Baseline

Spatial distribution and contamination assessment of heavy metals in marine sediments of the southern coast of Sfax, Gabes Gulf, Tunisia

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ABSTRACT

In order to investigate the current distribution of metal concentrations in surface marine sediments of the southern coast of Sfax (Tunisia), thirty-nine samples were collected in the vicinity of a mixed industrial and domestic wastewater effluent discharge. In comparison with the threshold effect level and probable effect level, the majority of metals had high ecological and biological risks. Enrichment factor and geoaccumulation Index showed that the majority of sediments are unpolluted by As, Ni and Pb, moderately polluted by Cr and Cu and moderately to strongly polluted by P, Y, Zn. Besides, all sites are extremely polluted by Cd. Principal component analysis indicates that As, Cu and Ni were mainly from lithogenic sources, whereas Cd, Cr, F, P, Pb, Y and Zn were mainly derived from anthropogenic source. Findings of this research can be used as suitable reference for future studies and environmental management plans in the region.

Integrated management of coastal areas takes into account all environmental parameters that may affect its development. In this context, Tunisian coastal areas (southern Mediterranean Sea) are the focus of many studies including Sfax area (Gulf of Gabes GG) which is considered as the second principal pole of economic activities. Due to the numerous industrial activities, the southern coast of Sfax, became one of the most damaged Mediterranean coasts inducing significant degradations of the environment (ecosystem, quality of life, local population …).

Marine environment can be considered as one of the most fragile areas, and as a result, the extension of urban activities on the south-eastern Tunisian coasts increased marine pollution, especially in Sfax coasts. This city is one of the most industrialized cities. The main operating industries, such as the phosphate treatment factory (Tunisian Chemical Group (GCT)/SIAPE) and the lead secondary melting industries are collectively generating many liquid and solid wastes. Those are usually loaded with both mineral and organic pollutants that are released within the littoral zone without treatment (Bouzid et al., 1993; Azri et al., 2007; Azri et al., 2008).

Due to their toxicity, non-biodegradability and accumulative behaviors, heavy metals are considered as dangerous environmental pollutants that need to be monitored with care (Billah et al., 2017; Pekey, 2006; Yu et al., 2008). These elements play a role in many biological and geochemical cycles due to their presence in both solid

and dissolved form. Marine coastal sediments are usually dominated by terrigenous particles and shell debris; they are considered as a reservoir where an important range of pollutants such as heavy metals can be stored (Pekey, 2006; Santos et al., 2005; Sin et al., 2001).

Heavy metals have a rapid and efficient tendency to be associated with solid sediments when dropped in solution to the natural environment through different mechanism: adsorption or incorporation into a biogenic material or precipitation (Szefer et al., 1996). Heavy metals in sediments casue various deletrious effects to both benthic and aquatic biota as they can be released into the overlying water via biological and chemical processes (Ip et al., 2007). Their distribution and accumulation are influenced by many factors, including sediment texture, mineralogical composition and hydrodynamic conditions.

Most of recent studies aiming at the assessment of marine environment quality in GG revealed an enrichment of surface sediments with a wide range of pollutants especially in heavy metals, showing a potential degradation of sediments quality (Serbaji, 2000; Ayadi et al., 2014;Gargouri et al., 2011; Ghannem et al., 2011; Houda et al., 2011; El Zrelli et al., 2015; Rabaoui et al., 2017). It also resulted in the appearance of red tides (Hamza and EL Abed, 1994), the disappearance of some marine species (El Kateb et al., 2016), unbalance in different local benthic communities (Rabaoui et al., 2015) and malformations in different benthic foraminifera species (Ayadi et al., 2016). However, none of the studies in the southern coast of Sfax have reported the

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distributional patterns of heavy metals according to the granulometric and mineralogical characteristics of the surface marine sediments.

In this context, metals like As, Cd, Cr, Ni, Mn, Sr, V, Zn… are often used for marine contamination monitoring and assessment due to their dependence on anthropogenic activities (Caccia et al., 2003; Burton et al., 2004). The evaluation of their distribution in surface marine sediment is useful to assess the pollution status of the studied area. For this purpose, we investigated the current metals distribution and concentrations in coastal sediments of Sfax to evaluate its environmental status after > 65 years of industrialization and to update the relevant data for an effective environmental management in the region.

We analyzed many geochemical and some physical parameters, such as pH, heavy metals, fluoride and granulometry in both waters and coastal sediments. Then, the distribution maps of concentrations were established using a geographic information system (GIS) approach coupled with geostatistical and multivariate statistical techniques to identify covariations among them and to discuss their significance and potential source.

The studied area covers the southern coastal line of Sfax to the northern edge of the Gabes Gulf (south-east of Tunisia). It is characterized by a semi-arid Mediterranean climate influenced mainly by a mild and gentle topography. This coast experiences a semidiurnal and low tide with an amplitude approximately 1.4 m during spring tides and 0.3 m during neap tides. The wave currents precede towards the N-NW and those of ebb towards the S-SE (Amari, 1984).

Sfax region contains large flat plains characterized by soils rich in limestone, siliciclastic sediments, and gypsum (Watson, 1985; Mtimet, 1999). From a sedimentological viewpoint, surface sediments are dominated by slightly gravelly, sandy mud and poorly sorted, muddy sand. This coastline is subjected to an increasing pressure due to the development of several industrial activities that generate industrial and domestic wastewaters. These effluents are drained to the sea causing deleterious effects to waters, marine sediments and the whole natural ecosystem (Illou, 1999; Ghannem et al., 2011; Gargouri et al., 2011).

Our study area, is located downstream a mixed industrial and domestic wastewater effluent on the southern coast of Sfax (latitude 34°43′N and longitude 10°46′E) transported through a three kilometers long channel. Its outlet is connected directly to the sea (Fig. 1). This channel drains together an acidic industrial effluent originated from the phosphate treatment factory since 1952 and the wastewater generated by the Wastewater Treatment Plant (WWTP) of Sfax City since 1983. This effluent also contains phosphogypsum particles; it causes a severe contamination of marine waters and sediments by heavy metals (Illou, 1999; Gargouri et al., 2011), fluoride and phosphorus (Ayadi et al., 2014) and hydrocarbons (Fourati et al., 2017; Aloulou Ben Ayed, 2010; Serbaji, 2000). These pollutants pose a potential ecological risk to marine organisms and human health (Wong et al., 2000).

Thirty nine surface marine sediments were sampled, in March 2016, from the southern coast of Sfax receiving the mixed industrial and domestic effluents. Sampling was performed in spaced sites (from 150 to 250 m) through different radials covering an area approximately of 4.3 km². Location was recorded using a Global Positioning System (GPS) technology (Fig. 1). Eleven samples were collected from the upper shoreface where water depth does not exceed 0.3 m. For other stations, the depth of water varied from 0.5 to 2 m. At each sampling station, the upper 0–10 cm layer of surface sediment was collected using a Van Veen grab sampler. Immediately after their collection, samples were transported to the laboratory and stored in polyethylene bags at 4 °C for subsequent analysis.

Samples were oven dried at 60 °C for five days and lightly ground to reduce aggregates, then sieved to < 63 μm to be used later in the chemical analysis. Grain size plays a significant role in the determination of heavy metals concentrations in sediments. Fine-grained sediments tend to have relatively high metal contents (Horowitz, 1991; Tam and Wong, 2000; Morillo et al., 2004) because of their high specific surface (Horowitz and Elrick, 1987). pH was measured for both of marine waters (pH$_L$) and sediments (pH$_S$) using a pH meter (INOLAB WTW 720). The granulometric analysis was performed on the bulk sample

sieved below 1 mm using the laser analyzer (Malvern Masteriser 2000).

Chemical analysis was performed on the particle size fraction of < 63 μm. About 1 g of calcinated sediments was dissolved with Aqua Regia (3:1 HNO$_3$: HCl). The concentrations of Al, Ca, Fe, Mn, P, Zn and Y were measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Jobin Yvon 138 Ultrace). As, Cr, Cu, Cd, Ni and Pb concentrations were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7800). Data reported in this study are recalculated on a dry weight basis.

Fluoride concentrations were determined by dissolving 1 g of marine sediment samples in 3 ml of 6 M HCl and diluted to 100 ml with deionized water. Then, an aliquot of the extract was used for the determination of fluoride by selective electrode method (perfectION™) (Abu Hilal, 1985).

A subset of the collected fine-grained fractions (< 63 μm) was analyzed by X-rays Diffraction (XRD) to assess the mineralogy of the marine material, and to compare their content with the solids collected in the bedload of the wastewater channel.

In order to assess the impact of the anthropogenic activities through the abundance of trace metals, enrichment factor (EF) was calculated using the following equation (Ergin et al., 1991; Choi et al., 2008; Garcia et al., 2008):

$$EF = \frac{\left(C/_{Al}\right)S}{\left(C/_{Al}\right)B}$$

(1)

where $(C/Al)_S$ is the metal to reference ratio in the samples of interest and $(C/Al)_B$ is the same ratio for the used background reference (earth crust or unpolluted reference baseline). To minimize the influence of grain size and mineral composition on elemental concentrations and to identify possibly anomalous metal concentrations, heavy metal concentrations were generally normalized by conservative elements, such as Al, Fe and Sc (Aloupi and Angelidis, 2001; Amin et al., 2009). In this study, we selected Al as the commonly used normalizer element (Din, 1992; Zhang and Liu, 2002). The choice of background values plays an important role in the assessment of pollution status. The average shale value (Turekian and Wedepohl, 1961) or the average crustal abundance data (Taylor and Mc Lennan, 1995) can be used as background metal values. However, the use of these data for a specific area may give misleading results. The regional background values might be more appropriate (Gao et al., 1998; Xu et al., 2016). Moreover, in the case of partially digested samples, it seems more appropriate to use a sample processed with the same analytical protocol as a reference. In this study, a sample of marine sediment (S$_T$), 8 km apart from the study area, was employed as the reference for the background values (Table 2).

According to Zhang and Liu (2002), an EF value of < 1.5 suggests a geogenic origin of the studied metal (may be entirely from crustal materials or natural weathering processes). A high EF (> 1.5) means a significant input of trace metal derived from non-crustal materials. Instead, they are provided by an anthropogenic source. Sutherland (2000) used a five categories ranking system to assess the degree of contamination: EF < 2: deficient to minimal contamination; 2 < EF < 5: moderate contamination; 5 < EF < 20: significant contamination; 20 < EF < 40: very high contamination and EF > 40: extremely high contamination.

According to Müller (1979), the geoaccumulation index (Igeo) may contribute to the estimation of the degree of pollution by heavy metals. The Eq. (2) that describes Igeo is as follows:

$$Igeo = \log 2 \frac{C_x}{K \times B_x}$$

(2)

where C_x and B_x are concentrations of metal (x) in the sediment and in the background, respectively. To eliminate the effect of possible lithological variations in sediments that can affect background data, a correction factor (K = 1.5) was used accordingly. Based on Igeo values, sediments can be classified into seven levels as follows: < 0: unpolluted; 0–1: unpolluted to moderately polluted; 1–2: moderately polluted; 2–3: moderately to