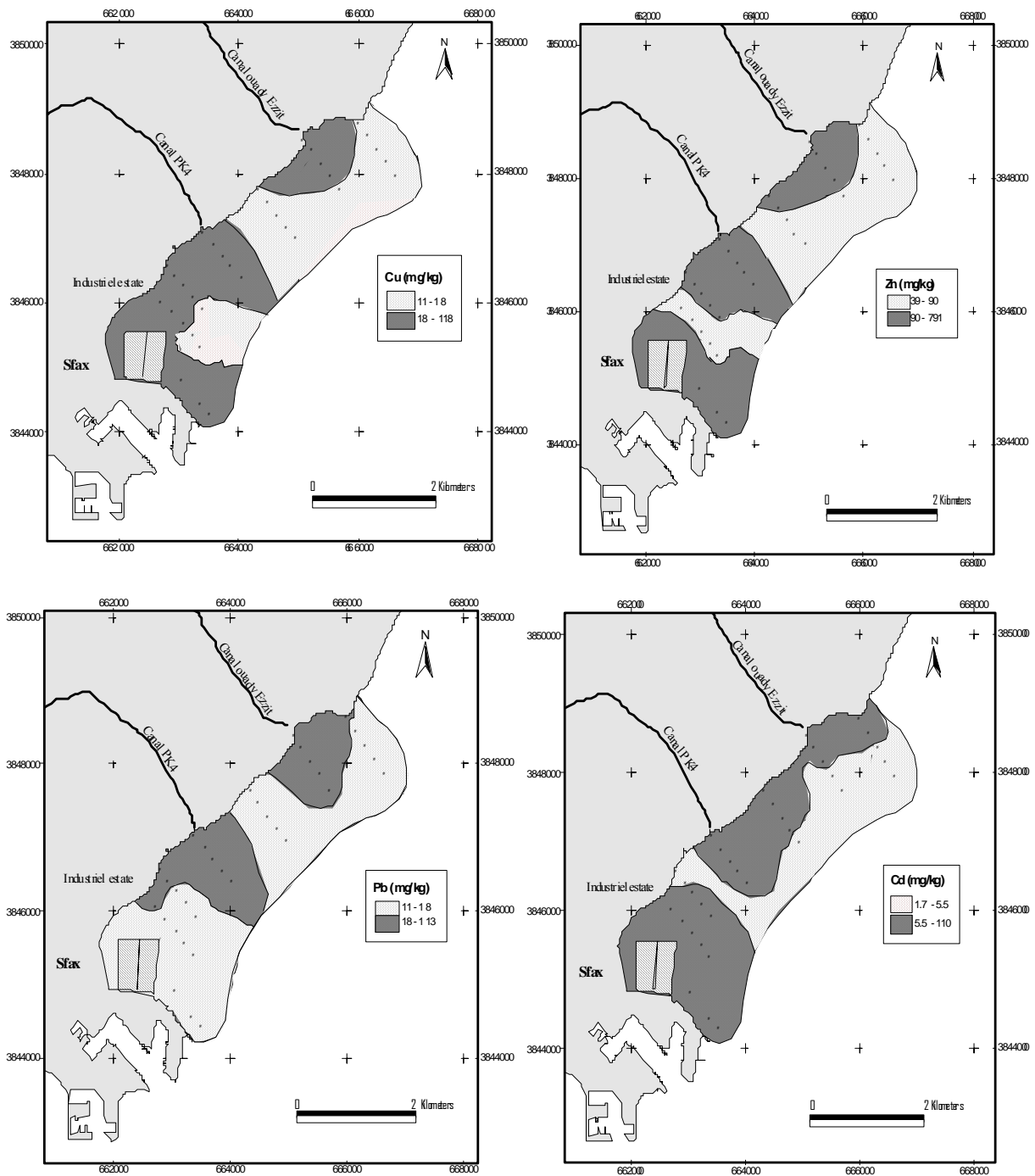| Study area	Heavy metal	Median	SD	Range
Surface	Cu	19	22.74	11-118
	Zn	106	156.79	45-791
	Pb	20	23.52	11-113
	Cd	7,75	20.65	1,7-110
	Cr	56	79.43	26- 467
	Mn	132.5	45.94	3-199
	Fe	15190	4974.42	390-21920
	Al	38030	12016.71	1360-50240
Sub-surface	Cu	13.9	3.96	7-24.1
	Zn	47	96.09	17- 495
	Pb	19.5	14.67	10-78
	Cd	2.1	4.93	1-26.7
	Cr	41	11.85	26- 69
	Mn	123.5	46.76	5-299
	Fe	15571	5639.02	981-28359
	Al	36655	11111.22	4453-58406

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Fig. 2. Distribution maps of Cu, Zn, Pb and Cd concentrations in surface marine sediments of the northern coast of Sfax

$C(X)^{sub-surface\ aera}$: Concentration of the selected

heavy metal (X) in the sediment sampled in the sub-surface area;

Due to the absence of Tunisian guidelines for coastal sediments, Cu, Zn, Pb, Cd and Cr concentrations were compared with the China sediment quality assessment guidelines (i.e., the threshold effect levels or TEL) (Junhong *et al.,* 2011). The values of TEL for each metal species and the number of samples exceeding TEL are also presented in Table 2. The TEL, as defined by MacDonald et al. (1996), is the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries. Within this range, concentrations of sediment-
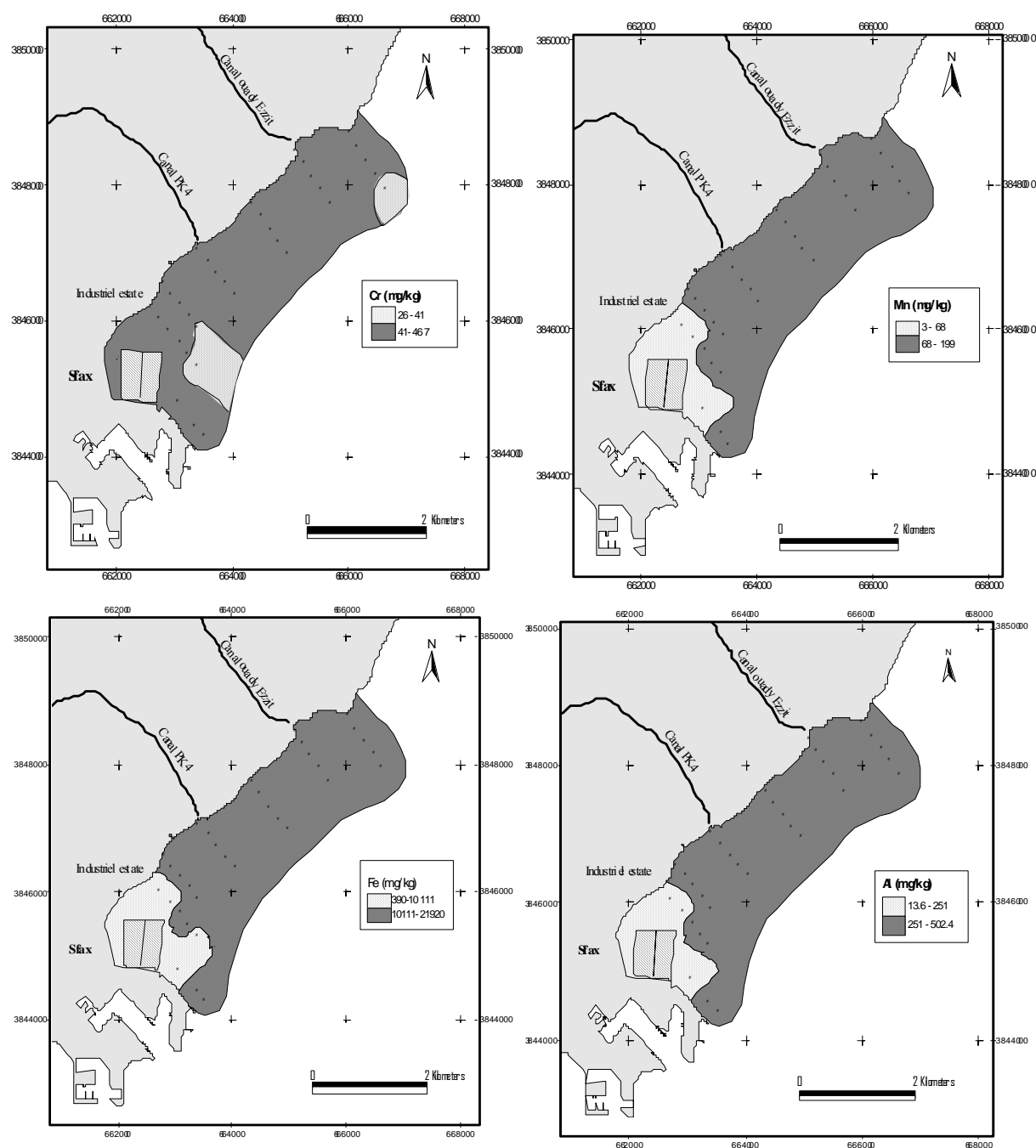
Fig. 2. (continued)- Distribution maps of Cr, Mn, Fe and Al concentrations in surface marine sediments of the northern coast of Sfax

associated contaminants are not considered to represent significant hazards to aquatic organisms. The TEL can be calculated by the following equation (2):

$$TEL = \sqrt{(EDS-L) \times (NEDS-M)} \qquad (2)$$

Where (EDS-L) is the 15th percentile concentration in the effect data set and (NEDS-M) is the 50th percentile concentration in the no effect data set. An elaborate description of the numerical sediment quality

assessment guidelines and the TEL development can be found in MacDonald (1994) and Macdonald et al. (1996).

As shown in Table 2, metal concentrations of aforementioned metals exceeded the TEL values for both surface and sub-surface sediment samples. Moreover, it was revealed that approximately 61%, 42%, 24%, 100%, 52% of the sediment samples for Cu, Zn,
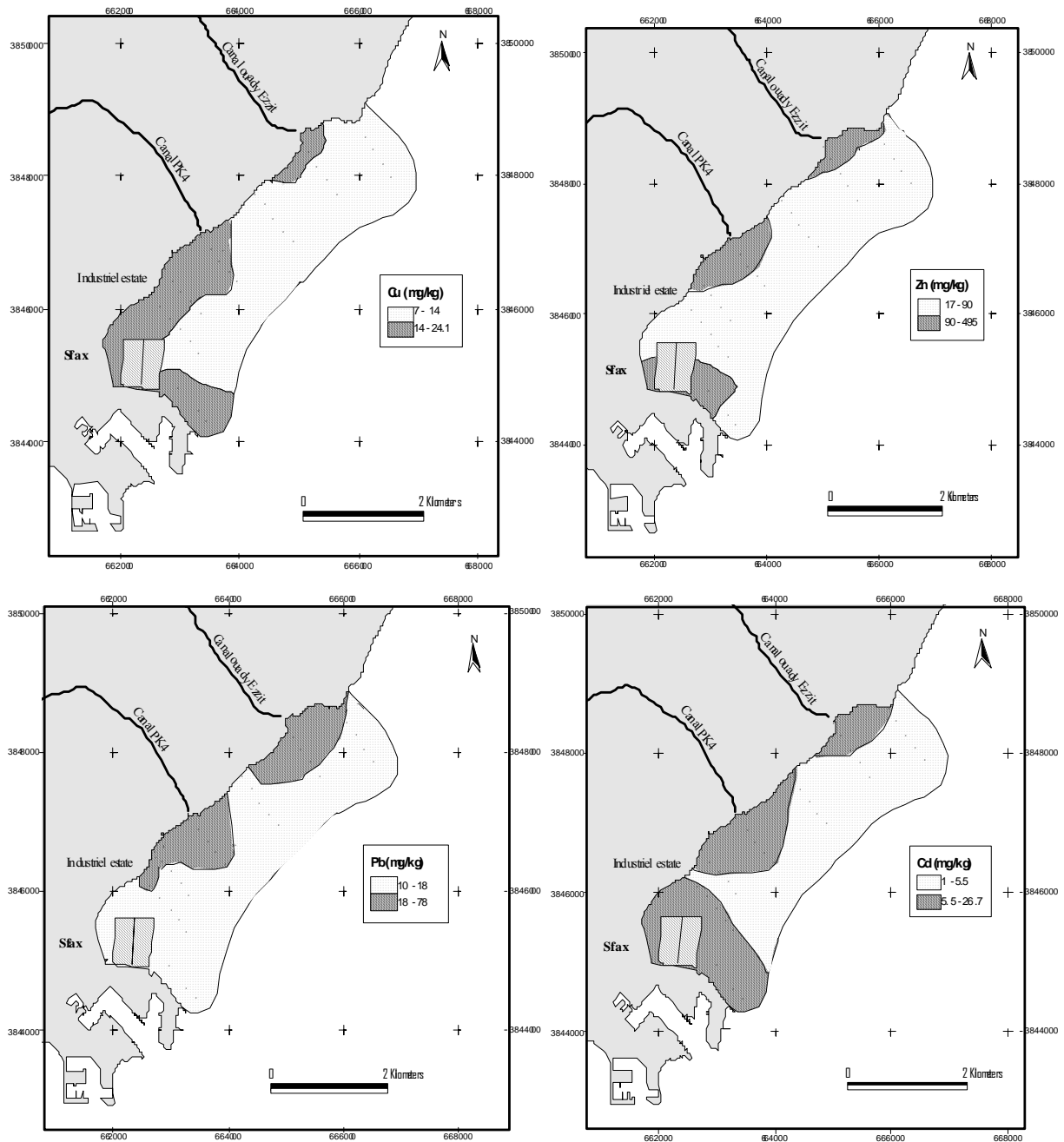
Fig. 3. Distribution maps of Cu, Zn, Pb and Cd concentrations in sub-surface marine sediments of the northern coast of Sfax

Pb, Cd and Cr, respectively, had concentrations exceeding the TEL values for superficial sediments (Fig. 5). Similar results, but with somewhat lower percentages, were obtained for sub-surface sediments. That is, approximately 15%, 12%, 9%, 85 and 21% of the sediment samples for Cu, Zn, Pb, Cd and Cr, respectively, had concentrations exceeding the TEL values (Fig. 5). These data indicated that heavy metal sediment pollution occurred primarily at the surface

sediments which are more polluted than the sub-surface sediments.

The results show that the metal contamination found in the northern 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), Geoaccumulation index (I_{geo}) and Principal Component Analysis (PCA) were used.
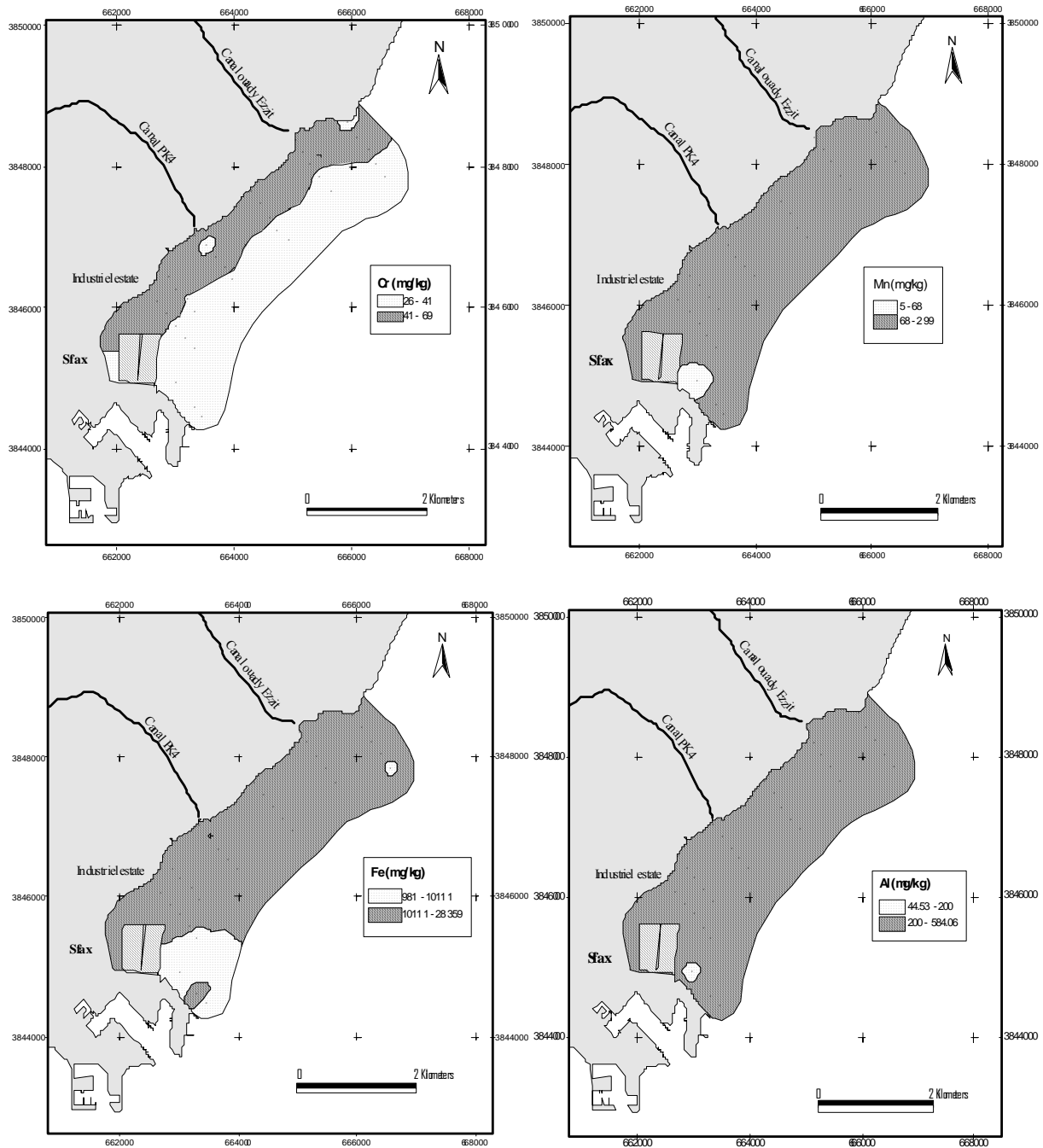
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Fig. 3. (continued)- Distribution maps of Cr, Mn, Fe and Al concentrations in sub-surface marine sediments of the northern coast of Sfax

The composition of sediments would be significantly influenced by contributions from various man-made sources (Atgin *et al.,* 2000). Generally, enrichment factor (EF) values less than 10 are not considered significant, since such small enrichments may arise from differences in the composition of local soil material and reference soil used in EF calculations. An enrichment factor (EF) technique is used in the area of atmospheric aerosols (Güllü *et al.,* 1998 and Odabaşi *et al.,* 2002), sediments (Szefer *et al.,* 1999, Rubio *et al.,*

2000, Selvaraj *et al.,* 2004), soil (Obiajunwa *et al.,* 2002 and Bergamaschi *et al.,* 2002) and solid wastes (Obiajunwa *et al.,* 2002) to determine the degree of modification in the composition.

Using the data obtained in the analysis, the EF of all the elements can be calculated by the following equation (3):

$$EF = \frac{\left(C_x/C_{Al}\right)_{sample}}{\left(C_x/C_{Al}\right)_{reference}} \qquad (3)$$
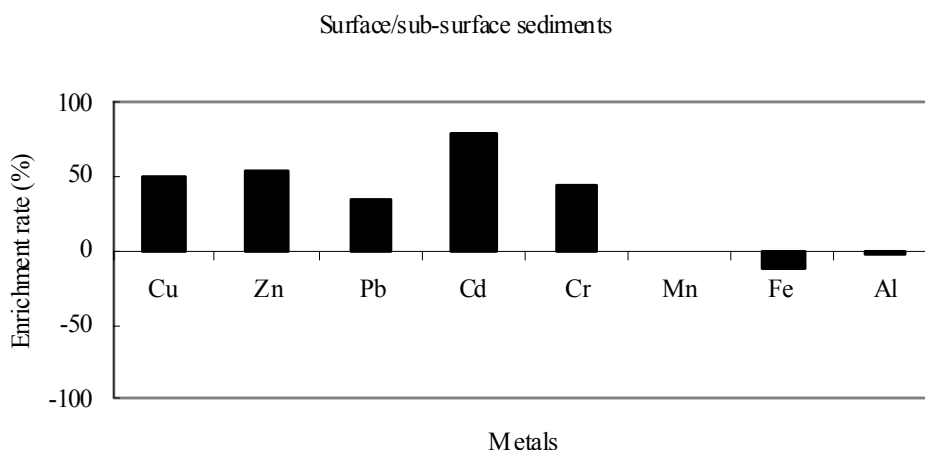
Surface/sub-surface sediments

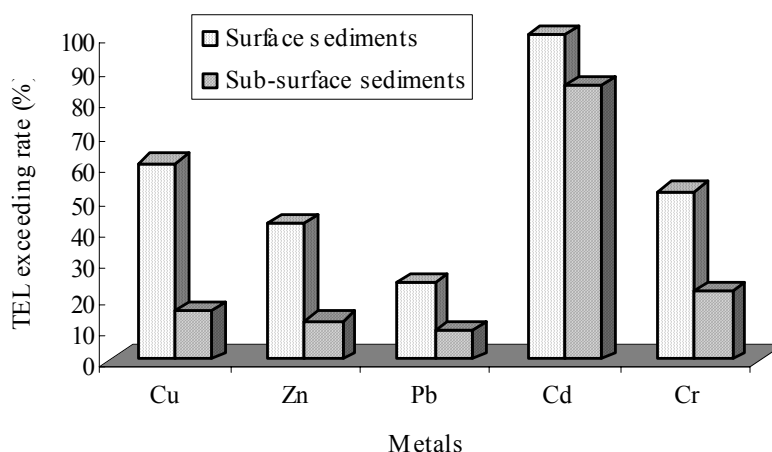**Fig. 4. Inter-level enrichment rate for selected heavy metals**

Fig. 5. TEL exceeding rate

where $(C_x/C_{Al})_{sample}$ is the ratio of concentration of the element being tested (C_x) to that of Al (C_{Al}) in the sediment sample and $(C_x/C_{Al})_{refrence}$ is the same ratio in unpolluted reference baseline.

Elemental concentrations can be compared with reported natural abundances of metals in soils and/or crustal rocks, by normalizing against geochemical markers (e.g., Al, Fe, Cs, Rb, Li, Si, total organic carbon, grain size) of the predominant natural mineralogical phases (Ackerman, 1980; Loring, 1990; Loring *et al.,* 1995). These markers can also compensate for constituent variability in sediments resulting from granulometric variations. Aluminium is a conservative element and a major constituent of clay minerals and it has been used successfully by several researchers. Several authors such as Vinogradov (1959), Mason (1966), Wedepohl (1968) and Taylor (1972) have also used the same to provide reference concentrations. In this study, Mason's soil composition (1966) was used

as the reference and Al was used as normalizing element.

The computed metal enrichment factors (EFs) in the studied surface sediments (Table 3) showed that the EF of Cu ranges from 0.42 to 25, EF of Zn from 1.6 to 192.7, EF of Pb from 1.6 to 22.9, EF of Cd from 35.3 to 17390.4, EF of Cr from 0.1 to 26, EF of Mn from 1.1 to 4.2 and EF of Fe from 0.4 to 0.8. At the sub-surface sediments, they showed that the EF of Cu ranges from 0.2 to 15.4, EF of Zn from 0.9 to 80.8, EF of Pb from 1.7 to 11, EF of Cd from 15.8 to 4431.6, EF of Cr from 0.1 to 17, EF of Mn from 0.1 to 0.5 and EF of Fe from 0.4 to 0.9 (Table 3). It appears that the majority of analyzed metals (except for Mn and Fe) present enrichment factor values greater than 10, both in the surface and sub-surface levels, indicating a significant contribution of man made-source effects.

In order to determine the degree of metal contamination in sediments, another criterion based

on the geoaccumulation index (I_{geo}) was adopted. It was originally defined by Müller (1981). It is based on the comparison of current concentrations with Mason's soil and can be calculated by the following equation (4):

$$I_{geo} = Log_2(\frac{C_n}{1.5B_n}) \qquad (4)$$

Where C_n is the measured concentration of the examined metal (n) in the sediment and B_n is the Mason's soil 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 4). It appears that Zn, Pb, Cd and Cr can be considered as

moderate to extreme pollutants both in surface and sub-surface sediments. A particular behaviour concerned Cu, which is demonstrated by its calculated I_{geo} as a moderate pollutant.

Results of the descriptive study presented above were refined by a principal component analysis (PCA). It is applied to all data (elementary concentrations), using the ITCF statistical software package (STATIT-CF 1987). It 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 0.35 after a test of student (n=33). The significant correlations between selected parameters (variables) and the components represent approximately 89 and 85 % of the total variance for

Table 2. Trace element concentrations (mg/kg dry weight) compared to marine Sediment Quality Standards

	Class	Cu	Zn	Pb	Cd	Cr	Reference
Our study							
Superficial sediments		11-118	45-791	11-1136	1.7-110	26-467	This study
Sub-surface sediments		7-54.1	17-495	10-78	1-26.7	26-69	
China sediment quality assessment guidelines	TEL	18.7	124	30.2	0.68	52.3	Junhong et al. (2011)
Number of surface samples exceeding TEL/Total number of samples		20/33	14/33	8/33	33/33	17/33	
Number of sub-surface samples exceeding TEL/Total number of samples		5/33	4/33	3/33	28/33	7/33	

Table 3. Metal enrichment factors in the surface and sub-surface marine sediments from northern coast of Sfax

Study area	Heavy metal	Median	SD	Range
Surface	Cu	0.78	4.90	0.42-24.99
	Zn	3.57	46.31	1.60-192.66
	Pb	3.25	4.36	1.64-22.92
	Cd	134.01	3995.73	35.30-17390.37
	Cr	0.45	4.37	0.11-26.3
	Mn	2.81	0.61	1.10-4.16
	Fe	0.64	0.06	0.46-0.80
	Cu	0.58	0.87	0.25-15.37
	Zn	1.27	14.15	0.91-80.85
	Pb	2.85	2.19	1.71-10.66
Sub-surface	Cd	41.57	843.17	15.84-4431.55
	Cr	0.21	2.98	0.1-17.2
	Mn	0.28	0.08	0.09-0.49
	Fe	0.67	0.09	0.35-0.87

Table 4. Geoaccumulation index (I_{geo}) values of heavy metals in the surface and sub-surface marine sediments from northern coast of Sfax

I_{geo} value	Class	Quality of sediment	Study area	Heavy metal	I_{geo} range	Quality of studied sediment
≤0	0	Unpolluted		Cu	-2.91→ 0.52	From unpolluted to moderately polluted
0-1	1	From unpolluted to moderately polluted		Zn	-1.22→ 2.91	From unpolluted to strongly polluted
1-2	2	Moderately polluted		Pb	-0.83→ 2.53	From unpolluted to strongly polluted
2-3	3	From moderately to strongly polluted	Surface	Cd	3.36→ 9.38	From strongly to extremely polluted
3-4	4	Strongly polluted		Cr	-2.53→ 1.64	From unpolluted to moderately polluted
4-5	5	From strongly to extremely polluted		Mn	-12.21→ -6.16	Unpolluted
>5	6	Extremely polluted		Fe	-7.59→ -1.77	Unpolluted
				Cu	-3.55→ 0.37	From unpolluted to moderately polluted
				Zn	-2.62→ 2.23	From unpolluted to strongly polluted
			Sub-surface	Pb	-0,96→ 2	From unpolluted to moderately polluted
				Cd	2,59→ 7.33	From strongly to extremely polluted
				Cr	-2,52→1.12	From unpolluted to moderately polluted
				Mn	-11,47→-5.57	Unpolluted
				Fe	-6,25→ -1.40	Unpolluted

surface and sub-surface data, respectively. For surface data, the first, second and third PCs explained 43, 35 and 11% of the total variance respectively. For sub-surface data, they described 51, 21 and 13% of the total variance respectively.

The projection over the (1x2) factorial plane of both surface and sub-surface data (presenting 78 and 72 % of inertia, respectively) shows similar repartitions with two distinct groups (Fig. 6):

- The first group (G_1), which is negatively displayed over axis 1, is representative of Al (selected as natural tracer), Fe and Mn. It is representative of the natural component;

- The second group (G_2), which is positively displayed over axis 2, is articulated around Zn, Cd, Cu, Cr and Pb. They present among each other highly significant positive correlation coefficients. These metals which did not show any correlations with metals of the first group imply the significant impact of man-made sources. The estimated contributions of these sources (based on equations 5 to 7; Azri *et al.,* 2009) in terms of sediment's enrichment by aforementioned metals showed very high rates exceeding 98 % (Table 5).

$$\text{Anth}(X)\,(\%) = \frac{[X]_{sample}^{anthropogenic}}{[X]_{sample}^{measured}}\, x100 \quad (5)$$

$$[X]_{sample}^{anthropogenic} = [X]_{sample}^{measured} - [X]_{sample}^{crust} \quad (6)$$

$$[X]_{sample}^{crust} = ([X]\times[Al]^{-1})_{crust} \times [Al]_{sample}^{measured} \quad (7)$$

Were

$\text{Anth}(X)(\%)$: Anthropogenic contribution for the metal (X) (%);

$[X]_{sample}^{anthropogenic}$: Estimated concentration of the heavy metal (X) in the sediment sample derived from man-made sources (anthropogenic component);

$[X]_{sample}^{measured}$: Actual concentration of the heavy metal (X) in the sediment sample;

$[X]_{sample}^{crust}$: Estimated concentration of the heavy metal (X) in the sediment sample derived from the crust (natural component);
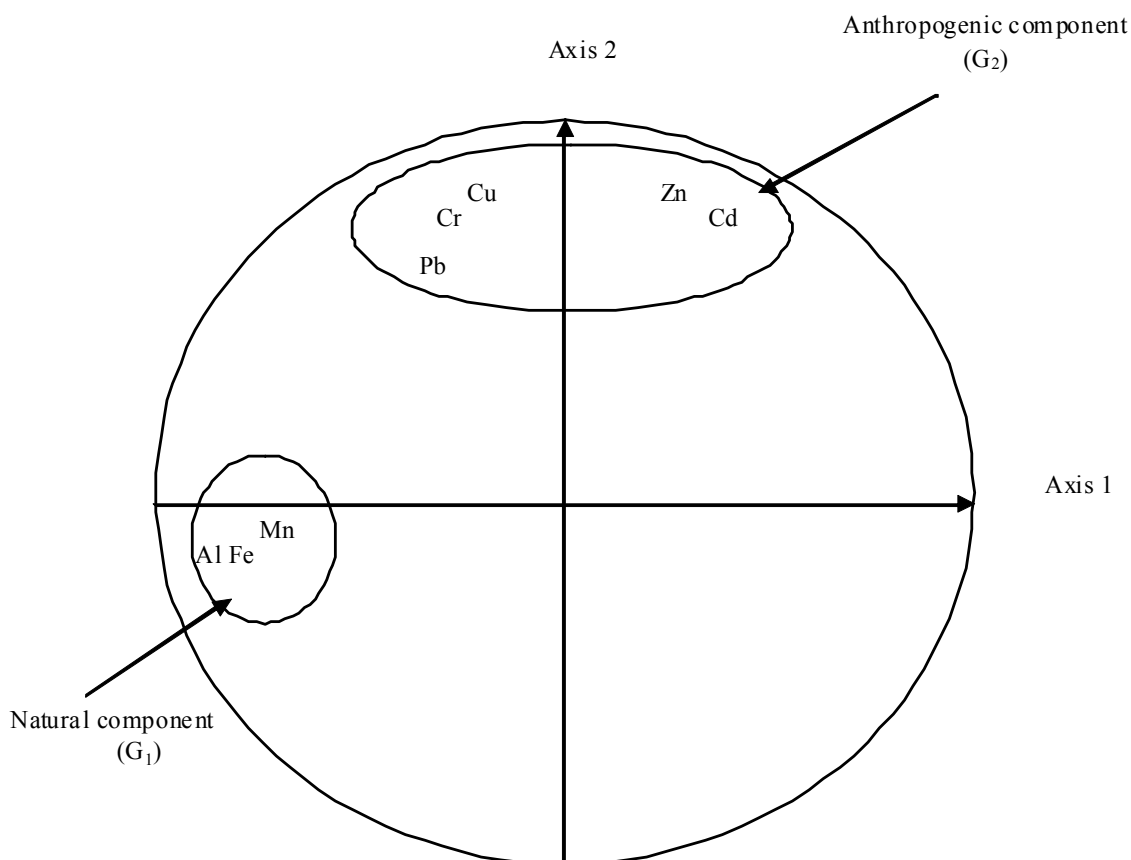

Fig. 6. Projection of variables (metal concentrations) in the (1×2) factorial plane

Table 5. Estimated anthropogenic contributions of heavy metals

	Study area	Cu	Zn	Pb	Cd	Cr
Estimated anthropogenic concentration (mg/kg)	Surface	26.642	163.759	26.541	14.499	78.759
	Sub-surface	13.485	76.116	17.488	2.999	42.803
Actual mean concentration (mg/kg)	Surface	26.879	164.061	26.597	15	78.879
	Sub-surface	13.727	76.424	17.545	3	43.242
Anthropogenic contribution (%)	Surface	99.11	99.82	99.79	99.99	99.85
	Sub-surface	98.24	99.6	99.67	99.97	98.98

$[Al]_{sample}^{measured}$: Actual concentration of Al in the sediment sample;

$([X])_{crust}$: Concentration of the heavy metal (X) in the Mason's soil composition;

$([Al])_{crust}$: Concentration of Al in the Mason's soil composition (reference)

CONCLUSION

The geochemical analysis of selected heavy metals (Cu, Zn, Pb, Cd, Cr, Mn, Fe and Al) in the surface and sub-surface sediments in the northern coast of Sfax showed a wide spatial variation of the concentration values and significant inter-level enrichments, especially in terms of Cu, Zn, Pb, Cd and Cr. Their concentrations exceeding the threshold effect levels (TEL) indicated that heavy metal sediment contamination menaced not only the surface sediments but also the sub-surface sediments. Furthermore, the nearly superposition of surface and sub-surface maxima concentrations of Cu, Zn, Pb, Cd, Cr could testify the importance of their mobility until the surface. Enrichment factors (EFs) and Principal Component Analysis (PCA) related to both surface and sub-surface data revealed two distinct data groups. The first group contained Cu, Zn, Pb, Cd and Cr influenced by man-made sources and the second group contained Mn, Fe and Al originated from rock weathering. The estimated contributions of man-made sources in terms of sediment's enrichment by Cu, Zn, Pb, Cd and Cr showed very high rates exceeding 98 %. The computation of the geoaccumulation index (I_{geo}) showed that Zn, Pb, Cd and Cr can be considered as moderate to extreme pollutants both in surface and sub-surface sediments. A particular behaviour concerned Cu, which is demonstrated, by its calculated I_{geo}, as a moderate pollutant. Mn and Fe exhibit I_{geo} values <0 everywhere in the two study levels.

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