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# Trace element accumulation and elutriate toxicity in surface sediment in northern Tunisia (Tunis Gulf, southern Mediterranean)

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ABSTRACT

Metal concentrations in sediments were investigated in the Gulf of Tunis, Tunisia, in relation to anthropic activities along the Mejerda River and Ghar El Melh Lagoon, with effluents discharged into the gulf. Distribution of grain size showed that the silty fraction is dominant with 53%, while sand and clay averages are 34 and 12% respectively. Zn concentration increased in the vicinity of the Mejerda River while Pb was at its highest levels at the outlet of Ghar El Mehl Lagoon. Sediment elutriate toxicity, as measured by oyster embryo bioassays, ranged from 10 to 45% abnormalities after 24 h, but no relation was found between metal concentration and sediment toxicity. The AVS fraction that represents monosulfide concentrations in the sediment was higher in the central part of the gulf than in the coastal zone. The results reveal the influence of AVS, TOC and grain size on metal speciation and sediment toxicity.



## 1. Introduction

The accumulation of trace elements in marine sediments is heavily influenced by continental discharges and effluents largely due to fluctuations in the composition of suspended matter (Helali et al., 2016a, 2016b; Picone et al., 2016; Martins et al., 2015; Zaaboub et al., 2015). Trace metals are not definitely fixed within the sediment and many processes affecting metal concentrations in estuarine and coastal marine sediments have been reported as metal recycling through biological, chemical and physical processes (James, 1978; Carignan and Nriagu, 1985; Helali et al., 2016c). Metal accumulation in sediment may also have toxic effects on marine biotas and flora which an increasing number of studies have attempted to describe via differing approaches (USEPA, 2002; Kennedy et al., 2009; Galgani et al., 2009; Zaaboub et al., 2015; Martins et al., 2015; Helali et al., 2016c, Gimbert et al., 2017). SEM/AVS is an approach usually used to evaluate the toxicity of sediment contaminated with heavy metals. SEM are simultaneously extracted metals liberated from sediment by an HCl attack. AVS are acid-volatile sulfides extracted at the same time. Based on the chemical interactions between SEM and AVS, the ratio of these two parameters is used to assess the potential of metal bioavailability and thus sediment toxicity. When SEM/AVS exceeds the value 1, the sediment is considered toxic because there is not enough AVS to scavenge bioavailable metals (SEM).

The coast of northern Tunisia is characterized by important industrial and urban centers with well-developed mining activities producing large quantities of effluent discharges in the region including heavy metals (Jdid et al., 1999; Mlayah et al., 2009; Oueslati et al., 2010a,b; Helali et al., 2013; Zaaboub et al., 2014; Ennouri et al., 2015; Helali et al., 2015) and nutrients (Helali et al., 2016a). Most of this effluent, including both sewage and industrial discharge, flows into the 253-km long Mejerda River which in turn flows into the Gulf of Tunis. In recent decades, extraction of Pb, Zn and Ba from mines located in the Mejerda River catchment area have led to large amounts of discharges (Ayari et al., 2016) posing a serious threat to public health (Abidi et al., 2014) and the marine environment. Organic pollution sources have also been evaluated, with concentrations of polycyclic aromatic hydrocarbons in the gulf sediments found within the 0.01 to 2.6 μg $g^{-1}$ range (Mzoughi et al., 2010).

Geochemical studies have therefore been conducted in the Gulf of Tunis, especially in the prodelta of the Mejerda River (Essonni, 1998; Helali et al., 2013; Zaaboub et al., 2014) to investigate by means of simultaneously extracted metals (SEM)/acid volatile sulfide (AVS) the possible toxicity of metals in the marine waters and sediments. The results suggest that there is enough AVS to scavenge metals, thus avoiding

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their toxicity (Helali et al., 2016c). However, works of Helali et al. (2016b,c), using other geochemical approaches such as chemical fractionation of metals in sediments and suspended matter, showed that some elements and especially Pb and Zn are sufficiently bound to the exchangeable fraction making them relatively bioavailable and therefore potentially toxic. To circumvent this paradox, we (1) used the embryo-toxicity bioassay to evaluate sediment toxicity, and (2) examine possible relationships between the observed toxicity and chemical properties of sediments.

## 2. Material and methods

### 2.1. Study site

The Gulf of Tunis (Fig. 1) is located on the northeastern coast of Tunisia (36°42′–37°10′ N, 10°15′–11°5′ E) and receives sediments and waters essentially from the Mejerda River, the Khlij Channel, and Ghar El Melh Lagoon (Dhib et al., 2013). The Mejerda catchment contains a large number of lead and zinc mines. Ghar El Melh Lagoon, which is the former mouth of the Mejerda, is surrounded by an industrial zone and is connected to the sea via a channel. The Mejerda River Delta is subject to two directions of prevailing winds that differ according to season: from north to northwest during the winter and east to southeast during the summer (Ben Charrada, 1997). The sea surface currents depend on wind direction and are mostly from north to south.

### 2.2. Sampling

Twenty-one surface sediments were sampled using a Van-Veen grab (0–5 cm) from operations aboard the oceanographic vessel "Hannibal" (Fig. 1). All samples were taken from the northern part of the gulf between 6 and 75 m depth. Sediments were immediately placed in polyethylene flasks and stored at −4 °C for immediate or short-term analysis, or conserved at −80 °C for later bioassays.

### 2.3. Grain size distribution

Sediment was sieved to collect the fine fraction (63 μm) using nylon mesh. Grain size (0.01–63 μm) was measured in all samples using a laser granulometer (Mastersizer, 2000). Grain size was determined using Stokes Law to characterize particle size distribution for all surface sediment samples. Sediment was placed on the top of a sieve column for a specific time or until it passed through the sieve at a constant low rate, separating different sediment fractions of clay, silt or sand. Duplicate measurements showed fine fraction percentages were reproducible with an analytical <5%.

### 2.4. Scanning microscope observations

Sediment surface was observed by means of a SEM Type JEOL JSM-5400 scanning microscope. Observations were made on total sediment.

### 2.5. Total organic carbon (TOC)

Measurements were carried out on total sediment subsamples (<63 μm) by means of a Perkin Elmer PE 2400 CHN. Samples were decarbonated using 1 M HCl solution and dried at 60 °C. Method analysis was detailed in Zaaboub et al. (2014). Duplicate analyses were generally <8%.

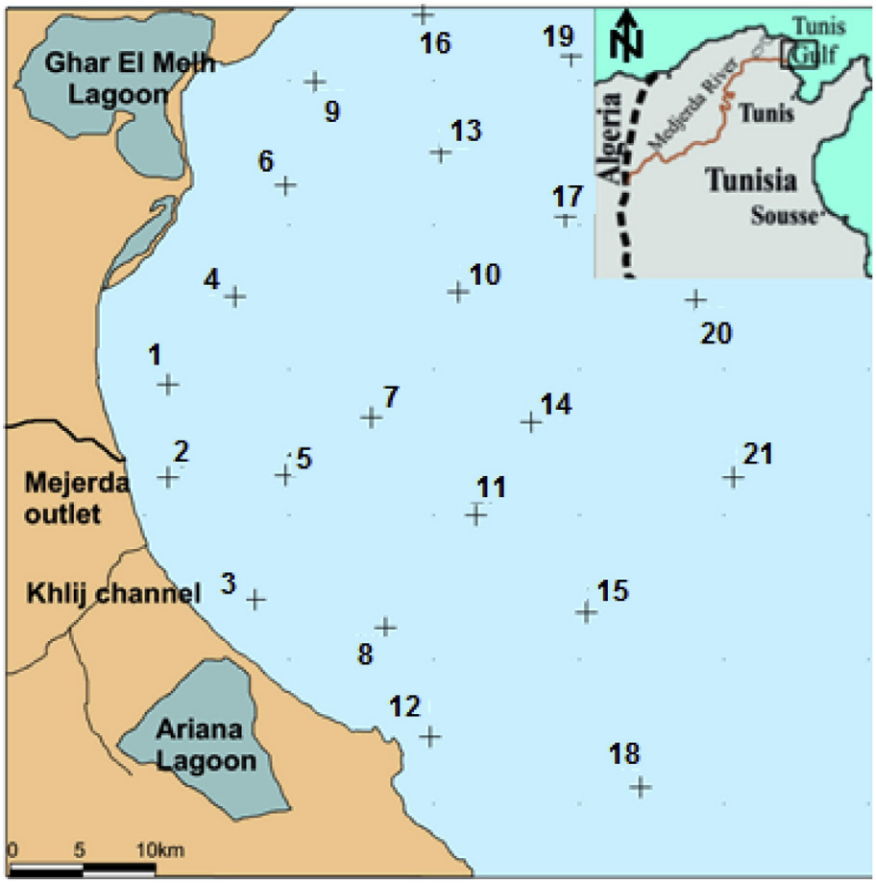


**Fig. 1.** Sampling sites of surface sediment in the Gulf of Tunis.