



# Bioavailability and assessment of heavy metal pollution in sediment cores off the Mejerda River Delta (Gulf of Tunis): How useful is a multiproxy approach?



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## ABSTRACT

Three core samples were taken from zones offshore from the Mejerda River Delta (Tunisia) and analyzed for major and trace elements to assess their relationships with organic matter, monosulfides and carbonates, as well as for pollution and bioavailability. Chemical speciation,  $\sum$  SEM/AVS, the enrichment factor (EF) and the geo-accumulation index (I-geo) were used. Iron, cadmium, lead and zinc – the most frequently mined metals in the Mejerda catchment – were found as contaminants in the offshore areas. Estimations of trace element accumulation using the EF and the I-geo index show that lead, and to a lesser extent zinc, are the most polluting metals off the Mejerda outlet. According to their bioavailability, these metals are also the most toxic. Only cadmium is heavily present in delta sediment (EF > 100) though deeply sequestered (100% bound to the residual fraction) and thus presents no toxicity.

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## 1. Introduction

Sediment in coastal areas, especially in river mouths, is highly prone to heavy metal pollution (Sprovieri et al., 2006; Ogston et al., 2008; Cossa et al., 2014). Though heavy metals are involved in the geochemical reactions occurring in the water column and sediment, these inorganic pollutants are persistent and remain toxic for marine organisms. The use of chemical speciation (Tessier et al., 1979) and Simultaneously Extracted Metals (SEM)/acid volatile sulfide (AVS) has been proposed as a possible indicator of heavy metal toxicity for biotas, particularly considering the physicochemical state and availability of reactive metals (Di Toro et al., 1992, 1999; Ankley et al., 1994; Allen et al., 2009; Nasr et al., 2014). In addition, various approaches have been used to estimate the anthropogenic impact of heavy metals in sediments, such as the enrichment factor (EF) (Di Toro et al., 1992, 1999) and geo-accumulation indexes (I-geo) (Müller and Süss, 1979).

The Mejerda River in northern Tunisia, with an extensive mining activity located in its watershed, appears to be a good subject for study using a multiproxy approach in order to establish the pollution status of its delta. It must be pointed out, however, that other sources of metal contamination (Ghar El Melh Lagoon, the Khlij Channel and Sebket Ariana) (Helali et al., 2013; Boussen, 2010; Sebai, 2007; Essoni 1998) are also present in the area. Two tasks were undertaken in this

study: 1) assessment of metal accumulation via different approaches (geoaccumulation indexes, the enrichment factor) in three marine sediment cores taken from the zone offshore from the Mejerda River mouth and 2) estimation of the importance of the reactive metals that may be available and which may potentially threaten marine biotas, also using two approaches (AVS/SEM ratio and chemical speciation).

## 2. Material and methods

### 2.1. Study site

The Mejerda River, with its delta located on the western shore of the Gulf of Tunis, is the gulf's principal source of water and sediments. With a catchment of 23,700 km<sup>2</sup>, an approximate water flow of 30 m<sup>3</sup> s<sup>-1</sup> and a sediment flow varying from 10 to 30 g L<sup>-1</sup> (Essoni, 1998), the Mejerda basin supports an abundant mining activity (polymetallic deposits: Pb > Zn > Cu > Hg and As). The principal mines are shown in Fig. 1.

Mining in the Mejerda catchment began during the Roman period and reached its maximum development during the 19th and 20th centuries. For example, the Boujerda mine (Fig. 1), in operation from 1897 to 1914, was temporarily closed but then re-opened from 1929 to 1947. The J. Slata mine opened in 1904 and remained in operation until the 1950s. The Fej Lehdhoum mine reached its maximum level of activity after 1948 and was then progressively shut down in last decades of the 20th century (Sebai, 2007). Mining in the Mejerda catchment is currently much reduced compared to the first decades of the 20th century.

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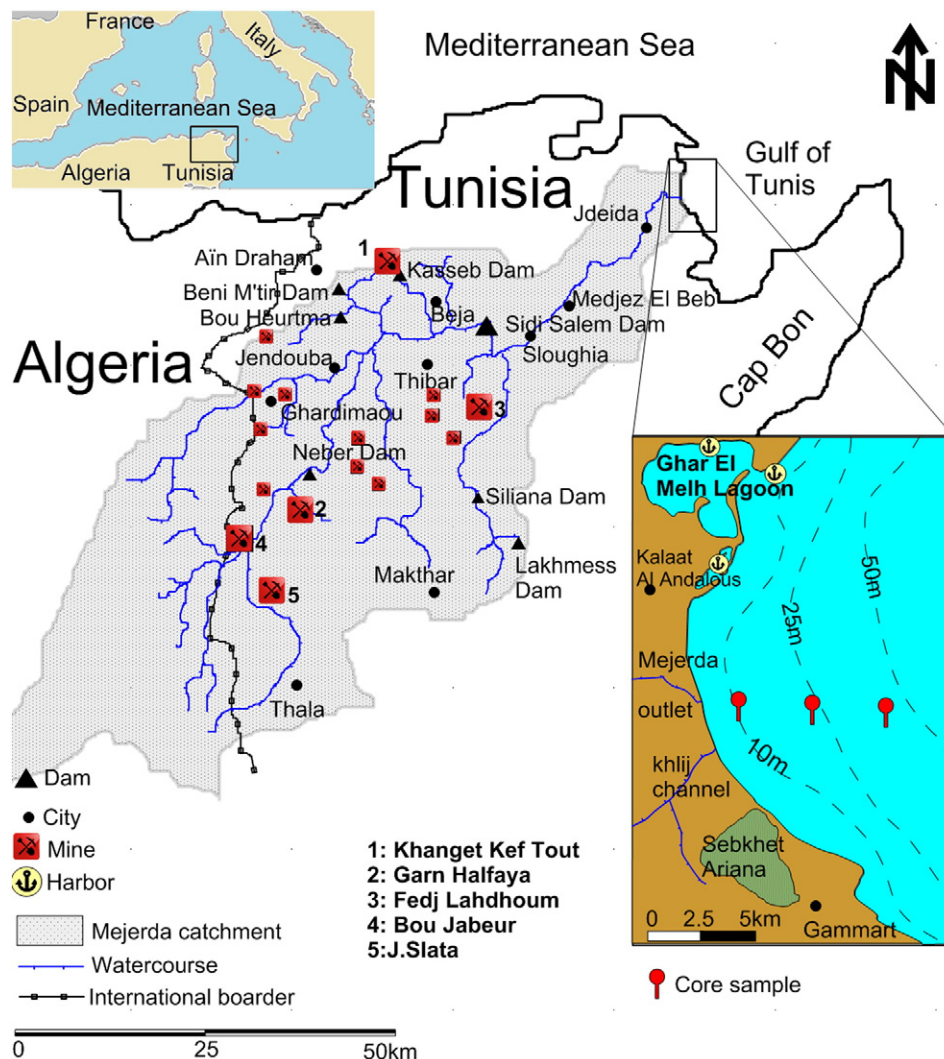


Fig. 1. Mejerda catchment and study site.

Today, the Mejerda River and its tributaries occupy an important position in the mobilization of Tunisia's water resource strategy. Though the waters of the Mejerda constitute the main source of polluting metals in the Gulf of Tunis, the zones off the delta are also subject to influences from three other sources: the Khlij Channel, Ghar El Melh Lagoon and Sebkhet Ariana, all of which are connected to marine waters (Fig. 1). Several studies have been conducted in the Gulf of Tunis, and especially off the Mejerda outlet, describing the lateral variation of granulometry and mineralogical composition of the sediment (Helali et al., 2013; Essoni, 1998; Brahim et al., 2015). The western part of the gulf is subject to prevailing winds that change directions according to season, from north to northwest in winter and from east to southeast in summer (Ben Charrada, 1997). The sea surface currents depend upon wind direction (Fig. 2) and flow mainly from north to south (Brahim et al., 2007 and 2015).

## 2.2. Sampling and sample processing

A recent geochemical study shows that pollution by heavy metals in surface sediment in the Gulf of Tunis varies from coastal areas to offshore zones, (Helali et al., 2013) with small or absent variations from north to south facing the Mejerda outlet. The present study was therefore conducted at three points (stations) forming a radial

perpendicular to the coast opposite the mouth (Fig. 1) at depths of 10, 20 and 40 m (Table 1).

Core samples were taken by divers using polyvinyl chloride pipes ( $\phi$ : 50 mm and length: 50–90 cm). The cores were sliced under an inert atmosphere ( $N_2$ ) into 1- to 2-cm sections from the top 20 cm, and into 5 cm sections for the rest of the core. Each section was placed in a polypropylene beaker previously washed with bi-distilled water (Milli-Q) and sealed under an inert atmosphere. Handling and analysis of samples were performed in a clean laboratory using plastic LabWare containers (LabWare, Wilmington, Delaware, USA). By means of a 63- $\mu$ m nylon mesh the sediments were sieved to collect the finer fraction and then oven-dried at 60 °C. Wet sediment was sub-sampled for acid volatile sulfide (AVS) analysis. 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 analyzed for Al, K, Fe, Mn, Pb, Zn, Cd, Cu, Co, Ni and Cr by flame atomic absorption spectrometry (Thermo Scientific ICE 3300 AA Spectrometer). The procedures used for heavy metal analysis were checked for accuracy using the BCR-032 certified reference material, obtaining good concurrence (<13%); the certified values and the relative standard deviations (RSDs) obtained from 10 replicates of one sample were typically <4.5% (Tables 2 and 3). The AVS concentrations in the sediments were analyzed using the cold-acid purge-and-trap technique described in detail by Added (2002). Ten grams of

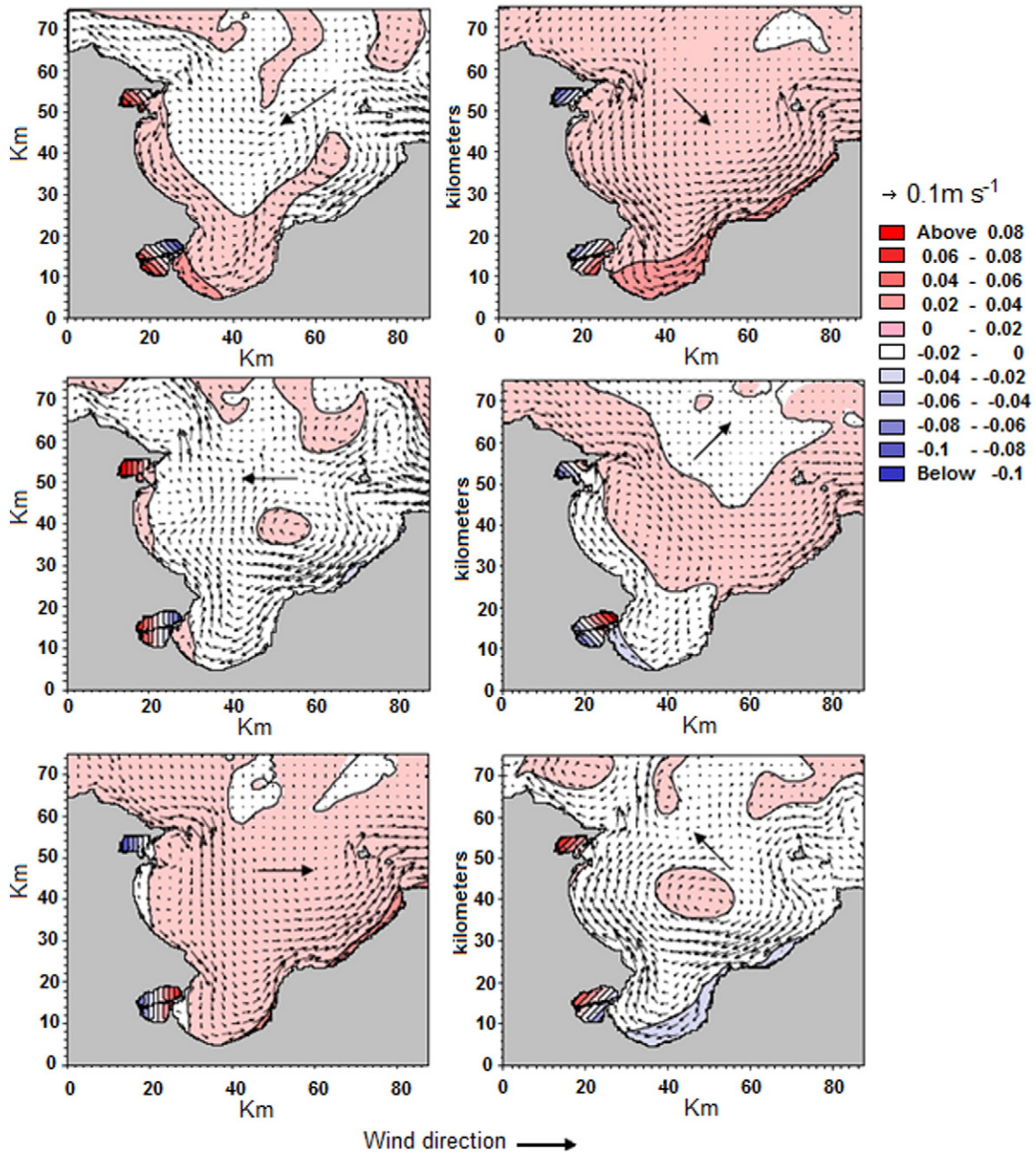


Fig. 2. Wind direction and marine currents (Brahim et al., 2007 and 2015).

accurately weighed sediment was placed in a 500 mL round bottom flask and purged for 10 min with nitrogen at a flow rate of  $40 \text{ cm}^3 \text{ min}^{-1}$ , before addition 20 mL of HCl (6 N). Nitrogen was then bubbled through the sample for 20 min at a flow rate of  $20 \text{ cm}^3 \text{ min}^{-1}$ . While the sample was heating,  $\text{H}_2\text{S} + \text{N}_2$  was passed through 0.1 N iodine solution and simultaneously stirred magnetically to trap the  $\text{H}_2\text{S}$  volatilized from the acidified sediments. The excess iodine was titrated with sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$  (0.1 N). Total carbon and nitrogen were measured using a

Table 1  
Sampling locations and water depths.

Station	Latitude	Longitude	Depth (m)
10 m	37°0.468'N	10°13.821'E	10
20 m	37°0.440'N	10°16.188'E	20.5
40 m	37°0.419'N	10°17.881'E	38

PerkinElmer PE 2400CHN on dry sediment. Calcium carbonate in sediment was assessed using a Bernard calcimeter. Each sample was measured three times and an average value calculated. The sequential extraction procedure applied in this study was developed by Tessier

Table 2  
Accuracy of heavy metal analysis (%).

Element	BCR-032	This study	% error
Fe	1.15	1.221	6
Mn	18.8	22.12	7
Zn	0.253	0.286	10
Cu	33.7	34.2	1.5
Cd	0.02	0.024	12
Co	0.59	0.66	11
Ni	34.6	30.2	13
Cr	257	250	2.7
Al	2.75	2.551	7.3
K	0.45	0.605	3.4



**Table 3**  
Relative standard deviation (RSD) of analyzed elements (%).

Element	RSD (%)	Element	RSD (%)
K	1.12	Co	0.27
Al	1.55	Ni	0.65
Fe	0.96	Cr	3.38
Mn	4.40	Cu	1.97
Pb	2.49	AVS	5.22
Zn	2.20	Cd	0.22

et al. (1979). Extractions were in the following order with the associated chemical reagents and conditions (to 1 g sediment):

- (1) exchangeable fraction: 8 mL of  $MgCl_2$  (1 M) adjusted to pH 7.0 with ammoniac + continuous agitation for 1 h;
- (2) bound to carbonates: 8 mL of NaOAc (1 M) adjusted to pH 5.0 with acetic acid plus agitation for 6 h;
- (3) bound to Fe and Mn oxides 20 mL of  $NH_2OH$ , HCl (0.04 M) in 25% (HOAc) heated for 6 h at 95 °C with occasional agitation;
- (4) Bound to organic matter: 3 mL of  $NH_4OAc$  plus 5 mL of 30%  $H_2O_2$  adjusted to pH 2 with  $HNO_3$ ; and
- (5) the residual fraction: mixture of 20 mL HF plus 10 mL  $HClO_4$  (total digestion).

After each successive extraction, separation was performed by centrifuging the sample at 4000 rpm for 15 min. The supernatant was then separated using a micropipette. Metal concentrations were determined by flame atomic absorption spectrometry (with a Thermo Scientific ICE 3300 AA Spectrometer).

Correlations of different elements are calculated by the XLstat and STATISTICA.10 software.

The enrichment factor for each heavy metal is calculated relative to the aluminum content as Al is a conservative element, unaffected by human activity, which is why it is considered as the detrital fraction of sediment. The EF is calculated by normalizing metal levels in comparison with those of aluminum (Zoller et al., 1974; Hakanson, 1980; Alvarez-Iglesias et al., 2003; Maanan et al., 2004) and compared with the levels recorded in the NASC (North American Shale Composite). The formula used is as follows (Salomons and Forstner, 1984):

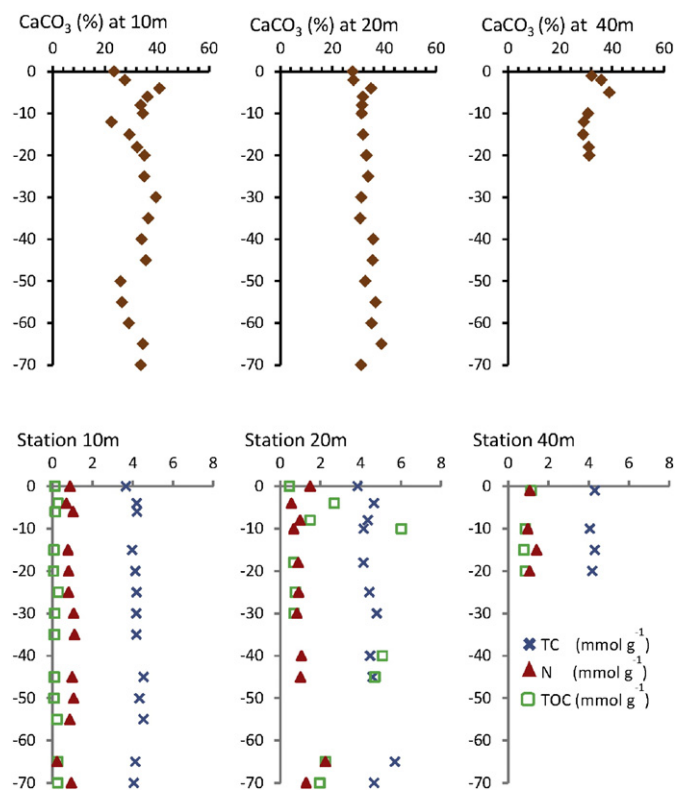
$$EF = [Me/Al]_{\text{sample}} / [Me/Al]_{\text{NASC}}$$

$Me_{\text{NASC}}$ : Al = 80.9 mg  $g^{-1}$ ; Fe = 30 mg  $g^{-1}$ ; Zn = 71  $\mu g$   $g^{-1}$ ; Co = 17  $\mu g$   $g^{-1}$ ; Cr = 83  $\mu g$   $g^{-1}$ ; Ni = 44  $\mu g$   $g^{-1}$ ; Mn = 600  $\mu g$   $g^{-1}$ ; Cu = 25  $\mu g$   $g^{-1}$ ; Cd = 0.09  $\mu g$   $g^{-1}$ ; Pb = 17  $\mu g$   $g^{-1}$ .

Introduced by Müller and Suess (1979), geoaccumulation is calculated using the equation:  $I\text{-geo} = \log_2 (C_m / 1.5C_b)$ , where  $C_m$  is the metal concentration and  $C_b$  is the metal concentration with the geochemical background. In this study,  $C_b$  was calculated from five of the lowest values measured for each element in all three cores (Tessier, 2012). The geoaccumulation indexes are classified into seven categories, each representing a degree of pollution:  $I\text{-geo} < 0$ : no pollution;  $0 < I\text{-geo} < 1$ : no pollution or moderate pollution;  $1 < I\text{-geo} < 2$ : moderate pollution;  $2 < I\text{-geo} < 3$ : moderate to strong pollution;  $3 < I\text{-geo} < 4$ : heavy pollution;  $4 < I\text{-geo} < 5$ : strong to extreme pollution; and  $I\text{-geo} > 5$ : extreme pollution.

### 3. Results

The sediments in the three cores are characterized by their homogeneity, where the fine fraction ( $< 63 \mu m$ ) represent 100% of the sediment from top to the bottom of each core. This is the case of the sediment collected off the Mejerda outlet beyond the 6 m depth (Helali et al., 2013; Essoni, 1998).



**Fig. 3.** Vertical profiles of carbonates, TC, N and TOC.

In the top 10 cms of sediment, carbonate concentrations increase from 20 to 40% at the 10 m station and from 30 to 40% at the 20 and 40 m stations (Fig. 3). In all cores, the carbonate content exhibits great variation, though no specific trend emerges. Levels do not exceed 40%, therefore the carbonate content in the delta sediments remain relatively low. The organic content of both carbon and nitrogen is relatively high (Fig. 3) which is generally characteristic of silty clay sediments and is also the case in this study (Helali et al., 2013). The average concentration of organic carbon is 0.86 mmol  $g^{-1}$  and 1.08 mmol  $g^{-1}$  at the 10 and 20 m stations, respectively. The change in concentration in both cores is irregular and the profiles do not show the exponential variation which characterizes degradation of organic matter.

This is also the case for total nitrogen which changes at the 20 m station, showing peaks at 10 cm and from 40 to 50 cm below the sediment–water interface, evolving almost steadily at the 10 and 40 m stations with an average of 0.16 and 0.9 mmol  $g^{-1}$  (Fig. 3), respectively.

The  $Al_2O_3$  content varies from 60 mg  $g^{-1}$  to 80 mg  $g^{-1}$  at the three stations with a slight decrease in the first 10 to 15 cm of each core. The maximum aluminum content (85 mg  $g^{-1}$ ) is observed in the surface sediment at the 20 and 40 m stations (Fig. 4). Iron decreases from 40 to 25 mg  $g^{-1}$  in the first few centimeters of the three cores. The 20 m station is characterized by a less marked variation in the iron content at the bottom of the core, unlike the 10 m station (Fig. 4).

The manganese concentration on the surface varies slightly among the three stations (from 230 to 260  $\mu g$   $g^{-1}$ ), with the concentration profile characterized by a slight increase just below the sediment–water interface. The highest levels are observed in the deep sediment at the 10 m station, where the concentration reaches 337  $\mu g$   $g^{-1}$  at 60 cm depth (Fig. 5). At the 10 m station, lead and zinc contents are maximal, between 50 and 60 cm depth (120  $\mu g$   $g^{-1}$  for Pb and 300  $\mu g$   $g^{-1}$  for Zn), while at the 20 and 40 m stations, the maximum accumulation is found between 20 and 40 cm where more than 70  $\mu g$   $g^{-1}$  for Pb and more than 300  $\mu g$   $g^{-1}$  for Zn have been recorded. The copper content varies from 25  $\mu g$   $g^{-1}$  (surface sediment) to at least 20  $\mu g$   $g^{-1}$  at 10 cm depth (Fig. 5), whereas in the lower sediment the levels are almost constant,

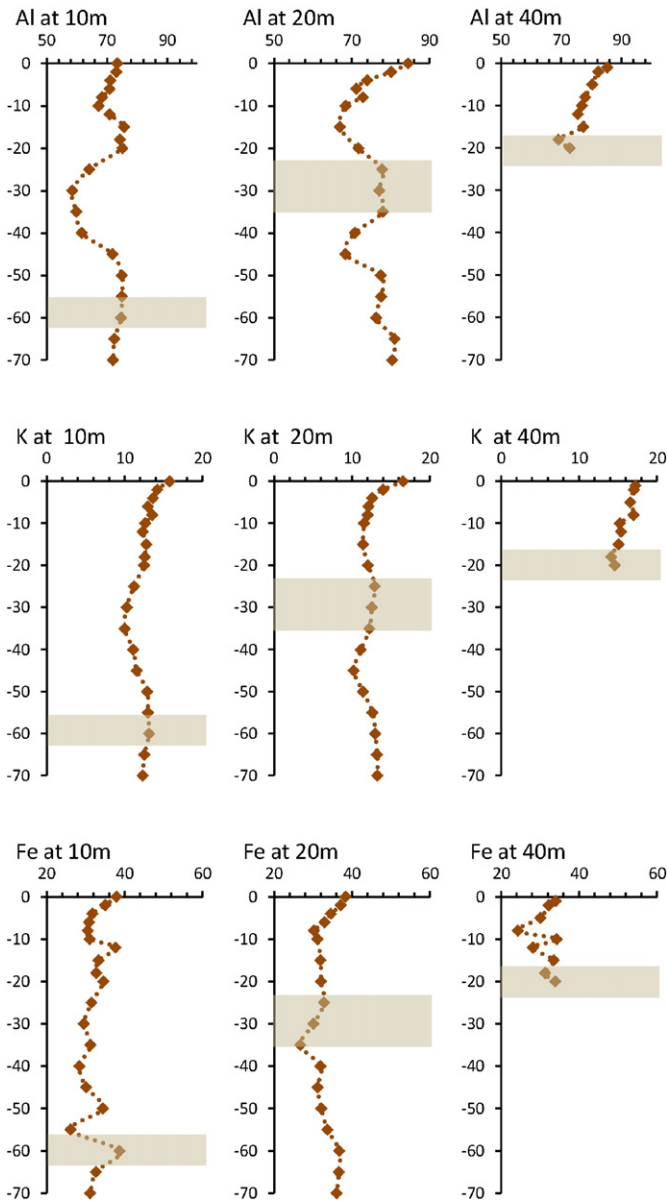


Fig. 4. Vertical profiles of Al, K and Fe in  $\text{mg g}^{-1}$ .

except for the enrichment layer of copper at the 10 m (approx. 50 cm) and at 20 m stations (approx. 30 cm) which correspond to the enrichment zones observed for lead and zinc. The cadmium content remains constant along the 20 m station core (from 2.8 to  $3.1 \mu\text{g g}^{-1}$ ), while slight changes in the Cd concentration are observed at the 10 and 40 m stations, with 3.65 and  $4.8 \mu\text{g g}^{-1}$ , respectively. As for spatial distribution in the delta (Helali et al., 2013), Ni and Cr appear to correlate deeply within the three cores, with varying levels of 20 to  $40 \mu\text{g g}^{-1}$  for Ni and 90 to  $110 \mu\text{g g}^{-1}$  for Cr. Though cobalt does not correlate well statistically with Ni and Cr, ( $R < 0.42$ ) its vertical evolution is quite similar to that of these two metals, as a progressive decrease in concentration is observed in the first levels of each core, with the appearance of the enriched layers at 60, 30 and 15 cm depth at the 10, 20 and 40 m stations, respectively. Peak levels for these metals at the 10, 20 and 40 m stations, respectively, were: 3.3, 6.5 and  $4.25 \mu\text{g g}^{-1}$  for Co; 30, 33 and  $27 \mu\text{g g}^{-1}$  for Ni and 111, 107 and  $101 \mu\text{g g}^{-1}$  for Cr (Fig. 6).

The AVS contents were measured at the three stations over two seasons (in March and August 2012). Concentrations were low, varying from 1 to  $7 \mu\text{mol g}^{-1}$ . Lateral variations are more important than seasonal ones; in fact, it is at the 40 m station that the maximum AVS is

reached (2 to  $7 \mu\text{mol g}^{-1}$ ), while near the coast AVS contents range between 1 and  $2 \mu\text{mol g}^{-1}$  at the 10 and 20 m stations, with peaks of 3 and  $4 \mu\text{mol g}^{-1}$  at 30 and 55 cm depth (at the 20 m station) (Fig. 6). Overall, concentrations increase below the sediment water interface, especially at the 40 m station, though the recorded values are low compared with those observed in other marine sediments. Despite the fluctuations and peak production in the first few centimeters below the sediment–water interface, AVS contents are characterized by a constant evolution in accordance with the sediment characteristics, namely a homogeneous color with gradual decline in the Eh (Helali et al., 2015).

## 4. Discussion

### 4.1. Carbonates and organic matter

The carbonate content measured in the three cores is relatively small and is observed in all the delta surface sediments (Essoni, 1998; Helali et al., 2013), with only the southern area of the Gulf possessing a higher concentration ( $>40\%$ ). The carbonate content correlates with the sandy sediment content ( $R > 0.82$ ) which, in this study, is absent in all three cores. In addition, no shells have been observed in the delta sediment at 6 m depth (Helali, 2010), which is why the carbonate concentrations remain consistently below 40%. Variation in the organic carbon contents among the three stations is similar to that observed for all of the delta surface sediments (Helali et al., 2013), as well as for the entire Gulf of Tunis (Essoni, 1998), whereas the lower organic matter values are observed in the coastal sediments of the delta and in the southern area of the Gulf where sediment composition is sandy. Clay/silt sediments provide more molecular sites capable of binding organic particles than do sandy sediments (Hedges, 2002; Wakeham, 2002). However, this is not always found in the delta sediments; in fact, the organic carbon content is low ( $<0.5\%$ ) in some core layers, despite the fact that the sediment contains both clay and silt. Rojas and Silva (2005) found low concentrations of organic matter in a fine-grained sediment, caused by the large sediment inputs found near the river mouths of the Aysen Cuervo and Condor Rivers in Chile. As the contribution of the Mejerda River varies widely between the dry and wet seasons, especially during flood periods, a gap in the provision of the fine material cannot be excluded.

The constant evolution of organic matter content is characteristic of a strongly agitated area, either because of the bioturbation, to be excluded in the case of the Mejerda River Delta (Helali, 2015), or by marine currents; indeed, in the sheltered and stationary areas, early diagenesis may be responsible for an exponential decrease in the organic matter. In the case of the Mejerda Delta, the levels tend to blend below the sediment–water interface (Helali, 2015). A constant vertical distribution of organic carbon may also be observed in those environments characterized by high sedimentation rates, where organic carbon is quickly removed from the area of intense degradation of organic matter within a very short period (Rojas and Silva, 2005) and where oxidation is the most intense. In the three cores, the C/N ratio is low ( $<10$ ), except at some levels at the 10 m station (Fig. 7) where the ratios are greater than 15. Considering the classifications of C/N ratios proposed by several authors (Deevy, 1973; Rullkötter, 2000) organic matter is largely marine in origin with continental inputs at some intense moments which especially affect the sediment in zones facing the mouth of the Mejerda.

### 4.2. Heavy metals

The fact that in our study area the sediments are clayey (Helali et al., 2013) explains why the aluminum content exceeds  $80 \text{ mg g}^{-1}$ . Al and K are correlated ( $R > 0.84$ ) in the three cores (Fig. 4), suggesting that the Illite group, with the general formula  $(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{Al}_2)(\text{OH})_2(\text{K})$  with  $x$  close to 0.5 (Fütterer, 2006; Tessier, 2012), includes a large proportion of the sediments. In contrast, statistical analysis shows that Al or K are generally negatively correlated with  $\text{CaCO}_3$  ( $R = -0.7$  to  $-0.85$ ), showing

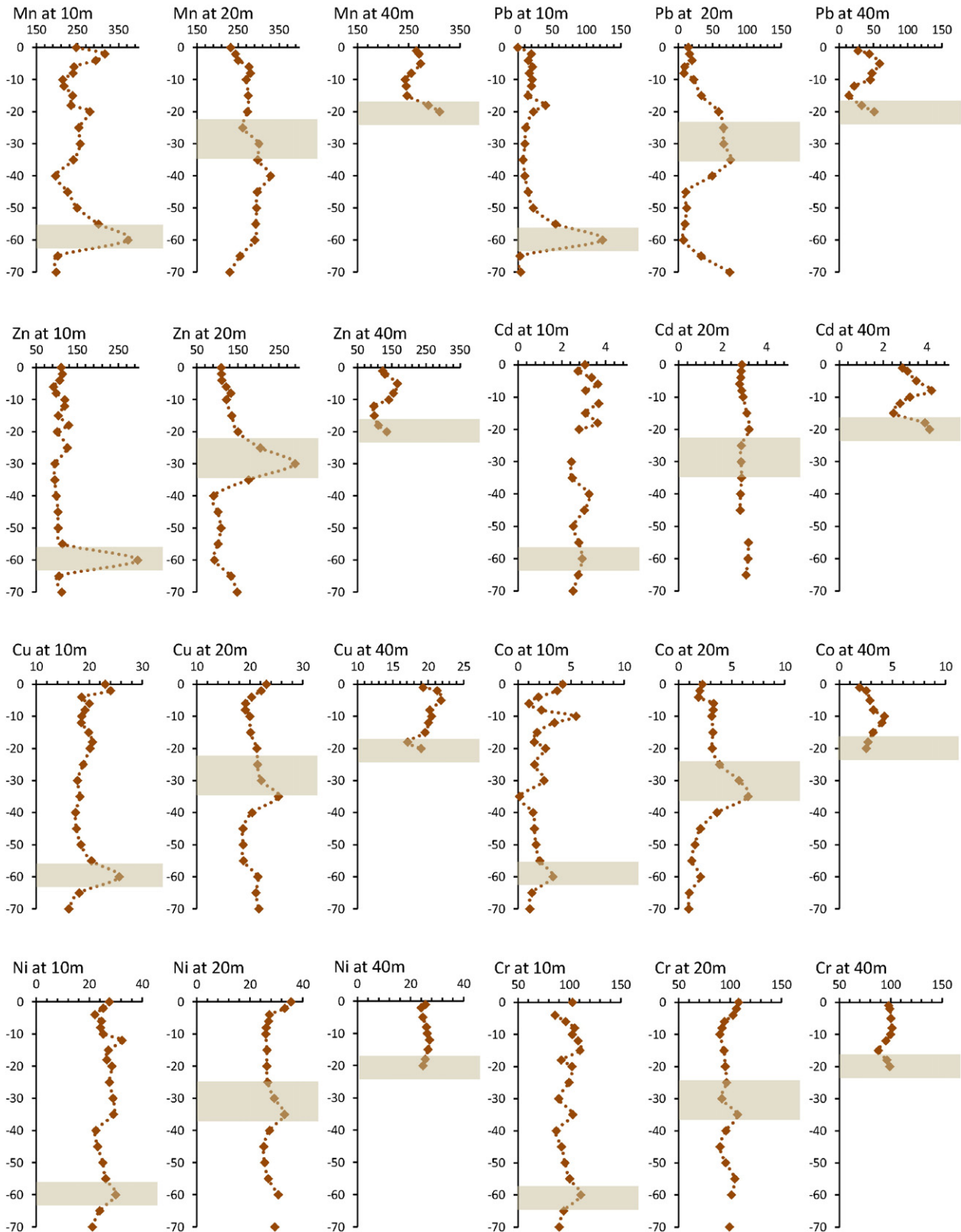


Fig. 5. Vertical profiles of heavy metals in  $\mu\text{g g}^{-1}$  (enrichment level is marked in gray.)

that the carbonates are not of the same origin as the aluminum. Iron is correlated with the Al at the 10 m station ( $R = 0.89$ ), whereas at the 20 and 40 m stations, Al and Fe exhibit completely different behaviors ( $R < 0.3$ ). This is due to the fact that either the origin of the iron is different at the 10 m station from at the 20 and 40 m stations, or that the kinetics of

early diagenesis, which has a great influence on the iron-to-aluminum process, occur at different rates (Tessier, 2012; Added, 1981). The iron content at the tops of the cores is higher than that observed to the north of the mouth of the Mejerda or in the southern area of the Gulf ( $22 \text{ mg g}^{-1}$ ) (Essoni, 1998; Helali et al., 2013), yet it is similar to that

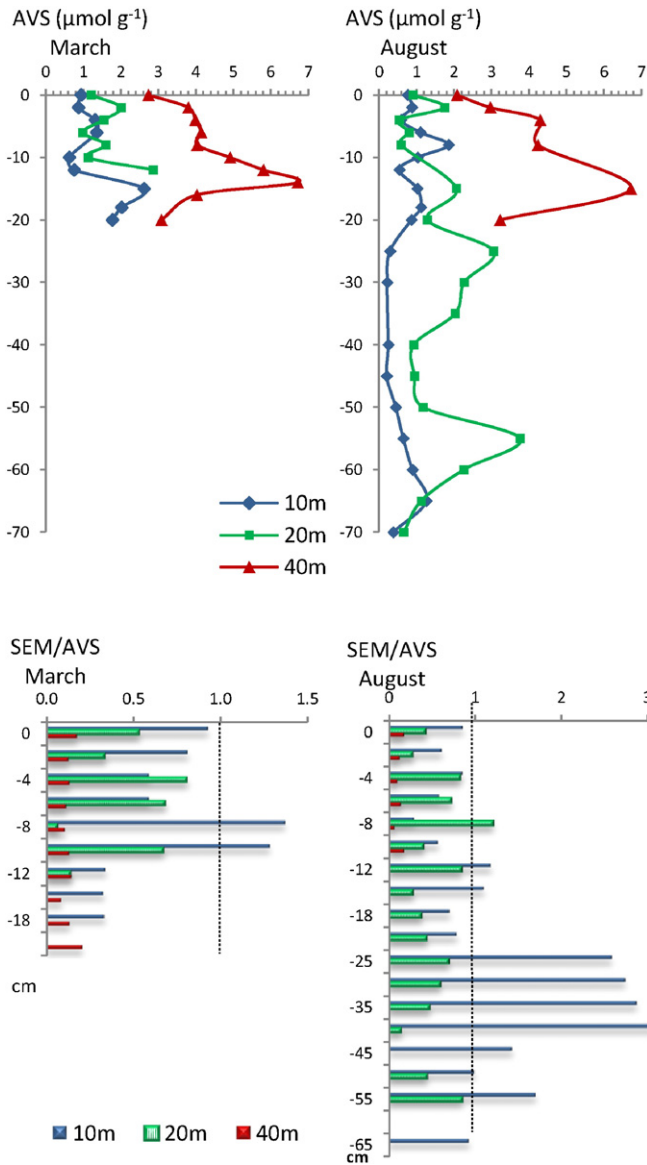


Fig. 6. Vertical profiles of SEM and SEM/AVS.

observed in other marine environments moderately polluted and subject to anthropogenic sources of heavy metals such as the Persian Gulf (Karbassi et al., 2005), the Gdansk Basin (Belzunce-Segarra et al., 2007) and Cardiff Bay (Hitchcock and Thomas, 1992) (Table 4).

Lead and zinc are perfectly correlated across the sediments of each core as is also the case for their spatial distribution in the delta (Helali, 2010). The correlation coefficients between Pb and Zn are,  $R = 0.98, 0.86$  and  $0.96$ , respectively, at the 10, 20 and 40 m stations. The high Pb and Zn levels observed probably correspond to the peak of the mining activities in the Mejerda catchment, as the different sedimentation rates among the three points studied explain the reason for the enrichment zones occurring at different levels (more inputs at the 10 m station than at the 20 or 40 m stations). The accumulation layer is deeper in the coastal station sediments. The cessation of mining activity explains why Pb and Zn concentrations decrease in the tops of the cores, but remain relatively high ( $30$  to  $50 \mu\text{g g}^{-1}$  for Pb, and  $100 \mu\text{g g}^{-1}$  for Zn in surface sediments). For example, the Zn content in Monastir Bay (Tunisia) is about  $30 \mu\text{g g}^{-1}$  (Sahnoun, 2000) and  $50 \mu\text{g g}^{-1}$  in the Gulf of Gabes (Elkikhel, 1995). The lead content attained  $15 \mu\text{g g}^{-1}$  in the Rhône Delta (Addad, 1981) and  $10$  to  $20 \mu\text{g g}^{-1}$  in the Gulf of Trieste (Faganelli et al., 1991). Such high values currently observed in surface

C/N at 10m, 20m and 40m

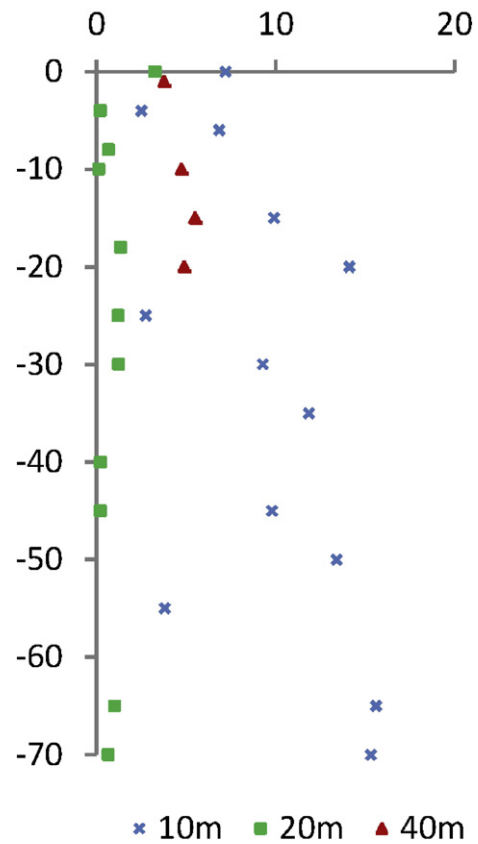


Fig. 7. Vertical profiles of C/N.

sediment despite the end of mining are probably due to the emergence of new sources for these metals, likely industrial development in the coastal areas of the Gulf of Tunis and the building of the Khlij Channel which drains the waste water south of the mouth of the Mejerda, both of which are possible sources of lead and zinc.

For manganese, the correlation of this element with other metals is not clearly established. At the 10 m station, Mn is correlated with Pb, Zn and Cu (respectively,  $R = 0.85, 0.83$  and  $0.87$ ), though it does not correlate with these elements further offshore (at the 20 and 40 m stations). Manganese accumulation is limited to the coastal area (10 m station). Moreover, it is at this station that the higher manganese levels are observed (more than  $300 \mu\text{g g}^{-1}$  a few centimeters below the sediment-water interface, and more than  $380 \mu\text{g g}^{-1}$  between 50 and 60 cm depth) (Fig. 5). But manganese may be affected by the different chemical reactions of early diagenesis occurring in the sediment, which is the case in our study area (Helali et al., 2015); in addition, the formation of manganese oxides is also prevalent in marine environments. Variation in manganese content in the delta sediments may be the result of continental inputs affecting the sediment near the Mejerda outlet rather than a native chemical formation offshore.

Copper contents resemble those observed in the rest of the Gulf of Tunis. Variations observed in this study were reported by Essoni (1998). The sediments found at the mouth of the Mejerda River are the most copper-enriched. The river's actual impact is clearly established in the delta surface sediments; indeed, the copper maximum ( $> 17 \mu\text{g g}^{-1}$ ) is observed spread across the outlet (Helali et al., 2013). Though copper is produced in the same manner as Pb and Zn (peak concentrations reached at 50 and 30 cm depth at the 10 and 20 m stations, respectively), an important and continuous input of copper appears to have accumulated over recent decades which explains why its contents have increased at the sediment surface, unlike for Pb and Zn. Copper is a common product



**Table 4**  
Average contents of heavy metals in  $\mu\text{g g}^{-1}$  (except for Fe in  $\text{mg g}^{-1}$ ) in other moderately polluted coastal areas: (1) Helali (2010); (2) Liu et al. (2011); (3) Spencer and MacLeod (2002); (4) Karbassi et al. (2005); (5) Belzunce-Segarra et al. (2007); (6) Hitchcock and Thomas (1992).

Location	Fe	Mn	Pb	Zn	Cd	Cu	Ni	Co	Cr
(1) Surface sediment of the Mejerda Delta	16 to 34	200 to 380	20 to 120	80 to 180	0.5 to 8	7 to 18	11 to 30	0.5 to 11	20 to 150
(2) Pearl River Estuary (China)	***	***	32 to 88	100 to 274	0.29 to 1.55	53 to 105	39 to 76	16 to 24	84 to 138
(3) Medway Estuary (England)	***	***	20 to 296	61 to 338	***	21 to 343	14 to 49	***	31 to 144
(4) Persian Gulf	22 to 29.2	402 to 513	33 to 80	34 to 67	***	15 to 31	97 to 133	***	106 to 180
(5) Gdansk Basin (Poland)	17.9 to 50.2	188 to 434	21 to 83	56 to 210	***	21 to 71	20 to 48	9 to 21	65 to 107
(6) Cardiff Bay (England)	32	668	138	234	***	61	26	***	44

of urbanization: the building of the Khlij Channel and the increased urban development along the Gulf of Tunis and near Ghar El Melh Lagoon are probably the most important causes for this increase. Despite its increased concentrations, copper does not appear to be problematic here when compared to other marine environments where the contents remain similar or lower, for example from 21 to  $343 \mu\text{g g}^{-1}$  in the Medway Estuary (Spencer and MacLeod, 2002), 15 to  $31 \mu\text{g g}^{-1}$  in the Persian Gulf (Karbassi et al., 2005), up to 71 and  $61 \mu\text{g g}^{-1}$ , respectively, in the Gdansk Basin (Belzunce-Segarra et al., 2007) and Cardiff Bay (Hitchcock and Thomas, 1992) (Table 4).

In general, the best correlations of Fe, Mn, Pb, Zn and Cu with aluminum are observed at the 10 m station; yet, this correlation tends to either decrease or disappear at the 20 and 40 m stations. Moreover, these metals are negatively correlated with the more marine elements such as Ca and Sr (Helali, 2015), especially at the 10 m station ( $r = -0.69$  for Fe,  $-0.67$  for Mn,  $-0.61$  for Pb and Zn and  $-0.52$  to  $-0.75$  for Cu). All these observations reinforce the hypothesis of a detrital origin for these metals. Though not correlated with Pb and Zn, cadmium is produced from the mining activity in the Mejerda catchment where many outcrops rich in cadmium carbonates (Sebai, 2007; Boussem, 2010) also help to explain why the element's levels are consistently high in the delta sediments and not only in a few layers as is the case for lead or zinc in the three cores. Cadmium levels are relatively high here when compared with other marine environments such as the Pearl River Estuary (China) where the measured levels vary from 0.29 to  $1.55 \mu\text{g g}^{-1}$  (Liu et al., 2011) and Lake Wigry in Poland where it varies from 0.33 to  $11 \mu\text{g g}^{-1}$  (Aleksander-Kwarczak and Kostka, 2011).

Nickel and chromium evolution in the three cores is similar to that previously reported by Essoni (1998) to the north of the Mejerda outlet and throughout the Gulf of Tunis, with the exception of offshore sediments (beyond 50 m depth). Enrichment of these metals in the delta sediments is found to be to the same degree as for Pb and Zn. Ni, Cr and Co also appear to be of human origin, though levels are not sufficient to cause any pollution. For example, the nickel content in the Persian Gulf exceeded  $100 \mu\text{g g}^{-1}$  (Karbassi et al., 2005) and attained nearly  $50 \mu\text{g g}^{-1}$  in the Gulf of Gabes (Elkhihel, 1995) and in the Gdansk Basin in Poland (Belzunce-Segarra et al., 2007). Similar values have been recorded in Monastir Bay in Tunisia (Sahnoun, 2000) and Cardiff Bay (25 to  $30 \mu\text{g g}^{-1}$ , Hitchcock and Thomas, 1992). The cobalt content in the Mejerda Delta is even lower, as observed in other similar marine environments: 15 to  $21 \mu\text{g g}^{-1}$  in the Gediz Delta (Parlak et al., 2006.),  $8 \mu\text{g g}^{-1}$  in the Rhône Delta (Added, 1981) and 16 to  $24 \mu\text{g g}^{-1}$  in the Pearl River Estuary in China (Liu et al., 2011). Only chromium levels appear to be slightly higher as only 20 to  $25 \mu\text{g g}^{-1}$  are observed in the Rhône Delta (Added, 1981) and in Monastir Bay (Sahnoun, 2000) and  $44 \mu\text{g g}^{-1}$  in Cardiff Bay (Hitchcock and Thomas, 1992).

#### 4.3. Enrichment factor (EF)

Overall, the EF distribution is similar to that found in surface sediments (Helali et al., 2013), in fact, it is Pb, Zn and Cd, which show greater enrichment. The EF is the lowest for Pb (EF = 1) and Zn (EF = 2) in the first centimeters below the sediment–water interface. Below, in the cores, some layers are observed to be relatively enriched with Pb and

Zn; the enrichment is observed from 10 cm at the 40 m station, from 20 cm at the 20 m station and below 35 cm at the 10 m station (Fig. 8). Two aspects characterize the cadmium enrichment factor: a very high degree of enrichment (average of 30 to 40 at all three stations), and distribution consistency. In fact, except for slight fluctuations at the 40 m station, the Cd enrichment factor is constant along the entire 70 cm of the cores at the 10 and 20 m stations.

All these metals are originated mainly in the mines of northwestern Tunisia; in fact, several former lead–zinc mines are located in the Mejerda catchment area (Mauldenauer et al., 2008). This clearly shows that the contaminated sediment inputs changed over time, especially during the last century (Paskoff, 1994). In addition, the course of the Mejerda River evolved over the same period (Currently, the measurements observed in the deep sediment from the core samples at

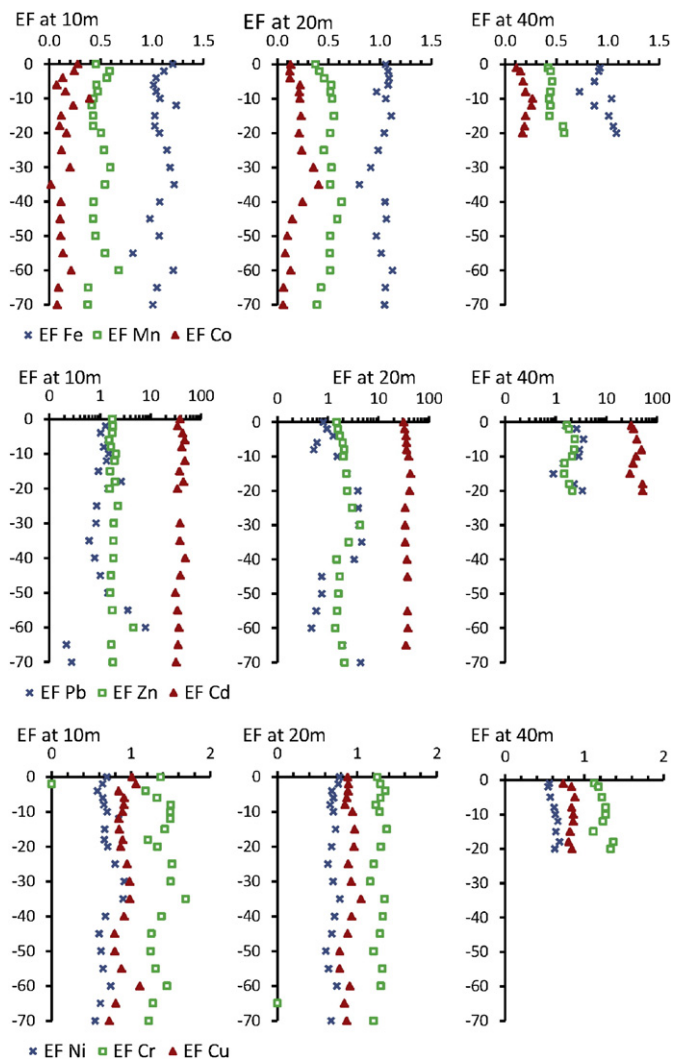


Fig. 8. Vertical profiles of enrichment factor.



the 10 and 20 m stations, are not from the present Mejerda mouth but from the former one (Fig. 1). In addition, the Mejerda flow has evolved tremendously over time as several dams have been built in order to exploit the river's waters. This probably explains the trend observed in the enrichment factor. Cadmium did not originate only in the mines; indeed, the carbonate outcrops in northwestern Tunisia, including those of the Mejerda catchment area are characterized by their high cadmium levels. Although mining is currently reduced, the erosion of the outcrops exploited in the past continues to feed the Gulf of Tunis. The enrichment factors of the other metals (Mn, Cu, Co and Ni) are relatively low, only chromium and iron showing enrichment greater than 1 at some core depths. The chromium enrichment begins on the surface, suggesting that even today chromium input in delta sediments is continuous. This is also the case for iron (Fig. 8). Fe and Cr are usually associated with pollution originating in mining activities. Vertical variation of the iron EF is different from that of lead or zinc; this suggests that there are other sources for these elements, in addition to the mining activities (Helali et al., 2016).

The deeper sediment is not enriched in manganese, cobalt, copper or nickel and the enrichment factor for these elements remains below 1.

A striking contrast is observed, not only between Pb, Zn and Cd, but also between the spatial distribution of the enrichment factors (Helali et al., 2013) and their evolution towards the three cores under investigation. If the deeper sediment is not enriched in certain metals such as copper, some surface sediment will be, probably as the result of some great geo-morphological change:

- transfer of the Mejerda outlet from the south to the north (towards Ghar El Melh Lagoon) and the subsequent building of the Henchir Toubias Channel (the current Mejerda outlet),
- intermittent mining operations in the Mejerda catchment area,
- greater demand for Mejerda water and
- modification of the coastline with the opening of new channels (Sebkhet Ariana and Khlij Channel).

#### 4.4. Geoaccumulation index

As stated in the Introduction, the geoaccumulation index is another approach used in estimating the pollution of marine sediments, and may, in the case of this study, support the finding generated by EF calculation. In the Mejerda River Delta, the I-geo of all metals is between 0 and 1, corresponding to a moderate or absent pollution, except for lead, whose levels are high, greater than 1.5 between 15 and 20 cm, and then from 50 to 60 cm at the 10 m station, 2 to 2.5, and even more in some layers at the 20 and 40 m stations, which corresponds to moderate to strong pollution (Fig. 9). Contrary to expectations, the I-geo of zinc is low, even though it is close to 1 at some levels at the 10 and 20 m stations. The I-geo of cadmium is also low, and does not exceed 0.5 despite the fact that this element, according to its EF, is the greatest pollutant in the delta. This is probably due to the fact that calculation of the enrichment factor is based on the standard of the continental crust values, whereas calculating the I-geo is based on the concentration of metal present in the outcrops of the Mejerda watershed where, according to the NASC, cadmium concentrations are higher than in the earth's crust. There is no I-geo < 0 in the studied location, meaning that the human impact is, therefore, echoed in all sediments for all studied heavy metals. For most of the metals under study, the I-geo reflects the same conclusions reached via calculation of the enrichment factor, though except for Zn and Cd this is not always true in the case of the Mejerda Delta.

#### 4.5. Monosulfides

The  $\sum \text{SEM}/\text{AVS}$  ratio is a simple and quick approach used to estimate the toxicity of marine sediments with respect to the metals: Pb,

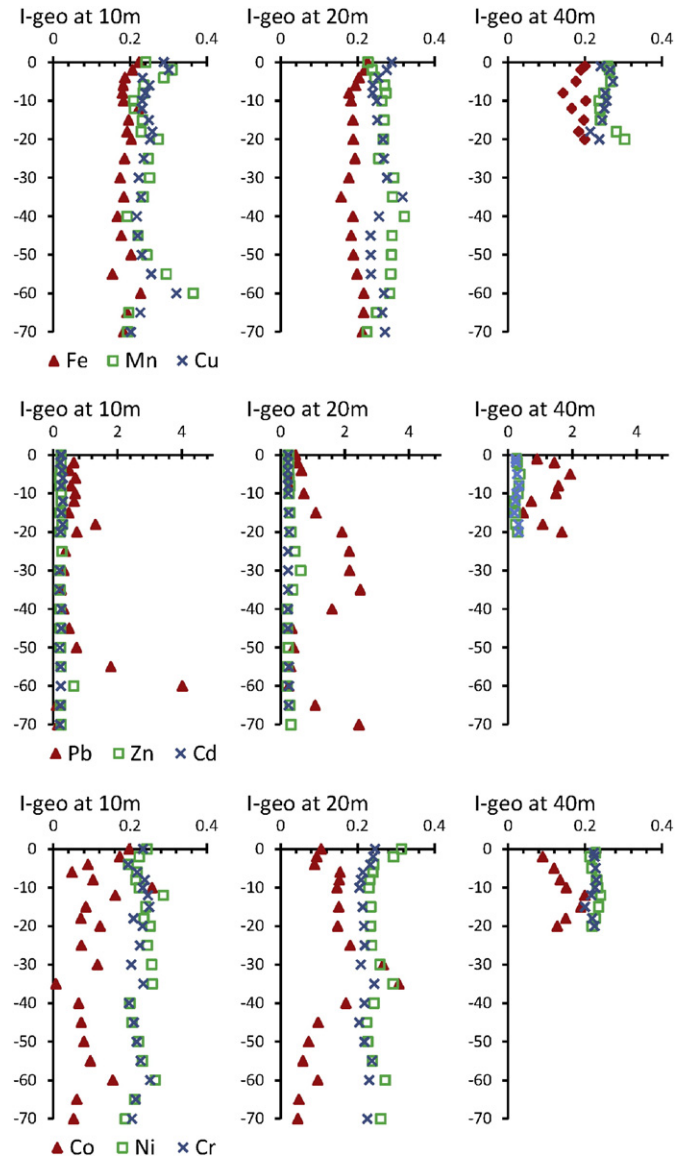


Fig. 9. Vertical profiles of geoaccumulation index.

Zn, Cu, Cd and Ni. Parallel to AVS extraction, Pb, Zn, Cd, Cu and Ni are also extracted, constituting the “Simultaneously Extracted Metals” (SEMs). These metals show a strong affinity for sulfides, which are metal traps and greatly limit metal mobility (Di Toro et al., 1999; Added, 2002). The  $\sum \text{SEM}/\text{AVS}$  ratio, therefore, reflects the ability to trap these metals during remobilization (Clarisse et al., 2003). If the ratio  $\sum \text{SEM}/\text{AVS}$  is less than ‘1’ then the sediment is considered non-toxic; however, if the ratio is greater than ‘1’ toxicity is not confirmed, showing only that the metals are considered bioavailable and that the sediment is potentially toxic. Monosulfide contents have been poorly studied in Tunisian marine sediments; only AVS contents in Ghar El Melh Lagoon sediment have been examined, varying from 10 to more than  $100 \mu\text{mol g}^{-1}$  (Oueslati, 2011; Added, 2002). In other parts of the world, AVS contents are significantly greater:  $18 \mu\text{mol g}^{-1}$  in the Sergipe Estuary in Brazil (Alves et al., 2007) and up to  $1.5 \text{mmol g}^{-1}$  in Florida Bay (Rude and Aller, 1991). The  $\sum \text{SEM}/\text{AVS}$  ratio is shown in Fig. 6. Even if the ratio is less than 1 in most cases, it appears clear that it is at the 10 m station that maximum toxicity is recorded, where the sediment concentrates a lower level of monosulfide content. Therefore a fraction of heavy metals is not fixed by the sulfide and so remains potentially bioavailable. In contrast, though the highest AVS levels were recorded at the 40 m station, no apparent toxicity is observed since the

$\sum$  SEM/AVS ratio did not exceed 0.2. The same trend is observed during both seasons, though the summer campaign clearly shows high toxicity between 25 and 35 cm below the sediment–water interface at the 10 m station, where  $\sum$  SEM/AVS reaches a value of 3.

Overall, AVS profiles first show an increase below the sediment–water interface, followed by a gradual decline moving down the core. This type of evolution is typical of the sedimentary environments running in a non-stationary regime, as is the case of the sediment off the Mejerda outlet (Helali et al., 2015), characterized by instability during sedimentation: changes in particle size, permeability, porosity etc. (Van Den Berg et al., 2001). The delta sediments are homogeneous, though porosity is variable, especially at the top of the sediment cores. Contrary to expectations, the highest AVS values attained at the 40 m station are associated with the lowest organic carbon contents, yet the 10 m station is where the maximum amount of organic material is dissolved and also where the minimum monosulfide content is recorded. The lowest monosulfide contents are observed in the first centimeters of the sediment which are in constant contact with the dissolved oxygen in the water column. The presence of oxygen causes the monosulfides to oxidize, explaining the decrease in their concentration. However, since the sediment along the entire length of the core is suboxic, the monosulfide contents are very low compared with those recorded in the anoxic sediment of Ghar El Melh Lagoon (Added, 2002; Oueslati, 2011). According to the  $\sum$  SEM/AVS ratio, delta sediments are relatively non-toxic for marine organisms. Even when toxicity is suspected, it is restricted to certain layers at the coastal station (10 m).

#### 4.6. Chemical speciation

Lead is one of the most toxic metals for marine organisms, and, in the case of the Mejerda Delta, is one of the most polluting, being present in high concentrations in the sediments. This element is moderately sequestered in the sediment as only 30 to 40% of it is bound to the residual fraction (Fig. 10). Chemical speciation of lead shows the same trend between the top and bottom of the studied cores, and a high part of lead is bound to the residual fraction (an average of 20% and from 5 to 15% at the 10 and 20 m stations, respectively). In general, lead is bound to all five of the sediment fractions. Like lead, copper is also bound to the five fractions, but only at lower depths. In the surface sediment Cu is bound to oxyhydroxydes, to organic matter and to the residual fraction. Bioavailability of copper in the sediments appears to be more pronounced at depth than on the surface. At greater depths (below 20 cm) copper is bound to the exchangeable fraction (10 to 20%) and to carbonates, making it bioavailable in these fractions. Only 40 to 50% of copper is bound to the residual fraction and this part of copper is highly sequestered in the sediment.

Zinc and iron are even more sequestered in the sediment, with the exception of surface levels where Zn is bound to the exchangeable fraction (20%), to oxyhydroxydes (40%) and to organic matter (5 to 10%) (Fig. 10). In the deeper layer of the cores, Zn is essentially bound to the residual fraction; despite it having the highest contents and the highest calculated EF, zinc is of limited toxicity as more than 90% of it is not bioavailable. Iron is also among the metals whose concentrations

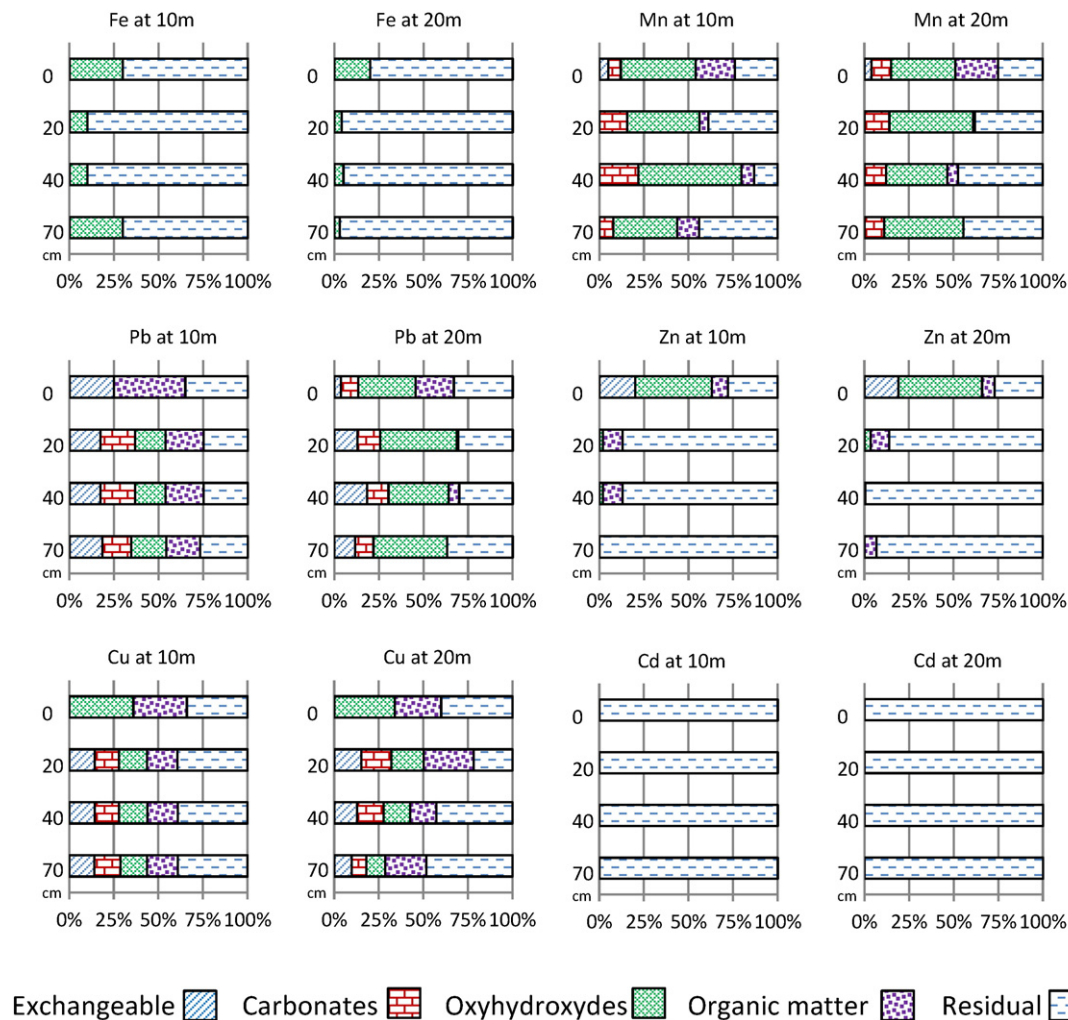


Fig. 10. Chemical speciation of Fe, Mn, Pb, Zn, Cu and Cd (in %).

are high but with limited toxicity: only 20 to 25% of it is bound to oxyhydroxydes and more than 80% bound to the residual fraction (Fig. 10).

Cadmium is one of most toxic metals for marine biotas, and in the case of the Mejerda Delta, it is the most polluting, according to its enrichment factor. However, it is bound only to the sediment's residual fraction (100%) in the cores and at all depths (Fig. 10). This trend confirms the latest studies of cadmium speciation in surface sediments in the western Gulf of Tunis (Helali et al., 2013). With its abundant mining activities and high Cd values in the catchment, and though the Mejerda Delta has a high level of cadmium in comparison to other coastal areas, the offshore cadmium accumulation is nevertheless so deeply sequestered in the sediment that it is not bioavailable.

## 5. Conclusion

Heavy metal accumulation in the Mejerda Delta sediments is clearly dependent upon the different water flows connected to the Gulf of Tunis. Variation in content from the coast to the offshore zones is highly pronounced, as the influence of the Mejerda River is significant at the 10 m station but decreases towards the 40 m depth station. Organic matter shows that the shallower areas are more prone to detrital accumulation than the deep areas. Profiles of the most polluting metals, directly related to the Mejerda catchment mining activity, suggest that the sedimentation rate is higher near the mouth and that this river's contributions have varied much over time; the appearance of the enriched elements related to the mining activities, such as Pb and Zn, indicates that mining has also evolved over time. In general, the delta sediments do not appear to be highly polluted by heavy metals, though the human impact is clearly established. Estimation of trace element accumulation using the enrichment factor and the geoaccumulation index show that lead, cadmium and to lesser extent zinc are the most polluting metals in the delta. The  $\sum$  SEM/AVS ratio suggests possible bioavailability of heavy metals, especially at the 10 m station. High cadmium levels compared with other similar marine environments are not only related to human activity, but may also be attributed to the cadmium-rich carbonate outcrops in the Mejerda catchment. Therefore, the calculation of the enrichment factor and the geoaccumulation index points to completely different conclusions for the Cd. For other metals, the two estimation techniques for pollution result in nearly the same findings, but do not provide any clue regarding the toxicity of the sediment. The SEM/AVS ratio is a simple technique used to estimate sediment toxicity, but has some drawbacks; ultimately it is chemical speciation that offers the best estimation.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marpolbul.2016.02.077>.

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