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Suspended particulate matter fluxes along with their associated metals, organic matter and carbonates in a coastal Mediterranean area affected by mining activities

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ABSTRACT

A study of suspended particulate matter (SPM) fluxes along with their associated metals, organic matter and carbonates, was conducted off the Mejerda River outlet in May 2011 and in March and July 2012 at depths of 10, 20 and 40 m using sediment traps. SPM fluxes are more significant near the Mejerda outlet, especially in winter, but dissipate further offshore. Normalization reveals that the Mejerda is a major source of Pb, Zn, Cd, Cu, Ni, and Co, all of which are the result of human activities. In contrast, Fe, Mn and N are of authigenic origin. The enrichment factor shows that Pb, Zn and especially Cd are the most highly polluting metals off the Mejerda outlet. This confirms the trend observed on the shores of the Mejerda prodelta and is consistent with the type of mining activities conducted in the Mejerda catchment.

1. Introduction

In both river catchment areas and deltaic zones, spatial and temporal differences in concentrations of trace elements in sediments have been linked to changes in physico-chemical and biogeochemical conditions in bottom water and also to sediment redox conditions (Loring and Rantala, 1992; Rivaro et al., 2011; Kontas, 2012). For trace element enrichment or depletion relative to detrital concentration assessment the ratios of trace elements to Al are often used (Yiğiterhan and Murray, 2008; Spagnoli et al., 2014; Little et al., 2015). Heavy metals are one of the contaminants most often discharged into the marine coastal areas from rivers. Apart from their natural origins, heavy metals frequently originate in industrial and mining activities, as in the case of the Mejerda River and its neighboring wet zones (Oueslati et al., 2010; Helali et al., 2013; Zaaboub et al., 2014, 2015). These metals are dissolved, but are also associated with sediment particles in rivers (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Balkis et al., 2009; Lam et al., 2015). Transport and sedimentation of heavy metals are therefore also associated with the fate of suspended particulate matter (SPM) released into the sea. It is noteworthy that another source of metal may also contribute to SPM fluxes, Saharan dust which is composed mainly of Al, Si, Fe and Ti, as well as Ca, Na, K oxides (Marconi et al., 2014). The settling and distribution of contaminants in coastal areas are influenced essentially by both prevailing marine currents (Palanques and Díaz, 1994; Action, 2011; Spagnoli et al., 2014) and the nature of the SPM (organic matter, carbonates, clays, silts, etc.). After sedimentation, metals and associated particles may be re-suspended by bioturbation or marine currents (Palanques and Díaz, 1994; Spagnoli and Bergamini, 1997; Spagnoli et al., 2008; Marconi et al., 2014).

This study is a continuation of various geochemical investigations of sediment in the waters off the Mejerda outlet (Zaaboub et al., 2014; Helali et al., 2015, 2016). The Mejerda is an important North African river; assessment of its inputs is therefore necessary, especially since extensive mining activity is found within its catchment (Moldenhauer et al., 2008) and the region is subject to two contrasting climates: wet and dry (Ben Charada, 1997). The Mejerda is thus a significant source of heavy metals which are transported into the prodelta along with suspended particle matter.

The objectives of this study are to (i) determine the SPM fluxes along with their associated organic matter, carbonates and heavy metals, and also their seasonal, lateral or vertical variations, if any, (ii) estimate the degree of pollution by the heavy metals associated with the particulate matter by calculating the enrichment factor (EF), and (iii) determine the degree to which the Mejerda River contributes to the accumulation of heavy metals offshore.

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2. Materials and methods

2.1. Sampling site

The Mejerda River prodelta is located in the western Gulf of Tunis. Mejerda is the most important river in Tunisia, and the main source of water and sediments in the gulf, it has a flow of 30 $m^3 s^{-1}$. The Mejerda catchment extends over 23,700 km^2 and supports extensive mining operations, including polymetallic deposits, in the regions of Chemtou, Ain Ksir, Bou Hertma, Sidi Abdallah, Ben Béchir, Bou Salem and Jendouba (Fig. 1). The Mejerda prodelta 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 Charada, 1997). The sea surface currents depend upon wind direction (Fig. 2) and flow mainly from north to south (Brahim et al., 2007, 2015). While the waters of the Mejerda constitute the main source of erosive influences, the prodelta is also affected by three other water inflows from the Khlij Channel, Ghar El Melh Lagoon and Sebkhet Ariana, also connected to the marine waters (Fig. 1).

This study was conducted in the offshore waters facing the mouth of the Mejerda River. Sampling locations are shown in Fig. 1. Seasonal variation was studied only at the three points forming a radial perpendicular to the coast opposite the mouth (B1, B2 and B3 stations) (Fig. 3a and b) in March (winter) and July 2012 (summer) corresponding respectively to the wet and dry seasons in North Africa. At 9 stations (A1, A2, A3, B1, B2, B3 and C1, C2, C3) (Fig. 1) spatial distribution was studied only after the wet season in May 2011.

2.2. Sample processing

The sediment traps constructed for this study were designed based on the research of Butman (1986), taking into account the marine currents in the area off the Mejerda outlet studied during extreme conditions (Brahim et al., 2007). The traps were composed of a 110 × 9 cm cylinder of inert material (PVC) resistant to marine conditions and causing no interference with geochemical analysis. A small volume of chloroform was first placed into the sediment trap to prevent bacterial activity. Fig. 3a and b show the lateral and vertical dispositions of the traps at the three stations. After four weeks of immersion, the traps were recovered; the suspended particles were decanted and then centrifuged at 3500 rpm for 15 min. Suspended particulate matter in the Mejerda River was collected after filtration onto 0.45 μm cellulose acetate filters. After several washings with bi-distilled water to remove the salts, the SPM was dried (60 °C) and weighed.

2.3. Metal analysis, SPM and metal flux calculations

The samples thus obtained were digested by mixing 1 g of sediment with a solution of 20 ml concentrated HF, 10 ml $HClO_4$ and 10 ml HNO_3 in Teflon bombs. The resulting digestates were analyzed by flame atomic absorption spectrometry (using the Thermo Scientific ICE 3300 AA Spectrometer) for the presence of Fe, Mn, Pb, Zn, Cd, Cu, Co, Ni and Cr. The accuracy of the analytical procedures employed for heavy metal analysis was checked using the BCR-032 certified reference material; good concurrence with certified values was obtained (Table 1). Relative

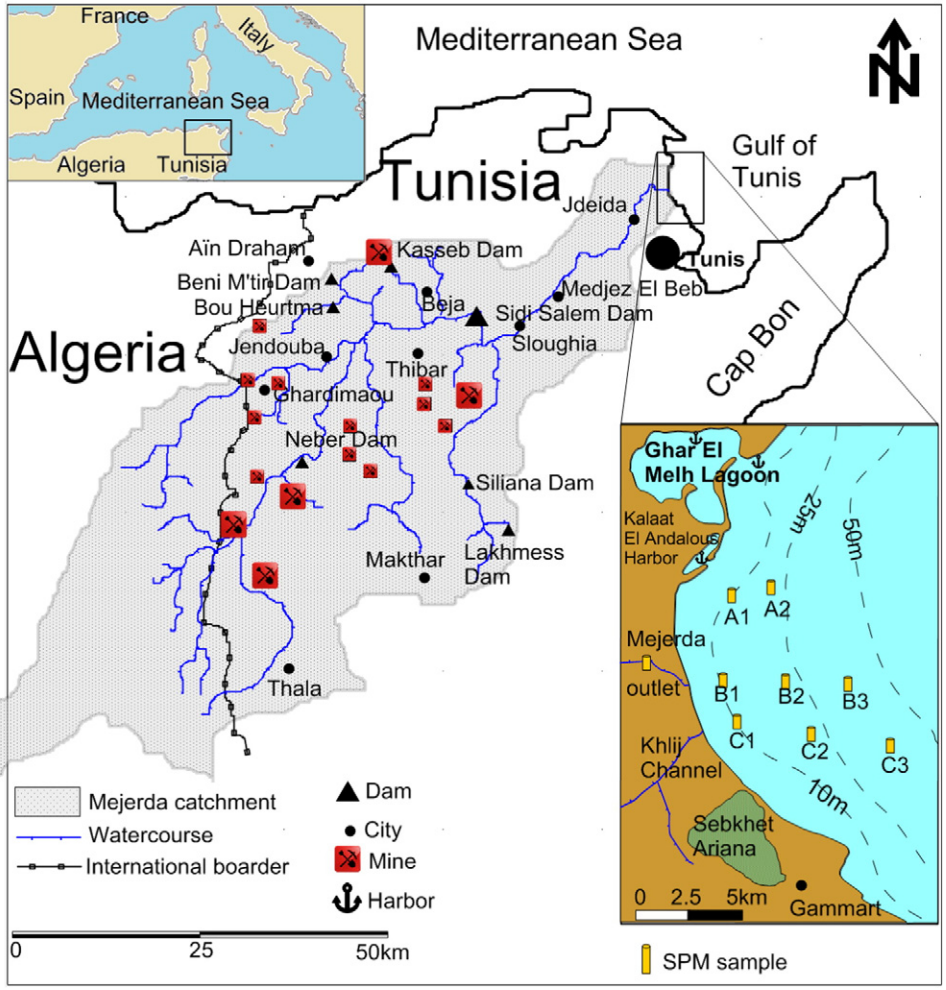

Fig. 1. Study area and sample locations.

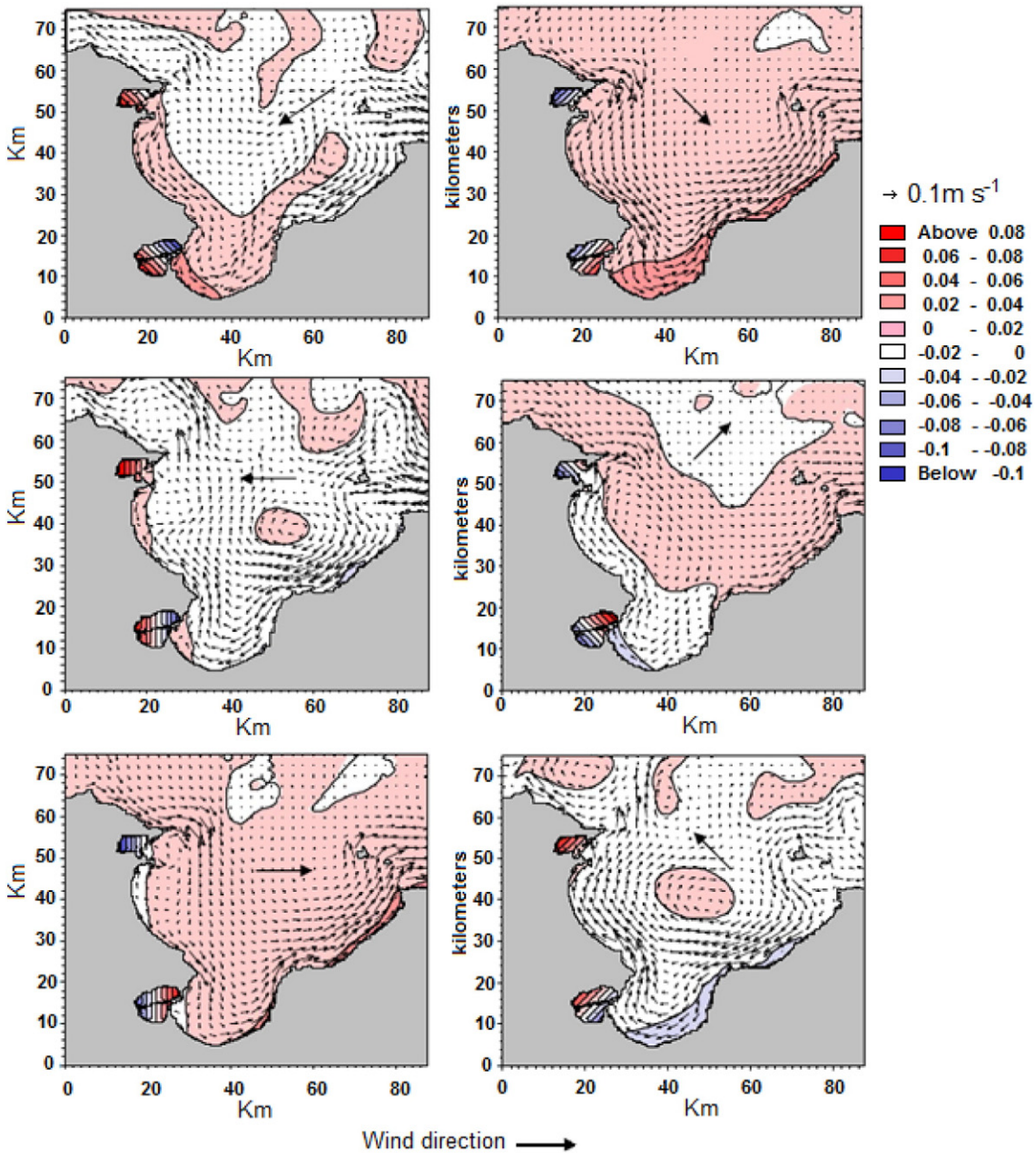

Fig. 2. Marine currents versus wind direction in the Gulf of Tunis (Brahim et al., 2007, 2015).

Standard Deviations (RSDs) were calculated from 3 replicates for heavy metals and 2 replicates for $CaCO_3$ and organic matter. RSD were in all cases <11% (Table 2).

SPM flux is calculated by taking into account the duration of immersion of sediment traps, their surface and the quantity of trapped suspended matter. Sedimentation flux (Js, in g m^{-2} day^{-1}) = m/S/n; m = the total mass of trapped suspended matter (in grams); S = section of sediment trap (in m^2); N = number of days of immersion.

Metal flux (μg m^{-2} day^{-1}) was calculated using the relation [Me] × Js with Me being the concentration of metal in the SPM (in μg g^{-1}). Sedimentation flux (Js) was measured at all marine stations, while in the waters of the Mejerda the concentration of suspended particles (mg l^{-1}) was calculated directly using SPM weight and the volume of filtered water. Metals associated with SPM in the river (C_{Me}) are listed in μg l^{-1} and calculated from the total SPM concentration: $C_{Me} = C_{SPM} \times [Me]$, Me = metal concentration in SPM (in μg g^{-1}) and C_{SPM} the concentration of SPM in water (g l^{-1}).

2.4. Carbonate analysis

Calcium carbonate in sediment (Total Carbonates, TC: $CaCO_3$, $MgCO_3$ etc): was performed using a Bernard calcimeter on 0.25 g dry sediment, with 10% HCl solution. Each sample was measured three times and an average value calculated.

2.5. Total organic carbon and nitrogen

Organic matter and nitrogen were measured using a PerkinElmer PE 2400CHN on dry sediment. Total Organic Carbon (TOC) was determined in sediment samples by means of a Perkin Elmer PE 2400 CHN. Subsamples for TOC analysis were decarbonated using 1 M HCl and dried at 60 °C. Total Carbon (TC) and nitrogen (N) analysis were carried out on subsamples without HCl treatment.

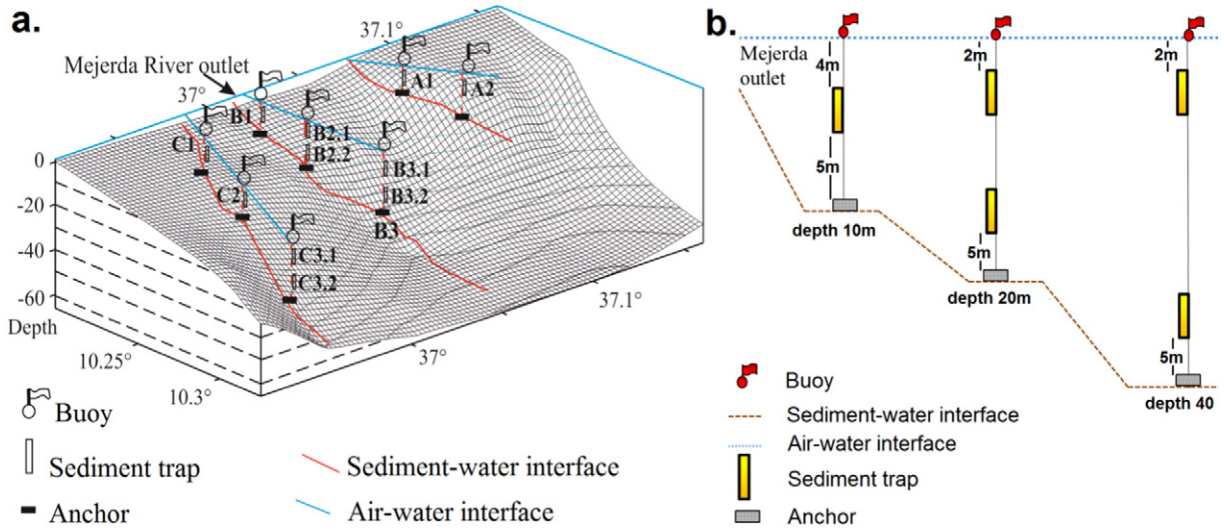

Fig. 3. Horizontal and vertical disposition of sediment traps.

2.6. Statistical analysis

Principal Component Analysis (PCA) was used to elucidate 1) the origin of SPM metal fluxes in the gulf and 2) whether SPM metal fluxes are related to the Mejerda River. Potential correlations between the river's suspended particulate matter discharge, including trace elements and suspended particulate matter offshore from the prodelta were also calculated. Statistics were established with the SPSS program.

3. Results

3.1. Spatial distribution

3.1.1. Suspended particulate matter (SPM)

Fluxes of suspended particles are the highest along the coastal stations (10 m depth) in the north (A1 station: 28.6 g m^{-2} day^{-1}) and south (C1 station: 27.7 g m^{-2} day^{-1}) of the Mejerda outlet, while further offshore (depth > 20 m) they gradually decrease to 17.4 g m^{-2} day^{-1} (A2 station) and 15.3 g m^{-2} day^{-1} off the Mejerda outlet (B2 station) (Table 3). Both 40 m stations show a significant vertical difference as the maximum SPM was recorded in the traps near the bottom, while the subsurface traps accumulated very little: approximately 3.9 at the top and 15.5 g m^{-2} day^{-1} at the bottom of the water column off the Mejerda outlet (B3), and 2 at the top and 21.6 g m^{-2} day^{-1} at the bottom off the Khlij Channel (C3).

3.1.2. Aluminum and potassium

Aluminum flux ranges between 0.085 and 1.5 g m^{-2} day^{-1} (Table 3). As for SPM, maximum fluxes are observed near the coast (10 m depth) while further offshore (>20 m depth) the flux decreases: 1.25 to 0.71 g m^{-2} day^{-1} (respectively at stations C3 and B2). Potassium flux is linked to that of aluminum whose maximum is also observed near the coast: 0.6 to 1.25 g m^{-2} day^{-1} (stations A1 and C1) and 0.4 g m^{-2} day^{-1} further offshore (Table 3). Iron flux is at its maximum off the Khlij Channel (790 mg m^{-2} day^{-1}) and north of the Mejerda outlet (751 mg m^{-2} day^{-1}). Although a declining trend is noted further offshore, iron flux is still relatively high at 20 m depth near Kallaat El Andalous Harbor (A2) and on the sea bottom at the 40 m stations where fluxes reached 422 and 621 m g m^{-2} day^{-1} at stations B3 and C3, respectively (Table 3).

3.1.3. Heavy metals

Maximum fluxes of Mn, Pb and Zn are observed near the coast, in the northern and southern areas off the Mejerda outlet (Table 4). However, Pb flux is relatively high off the Kalaat El Andalous Harbor: 1.3 m g m^{-2} day^{-1} (station A2), probably due to human activity in Kalaat El Andalous harbor (Table 4). In contrast to other metal fluxes, maximum Pb flux is found in subsurface sediment traps (0.9 and 1.7 mg m^{-2} day^{-1}) and not in those at the bottom of the water column (0.6 and 0.7 mg m^{-2} day^{-1}) (Table 4). This difference may be explained by an additional supply of Pb from the atmosphere.

When cadmium content in SPM is undetectable, the corresponding flux is then considered void (Table 4). The copper flux was measured to the north of the Mejerda outlet (627 μg m^{-2} day^{-1}) and only on the sea floor, at the 40 m stations (86 and 227 μg m^{-2} day^{-1}) (Table 4). The maximum fluxes of nickel and chromium were found off the Khlij Channel at the 10 m station, at 500 μg m^{-2} $day^{-1}$and 3 mg m^{-2} day^{-1} (Table 4). The fluxes of these two elements, unlike for other metals, are apparently lower to the north of the Mejerda outlet (Table 4); in contrast, the offshore fluxes (40 m stations) are relatively more significant: from 377 to 424 μg m^{-2} day^{-}1 for Ni, and 1.5 to 1.7 mg m^{-2} day^{-1} for Cr. The Mejerda River and the Khlij Channel appear to be the prodelta's main sources of nickel and chromium.

Table 1
Accuracy (%) compared to certified material (BCR-0.32).

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

Table 2
RSD (relative standard deviations) of analyzed component (%).

Component	RSD (%)	Component	RSD (%)
$CaCO_3$	10.22	Zn	2.20
CT	1.21	Cd	0.22
K	1.12	Cu	1.97
Al	1.55	Co	0.27
Fe	0.96	Ni	0.65
Mn	4.40	Cr	3.38
Pb	2.49		

Table 3
Spatial variation of fluxes of SPM (suspended particulate matter), Al, K and Fe at top and bottom of water column in May 2011. (− = missing data).

Sites	SPM ($g\ m^{-2}\ day^{-1}$)	Fe ($mg\ m^{-2}\ day^{-1}$)	Al ($g\ m^{-2}\ day^{-1}$)	K ($g\ m^{-2}\ day^{-1}$)
A1	28.6	751	1.5	0.59
A2	17.4	422	0.89	0.36
B1	–	–	–	–
B2	15.3	313	0.71	0.31
B3.1	3.9	25	0.1	0.068
B3.2	15.54	422	0.88	0.35
C1	27.7	790	1.46	1.58
C2	–	–	–	–
C3.1	2	23	0.085	0.038
C3.2	21.6	621	1.25	0.5

Table 5
Seasonal variation of $CaCO_3$, TC (Total carbon), TOC (Total organic carbon) and N contents in SPM in Mejerda outlet and sediment traps.

	$CaCO_3$ ($g\ g^{-1}$)	TC ($g\ g^{-1}$)	TOC ($g\ g^{-1}$)	N ($mg\ g^{-1}$)
Summer				
Mejerda	0.236	0.161	0.133	5.6
B1	0.069	0.025	0.017	0.8
B2.1	0.054	0.042	0.036	1.834
B2.2	0.054	0.032	0.026	1.3
B3.1	0.253	0.044	0.014	1.502
B3.2	0.076	0.023	0.014	2.0
Winter				
Mejerda	0.201	0.149	0.125	2.82
B1	0.202	0.047	0.023	0.80
B2.1	0.084	0.028	0.018	1.30
B2.2	0.130	0.034	0.019	1.101
B3.1	0.102	0.036	0.024	1.401

3.2. Seasonal variation

3.2.1. Carbonates

Carbonate content in SPM in the waters of the Mejerda River is 0.201 g g^{-1} in winter and 0.236 g g^{-1} in summer (Table 5). Carbonate fluxes at the 10 (B1), 20 (B2) and 40 m (B3) stations range from 1 to 7.66 g m^{-2} day^{-1} in winter and 0.32 to 1.16 g m^{-2} day^{-1} in summer (Table 6).

3.2.2. Organic matter

Total carbon (TC) concentration is higher in SPM in the open waters off the mouth of the Mejerda River (0.149 to 0.162 g g^{-1}) (Table 5). This is also the case for TOC and nitrogen. Therefore, the highest concentrations are observed also in the SPM of the Mejerda River: 2.8 and 5.6 mg g^{-1} for N and 0.12 and 0.13 g g^{-1} for TOC, as shown in Table 5. Although the waters of the Mejerda concentrate more SPM in winter, the organic matter content in SPM varies only slightly between seasons. TC content is practically the same at the marine stations: 0.023 to 0.0 44 g g^{-1} in summer and 0.028 to 0.046 g g^{-1} in winter, depending on the station (Table 5). Organic matter flux varies from the coast to offshore but shows little variability between the seasons. Maximum TOC flux (0.86 g m^{-2} day^{-1}, Table 6) is observed facing the Mejerda outlet (station B1) in winter. Nitrogen fluxes are significantly different from those of the TOC because maximum flux is observed at the 40 m station: 41.5 mg m^{-2} day^{-1} in winter and 22.3 mg m^{-2} day^{-1} in summer (Table 6).

Major and trace elements:

- Aluminum: due to its detrital nature, Al flux is similar to that of SPM and is observed at its maximum near the Mejerda outlet. Further offshore, however, its fluxes are relatively lower at the 20 (B2) and 40 m (B3) stations: 0.14 to 0.41 g m^{-2} day^{-1} in summer and 0.9 to 1.59 g m^{-2} day^{-1} in winter (Table 7). Seasonal variation in Al flux is wide and of great significance, with the Mejerda's contributions lower in summer; the flux is five times lower during summer at the 10 m station (B1). It is noteworthy that the Al flux is greater in sediment traps at the bottom than in the subsurface, probably due to re-suspension of rich aluminum sediment from the seabed.
- Iron: flux is significant near the coast at 384 mg m^{-2} day^{-1} in winter and 260 mg m^{-2} day^{-1} in summer, while further out it varies from 58 to 230 mg m^{-2} day^{-1} in winter and 37 to 344 mg m^{-2} day^{-1} in summer (Table 7).
- Manganese: unlike SPM, the amount of Mn provided by the Mejerda River is higher in summer (78 μg g^{-1}) than in winter (10.1 μg g^{-1}) (Table 8). This is also the case at the 10 m station (B1) which is directly influenced by the contributions of the Mejerda, where a much greater flux of Mn is observed in summer (18 mg m^{-2} day^{-1}) opposed to only 5.5 mg m^{-2} day^{-1} in winter (Table 7).
- Lead: flux in winter is estimated at 1446 μg m^{-2} day^{-1} at the 10 m (B1) station and 4747 μg m^{-2} day^{-1} at the 20 m station (B2). In summer, lead flux at the bottom of the water column is estimated at 1164 and 1490 μg m^{-2} day^{-1} at the 20 (B2.2) and 40 m (B3.2) stations, respectively, whereas it is only 538 μg m^{-2} day^{-1} at the 10 m (B1) station (Table 7).
- Zinc: in contrast to lead, maximum Zn flux is observed in winter at the bottom of the water column, with the exception of the 20 m station (B2.2), where Zn flux is slightly higher in summer (2900 μg m^{-2} day^{-1}) than in winter (2660 μg m^{-2} day^{-1}). Elsewhere maximum Zn flux is measured as follows: at the 10 m station (4520 μg m^{-2} day^{-1} in winter and 2308 μg m^{-2} day^{-1} in summer), a little less further offshore, at the 20 m station (B2) (between 784 and 2902 μg m^{-2} day^{-1}, and at the 40 m station (B3) between 566 and 2802 μg m^{-2} day^{-1} (Table 7).
- Copper: Cu flux is detected in winter only in the sediment traps at the bottom at the 20 m (B2) and 40 m (B3) stations, where flux is respectively 247 and 856 μg m^{-2} day^{-1} (Table 7). In summer, copper flux is much higher, with the maximum observed at the 10 m station (B1) (1285 μg m^{-2} day^{-1}). Offshore, greater flux is recorded at 40 m

Table 4
Spatial variation of trace element fluxes at top and bottom of water column in May 2011(BDL = below detection limits).

Sites	Mn $mg\ m^{-2}\ day^{-1}$	Pb $mg\ m^{-2}\ day^{-1}$	Zn $mg\ m^{-2}\ day^{-1}$	Cd $\mu g\ m^{-2}\ day^{-1}$	Cu $\mu g\ m^{-2}\ day^{-1}$	Ni $\mu g\ m^{-2}\ day^{-1}$	Cr $mg\ m^{-2}\ day^{-1}$
A1	6.1	2.4	7	BDL	627	171	1.1
A2	2.9	1.3	3.7	BDL	BDL	342	1.5
B1	–	–	–	–	–	–	–
B2	3.5	0.4	3.4	BDL	BDL	411	0.74
B3.1	0.3	0.9	1	BDL	BDL	97	0.2
B3.2	4.9	0.6	3.6	BDL	86	377	1.7
C1	6.5	1.9	5.7	BDL	BDL	501	3
C2	–	–	–	–	–	–	–
C3.1	0.4	1.7	0.9	BDL	25	BDL	0.12
C3.2	5.2	0.7	5.3	BDL	227	424	1.5

Table 6
Seasonal variations in flux of SPM, $CaCO_3$, CT, TOC and N.

	SPM ($g\ m^{-2}\ day^{-1}$)	$CaCO_3$ ($g\ m^{-2}\ day^{-1}$)	TC ($g\ m^{-2}\ day^{-1}$)	TOC ($g\ m^{-2}\ day^{-1}$)	N ($mg\ m^{-2}\ day^{-1}$)	C/N
Summer						
B1	16.98	1.16	0.42	0.28	13.59	20.80
B2.1	6	0.32	0.25	0.21	11	19.55
B2.2	16.41	0.88	0.53	0.42	21.33	19.93
B3.1	4.83	1.22	0.21	0.06	7.25	9.34
B3.2	11.16	0.84	0.25	0.15	22.32	6.95
Winter						
B1	38	7.66	1.78	0.86	30.40	28.39
B2.1	12.94	1.08	0.36	0.23	16.82	13.8
B2.2	24.56	3.18	0.84	0.46	27.03	17.02
B3.1	11.57	1.18	0.41	0.27	16.20	16.89
B3.2	21.87	4.31	0.96	0.44	41.56	10.74

($1142\ \mu g\ m^{-2}\ day^{-1}$) than at 20 m ($589\ \mu g\ m^{-2}\ day^{-1}$) (Table 7).

- Cadmium: Cd flux is found in SPM only in winter; these fluxes are the lowest among the metals studied: $45\ \mu g\ m^{-2}\ day^{-1}$ at the 10 m station, between 33 and 49 $\mu g\ m^{-2}\ day^{-1}$ at 20 m (B2) and from 15 to 22 $\mu g\ m^{-2}\ day^{-1}$ at 40 m (B3) (Table 7).
- Cobalt: flux is significantly greater in winter at the 10 m station (B1), with 253 $\mu g\ m^{-2}\ day^{-1}$, while offshore it varies between 20 and 148 $\mu g\ m^{-2}\ day^{-1}$. In summer, despite a decrease in SPM flux, cobalt flux is more significant off the Mejerda outlet, where a flux of 1834 $\mu g\ m^{-2}\ day^{-1}$ is observed at 20 m and of 400 $\mu g\ m^{-2}\ day^{-1}$ at 40 m (Table 8).
- Nickel: Ni content in SPM varies slightly between winter (average $67\ \mu g\ g^{-1}$) and summer ($46\ \mu g\ g^{-1}$) (Table 6). The fluxes are stronger in winter, especially at the 10 m station (2637 $\mu g\ m^{-2}\ day^{-1}$) and a little less further offshore: 1639 and 1656 $\mu g\ m^{-2}\ day^{-1}$, respectively, at 20 and 40 m (Table 7).
- Chromium: fluxes range from 778 to 3200 $\mu g\ m^{-2}\ day^{-1}$ in winter and show a marked decrease in summer with 292 to 1480 $\mu g\ m^{-2}\ day^{-1}$. In fact, Cr flux decreases in summer, along with that of SPM.

4. Discussion

4.1. Suspended particulate matter (SPM)

4.1.1. Lateral SPM

This accumulation is contrary to expectations as the accumulation of solids is generally at its maximum at the top of the water column, decreasing with depth (Violintzis et al., 2009). Our finding, however, is consistent at each installation of the two sediment traps at a single station and is probably the result of re-suspension from the sediment surface. SPM distribution is almost equal between areas to the north and south of the Mejerda outlet despite the north–south long-shore current predominance in the region due to the weather conditions in May 2011 (Fig. 4). Accumulation of SPM north of the outlet is due either to the sudden changes in wind direction and speed or to an extra supply of SPM from a source other than the Mejerda River (e.g. Ghar El Melh Lagoon). Furthermore, previous studies (Helali et al., 2013) have shown that accumulation of heavy metals in sediments occurs on both sides of the Mejerda outlet and that current modeling has demonstrated presence a south–north drift stream passing before the outlet. Seasonal and lateral distributions of SPM fluxes are consistent with the prevailing wind direction (north to northwest sector) most often resulting in the formation of marine currents, which is consistent with the SPM contents recorded in the waters of the Mejerda. Excess of suspended particles collected in the traps at the bottom of the water column is due to resuspension affecting the seabed; in fact, even though the sediment traps placed at the bottom of the water column were positioned 5 cm above the bottom, they still accumulated the suspended particles from the seabed in addition to particles carried and discharged by the Mejerda. Due to the fine grain size characterizing the sediment particles in our study area (Helali et al., 2013), and according to the recent measurements of the currents in the Gulf of Tunis (Brahim et al., 2015), it appears that the re-suspension affecting the seabed cannot be ruled out and is even very likely present in the area facing the Mejerda mouth where the recorded currents were most intense. According to Ben Charada (1997) and Brahim et al. (2007, 2015), frequent strong NW winds generate weak counter-clockwise littoral currents in the central part of the gulf, thereby controlling suspended matter and surface sediment accumulation there.

Table 7
Seasonal variation in heavy metal flux in $\mu g\ m^{-2}\ day^{-1}$ (Fe in $mg\ m^{-2}\ day^{-1}$) and of SPM ($g\ m^{-2}\ day^{-1}$) in the sediment trap at top and bottom of the water column. (BDL = below detection limits).

	Al $g\ m^{-2}\ day^{-1}$	Fe $mg\ m^{-2}\ day^{-1}$	Mn $\mu g\ m^{-2}\ day^{-1}$	Pb $\mu g\ m^{-2}\ day^{-1}$	Zn $\mu g\ m^{-2}\ day^{-1}$	Cu $\mu g\ m^{-2}\ day^{-1}$	Cd $\mu g\ m^{-2}\ day^{-1}$	Co $\mu g\ m^{-2}\ day^{-1}$	Ni $\mu g\ m^{-2}\ day^{-1}$	Cr $\mu g\ m^{-2}\ day^{-1}$
Summer										
B1	0.37	258	18194	538	2308	1285	BDL	592	647	920
B2.1	0.27	37	902	1253	784	762	BDL	561	251	405
B2.2	0.40	46	1125	1164	2902	589	BDL	1834	910	299
B3.1	0.14	85	610	324	566	199	BDL	58	115	292
B3.2	0.41	344	1505	1490	2205	1142	BDL	407	813	1480
Winter										
B1	1.65	384	5575	1447	4521	BDL	45	253	2637	3225
B2.1	1.02	59	1732	1421	859	BDL	33	47	846	826
B2.2	1.20	203	3711	4747	2663	248	49	148	1640	1948
B3.1	0.89	75	1007	2030	1287	BDL	15	20	763	778
B3.2	1.59	229	4836	1512	2802	856	22	98	1556	2123
B1	1.65	384	5575	1447	4521	BDL	45	253	2637	3225

Table 8
Heavy metal contents in μgg^{-1} (in mg g^{-1} for Al and Fe) in SPM in Mejerda River outlet.

	Al	Fe	Mn	Pb	Zn	Cd	Cu	Ni	Co	Cr
Summer	30.1	17.7	78.0	61.3	246.4	0.0	37.3	65.5	8.7	61.2
Winter	44.6	17.0	10.1	67.8	142.5	0.4	BDL	82.0	18.2	106.0

4.2. Organic matter and carbonates

The C/N ratio in the SPM is higher than in the sediment cores measured by Essoni (1998) and those recorded in this study (data not shown). The highest value observed is for SPM in the Mejerda River in winter (C/N = 44). Of the three marine stations, the 10 m station is always the one revealing a high ratio at 28 in winter and 20 in summer, while further offshore the C/N ratio decreases above 40 m (16 to 10 in winter and 7 to 9 in summer). Even though the ratio is lower at the 10 m station, it remains high at 20 m at 13–19 indicating that the 20 m station, too, is subject to a significant contribution of organic matter of detritic origin. At the 20 and 40 m stations, the C/N ratio is lower in the bottom sediment traps than in the subsurface, implying that the detritic organic matter probably comes from the top of the water column, while further down, the suspended organic matter particles are of mixed detrital and marine origins. At all the studied sites the C/N ratio tended to decrease in summer, probably due to the reduction in the detritic supply from the Mejerda River, Ghar El Melh Lagoon and the Khlij Channel. Over the entire period of immersion of the sediment traps, easterly winds (Fig. 4), more present in summer, tended to alter the marine current in the prodelta waters. Whereas the C/N ratio at the 10, 20 and 40 m stations represents average values over four weeks, the C/N ratio off the Mejerda River outlet represents a value measured at a given time, which explains why the C/N ratio is lower at the Mejerda River mouth in summer (C/N = 14.16) than at the 10 and 20 m stations (C/N = 20.8 and 19.5, respectively), though the origin of the organic matter was not shown to be mainly detritic.

Carbonate fluxes are significantly greater at the 10 m station (B1) than at 20 (B2) and 40 m (B3), not only because SPM flux is greater, but also because carbonate content is more significant near the coast (Table 5). This is probably due to the origin of the carbonates, from both biogenic precipitation and detritic sources. The Mejerda is the main source of detritic carbonates, but the other likely contributor is the Ghar El Melh Lagoon.

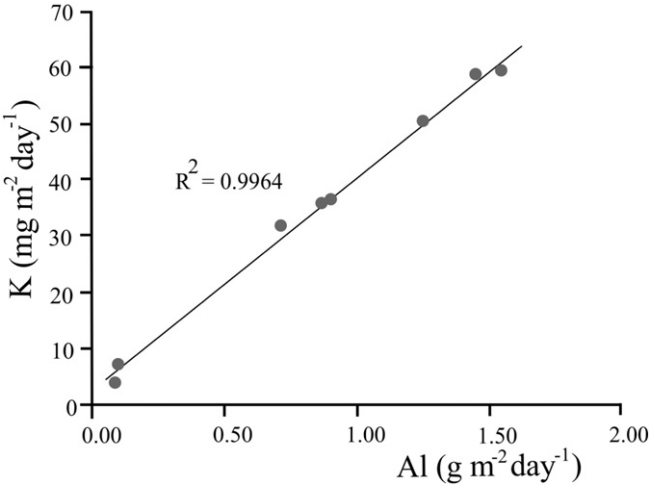

Fig. 5. Aluminum flux vs potassium flux correlation.

4.3. Aluminum and potassium

Though the number of samples is limited, the correlation of Al to K (Fig. 5) is almost perfect (R = 0.9982). In the case of deep sediment from the prodelta (data not shown), the correlation of Al/K suggests that the illite group—general formula $(Si_{(4-x)}\ Al_x)\ O_{10}\ (Al_2)\ (OH)_2\ (K)$ x with x close to 0.5 (Fütterer, 2006; Tessier, 2012)—is probably the most abundant clay component of SPM. As aluminum is a product of the weathering of continental rocks, it is normal for its fluxes to be similar to those of SPM, since a maximum amount of fluxes are observed near the coast, decreasing offshore.

When compared to other studies, it becomes apparent that aluminum fluxes off the Mejerda outlet are similar to those generally observed along the rivers of the Vigo estuary (northern Spain), where aluminum flux ranges from 1.27 to 2.39 to g m^{-2} day^{-1} (Santos-Echeandía et al., 2011), and in the Vöra estuary in Finland, where it ranges from 0.27 to 9.72 g m^{-2} day^{-1} (Nordmyr et al., 2008). In the Baltic Sea aluminum flux is much lower, from 0.01 to 0.09 g m^{-2} day^{-1} (Leivuori and Valliusb, 1998). The trend remains similar where aluminum fluxes are more significant in coastal areas near the river outlets, but decreasing in offshore areas, due to the metal's detrital character. In winter Al content in SPM is similar to that measured in deltaic

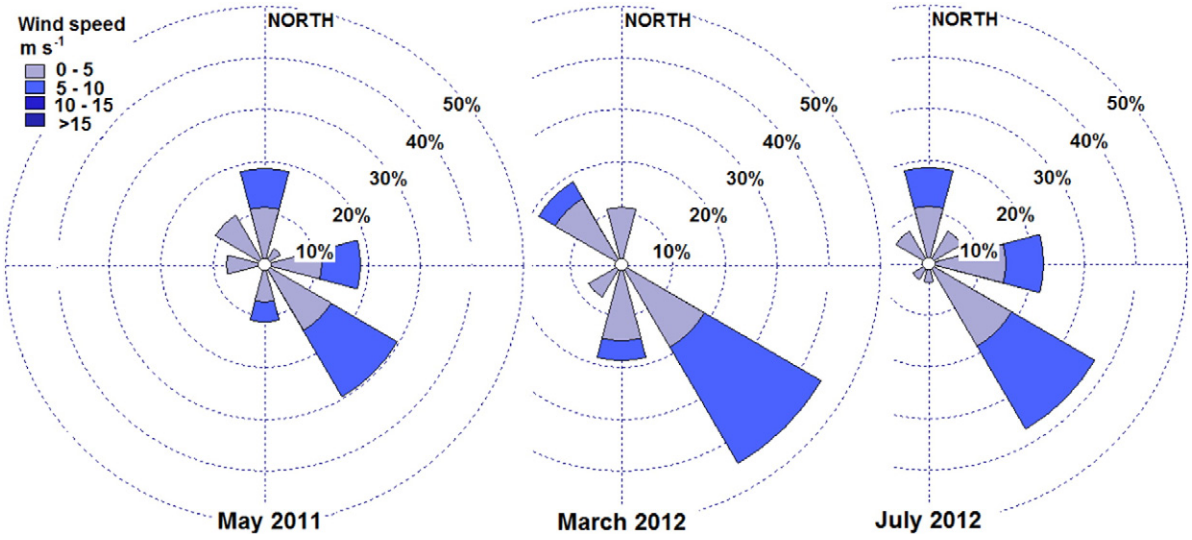

Fig. 4. Average wind speed and direction during sampling campaigns.

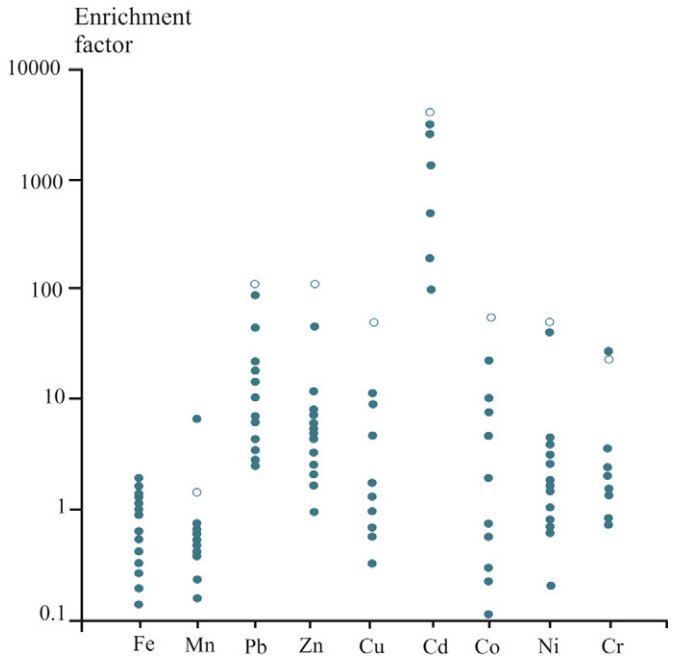

Fig. 6. Enrichment factor of heavy metals (circles represent enrichment at Mejerda outlet).

sediments (Helali et al., 2013), though it is lower in summer (Table 6) due to lower summer detrital output.

4.4. Enrichment factor

The enrichment factor (EF) is the value calculated for each heavy metal when estimating the proportion of the anthropogenic activity in the uptake of heavy metals in sediments. Aluminum is a conservative element, unaffected by human activity and is thus regarded as the detrital fraction of sediment. The EF is therefore calculated in relation to Al content; the levels of the other metals are normalized in comparison with those of aluminum (Zoller et al., 1974; Hakanson, 1980; Alvarez-Iglesias et al., 2003; and Maanan et al., 2004) and then compared to the levels recorded in the NASC (North American Shale Composite). The formula used is as follows EF = [Me/Al] sample / [Me/Al] (Salomons and Forstner, 1984).

Enrichment factors calculated for the heavy metals at all the stations and in both seasons are shown in Fig. 6. Three categories are distinguished:

- Non-polluting metals: The best examples are iron and manganese (with an EF of 0.1 to 1), with the exception of values corresponding to the Mejerda outlet and the 10 m stations, characterized by an EF > 1 in summer.
- Moderately polluting metals: Here pollution occurs only at some stations or in certain seasons. For example, in nickel, cobalt, copper and chromium, the EF range is from less than 1 to almost 50, but most of them range between 1 and 10. The highest values are found in the Mejerda River water itself and not in the marine waters off the outlet: EF = 41 to 48 for Ni, 24 to 28 for Cr, 23 to 55 for Co and more than 40 for Cu in the summer (Fig. 6). EF can also reach high values off the Mejerda outlet, as is the case of Cu at the 10 m station in summer (EF = 11) and Co at the 20 m station where the EF = 2.1.
- Polluting metals: This is seen in the cases of lead, zinc and cadmium where the enrichment factor is high (up to 115 for Pb and Zn) or extremely high (up to 3000 for Cd). Regarding the aforementioned metals, the highest enrichment values are observed in the Mejerda outlet: 89 to 117 for Pb and 44 to 114 for Zn, and up to 3180 for Cd (Fig. 6).

Overall, the estimates of pollution from the enrichment factors calculated in SPM reflects the same values reported in the surface sediment (Helali et al., 2013) and sediment cores from the Mejerda River Delta (data not shown), with Pb, Zn and Cd as the most polluting metals there. Enrichment is a natural process, whose occurrence has, in fact, been observed to be high in this mining area. However, the production of some metals is closely linked with human activity: wastewater discharge and mining activity in the Mejerda catchment. Other metals are not a factor of heavy pollution in the prodelta. Clearly, the waters of the Mejerda are an important source of heavy metal in the prodelta which are then dispersed into the offshore waters and probably into the rest of the Gulf of Tunis.

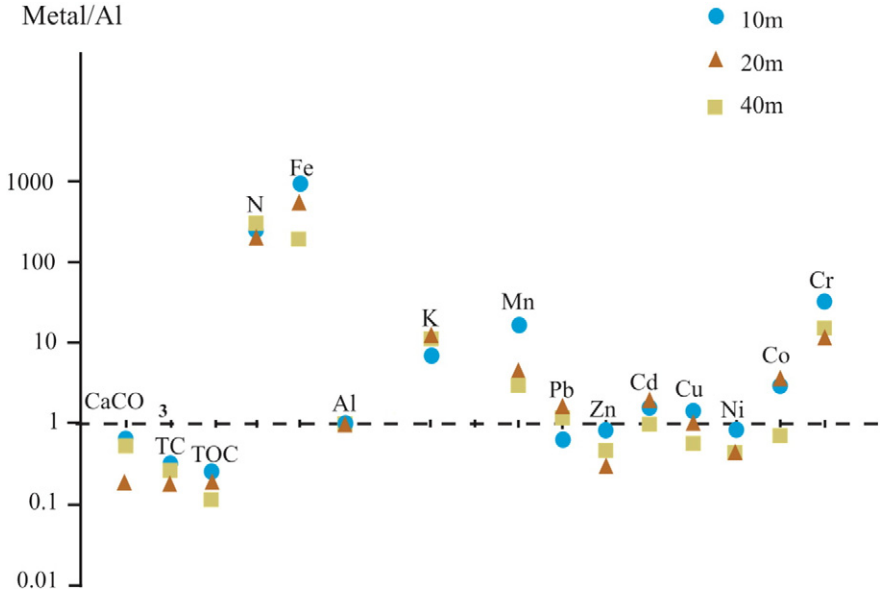

Fig. 7. Normalization of $CaCO_3$, TC, TOC, and trace elements compared to aluminum in top-level Mejerda outlet SPM.

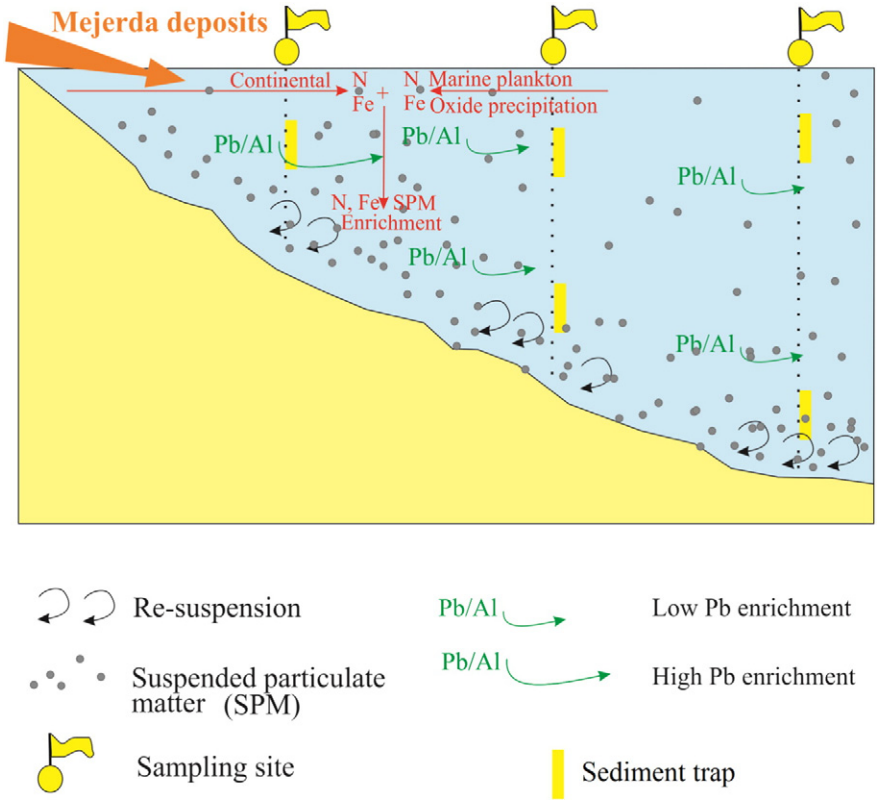

Fig. 8. Nutrient and trace element enrichment in SPM in offshore zones facing Mejerda River outlet.

4.5. Normalization towards aluminum

The same calculation was used to determine the enrichment factor as was used to estimate the significance of the contribution of the Mejerda outlet for each metallic element in the marine waters. To achieve this, the values of each component (carbonates, organic matter and metals) were normalized in relation to its own concentration level in the Mejerda water SPM. No seasonal variation in results was obtained, thus it is the average annual measurements that are represented (Fig. 7).

Two categories of component are conspicuous:

- Elements contributing to enrichment in the Mejerda waters: This is especially true for nitrogen and iron (Fig. 8), whose enrichment exceeds 100. Nitrogen and iron should show an authigenic origin, and, in the case of nitrogen, also biogenic as this component is abundant in marine plankton; this was explained above in the calculation of the C/N ratio and the precipitation of iron oxides off the Mejerda outlet regarding iron.

Other components are also enriched in the waters of the prodelta:

- Potassium, for example, is widely present in clays; potassium enrichment in the prodelta indicates that the clays present in the marine waters have likely originated elsewhere, probably in Ghar Melh Lagoon.
- Manganese has limited enrichment. It is more significant near the coast (15 at the 10 m station) and slightly less at the 20 and 40 m stations (3–4).
- Similar to iron, the enrichment manganese is restricted to the 10 m station, which may come from a source other than the Mejerda, probably Ghar El Melh Lagoon, from which manganese enters the mouth of the Mejerda via the north–south littoral drift.

Table 9
Correlation of heavy metal flux in SPM facing Mejerda River outlet.

Variables	Al	Fe	Mn	Pb	Zn	Cd	Cu	Ni	Co	Cr
Al	**1.00**									
Fe	−0.43	**1.00**								
Mn	−0.29	0.52	**1.00**							
Pb	−0.45	0.30	−0.01	**1.00**						
Zn	−0.53	**0.79**	0.42	0.43	**1.00**					
Cd	−0.30	0.41	0.07	**0.72**	0.54	**1.00**				
Cu	−0.40	0.43	0.56	−0.04	0.27	−0.39	**1.00**			
Ni	−0.44	**0.73**	0.26	0.56	**0.91**	**0.82**	−0.04	**1.00**		
Co	−0.30	−0.05	0.11	−0.04	0.36	−0.30	0.42	0.04	**1.00**	
Cr	−0.42	**0.86**	0.31	0.51	**0.84**	**0.76**	0.08	**0.95**	−0.16	**1.00**

Significant correlations (> 0.7) are in bold.

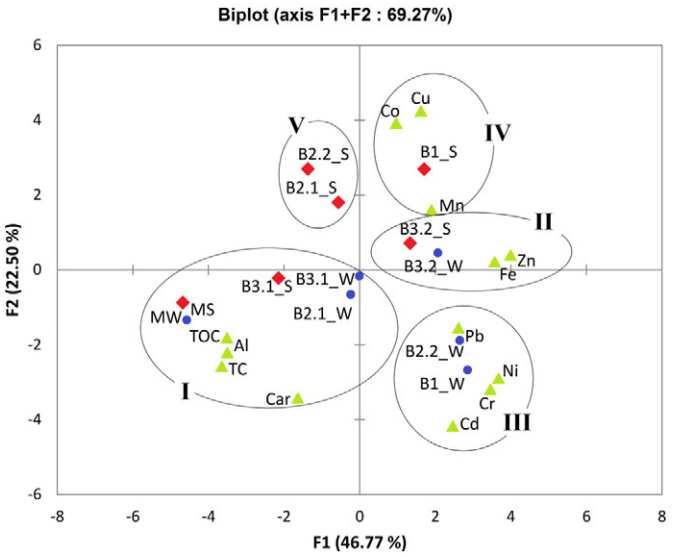

Fig. 9. ACP analysis in SPM flux and metal-associated flux in the Mejerda (M) and in offshore zones (B1, B2 and B3 stations). Blue circle = winter and red lozenge = summer.

- Metal enrichment as regards Mejerda River sediment deposits: metals with no enrichment or very little, a state particularly true of most heavy metals (Fig. 7) in relation to human activity in the Mejerda catchment, which is a major source of these metals in the prodelta. With the exception of Pb, most of the metals undergo a "dilution" in the sea, since maximum enrichment is observed at the coastal stations (0.8 for Zn and Ni, 1 for Cu and Cd, and 3 for Co). Lead enrichment (Fig. 8) confirms that this element has a source contributing to its enrichment other than the Mejerda; this may be due to atmospheric inputs or the region's fishing activity, as well as the inputs from Ghar El Melh Lagoon. Cadmium enrichment is almost constant and does not show significant differentiation (around 1) as it is linked to organic matter, as mentioned previously, and itself originates essentially in the Mejerda. As presented in Fig. 7 the enrichment of Co and Cr cannot be related to Mejerda discharge since Mejerda deposits are not enriched with Co and Cr (Decrée et al., 2010). The Co and Cr enrichment is related to other sources such as Ghar El Melh Lagoon and, mainly, the Khlij Channel (Essoni, 1998). Trace elements such as cobalt may be present at $\mu g\ g^{-1}$ levels in biogenic materials and particulate organic carbon (POC). In the future, for a better understanding of SPM and the role of trace elements in the biogeochemical cycle (Roberts et al., 2009; Boss et al., 2015), a good knowledge of chemical fractionation will be essential.

4.6. Statistical analysis

Correlation between metal flux during the wet and dry seasons in the Mejerda River and offshore facing the Mejerda outlet shows positive correlation between metal fluxes with a high positive correlation of Cr to Fe, Zn, Ni and Cd (Table 9). Iron is positively correlated with Cr, Zn and Ni with $r = 0.86$, $r = 0.79$ and $r = 0.73$ for $p < 0.05$, respectively. ACP analysis shows that the two first axes explain 71.5% of total variance (Fig. 9). Five groups are distinguished: the first includes the Mejerda in both winter and summer, with Al representing the continental origin of SPM flux in both seasons and SPM flux at the 40 m depth sites in winter. Results agree with the hypothesis that the counter-clockwise current carries all outflow deposits from the Mejerda during the winter period to the central part of the gulf. In the second group Fe is associated with SPM flux in both summer and winter, associated with Zn flux which is accumulated with strong diagenetic processes as explained by Helali et al. (2015). The third and fourth groups associate other SPM fluxes at 10 and 20 m with other groups of metals. Group 5 is composed of summer intermediate sites at 20 m that have no metal association or metal flux association.

5. Conclusion

Normalization shows that in the marine waters off the Mejerda River outlet, it is the river itself which is a major source of Pb, Zn, Cd, Cu, Ni, and Co (all of which are related to human activities). In addition to the Mejerda, Ghar El Melh Lagoon may be a potential source of Fe and the essential source of Mn, as well as the probable source of clays in these coastal waters. The prodelta shows some metal accumulation of zinc, lead and cadmium, the heavy metals essentially found present in Mejerda catchment mining activity. Enrichment factor calculation shows that Cd is likely the most heavily accumulated metal in the SPM off the Mejerda outlet, confirming the results of other studies conducted in the area. The Mejerda is also an important source of other heavy metals which, though not major polluting factors, are dispersed into the marine waters off the outlet from which they likely spread into the rest of the Gulf of Tunis.

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References

Action, Q.A., 2011. Issues in Global Environment: Freshwater and Marine Environments, Scholarly Editions, Atlanta, Georgia. pp. 318–1287.
Alvarez-Iglesias, P., Rubio, B., Vilas, F., 2003. Pollution in intertidal sediments of San Simon Bay (Inner Ria de Vigo, NW of Spain): total heavy metal concentrations and speciation. Mar. Pollut. Bull. 46, 491–521.
Balkis, N., Aksu, A., Okus, E., Apak, R., 2009. Heavy metal concentrations in water, suspended matter, and sediment from Gökova Bay, Turkey. Environ. Monit. Assess. 167, 359–370.
Ben Charada, R., 1997. Etude hydrodynamique et écologique du complexe Golfe - Lac de Tunis. Contribution à la modélisation de l'écosystème pélagique des eaux côtières de Tunis Thèse de doctorat Ecole d'Ingénieurs de Tunis (400 pp.).
Boss, E., Guidi, L., Richardson, M.J., Stemmann, L., Gardner, W., Bishop, J.K.B., Anderson, R.F., Sherrell, R.M., 2015. Optical techniques for in-situ characterization of particles pertinent to GEOTRACES. Prog. Oceanogr. 133, 43–54.
Brahim, M., Atoui, A., Sammari, C., Aleya, L., 2015. Surface sediment dynamics along with hydrodynamics along the shores of Tunis Gulf (north-eastern Mediterranean). J. Afr. Earth Sci. 103, 30–41.
Brahim, M., Koutitonsky, V., Bejaoui, B., Sammari, C., 2007. Simulation numérique du transport du sable sous l'effet des vents dans le golfe de Tunis. Bull. Inst. Nat. Sci. Tech. Mer.
Butman, C.A., 1986. Sediment trap biases in turbulent flows: results from a laboratory flume study. J. Mar. Res. 44, 645–693.
Decrée, S., Ruffet, G., Putter, T., De Baele, J.M., Recourt, P., Jamoussi, F., Yans, J., 2010. Mn oxides as efficient traps for metal pollutants in a polyphase low-temperature Pliocene environment: a case study in the Tamra iron mine, Nefza mining district, Tunisia. J. Afr. Earth Sci. 57, 249–261.
Essoni, N., 1998. Etude de la dynamique des sels nutritifs et des métaux lourds en relation avec la sédimentologie et l'hydrodynamique dans le large du golfe de Tunis Thèse de Doctorat en Géologie Université De Tunis II (229 pp.).
Forstner, U., Wittmann, G.T.W., 1981. Metal Pollution in the Aquatic Environment. second ed. Springer-Verlag, New-York (468 pp.).
Fütterer, D.K., 2006. In: H.D., Schulz, M., Zabel (Eds.), The Solid Phase of Marine Sediments. Marine Geochemistry. Springer, Berlin Heidelberg, pp. 1–25.
Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001.
Helali, M.A., Oueslati, W., Zaaboub, N., Added, A., Abdeljaouad, S., 2013. Geochemistry of marine sediments in the Mejerda River delta, Tunisia. Chem. Speciat. Bioavailab. 25, 247–257.

Helali, M.A., Zaaboub, N., Oueslati, W., Added, A., Aleya, L., 2015. Diagenetic processes and sediment–water exchanges of heavy metals in the Mejerda River Delta (Gulf of Tunis). Environ. Earth Sci. 74 (9), 6665–6679.

Helali, M.A., Zaaboub, N., Oueslati, W., Added, A., Aleya, L., 2016. Nutrient exchange and oxygen demand at the sediment–water interface during dry and wet seasons off the Medjerda River Delta (Tunis Gulf, Tunisia). Environ. Earth Sci. 75 (25). http://dx.doi.org/10.1007/s12665–015-4820-x.

Kontas, A., 2012. A case study of trace metals in suspended particulate matter and biota before wastewater treatment plant from the Izmir Bay, Turkey. Environ. Monit. Assess. 184, 2605–2616.

Lam, P.J., Twining, B.S., Jeandel, C., Roychoudhury, A., Resing, J.A., Santschi, P.H., Anderson, R.F., 2015. Methods for analyzing the concentration and speciation of major and trace elements in marine particles. Prog. Oceanogr. 133, 32–42.

Leivuori, M., Valliusb, H., 1998. A case of seasonal variation in the chemical composition of accumulating suspended sediments in the central Gulf of Finland. Chemosphere 36, 2417–2435.

Little, S.H., Vance, D., Lyons, T.W., McManus, J., 2015. Controls on trace metal authigenic enrichment in reducing sediments: insights from modern oxygen-deficient settings. Am. J. Sci. 315, 77–119.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev. 32, 235–283.

Maanan, M., Zourarah, B., Carruesco, C., Aajjane, A., Naud, J., 2004. The distribution of heavy metals in the sidi Moussa lagoon sediments (Atlantic Moroccan Coast). J. Afr. Earth Sci. 39, 473–483.

Marconi, M., Sferlazzo, D.M., Becagli, S., Bommarito, C., Calzolai, G., Chiari, M., di Sarra, A., Ghedini, C., Gómez-Amo, J.L., Lucarelli, F., Meloni, D., Monteleone, F., Nava, S., Pace, G., Piacentino, S., Rugi, F., Severi, M., Traversi, R., Udisti, R., 2014. Saharan dust aerosol over the central Mediterranean Sea: PM_{10} chemical composition and concentration versus optical columnar measurements. Atmos. Chem. Phys. 14, 2039–2054.

Moldenhauer, K.M., Christophe, Z., Dominik, F., 2008. Heavy metals as indicators for Holocene sediment provenance in a semi-arid Mediterranean catchment in northern Tunisia. Quat. Int. 189, 129–134.

Nordmyr, L., Österholm, P., Åström, M., 2008. Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils. Mar. Environ. Res. 66, 378–393.

Oueslati, W., Added, A., Adeljaouad, S., 2010. Evaluation of metal contamination in a changed sedimentary environment: Ghar El Melh Lagoon, Tunisia. Chem. Speciat. Bioavailab. 22, 227–240.

Palanques, A., Díaz, J.I., 1994. Anthropogenic heavy metal pollution in the sediment of the Barcelona continental shelf (Northwestern Mediterranean). Mar. Environ. Res. 38, 17–31.

Rivaro, P., Çullaj, A., Frache, R., Lagomarsino, C., Massolo, S., De Mattia, M.C., Ungaro, N., 2011. Heavy metals distribution in suspended particulate matter and sediment collected from Vlora Bay (Albania): a methodological approach for metal pollution evaluation. J. Coast. Res. 58, 54–66.

Roberts, K.A., Xu, C., Hung, C.-C., Conte, M.H., Santschi, P.H., 2009. Scavenging and fractionation of thorium vs. protactinium in the ocean, as determined from particle–water partitioning experiments with sediment trap material from the Gulf of Mexico and Sargasso Sea. Earth Planet. Sci. Lett. 286, 131–138.

Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin (349 pp.).

Santos-Echeandía, J., Prego, R., Cobelo-García, A., Caetano, M., 2011. Metal composition and fluxes of sinking particles and post-depositional transformation in a Ria Coastal System (NW Iberian Peninsula). Mar. Chem. 134, 36–46.

Spagnoli, F., Bergamini, M.C., 1997. Water-solid exchanges of nutrients and trace elements during early diagenesis and resuspension of anoxic shelf sediments. Water Air Soil Pollut. 99, 541–556.

Spagnoli, F., Bartholini, G., Dinelli, E., Giordano, P., 2008. Geochemistry and particles size of surface sediments of Gulf of Manfredonia (Southern Adriatic Sea). Estuar. Coast. Shelf Sci. 80, 21–30.

Spagnoli, Federico, Dinelli, Enrico, Giordano, Patrizia, Marcaccio, Marco, Zaffagnini, Fabio, Frascari, Franca, 2014. Sedimentological, biogeochemical and mineralogical facies of Northern and Central Western Adriatic Sea. J. Mar. Syst. 139, 183–203.

Tessier, E., 2012. Diagnostic de la contamination sedimentaire par les metaux/metalloids dans la rade de Toulon et Mecanismes controlant leur mobilité Thèse Chimie de l'environnement Université du Sud Toulon Var (291 pp.).

Violintzis, C., Arditsoglou, A., Voutsa, D., 2009. Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay, Greece: Delineating the impact of inland waters and wastewaters. J. Hazard. Mater. 166, 1250–1260.

Yiğiterhan, O., Murray, J.W., 2008. Trace metal composition of particulate matter of the Danube River and Turkish rivers draining into the Black Sea. Mar. Chem. 111, 63–76.

Zaaboub, N., Alves Martins, M.V., Dhib, A., Béjaoui, B., Galgani, F., El Bour, M., Aleya, L., 2015. Accumulation of trace metals in sediments in a Mediterranean Lagoon: usefulness of metal sediment fractionation and elutriate toxicity assessment. Environ. Pollut. 207, 226–237.

Zaaboub, N., Oueslati, W., Helali, M.A., Abdeljaouad, S., Huertas, J.F., Galindo, A.L., 2014. Trace elements in different marine sediment fractions of the Gulf of Tunis, Central Mediterranean Sea. Chem. Speciat. Bioavailab. 26, 1–12.

Zoller, W.H., Gladney, E.S., Gordon, G.E., Bors, J.J., 1974. Emissions of trace elements from coal fired power plants. In: Hemphill, D.D. (Ed.)Trace Substances in Environmental Health 8. University of Missouri, Colombia, Rolla, pp. 167–172.