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ABSTRACT

Over several decades, the mouth of the Mejerda River (northern Tunisia) has received large amounts of mining tailings mainly containing Pb, Zn and Ba. We have measured the concentrations of major and trace elements (Al, Ti, P, K, Mg, Na, Ca, S, Fe, Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, I, Ba and Pb) in three different fractions of 45 surficial sediments using wavelength dispersive X-ray fluorescence. The size distribution of fine particles (<2 µm, 2–20 µm, 20–63 µm) revealed that clay and silt compounds were predominant (75–95%) in the deeper estuarine region. These condensed clay phases were mainly dioctahedral smectite, illite and kaolinite. The total organic carbon (TOC) concentration varies from 0.08 to 1.37 %. The C:N ratio varies from 1 to 17 indicating that the organic matter has a mixed marine and continental origin principal component analysis was used to determine the associations of trace elements with organic and/or inorganic phases of the sediment fractions. The correlations of Fe_2O_3, MnO_2 and P_2O_5 with trace elements showed that amorphous Fe and Mn were the most active scavengers of dissolved metals from the Mejerda River. Cluster analysis clearly distinguished local trace element accumulations according to grain size fractions (< 2 µm and 2–20 µm) near the Ghar el Melh Lagoon and the Mejerda River.

Keywords: marine sediments, Gulf of Tunis, trace element, grain size particle, pollution

INTRODUCTION

Most of the metal discharged into estuarine environments is the result of human activity, leading to the formation of sediments that are large repositories of potentially toxic compounds. Over the past decade research into near shore contamination of the Mediterranean Sea by trace metals (*e.g.*, Rubio *et al., 2000*; Buccolieri *et al., 2006*; Violintzis *et al., 2009*) has reported extensive accumulation of suspended particles in surface sediments caused by man-made erosion from continental sediments. For example, Martínez-Sánchez *et al.* (2008) discovered that millions of tons of mine tailings had been dumped into Portman Bay (Spain) over a long period.

In north-western Tunisia, the Mejerda River is the main source of continental water and sediment discharge into the Gulf of Tunis (Figure 1). The Mejerda River originates in eastern Algeria and has a catchment area of approximately 25,000 km², covering most of northern Tunisia. Its total annual discharge is around 1100 Mm³ yr⁻¹, with a total sediment load of 2106 tons yr⁻¹. The Lake of Tunis and Ghar El Melah Lagoon are two large sheets of water communicating with the Gulf.

Because of its proximity to lead and zinc mines, the catchment area of the Mejerda River has been subject to multiple sources of trace element contamination for several decades. Industrial activity has produced considerable amounts of residues in waste dumps in the vicinity of the river. For example, previous researchers have pointed out that the discharge of mining rejects in this area constitutes a potential source of contamination (Ben Hamza, 1994; Jdid *et al.* 1999; Moldenhauer *et al., 2008*; Mlayah *et al., 2009*).

Quantitative analysis of heavy metals in coastal environments provides useful information for determination of their distribution in near shore sediments. The concentrations of trace element are usually controlled by a variety of

Figure 1 Catchment area of Mejerda River and deleta outflow.

physical and chemical factors (Villaescusa-Celaya *et al., 2*000; Angelidis 2005) such as grain particle size distribution, composition, particle transport, mineralogical composition, oxidation/reduction reactions and adsorption/desorption processes. As trace elements and organic carbon are usually associated with fine-grained sediments because of their high surface to volume ratios and adsorption capacities (Burdige, 2006), <63 μm particles are usually selected for control of sediment contamination (Szava-Kovats, 2008). Grain size is an important factor in considering the variability of sediment-trace element concentrations in time and space (Forstner and Wittmann, 1981; Horowitz and Elrick, 1986; Cauwet, 1987, Ujevic *et al*., 2000). As grain size decreases, trace element concentrations increase, reflecting changes in the physical and chemical factors affecting them (Forstner and Wittmann, 1981; Horowitz, 1985).

Sediment dynamics along a littoral zone are usually closely dependent on the direction and intensity of littoral currents generated by winds, waves and tides. At the mouth of the Mejerda River, frequent strong NW winds generate weak anticlockwise littoral currents in the middle of the gulf, thereby controlling suspended matter and surface sediment accumulation (Ben Charrada *et al*., 1997). In the past, the Mejerda River discharged into the Ghar El Melh lagoon, which is connected to the gulf of Tunis, but towards the end of the nineteenth century its course shifted to a channel south of the lagoon during a major flood (Ayache *et al*., 2009). Several decades later, the Mejerda River mouth moved to its current position 10 km south of the lagoon. Previous studies

on the gulf of Tunis (over 30 m deep) detected accumulation areas for Pb, Cu, Zn and Fe near the Mejerda River and in the central sector of the gulf (Essonni, 1998; Added *et al*., 2003; Ennouri *et al*., 2010). The distribution of these element shows that they originated in the Mejerda river. In this study, we took sediment samples from depths of 6–70 metres in order to better understand trace element accumulation.

The objectives of this study are (1) to analyse the distribution patterns of minerals, trace elements and organic carbon in the mouth of the Mejerda River (Gulf of Tunis); (2) to outline the extent of metal accumulation in sediment and the consequences of its contamination in this area.

MATERIALS AND METHODS

In September 2008, on board the oceanographic vessel "Hannibal", 52 surface sediment samples were collected from the distal end of the Mejerda River (Figures 2 and 3) (about 8 km from the coast and at a depth of 75 m). A Van Veen bottom grab (2000 cm²) was used to sample the upper 15–18 cm of the sediments. The bulk material collected was placed in polyethylene jars and immediately frozen at –4°C for future analysis.

Mineralogical analyses were performed by X-ray diffraction (XRD) for the bulk sediment powders in the <2 μm, 2–20 μm and 20–63 μm size ranges, using a Philips PW 1800 diffractometer equipped with automatic slit, CuKα
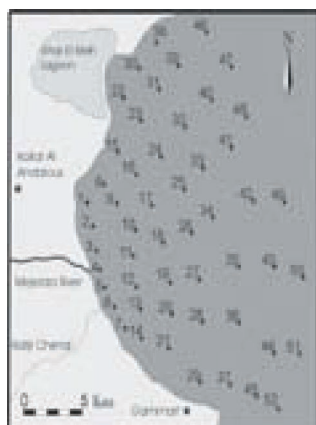
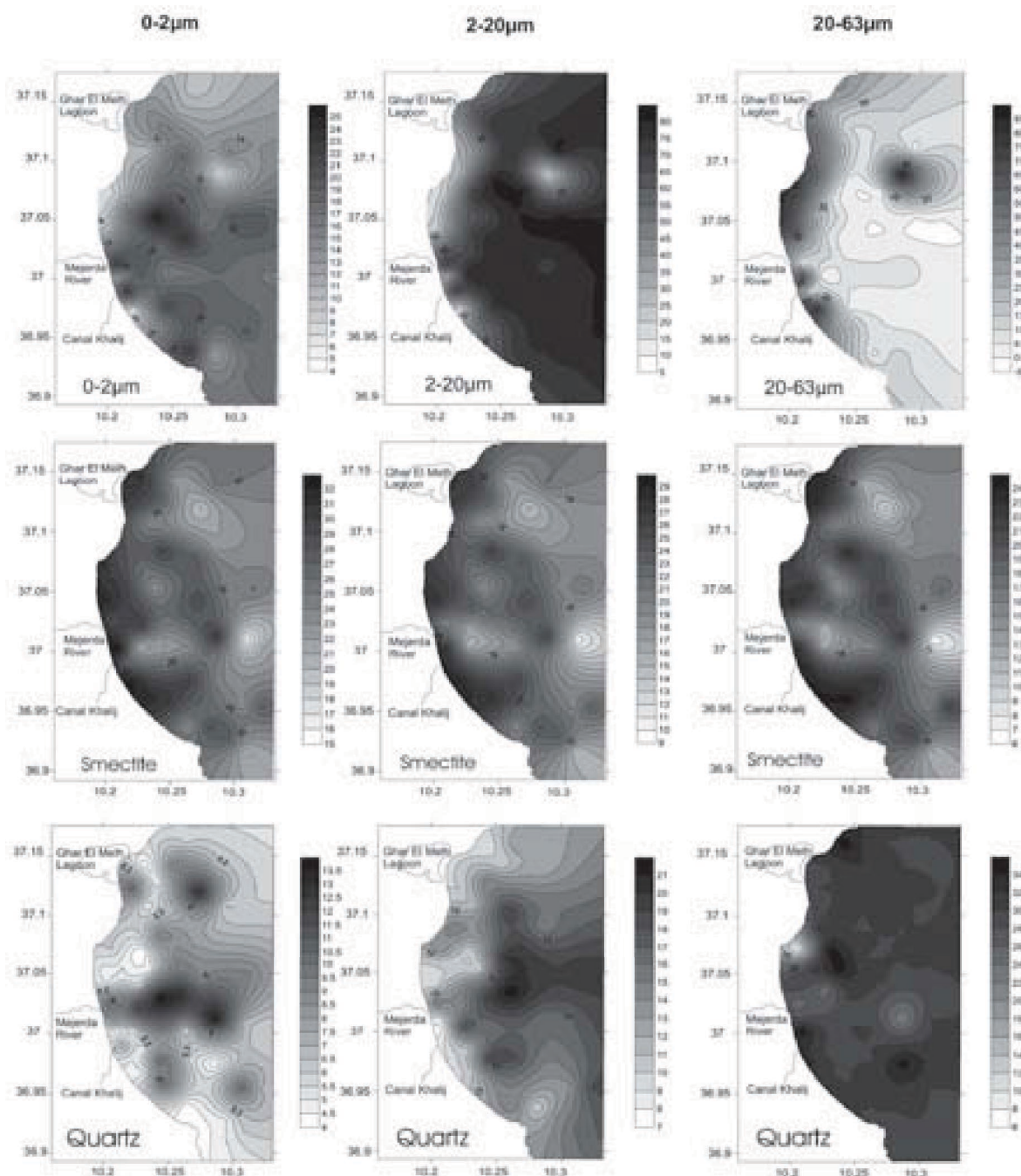**Figure 2** Sampling sites of surface sediment in northern Tunisia

Figure 3 Granulometry (0–2 µm, 2–20 µm, 20–63 µm) and mineralogical distribution (smectite and quartz)

radiation, Ni filter and scan speed of 2º/minute. Quantification of the three phases was carried out by the standard method of area measurement of peaks and reflective power (*cf.* Mellinger, 1979; Pevear and Mumpton, 1989).

For the analysis of the < 2 µm, 2–20 µm and 20–63 µm particles, each bulk sample was de-carbonated with HCl 1 N and the particles separated by settling in a water column. The samples were then mounted on glass slides to monitor the X-ray patterns in natural conditions (air-dried), and after ethylene glycol and heat (550ºC) treatments, semi-quantitative analysis was performed following Biscaye (1965).

Total organic carbon (TOC) and total nitrogen (TN) were measured by a Perkin-Elmer 2400 CHN analyser. The subsamples for TOC were decarbonated using 1 M HCl and dried at 60 °C. Oxygen was used for combustion of sample materials, and either helium or argon used as carrier gas. In the presence of an excess of oxygen and combustion reagent, samples were combusted to elemental gases CO_2, H_2O and N_2. After homogenisation in the gas phase, they were first placed in a separation zone, and then in a detection zone.

Metals were characterised and identified using a commercial wavelength dispersive X-ray fluorescence instrument (Bruker S4 Pioneer) equipped with an Rh anode X-ray tube (60 kV, 150 mA), three analyser crystals (OVO-55, LiF 200 and PET), a flow proportional counter for light element detection and a scintillation counter for heavy elements. Quantitative analysis was made by the fundamental parameters method using software linked to the equipment (SpectraPlus). Five grams of each powdered sample were mixed with 0.5 g binder (Hoechst wax C micropowder) and homogenised in an agate mortar. To obtain an XRF-pellet, we used a small aluminium sample holder approximately 4 cm in diameter. The pellets were pressed at 90 bars in a Nannetti hydraulic press for 30 s. To determine loss on ignition (LOI), the samples were heated to 900ºC for 1 hour.

Principal components analysis (PCA) was used to reduce the number of geochemical and mineralogical data (Davies, 1986; Howard, 1991). The original data were transformed with a Z function to reduce the scales effect. Eigenvectors or components were calculated from a variance ± covariance matrix of the standardised data, and the resulting loadings were plotted for each component. To identify the spatial distribution of heavy metal contamination in the sediments, we used a hierarchical clustering technique (Anders, 1972; Poulton, 1989). In addition, SPSS statistical software was used for principal components and cluster analyses. Particle-size distribution was determined by laser grain size meter (Malvern Mastersizer 2000s) for < 63 µm particles.

RESULTS

Particle size distribution

Our data on surficial sediment from the Gulf of Tunis indicate 30–90% contents of presence of clay (<2 µm) and fine silt (2–20 µm) (Figure 3), together with fine and coarse silt (20–63

Table 1 Average of grain size, TOC and N of surficial sediment

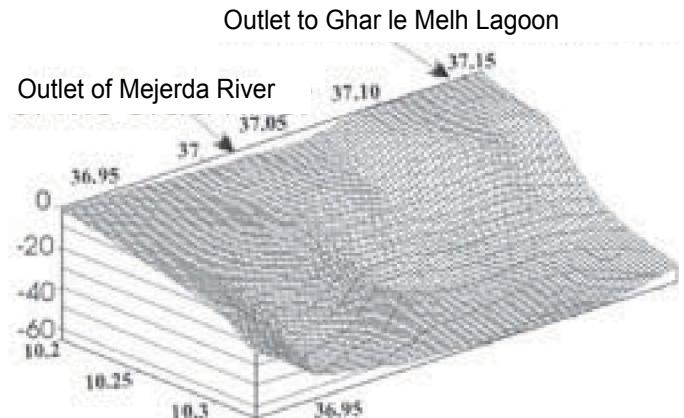|	Grain size <2 µm(%)	Grain size 2–20 µm(%)	Grain size 20–63 µm(%)	COT(%)	N(%)	C/N
Avg	16	64	19	0.68	0.11	7.15
Max	26	82	87	1.37	0.15	16.84
Min	5	7	0	0.08	0.04	0.67

Figure 4 Topography of the Gulf of Tunis

µm) downstream from the Mejerda River between Ras Fartas and Gammarth (Table 1, Figure 3). In the deeper sediments, from more than 25 m deep, our results show that clay and fine silt particles were predominant (75–95%), but fine and coarse silt particles were only found at one sampling station (41) (Figure 2). We can distinguish two streamlines of channels originating from the coastal zone with a low percentage of fine particles, one off the Mejerda River and one off the Ghar El Melh lagoon (Figure 4).

Mineralogy

The dominant clay phases were dioctahedral smectite, illite and kaolinite. Chlorite and interstratified illite-smectite were also present in amounts representing less than 10% (Table 2). The distribution of the aforementioned components clearly showed different accumulation zones of clay minerals as well as the hydrodynamics of the area. The distribution of smectite in the three fractions smaller than 63 µm correlated exactly with <2

Table 2 Average of clay minerals and quartz in surficial sediment

	Coastal zone (%)					
	Smectite	Illite	Kaolinite	Chlorite	I–S	Quartz
< 2 µm	28	25	34	5	8	7
2–20 µm	30	24	34	6	6	13
20–63 µm	18	33	32	6	11	29
	Central zone (%)					
	Smectite	Illite	Kaolinite	Chlorite	I–S	Quartz
< 2 µm	23	25	40	5	8	7
2–20 µm	24	25	39	6	6	15
20–63 µm	12	34	37	6	11	30

μm grain size sediment (Figure 3). According to Morris and Żbik (2009), the presence of smectite in fractions larger than 2 μm indicates an aggregate form of smectite. Kaolinite is dominant in the central zone of the gulf with an average of 40% in the fine fraction, whereas smectite has a high average (30 %) in the fine silt fraction in the coastal zone (Table 2).

Quartz distribution indicates a homogenous size distribution of 20–63 μm particles over the Mejerda River end tail, with an average of 30%. In the <2 μm fine fraction the quartz had an average around 8%, with two distribution areas: one close to Ghar el Melh Lagoon and the other downstream of the Mejerda River (Table 2; Figure 4).

Total organic carbon and total nitrogen

Our data indicate an accumulation of total organic carbon close to the Mejerda River and Ghar El Melah Lagoon shores, where TOC exceeds 1%, mainly in the central part of the Gulf (Figure 5). This zone presented a bathymetric variation area (Figure 4) which facilitated the accumulation process. The total organic carbon content in surface sediments of the Gulf of Tunis varied between 0.08% and 1.37 % (avg. 0.68%; Figure 5). Nitrogen was present off the Mejerda River and Ghar El Melah Lagoon, as well as in the central part of the Gulf (avg. 0.11%; Table 1).
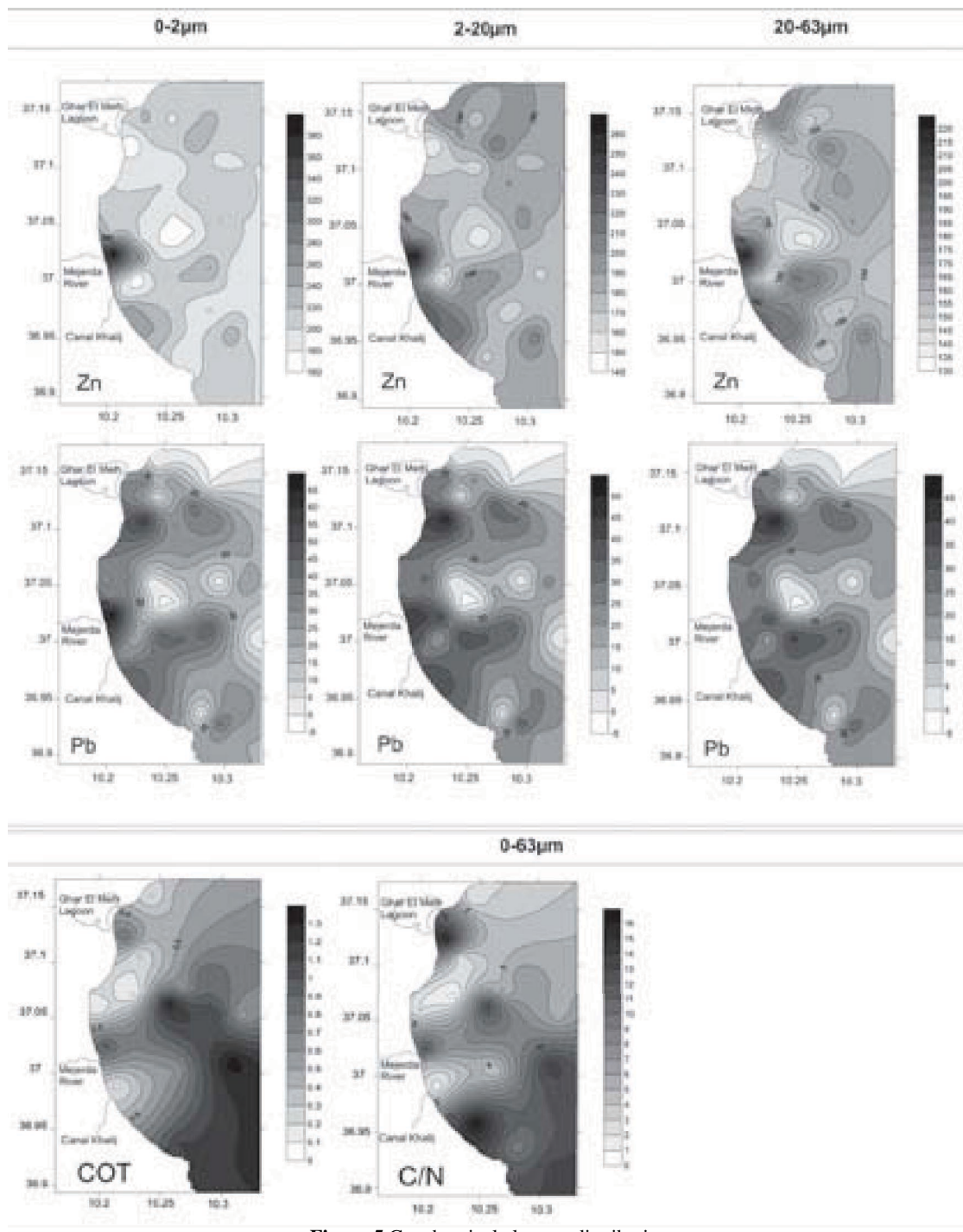

Figure 5 Geochemical element distribution

Geochemistry of major and trace elements

Forty-five surface sediment samples were analysed for the following elements: Al, Ti, P, K, Mg, Na, Ca, S, Fe, Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, I, Ba and Pb. Table 3 summarises the mean chemical compositions of three grain size fractions. The coarse fraction (20–63 μm) was richer in SiO_2 than the fine fraction (<2 μm) suggesting the presence of non-clay minerals such as quartz, whereas the reverse was true for Al_2O_3 and Fe_2O_3. The weight percentage of MnO remained constant in both fractions with an average of 0.02%. Finally, the fine particles (<2 μm) were richer in alkalis (Na and K) and Mg indicating the extensive presence of phyllosilicate minerals. P_2O_5 averaged 0.15% in the three fractions.

Trace element distribution showed a relative accumulation of Zn, downstream of the Mejerda River, reaching a concentration of 398 μg g^{-1} for fine particles (<2 μm). The distribution of Pb was homogenous in the three fractions, mainly off Ghar el Melh lagoon, and little accumulation (68 μg g^{-1}) was observed in the fine particles (<2 μm) at the distal end of the Mejerda River (Figure 5, Table 3). The distribution of Cu showed a higher concentration (62 μg g^{-1} in average) in the fine fraction (<2 μm) when compared with coarser grain sizes (55 μg g^{-1} in the 2–20 μm fraction and 48 μg g^{-1} in the

20–63 μm fraction). An accumulation of V was observed in the fine fraction, reaching a concentration of 305 μg g^{-1}. Sr showed a different punctual accumulation depending on the particle size distribution, with the highest concentration of 338 μg g^{-1} recorded for the fine fraction <2 μm (Table 3).

Correlation

We carried out a Pearson correlation between trace metals (Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, I, Ba and Pb) and sediment properties, principal clay minerals composition (smectite, illite, kaolinite) and percentages of TOC as shown in Table 4.

Our results showed a positive correlation of MnO_2, Fe_2O_3 and P_2O_5 with several trace elements, for <2 μm particles. In this fine fraction, MnO_2 correlated significantly with Y, Zn, Cu, Ni, Ba, Cl, Pb and Cr; Fe_2O_3 correlated with Zn, Ni, Y, Ba, Cu and Cr; and P_2O_5 correlated significantly with Zn, Y, Cu, Ni, Cr, Ba, Cl, Pb. For particle sizes ranging from 2 to 20 μm, there was a correlation of Fe_2O_3 with Zr, Zn, Ni, Cl, Ba and Y. MnO_2 and P_2O_5 were both correlated with Y and Zn. For particles sizes between 20 and 63 μm, there were correlations of MnO_2 with Zn, Fe_2O_3 with Zr and Ba, and P_2O_5 with Y and

Table 3 Average of major element (%) and trace element (μg g^{-1}) in surficial sediment

	< 2 μm			2–20 μm			20–63 μm		
	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min
Cl	429	1005	149	380	865	134	333	892	122
V	223	305	0	197	234	0	172	203	0
Cr	218	319	153	192	241	138	167	210	125
Co	5	37	0	4	34	0	4	31	0
Ni	72	93	61	64	75	56	56	63	46
Cu	62	104	46	55	69	42	48	57	39
Zn	209	398	161	184	267	145	160	221	133
Ga	31	39	15	27	34	13	24	29	11
Br	47	270	8	42	236	7	36	189	6
Rb	120	147	82	106	130	73	93	110	60
Sr	196	338	155	173	217	141	151	182	116
Y	14	35	8	12	24	7	11	19	6
Zr	300	885	152	266	780	138	230	646	125
Nb	28	35	16	25	31	14	22	26	12
I	45	330	0	40	289	0	35	231	0
Ba	271	463	166	239	405	146	208	324	127
Pb	25	68	0	22	50	0	19	46	0
SiO_2	45,91	52,90	40,53	51,33	58,30	44,71	59,62	65,9	55,79
Al_2O_3	22.69	26.37	18.97	20.32	23.33	16.71	17.35	19.0	13.84
Fe_2O_3	8.87	11.25	7.14	7.88	9.90	6.44	6.39	7.9	5.08
MnO	0.02	0.06	0.02	0.02	0.04	0.01	0.02	0.09	0.01
MgO	2.08	2.54	1.69	1.85	2.24	1.53	1.61	1.8	1.41
CaO	0.95	1.41	0.70	0.85	1.24	0.63	0.75	1.0	0.52
Na_2O	0.29	0.49	0.11	0.26	0.43	0.10	0.23	0.4	0.09
K_2O	2.55	3.08	2.15	2.26	2.62	1.67	1.97	2.2	1.45
TiO_2	1.22	1.46	0.92	1.09	1.28	0.78	0.95	1.1	0.67
P_2O_5	0.17	0.43	0.10	0.15	0.29	0.09	0.13	0.2	0.08
SO_3	0.23	0.85	0.00	0.25	2.60	0.00	0.21	2.2	0.00

Table 4 Pearson correlation between trace metal and sediment properties

		Cl	V	Cr	Co	Ni	Cu	Zn	Ga	Br	Rb	Sr	Y	Zr	Nb	I	Ba	Pb	Somme
0–2μm	Group 1	964	181	239	5	77	73	260	28	54	116	188	21	443	26	55	339	40	3108
	Group 2	264	237	219	2	74	61	206	30	52	118	197	14	321	28	52	288	17	2181
	Group 3	355	0	189	0	64	62	216	15	8	82	165	22	885	18	0	434	42	2557
	Group 4	640	238	234	5	75	63	223	35	54	128	204	16	288	30	28	261	28	2551
	Group 5	375	226	206	7	70	60	194	32	41	121	196	12	217	28	45	234	26	2091
2–20μm	Group 1	681	178	189	4	64	56	198	27	48	103	177	15	304	24	30	253	29	2379
	Group 2	250	101	179	0	62	55	194	17	10	77	150	17	633	18	15	326	32	2134
	Group 3	241	212	193	2	65	54	181	28	35	105	174	12	267	25	30	244	15	1884
	Group 4	346	206	192	6	63	54	177	29	36	110	171	11	199	26	42	208	24	1899
	Group 5	205	194	213	0	68	63	196	28	236	123	215	19	341	30	289	405	0	2623
20–63μm	Group 1	596	153	161	4	56	48	170	23	44	90	152	13	271	21	28	224	21	2074
	Group 2	202	181	167	2	56	47	157	23	39	90	151	11	245	22	39	219	13	1665
	Group 3	259	182	168	2	56	47	156	24	41	92	152	11	233	22	40	218	13	1715
	Group 4	892	138	161	0	48	46	154	21	11	65	139	15	125	16	0	127	36	1994
	Group 5	321	183	169	5	57	48	160	26	32	98	153	10	184	23	34	191	22	1716

Zn. The application of PCA and cluster analysis allows for better understanding of these results.

Application of PCA to the surface sediments of the Gulf of Tunis resulted in the identification of two components that explained 67% (<2 μm), 94% (2–20 μm) and 64% (20–63 μm) of the total variance in the three fractions. The PCA diagram for mineralogical and geochemical parameters in each fraction downstream of the Mejerda River estuary sediments showed a different group distribution (Figure 6). As shown in group I, Fe_2O_3, P_2O_5 and MnO were associated with Zn, Cu, Ni and Y traces, for particle sizes less than 2 μm. In group II, Al_2O_3, TiO_2 and quartz were associated with Br, Sr, V, Nb, Rb and Ga. Groups III and IV were represented respectively by TOC and smectite. In the 2–20 μm grain size, TOC was associated with quartz and Kaolinite in Group III, and smectite was associated with Pb in group IV. For the 20–63 μm fraction in group I,
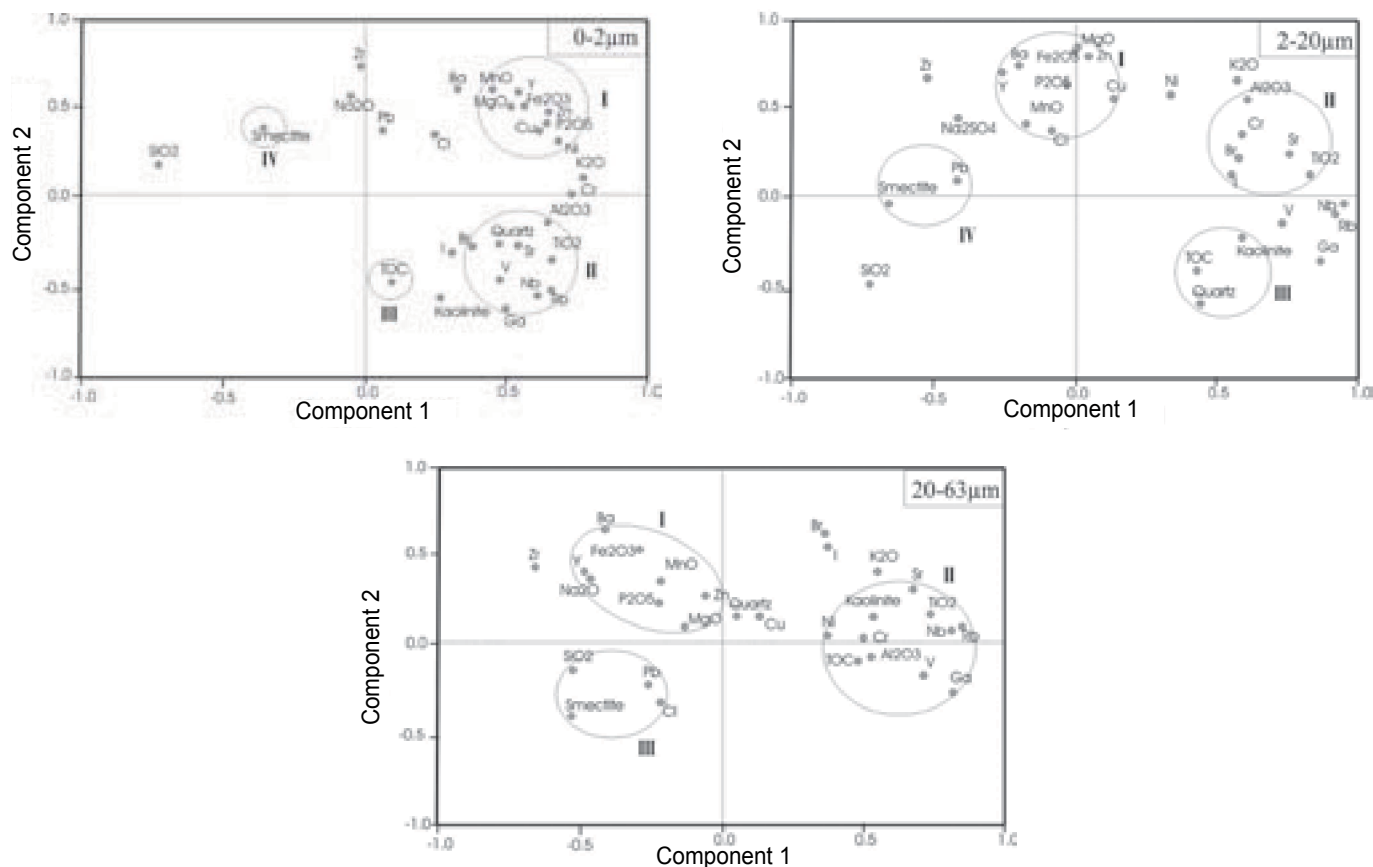

Figure 6 Loading of variables on the first two principal components

Fe_2O_3, P_2O_5 and MnO were associated with trace Zn, Ba and Y. TOC was associated with kaolinite, Al_2O_3, TiO_2, Ni, Sr, Cr, V, Nb, Rb and Ga in group II (Figure 6).

By means of cluster analysis we can classify the sediments in terms of their inter-metallic and compositional ratios. In other words, sediment samples (45 sites) that are similar in origin tend to be associated with one group, whereas sediments affected by some factors, such as transport pattern or proximity to punctual sources of pollution, tend to separate into independent groups. In this study we have identified five groups (Figure 7).
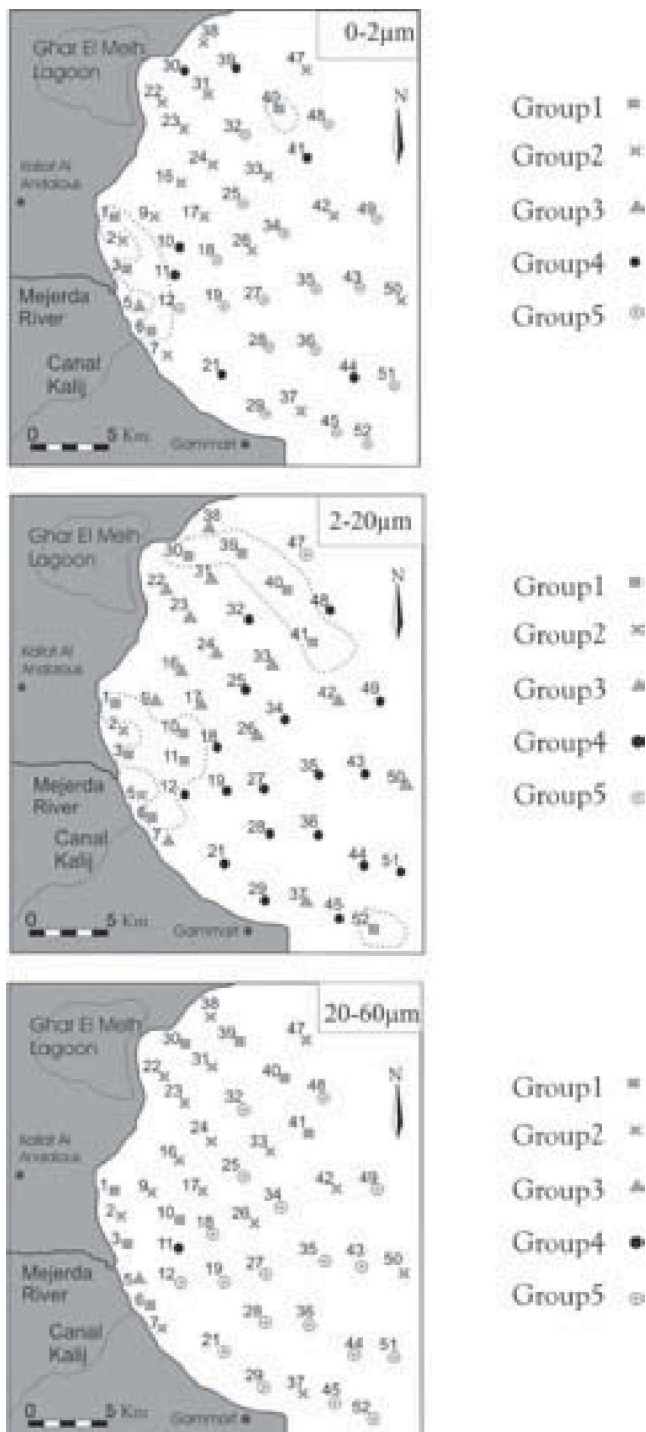

Figure 7 Classification of the sites based on cluster analysis

DISCUSSION

Grain particle size

According to Szava-Kovats (2008) and Horowitz (1991), a less than 63 µm grain size affects trace element chemistry in marine sediments. At the mouth of the Mejerda River there is a substantial accumulation of fine particles, in sediment, in the 2–20 µm and <2 µm ranges. The grain-size distribution of the fine particles is largely related to the currents affecting their transport and sedimentation settling along with trace elements in the Gulf of Tunis. The local accumulation of these fine particles leads to an accumulation of trace metal concentrations, generally because of the increase in specific surface area and to the surface properties of clay minerals (Förstner *et al*., 1982; Pache *et al*., 2008). The sea floor morphology shows two types of seabed structures – a pit between Mejerda River and Ghar el Melh lagoon in the costal zone and a pair of channels in front of the Mejerda River and Ghar el Melh lagoon (Figure 4). The grain size and metal distribution are extensively affected by seabed morphology (Molinaroli *et al*., 2009).

Total organic carbon and total nitrogen

Accumulation of TOC is noticeable in the southern region of the Gulf of Tunis and at the distal end of the Mejerda River and Ghar el Melh lagoon. Generally, marine organic matter has a C:N ratio lower than 10, whereas the C:N ratio for terrestrial organic matter is over 20 (Burdige, 2006). We observed, however, a significant infiltration of terrestrial organic compounds upstream of Ghar el Melh lagoon (C:N= 17) and in the southern region of the Gulf (C:N = 16). Moreover, the current with its mainly north to south direction (Ben Charrada, 1997) constitutes another factor that can facilitate the accumulation of organic matter in the southern region of the Gulf. According to Essonni (1998) this local accumulation of TOC is mainly due to a weak decomposition of organic matter in surface sediment. The low rate of decomposition of organic matter reduces premature diagenesis and complexation of organic matter to metals (Schultz and Urban, 2008).

Mineralogy and Geochemistry of major and trace elements

Our results showed a significant correlation between particle size and type and concentration of trace elements. Trace elements in different grain size fractions were enriched in Pb and Zn off the mouth of the Mejerda River (Figure 5) compared with coastal zone of Sfax, Tunisia. For example, Gargouri *et al*. (2010) found a deficiency of Zn and Pb in the coastal zone of Sfax compared with Gulf of Tunis values. Therefore trace elements contents in surface sediments are clearly affected by anthropogenic inputs that can be evaluated by calculating the enrichment factors. Geochemical normalisation based on the

concentration of a conservative element such as aluminium is commonly used to identify anomalous metal concentrations. The enrichment factor (EF) is defined as the observed metal/Al ratio in the sample of interest divided by the background metal/Al ratio (Guerra-Garcia and Garcia-Gomez, 2005). The enrichment factor (EF) is expressed as: EF = (M/Al sample)/(M/Al background) where (M/Al) sample is the metal/Al ratio in the sample of interest and (M/Al) background is the natural background value of the metal/Al ratio. Concentrations of heavy metals in the reference estuarine sediment MESS-1 (NRCC) were used for the natural background values.

According to values of EF between 0.5 and 1.5 indicate that the metal is entirely from crustal materials or natural processes; whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic (Zhang and Liu 2002). Figure 8 shows EF calculated values for Cr, Zn, Pb, Ni, Cu and Co. The values of EF suggest that Cr, Zn, Pb, Ni and Cu are from anthropogenic inputs.

Five degrees of contamination are commonly defined (Sutherland, 2000):

EF < 2, deficiency to low enrichment;
EF 2–5, moderate enrichment;
EF 5–20, significant enrichment;
EF 20–40, very high enrichment; and
EF >40, extremely high enrichment.

The resulting EF values demonstrate that Pb, Zn, Ni, Cr and Cu are enriched in the surface sediments of the Gulf of Tunis (Figure 8). The EF values for Zn are the highest among the metals, indicating significant enrichment. The average EF values indicate that Zn, Pb, Cr and Cu have moderate enrichment, while the average values of Ni and Co indicate deficiency to low enrichment. The enrichment of metals in the sediments from the study area is due to discharges from the main flow of the Mejerda River into the Gulf of Tunis.

Trace elements in different sediment grain size of sediments show an accumulation of Zn, Cu and Cr; compared to the background value in the gulf of Tunis (Figure 8), suggesting a significant anthropogenic contribution mainly for Zn and Cu. In another Mediterranean area, the sediment quality to the north of Greece (Thermaikos Gulf) is considered as "moderately contaminated" by trace elements (Figure 8), although the sediments of Thermaikos bay are considered to be
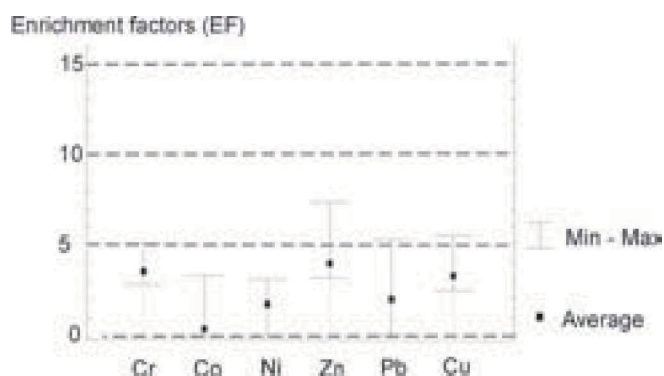

Figure 8 Enrichment factor of trace metal in surface sediment of the Gulf of Tunis

"highly to very highly contaminated" by Pb (Christophoridis *et al*., 2009). As regards heavy metal contents, the comparison of marine sediments in the Gulf of Tunis with Thermaikos Gulf (Greece) shows that Zn and Cr predominate in the Gulf of Tunis (Figure 8). The enrichment of trace element in the Gulf of Tunis is notable in the fine fraction. In the Adriatic Sea, the Manfredonia Gulf is characterised by relatively high concentrations of trace elements such as Cr and Ni. This geochemical accumulation of trace elements denotes fine sediment enrichment (Spagnoli *et al*., 2008).

It appears that grain size, mineralogy and organic matter (TOC) are so interrelated that it may be difficult to differentiate among the individual effects of all three on the distribution of trace elements, hence the importance of statistical interpretation. The PCA and cluster analysis were applied to demonstrate the importance of theses interrelations. There are difficulties associated with selecting an appropriate grain size particle or range for dealing with the grain-size effect, so that spatial trends of associated trace elements can be determined.

Correlation

There is no direct relationship between trace element concentrations and sediment properties, these results are in agreement with those found in other Mediterranean coastal zones such as the Gulf of Lions (NW Mediterranean Sea) (Roussiez *et al*., 2006; Sabatier *et al*., 2010). Trace elements concentrations present weak correlation to TOC, as was observed in surface sediments in a previous study carried out in the Gulf of Tunis (Essonni, 1998). This author attributes the low correlation to different geochemical associations of trace elements (Cu, Zn, Pb, Cr and Ni) in the catchment area and in the delta zone. On the other hand, we note that the surface distribution of trace elements present an accumulation off the mouth of the Mejerda River and the Ghar el Melh lagoon.

The use of PCA allowed us to identify separately the organic and inorganic phases associated to the metal contaminants. In different sediment fractions, PCA statistical analysis shows association of Fe and Mn to trace elements as confirmed by correlation. The hydrogenous fraction of sediments was dominated by Fe and Mn, the oxyhydroxide major components which were among the most dominant colloid systems leading to strong downstream retention of trace metals (Jenne, 1968; Wells, 1999; Wells *et al., 2000*). Thus, amorphous iron oxyhydroxides were among the most active scavengers of dissolved metals (Withney 1975; Hassellöv and Von Der Kammer, 2008). Furthermore, iron occurs as a Fe and Mn oxyhydroxide capable of chemical exchanges with metals, depending on the redox conditions, due to its large specific area and high zeta potential responsible for fixing the dissolved trace elements. Thus, iron oxyhydroxides are associated with trace elements from the catchment area of the Mejerda river. The previous work of Mlayah *et al.* (2009) and Decrée *et al.* (2009) suggests that weathering and oxidation produce a prevalent Fe–Mn oxyhydroxide surface in the stream sediment hydrogenous phase, which is capable of scavenging toxic metals. Lead was

the only element associated with clay minerals, particularly smectite in the 2–20 µm and 20–63 µm fractions. Sorption experiments by Helios Rybicka *et al.* (1995) showed that Pb is preferentially adsorbed by smectite.

Figure 6 shows that TOC was associated with kaolinite and quartz in the 2–20 µm range, and with major trace elements in the 20–63 µm range. For the fine particles (<2 µm) where TOC forms a single group, organic matter in the sediments was present in two major forms, as coatings on sediment grains and as discrete particles (Horowitz and Elrick, 1987). Regarding grain size and the geochemical phase, our results indicate that the coatings (more common in fine grained sediment) acted as inhibitors. Organic coating on clay minerals may significantly affect size distribution and the settling rate of inorganic sediment flocculation at the river–sea mixing zone (Figure 6). It may also contribute to the ubiquitous increase of organic matter in coastal marine sediment (Scholkovitz, 1967; Muraleedharan Nair and Ramachandran, 2002). This process induces a weak decomposition of the organic matter as demonstrated by Essonni (1998) downstream of the Mejerda River. Discrete particles (more common in the coarse-grained sediment) act as contributors to the association of organic matter with geochemical phases (Horowitz and Elrick, 1987).

Using the similarity matrix with the ratio matching, cluster analysis supports the choice of the mineralogical and geochemical sediment parameters as representative in the three sediment fractions (<63 µm). Clustering can also occur among sites that are geographically separated but have similar metal ratio concentrations or similar levels of pollution (Poulton, 1989; Villaescusa-Celaya *et al.*, 2000; Tranchina *et al.*, 2008). As shown in Figure 7, the dendrogram suggests a separation into five different groups:

In grain particles finer than 2 µm (Figure 7), Group 1 (four sites) is the most important and is characterised by high average metal concentrations of Fe, Pb, Zn, Ni and Cr, occurring mostly upstream of the Mejerda river. Group 3 (Site 5) is characterised by the highest concentrations of Pb and Zr with high smectite contents; Group 2 (16 sites) is characterised by weak trace element contents. In coarser grain size sediments (2–20 µm) (Figure 7), the 10 sites upstream of the Mdejerda river and Ghar el Melh Lagoon form Group 1 and are considered a potential source of Zn, Cu and Pb. Group 2 (sites 2 and 5), located respectively north and south of the Mejerda River and close to the coast, with dominance of smectite in the clay fraction (average 34%) and high concentrations of Fe and Pb. Group 5 contains the site furthest from potential sources of metals in the region, close to open sea influence in the north (Figure 7). In the 20–63 µm range (Figure 7), there is an agreement in Group 1 with the last fraction (2–20 µm) that has a high average of Zn and Br corresponding to sites at the proximal end of the Mejerda River and Ghar el Melh Lagoon. The sites of Group 5 (south) are characterised by a high average of Pb (Figure 7). In the three grain size fractions, group 1 of cluster analysis is characterised by accumulation of trace elements compared with other groups (Figure 7). This observation shows that trace element accumulation is concentrated off the mouth of

the Mejerda River in the fine fraction (2 µm), and there is a more extensive area of trace element accumulation in the coarser grain size (Figure 7). The estimated trace element accumulation level in a particular area is heavily affected by current. The fine grain size is dispersed in the low current area depending on current direction. Sediments can reflect the current quality of an environment as well as providing a history of the chemical parameters Cauwet, (1987).

In the three fractions, Group 1 constitutes the accumulation area of trace elements in sediments off the two principal water flows into the northern Gulf of Tunis. For other groups (Figure 8) in different sediment fractions, the observed area distribution shows a high degree of variability as regards element abundance. We note that groups 2, 3, and 2 respectively for sediment fractions 2 µm, 2–20 µm and 20–63 µm represent an average value of trace elements, whereas groups 5, 4, and 5 of the same respective sediment fractions represent the distribution area of trace elements with low accumulation of Zn. The differences between widely dispersed elements of the same group can be explained by sediment mixing from various sources. Because of resuspension caused by currents, at in-shore stations coarse-grained particles are the predominant fraction, while at deep water stations resuspension of sediments is negligible and fine-grained sediments are more prevalent.

CONCLUSION

Trace elements are associated with the Fe–Mn oxyhydroxide fractions from water outlets (catchment area of the Mejerda River); Pb was associated with smectite. A second group of trace elements is associated with alluminosilicates in the three fractions.

Organic matter is not associated with trace elements in fine grain size, and only slightly associated with a few elements in coarser particles; this may be due to the poor decomposition of organic matter that delays mineralisation.

Cluster analysis clearly distinguished trace elements area accumulations in the < 2 µm fraction, which is characterised by a relatively high average content in Fe, Pb, Zn, Ni and Cr. Most of the sites of this group are off the mouth of the Mejerda River. In a coarser grain size fraction (2–20 µm), samples characterised by high metal content spread over an extended area off the mouth of Mejerda River and Ghar El Melh lagoon. These areas are potential sources of metal contaminants in the region, mainly Zn, Cu and Pb.

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