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Assessment of physicochemical water and sediment quality of Sfax-Kerkennah plateau, Tunisia

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ABSTRACT

This study has been undertaken to evaluate the physicochemical water quality of the Sfax-Kerkennah plateau. Thirteen surface seawater and sediment samples were collected. Different tests, including turbidity, suspended matter (MES), dissolved organic carbon (DOC), and nutritive salts (i.e. total phosphorus "P_{tot}" and nitrate "NO_3") were used. Trace metals (Zn, Ni, Cu, Cd, and Fe) were also analyzed by using Inductively Coupled Plasma-Atomic Emission Spectrometry. The results indicated high values of turbidity, suspended matter, DOC, and nutritive salts in seawater samples near the coastal line of Sfax City. Those high values seemed to be related to the huge volumes of domestic wastewater discharged in the ecosystem. Trace metals analyzed in surface seawater and sediment samples showed also significant concentrations at the same sites (close to Sfax coast). The study of the metal spatial distributions in sediment samples refined by complementary approaches including enrichment factors and geoaccumulation index highlighted significant impact of multiple anthropogenic sources, generated by many industrial activities located on the coast of Sfax.

Keywords: Coastal zone; Seawater; Sediment; Physicochemical parameters; Trace metals

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1. Introduction

The quality of aquatic environment is governed by both natural processes (such as precipitation rate, weathering processes, and soil erosion) and anthropogenic effects (such as urban, industrial and agricultural activities, and the human exploitation of water resources) [1–4]. High urbanization and industrialization rates in coastal cities are the main sources of anthropogenic generated pollutants, (i.e. mineral and organic micropollutants), that are usually released in

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the littoral zones. Trace metals are one of the severe pollutants introduced into aquatic system, due to their toxicity, persistence, and bioaccumulation problems [5,6]. Unlike organic contaminants, trace metals are non-biodegradable; they are distributed among water-soluble species, colloids, suspended matter, and sedimentary phases. Most of the trace metals are present in seawater in trace concentrations, whereas excessive concentration can affect marine biota and pose risk to consumers of sea food [7,8]. Pollution of the natural environment by trace metals is a worldwide problem [9–12] resulting in deterioration of the water and sediment quality [13].

The aim of this study is to recognize the affect of telluric pollution sources on the seawater and sediment quality parameters through determination of physicochemical parameters through 13 sampling stations of Sfax-Kerkennah plateau.

2. Materials and methods

2.1. Sample collection

Surface seawater and sediment samples were collected in various locations (13 sites) in the Sfax-Kerkennah plateau, south-eastern Tunisia (Fig. 1).

Seawater samples were collected in plastic bottles as folowings: (1) 1 L plastic bottles were cleaned with bidistilled water first, and then rinsed with methanol, acetone, and hexan, for physicochemical parameter measurements and (2) 1L plastic bottle was washed with deionized water, immersed in 3% nitric acid solution overnight, and then rinsed with bidistilled water, for trace metal analysis. Water samples were first filtered through 0.45 μm Millipore filter paper and then acidified to pH <2 using concentrated nitric acid. The obtained water samples were stored at 4°C until processing and analysis.

Sediment samples were collected with an Ekman bucket. The top 5 cm of the sediment was removed with an acid-washed spatula to prevent contamination. Immediately after collection, samples were placed in polyethylene bags, refrigerated, and transported to the laboratory [14].

2.2. Analytical methods

Turbidity test was performed by using HACH 2100AN turbidimeter, the detection limit was 0.5 NTU. MES was determined in filtered water samples (1 μm) by gravimetry. dissolved organic carbon DOC concentrations were obtained by a model 700 TOC analyzer (Detection limit: 0.4 mg/l).

NO_3 and P_{tot} were analyzed using HACH DR2800 spectrophotometer. The detection limits were 0.1 and 0.02 mg/l, respectively. All the analyses were based on standard methods as appropriate to seawater quality parameter [15].

Sediment samples were dried at 60°C and sieved to collect the desired fraction of <63 μm, to which metals are most often associated [16]. Dried samples (<63 μm sized grains) were digested with HNO_3–H_2O_2–HCl according to US EPA method 3050B [17], filtered, and made up to volume with Milli-Q water (Millipore corp., Ireland). Then, trace metals (Zn, Ni, Cu, Cd, and Fe) in digested sediments and acidified

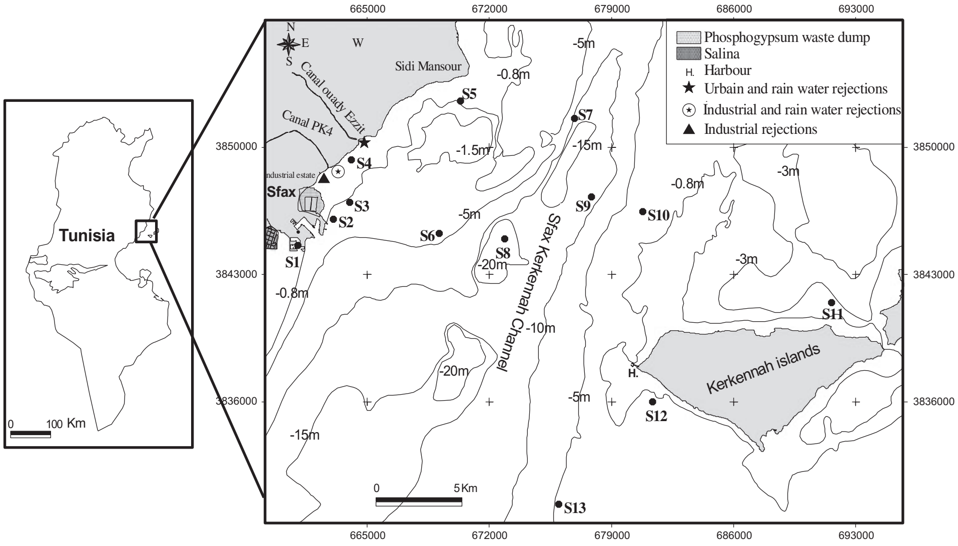

Fig. 1. Location map of study area and sampling sites.

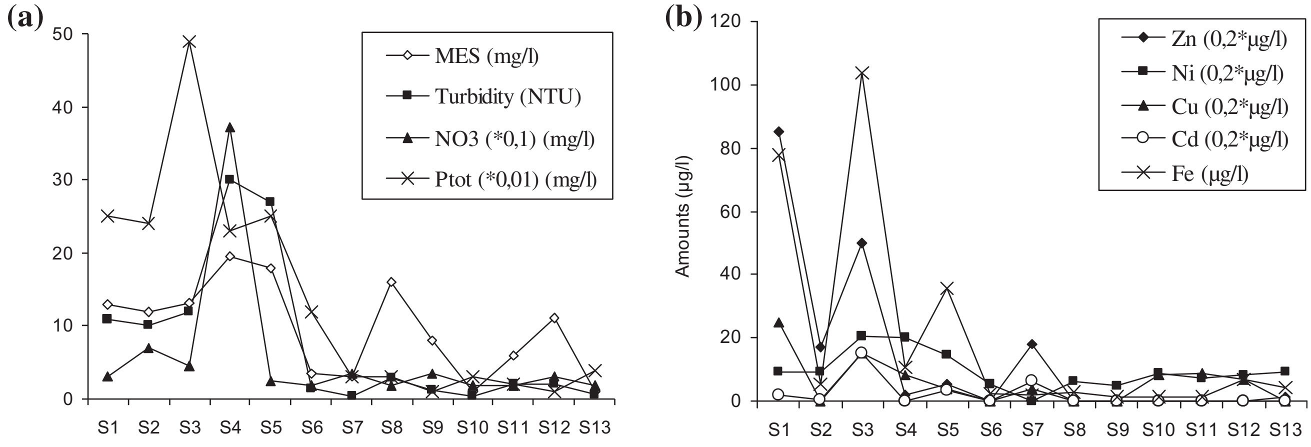

Fig. 2. Variation of the physicochemical parameters (a) and heavy metals (b) in water samples.

water samples were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry [18] in triplicate. The instrument is equipped with a cross-flow nebulizer and double pass spray chamber under RF power of 1,150 W. The method detection limits (µg/l) were 0.03 for Zn, 0.018 for Ni, 0.01 for Cu, 0.007 for Cd, and 0.13 for Fe. The accuracy and precision of the analytical methodology were assessed by triplicate analyses of standard reference materials. Precision was generally <10%.

Analyses of blank and standard samples were also performed to control physicochemical parameters in seawater samples during the experimental work.

3. Results and discussion

The assessment of turbidity, MES, DOC, P_{tot}, NO_3, and selected metal concentrations (Zn, Ni, Cu, Cd, and Fe) in surface seawater and sediments of Sfax-Kerkennah plateau is needed to evaluate the impact of various anthropogenic pollutants on the receiving ecosystem.

3.1. Physical and chemical characteristics of surface water

The variation of turbidity, MES, DOC, P_{tot}, and NO_3 of different water samples are shown in Fig. 2(a). High values of turbidity and MES were found near Sfax City coastal line (S1–S5). This turbidity is generated by the suspended particles from phosphogypsum waste dump. For DOC, P_{tot}, and NO_3, the highest levels were recorded also at the coast of Sfax.

The metal concentrations in water samples ($\mu g\ l^{-1}$) varied from 0.3 to 17 for Zn, 1–4.1 for Ni, 0.8–5 for Cu, 0.11–3 for Cd, and 1.4–104 for Fe. The maximum levels were recorded at S1–S5 study sites near Sfax coast (Fig. 2(b)) where the accumulation of trace metals is explained by the proximity to pollution sources. Anthropogenic activities and urban effluents are known to be significant sources of the metals, resulting in the deterioration of water quality.

3.2. Trace metal contamination of the sediment

Averages, standard deviations, and ranges of tarce metal concentrations in studied superficial sediments are summarized in Table 1. The metal concentrations (mg kg^{-1} dry weight) varied from 13 to 181 for Zn, 4.40–19.24 for Ni, 3.25–22 for Cu, 0.11–22 for Cd, and 9024.78–14,353 for Fe. Table 1 showed that averages and maxima of the selected metals exceed by far natural concentrations, indicating a metallic pollution of sediments with the exception of Fe, where concentration values were in agreement with natural levels.

Table 1
Averages, standard deviations, and ranges of heavy metals in sediment samples (mg/kg)

	Average	SD	Range	Background levels [19]
Zn	62.72	37.09	34.98–181.00	61
Ni	9.26	5.43	4.40–19.24	7
Cu	11.26	5.32	3.25–22.00	10
Cd	2.87	5.84	0.11–22.00	4
Fe	9829.57	405.24	9024.78–10353.00	10,000

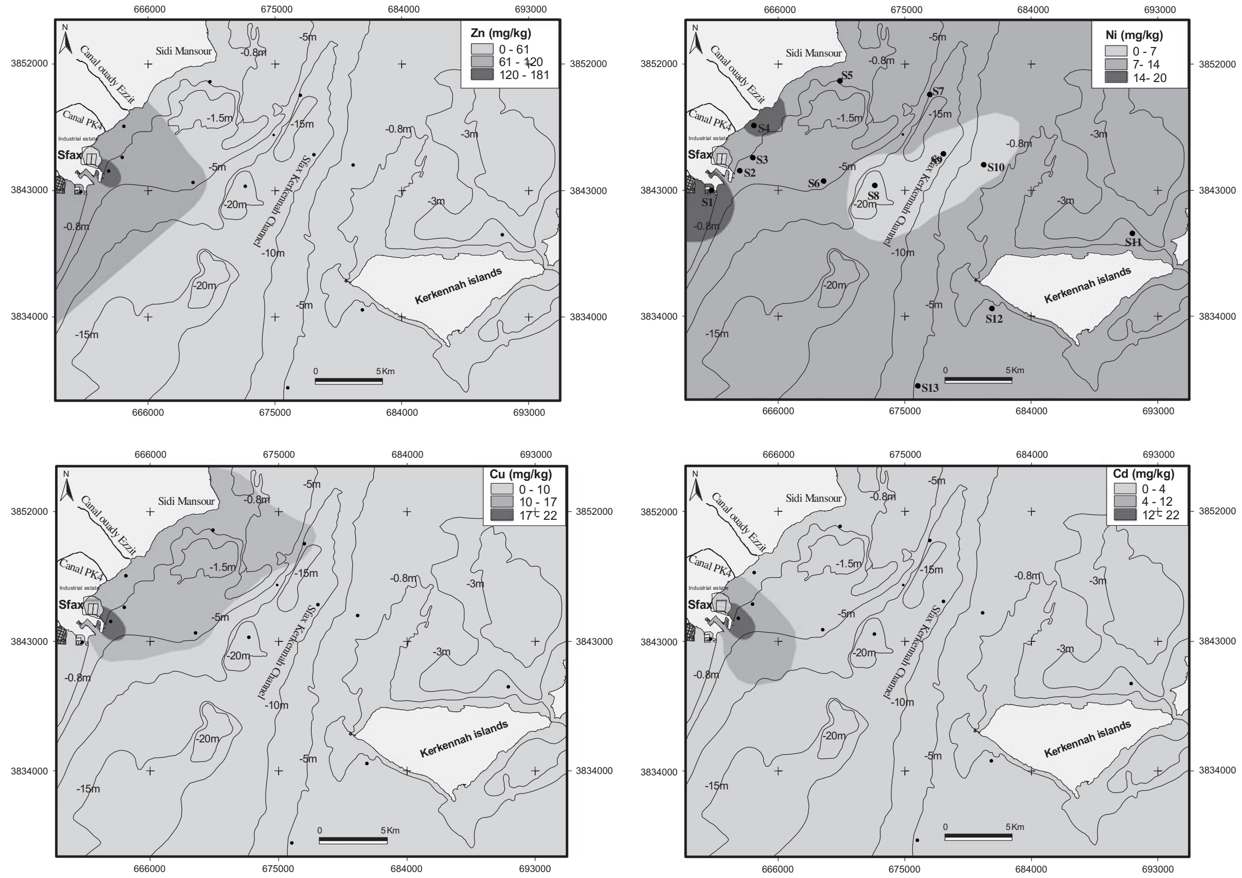

Fig. 3. Distribution maps of Zn, Cu, Cd, and Ni concentrations in surface marine sediments.

The horizontal distribution patterns of the studied metals, mapped through the interpolation of elemental data by using Arc View GIS 3.2, showed different spatial distributions (Fig. 3). Maximum value of Zn, Cu, and Cd was recorded near the phosphogypsum deposit, a by-product of old phosphates processing plants. Those metals were also found in the coastline downstream because of the principal anthropogenic effluents of Ouady Ezzit and phosphate processing site (PK4). For Ni, the highest concentrations were located around the mouth of canal Ouady Ezzit. Those high metal concentrations were recorded in zones with muddy facies and high organic matter content (TOC varying between 5 and 8% in superficial sediments) [19].

The spatial distributions of the above described metals, which were shown to be very different from those of Fe (Fig. 4), suggested a localized impact of the potential anthropogenic sources.

By comparing the accumulation of trace metals in water and sediments, it can be concluded that trace metals were accumulated in sediments rather than water since the sediments are potential adsorbent for trace metals as well as for organic compounds [20,21].

In order to assess the impact of the anthropogenic activities related to the abundance of trace metals in the studied sediments, the computation of enrichment factor (EF) is required.

Commonly, geochemical normalization of the trace metals data to conservative elements, such as Al or Fe, is employed in order to identify anomalous metal concentration. Al concentration was not analyzed in the studied sediments. Instead, Fe can be used as a crustal reference [22,23].

According to [24], EF is defined by the following Eq. (1).

$$\mathrm{EF} = \frac{(C_x/C_{\mathrm{Fe}})_{\mathrm{sample}}}{(C_x/C_{\mathrm{Fe}})_{\mathrm{reference}}} \tag{1}$$

where $(C_x/C_{\mathrm{Fe}})_{\text{ sample}}$ is the ratio of concentration of the element being tested (C_x) to that of Fe (C_{Fe}) in sediment sample and $(C_x/C_{\mathrm{Fe}})_{\text{ reference}}$ is the same ratio in unpolluted baseline samples.

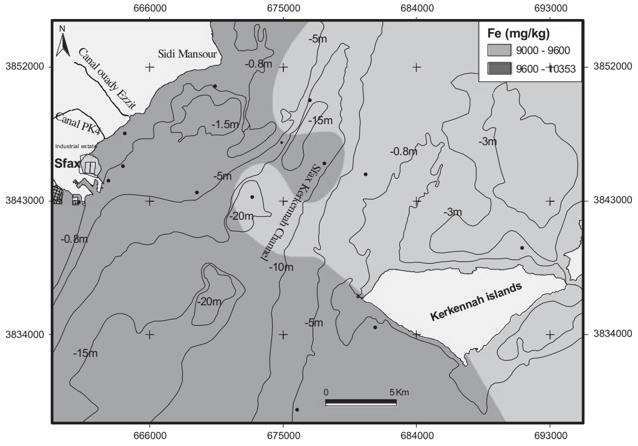

Fig. 4. Distribution map of Fe concentrations in surface marine sediments.

Table 2
Metal EFs in sediment samples

	Average	SD	Range
Zn	1.04	0.59	0.58–2.94
Ni	1.37	0.67	0.62–2.72
Cu	1.14	0.50	0.37–2.18
Cd	0.72	1.44	0.03–5.45

If an EF value is less than 1.5, it suggests that the trace metals may be entirely from crustal materials [25]. However, if it is greater than 1.5 (EF >1.5), it suggests that a significant portion of trace metal is delivered from non-crustal materials.

The computed EFs in the sediments (Table 2) with respect to metal background levels [19] showed that only the maxima of all metals are higher than 1.5, indicating a localized contamination by anthropogenic sources.

Another criterion based on the geoaccumulation index (I_{geo}) was adopted, in order to determine the degree of metal contamination in the studied sediment samples. It was originally defined by [26]. It is based on the comparison of current concentrations with pre-industrial levels and can be calculated by the following Eq. (2):

$$I_{\text{geo}} = \text{Log}_2\left(\frac{C_n}{1.5B_n}\right) \tag{2}$$

where C_n is the measured concentration of the examined metal (n) in the sediment and B_n is the background concentration of the metal (n). The background matrix correction factor is 1.5 due to lithogenic effects.

Table 3
Geoaccumulation index (I_{geo}) Muller's classification and ranges of heavy metals in surface sediments of Sfax-Kerkennah plateau

I_{geo} value	Class	Quality of sediment	Metal	I_{geo} range	Quality of sediment
≤0	0	Unpolluted	Zn	−1.39 to 0.98	From unpolluted to moderately polluted
0–1	1	From unpolluted to moderately polluted	Ni	−1.25 to 0.87	From unpolluted to moderately polluted
1–2	2	Moderately polluted	Cu	−2.10 to 0.55	From unpolluted to moderately polluted
2–3	3	From moderately to strongly polluted	Cd	−5.77 to 1.87	From unpolluted to moderately polluted
3–4	4	Strongly polluted	Fe	−0.73 to −0.53	Unpolluted
4–5	5	From strongly to extremely polluted			
>5	6	Extremely polluted			

According to Müller scale, the calculation of geoaccumulation index related to studied samples showed different values (Table 3).

For all studied metals (except for Fe), the maximum of I_{geo} showed positive values testifying localized zones of sediment which are moderately polluted by these metals.

4. Conclusion

This study has been undertaken to assess the effects of possible anthropogenic sources of pollution on the Sfax-Kerkennah plateau. The obtained results showed that MES, DOC, P_{tot}, and NO_3 in the water samples were higher near the coast of Sfax City. The same observation can be adopted for the analyzed trace metals.

As for sediment samples, metals' concentrations showed a clear increase when compared with those of surface seawater. Those high concentrations (except for Fe) exceeded largely the natural values, indicating an anthropogenic contamination sources. This was further confirmed by the computed metal Efs. The spatial distribution of metal concentrations showed different patterns with localized higher concentrations close to the coastline of Sfax city. They were attributed to the effect of urban activity in Sfax City that is usually characterized by numerous industrial activities, municipal discharges, and illegal discharges. Based on the geoaccumulation index approach, it was found that many localized sites of the Sfax-kerkennah plateau suffer from moderate pollution by various trace metals (e.g. Zn, Ni, Cu, and Cd).

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