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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 g m^{-2} day^{-1}), but dissipated further offshore, 24.5–6 g m^{-2} day^{-1} at the 20 m and 21.8–4.8 g m^{-2} 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).

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 m^3s^{-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 km^2, 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 Sebkhet 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 $HClO_4$, 10 ml HF and 20 ml HNO_3 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 $MgCl_2$ (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 $NH_2OH.HCl$ (0.04 M) in 25% (HOAc) heated for 6 h at 95 °C with occasional agitation;
(4) bound to organic matter: 3 mL of HNO_3 plus 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3; samples were heated to 85 °C for 2 h with occasional agitation; a second 3 ml aliquot of (30% H_2O_2) 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 NH_4OAc added; samples were agitated continuously for 30 min;
(5) 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. 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 m^2); 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 $C_{Me} = C_{SPM}$ x [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.