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Baseline

Assessment of anthropogenic inputs in the surface waters of the southern coastal area of Sfax during spring (Tunisia, Southern Mediterranean Sea)

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ABSTRACT

The coastal marine area of Sfax (Tunisia), which is well-known for its high productivity and fisheries, is also subjected to anthropogenic inputs from diverse industrial, urban and agriculture activities. We investigated the spatial distribution of physical, chemical and biogeochemical parameters in the surface waters of the southern coastal area of Sfax. Pertinent tracers of anthropogenic inputs were identified. Twenty stations were sampled during March 2013 in the vicinity of the coastal areas reserved for waste discharge. Phosphogypsum wastes dumped close to the beaches were the main source of PO_4^{3-}, Cl^- and SO_4^{2-} in seawater. The high content in total polyphenolic compounds was due to the olive oil treatment waste water released from margins. These inorganic and organic inputs in the surface waters were associated with elevated COD. The BOD_5/COD (<0.5) and COD/BOD_5 (>3) ratios highlighted a chemical pollution with organic load of a low biodegradability.

The Gulf of Gabes, located in the Southeast of Tunisia, owns one of the largest continental shelves in the Eastern Mediterranean Basin. Despite its importance to the economy and for wildlife conservation, the Gulf of Gabes is now undergoing a high stress caused by urbanization, industry, over-fishing, tourism and leisure sites (Hamza-Chaffai et al., 1997; Smaoui-Damak et al., 2003, 2006). Sfax is the second largest city and the second economic pole in Tunisia. It is heavily industrialized with important fishing and harbor activities (Zaghden et al., 2005). The southern coastal area of Sfax has undergone an increased anthropogenic pressure for many years. Due to the phosphoric acid plant (SIAPE), huge amounts of phosphogypsum and associated organic and inorganic contaminants have been discharged in this region for 40 years, altering the marine environment and its biodiversity (Zaghden et al., 2005; Gargouri, 2006; Aloulou et al., 2012). In addition, this coastal area is impacted by a pronounced shipping activity with the commercial harbor and the new fishing harbor of Sfax, by a strong agricultural activity including salt marshes and the storage of olive oil wastes (margins) and by numerous urban wastes attributable to the ex-Thyna household waste landfill and the municipal wastewater treatment plants. Hence, in the Southern part of Sfax, a great variety of sources can release diverse contaminants in marine waters such as phosphates, fluorides, sulfates, naturally occurring radionuclides, trace metals and other trace elements, organic matter, hydrocarbons, polyphenolic and flavonoid compounds (Illou, 1999; Serbaji, 2000; Serbaji et al., 2012; Louati et al., 2001; Louati, 2003; Zaghden et al., 2005, 2014; Gargouri, 2006; Tayibi et al., 2009; Mezghani-Chaari et al., 2011).

These contaminants may enter the southern coastal area of Sfax through the Sidi Salem, Hakmouni and El Maou wadis (Illou, 1999; Serbaji, 2000; Louati, 2003) but also runoffs and atmospheric depositions. These inputs of anthropogenic material may impact marine ecosystems. For instance, it has been shown that large amounts of allochthonous phosphorus and organic matter affected the structure and functioning of the plankton communities, namely phytoplankton, ciliates and crustacean zooplankton (Rekik et al., 2012), and led to blooms of toxic dinoflagellate *Alexandrium minutum*, coastal eutrophication and public health problems (Abdenadher et al., 2012). Also, Ben Brahim et al. (2010) found that the spatial variability of the macro-epiphyte assemblages of *Posidonia oceanica* leaves was influenced by anthropogenic inputs. In this coastal area, several works have highlighted some bioindicators of pollution such as benthic foraminifera assemblages (Aloulou et al., 2012), benthic fish species (Barhoumi et al., 2009) and bivalves (Hamza-Chaffai et al., 2003). Although many studies have reported concentrations of anthropogenic compounds in surface sediments (Louati et al., 2001; Zaghden et al., 2005, 2014; Ghannem et al., 2010; Gargouri et al., 2011) and living organisms (Hamza-Chaffai

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et al., 1999; Barhoumi et al., 2009, 2012), little is known, to our knowledge, about the distribution of anthropogenic tracers in the surface waters of the coastal area of Sfax. Therefore, in this context, the objectives of the present study are 1) to assess the spatial distribution (coast-open sea and North–South gradients) of physical, chemical and biogeochemical parameters, including temperature, salinity, pH, major ions, nutrients, turbidity, suspended particulate matter, polyphenolic and flavonoid compounds, 2) to determine the level of biodegradability of these compounds through the estimation of chemical oxygen demand (COD) and biological oxygen demand (BOD_5) and 3) to identify relevant tracers of anthropogenic inputs in the Sfax coastal area.

The study area is the coastline of Sfax city (34°44′N, 10°46′E), located in the Southeast of Tunisia in the Northern part of the Gulf of Gabes (Southern Mediterranean Sea) (Fig. 1). Twenty stations were sampled at high tide during a spring cruise conducted on the 19th of March 2013 along the Southern coast of Sfax on board the vessel "Taparura". Depth of the stations ranged from 0.3 to 3.5 m. Seawater samples were taken at ~0.1-m depth using PVC Van Dorn bottles (1.5 l volume) deployed horizontally. All the samples were transferred into Teflon bottles which were rinsed three times with the respective sample before filling and stored in the dark in the cold (4 °C). Before the cruise, bottles were washed with 10% nitric acid and then thoroughly rinsed with double distilled water and Milli-Q water.

Temperature, salinity, conductivity, pH and turbidity were immediately measured on board upon sample collection. Temperature, salinity and pH were obtained using a portable multi-kit meter (WTW Multi 340i/SET), while turbidity was measured with a HACH RATIO 2100A turbidity-meter and the conductivity with a Tacussel model 123 conductometer.

Concerning major anions, sulfate (SO_4^{2-}) and chloride (Cl^-) concentrations were determined by gravimetric (JIS K 0102. 41. 2.) and argentometric (Mohr) methods, respectively. Bicarbonate (HCO_3^-) concentration was determined by titration with 0.01 or 0.1 M HCl against methyl orange and bromocresol green indicators according to the French Association for Normalization (NFT 90-036). Fluoride (F^-) concentration was estimated by using an ion-selective electrode according to Soto-Rojas et al. (2004). Briefly, 20 ml of water samples was added to 20 ml of Total Ionic Strength Adjustment Buffer (TISAB)-EDTA solution. The mixture was directly placed under the electrode with continual stirring and the F^- content was obtained by the comparison of the millivolt reading of the sample to a standard curve. Major cations, i.e. calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), manganese (Mn^{2+}) and iron ($Fe^{2+} + Fe^{3+}$), were measured by atomic absorption spectrometry (AAS) by using a Zeenit 700 instrument (Analytik Jena AG).

Nutrients, i.e. nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), silicate ($Si(OH)_4$), total nitrogen (T-N) and total phosphate (T-P), were analyzed with a BRAN and LUEBBE type 3 autoanalyzer and their concentrations were determined colorimetrically using a UV–visible 6400/6405 spectrophotometer (APHA, 1992). Concentrations in suspended particulate matter (SPM) were determined by measuring the dry weight of the residue after filtration of 2 l of seawater onto pre-combusted (5 h, 450 °C), pre-weighted Whatman GF/F glass fiber filters (0.7 μm pore size filter and 47 mm-diameter) according to Neukermans et al. (2012). After filtration, filters were rinsed with Milli-Q water to remove salt and stored at −20 °C until further analysis, within one week. After drying for 48 h at 60 °C, filters were reweighed on the same balance. SPM concentration was calculated as the difference between filter weight before and after sample filtration, normalized to the filtration volume (Neukermans et al., 2012). The total polyphenolic content was determined spectrometrically using the Folin–Ciocalteu method, as suggested by Singleton et al. (1999) and slightly modified according to Dewanto et al. (2002). Total polyphenolic concentrations were estimated at the wavelength of 415 nm using Quercetin as reference. The total flavonoid content was determined using the method of Djeridane et al. (2006), slightly modified according to Akrout et al. (2011). Total flavonoid concentrations were estimated at the wavelength of 725 nm using Gallic acid as reference. COD was estimated according to Rodier's (1996) method using a VARIO photometer type HACH/HDR/2000, whereas BOD_5 was assessed according to the French standard AFNOR (2001).

We used the Arc-Geographic Information Systems (GIS) version 9 software to make contour plots. Pearson linear correlation analyses were conducted using the XLStat software (version 2014). One-way analysis of variance (ANOVA) was performed to detect significant differences between Northern (1–10) and Southern (11–20) stations in terms of physical, chemical and biogeochemical parameters. Moreover,

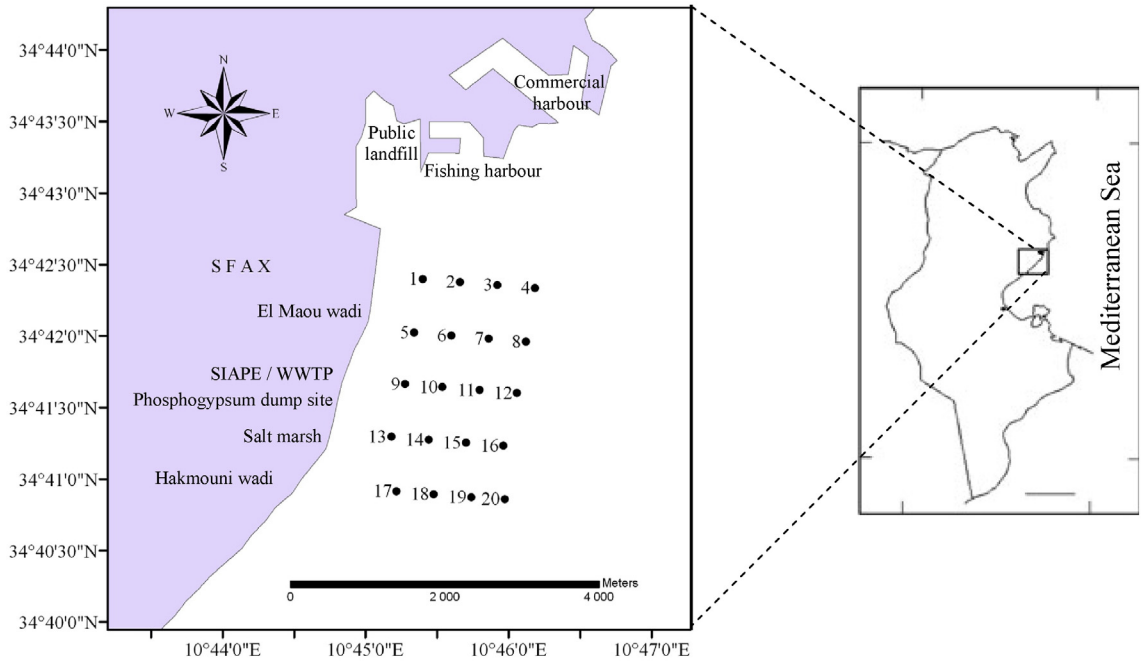

Fig. 1. Location of the study stations in the southern coastal area of Sfax (Tunisia, Southern Mediterranean Sea), sampled during spring (March 2013): Northern (1–10) and Southern (11–20) stations, SIAPE/WWTP: WasteWater Treatment Plant (in front of station 9), Fishing harbor (near stations 1 and 2), Salt marsh (station 13).

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