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

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ABSTRACT

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

1. Introduction

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

The Mejerda River in northern Tunisia, with an extensive mining activity located in its watershed, appears to be a good subject for study using a multiproxy approach in order to establish the pollution status of its delta. It must be pointed out, however, that other sources of metal contamination (Ghar El Melh Lagoon, the Khlij Channel and Sebkhet Ariana) (Helali et al., 2013; Boussen, 2010; Sebai, 2007; Essoni 1998) are also present in the area. Two tasks were undertaken in this study: 1) assessment of metal accumulation via different approaches (geoaccumulation indexes, the enrichment factor) in three marine sediment cores taken from the zone offshore from the Mejerda River mouth and 2) estimation of the importance of the reactive metals that may be available and which may potentially threaten marine biotas, also using two approaches (AVS/SEM ratio and chemical speciation).

2. Material and methods

2.1. Study site

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

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

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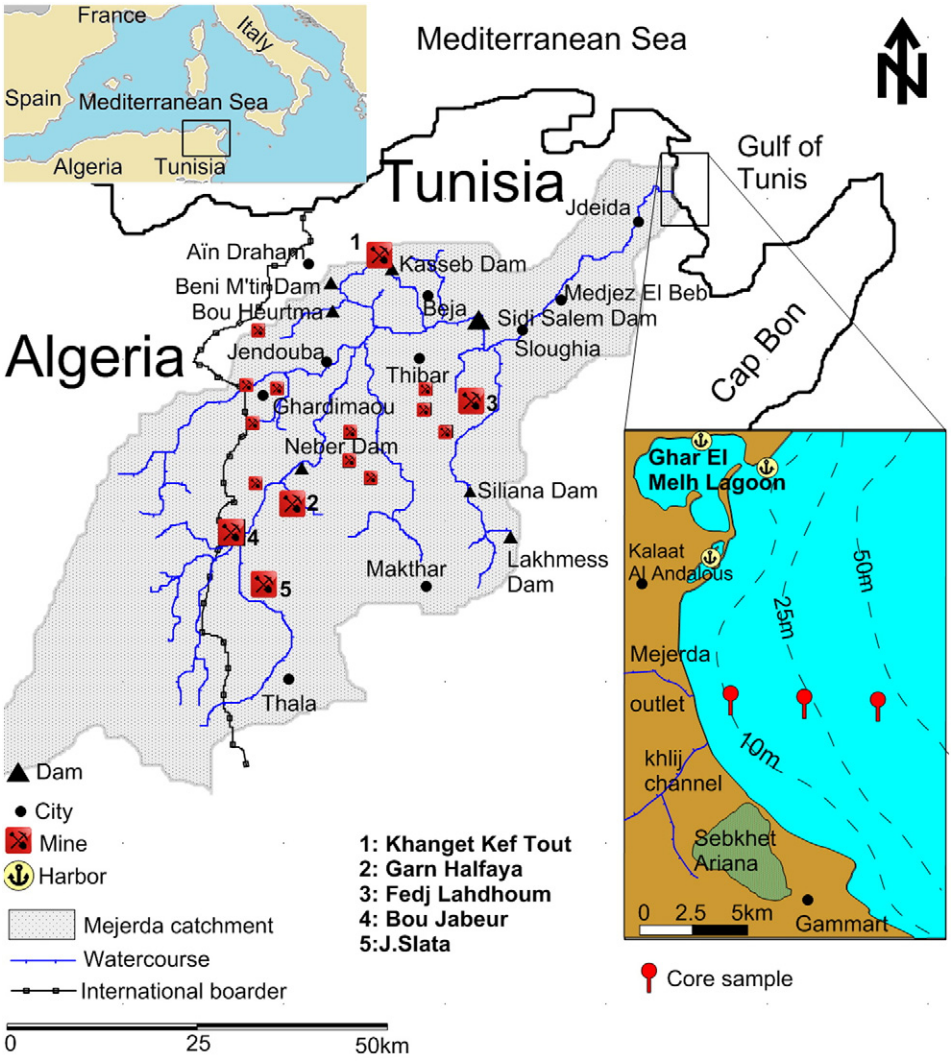

Fig. 1. Mejerda catchment and study site.

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

2.2. Sampling and sample processing

A recent geochemical study shows that pollution by heavy metals in surface sediment in the Gulf of Tunis varies from coastal areas to offshore zones, (Helali et al., 2013) with small or absent variations from north to south facing the Mejerda outlet. The present study was therefore conducted at three points (stations) forming a radial perpendicular to the coast opposite the mouth (Fig. 1) at depths of 10, 20 and 40 m (Table 1).

Core samples were taken by divers using polyvinyl chloride pipes (ϕ: 50 mm and length: 50–90 cm). The cores were sliced under an inert atmosphere (N_2) into 1- to 2-cm sections from the top 20 cm, and into 5 cm sections for the rest of the core. Each section was placed in a polypropylene beaker previously washed with bi-distilled water (Milli-Q) and sealed under an inert atmosphere. Handling and analysis of samples were performed in a clean laboratory using plastic LabWare containers (LabWare, Wilmington, Delaware, USA). By means of a 63-μm nylon mesh the sediments were sieved to collect the finer fraction and then oven-dried at 60 °C. Wet sediment was sub-sampled for acid volatile sulfide (AVS) analysis. The samples thus obtained were digested by adding a mixed solution of concentrated 20 mL $HClO_4$, 10 mL HF, and 20 mL HNO_3 to 1 g sediment in Teflon bombs. The resulting digestates were analyzed for Al, K, Fe, Mn, Pb, Zn, Cd, Cu, Co, Ni and Cr by flame atomic absorption spectrometry (Thermo Scientific ICE 3300 AA Spectrometer). The procedures used for heavy metal analysis were checked for accuracy using the BCR-032 certified reference material, obtaining good concurrence (<13%); the certified values and the relative standard deviations (RSDs) obtained from 10 replicates of one sample were typically <4.5% (Tables 2 and 3). The AVS concentrations in the sediments were analyzed using the cold-acid purge-and-trap technique described in detail by Added (2002). Ten grams of