Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1149107

57 (2016) 24765–24777
November

The Tunisian Mediterranean coastline: potential threats from urban discharges Sfax-Tunisian Mediterranean coasts

Hatem Zaghden[a,b,*], Mohamed Moncef Serbaji[c], Alain Saliot[a], Sami Sayadi[b]

[a]*Laboratoire d'Océanographie et du Climat, Expérimentation et Approches Numériques LOCEAN, UMR CNRS 7159, CNRS/IRD/UPMC/MNHN, Université Pierre et Marie Curie, Case courrier 100, 4 Place Jussieu, 75252, Paris, Cedex 05, France, Tel./Fax: +216 74 874 452; emails: hatem.zaghden@gmail.com (H. Zaghden), alain.saliot@upmc.fr (A. Saliot)*
[b]*Laboratoire des Bioprocédés, Pôle d'Excellence Régional AUF (PER-LBP), Centre de Biotechnologie de Sfax, BP, 1177, 3018 Sfax, Tunisia, email: sami.sayadi@cbs.rnrt.tn (S. Sayadi)*
[c]*Study and management of coastal and urban environments, National School of Engineers of Sfax, University of Sfax, Soukra, Sfax 3038, Tunisia, email: moncef.serbaji@fss.rnu.tn*

Received 26 June 2015; Accepted 27 January 2016

ABSTRACT

There have been growing concerns over the alarming threats to marine and terrestrial ecosystems from the improper discharge of effluents into water bodies worldwide, including Tunisia. Despite the large flow of data on the environmental pollution of various sites, little data is currently available on the physicochemical, geochemical conditions of the seawater of the Gulf of Gabes (South East Tunisia). Accordingly, the present study was undertaken to investigate and evaluate the physicochemical, biochemical and geochemical properties and attributes of the water and sediment samples from the coastal dumping sites of the Boudriere PK4, Ouady Ezzit, Ouady Maou, Sidi Salem, Sidi Mansour, Thyna and Sfax harbour. The results revealed that the marine environment in the title sites was alarming, suffering from heavily loaded pollutants from various sources that are predominantly discharged without preliminary or inadequate treatment. The total suspended matter (TSM) values recorded in the waters along the coastal sites were higher than the standard norms. In fact, more than 4350 mg/l of TSM were recorded at the coast, and the biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) values exceeded the standard limits, reaching 300 mg/L and 1050 mg/L, respectively. The total oxidizable matter, representing BOD_5 and COD, also exceeded 1360 mg/L. Low dissolved oxygen (DO) concentrations fluctuating between 0 and 2.95 mg/L were observed, except for some oueds. This reflected high levels of DO depletion and a tendency towards anoxic conditions. High hydrocarbon loads were also observed. Heavy metal pollution was equally alarming. Overall, the results indicated that the serious organic and mineral contamination of the Tunisian Mediterranean coastline calls for urgent action from state authorities and the public to remediate polluted sites and better control non-complying effluent discharge activities.

Keywords: Tunisian Mediterranean coastline; Pollution; Organic charge; Hydrocarbons; Heavy metals

*Corresponding author.

1. Introduction

There have been growing concerns during the last decades over the alarming threats posed by the discharge of chemicals from various urban and industrial sources into surrounding water bodies worldwide. The Mediterranean Sea represents about 1% of the global ocean surface, and its coasts are home to several unique species of fauna and flora [1]. The Mediterranean coastline, which correspond to a semi-enclosed basin where waters are renewed slowly (15 years for deep waters), is vulnerable to high environmental pollution pressures from various urbanization and industrialisation processes [2]. Of particular interest, the Tunisian Mediterranean coastline is exposed to various loads of pollution due to the intense anthropogenic development and huge industrial activity based in this area. With a total length of about 1,300 km, the Tunisian coastline is the home of almost 64% of the total population and supports most of the industrial activities of the country [3]. The effluents discharged in several sea ports and rivers around the Mediterranean Sea have been reported to represent significant pollution sources [4]. The latter have varied annual weather events and irregular monthly and yearly precipitation patterns.

The growing concerns over the impacts of the deteriorating seawater quality in Tunisian coasts have attracted increasing attention in recent research. The Tunisian coastline is subjected to large amounts of pollution loads from various sources. The water pollution in Tunisia is issued from industrial units concentrated mainly in and around big cities [5]. Two types of industries can be distinguished. The first type includes industrial facilities whose discharges are primarily organic, such as sugar refineries and oil extraction facilities. The second type encompasses industrial units, whose discharges contain toxic elements, such as tanneries and textile factories. The effluents discharged from those industrial activities contain ordinary organic substances, organic synthesis, petroleum, minerals, heavy metals, polychlorinated biphenyls, chlorides, sulphates, cyanides and arsenic salts. Furthermore, some agricultural activities represent another significant source of pollution, releasing various forms of pollution, such as nitrates, phosphates, pesticides and organic matter, directly into the surrounding waterways [6]. Urban and municipal effluents can also comprise wastewater from domestic and commercial activities. The latter contribute essentially by organic forms of pollution (organic matter, detergents, solvents, antibiotics, micro-organisms, etc.). In addition to these types of pollutants from continental origins, the marine environment is subjected to other pollution loads from marine traffic and harbour activities.

The pollutants derived from anthropogenic, agricultural, domestic or marine activities pose serious contamination threats to aquatic environments and ecosystems [7]. They involve pollution manifested by a microbial contaminations, hydrocarbon and heavy metal accumulation and/or eutrophication, which causes anoxia or the appearance of harmful algal blooms.

Several studies have been performed to investigate and evaluate the environmental pollution in the gulf of Tunis (North), gulf of Hammamet (East) and gulf of Gabes (North). Most of the currently available studies have, however, been limited to one region as a representative site of the entire area. In fact, the Gulf of Gabes covers several cities (including Mehdia, Gabes, Sfax, Zarsis and Jerba) and involves about 18 ports. Most of the previous studies have also used various marine species or water and sediment samples as indicators of pollution, with little focus on the potential links that might hold between the physicochemical and geochemical parameters of the sites under investigation. Accordingly, the present study aimed to investigate, characterize and evaluate the physicochemical and geochemical parameters of the urban discharges in different sites within the Gulf of Gabes (coastline of Sfax).

2. Materials and methods

2.1. Sampling sites and procedures

The coastal sites under investigation were submitted to a weekly sampling programme followed during April, May, June and July 2002, 2003, 2004, 2005, 2006 and 2008. Water and sediment samples were taken from different points along of the various canals, out of rainfall periods to avoid the eventual dilution of sewage.

Sampling points of water and sediment collection were selected according to their closeness to industrial and urban discharge points (Fig. 1). Water samples were collected manually using glass bottles previously cleaned according to Rodier process and placed in iceboxes at of 4°C to reduce the risks of precipitation, adsorption, contamination or evaporation [8]. Sediment samples were collected from accumulation zones using a PVC tube of 75 mm of diameter.

2.2. Analytical parameters

Temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured *in situ*. Total

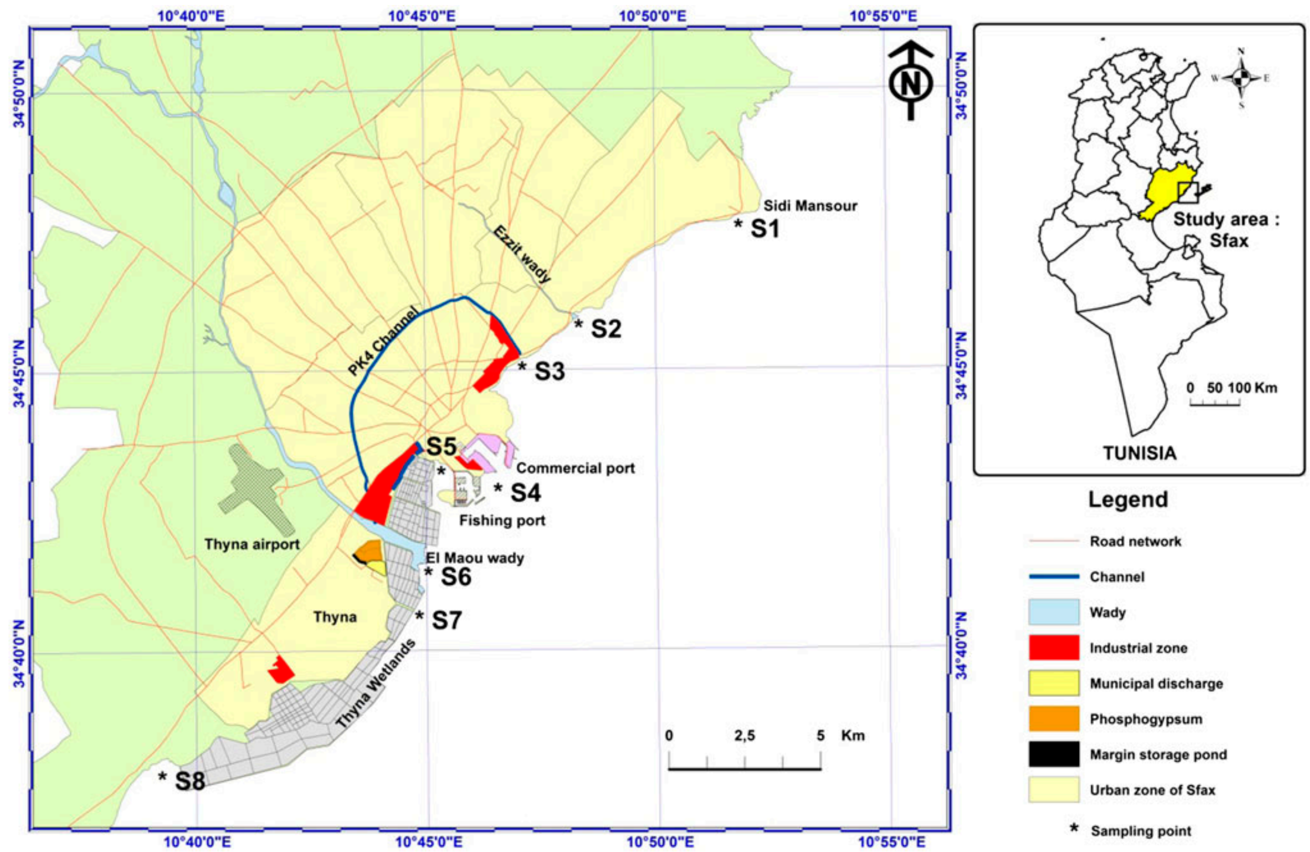

Fig. 1. Map of the coast of Sfax showing sampling locations.

suspended matter (TSM) was determined by the filtration and subsequent analysis of a known water volume. The measurement of biochemical oxygen demand (BOD_5) was performed by a respirometric apparatus (respirometric system of SIERP) that quantified the oxygen produced to re-establish initial pressure. Chemical oxygen demand (COD) was determined by oxidization with potassium dichromate in acidic media and in the presence of silver sulphate and mercury [8]. Total organic carbon (TOC) was measured by a LECO CR-412 Carbon Analyzer.

To determine heavy metals, samples were oven-dried at 60˚C for 4 d, lightly ground in an agate mortar for homogenization, sieved to pass <63 μm (metals are most often associated with small grains) [4]. The dry samples were digested with HNO3–H2O2–HCl according to US EPA method 3050B (US EPA, 1999) and the digestate made up to volume with Milli-Q deionized (DI) water (18 MΩ). Afterwards, the digests were analysed for the amount of Zn, Cu, Cr, Cd, Pb and Fe by inductively coupled plasma-atomic emission spectrometry (ICP-AES) in triplicate (US EPA, 1996). The instrument was equipped with a cross flow nebulizer and a glass spray chamber. The detection limits (mg/L) were 0.007 for Zn, 0.004 for Cu, 0.006 for Cr, 0.007 for Cd, 0.035 for Pb and 0.013 for Fe. Analytical procedures were described in details [9]. Data reported in this study were calculated on dry weight basis.

Hydrocarbon compounds were extracted by a Soxhlet extractor for sediments (8 h). An amount of 5 g of samples, previously freeze-dried, blended and homogenized, were extracted using 250 ml of dichloromethane/methanol (70:30). In case of non-filtered water sample, a liquid/liquid extraction by chloroform from a volume of 10 l was employed. Two internal standards (C18 and 9, 10 dihydroanthracene) were added to the samples to determine the recoveries during the analytical procedure. The extracts were purified and separated into nonaromatic hydrocarbons (NAH) and polycyclic aromatic hydrocarbons (PAH) using chromatographic column on neutral alumina/silica for sediments and waters. The silica and alumina, previously cleaned with methanol and hexane for 8 h, were reactivated at 140˚C for 2 h and partially deactivated with 5% of water. The chromatography column was prepared with 0.4 g of silica (100–200 mm in mesh), and kept in suspension in hexane. Elution was performed using hexane (3 ml) and toluene/dichloromethane (9:1) for NAH and PAH, respectively. The NAH fraction was analysed by gas chromatography using an HP AGILENT 6,890 series chromatograph, equipped with a flame ionisation detector and a capillary column (30 m × 0.25 mm). The column temperature was programmed from 60°C to 290°C with a heating ratio of 3°C/min. The maximal temperature (290°C) was maintained for 15 min. Helium served as a vector gas at a flow rate of 2 ml/min, whereas nitrogen was used as a carrier gas. Standard reference materials certified by the International Atomic Energy Agency were used for comparisons. The fluorescence spectra of PAH were measured by a spectrofluorimeter (Perkin Elmer, type L. S30).

For the different hydrocarbons, the detection limits ranged from 0.1 to 0.5 ng g^{-1}. Instrumental reproducibility, evaluated from samples Ouady Ezzit and Sidi Mansour, was on average ±10%. All the concentration values, given in μg g^{-1} (AHs) sediment dry weight (sed. dw), were blank—and recovery-corrected.

3. Results

3.1. Physicochemical, biochemical and geochemical analyses

The physicochemical, biochemical and geochemical analyses performed on the water and sediment samples from the various sites and leachate samples from various discharge points revealed the presence of highly significant pollution load. In fact, most of the effluents discharged through the various river mouths into the coastal waters were released without preliminary or adequate treatments. The values recorded for the various parameters under investigation are presented in Tables 1 and 2.

The temperature values recorded for the liquid discharges ranged between 15 and 25°C, largely depending on climate and air temperature. The pH values were relatively normal, ranging from 7 to 8.5 because station selected were near effluents rejected. High EC values were detected, particularly for the effluents at the Boudriere PK4 site. The average EC rates ranged between 65,000 and 20,000 μs/cm. The EC values registered for the PK4 and Sidi salem canals were 55,000–62,000 μs/cm, respectively, whereas for the other sites EC values did not generally exceed 50 μs/cm.

For TSM, which refer to the solid matters retained by filtration or centrifugation and may be linked to terrestrial pollution, such as domestic and industrial wastes, the different effluents showed considerable load that varied between 50 and 3,535 mg/L and exceeded 1,000 mg/L in large agglomerations. At the PK4, Maou and Sidi Salem canals, the values recorded for TSM were 2,495, 2015 and 3,535 mg/L, respectively (Table 1).

The determination of biochemical parameters, particularly DO, COD and BOD_5 is necessary to determine the water quantity and quality of water bodies exposed to urban and industrial wastes. These parameters are interrelated in such a way that, for instance, total oxygen demand depletes DO, and that the COD and BOD_5 translate the rate of total oxidizable matter. The values of DO contents, which play a key role in the maintenance of aquatic life and regulation of self-purification processes, were often very low, fluctuating between 0 and 2.95 mg/L, except for the Sidi Salem canal, Sfax harbour and PK4 canal, where DO rates of 7.5,10 and 6.5 mg/L were recorded, respectively. Lower rates of oxygenated waters were detected for Sidi Mansour, Canal Ouady Ezzit and Thyna, with DO values of 2.25, 2 and 0.75 mg/L, respectively (Table 1).

The BOD_5 content, which corresponds to the quantity of oxygen consumed during the biological decomposition processes of organic (vegetable or animal) and inorganic (sulphide, salts, ferrous, etc.) matters in a water sample is a function of pollution degree. The average values measured at the different river mouths and harbours ranged from 10 to 300 mg/L. The most important values were recorded in Sidi Mansour, Sfax harbour and Canal Ouad Maou, with average values (mg/L) of 200, 190 and 300, respectively (Table 1).

The COD content, which represents the quantity of oxygen consumed during chemical decomposition processes of organic matters, showed average values of up to 1,050 mg/L. The highest COD values were recorded in Sidi Mansour, Thyna, Sidi Salem canal and Sfax harbour, with 500, 725, 600 and 1,050 mg/L, respectively.

3.2. Geochemical analyses

The TOC, reflecting the accumulated and preserved organic matter rate, was determined in the samples of the superficial sediments along the canals under investigation. The TOC values are reported as percentage of the total dry weight of the fine fraction (lower than 63 μm). The TOC contents recorded at the Sidi Mansour, sfax harbour and Thyna canals ranged from 2.75 to 8% (Table 2).

High total hydrocarbon concentrations were recorded at the different sites under investigation, ranging between 8 and 65 mg/L. The highest hydrocarbon

Table 1
Biochemical and geochemical data of water samples from harbours and the most important effluent of the Sfax-Tunisian Mediterranean coasts, TSM: total suspended matters, DO: dissolved oxygen, BOD_5: biochemical demand in oxygen and COD: chemical demand in oxygen

Samples			Physicochemical parameters (water samples)		
		TSM (mg/l)	DO (mg/l)	BOD_5 (mg/l)	COD (mg/l)
Sidi Mansour	S1	2,495 ± 391.92	2.25	200 ± 44.9	500 ± 93.90
Canal ouady ezzit	S2	2,015 ± 563.38	2	115 ± 48.99	350 ± 69.40
Canal PK4	S3	1,350 ± 81.65	6.5	120 ± 65.32	395 ± 73.84
Sfax Harbour	S4	635 ± 110.23	10	190 ± 20.41	1,050 ± 134.72
Canal Sidi Salem	S5	500 ± 75	7.5	25 ± 10	550 ± 205
Canal Ouady Maou	S6	365 ± 28.58	5.9	300 ± 93.90	600 ± 285.77
Canal SIAPE ONAS	S7	4,350 ± 510	10.5	130 ± 35.42	595 ± 83.5
Thyna	S8	3,535 ± 432.74	0.75	42.5 ± 7.5	725 ± 61.24

Table 2
Geochemical data of water and sediment samples from harbours and the most important effluent of the Sfax-Tunisian Mediterranean coasts, TOC: total organic carbon, THC: total hydrocarbons and (Pb, Cu, Zn, Cd, Cr and Ni): Heavy metals (the underlined values are of Blinda (2007) and the values in bold type are of Bloundi (2005))

		Geochemical parameters (sediment samples)									
			THC (ppm)			Heavy metals (mg/l)					
Samples		TOC (%)	Eau	Sediment	%Extract of Hc in TOC	Pb	Cu	Zn	Cd	Cr	Ni
Sidi Mansour	S1	2.25	29 ± 1.6	528.1	23.5	1.2	9.2	26.9	0.800	20.9	17.4
Canal ouady ezzit	S2	4	38 ± 4.08	276.25	6.90	11	6.3	41.6	1.9	196.9	15.2
Canal PK4	S3	6.7	41 ± 3.27	418.5	54	125.2	8.1	270.1	6.8	21.3	19.24
Sfax Harbour	S4	8	65 ± 4.08	1,027	34.66	20.2	2.6	207.7	36	1.6	10.5
Canal Sidi salem	S5	7.8	35 ± 0	839	28.3	25.8	81.4	281.9	20.5	185.8	10.85
Canal Ouady Maou	S6	2.75	17 ± 3.27	209.5	8.95	16	10	61	4	15.5	7
Canal SIAPE ONAS	S7	6.8	35 ± 0	549	18.4	23.5	31.4	181.2	23.5	125.3	16.75
Thyna	S8	3.5	8 ± 0.4	234	7.9	1	9	10.9	0.7	2.9	1.4

concentrations were detected at the sfax Harbour, PK4, Ouady Ezzit and Sidi Salem, with 65, 41, 38 and 35 mg/L, respectively. At the other sites, hydrocarbon concentrations ranged from 8 to 29 mg/L. The total hydrocarbons recorded for the sediment samples collected from river mouths were also significant. The values ranged between 209.5 and 1,027 μg/g dry weight (dw). The results revealed that hydrocarbon concentrations (mg/g dw) of 528.1 were recorded at Sidi Mansour, 276.25 at canal Ouady Ezzit, 418.5 at Canal PK4, 209.5 at canal Ouady Maou, and 839 at canal Sidi Salem (Table 2).

Several chemical substances can cause the degradation of water quality, including heavy metals. The findings revealed that the water samples collected from the various river mouths and canals displayed various concentrations of toxic trace elements (Pb, Zn, Cu, Cr, Ni and Cd) with harmful effects on the environment (Table 2).

The findings indicated the presence of high Pb concentrations (mg/l) of 125.2, 25.8 and 20.2 at the PK4, Sidi Salem and Sfax Harbour canals, respectively. The Pb values recorded at the other sites values ranged between 1.1 and 16 mg/L. The Zn concentrations were generally low and fluctuated between 10 and 282 mg/l. The highest levels were detected at Canal Sidi Salem (281.9), Canal PK4 (270.1) and Sfax harbour (207.7). The copper content showed a maximum concentration of 81.4 mg/L at Canal Sidi Salem. The highest Cr concentrations were detected at canal Ouady Ezzit (196.9), Canal Sidi Salem (185.8), with the other sites showing Cr concentrations of less than 22 mg/L. Furthermore, the highest rates Ni content were recorded at Canal PK4, Sidi Mansour and canal Ouady Ezzit, with concentrations of 19.24, 17.4 and 15.2 mg/L, respectively. At the other sites, Ni concentrations did not exceed 11 mg/L. As for Cd content, the highest concentrations were recorded for the Sfax Harbour and Sidi Salem Canal, corresponding to 36, 20.5 mg/L, respectively (Table 2).

4. Discussion

The results obtained were analysed in terms of flow rate expressed by the gross load of effluent in (mg/L) and compared to the standard limits of the Tunisian project on certain substances discharged into the aquatic environment (surface water, etc.). The results showed the extent of pollution flows released at sea by the large cities on the Tunisian Mediterranean coast. The wastewaters discharged from the urban and industrial facilities into the river mouths and coastal waters of the Mediterranean basin without preliminary or inadequate treatment were characterized by significant organic and mineral loads. The comparison of physicochemical (BOD_5, COD, DO and TSM) and geochemical (heavy metals and hydrocarbons) variables of the sample water, sediment and leachate samples with standard reference values confirmed the bad water quality of the sites under investigation. The waters discharged into the coastal sites were noted to display high TSM loads. The TSM contents are of mineral or organic nature, together with several other chemical pollutants. These TSM create conditions favourable for pathogenic bacteria species that might affect the marine ecosystem. The Sfax harbour was, for instance, noted to display a high bacterial load of about 10^5/ml and high quantities of faecal coliforms that exceeded 10^3/100 ml.

The monitoring of the bacteriological quality of coastal waters of the Mediterranean basin allowed to conclude that some areas are subject to marked rates of contamination due to the accumulation of heavy metals in the soil and water bodies as a result of heavy rain, run off and leaching events, especially during spring period. Increasing turbidity and TSM may alter various physical and chemical properties of water, thus inhibiting photosynthesis and, consequently, the oxygenation and respiration in the medium.

The EC values recorded at the studied sites reflected the high mineralization degree of urban water compared to the established standard limits [10]. The salinity rate was also significantly important. A clear correlation was observed between the concentrations of major ions responsible for the salinity of sewage and electrical conductivity.

The nitrogen presence in wastewater can be organic or mineral. The organic nitrogen is mainly a constituent of proteins, polypeptides, amino-acids and urea. The mineral nitrogen which includes ammonium (NH_4^+), nitrites (NO_2^-) and nitrates (NO_3) constitutes the major part of total nitrogen. The nitrate concentrations recorded in the water samples showed a maximum of 6.95 mg/L, thus remaining lower than the standard values. The low nitrite concentration detected in the wastewater of the studied effluents could be explained by the fact that the nitrite ion (NO_2^-) is an intermediate compound, unstable in the presence of oxygen, whose concentration is usually much lower than that of the two forms that are linked, namely nitrate and ammonium ions [6].

The results also revealed high loads of organic pollution. The BOD_5 and COD values reached 300 mg/L and 1,050 mg/L, respectively, far exceeding the permitted limits (Fig. 2(b)). The total oxidizable matter, representing the total amount of BOD_5 and COD drain in the sea exceeded 1,360 mg/L. The limit values are 10 and 40 mg/L, respectively. Low total DO rates were also observed, fluctuating between 0 and 2.95 mg/L, except for some oueds. This reflected a tendency of different media to anoxia, which was further confirmed by the important organic matter accumulation rates. In fact, high TOC values were recorded, ranging between 5 and 8% of dry weight, which promotes redox conditions favourable for the accumulation and preservation of organic matter. This high organic matter content can be explained by the high load of municipal biodegradable matter discharges that can contain up to 55% of organic matter [11].

In the absence of free oxygen, reactions of organic matter degradation starts, initially by the intervention of anaerobic nitrate and sulphate-reducing bacteria. In the ultimate stage, degradation takes place by methanogenic bacteria that produce CH_4 from the CO_2 reduction or by attacking acetates or methanol, which explained the presence of unpleasant smells at the shores of the effluents.

The COD/BOD_5 ratios at the effluents in large agglomerations marked by intense industrial activity, such as Sidi Mansour, Thyna and Sfax harbour, were higher than 2.5, thus reflecting the predominant effects of effluent discharges from industrial origin. Overall, the contribution of industry to the effluent discharges in the coastal waters is estimated to attain 55% [12]. The ratio indicates the presence of industrial effluents loaded with non-biodegradable substances [8,13].

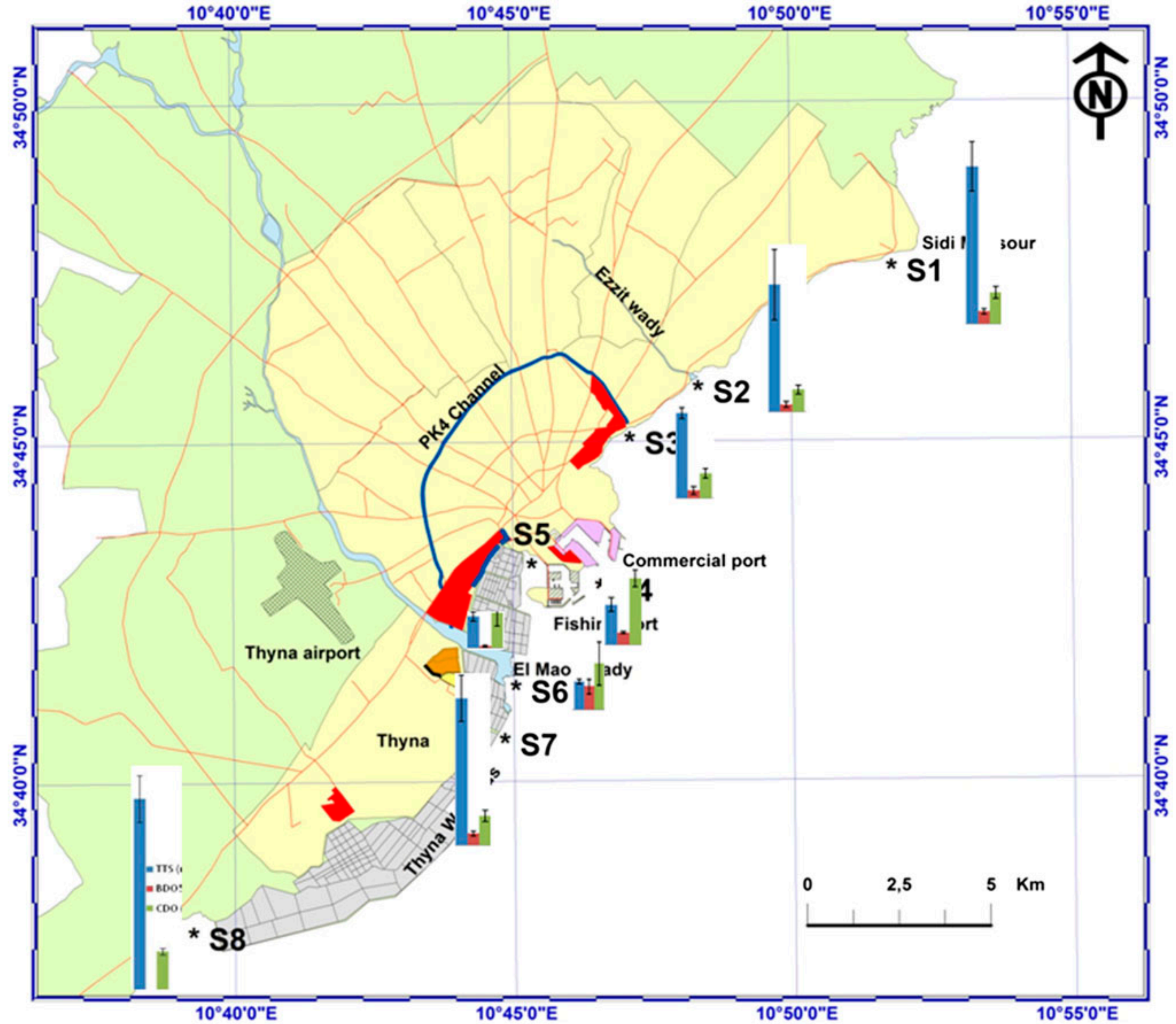

Fig. 2. The TSM quantities and The total oxydable matters (expressed in mg/L) discharged at the Sfax-Tunisia Mediterranean coastline.

Micropolluants from diverse origins contaminate water, sediments and organisms living in the medium. They are present in the different forms (aqueous, solid and biotic) and different chemical structures. Microelements and heavy metals, such as copper and zinc, are essential for the functioning of all living organisms at certain concentrations beyond which they become toxic [14]. Some other metals (mercury, lead and cadmium) and organic microelements are toxic even at very low concentrations. The results revealed the water samples from the studies sites were highly charged in hydrocarbons fractions, far exceeding the accepted standard limit of 1 mg/L. The flows of pollution discharges drained into the Tunisian Mediterranean coasts were high, reaching 270 mg/L at the Sfax harbour. The total hydrocarbon content released into the coast exceeded 1,000 µg/g. This high level of hydrocarbon contamination could be explained by the presence of small ports, fishing communities and small villages on the coastline. The sediments, which represent a large reservoir that provides information on the geochemical cycle of elements [15] showed high amounts of hydrocarbons ranging from 295 to 1,027 µg/g. Expressed as a TOC percentages, hydrocarbons represented 8–54% of TOC and exceeded the quantities usually extracted from the recent immature sediments that generally have a maximum of 3% of TOC, corresponding to free hydrocarbons inherited from original biomass [16]. This reflects the contamination of the sites under investigation by allochthonous hydrocarbons corresponding to pollution products from industrial units and dumps [17].

The qualitative analysis confirmed the origin of petroleum hydrocarbon compounds, with the oil fraction collected from the effluent being predominantly composed by polar material. Light hydrocarbons migrate more easily, at the expense of polar compounds which, owing to their functional groupings, remain attached to the mineral matrix by adsorption [18,19]. The composition of the hydrocarbons of the sediment samples taken from the coast was dominated by the fraction of light compounds, which reached up to 70%. In fact, the hydrocarbons rates identified in samples of superficial sediment, water and benthic organisms with marked filtering ability collected from different sites in the Tunisian Mediterranean coasts (Sfax—Thyna) showed important levels of contamination [20,21]. The Sfax harbour, Thyna and Sidi Mansour represented the zones most exposed to urban and industrial discharges. The contamination rates corresponding to NAHs and PAHs were significantly higher than the allowed standards values. Qualitative analyses, made by gas chromatography-mass spectrometry (GC-MS) and estimated geochemical parameters (Pr/Ph, CPI, UCM/NA), allowed to conclude that the origin of hydrocarbons could be linked to petrogenic inputs attesting to oil contamination (Figs. 3a–3c) [20].

Some heavy metals appeared to make part of chemical substances that could be at the origin of water quality degradation. In aquatic ecosystems, the concentrations of trace elements depend on the TSM.

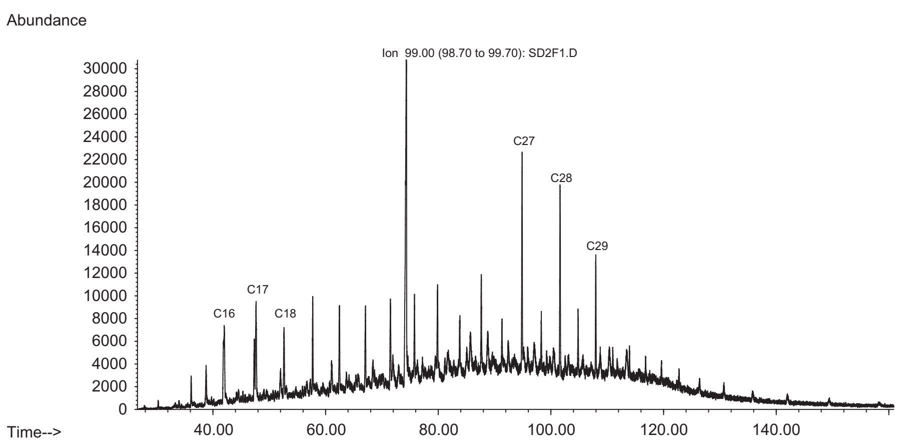

Fig. 3a. Gas chromatogram of saturated and unsaturated non aromatic hydrocarbons from sediment at Sidi Salem canal site (mouth). The n-alkanes distribution is designated as C17–C35.

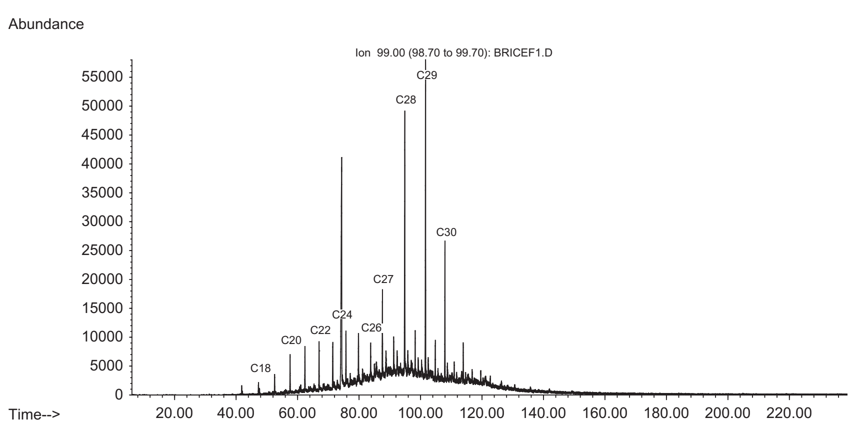

Fig. 3b. Gas chromatogram of saturated and unsaturated non aromatic hydrocarbons from sediment at PK4 canal site (mouth). The n-alkanes distribution is designated as C17–C35.

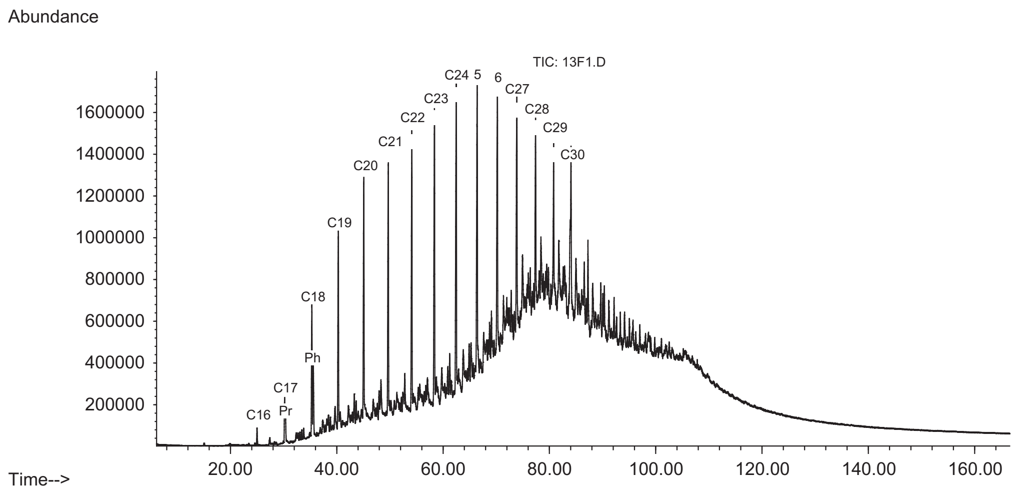

Fig. 3c. Gas chromatogram of saturated and unsaturated non aromatic hydrocarbons from sediment at Sfax harbor (mouth). The n-alkanes distribution is designated as C17–C35.

In fact, the TSM content drained into the coast were important in quantity (more than 4,350 mg/L of TSM in total). Those materials clearly contained heavy metals. The trace element concentrations also depend on the pH. Thus, for instance, copper trapped by the particulate phase is desorbed with acid pH; it becomes labile and bioavailable to aquatic life. The contrary effect occurs at high pH, where the dissolved copper is associated with the particulate phase [22].

The results revealed significant rates of metal pollution, represented by heavy loads of lead, cadmium, chromium and nickel which, in certain sites, were present at alarming concentrations and far exceeded the standard limits. The heavy metal accumulations expressed in mg/L reached 125 for Pb, 23 for Cd, 196 for Cr and 19.2 for Ni. For Cu and Zn concentrations, the values amounted to 81 and 270, respectively (Fig. 4). Those heavy metals came from various anthropogenic and industrial sources, including municipal and industrial effluents and inputs from rural areas (pesticides), or atmospheric sources, such as fuel combustion. Heavy metals are distinguished from other chemical pollutants by their low biodegradability and high bio-accumulative capacity along the food chain. They enter various compartments of the aquatic ecosystem (water, suspended matter, fish) and accumulate in several food chains, causing significant environmental and health problems [23–25]. Living beings that inhabit these environments and organisms including bivalves are endowed with a great filtration potential and are generally exposed to metal pollution. This explains why even at concentrations not exceeding the established standard values, certain metals can pose serious effects on natural ecosystems [9].

Compared to some countries in the Mediterranean basin, the Rhone river (France) has been reported to be subject to important anthropogenic pressure in terms of pollution and physical disturbances, thus displaying high chemical contamination by persistent elements (hydrocarbons, heavy metals and organic micropollutants) presenting harmful threats to the marine environment and its living organisms [26]. The situation in Algeria has been reported to be even worse, with the waters of the Tafna and Mouillah oueds, serving the Oran city via the Hammam Boughrara dam, being confronted to intense pollution loads from urban, agricultural and industrial activities.

The study of physicochemical parameters is important to obtain accurate data on the seawater quality. The pH is one of the most important factors in the coastal ecosystems. In fact, several biological activities can occur only within a narrow pH range. The wide variety of aquatic animals prefers pH values ranging between 6.5 and 8. Accordingly, the pH values recorded for the sites under investigation were within the accepted range. The water temperature controls the rate of all chemical reactions, and affects fish growth, reproduction and immunity. The results indicated that the surface water temperature was governed by atmospheric temperature.

Furthermore, the samples were rich in Na, Ca, Mg and K minerals, which could explain the important EC and, hence, salinity values recorded at the studied sites. In fact, salinity is quantified as the total concentration of soluble salts and is expressed in terms of

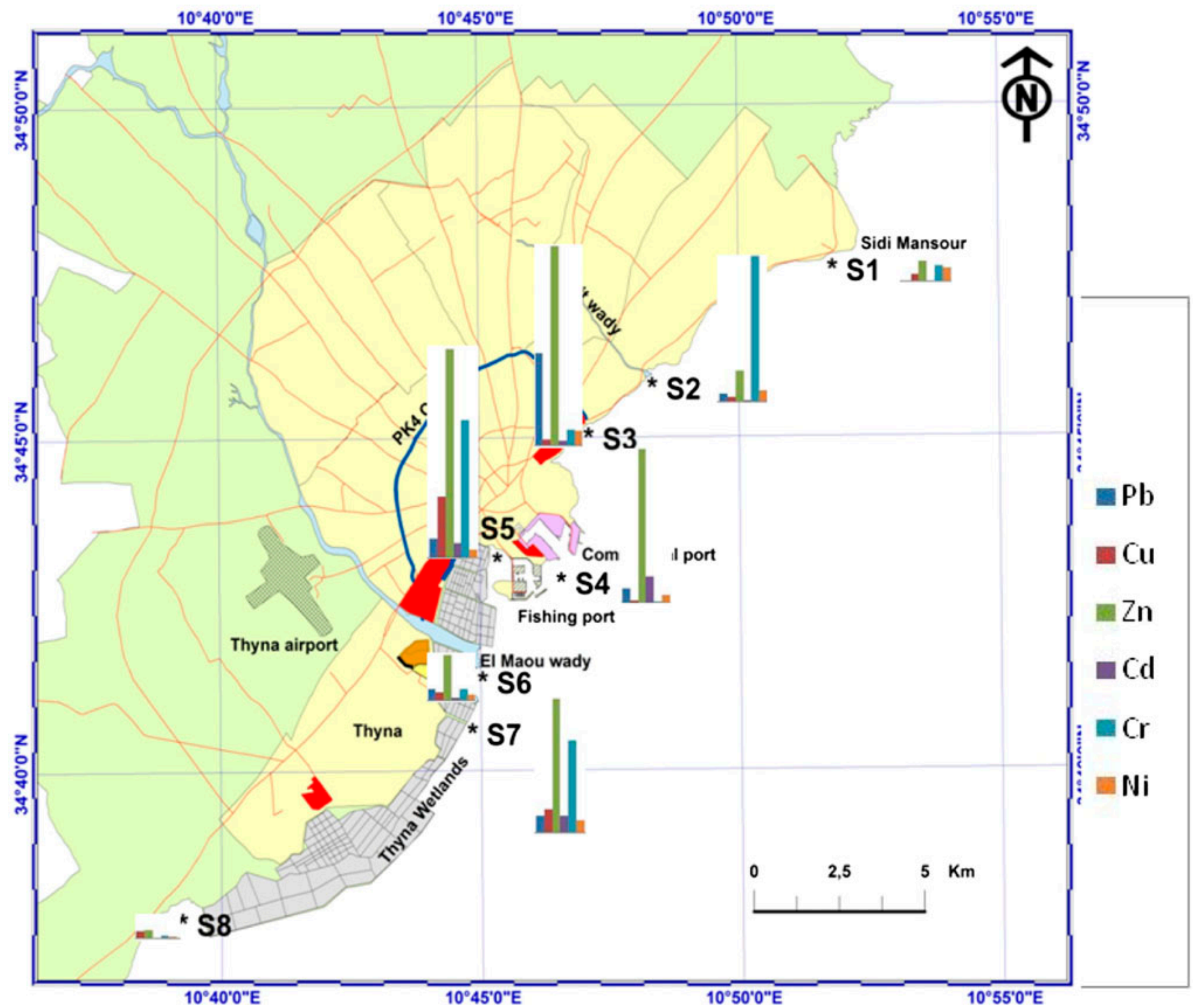

Fig. 4. The heavy metals' flows (expressed in mg/L) discharged at the Sfax-Tunisa Mediterranean coastline.

electrical conductivity. Salinity refers to the presence of dissolved inorganic ions, such as Mg^{++}, Ca^{++}, K^{+}, Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} and CO_3^{2-}, in the aqueous solution.

The minimal concentration of heavy metals reported for water quality criteria (WQC, 1972) are 50 μg/L for Fe; 20 μg/L for Zn; 10 μg/L for Cu and 2 μg/L for Ni. The results indicated the accumulation of heavy metals in the water samples. This contamination could be attributed to industrial effluents, fishing activities, ship traffic and inputs from municipal wastewater.

The TOC can be considered as a direct indicator on the extent, type and origin of organic contamination in seawater. The results showed that the organic carbon values were higher than the inorganic carbon values. The BOD_5 and COD values are also important indicators of organic load in water according to reference standards (NT106, 1989). If COD/BOD are higher than 2, then there is recalcitrant chemical pollution that couldn't be efficiently treated with biological methods. The results revealed that the COD/BOD, particularly in the Harbour of Sfax, were higher than 2, thus indicating the high degree of chemical pollution in this area. The findings also indicated that most of the organic matter in the water samples from this site was biodegradable. Those heavy loads of chemical pollution could be due to industrial effluents and intense fishing and maritime traffic which generate various pollutants such as hydrocarbons. In fact, the GC/MS data indicated the presence of a large group of hydrocarbons, including n-alkanes from C12 to C25 as well as individual isoprenoid hydrocarbons, pristane and phytane, thus suggesting the seawater at the harbour of Sfax exhibited petroleum contamination. The pristane (2,6,10,14-tetramethylpentadecane, Pr) and phytane (2,6,10,14-tetramethylhexadecane, Ph) hydrocarbons are common isoprenoids detected in coastal marine sediments (pristane phytane turkey). They are commonly present in most petroleum media, usually as the major constituents among a much wider distribution of isoprenoid alkanes. Therefore, they are often considered as good indicators of petroleum contamination [27,28].

The contamination sources of coastal sediments from the region of Sfax have been extensively investigated during the last few decades [29]. Louati et al. reported that the hydrocarbon concentrations are relatively high in the coastal area of the city of Sfax compared to other coastal Mediterranean sites. The impact of this hydrocarbon contamination has become significant in areas of harbour activities, where the concentration of total petroleum hydrocarbons reached 772 $\mu g\ g^{-1}$ and total of PAHs amounted to 11 $\mu g\ g^{-1}$ [27].

The region receives hydrocarbons from several origins, such as fisheries activities, ship traffic, inputs associated with municipal and industrial sewage waters, especially from crude oil storage and phosphogypsum stockpiles at the coast.

The physicochemical characterization of the samples showed a heavy contamination by organic and inorganic micropollutants. These are among the most toxic compounds due to their low biodegradation, and they represent excellent indicators of urban and industrial pollution [30]. Their presence requires regular monitoring, preventive measures and stringent provisions that ban their discharge along the coast of Sfax. The increasing of anthropogenic and industrial activities with organic contamination represents the most serious sources for the deteriorating water quality.

The permanent threats to coastal and marine environments and their detrimental effects on natural habitats and ecosystems call for vigilance, planning and commitment to preserve aquatic environment and ensure the sustainability of its resources. In fact, several measures have been taken in the Tunisian context to achieve those purposes. The currently available regulatory documents are, however, characterized by a multitude of fragmented texts with little focus and poor coordination. State agencies seem to have given priority to installations with economic impact where the need for coherent integrated management is needed. Local authorities have opted for the installation of sewage treatment plants to control the wastewater flows drained into the coastline. The stations have different process performances and removal efficiencies. The wastewater treatment facility of South Sfax has, for instance, a limited drawdown rate of 30%. The treated wastewater is discharged at sea via a 3-km-long emissary submarine outfall. The discharged water is still loaded in various contaminants (hydrocarbons, heavy metals and toxic elements). The self-purification ability of the sea on which the authorities rely for additional treatment is not sufficient. In fact, the flows of TSM, oxidizable matter, hydrocarbons and heavy metals discharged into the coast are high, constituting a serious problem for the health and stability of the Mediterranean ecosystem and its biota. The need to draft a comprehensive authoritative legal text for the protection, management and control of the Tunisian coastline has become more urgent than ever before. This is consistent with the current gradual efforts in Tunisia to adapt its national environmental rules and bilateral, multilateral and regional agreements so as to match them with its international commitments. These efforts have been further enhanced by international engagements that involve participation in specific programs, particularly in the Mediterranean. These programs often result in the implementation of resolutions and recommendations targeted to implement a rigorous policy of sustainable development of marine and coastal environments [5,14].

5. Conclusion

The results from the physicochemical, biochemical and geochemical analyses of water, sediment and leachate samples for various harbours along the Tunisian Mediterranean coastline revealed that the pollution flow released into the sea from anthropogenic and industrial activities in the region is alarming. Those loaded waters are discharged into the sea via various channels, including river mouths and canals, without adequate or preliminary treatment.

The results indicated that the wastewaters released into the sea are loaded with TSM, reaching a value of 4,350 mg/L and, hence, far exceeding the established standard limits. The organic load was also significant. The COD and BOD_5 values were far above the permitted limits, reaching 300 mg/L and 1,050 mg/L, respectively, thus reflecting that the discharges had a predominantly industrial origin. The total oxidizable matters, representing the amount of BOD_5 and COD, released into the sea exceeded 1,360 mg/L. The DO rates were also low, fluctuating between 0 and 2.95 mg/L, except for some oueds. This reflected the tendency of different media towards anoxic conditions.

High hydrocarbon loads were also observed, taking several small ports, fishing zones and small villages along the coastline into account. Significant rates of metal pollution were also recorded, represented by heavy and intolerable loads of lead, cadmium, chromium and nickel, which, in some places, were present at high concentrations that far exceeded the standard limits. Considering the serious impacts of the organic and mineral contamination of the Tunisian Mediterranean coastline, further state and public efforts are needed to protect the Mediterranean ecosystem and its habitat.

Acknowledgements

We would like to thank Pr. Jean-Louis Reyss (Laboratoire des Sciences du Climat et de l'Environnement, UMR CEA-CNRS 1,572, Avenue de la Terrasse, F-91,198 Gif sur Yvette Cedex) for providing access to CHN and isotope ratio monitoring equipment. We also appreciated Anne Lorre's help during analytical procedure during sedimentary OC and heavy metals' analysis.

References

[1] K.A. Burns, A. Saliot, Petroleum hydrocarbons in the Mediterranean Sea: A mass balance, Mar. Chem. 20 (1986) 141–157.

[2] T. Hopkins, Physical processes in the Mediterranean basins, Estuar. Trans. Process. USA. (1978) 269–310.

[3] A. Saliot, Évolution de la pollution de l'océan mondial et de la Méditerranée par les hydrocarbures sur les quarante dernières années (Evolution of the pollution in World Ocean and the Mediterranean by oil on past forty years) (1960–2000), Oceanis 30 (2004) 449–459.

[4] N. Ghannem, D. Gargouri, M.M. Sarbeji, C. Yaich, C. Azri, Metal contamination of surface sediments of the Sfax-Chebba coastal line, Tunisia, Environ. Earth Sci. 72 (2014) 3419–3427.

[5] S. Illou, Impact des rejets telluriques d'origines domestique et industrielle sur les environnements côtiers: Cas du littoral Nord de la ville de Sfax (Tunisie), Thesis Dr. Geol. Tunis Univ. Tunisie, 1999, p. 259.

[6] G. Nedia, S.M. Moncef, G. Dorra, M. Khaled, A. Chafai, Assessment of physicochemical water and sediment quality of Sfax-Kerkennah plateau, Tunisia, Desalin. Water Treat. 1–6 (2013).

[7] S. Bouzid, A. Raissouni, S. Khannous, A. El Arrim, I. Bouloubassi, A. Saliot, Distribution and origin of aliphatic hydrocarbons in surface sediments of strategical areas of the western moroccan Mediterranean Sea, Open Environ. Pollut. Toxicol. J. 3 (2012) 13–22.

[8] J. Rodier, L'analyse de l'eau. Eaux naturelles, eaux résiduaires, eau de mer (The analysis of the water. Natural waters, waste waters, sea water), 8ème édition—Collectif, Jean Rodier—Livres, 8ème Édition., Ed. Dunod, Paris, Fr, (1996) 1383.

[9] C. Amiard-Triquet, C. Metayer, J.C. Amiard, B. Berthet, études *in situ* et experimentales de l'écotoxicologie de quatre métaux (Cd, Pb, Cu, Zn) *chez* des algues et des mollusques gastéropodes brouteurs, Water Air Soil Pollut. Kenitra, Morocco, 34 (1987).

[10] M. Nisbet, J. Verneaux, Composantes chimiques des eaux courantes. Discussion et proposition de classes en tant que bases d'interprétation des analyses chimiques (Chemical components running water. Discussion and proposed classes as a basis for interpretation of chemical analyzes), Ann. Limnol. 6 (2011) 161–190.

[11] S.A. Waksman, Humus: Origin, Chemical Composition and importance in nature de Selman A. Waksman: Williams & Wilkins Hardcover—World of Rare Books, Editor, Williams Wilkins (1938) 526.

[12] D. Belghyti, Y. El Guamri, G. Ztit, M. Ouahidi, M. Joti, A. Harchrass, H. Amghar, O. Bouchouata, K. EL Kharrim, H. Bounouira, Caractérisation physico-chimique des eaux usées d'abattoir en vue de la mise en oeuvre d'un traitement adéquat: Cas de Kénitra au Maroc, Afrique Science. Revue Internationale des Sciences et Technologie 5(2) (2010) 199–216.

[13] L.J. C.J., E. A, M. Henze, P. Harremoes, Wastewater Treatment—Biological and Chemical Processes, Springer Verlag, Berlin, (1997) 143–92.

[14] L. Chouba, N. Mzougui-Aguir, Les métaux traces (Cd, Pb, Hg) et les hydrocarbures totaux dans les sédiments superficiels de la frange cotière du golfe de Gabès, 2006.

[15] S.N. Luoma, Bioavailability of trace metals to aquatic organisms—A review, Sci. Total Environ. 28(1–3) (1983) 1–22.

[16] X. Durrieu de Madron, C. Guieu, R. Sempéré, P. Conan, D. Cossa, F. D'Ortenzio, C. Estournel, F. Gazeau, C. Rabouille, L. Stemmann, S. Bonnet, F. Diazd, P. Koubbi, O. Radakovitch, M. Babin, M. Baklouti, C. Bancon-Montigny, S. Belviso, N. Bensoussan, B. Bonsang, I. Bouloubassi, C. Brunetl, J.-F. Cadiou, F. Carlotti, M. Chami, S. Charmasson, B. Charrière, J. Dachs, D. Doxaran, J.-C. Dutay, F. Elbaz-Poulichet, M. Eléaume, F. Eyrolles, C. Fernandez, S. Fowler, P. Francour, J.C. Gaertner, R. Galzin, S. Gasparini, J.-F. Ghiglione, J.-L. Gonzalez , C. Goyet, L. Guidi, K. Guizien, L.-E. Heimbürger, S.H.M. Jacquet, W.H. Jeffrey, F. Joux, P. Le Hir, K. Leblanc, D. Lefèvre, C. Lejeusne, R. Lemé, M.-D. Loÿe-Pilot, M. Malleti, L. Méjanelle, F. Mélin, C. Mellon, B. Mérigotf, P.-L. Merle, C. Migon, W.L. Miller, L. Mortier, B. Mostajir, L. Mousseau, T. Moutin, J. Para, T. Pérez, A. Petrenko, J.-C. Poggiale, L. Prieur, M. Pujo-Pay, Pulido-Villen, P. Raimbault, A.P. Rees, C. Ridame, J.-F. Rontani, D. Ruiz Pino, M.A. Sicre, V. Taillandier, C. Tamburini, T. Tanaka, I. Taupier-Letage, M. Tedetti, P. Testor, H. Thébaulto, B. Thouvenin, F. Touratier, J. Tronczynski, C. Ulses, F. Van Wambeke, V. Vantrepotte, S. Vaz, R. Verney, Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean, Prog. Oceanogr. 91 (2011) 97–166.

[17] N. Venturini, M.C. Bícego, S. Taniguchi, S.T. Sasaki, F. García-Rodríguez, E. Brugnoli, P. Muniz, A multi-molecular marker assessment of organic pollution in

shore sediments from the Río de la Plata Estuary, SW Atlantic, Mar. Pollut. Bull. 91 (2015) 461–475.
[18] B. Tissot, R. Pelet, J. Roucaché, A. Combaz, Utilisation des alcanes comme fossiles géochimiques indicateurs des environnements géologiques, Org. Geochem. 117–54 (1975).
[19] D.H. Welte, Petroleum exploration and organic geochemistry, J. Geochem. Explor. 1 (1972) 117–136.
[20] H. Er-Raioui, S. Bouzid, M. Marhraoui, A. Saliot, Hydrocarbon pollution of the Mediterranean coastline of Morocco, Ocean Coastal Manage. 52 (2009) 124–129.
[21] F. Aloulou, M. Kallel, M. Dammak, B. Elleuch, A. Saliot, Even-numbered n-alkanes/n-alkenes predominance in surface sediments of Gabes Gulf in Tunisia, Environ. Earth Sci. 61 (2009) 1–10.
[22] G. Bordin, Distribution et évolution saisonnière du cuivre dissous dans un écosystème estuarien macrotidal d′ Europe occidentale (estuaire de l′ Aulne, France), Oceanlogica ACTA 14(5) (1991) 445–457.
[23] M.W. Neathery, W.J. Miller, Metabolism and toxicity of cadmium, mercury, and lead in animals: A review, J. Dairy Sci. 58 (1975) 1767–1781.
[24] C.R. Dorn, Cadmium and the food chain, Cornell Vet. 69 (1979) 323–344.
[25] G. Cumont, La contamination des aliments par le mercure, in: Sess. Themat. Contam., 25 Jan 1984, Paris (France), 1984, pp. 309–320.
[26] B. Saïda, A. Houda, A. Khadija, E. Hassan, Urban effluent pollution from the Mghogha flow of the west, margin of the Mediterranean sea, Morocco, Afr. J. Environ. Sci. Technol. 2 (2008) 116–123.
[27] H. Zaghden, M. Kallel, B. Elleuch, J. Oudot, A. Saliot, Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Sfax, Tunisia, Mediterranean Sea, Mar. Chem. 105 (2007) 70–89.
[28] J.K. Volkman, D.G. Holdsworth, G.P. Neill, H.J. Bavor, Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments, Sci. Total Environ. 112 (1992) 203–219.
[29] A. Louati, B. Elleuch, M. Kallel, A. Saliot, J. Dagaut, J. Oudot, Hydrocarbon contamination of coastal sediments from the Sfax Area (Tunisia), Mediterranean Sea, Mar. Pollut. Bull. 42 (2001) 444–451.
[30] D. Gargouri, C. Azri, M.M. Serbaji, Y. Jedoui, M. Montacer, Heavy metal concentrations in the surface marine sediments of Sfax Coast, Tunisia, Environ. Monit. Assess. 175 (2011) 519–530.