



Chemical speciation of Fe, Mn, Pb, Zn, Cd, Cu, Co, Ni and Cr in the suspended particulate matter off the Mejerda River Delta (Gulf of Tunis, Tunisia)



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ABSTRACT

Fluxes of suspended particulate matter (SPM) and their associated metals were performed off the Mejerda River Delta during both the wet (March) and the dry (July) seasons in 2012, using sediment traps at study stations at depths of 10, 20 and 40 m. Fluxes nearest to the Mejerda outlet were more significant, especially during winter ($36 \text{ g m}^{-2} \text{ day}^{-1}$), but dissipated further offshore, $24.5\text{--}6 \text{ g m}^{-2} \text{ day}^{-1}$ at the 20 m and $21.8\text{--}4.8 \text{ g m}^{-2} \text{ day}^{-1}$ at the 40 m stations. Many variations observed in seasonal and spatial metal fluxes are similar to those of SPM, in particular Pb and Zn, probably because they are associated with the mining activity characteristic of the Mejerda catchment. Chemical speciation reveals that most of the metals (20–100%) are bound to the residual fraction. The most toxic metals (Pb, Zn) are bound in part to the exchangeable fraction (20–50% for Pb and 5–15% for Zn) making them relatively bioavailable and therefore potentially toxic. While Cu and Cd fluxes are not always clearly established according to season, both metals are apparently sequestered deep in the sediment, bound especially to clays (40–80% for Cd and up to 100% for Cu).

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1. Introduction

Suspended particulate matter (SPM) in coastal ecosystems is essential as it contributes to the structuring of water masses along with providing the environmental conditions to support the production and the growth of plankton and fish species. However, SPM can also be loaded with contaminants such as heavy metals, mainly transported as both inorganic and organic suspended particles and deposited along the coast leading to disruption in the delicate food web (Belabed et al., 2003; Islam and Tanaka, 2004; Zaaboub et al., 2015; Martins et al., 2015). Various chemical reactions within the suspended particles occur prior to sedimentation of organic matter. For example, suspended particles are the subject of several physico-chemical processes including flocculation/coagulation (Sholkowitz, 1978; Erisma, 1986; Morris, 1986), desorption from suspended

particle surfaces (Van der Weiden et al., 1977) and biological uptake (Turekian, 1977; Kuss and Kremling, 1999). Sediment traps were therefore adopted as a means to measure SPM and metal fluxes along the water column of different marine systems (Broman et al., 1994; Leivuori and Valliusb, 1998; Kuss and Kremling, 1999; Matthai et al., 2002; Ergül et al., 2008; Nordmyr et al., 2008; Santos-Echeandía et al., 2011), yet no such studies have previously been conducted in western environments and certainly not in the Gulf of Tunis. Located in the western Gulf of Tunis, the Mejerda River is Tunisia's most important river and the main source of water and sediments for the gulf, with approximately $30 \text{ m}^3 \text{ s}^{-1}$ water flow (Oueslati et al., 2006). As mining is extensive in the Mejerda catchment (Mauldenauer et al., 2007), the location appeared ideal for the study of the qualitative and quantitative characteristics of SPM and its associated metals, with the additional hypothesis that clarification of the chemical speciation of metals bound to suspended particles would provide insight into the mechanisms of binding and transport of metals, helping to improve our knowledge as to their sequestration and bioavailability.

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The objectives of the present study were to (i) determine the level of heavy metal flux off the delta and its seasonal, lateral and vertical variations, (ii) compare these fluxes with those of other similar marine areas in the world so as to evaluate the degree of heavy metal pollution in the delta and (iii) determine the contribution of the various phases of sedimentation to the settling of these metals.

2. Study site

The Mejerda catchment extends over 23,700 km², its mining activity including polymetallic deposits of Pb > Zn > Cu > Hg and As, in the regions of Chemtou, Ain Ksir, Bou Hertma, Sidi Abdallah, Ben Béchir, Bou Salem and Jendouba. The delta is subject to winds that change direction with the season, from north to northwest during the rainy season (March) and from east to southeast during the dry season (July) (Ben Charada, 1997; Brahim et al., 2014). Sea surface currents depend upon wind direction, moving mainly from north to south (Brahim et al., 2014). While the waters of the Mejerda River constitute the main source of erosion products (Oueslati et al., 2006), the delta is also influenced by three other water inflow sources: the Khlij Channel, Ghar El Melh Lagoon and Sebkheth Ariana, all of which are also connected to marine waters (Fig. 1).

This study took place in the offshore zones opposite the mouth of the Mejerda River, at three points situated along a radial perpendicular to the coast (Fig. 2). Fig. 1 and Table. 1 show the sampling locations and the seasonal study which was conducted in March and July 2012.

3. Material and methods

The sediment traps constructed for this study were designed after the research of Butman et al. (1986), taking into consideration the extreme conditions of the marine currents in the zones off the delta (Brahim et al., 2014). The traps are composed of a 110 × 9 cm cylinder of inert material (PVC) resistant to marine conditions and which caused no interference with geochemical analysis. A small volume of chloroform was placed into the sediment trap beforehand to prevent bacterial activity. Fig. 2 shows the coastal-offshore and vertical dispositions of the sediment traps at the three stations. After four weeks of immersion, the sediment traps were recovered and decanted; the suspended particles were removed from the water and centrifuged at 3500 rpm for 15 min. Suspended particulate matter from the Mejerda River was collected by filtering (0.45 μm). After several washings with bi-distilled water to remove the salts, the SPM was dried (60 °C) and weighed.

The samples thus obtained were digested by adding a mixed solution of 20 ml concentrated HClO₄, 10 ml HF and 20 ml HNO₃ to 1 g of sediment in Teflon bombs. The resulting digestates were analysed by flame atomic absorption spectrometry (using the Thermo Scientific ICE 3300 AA Spectrometer) for presence of Fe, Mn, Pb, Zn, Cd, Cu, Co, Ni and Cr. The accuracy of the analytical procedures used for heavy metal analysis was verified using the BCR-032 certified reference material, obtaining good occurrence with the certified values. Relative Standard Deviations (RSDs) were typically <11% (Tables. 2 and 3). Chemical speciation is the most popular approach used to evaluate pollution and mobility in marine sediments. The sequential extraction procedure applied in this work was developed by Tessier et al. (1979) and consists of extractions, with the associated chemical reagents and conditions (to 1 g sediment), in the following order:

- (1) exchangeable fraction: 8 mL of MgCl₂ (1 M) adjusted to pH 7.0 with ammoniac + continuous agitation for 1 h;
- (2) bound to marine 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 NH₂OH.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 HNO₃ plus 5 ml of 30% H₂O₂ adjusted to pH 2 with HNO₃; samples were heated to 85 °C for 2 h with occasional agitation; a second 3 ml aliquot of (30% H₂O₂) were added and the samples were heated to 85 °C for 3 h with occasional agitation; after cooling, the samples were diluted to 20 ml, with 5 ml of NH₄OAc added; samples were agitated continuously for 30 min;
- (5) residual fraction: mixture of 20 ml HF plus 10 ml HClO₄ (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. The sediment was once again washed in 10 ml of bi-distilled water, then centrifuged and the water discarded. Metal concentrations were determined by flame atomic absorption spectrometry with a Thermo Scientific ICE 3300 AA Spectrometer. The SPM flux was calculated by taking into account the duration of immersion of the sediment traps, their surface and their quantity of trapped suspended matter: Sedimentation flux (Js) = m/S/n; with: m: the total mass of trapped suspended matter (in grams); S: section of sediment trap (in m²); N: number of days of immersion; Js: g m⁻² day⁻¹.

Metal flux (μg m⁻² day⁻¹) is calculated using the relation [Me] x Js with Me being the concentration of the metal in the SPM (in μg g⁻¹). The sinking flux (Js) was measured at all three stations (10, 20 and 40 m), while in the waters of the Mejerda River the concentration of the suspended particles (mg l⁻¹) was calculated directly. Metals associated with SPM in the Mejerda (C_{Me}) are listed in μg l⁻¹ were calculated from the total concentration of SPM in the water, with C_{Me} = C_{SPM} × [Me]; with Me: metal concentration in the SPM (in μg g⁻¹) and C_{SPM} the concentration of SPM in water (g l⁻¹).

4. Results

4.1. Suspended particulate matter (SPM)

The concentration of suspended particles in the Mejerda River varies between the two seasons: in the rainy season (March) it is 90 mg l⁻¹, while in the dry season (July) the concentration does not exceed 40 mg l⁻¹ (Table. 4). The suspended particle concentration is closely related to the amount of precipitation in the Mejerda catchment, as well as to the direction of the prevailing winds in the Gulf of Tunis. As the Mejerda is the gulf's main source of SPM, maximum flux is observed at the 10 m station with 38 g m⁻² day⁻¹ during the rainy season, but only 18 g m⁻² day⁻¹ in the dry season (Table. 6). Further offshore, the SPM flux decreases rapidly; it is only at the 40 m station that the minimum flux is observed (from 10 to 25 g m⁻² day⁻¹ and 5–11 g m⁻² day⁻¹) depending on the season and depth of the sediment traps (Table. 6). Conversely, a fairly pronounced vertical stratification is observed at the 20 and 40 m stations, resulting in a distribution pattern contrary to expectations, in fact, quite opposite to the general observations in the oceans and the open sea. Here, more SPM flux is observed in the rainy season at the bottom (5 m above the seabed) than on the surface, at 13 g m⁻² day⁻¹ at the subsurface compared to 25 g m⁻² day⁻¹ at the bottom of the water column at the 20 m station, and 12 g m⁻² day⁻¹ at the subsurface compared to 22 g m⁻² day⁻¹ at the bottom at the 40 m station (Table. 6). The same trend is also observed during summer, where the minimum SPM flux is measured in the subsurface sediment traps.

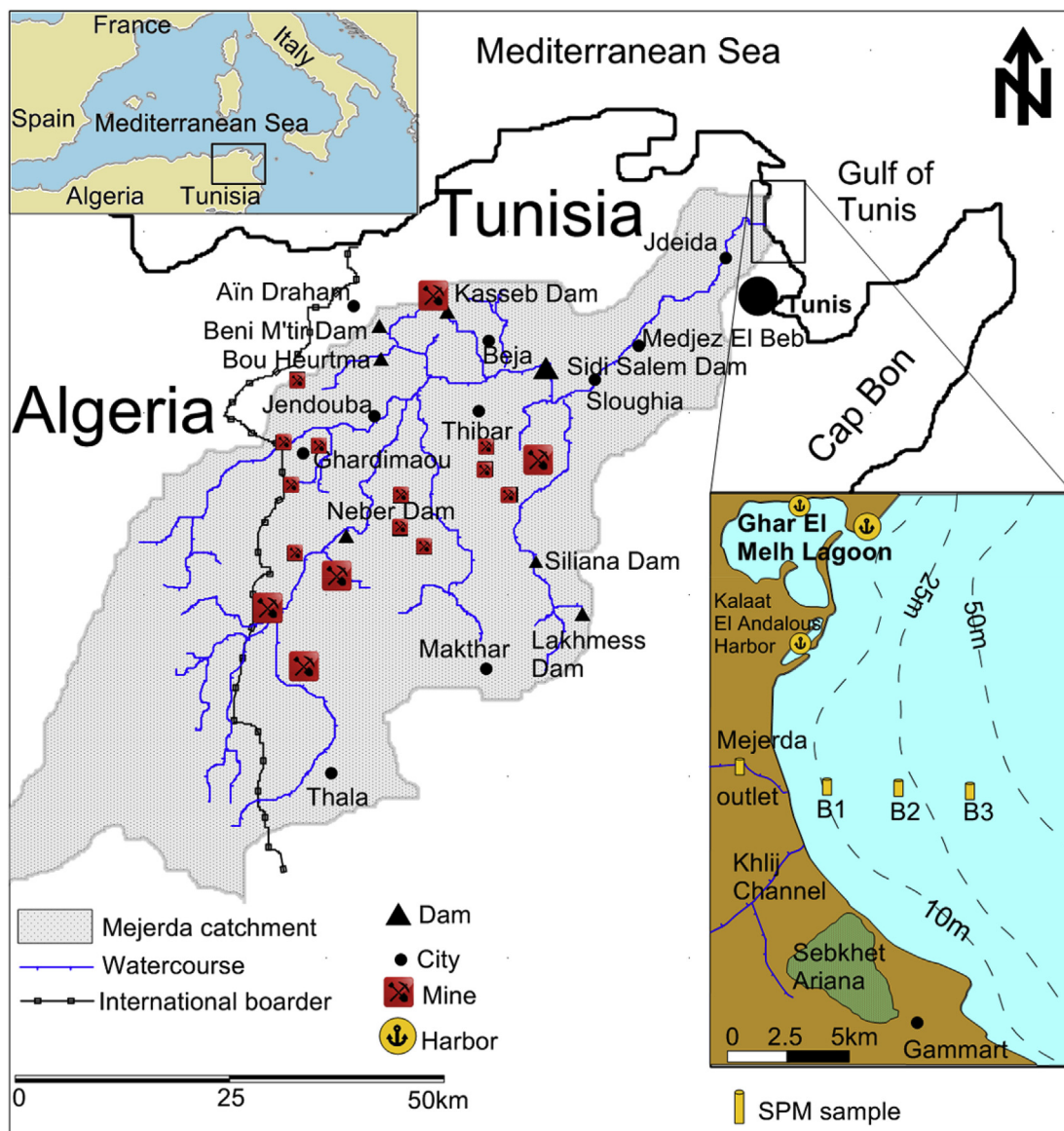


Fig. 1. Study site.

4.2. Iron

This flux is significant near the coast with $384 \text{ g m}^{-2} \text{ day}^{-1}$ in the wet season and $260 \text{ g m}^{-2} \text{ day}^{-1}$ in the dry season, while further out, the flux varies from 58 to $230 \text{ g m}^{-2} \text{ day}^{-1}$ in the wet season and $37\text{--}344 \text{ g m}^{-2} \text{ day}^{-1}$ in the dry season, seasonal variations not being considered significant (Table 6).

4.3. Manganese

Unlike SPM, the amount of manganese carried by the Mejerda River is higher during the dry season ($2.89 \mu\text{g l}^{-1}$) than in the wet season ($0.88 \mu\text{g l}^{-1}$) (Table 4). This is also the case at the 10 m station which is directly influenced by the contributions of the Mejerda River, where a much greater flux of Mn is observed in the dry season ($18 \text{ mg m}^{-2} \text{ day}^{-1}$) compared to only $5.5 \text{ mg m}^{-2} \text{ day}^{-1}$ in the wet season (Table 6).

4.4. Lead and zinc

Lead flux in the wet season is estimated at $1446 \mu\text{g m}^{-2} \text{ day}^{-1}$ and $4746 \mu\text{g m}^{-2} \text{ day}^{-1}$ at the 10 and 20 m stations, respectively. In the dry season, the lead flux at the bottom of the water column is estimated at 1164 and $1490 \mu\text{g m}^{-2} \text{ day}^{-1}$, at the 20 and 40 m stations, respectively, while it is only $538 \mu\text{g m}^{-2} \text{ day}^{-1}$ at the 10 m station (Table 6).

Maximum lead flux is observed during the rainy season except at the 20 m station—at the bottom of the water column—whereas Zn flux is slightly higher during the dry season ($2900 \mu\text{g m}^{-2} \text{ day}^{-1}$) than during the rainy season ($2660 \mu\text{g m}^{-2} \text{ day}^{-1}$). At the other stations, maximum flux is observed at the 10 m station ($4520 \mu\text{g m}^{-2} \text{ day}^{-1}$ during the rainy season and $2308 \mu\text{g m}^{-2} \text{ day}^{-1}$ during the dry season) and a little closer inshore (ranging from 783 to $2901 \mu\text{g m}^{-2} \text{ day}^{-1}$ at the 20 m station and from 566 to $2801 \mu\text{g m}^{-2} \text{ day}^{-1}$ at the 40 m station).

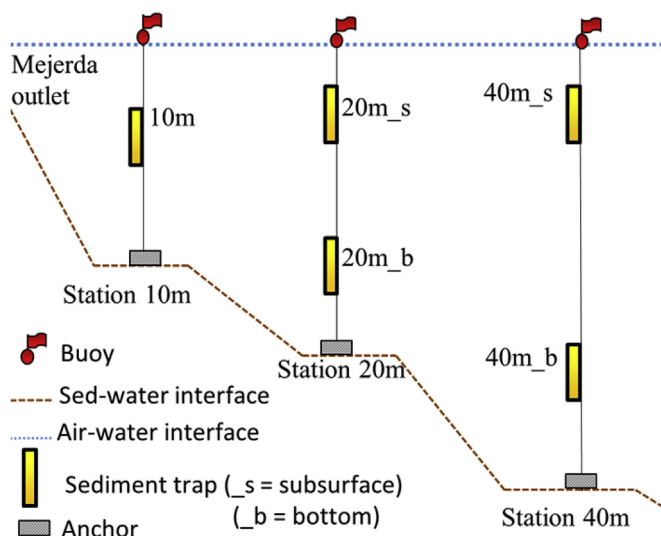


Fig. 2. Vertical disposition of sediment traps.

Table 1
Location and depth of study stations.

Station	Latitude	Longitude	Depth (m)
10 m (B1)	37°0.468'N	10°13.821'E	10
20 m (B2)	37°0.440'N	10°16.188'E	20.5
40 m (B3)	37°0.419'N	10°17.881'E	38
Mejerda outlet	37°0.1678'N	10°8.448'E	2

Table 2
Relative standard deviations.

Element	RSD (%)	Element	RSD (%)
Fe	0.96	Co	0.27
Mn	4.40	Ni	0.65
Pb	2.49	Cr	3.38
Zn	2.20	Cu	1.97
Cd	0.22		

Table 3
Accuracy of analytical procedures employed for 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

Table 4
Concentration of SPM (in mg l⁻¹) and particulate heavy metals (in µg l⁻¹) in the Mejerda outlet.

	SPM	Fe	Mn	Pb	Zn	Cd	Cu	Ni	Co	Cr
March	87	1.48	0.88	5.9	12.4	0.033	NC	7.13	1.58	9.22
July	37	0.65	2.89	2.27	9.12	0.00	1.38	2.42	0.32	2.27

4.5. Copper

Copper is not detected in the wet season. It is found only in the sediment traps at the bottom at the 20 and 40 m stations, where the flux is 247 and 856 µg m⁻² day⁻¹, respectively. During the dry season copper flux is much higher, the maximum being observed at the 10 m station (1284 µg m⁻² day⁻¹). Offshore, greater flux is recorded at the 40 m station (1142 µg m⁻² day⁻¹) than at the 20 m station (588 µg m⁻² day⁻¹) (Table. 6).

4.6. Cadmium

Cadmium is found in SPM only during the rainy season; these fluxes are the lowest among the metals studied: 45 µg m⁻² day⁻¹ at the 10 m station, from 33 to 49 µg m⁻² day⁻¹ at 20 m and from 15 to 22 µg m⁻² day⁻¹ at the 40 m station (Table. 6).

4.7. Cobalt

During the rainy season, Co flux is significantly greater at the 10 m station, with 253 µg m⁻² day⁻¹, while offshore it varies from 20 to 148 µg m⁻² day⁻¹. In the dry season, despite a decrease in SPM flux, cobalt flux is more significant off the Mejerda outlet, where fluxes of 1833 µg m⁻² day⁻¹ and 400 µg m⁻² day⁻¹ are observed at the 20 m and 40 m stations, respectively (Table. 6).

4.8. Nickel

The Ni content in SPM varies slightly between the rainy season (average 67 µg g⁻¹) and the dry season (46 µg g⁻¹) (Table. 5). The fluxes are stronger during the rainy season, especially at the 10 m station (2637 µg m⁻² day⁻¹) and a little closer inshore: 1639 and 1656 µg m⁻² day⁻¹, respectively, at the 20 and 40 m stations (Table. 6).

4.9. Chromium

Fluxes range from 778 to 3200 µg m⁻² day⁻¹ in the rainy season and show a marked decrease during the dry season when a flux of 292–1480 µg m⁻² day⁻¹ is observed (Table. 6). In fact, chromium flux decreases along with SPM during the dry season, though the Mejerda's concentration of particulate chromium ranges from 9.22 µg l⁻¹ in winter to 2.27 µg l⁻¹ in the dry season (Table. 4).

5. Discussion

5.1. Suspended particulate matter

Seasonal and coastal-offshore distribution of SPM fluxes is consistent with the prevailing wind direction (most often north to northwest) and thus with marine currents, and is also consistent with the measured SPM content of the Mejerda River. The excess of suspended particles collected in the traps at the bottom of the water column is probably due to the re-suspension affecting the seabed. In fact, though the sediment traps were placed at the bottom of the water column where they were perched 5 m above the sea floor, thus they still accumulated particles resuspended from the bottom, in addition to the particles transported and discharged by the Mejerda waters. Due to the fine size of the sediment particles at the study site (Helali et al., 2013, 2016), and based on recent current measurements in the Gulf of Tunis (Brahim et al., 2014), it appears that re-suspension affecting the seabed is not ruled out and that occurrence is even very likely, including in the zone facing the Mejerda River mouth where the strongest currents were observed (Brahim et al., 2014).

Table 5
Heavy metal contents in SPM (BDL: below detection limit).

Rainy season	Fe (mg g^{-1})	Mn ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Co ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)
Mejerda	17.0	10.1	67.8	142.5	0.4	BDL	82.0	18.2	106.0
10 m	10.1	146.7	38.1	119.0	1.2	BDL	69.4	6.7	84.9
20 m_s	4.6	134.3	110.2	66.6	2.6	BDL	65.6	3.7	64.1
20 m_b	8.3	151.5	193.8	108.7	2.0	10.1	66.9	6.0	79.5
40 m_s	6.5	87.1	175.4	111.2	1.3	0.0	66.0	1.8	67.3
40 m_b	10.5	221.1	69.1	128.1	1.0	39.1	71.2	4.5	97.1
Dry season	Fe (mg g^{-1})	Mn ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Ni ($\mu\text{g g}^{-1}$)	Co ($\mu\text{g g}^{-1}$)	Cr ($\mu\text{g g}^{-1}$)
Mejerda	17.7	78.0	61.3	246.4	BDL	37.3	65.5	8.7	61.2
10 m	15.2	1071.5	31.7	135.9	BDL	75.7	38.1	34.8	54.2
20 m_s	6.2	150.4	208.8	130.7	BDL	127.0	41.8	93.6	67.5
20 m_b	2.8	68.5	70.9	176.8	BDL	35.9	55.4	111.7	18.2
40 m_s	17.5	126.4	67.1	117.2	BDL	41.2	23.9	12.1	60.5
40 m_b	30.8	134.9	133.5	197.6	BDL	102.3	72.8	36.5	132.6

Table 6
Heavy metal flux and SPM in sediment traps at the subsurface (_s) and at the bottom (_b) of the water column.

Rainy season	SPM $\text{g m}^{-2} \text{d}^{-1}$	Fe $\text{mg m}^{-2} \text{d}^{-1}$	Mn $\mu\text{g m}^{-2} \text{d}^{-1}$	Pb $\mu\text{g m}^{-2} \text{d}^{-1}$	Zn $\mu\text{g m}^{-2} \text{d}^{-1}$	Cu $\mu\text{g m}^{-2} \text{d}^{-1}$	Cd $\mu\text{g m}^{-2} \text{d}^{-1}$	Co $\mu\text{g m}^{-2} \text{d}^{-1}$	Ni $\mu\text{g m}^{-2} \text{d}^{-1}$	Cr $\mu\text{g m}^{-2} \text{d}^{-1}$
10 m	38	384	5575	1447	4521	BDL	45	253	2637	3225
20 m_s	12.94	59	1732	1421	859	BDL	33	47	846	826
20 m_b	24.56	203	3711	4747	2663	248	49	148	1640	1948
40 m_s	11.57	75	1007	2030	1287	BDL	15	20	763	778
40 m_b	21.87	229	4836	1512	2802	856	22	98	1556	2123
Dry season	SPM $\text{g m}^{-2} \text{d}^{-1}$	Fe $\text{mg m}^{-2} \text{d}^{-1}$	Mn $\mu\text{g m}^{-2} \text{d}^{-1}$	Pb $\mu\text{g m}^{-2} \text{d}^{-1}$	Zn $\mu\text{g m}^{-2} \text{d}^{-1}$	Cu $\mu\text{g m}^{-2} \text{d}^{-1}$	Cd $\mu\text{g m}^{-2} \text{d}^{-1}$	Co $\mu\text{g m}^{-2} \text{d}^{-1}$	Ni $\mu\text{g m}^{-2} \text{d}^{-1}$	Cr $\mu\text{g m}^{-2} \text{d}^{-1}$
10 m	16.98	258	18,194	538	2308	1285	BDL	592	647	920
20 m_s	6	37	902	1253	784	762	BDL	561	251	405
20 m_b	16.4	46	1125	1164	2902	589	BDL	1834	910	299
40 m_s	4.8	85	610	324	566	199	BDL	58	115	292
40 m_b	11.1	344	1505	1490	2205	1142	BDL	407	813	1480

5.2. Iron

The chemical speciation performed on SPM shows that iron is largely bound to the oxyhydroxide fractions, to organic matter and to the residual fraction (Fig. 3). While the latter is the major fraction fixing iron in the SPM (60–90% at all stations in both seasons), it appears that the percentage of iron bound to oxyhydroxides is lower near the bottom than at the top of the water column. Since SPM is partially provided from the re-suspension of the poorly oxygenated seabed, oxyhydroxides are probably partly destroyed, with the associated iron appearing to be released and then bound to the residual fraction. The chemical speciation of iron in the suspended matter reflects the observations noted in the delta surface sediments, i.e. more iron was bound to the residual fraction and less to the oxyhydroxides (Helali et al., 2013; Essoni, 1998). The iron content in the sediment is greater than in the suspended matter from the Mejerda. It could be inferred that iron in the delta sediment is not only detritic but is also accumulated due to authigenic processes. Compared with other similar marine environments, iron fluxes off the Mejerda River Delta are low. For example, in the Vora River Estuary (Finland), iron flux is $0.19\text{--}5 \text{ g m}^{-2} \text{ day}^{-1}$ (Nordmyr et al., 2008), $10\text{--}50 \text{ mg m}^{-2} \text{ day}^{-1}$ in the Baltic Sea (Leivuori and Valliusb, 1998) and $60\text{--}250 \text{ mg m}^{-2} \text{ day}^{-1}$ in the Black Sea (Ergül et al., 2008). In the Ria de Vigo (Spain), the iron flux ranges from 0.57 to $1.1 \text{ g m}^{-2} \text{ day}^{-1}$ (Santos-Echeandia et al., 2011) (Table. 7).

5.3. Manganese

As for iron, the seasonal variation of Mn flux is more pronounced near the bottom of the water column than at the top; in fact, more agitation and thus re-suspension of surface sediment in the rainy season creates more fluxes in the bottom sediment traps.

Chemical speciation showed that manganese was identified in the five fractions of the SPM, preferentially bound to carbonates (20–80%) and to oxyhydroxides (15–40%) (Fig. 3). Manganese bound to carbonates in the Mejerda's SPM is estimated at 5–10%, while in the marine stations it attained 40–60% due to the lower carbonate in seawater. However, in surface sediments, manganese is also bound to the five sediment fractions (Helali et al., 2013; Essoni, 1998). Evidently, once settled into the sediment, the proportion of manganese that is associated with carbonates decreases to a level similar to that in the SPM in which the carbonates are mainly associated with manganese oxyhydroxides, likely due to the dissolution of carbonates in the sediment, once pH values decrease (Essoni, 1998). Various studies have shown that manganese flux presents regional variations: in the Vora River Estuary (Finland), for example, it has been seen to vary from 4 to $11 \text{ mg m}^{-2} \text{ day}^{-1}$ (Nordmyr et al., 2008), and from 3.9 to $8 \text{ mg m}^{-2} \text{ day}^{-1}$ in the Ria de Vigo on the Atlantic coast of Spain (Santos-Echeandia et al., 2011). In the Black Sea (Ergül et al., 2008), manganese flux ranged from 7 to $57 \text{ mg m}^{-2} \text{ day}^{-1}$ (Table. 7). Thus, the fluxes measured in the Mejerda Delta do not show the presence of excessive manganese intake.

5.4. Lead

Chemical speciation of lead shows that, like manganese, it is bound to all SPM fractions, though essentially to oxyhydroxides and carbonates (Fig. 3). However, a relatively large fraction of lead is bound to the exchangeable fraction, as is the case for the surface sediments (Helali et al., 2013; Essoni, 1998). This bioavailable lead is observed mainly during the dry season (5% in Mejerda SPM, 15% at the 10 m station and up to 20% at the 20 m station). At the 20 and 40 m stations, which face the outlet of the Khlij Channel, lead flux appears to be affected from another source. Since lead is widely

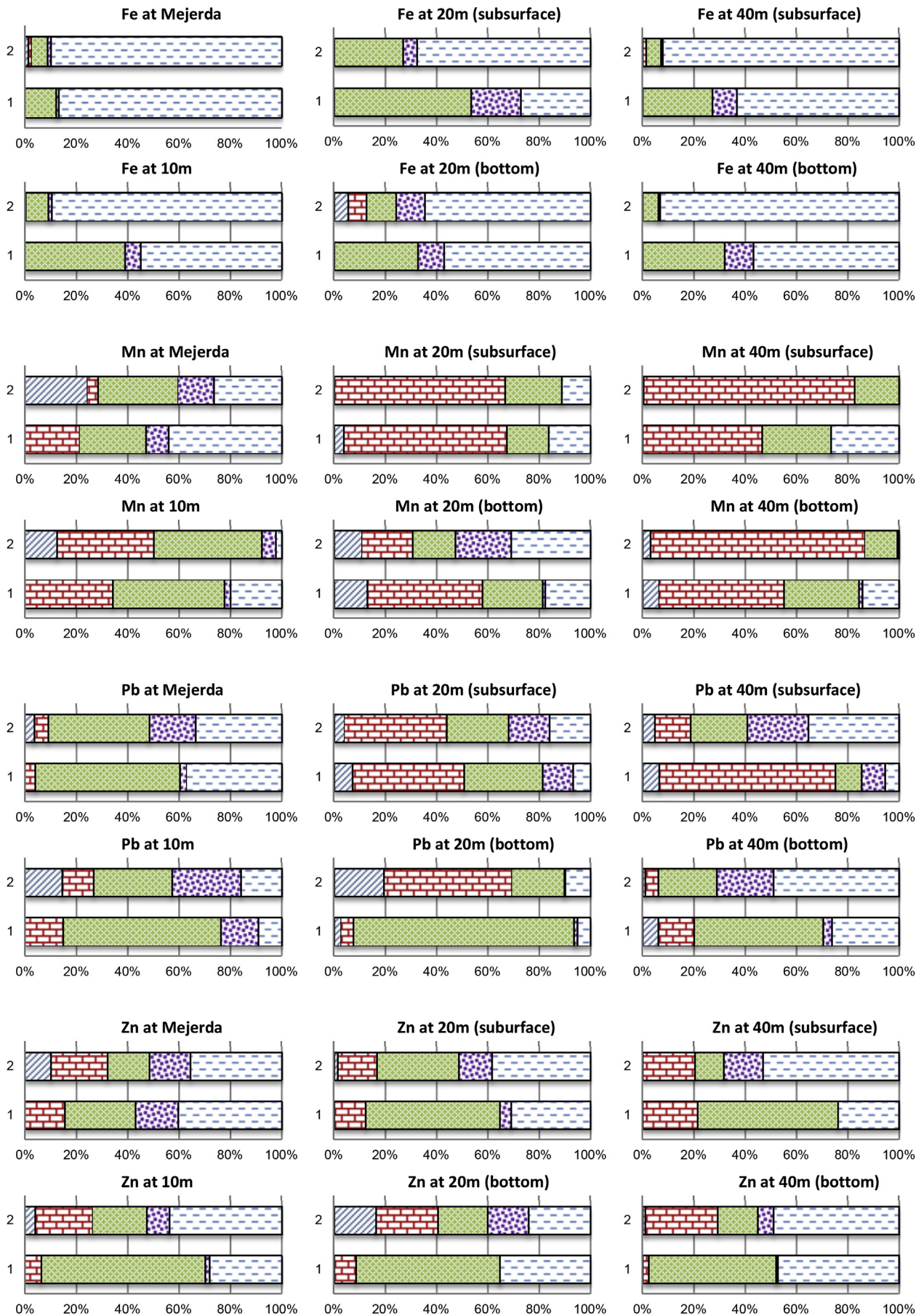


Fig. 3. Chemical speciation of Fe, Mn, Pb and Zn in SPM (1: rainy and 2: dry season) Exchangeable Carbonates Oxyhydroxydes Organic matter Residual

Table. 7
Heavy metal flux in different marine environments.

Site	SPM gm ⁻² d ⁻¹	Fe mgm ⁻² d ⁻¹	Mn mgm ⁻² d ⁻¹	Pb µgm ⁻² d ⁻¹	Zn mgm ⁻² d ⁻¹	Cd µgm ⁻² d ⁻¹	Cu µgm ⁻² d ⁻¹	Co mgm ⁻² d ⁻¹	Ni mgm ⁻² d ⁻¹	Cr mgm ⁻² d ⁻¹
Black sea	9.4 to 56.4	60 to 250	7.17 to 57.6	230 to 2440	1.64 to 7.49	11 to 13	420 to 3180	0.19 to 0.99	0.11 to 1.38	0.52 to 5.88
Baltic sea	0.55 to 1.66	10 to 50	0.01 to 0.02	10 to 50	0.08 to 0.25	0.4 to 3	10 to 60	0.01 to 0.03	0.01 to 0.06	0.02 to 0.11
Baltic sea	1.1 to 7.2	50 to 330	4 to 10	10 to 3000	0.5 to 5	1 to 23	10 to 2000	0.03 to 0.15	0.03 to 0.23	0.06 to 0.7
Võra Estuary	5 to 120	190 to 5000	4.1 to 11.16	–	1.52 to 67.9	–	160 to 8520	0.16 to 11.4	0.3 to 9.96	0.2 to 5.76
Ria de Vigo	14.1 to 27.2	570 to 1100	3.9 to 8.07	4100 to 4220	2.31 to 3.21	1.66 to 3.2	2790 to 3140	0.14 to 0.25	1.23 to 1.46	2.2 to 2.57

present in wastewater, the channel may be an additional source of an excessive amount of it in the study area. The proximity of the 10 m station to the Mejerda outlet, however, ensures that this station is constantly subject to the influence of the Mejerda River, regardless of the prevailing hydrodynamic configuration in the delta and may therefore be unaffected by the contributions from the channel. Though the 10 m station receives more SPM than the 20 and 40 m stations (regardless of season) a small proportion of particles trapped at the latter stations does come from the Khlij Channel. In addition, other sources may also help to explain the appearance of lead further offshore, such as atmospheric inputs or commercial fishing, quite important in the area. Trapped offshore, this SPM definitely concentrates more lead than SPM from the Mejerda River or from Ghar El Melh Lagoon.

Lead is generally found to be essentially bound to organic matter and clay (Helali et al., 2013). Its distribution among the five Mejerda SPM fractions resembles more closely the distribution recorded at the 10 m station than that observed at the 20 and 40 m stations. The association of lead to carbonates and oxyhydroxides is limited to suspended matter since the sediment, once the sedimentation process is complete, will release its accumulated quantity. When transported by wind, the lead thus provided is dissolved in the sea where it forms soluble carbonates which, once settled, will also release their lead which is then taken up by oxyhydroxides or clays. Lead fluxes off the delta are similar to those observed in the open sea (Table. 7); in the Black Sea, it has been observed from 230 to 2440 mg m⁻² day⁻¹ (Ergül et al., 2008), but from only 10–50 mg m⁻² day⁻¹ in the Baltic Sea (Leivuori and Valliusb, 1998). In estuaries, however, lead flux may be more significant; Santos-Echeandia et al. (2011) measured a flux of more than 4000 mg m⁻² day⁻¹ in the Ria de Vigo (Table. 7).

5.5. Zinc

Chemical speciation shows that zinc is bound to all five fractions of SPM, with the residual fraction (25–50%) as the preferred association, depending on stations and seasons. Next come oxyhydroxides, attaining 20–30% in the rainy season and up to 60% in the dry season (Fig. 3). This association of Zn with clays and oxyhydroxides in the sediment has previously been reported by other authors (Tessier et al., 1986; Fernex et al., 1986; Tessier et al., 1979), and is likewise found in the delta surface sediments (Helali et al., 2013). Zinc is also bound to the exchangeable phase and carbonates, making it one of the most bioavailable metals. At the 10 m station the Mejerda SPM concentrates more zinc-bound particles in the exchangeable and carbonate phases, especially during the rainy season (25–35%). SPM carbonates concentrate zinc in a manner unlike surface sediment (Helali et al., 2014), likely due, as is also the case for manganese, to the carbonate dissolution present in the sediment and the release of the associated zinc. Overall, the zinc fluxes measured off the delta (at all three stations and in both seasons) are comparable to or lower than those observed in other marine environments (Table. 7), for example, from 2310 to 3210 mg m⁻² day⁻¹ in the Ria de Vigo (Santos-Echeandia et al.,

2011), depending on the season. In the Baltic Sea, zinc flux is highly variable from 80 to 5000 mg m⁻² day⁻¹ (Leivuori and Valliusb, 1998; Broman et al., 1994) and it is much higher in the Vora Estuary, where fluxes are over 67900 mg m⁻² day⁻¹ (Nordmyr et al., 2008) (Table. 7).

5.6. Copper

Copper input from the Mejerda River is apparently very low during the rainy season, with the copper detected in the seabed sediment traps originating in re-suspended sediment during brief episodes of agitation. The coastal-offshore and vertical variations of copper fluxes are not clear. It therefore appears that various copper inputs during the dry season are associated with an additional supply of organic matter from the Mejerda. Chemical speciation shows that copper observed during the rainy season is bound only to the residual fraction, while copper noted during the dry season is shared by the five fractions of the sediment. This distribution in both the river and marine stations shows very little change, since it is the residual fraction and organic matter that absorb the larger quantities of copper: 20–50% and 10–35%, respectively (Fig. 4). However, a slight increase in copper was noted, associated with the organic matter offshore at the top of the water column and a decrease at the bottom, contrary to the copper bound to the exchangeable fraction. This reflects the change in the support for this metal during the sedimentation process. Compared with other studies, the copper fluxes in the delta are among the lowest or show values similar to those recorded in the Baltic Sea, from 10 to 2000 mg m⁻² day⁻¹ (Broman et al., 1994), whereas in river estuaries the flux is higher than in our study: 160–8520 mg m⁻² day⁻¹ in the Ria de Vigo (Nordmyr et al., 2008) and 2790–3140 mg m⁻² day⁻¹ in the Vora Estuary (Santos-Echeandia et al., 2011) (Table. 7).

5.7. Cadmium

Unlike in surface sediment, cadmium in SPM is bound to the organic matter as well as to the residual fraction. Cadmium is mainly bound to the organic matter in Mejerda SPM (65%) at the 10 m station, while further offshore it is mainly bound to the residual fraction (from 55% to 65%) at both the 20 m (more than 90%) and 40 m stations (Fig. 4). Cadmium flux bound to organic matter decreases in favour of the residual fraction. The Mejerda River may be the main source of Cd in organic matter; mineralization of the organic matter in the water column is probably responsible for the release of cadmium bound to this fraction. The latter is likely released once the organic matter is deposited on the seabed where it is incorporated into the clay. A source of cadmium-rich SPM other than the Mejerda appears to be present; in fact, the SPM taken from the 20 and 40 m stations shows a greater concentration of cadmium than the SPM at the 10 m station or when directly recovered from the Mejerda waters. As cadmium is chiefly present in wastewater, the Khlij Channel is likely to be its main source. Moreover, the location of the 20 and 40 m stations opposite the Khlij Channel

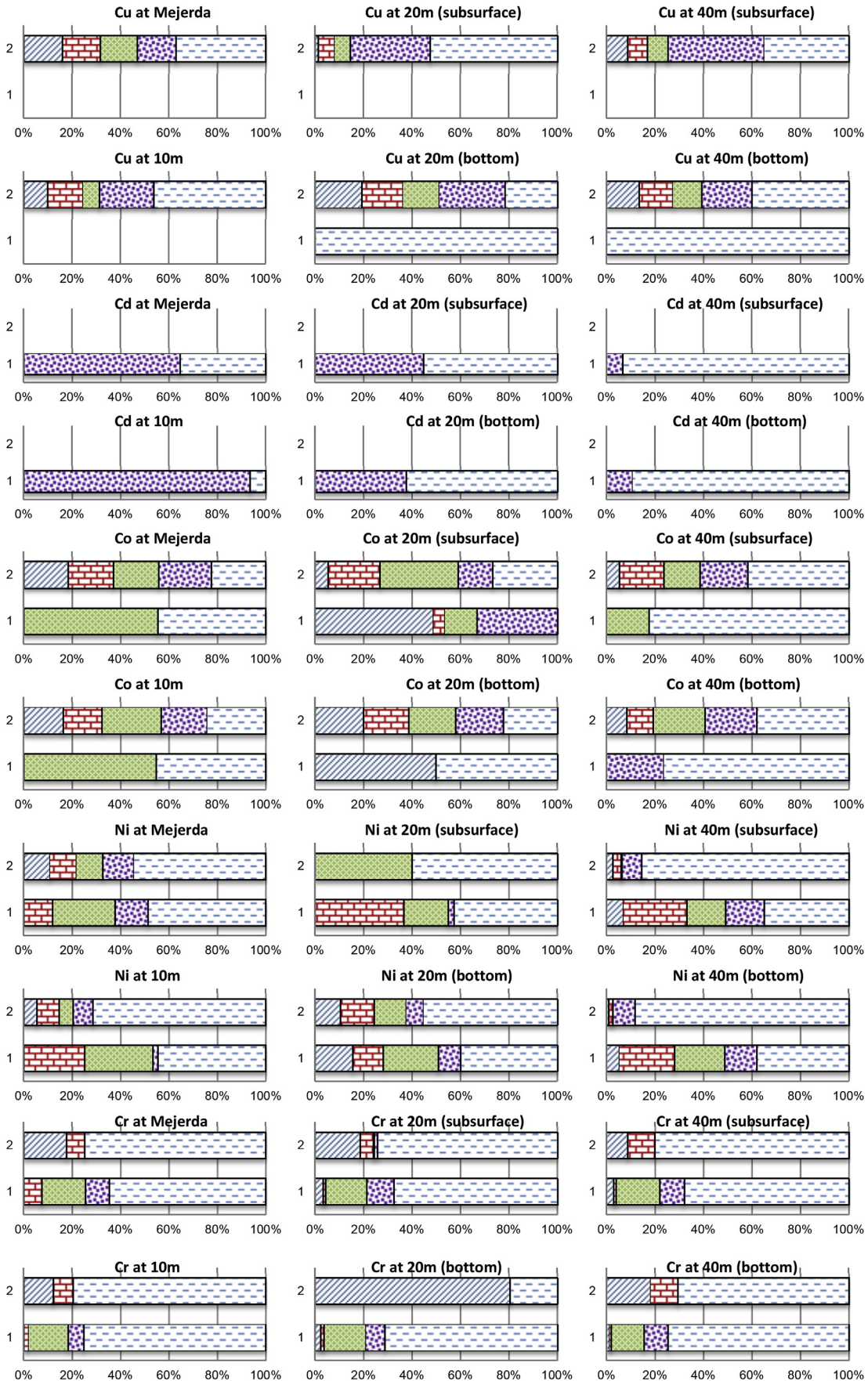


Fig. 4. Chemical speciation of Cu, Cd, Co, Ni and Cr in SPM (1: rainy and 2: dry season) Exchangeable Carbonates Oxyhydroxydes Organic matter Residual

outlet, strengthens this hypothesis, as the 10 m station, much closer to the Mejerda River mouth, is constantly subjected only to the input from the latter, and therefore may not be affected by the channel. In the Mejerda Delta, cadmium flux appears to be higher compared with that of the other studies (Table 7). In the Baltic Sea, cadmium flux reaches a maximum of $23 \text{ mg m}^{-2} \text{ day}^{-1}$ (Broman et al., 1994) though this is much lower (up to $0.4\text{--}3 \text{ mg m}^{-2} \text{ day}^{-1}$) according to Leivuori and Valliusb (1998). In the Ria de Vigo, the Cd flux is significantly lower than that recorded in this study, at $1.66\text{--}3.2 \text{ mg m}^{-2} \text{ day}^{-1}$, depending on the season (Santos-Echeandia et al., 2011), while in the Black Sea, the flux varies very little between the seasons and is only $11\text{--}13 \text{ mg m}^{-2} \text{ day}^{-1}$ according to Ergül et al. (2008) (Table 7). The absence of Cu during the rainy season and Cd in the dry season remains unexplained. However, it could be that these metals are delivered to the marine environment bound to organic matter of different origins, namely from the Mejerda River in winter and Khlij Channel in the dry season. Indeed, the contributions of the latter are subject to a dominant easterly wind in the dry season, while those from the Mejerda River are subject to the influence of the dominant north wind during the rainy season.

5.8. Cobalt

Chemical speciation shows that cobalt is transported by the Mejerda River and is equally associated to all five fractions (Fig. 4), whereas further offshore it is essentially bound to the residual fraction (30% and more than 40% at the 20 m and 40 m stations, respectively). This trend is valid only during the rainy season; in fact, during the dry season cobalt is largely bound to the residual fraction (50% and 80%, respectively, at the 20 and 40 m stations) and to oxyhydroxides at the Mejerda River outlet and the 10 m station (55%). Moreover, an increase in cobalt fluxes is observed during summer at the 40 m station in all five sediment fractions, while the decrease in flux near the bottom affects only the sediment's bioavailable fraction (exchangeable and carbonates). The association of cobalt with the residual fraction has already been identified in sediment cores taken in the Gulf of Tunis. Essoni (1998) recorded an association with cobalt oxyhydroxides at 35%, while at the surface cobalt oxyhydroxides are also linked at nearly 30% (Helali et al., 2013). The absence of cobalt bound to organic matter in the dry season suggests that this metal is of a natural and not anthropogenic origin, at least in summer. In fact, the anthropogenic cobalt is principally bound to the organic matter (Added, 1981; Essoni, 1998) but bound to the residual fraction if it is natural in origin (Tessier et al., 1979; Added, 1981; Essoni, 1998). In winter, cobalt is also bound to the organic matter (30% at the Mejerda outlet and at the 40 m station, as in Fig. 4). There is, therefore, a significant anthropogenic contribution of cobalt in the Gulf of Tunis, probably due to input from the Khlij Channel, as well as from the Mejerda.

5.9. Nickel

Chemical speciation shows that nickel is largely associated with the residual fraction (45–90% depending on the season) as well as the other sediment fractions, the oxyhydroxides in particular (20% at the 40 m station and slightly more at the 20 m station) (Fig. 4). The association of nickel to oxyhydroxides increases from the coastal areas seaward and is also reported in the deep sediments of the Gulf of Tunis (Essoni, 1998). Explained by the reduction of the dissolved oxygen in the offshore waters and a decrease in detritic fluxes, this finding has been shown by this study that it is not systematically checked since a fairly pronounced seasonal variation of the nickel flux bound to oxyhydroxides is observed. Moreover, the maximum flux of Ni bound to oxyhydroxides is observed at the

20 m station, whereas at the 40 m station, it is essentially bound to the residual fraction. It was also observed that more nickel is bound to oxyhydroxides at the bottom of the water column than at the surface. Therefore, a change in the chemical speciation of nickel between SPM and the sediment surface of the delta is noted. The Ni fluxes measured in this study are similar to those recorded in the estuaries of the Ria de Vigo (Spain) and Vora River estuary (Finland) Rivers where the fluxes are, respectively, $510\text{--}2920 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ (Santos-Echeandia et al., 2011) and $300\text{--}9960 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ (Nordmyr et al., 2008). In open seas Ni flux can be very low: $10\text{--}230 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ in the Baltic (Leivuori and Valliusb, 1998; Broman et al., 1994) and $110\text{--}1380 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ in the Black Sea (Ergül et al., 2008) (Table 7).

5.10. Chromium

Chemical speciation of chromium shows that this element is mainly bound to clays (as much as 60–80%) and oxyhydroxides during the rainy season (15–25%) and bound to clays and exchangeable fractions during the dry season (Fig. 4). Cr fluxes vary greatly from one place to another; they can be extremely low in the Baltic ($60\text{--}700$ and $20\text{--}110 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$) and relatively high ($520\text{--}2880 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$) in the Black Sea (Ergül et al., 2008). In estuaries, the chromium flux is extremely variable, as in the case of this study; for example, the Cr flux in the Ria de Vigo ranges from 880 to $6400 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ (Santos-Echeandia et al., 2011) and from 200 to $5760 \text{ } \mu\text{g m}^{-2} \text{ day}^{-1}$ in the Vora Estuary (Nordmyr et al., 2008), while the Cr flux off the Mejerda River Delta ranges from low to medium.

6. Conclusion

Chemical speciation of SPM shows that clays constitute the main carrier fraction for all metals. However, in the case of Pb and Zn, the exchangeable fraction and carbonates are also major carrier fractions, suggesting that a variable percentage of these metals is relatively toxic since it is bioavailable. Chemical speciation for other metals may show a substantially different result from that of surface sediment, as in the case of Fe and Cd which are bound to fractions in SPM, such as organic matter, to which they are not bound in sediment. Copper is also similar to SPM as it is bound to the exchangeable and carbonate fractions, whereas this is not the case in sediment. Insofar as metal availability is related to the carrier fraction, SPM may be capable of constituting a specific toxicity rather than the superficial sediment. Indeed, the chemical changes associated with early diagenesis occurring in the sediment (pH variations, change in redox conditions, the decrease in dissolved oxygen (Helali et al., 2015, 2016) are responsible for the release of a part of the metal associated with the suspended particles once they settle to the sea floor and become sediment. The degradation of organic matter and release of associated metals, as in the case of iron and cadmium, probably begins in the water column before sedimentation.

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