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ABSTRACT

Superficial sediments were collected from the Mejerda River delta between October and November 2008. Samples were analysed for 15 trace and major elements (Cd, Pb, Zn, Mn, Ni, Co, Cr, Cu, Sr, Fe, Al, Ca, Mg, Na, and K). Fine fractions, carbonates, total organic carbon, minerals and acid volatile sulfide (AVS) were also analysed to explain the spatial distributions of heavy metals.

There are two theories of metal spatial distribution: metals concentrated in coastal sediments (Ca, Mn, and Sr) and metals concentrated in offshore sediments (Al, Fe, Mg, Na, K, Pb, Zn, Cr, Co, Ni). Ca, Mn and Sr show similar distributions to those of carbonates, quartz and calcite; these elements show their greatest concentrations in the coastal sediments. However, Al, Fe, Pb, Zn, Cr, Co and Ni show a large concentration in offshore sediments, such as in the clay and silts (< 20μm). None of these metals has a visible affinity with the organic carbon or AVS, indicating that the carbonates and fine fraction are the essential factors which control the distribution of heavy metals in the delta. With regard to other heavy metals studied in the Mediterranean Sea, Cd, Pb and Zn constitute the main pollutants in the delta.

Keywords: Mejerda River delta, minerals, trace metals, sequential extraction, enrichment factor

INTRODUCTION

The Mejerda River delta is located in the western Gulf of Tunis. It is the most important river in Tunisia, and is the main source of water and sediments in the Gulf, with an approximate water flow of 30 m^3s^{-1} and sediment flow varying between 10 and 30 g L^{-1} (Essoni, 1999). The Mejerda catchment covers 23,700 km². Geological maps of the Tunisian northwest show that the main lithology is constituted of carbonates from the Cretaceous and the Jurassic, the clays and the sands of the Miocene, and recent alluviums of the Quaternary (Mauldenhauer *et al*., 2008). The catchment of the Mejerda River has abundant mining activity (polymetallic deposits : Pb > Zn > Cu > Hg and As) (Béjaoui, 2011). The principal mines are: Chemtou, Ain Ksir, Bou Hertma, Sidi Abdallah, Ben Béchir, Boussalem and Jendouba. The route of the Mejerda River has changed over time both naturally and artificially, and it is important to note that the mouth discussed in this study is that of "*Henchir Toubias*" canal built in the 1950s to prevent Mejerda flooding. (Oueslati *et al*., 2006).

The delta of the Mejerda River is subject to two directions of prevailing winds that differ according to season: from north to northwest during the winter and east to southeast during the summer (Ben Charrada, 1997). The sea surface currents depend on wind direction and are mostly from north to south (Brahim *et al*., 2007).

ANALYTICAL METHODS

A total of 52 samples were taken in October and November 2008 (Figure 1), and stored at 4°C for physical and chemical analysis. Handling and analysis of samples was carried out in a clean laboratory using plastic labware. Sediments were sieved using a 63-μm nylon mesh to collect the finer fraction and oven-dried at 50°C. Wet sediment was sub-sampled for
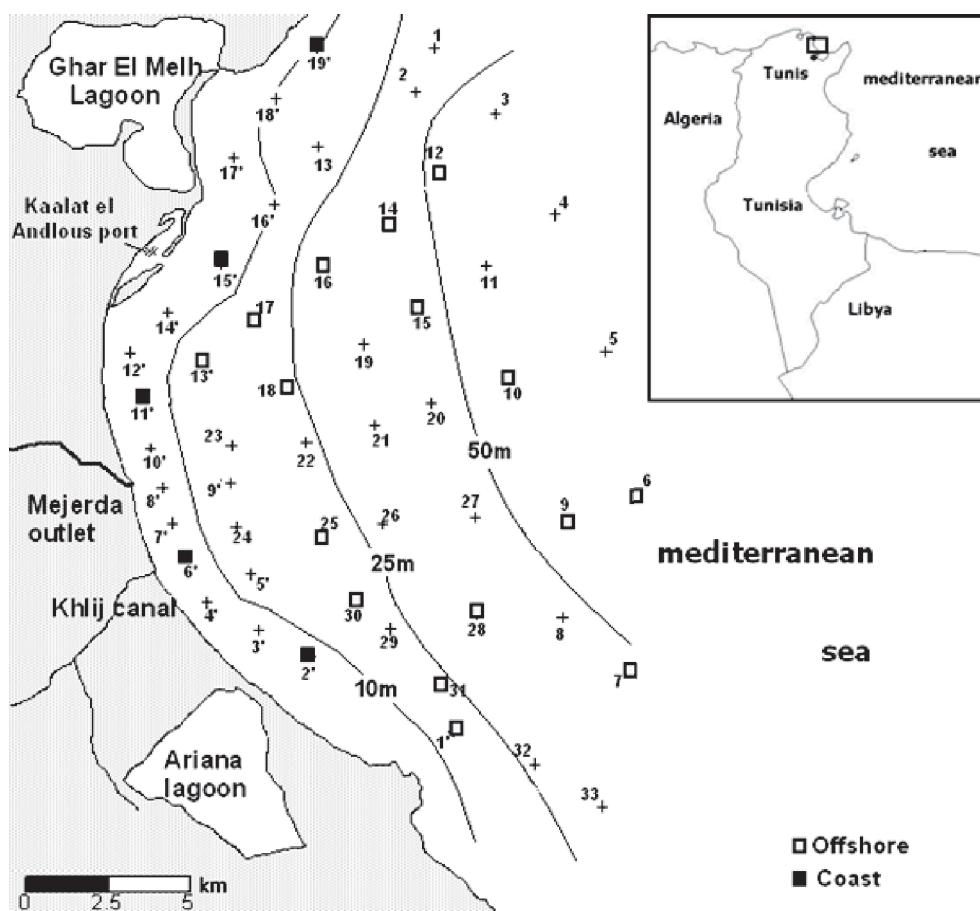
Figure 1 Sample location.

acid volatile sulfides (AVS) analysis. Minerals were analysed by X-ray diffractometry, and the fine fraction was analysed with the Mastersizer 2000 particle size analyser. The results are sub divided into three different groups : <2μm, 2–20μm and 20–63μm.

The samples thus obtained were digested by adding a mixed solution of concentrated 20 mL $HClO_4$, 10 mL HF, and 20 mL HNO_3 to 1 g sediment in Teflon bombs. The resulting digestates were analysed for Cr, Cu, Co, Ni, Pb, Mn, Sr, Zn, Cd, Al, Fe, Ca, Mg, Na and K, by flame atomic absorption spectrometry (FAAS SOOLAR). The accuracy of the analytical procedures employed for the heavy metal analysis was checked using the LKSD1: lakeside sediment (Lake Joe and lake Brady Ontario-Canada) certified reference material, obtaining good agreement with the certified values. Relative Standard Deviations (RSDs) were typically <11% (Table1).

Chemical speciation is the most popular approach to evaluate pollution and mobility in marine sediments. The

sequential extraction procedure applied in this work was developed by Tessier *et al*. (1979), and consists of extractions in the following order with associated chemical reagents and conditions (to 1 g sediment):

1. Exchangeable fraction : 8 mL of $MgCl_2$ (1M) adjusted to pH 7.0 with ammoniac + continuous agitation for 1h;
2. Bound to carbonates : 8 mL of NaOAc (1M) adjusted to pH 5.0 with acetic acid + agitation for 6 h;
3. Bound to Fe and Mn oxides 20 mL of $NH_2OH.HCl$ (0.04 M) in 25% (HOAc) heated during 6h at 95°C with occasional agitation;
4. Bound to organic matter : 3 mL of NH_4OAc + 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3, samples were heated to 85°C during 2h with occasional agitation + a second 3 mL aliquot of (30% H_2O_2) were added and the samples were heated to 85° during 3h with occasionally agitation, after cooling, samples were diluted to 20 mL and agitated continuously for 30 minutes; residual fraction : HF + $HClO_4$ total digestion.

After each successive extraction, a separation was performed by centrifuging the suspension at 3000 rpm for 15 min. The supernatant was then separated with a micropipette. The sediment was washed in 10 mL of deionised water and again centrifuged. The wash water was discarded. Metal concentrations were determined by FAAS.

Table 1 Accuracy and RSD of most important metals

LKSD1 (this study)	LKSD1 (certified)	Accuracy (%)	Element
1,26	1,2	5	Cd
296	331	11	Zn
722	700	4	Mn
40,46	45	10	Cu
85,43	82	4	Pb

Total organic carbon (TOC) was determined on sub-samples by chemical oxidation of organic matter with $K_2Cr_2O_7$: 0.1 g of dry sediment was mixed with 5 mL of concentrated H_3PO_4 and heated at 70°C for 30 min. After heating, 20 mL of acidified $K_2Cr_2O_7$ (0.1 N) was added and the sample was again heated for 5 minutes. Again, after cooling, 5 mL of H_3PO_4 and 100 mL of H_2O were added before a titration with Fe_2SO_4 (0.25 N) was performed in the presence of ferrozine indicator.

Analyses of AVS concentration in sediments were made with a cold-acid purge-and-trap technique described in detail by Added (2001). About 10 g of sediment (accurately weighed) was placed in a 500-mL round bottom flask and purged for 10 min with nitrogen at a flow rate of 40 cm³ min⁻¹, before 20 mL of HCl (6N) was introduced into the flask. Then, nitrogen was bubbled through the sample for 20 min at a flow rate of 20 cm³ min⁻¹, while the sample was heated, H_2S+N_2 was passed to 0.1 N iodine solution magnetically stirred at the same time to trap the volatilised H_2S from the acidified sediments. Excess of iodine was titrated with sodium thiosulfate $Na_2S_2O_3$ (0.1N).

RESULTS

Particle size analysis

The Mejerda River delta is poor in shell debris and marine flora. The fine fraction is more important than sand. Grain size analysis shows that the rate of the fine fraction (< 63μm) in most of the samples is more than 80%. The fine fraction is mainly located in offshore sediments, whereas less than 30% are found in the coastal sediments. The exceptions are north of the Mejerda mouth and near the Ghar El Melh lagoon where the percentage of the fine fraction (> 85%) reflects the presence of mudflats. The results of the fine fractions are grouped into three intervals depending on the particle size: clay: < 2 μm; silt: 2–20 μm and 20–63 μm. The results are expressed as a percentage of the total of the fine fraction (Table 2). Clay does not exceed 25% in sediments located offshore and in front of the Mejerda River and Khlij canal, so silts are dominant in the surface sediment. In the rest of coastal sediments and in the lagoon of Ghar El Melh, this level is below 10%. In offshore sediments, silts represent more than 60% of the total fine fraction.

Carbonates

Carbonates show a similar concentration in the sediments from the Mejerda River and the rest of surface sediment in the Gulf of Tunis. $CaCO_3$ contents vary between 30 and 40%, but with percentages > 50% in the North of the Mejerda mouth, near the Ghar El Melh lagoon and Khlij canal (Table 2).

Total organic carbon

TOC is less than 1% in the whole of the sediments of the delta (Table 2), the lowest concentrations are localised in

Table 2 Fine fraction, TOC, AVS and $CaCO_3$ in superficial sediments

Sample	<63μm (%)	<2μm (%)	2-25μm (%)	25-63μm (%)	AVS (%)	TOC (%)	CaCO₃ (%)
1	6.1	9.16	64.11	22.92	0.66	0.45	40.7
2	62.4	11.41	71.51	15.23	0.92	1	33.5
3	83.35	11.35	72.69	14.69	0.98	0.85	29.7
4	92.45	15.11	80.96	3.9	0.92	0.85	28
5	90	19.68	80.27	0.01	0.88	0.36	40.7
6	88.5	16.77	80.13	3.07	0.66	0.4	30.5
7	84.8	17.22	80.31	2.43	0.67	0.34	31.4
8	89.6	19.39	76.52	4.04	1.02	0.65	33.9
9	93.41	17.29	79	3.17	0.82	0.4	33.1
10	86.9	19.23	80.58	0.15	1.04	0.62	30.1
11	88.2	2.97	4.55	55.05	0.55	0.31	30.5
12	86.96	13.04	73.21	11.98	0.98	0.52	34.7
13	96.95	15.75	72.85	10.5	0.88	0.4	33.9
14	93.48	18.35	75.46	5.77	0.86	0.46	35.6
15	93.9	17.59	79.42	2.91	1.02	0.73	33.9
16	39.1	17.47	80.55	1.93	0.77	0.31	39
17	82.9	14.88	73.16	11.07	0.44	0.08	47.5
18	93.64	16.02	40.61	6.08	0.66	0.31	39.4
19	94.55	19.39	79.64	0.93	0.52	0.28	36.4
20	94.4	20.06	97.78	0.12	0.8	0.43	31.4
21	94.8	23.6	76.03	0.31	1.52	0.97	32.2
22	95.25	18.61	79.82	1.4	0.66	0.29	35.6
23	88.9	18.94	69.87	9.26	0.9	0.62	33.9
24	97	19.3	79.82	0.79	0.66	0.32	39
25	91.7	16.61	78.16	9.68	0.67	0.34	36.4
26	94.5	16.76	76.41	6.65	0.44	0.27	34.7
27	92	18.23	73.06	8.26	0.4	0.25	33.9
28	91.4	18.33	78.69	2.93	0.55	0.25	24.6
29	91.6	19.71	76.59	3.64	0.66	0.3	33.1
30	95.1	20.67	75.36	3.94	0.31	0.15	38.1
31	72.5	22.7	73.58	3.58	46.17	0.28	33.9
32	82.7	15.98	75.97	8.96	47.32	0.19	34.7
33	90.7	17.25	74.28	7.68	48.47	0.07	35.6
1'	55.46	11.52	74.96	12.88	48.47	0.51	35.6
2'	34.66	15.21	57.87	20.29	50.77	0.4	37.3
3'	10.2	13.1	56.06	31.47	0.56	0.27	44.1
4'	54.9	4.48	13.7	58.26	0.53	0.24	47.5
5'	25.6	15.97	64.16	15.78	0.2	0.6	37.3
6'	85.1	22.14	68.32	7.87	0.42	0.16	47.5
7'	28	7.82	21.38	44.98	0.42	0.16	42.4
8'	93.45	22.04	69.26	8.11	0.59	0.28	31.4
9'	96	18.8	63.66	12.66	0.37	0.12	50.8
10'	87.7	14.49	45.93	24.7	0.38	0.13	33.9
11'	62.16	7.76	17.6	44.69	0.47	0.2	46.6
12'	58.9	5.84	14.57	49.07	0.3	0.07	55.1
13'	76.3	14.24	43.82	27.86	0.29	0.07	47.5
14'	30.9	5.42	15.72	45.67	0.53	0.24	47.5
15'	12.6	7.98	21.23	39.08	0.81	0.45	47.5
16'	88.1	10.4	43.27	35.39	0.44	0.18	47.5
17'	54.42	10.5	33.08	41.08	0.34	0	48.3
18'	89.7	13.16	58.7	21.75	0.58	0.28	45.8
19'	88.2	11.49	47.56	31.2	0.53	0.24	42.4

the coastal sediments when the values are lower than 0.25%. This low content is associated with the lowest percentage of fine fraction, as has already been reported (Essoni, 1999) in the case of the small Gulf of Tunis. We find the strongest concentrations (>1%) in offshore sediments.

Monosulfides

Monosulfides show a similar distribution to that of organic matter. The coefficient of correlation of these two elements is $R^2 = 0.65$. Monosulfides concentrations vary between 0.2 and 1.5 g kg^{-1}, the highest values are observed near Ghar El Melh lagoon (> 0.8 g kg^{-1}). In coastal sediments, monosulfides are lower than 0.2 g kg^{-1} (Table 2).

Mineralogy of sediments

Non-clay minerals

Quartz, calcite, magnesium calcite, dolomite, ankerite, orthose, albite, aragonite and the phyllosilicates were identified by X-ray diffractometry. All the results are expressed in percentages of the total rock. quartz (16%) and the calcite (30%) are the most frequent minerals (Table 3).

Table 3 Non-clay minerals in superficial sediments (%)

Sample	Phyllos	Quartz	Calcite	Mg Cal	Arag	Dolom	Ank	Orth	Albite
1	17	40	17	16	5	1	0	3	1
2	40	15	28	8	4	0	2	0	3
3	38	17	23	8	4	1	2	4	3
4	57	10	20	4	2	2	2	2	1
5	58	9	27	1	0	1	1	2	1
6	60	9	26	0	0	0	2	1	2
7	61	10	25	0	0	0	1	2	1
8	52	11	29	2	0	0	2	2	2
9	57	8	27	0	0	4	1	1	2
10	55	9	31	1	1	1	1	0	1
11	55	10	29	2	0	0	1	1	2
12	56	10	20	5	2	0	2	3	2
13	49	13	28	0	0	2	4	3	1
14	56	11	28	0	0	1	2	1	1
15	60	10	26	0	0	0	1	2	1
16	54	11	24	0	0	1	3	4	3
17	38	20	30	0	0	0	3	6	3
18	49	13	28	0	0	2	3	3	2
19	60	9	25	0	0	1	1	2	2
20	61	9	27	0	0	0	0	2	1
21	62	9	26	0	0	0	0	2	1
22	54	12	28	0	0	0	2	3	1
23	59	10	21	0	0	1	4	4	1
24	60	8	25	0	0	1	0	4	2
25	49	12	30	0	0	1	4	2	2
26	59	10	25	0	0	1	1	2	2
27	58	9	29	0	0	0	1	2	1
28	57	9	29	0	0	1	1	2	1
29	54	10	31	0	0	1	1	2	1
30	15	36	29	0	0	4	8	6	2
31	50	15	28	0	0	1	2	3	1
32	40	15	32	1	0	1	4	5	2
33	57	9	29	0	0	0	3	1	1
1'	31	34	31	0	0	0	1	2	1
2'	34	26	31	0	0	1	1	5	2
3'	17	32	41	0	0	2	0	7	1
4'	20	30	31	0	0	7	4	6	2
5'	12	37	42	0	0	2	0	4	3
6'	37	15	37	0	0	0	5	4	2
7'	19	32	30	0	0	5	4	7	3
8'	56	15	28	0	0	0	0	0	1
9'	59	10	24	0	0	1	0	4	2
10'	39	23	30	0	0	4	1	2	1
11'	16	31	38	0	0	5	0	4	6
12'	17	22	43	0	0	8	0	6	4
13'	39	20	32	0	0	2	2	3	2
14'	17	25	38	0	0	3	3	10	4
15'	19	30	37	0	0	0	3	4	7
16'	42	14	32	0	0	2	4	3	3
17'	33	22	32	0	0	3	4	3	3
18'	42	18	30	0	0	2	4	2	2
19'	43	14	27	0	1	1	2	3	3

The spatial distribution shows that the quartz concentrates essentially in coastal sediments where the contents exceed 30% against less than 10% in offshore sediments. This is also observed for the calcite where the concentration exceeds 40% only in coastal sediments and especially in the north of the mouth of Mejerda River while they decrease towards the open sea and the percentages are lower than 27%.

Albite is a minor component among non-clay minerals concentrations < 7%. We observed maximum values (5–7%) in coastal sediments, in the north of the mouth River and near the port of Kalat El Andlous. The lowest contents (< 1%) were observed in offshore sediments (Table 3). Results showed that orthose is concentrated only in coastal sediments, where the contents exceed 5%, up to 10% north of the mouth of the Mejerda River. Towards the open sea, the content in orthose is lowest (< 2%).

Ankerite is found in coastal sediments near Ghar El Melh lagoon and Khlij canal (> 5%). To the north of the Medjerda River mouth and in offshore sediments, we observe low contents of ankérite (< 1.5%) (Table 3). The highest content in the dolomite is observed in coastal sediments (more than 5%) to the north of the Medjerda River mouth, near Ghar El Melh lagoon and Khlij canal. In the offshore sediments, the dolomite concentration is lower than 2% (Table 3). Dolomite, orthose and albite show a similar spatial distribution.

Aragonite and magnesium calcites also show a similar spatial distribution, (R^2 = 0.94). The magnesium calcite contents are higher (~ 15%) than aragonite (5%). Maximum values are observed in the north of the delta, near the Ghar El Melh lagoon. Most of the sediments contain little or no aragonite and magnesium calcite. (Table3).

Clay minerals:

Smectite, kaolinite, Illite and chlorite were identified by X-ray diffractometry. All results are expressed in percentage with regard to the total rock.

Phyllosilicates are less common in coastal sediments except in the Mejerda River and Ghar El Melh lagoon. The highest values are observed in offshore sediments (>60%) (Table 4). Spatial distribution of clay minerals is dependent on the structure of the mineral and other factors such as the climatic conditions, transporting mode, source of mineral, and the affinity of the mineral for the flocculation phenomena (Biscaye, 1965). In surface sediments of the Mejerda River delta, the chlorite content is lowest, with an average of 2.3%. Whereas, a high concentration of illite and smectite (with an average of 17%), and kaolinite (with an average of 37%) is observed (Table 4).

We observe the highest concentration of kaolinite in offshore sediments (more than 25%) while in coastal sediments the percentages remain relatively low except in near Ghar El Melh lagoon and the mouth of the Mejerda River (10%). We observe a maximum of 20% in the smectite concentrates especially near the mouth of Mejerda River. Elsewhere in the delta, the contents are globally weaker. Illite and chlorite also have a similar spatial distribution to that of the smectite and of the kaolinite, so we observe the highest contents in offshore sediments and near the mouth of Mejerda: more than 12% for Illite and 3% for the chlorite. Elsewhere in the delta, to the north of the Mejerda River and near the Ghar El Melh and Ariana lagoon, values are low: less than 7% for the illite and less than 1.5% for the chlorite. (Table 4).

Major elements

Aluminium and iron: Aluminium concentrations in the sediments of the delta vary between 20 and 40 mg g⁻¹. The highest concentrations were found in offshore sediments (>30 mg g⁻¹) while in globally coastal sediments, aluminium was lower than 25 mg g⁻¹, except near the Mejerda River mouth, near the Ghar El Melh lagoon and Ariana lagoon (Table 4). Iron concentrations are approximately 30 mg g⁻¹. Distribution of the iron in surface sediments is rather homogeneous, and the concentrations are only slightly different between the coast and offshore. But, as is the case for Al, the highest concentrations observed in coastal sediments are localised near the Ghar El Melh lagoon, near the mouth of the Mejerda River, and near the Ariana lagoon.

Calcium: Results show that CaO is the most important major element in sediments of the delta with an average concentration of 260 mg g⁻¹. The highest concentrations are localised in coastal sediments (> 300 mg g⁻¹) while in offshore sediments, the concentration is lower (< 250 mg g⁻¹). This distribution is similar to that of the calcite (Table 4).

Magnesium and potassium: MgO and K_2O showed similar spatial distribution (R^2= 0.77). The average concentration for K_2O is 21 mg g⁻¹ while that for MgO is 15 mg g⁻¹. We observe the highest concentrations in offshore sediments: >25 mg g⁻¹ for K_2O and >15 mg g⁻¹ for MgO. In coastal sediments, the highest levels are observed near the mouth of Mejerda River (30 mg g⁻¹ K_2O and 20 mg g⁻¹ MgO) (Table 4).

Sodium: The sodium concentration varies slightly across the delta between 10 and 20 mg g⁻¹, the highest values are observed north of the delta (40 mg g⁻¹) but, overall, values increase from the coast to offshore. In coastal sediments, the concentration of sodium is less than 10 mg g⁻¹, especially north of the mouth of the Mejerda River (5 mg g⁻¹) while offshore it exceeds 20 mg g⁻¹ (Table 4).

Distribution of trace metals

Standardisation of five heavy metals was carried out over the LKSD1 reference: typical lake sediment from Lake Joe Brady and Lake Ontario (Canadian Shield). These results show a maximum deviation of 11% (Table1).

Cadmium: Cd shows slight variations in the delta sediments (1 to 3 mg kg⁻¹), the highest values (8 mg kg⁻¹) are observed only to the north of the mouth (Table 5).

Nickel and chromium: Ni and Cr distribution are similar (R^2 = 0.95) (Table 5). Ni concentration varies between 10 and 30 mg kg⁻¹ and those of Cr between 40 and 130 mg kg⁻¹. The highest concentrations are observed offshore (> 20 mg kg⁻¹

Table 4 Clay minerals (%) and major elements (mg g^{-1}) in superficial sediments

Sample	Smectite	Illite	Kaolinite	Chlorite	Fe	Al	K$_2$O	Na$_2$O	MgO	CaO
1	14	31	42	5	15.6	39.4	20.1	38.6	19.7	335.7
2	13	31	40	7	25.7	34.7	23.2	13.9	17.4	299.6
3	16	30	42	5	27.6	34.6	23.9	11.1	17.3	186.2
4	19	26	43	5	32.3	34.3	26	14.3	17.1	209.4
5	26	22	40	5	28.8	31.2	24.9	18.4	15.6	238.6
6	24	27	37	6	28.5	30.5	25.4	20.4	15.2	223.7
7	33	18	39	4	29.7	32.2	25	17.1	16.1	249.8
8	18	26	40	6	29.9	32.2	25.7	17.7	16.1	243
9	11	28	43	7	31.1	35.1	27.7	17.8	17.6	230.2
10	14	24	46	6	31.9	34.4	26.7	19.5	17.2	150.2
11	18	25	43	6	33.3	37.4	29.2	20.9	18.7	203.4
12	10	28	45	7	30.9	33.5	23.9	10.4	16.7	205.3
13	27	23	38	5	30.9	33.1	22.9	16.7	16.6	281.5
14	22	23	43	5	32.2	35.6	26.8	18.9	17.8	222.6
15	30	18	41	4	30.8	33.8	26.7	13.9	16.9	227.2
16	27	28	33	4	32.6	35.2	25.8	16	17.6	250.4
17	25	23	37	6	30.1	27.9	18.4	9	13.9	347.5
18	28	24	34	6	31.7	33.5	23.3	14.5	16.7	284.9
19	28	26	37	4	30.3	32.9	25.1	19.7	16.4	241.4
20	30	21	38	4	30.9	34.9	26.2	17.3	17.5	238.1
21	25	25	39	5	31.1	36.3	26	17.6	18.1	240.5
22	20	28	39	5	31.4	32.8	25.5	9.9	16.4	243.2
23	27	28	32	5	29.6	32.4	24.4	11.3	16.2	263.3
24	34	18	34	6	27.6	31.1	24.7	14.7	15.5	288.4
25	23	23	38	6	32.1	31.7	22.4	10.2	15.9	304.9
26	21	24	40	6	28.6	31.8	23.5	15.4	15.9	259.6
27	33	16	40	4	32.3	33.6	26.3	12.3	16.8	232.1
28	28	17	43	5	32	35.1	25.7	16.1	17.5	239.3
29	24	20	45	4	28.8	31.3	24.1	15.9	15.6	274.6
30	21	24	43	5	33.2	29.8	21.8	21.7	14.9	248.4
31	19	27	42	5	31.3	35.4	29.8	16.1	177	181.1
32	22	26	40	5	29	30.6	24	8.8	15.3	259.2
33	29	23	34	6	29.7	32.6	24.1	15.3	16.3	229.8
1'	26	29	33	5	28.8	31.4	21.7	11.1	15.7	367.6
2'	23	27	39	4	30	30.3	22.2	8.3	15.1	449.5
3'	27	28	32	5	32.2	28.3	17.2	15.7	14.1	263.3
4'	31	30	26	5	27.4	24.1	14.4	9.3	12	340.1
5'	29	21	37	4	28.6	22.5	13.6	10.3	11.2	256
6'	31	27	30	5	26	23.7	15	4.4	11.8	333
7'	31	24	33	5	20.2	17.2	18.8	10.8	15.3	256.5
8'	32	22	34	5	31.4	32.6	29.5	18.2	16.3	200.6
9'	30	24	32	6	27.6	23.6	13.5	7.4	118	338.5
10'	24	22	38	6	29.2	27.6	22.3	7.9	13.8	207.7
11'	33	24	30	5	28.3	23.7	15.2	4.6	11.8	355.4
12'	31	25	30	5	27.1	21	10.6	3.1	10.5	306.6
13'	22	39	26	5	29.7	26.2	17.3	9.4	13.1	296.1
14'	29	21	36	6	29.7	22.7	13	3	11.4	271.7
15'	33	24	30	5	17	22.6	13.4	2.3	12	180.2
16'	28	29	30	5	27.7	25.7	17.2	4.4	12.9	286.3
17'	28	20	41	4	32.1	26	15.1	6.3	13	282.9
18'	27	22	40	4	29	29.6	19.8	7.1	14.8	309.5
19'	20	37	31	5	28.2	30.8	20.5	11.9	14.4	342.3

for Ni and > 120 for Cr). The concentrations are lower (20 mg kg^{-1} and 40 mg kg^{-1}) in the coastal sediments, except for sediments situated in front of the mouth of Mejerda River and of Ariana lagoon.

Copper: Cu shows a low spatial variation with contents varying essentially between 14 and 17 mg kg^{-1} (Table 5). The distribution of Cu towards the offshore seems to be rather uniform, but in the coastal sediment, it is not uniformly distributed. There is a zone with low Cu concentration (7–10 mg kg^{-1}) to the north of the mouth of Mejerda and another zone with strong concentration near the mouth of Mejerda River and Ariana lagoon.

Table 5 Trace elements in superficial sediments (µg g⁻¹)

Sample	Cd	Cu	Pb	Mn	Zn	Cr	Ni	Co	Sr
1	1.2	14	42	200	132	76	18	0.1	88
2	1.1	13	56	199	149	99	21	0.8	60
3	1.3	16	64	223	142	110	22	2.5	62
4	1.0	15	71	243	153	136	27	4.4	40
5	1.6	15	53	230	119	133	26	5.6	34
6	0.9	14	58	248	129	129	25	4.4	37
7	1.0	13	64	251	132	127	25	4.6	40
8	1.0	14	64	237	132	122	25	6.3	40
9	0.9	13	59	252	127	131	26	7.9	42
10	1.3	15	61	229	129	136	25	6.7	36
11	1.2	15	55	239	123	135	27	7.7	35
12	1.4	16	70	250	149	118	24	1.2	48
13	1.3	14	63	245	134	111	23	5.0	43
14	0.8	14	59	233	131	125	24	6.1	41
15	0.0	15	69	241	139	113	25	5.4	40
16	0.9	14	58	233	125	120	24	5.3	39
17	1.5	11	48	248	118	72	18	5.4	60
18	0.4	13	45	243	118	105	22	5.8	42
19	1.3	14	53	235	118	126	24	6.0	34
20	0.8	14	41	226	120	124	27	7.8	33
21	1.0	14	26	210	114	138	26	6.1	31
22	1.6	12	29	230	104	117	23	1.5	33
23	1.4	13	44	219	115	112	22	7.2	43
24	1.3	14	31	240	99	118	25	9.1	42
25	2.6	16	84	281	165	93	25	3.1	33
26	1.5	15	59	235	133	116	24	6.6	41
27	0.6	14	62	258	125	120	25	6.6	35
28	0.9	13	50	231	117	120	23	5.5	39
29	1.3	14	53	219	121	118	24	7.0	39
30	1.1	11	43	328	124	109	24	9.3	48
31	0.9	16	42	284	121	126	26	10.4	35
32	1.4	13	45	232	116	95	20	3.5	48
33	0.7	14	65	237	130	108	22	6.8	44
1'	0.6	14	43	269	127	88	21	1.3	41
2'	1.0	15	43	275	122	98	21	2.5	43
3'	1.2	12	43	340	133	62	18	3.5	46
4'	1.1	11	37	285	115	47	15	1.0	59
5'	1.1	12	45	377	129	74	18	3.1	46
6'	1.3	10	31	257	101	48	16	4.2	61
7'	1.0	15	29	237	89	45	17	8.9	40
8'	1.5	17	27	315	114	121	26	8.0	22
9'	1.5	10	39	296	103	43	15	1.6	76
10'	1.3	17	74	317	149	104	23	3.6	42
11'	8.0	12	41	290	121	57	18	5.2	67
12'	1.1	7	28	276	88	21	11	0.0	93
13'	1.9	11	36	270	107	54	16	1.0	62
14'	1.4	10	42	298	100	41	14	0.0	77
15'	0.8	7	44	379	136	83	22	10.7	62
16'	1.7	15	107	307	143	58	19	0.6	48
17'	1.2	12	35	327	87	54	18	0.2	65
18'	1.3	13	63	276	134	75	19	3.2	51
19'	1.3	13	55	258	123	85	18	1.6	53

Lead and zinc: The spatial variations of Pb and Zn are similar (R^2 = 0.75), overall highest concentrations (50–100 mg kg⁻¹ for Pb and 65–110 mg kg⁻¹ for Zn) are observed in offshore sediments, while it is minimal in the coastal sediments (20–45 mg kg⁻¹ for Pb and Zn) (Table 5). This distribution is similar to the fine fraction (<63 µm), except for two zones, one to the north of the mouth of the Mejerda and near Ghar El Melh lagoon associated with tidal reservoirs.

However, there is a third area near the mouth of the River where the contents of lead and zinc are also high.

Cobalt: Co and fine fractions show relatively similar spatial distributions (Table 5). Lowest concentrations (0.5–3 mg kg⁻¹) are localised in coastal sediments, while the highest contents (5–8 mg kg⁻¹) are observed offshore. However, the highest concentrations (10 mg kg⁻¹) are observed in the Ariana lagoon, near the mouth and in front of Kalaat El Andlouss port.

Manganese: Mn show similar distribution to that of carbonates (Table 5). Highest concentrations are observed in coastal sediments (300–350 mg kg⁻¹), offshore Mn concentrations are less than 250 mg kg⁻¹.

Strontium: The average concentration of Sr is 47 mg kg⁻¹ (Table 5). The highest levels are located in coastal sediments especially in the northern River delta and north of the mouth (more than 80 mg kg⁻¹) and near the Khlij canal (50 mg kg⁻¹). Offshore, levels are lower (< 30 mg kg⁻¹). Strontium shows correlation with some elements: negative correlation with potassium (R^2 = –0.7) and phyllosilicates particularly kaolinite (R^2 = –0.64). Strontium also shows positive correlations with Mn and carbonates (R^2 = 0.71).

Enrichment factor

The median enrichment factors (Grant and Middleton, 1990; Salomon and Forestner, 1984) calculated for the nine heavy metals in this study are shown in Figure 2. Most of the metals show no enrichment. Fe, Mn, Cu, Ni and Cr have enrichment factors less than 5, the maximum values between the 52 samples are 3.1 for Fe, 2.3 for Mn, 2.9 for Ni and Cu, 4 for Cr. For the most polluting metals: Pb, Zn and Cd, enrichment factors show relatively high values: 7 for Zn, 20 Pb and Cd more than 300. Moreover, spatial distribution of the EF is similar to that of total Pb and Cd concentration (R=0.87 for Pb and 0.98 for Cd) But the enrichment factor of zinc shows a slightly different distribution from that of zinc (R = 0.36), this difference is observed mainly off the Ghar El Melh lagoon.
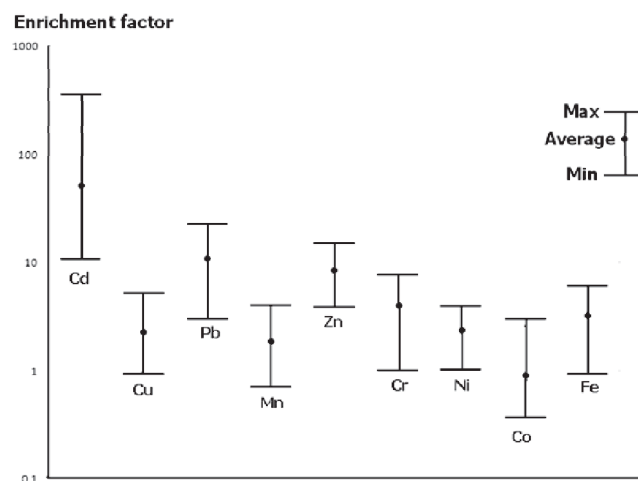

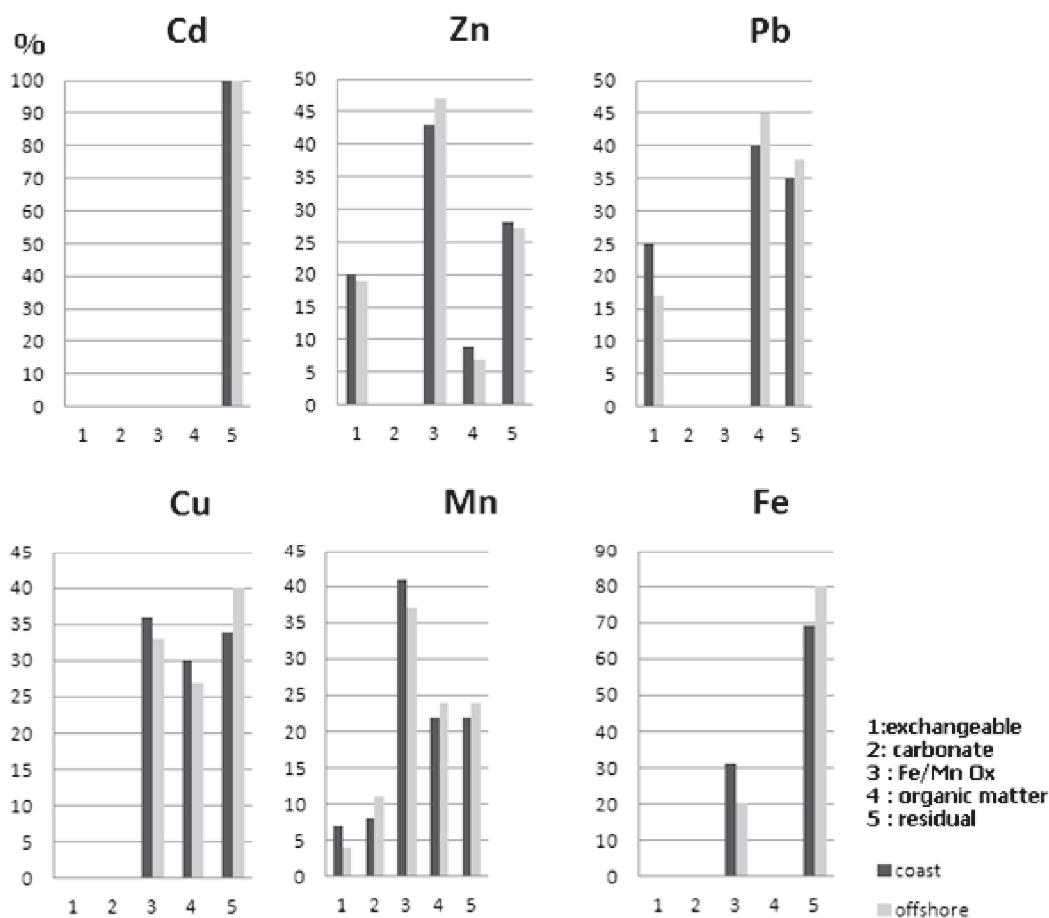**Figure 2** Minimum, median and maximum values of enrichment factors.

Figure 3 Average distributions of heavy metals between the five sediment fractions.

Chemical speciation

Chemical fractionation was carried out for the six most important metals: (Pb, Zn, Fe, Mn, Cd and Cu) on 23 samples, divided between coast and offshore. For each metal, we represent results in average distribution (in %) between the five fractions (1, exchangeable; 2, bound to carbonate; 3, bound to Fe/Mn oxides; 4, bound to organic matter; 5, residual). Results were grouped in two categories: 1, in coastal sediments; and 2, in offshore sediments (Figure 3).

Lead: Lead is found in the exchangeable fraction (17–25%), in the organic matter (39–47%) and in the residual fraction (39%). For the lead found in the residual fraction, there is no difference between coastal sediments and offshore sediments, but results show some difference in lead bound to the exchangeable phase (25% near the coast to 17% in offshore sediments) and lead associated with organic matter (from 38% in coastal sediments to 47% in offshore) (Figure 3).

Zinc: Zinc is mostly associated with Fe/Mn oxides (44–47%), with the residual fraction (27%), with the exchangeable fraction (20%), and with the organic matter (6–8%). There are no significant variations observed in the distribution of zinc between coastal sediments and offshore sediments.

Manganese: Manganese is found in five fractions of sediment, but it is mainly associated with Fe/Mn oxides (38–42%) and organic matter (28%). Results show a variation of the Mn

distribution between coastal sediments and offshore sediments. This variation is low and it concerns especially the Fe/Mn oxides fraction and carbonates (Figure 3).

Iron: This metal is mainly associated with the residual fraction of the sediment (67–79%) and Fe/Mn oxides (21–33%) (Figure 3). This association has been observed in surface sediments across the Gulf of Tunis (Essoni, 1999) and in the Ghar El Melh lagoon in northern Tunisia (Oueslati *et al*., 2006; 2010). Iron distribution between the two fractions (3 and 5) differs from coastal sediments and offshore sediments. The average iron associated with Fe/Mn oxides increases from 21 to 33% offshore, while iron bound to residual fraction decreases from 79 to 67%.

Copper: Copper is bound to the residual faction (35–43%), associated with Fe/Mn oxides and organic matter (22–27%). Cu associated with Fe/Mn oxides remains constant between coastal sediments and offshore sediments (35–37%), but copper bound to the organic matter and the residual fraction differs slightly from coast to open sea (Figure 3).

Discussion

Organic matter, carbonates and minerals

It has already been demonstrated (Essoni, 1999) by correlation with the total nitrogen, that the accumulation of the OM in

sediments of the Gulf, and particularly near the Ghar El Melh lagoon, is due to a low decomposition of the organic matter and not to an excessive intake. The distribution of OM is similar to that of the clay fraction (< 2 µm) near the Mejerda River, this distribution is probably due to the clay–OM flocculation mechanisms in the delta. In the rest of the gulf of Tunis, $CaCO_3$ varies between 30 and 40% (Essoni, 1999). Distribution of the aragonite and the magnesium calcite show that the highest contents are observed near the Ghar El Melh lagoon. Elsewhere, the percentages decrease while those of the calcite increase indicating a double origin of carbonates: continental (detrital calcite gains) and biogenic (shells of marine species). Quaternary emergences in the Mejerda watershed constitute probably the main source of quartz in River delta, when calcite may have two origins: chemical precipitation of Ca^{2+} HCO_3^- and dissolution of marine fauna shell. Kaolinite concentrates more in the centre of the Gulf of Tunis (Brahim and Chkioua, 2007), this indicates probably that the kaolinite is formed by sedimentation mechanisms in the least agitated areas. The presence of the smectite, very low granular size mineral, is made by electrochemical flocculation phenomena or by organo–mineral flocculation (Brahim and Chkioua, 2007). Essoni (1999) demonstrated that in the rest of the Gulf of Tunis, the smectite is essentially made by organo–mineral flocculation, because the distribution of the smectite coincided perfectly with that of the total organic carbon.

Aluminium and iron: Sediments near the Mejerda river mouth, the Ghar El Melh lagoon and the Ariana lagoon contain the most Al and Fe, the rest is concentrated in offshore sediments. This supposes that these three hydrographic systems constitute a source for Al and Fe. These two metals are produced from the sedimentary rocks of the Mejerda River watershed. This is particularly the case for Al which is considered as a detrital element, while the likely origin of Fe is from the mining activity in northwest Tunisia. Other studies have shown that the sediments of the Mejerda River and those of the offhsore have the highest Fe concentrations. In the rest of the Gulf (for example, the small Gulf of Tunis), the Fe concentration is less than 10 mg g^{-1} (Essoni 1999). Iron is mainly associated with the residual fraction and Fe-oxy-hydroxide; this association has been observed in surface sediments across the Gulf of Tunis (Essoni, 1999) and in

Ghar El Melh lagoon in northern Tunisia (Oueslati *et al*., 2006; 2010)

Cadmium: Cd shows no similarity in its spatial distribution with the granular size or any other substrate sediment. However, the association of this element with carbonates has been discussed by several authors (Added, 1981; Papadopoulos and Rowell, 1988), but it is limited to one area north of the mouth. Cadmium also has high levels (> 1 mg kg^{-1}) in all samples, varying from 0.1 to 0.25 mg kg^{-1} in other similar Mediterranean areas: Gediz Delta (Turkey) (Parlack *et al*., 2006); Nermut Bay (Turkey) (Esen *et al*., 2007). The highest content (5 mg kg^{-1}) is recorded in sediments of the Bay of Monastir (Tunisia) (Sahnoun, 2000), and in the Gulf of Gabes (southern Tunisia): 1 mg kg^{-1} (El Kihel, 1995), (Table 6).

Nickel and chromium: The concentration of Ni and Cd is relatively lower than that observed in other similar natural areas; in the bay of Monastir (Sahnoun, 2000) and the bay of Nice (Rapin, 1980; Span 1984). The concentration is lower than 30 mg kg^{-1} and is similar to that observed in the Rhône delta: 28 mg kg^{-1} (Added, 1981). Higher concentrations have been reported in the Mediterranean: in the delta of Gediz (Turkey), Parlak *et al*. (2006) observed a concentration reaching 57 mg kg^{-1}, and 63 mg kg^{-1} in the Bay of Nermut (Turkey) (Esen *et al*., 2007). In many parts of the Mediterranean, the Cr concentration is less than 60 mg kg^{-1}, the highest being observed in the delta of Gediz (Turkey): 488 mg kg^{-1} (Parlak *et al*., 2006), (Table 6).

Copper: The concentration of Cu is high near the mouth of the Mejerda River and the Ariana lagoon. These seem to be the main sources of the copper in the delta. Globally the concentration of the copper is low, and is similar to that observed in the bay of Nice: 15 mg kg^{-1} (Rapin, 1980; Span, 1984), or that of the Rhône delta: 20 mg kg^{-1} (Added, 1981). In other natural Mediterranean sites, the Cu concentration is higher; for example 20–40 mg kg^{-1} in the Gulf of Trieste (Faganneli *et al*., 1991) and 20–78 mg kg^{-1} in the bay of Algiers (Boudjellel *et al*., 1993). Copper is dominant in the organic and residual fractions, several authors stated that copper was transported to surface sediments in association with biogenic substances (Chester *et al*., 1988). In some coastal areas, one of the main sources of copper and zinc in

Table 6 Average concentration of trace metals in some Mediterranean areas

Zone	Cd	Pb	Zn	Co	Cr	Cu	Ni	Mn
G.G	1	–	50	–	–	–	45	
N.B	0.15	50	60	10	65	15	30	
M.B	5	30	30	–	25	6	30	100
R.D	–	15	60	8	20	20	28	
A.B	–	16–93	60–255	–	–	23–78	–	198–370
G.T	–	10–20	100–150	–	–	20–40	–	600–800
Nt.B	0.1–0.25	22–89	75–266	–	35–98	16–43	30–63	231–343
G.D	0.01–0.18	1.83–37	–	15–21	5–488	0.39–30	8–57	–

G.G , Golfe of Gabès (El Kihel, 1995) ; N.B , Nice bay (Rapin, 1980 ; Span, 1984) ; M.B ,Monastir bay (Sahnoun, 2000) ; R.D , Rhône delta (Added, 1981) ; A.B , Alger bay (Boudjellel *et al.,* 1993) ; G.T , Gulf of Trieste (Faganneli *et al.,* 1991) ; Nt.B , Nermut bay (Esen *et al.,* 2007) ; G.D , Gediz Delta (Parlak *et al.,* 2006).

surface sediments has been shown to be lithogenic minerals (Moussa 1984).

Zinc and lead: There are two probable origins of Pb and Zn: local contamination sources (lead fishing nets, shipwreck) and the Mejerda River and neighbouring wet zones (Ghar El Melh lagoon, Ariana lagoon and Khlij canal). Compared to other studies, Zn and Pb concentrations in the Mejerda River delta are high. In the bay of Alger, the Zn concentration exceeds 250 mg kg^{-1} (Boudjellel et al., 1993) and Pb exceeds 90 mg kg^{-1} in the Nermut Bay (Turkey) (Esen et al., 2007). Moreover, the concentration of Pb does not exceed 100 mg kg^{-1}, and Zn is between 30 and 60 mg kg^{-1} (Nermut Bay, Monastir Bay, Rhone delta, Gediz delta). These levels are much lower than that observed in the Mejerda River delta (Table 6). The association of lead with exchangeable, organic and residual fractions of the sediment does not support the observations across the Gulf of Tunis, where lead is mainly associated with carbonates up to 28% (Essoni, 1999). Other studies have shown that lead can be associated mainly with organic matter, especially in environments where there are anthropogenic sources (Espierre canal Belgium), this is probably due to anthropogenic pyritic compounds.

Zinc is preferentially associated with Fe/Mn oxides, as was previously observed (Fernandes 1997; Ma and Rao 1997). Ramos et al., (1999) showed that Zn has a high affinity for oxides-hydroxides in soils and sediments. Zn is also associated with organic matter, this may be explained by the fact that plankton biomass has a great ability to bind zinc (Collier and Edmon 1984), (Table 6).

Manganese: In the Mejerda River delta, Mn concentrations are globally less than that observed in other Mediterranean areas, where more than 800 mg kg^{-1} was found in the Gulf of Trieste and 250 to 350 mg kg^{-1} in Nermut bay. In the bay of Monastir, Mn values are less (<100 mg kg^{-1}) than that observed in the Mejerda River delta (Sahnoun 2000). The association of Mn with Mn oxide-hydroxides has been observed in other natural environments, and has been attributed to anthropogenic sources of this metal (Mamdouh et al., 2010), (Table 6). Across all of the Gulf of Tunis, Mn is mainly associated with carbonates (Essoni, 1999) and this has been explained as the result of a possible adsorption or co-precipitation of manganese with calcite.

In general, distribution of metals in the five fractions of the sediment varied slightly between coastal sediments and offshore sediments. It is possible that this region is not large enough to observe a change in the chemical speciation of metals between the coast and offshore. In fact, it is in the Mejerda River mouth to Zembra island where we can observe a significant variation. In general, Fe, Cd and Cu are highly sequestrated in sediments, most of it is associated with the residual fraction. Pb and Zn are bound to the residual fraction, so they are the most polluting metals in surface sediments. These results confirm the observation of the enrichment factor.

CONCLUSION

The Mejerda River and all neighbouring wet zones (Ghar El Melh lagoon, Ariana lagoon and Khlij canal) constitute the principal source of metallic elements in the delta. Trace metals are not distributed by tributaries to the fluvial or marine hydrodynamism but are connected to the sedimentary substrata: clays in offshore sediments and the carbonates near the coast.

Neither the sedimentation processes, nor those of the geochemistry of the Mejerda River are clearly established in the delta. This is due to the low flow of the river and the existence of other local sources of heavy metals. The dominant role of the Mejerda River in the metallic pollution of the Gulf of Tunis has declined since its flow decreased due to the construction of dams upstream.

The enrichment factor shows that human activity is largely responsible for the high levels of lead, zinc and cadmium; this is in accordance with the type of mining activity in the watershed of the Mejerda River. Despite the construction of dams, changes in the course of the river and the decline of mining activity in the north west of Tunisia, the levels of these metals in the surface sediments remain relatively elevated, but the chemical speciation confirms that these elements are deeply sequestered in the sediment, and do not constitute a particular toxicity towards marine organisms in the Delta.

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