Marine Pollution Bulletin 127 (2018) 445–452

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Seawater quality assessment and identification of pollution sources along the central coastal area of Gabes Gulf (SE Tunisia): Evidence of industrial impact and implications for marine environment protection

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ARTICLE INFO

Keywords:
Seawater contamination
Phosphogypsum
Anthropogenic impact
Trace elements
Southern Mediterranean

ABSTRACT

Temperature, pH and trace elements (F, P, Cr, Cu, Zn, Cd, and Pb) contents were determined in 16 stations as well as in 2 industrial and 2 domestic discharge sources, in the central coastal area of the Gulf of Gabes. Compared to the northern and southern areas of the study area, the highest contents of contaminants were reached in the central area which hosts the coastal industrial complex. The seawater in this central area was also found to be acid and of higher temperature. Based on the Water Pollution Index results, an increasing degradation gradient of the seawater quality was revealed from northern and/or southern stations to central ones, categorized as 'strongly to seriously affected'. Phosphogypsum wastes dumped by the Tunisian Chemical Group (GCT) seem to have continuously degraded the seawater quality in the study area. A rapid intervention is needed to stop the effects on the marine environment.

It is well known that the worldwide demographic expansion and the related industrialization of coastal areas have continuously generated an increasing pollution which led to various environmental problems and human health risks (Liu et al., 2011; Kerambrun et al., 2012; Andersen et al., 1996; Diop et al., 2014). Increasing industrial pressures on coastal systems were reported to be responsible of the deterioration of marine habitats, decline of marine resources and thus causing serious economic problems (Liu et al., 2011; Ali et al., 2013). According to Edgren (1993), it is estimated that up to 75% of the world population will be settled within a sixty-kilometer distance from the shoreline by 2020, which will most likely lead to increase more the anthropogenic pressures on coastal systems and to more serious environmental issues. In order to estimate the impact of the anthropogenic pressures on coastal marine ecosystems, it is necessary to conduct continuous monitoring programs of the quality and the health status of these ecologically and economically-important habitats (Zulfa et al., 2016; Cohen et al., 2001). Among the parameters to be monitored in coastal habitats, water quality is considered of special importance since its deterioration may be lethal for marine fauna and flora (Liu et al., 2011; Riani et al., 2014; Poonam et al., 2013). Within this context, it is worth noting that the enrichment of the seawater with metals leads to the accumulation of these pollutants in sediments and in marine species and hence to their biomagnification in the trophic chains of marine systems (Rabaoui et al., 2017). In fact, trace metals like other types of pollutants (Polycyclic aromatic hydrocarbons, PAHs and total petroleum hydrocarbons, TPHs) have a very wide range of sources and they are well-known with their toxicity, persistence and bioaccumulation through food chains (Yu et al., 2008; Tovar-Sánchez et al., 2010; Gao and Chen, 2012; Maanan et al., 2015). Anthropogenic activities including coastal industries, urbanization, extensive agriculture, tourism and aquaculture represent the major sources of pollutants which continually contribute to exacerbate the already serious situation of coastal systems (Tovar-Sánchez

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https://doi.org/10.1016/j.marpolbul.2017.12.012
Received 19 June 2017; Received in revised form 24 November 2017; Accepted 5 December 2017
Available online 21 December 2017
0025-326X/

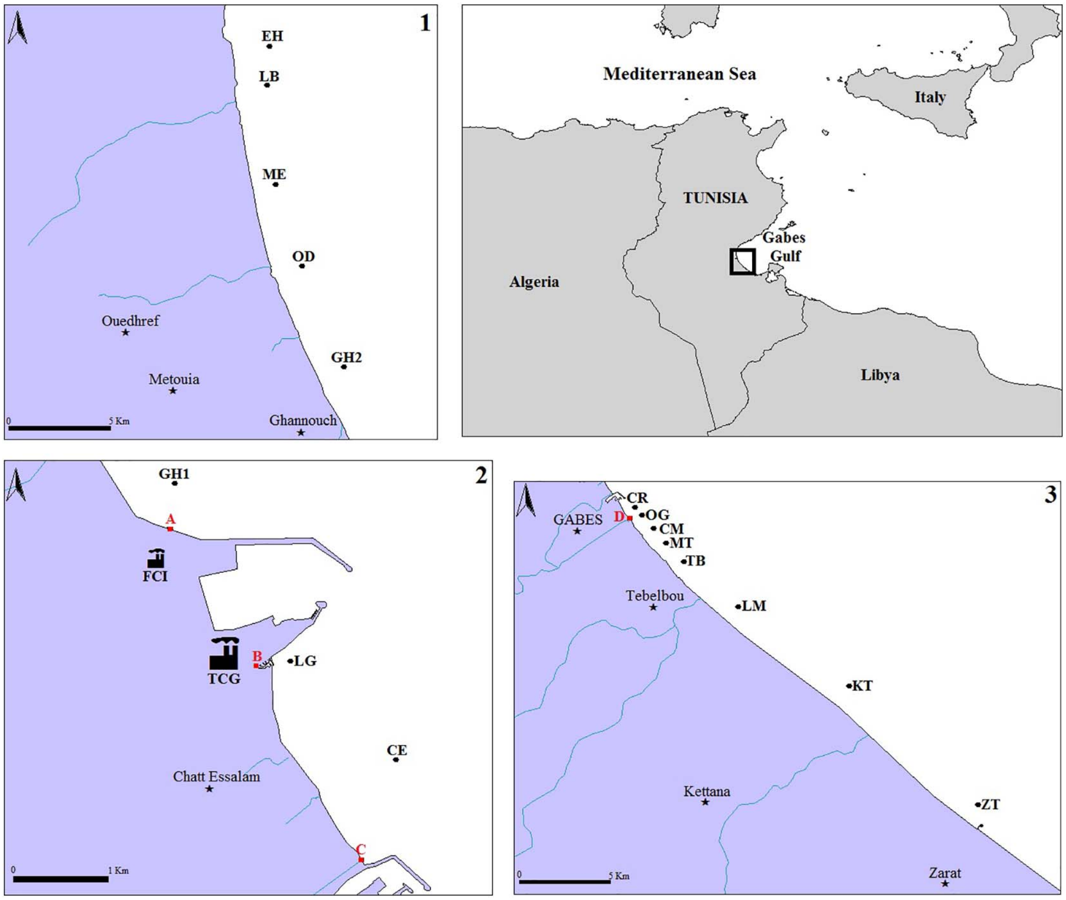

Fig. 1. Location of sampling stations in the northern (1), central (2) and southern (3) sectors of the central coastal area of Gabes Gulf. A: ICF marine emissary; B: TCG marine emissary; C: Ennaten Wadi marine emissary; D: Gabes Wadi marine emissary.

et al., 2010). Consequently, the seawater coastal pollution has become a worldwide serious and very worrying threat which requires rapid intervention (El Zrelli et al., 2015) through the application of monitoring programs and improvement of the water quality (Montefalcone, 2009) as well as the adoption of bioremediation solutions (Li et al., 2015).

The Gulf of Gabes (GG), located at the south-eastern coast of Tunisia, used to be considered until recently the main fishing zone in Tunisia and one of the most important in the Mediterranean Sea (Zaouali, 1993; Jabeur et al., 2000; Hattab et al., 2013; FAO, 2016; Colloca et al., 2017). For instance, the geomorphological features of GG in particular its continental margin and its shallow waters as well as its seagrass meadows made it one of the major nursery grounds for many Mediterranean fish and benthic invertebrate species. However, due to the rapid and uncontrolled industrialization of the central area of GG (Fig. 1), in particular in Gabes city, a continuous and increasing degradation of the local costal systems was reported since few decades (Darmoul et al., 1980; Darmoul and Vitiello, 1980; Darmoul, 1988; Ayadi et al., 2014; Rabaoui et al., 2014, 2015, 2017; El Zrelli et al., 2015, 2017). In fact, since the 70s, many untreated industrial wastes have been continuously discharged in the open sea from the industrial complex of Ghannouche-Gabes, one of the biggest industrial zones in Tunisia. These industrial wastes are mainly represented by phosphogyspum (PG) dumped by the Tunisian Chemical Group (TCG in english or GCT in french) as well as other discharges from the Fluorine Chemical Industry (ICF). The dispersion of PG was reported to follow a north-south direction, from the GCT, with a highest concentration in the area between Gabes and Ghannouch Ports (Fig. 1; El Zrelli et al., 2015). In addition to these industrial wastes, domestic wastes are also released in the marine environment of GG, from the local municipal wastewater discharges. In spite of these different pollution sources, there is still a knowledge gap about the water quality in the central part of GG. In fact, most of the recent studies assessing the quality of the marine environment in GG focused mainly on the enrichment of surface sediment with pollutants (mainly trace metals) showing an evident degradation of the sediment quality in this area (Ayadi et al., 2014; El Zrelli et al., 2015; Rabaoui et al., 2015). This has led to various environmental consequences passing from the local appearance of red tides (Hamza and El Abed, 1994) and unbalanced local benthic communities (Rabaoui et al., 2015) to the disappearance of some marine species (El Kateb et al., 2016) and decline in the fisheries production (Ben Othman, 1971). Based on these latter studies, it is expected that the water quality may also show similar pattern to that of surface sediments, and may then contribute partially to the environmental consequences abovementioned. The present study was carried out within this context aiming to describe the quality of the seawater in the central coastal area of GG, through the assessment of trace elements in several stations spread in this region including the industrial and urban discharge zones/sources. The aims of this work are then *i*) to describe the spatial distribution of six trace elements concentrated in seawater of the central coastal area of GG, *ii*) to assess the degradation level of seawater quality in this area through physicochemical characterization and Water Pollution Index, and *iii*) to identify the major sources feeding the marine environment of GG with pollutants. Knowing these information is necessary for any environmental management plan of the GG area aiming to improve the water quality and the "health status" of local marine habitats.

In September 2013, surface seawater samples were collected from 16 stations located along the central coastal area of GG, and spread in three sectors, northern, central and southern with respect to the location of the coastal industrial complex of Ghannouche-Gabes (Fig. 1).

Table 1
Detailed description of the characteristics (Area, GPS coordinates (DD) and depth) of sampling stations in the central part of Gabes Gulf.

Sectors	Stations	Area description	Latitude	Longitude	Depth (m)
Southern sector	ZT	No anthropogenic source of pollution, average coastal fishing activity and presumed as not polluted site.	33.73201	010.31936	4.5
	KT		33.79089	010.24704	4.0
	LM		33.83146	010.17958	4.3
	TB		33.85692	010.15088	4.3
	MT		33.86659	010.14185	4.0
	CM		33.87418	010.13390	4.1
	OG	In front of Gabes Wadi, important discharge of untreated urban wastewater, rare coastal fishing activity and presumed as polluted site.	33.88236	010.12665	4.2
	CR	In front of Corniche beach, rare coastal fishing activity and presuming as polluted site.	33.88973	010.12202	4.2
Central sector	CE	Located in the inter-harbor area (Chatt Essalam beach), important mix of industrial (phosphogypsum, fluoridated wastewater) and urban wastewater marine discharges, low coastal fishing activity and presumed as the most polluted site in Gabes.	33.90168	010.11238	4.0
	LG		33.91462	010.10442	1.2
	GH1	In front of the Fluorine Chemical Industry marine discharge, average coastal fishing activity and presumed as a polluted site.	33.92971	010.09028	1.7
Northern sector	GH2	No anthropogenic source of pollution, intensive coastal fishing activity and presumed as a non polluted site.	33.95895	010.07201	4.4
	OD		34.00586	010.04997	4.5
	ME		34.04186	010.03880	4.2
	LB		34.08678	010.04213	4.1
	EH		34.10376	010.04342	4.0

Five stations were sampled in the northern sector (EH, LB, ME, OD and GH2; Fig. 1), three in the central sector which surrounds the industrial complex and where industrial discharges take place (GH1, LG and CE; Fig. 1) and eight stations in the southern sector, in the direction of marine PG dispersion (CR, OG, CM, MT, TB, LM, KT and ZT; Fig. 1). Detailed description of the sampling stations including their exact GPS positions and their depth is given in Table 1. Additional samples were also collected directly from four known sources of discharges: two industrial discharge sources coming from GCT and ICF and two domestic discharge (wastewater) sources at the level of Ennaten Wadi and Gabes Wadi (Fig. 1). It is worth noting that the untreated wastewaters of Gabes city are being dumped in the wadis of Gabes (Gabes city), Ennaten (Chatt Essalam), Ettin (Ghannouch) and in particular through Legsuir Wadi at Chat Essalam which hosts the only functional purification station. These additional samples were collected directly from the discharge sources before the discharges reach the coastal seawater. In parallel to seawater sampling, seawater surface pH and temperature were measured in situ using a digital multi-parameter waterproof meter (Model pH 340i, WTW-Germany).

For the determination of dissolved trace metal concentrations, collected seawater samples were immediately filtered with 0.22 µm membrane and kept in polyethylene jerry cans, prewashed with acid and rinsed with de-ionized water. The seawater samples were thereafter acidified with ultrapure 10%HNO_3 and stored in polyethylene bottles. Sampling bottles were kept at 4 °C until analysis. In the laboratory, the concentrations of seven elements (F, P, Cr, Cu, Zn, Cd and Pb) were measured in the seawater samples using Inductively Coupled Plasma Mass Spectrometry, ICP-MS-Thermo iCAP Q (for P, Cr, Cu, Zn, Cd and Pb) and Ion Chromatography, IC-Dionex ICS 2000 (for F). The quality control of the trace elements analysis was enabled through the use of two certified reference materials for seawater, XSPEXF-2812 and XSPEXF-2782 (from SPEX CertiPrep®), preparation of blanks and spiked water samples throughout the complete procedure and analysis of triplicate samples. The concentrations determined herein correspond to the mean of triplicate samples and they are expressed as $\mu g{\cdot}L^{-1}$ for all elements except F which was expressed as $mg{\cdot}L^{-1}$. Analytical results of the quality control samples showed agreement with the certified values with recoveries < 10% for all studied trace elements.

The seawater quality status was assessed at the 16 sampling stations using the Water Pollution Index (WP_i; Lyulko et al., 2001; Filatov et al., 2005) which can be computed with the following equation:

$$WP_i = \sqrt{\frac{\left[\left(\frac{Ci}{Si}\right)^2_{\max} + \left(\frac{Ci}{Si}\right)^2_{\min}\right]}{2}} \quad (1)$$

where Ci is the measured water quality parameters, Si is the standard water quality parameters and $(Ci/Si)_{\max}$ and $(Ci/Si)_{\min}$ represent (Ci/Si) maximum and minimum, respectively. This index includes the five following classes: not affected ($WP_i < 1$), slightly affected ($1 \le WP_i \le 2$), moderately affected ($2 < WP_i \le 3$), strongly affected ($3 < WP_i \le 5$) and seriously affected ($WP_i > 5$).

To assess the pollutant loads of the examined pollution discharge sources, we used two different methods: (*i*) a comparison to the Tunisian standards for the discharge of industrial wastewaters in the maritime field (NT 106-02, 1989) and (*ii*) to the two following pollution indices:

- The Pollution Index (PI) proposed by Liu et al. (2011):

$$PI = \frac{M_i}{S_i} \quad (2)$$

where M_i is the measured concentration of pollutant i and S_i is the concentration of the stipulated standard of pollutant i. If PI > 1, the discharge of pollutant exceeds the stipulated standard; in the opposite case (PI ≤ 1), it is in accordance with this standard.

- The Compressive Pollution Index (CPI), which can be calculated using PI according to the following equation:

$$CPI = 1/n \sum_{i=1}^{n} PI \quad (3)$$

where n is the number of pollutants and PI is the single Pollution Index of each quality parameter. Based on the CPI values, Liu et al. (2010) distinguished four categories of seawater quality (Table 2).

pH and temperature records as well as the trace elements concentrations determined in the surface seawater samples collected from the sampling stations are given in Table 3. The surface seawater pH and temperature ranged from 3.61 (LG) to 8.15 (OD) and from 25.4 °C (LM) to 31.2 °C (LG), respectively. The concentrations of trace elements showed wide variations with all elements including F (from 0.35 ± 0.05 $mg{\cdot}L^{-1}$ in ME to 18.22 ± 0.19 $mg{\cdot}L^{-1}$ in GH1), P (from < 131.25 $\mu g{\cdot}L^{-1}$ in GH1 to 5605.21 ± 86.22 $\mu g{\cdot}L^{-1}$ in LG), Cr (from < 0.45 $\mu g{\cdot}L^{-1}$ in most stations to < 0.48 $\mu g{\cdot}L^{-1}$ in ME), Cu (from 3.02 ± 0.21 $\mu g{\cdot}L^{-1}$ in LG to 7.19 ± 0.14 $\mu g{\cdot}L^{-1}$ in LM), Zn (from 5.11 ± 0.91 $\mu g{\cdot}L^{-1}$ in GH2 to 21.21 ± 0.70 $\mu g{\cdot}L^{-1}$ in ZT), Cd

Table 2
Compressive Pollution Index categories (Liu et al., 2010).

CPI value	Class	Water quality
CPI ≤ 0.8	Qualified	Certain pollutants are detected but their concentrations accord with the standard.
0.8 < CPI ≤ 1	Basically qualified	Concentrations of certain pollutants exceed the standard.
1 < CPI ≤ 2	Polluted	Concentrations of quite a part of pollutants exceed the standard.
CPI > 2	Seriously polluted	Concentrations of quite a part of pollutants exceed the standard many times.

(from < 0.27 μg·L^{-1} in most stations to 1.99 ± 0.10 μg·L^{-1} in LG) and Pb (from 0.14 ± 0.01 μg·L^{-1} in LG to 0.94 ± 0.04 μg·L^{-1} in EH) (Table 3). In general, the highest concentration of trace metals in seawater were recorded in LG (for P and Cd), ME (for Cr), LM (for Cu), GH1 (for F), ZT (for Zn) and EH (for Pb). In contrast, the lowest concentrations of seawater trace elements were noted in GH1 (for P), LG (for Cu and Pb), ME (for F), GH2 (for Zn) and most of the sampling stations (for Cd and Cr) (Table 3). In addition, the decreasing order of trace elements concentrations in the seawater of the central coastal area of GG was found to be as follows: F > P > Zn > Cu > Cd > Cr > Pb.

The WP_i values calculated for the 16 sampling stations and their corresponding seawater quality categories are presented in Table 4. WP_i ranged between 0.66 (in LB) and 28.03 (in LG) and the descending order of sampling stations was found to be the following: LG > CE > CR > CM > OG > MT > TB > GH1 > LM > ZT > KT > GH2 > OD > ME > EH > LB. Based on WP_i results, the seawater was assessed as '*not affected*' in ME, LB and EH, '*slightly affected*' in ZT, KT, LM, TB, GH1, GH2 and OD, '*moderately affected*' in MT and OG, '*strongly affected*' in CM, CR and CE, and '*seriously affected*' in LG. Fig. 2 shows the spatial variations on the seawater quality in the central coastal area of GG, based on the WP_i estimates. This latter figure highlighted evidently that the central sector of the study area (mainly CE, LG and GH1 stations) which hosts the industrial complex of Gabes with its discharge sources, is the most affected having the worst quality of seawater. An increasing gradient of seawater quality improvement can be observed from the central sector toward the northern and southern ones which appeared to host better-quality seawaters. The seawater quality in the northern sector (GH2, OD, ME, LB and EH stations) seems to be less affected by the industrial pollution compared to the southern sector. This may be explained by the effect of the commercial harbor piers in Ghannouch, which seem to play a protective role of the northern area. In addition, the north-south direction of water currents seems to accentuate the transfer of pollutants toward the

Table 4
Water pollution index (WP_i) values and classification categories of surface coastal seawater of central part of Gabes Gulf.

Site	WP_i	Seawater quality classification
ZT	1.65	Slightly affected
KT	1.53	Slightly affected
LM	1.81	Slightly affected
TB	1.94	Slightly affected
MT	2.28	Moderately affected
CM	3.12	Strongly affected
OG	2.82	Moderately affected
CR	3.14	Strongly affected
CE	4.26	Strongly affected
LG	28.03	Seriously affected
GH1	1.82	Slightly affected
GH2	1.36	Slightly affected
OD	1.12	Slightly affected
ME	0.70	Not affected
LB	0.66	Not affected
EH	0.90	Not affected

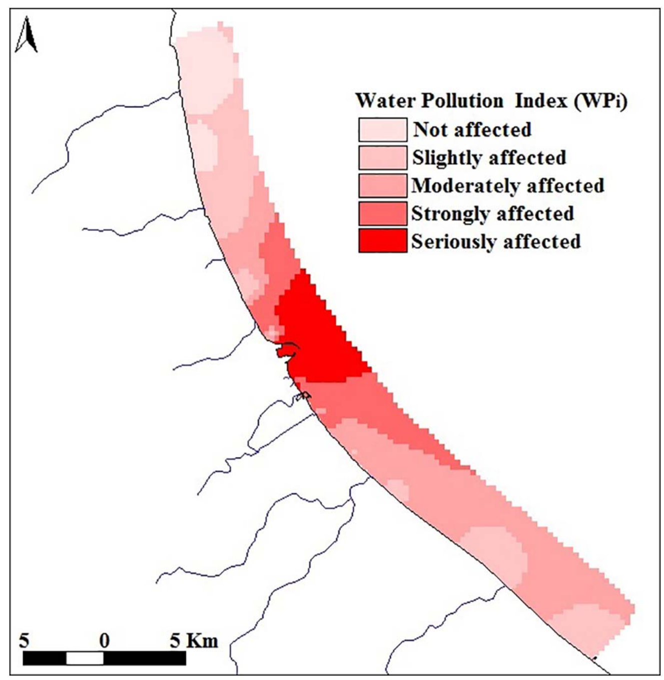

Fig. 2. Spatial distribution of the water pollution index (WP_i) in the central coastal area of Gabes Gulf.

Table 3
Surface pH, surface temperature and trace element concentrations recorded in the surface seawater samples collected from the sampling stations in the central coastal area of Gabes Gulf.

Stations	pH	T (°C)	F (mg·L^{-1})	P (μg·L^{-1})	Cr (μg·L^{-1})	Cu (μg·L^{-1})	Zn (μg·L^{-1})	Cd (μg·L^{-1})	Pb (μg·L^{-1})
ZT	7.98	26.2	0.39 ± 0.01	329.72 ± 121.27	< 0.45	6.82 ± 0.48	21.21 ± 0.70	< 0.27	0.25 ± 0.01
KT	8.06	25.9	0.56 ± 0.06	306.58 ± 37.96	< 0.47	5.09 ± 0.13	6.08 ± 0.63	< 0.28	0.23 ± 0.02
LM	7.89	25.4	2.20 ± 0.09	362.70 ± 75.75	< 0.47	7.19 ± 0.14	10.03 ± 2.59	< 0.29	0.55 ± 0.02
TB	8.13	26.7	2.61 ± 0.39	387.10 ± 99.25	< 0.45	6.93 ± 0.72	6.81 ± 0.40	< 0.27	0.29 ± 0.02
MT	7.34	27.0	0.60 ± 0.01	455.02 ± 60.68	< 0.45	6.04 ± 0.27	8.70 ± 0.67	< 0.28	0.37 ± 0.03
CM	7.94	27.1	2.80 ± 0.20	623.05 ± 158.35	< 0.45	5.41 ± 0.25	7.13 ± 0.17	< 0.27	0.27 ± 0.01
OG	8.05	26.4	0.63 ± 0.01	564.02 ± 103.28	< 0.45	5.45 ± 0.20	6.74 ± 1.08	< 0.27	0.22 ± 0.02
CR	7.32	26.9	0.67 ± 0.01	627.25 ± 123.27	< 0.47	5.61 ± 0.15	7.76 ± 0.55	< 0.29	0.24 ± 0.01
CE	4.35	28.4	2.96 ± 0.15	852.40 ± 144.17	< 0.45	6.29 ± 0.19	8.48 ± 0.63	0.74 ± 0.08	0.26 ± 0.02
LG	3.61	31.2	9.36 ± 0.59	5605.21 ± 86.22	< 0.47	3.02 ± 0.21	7.82 ± 0.66	1.99 ± 0.10	0.14 ± 0.01
GH1	3.89	30.9	18.22 ± 0.19	< 131.25	< 0.45	5.51 ± 0.25	8.32 ± 0.71	< 0.27	0.21 ± 0.01
GH2	7.62	27.5	2.08 ± 0.10	271.48 ± 97.52	< 0.45	5.13 ± 0.29	5.11 ± 0.91	< 0.27	0.26 ± 0.04
OD	8.15	25.9	2.67 ± 0.03	223.88 ± 40.69	< 0.45	5.20 ± 0.14	5.15 ± 0.22	< 0.27	0.26 ± 0.03
ME	7.84	26.7	0.35 ± 0.05	< 140.27	< 0.48	5.52 ± 0.35	6.41 ± 0.57	< 0.29	0.29 ± 0.01
LB	8.03	26.3	2.23 ± 0.07	< 131.37	< 0.45	5.60 ± 0.21	6.29 ± 0.95	< 0.27	0.32 ± 0.04
EH	7.79	26.1	3.03 ± 1.67	180.58 ± 48.11	< 0.45	6.71 ± 0.14	18.15 ± 5.47	< 0.27	0.94 ± 0.04

Table 5
Tunisian guidelines (NT 106-002) of trace element concentrations, as well as the corresponding pollution index (PI) and compressive pollution index (CPI) values and classes.

TN			pH	T (°C)	F ($mg \cdot L^{-1}$)	P ($mg \cdot L^{-1}$)	Cr ($mg \cdot L^{-1}$)	Cu ($mg \cdot L^{-1}$)	Zn ($mg \cdot L^{-1}$)	Cd ($mg \cdot L^{-1}$)	Pb ($mg \cdot L^{-1}$)
			6.5–8.5	< 35	5	0.1	2	1.5	10	0.005	0.5
Industrial pollution sources	GCT		3.11	39.2	336.97 ± 2.88	3.44 ± 0.04	11.81 ± 0.11	4.57 ± 0.09	105.47 ± 1.32	16.42 ± 0.24	1.38 ± 0.02
		PI	–	–	67.39	17.2	5.91	3.05	10.55	3284	2.76
		CPI	484.41								
		Class	Seriously polluted								
	ICF		3.52	37.4	428.31 ± 5.10	0.099 ± 0.01	6.70 ± 0.14	1.40 ± 0.02	1.59 ± 0.1	< $36.19\ 10^{-3}$	0.30 ± 0.07
		PI	–	–	85.66	0.99	3.35	0.93	0.16	< 7.24	0.60
		CPI	15.28[a]								
		Class	Seriously polluted								
Domestic pollution sources	Ennaten Wadi		7.46	26.3	1.22 ± 0.01	$2.89\ 10^{-3} \pm 0.05\ 10^{-3}$	$0.39\ 10^{-3} \pm 0.02\ 10^{-3}$	$0.52\ 10^{-3} \pm 0.01\ 10^{-3}$	$1.06\ 10^{-3} \pm 0.06\ 10^{-3}$	< $0.04\ 10^{-3}$	$0.05 \pm 0.002\ 10^{-3}$
		PI	–	–	0.24	$28.9\ 10^{-3}$	$0.195\ 10^{-3}$	$34.67\ 10^{-5}$	$1.06\ 10^{-4}$	< $8\ 10^{-3}$	$0.1\ 10^{-3}$
		CPI	0.04[a]								
		Class	Qualified								
	Gabes Wadi		8.01	26.1	0.57 ± 0.02	$0.82\ 10^{-3} \pm 0.01\ 10^{-3}$	$0.06\ 10^{-3} \pm 0.02\ 10^{-3}$	$0.63\ 10^{-3} \pm 0.01\ 10^{-3}$	$1.52\ 10^{-3} \pm 0.04\ 10^{-3}$	$0.11\ 10^{-3} \pm 0.02\ 10^{-3}$	$0.1 \pm 0.004\ 10^{-3}$
		PI	–	–	0.11	$8.2\ 10^{-3}$	$0.03\ 10^{-3}$	$0.42\ 10^{-3}$	$1.52\ 10^{-4}$	0.22	$0.2\ 10^{-3}$
		CPI	0.05								
		Class	Qualified								

[a] CPI values estimated for ICF and Ennaten Wadi did not consider the cadmium (Cd) concentrations.

southern areas, similarly to the findings of previous studies (Rabaoui et al., 2015; El Zrelli et al., 2015).

The concentrations of trace metals considered in the seawater samples collected from the four industrial and domestic discharge sources and their comparison with the Tunisian standards for the discharge of industrial wastewater in the maritime field (NT 106-02, 1989) are given in Table 5. Considerable differences were found between the concentrations estimated in the seawater samples collected from the industrial discharge sources and those indicated in the standard guidelines. For instance, the seawater sampled at the GCT industrial source, throwing mainly phosphogypsum wastes, exceeded all Tunisian guidelines for all water parameters considered (pH, surface seawater temperature, F, P, Cr, Cu, Zn, Cd and Pb), with PI values varying between 2.76 (for Pb) and 3284 (for Cd). The values of seawater parameters were in general worrying in the GCT industrial source showing very high values of surface seawater temperature, P, Cd, F and Zn and very low values of pH compared to the Tunisian standard levels (Table 5). Similar findings were observed with the seawater quality in the ICF industrial discharge source which was found to be within the standard Tunisian levels only with the concentrations of P (PI = 0.99), Cu (PI = 0.93), Pb (PI = 0.60) and Zn (PI = 0.16) (Table 5). In the case of the two domestic discharge sources of Ennaten Wadi and Gabes Wadi, all seawater parameters determined in the samples collected from these two latter sources were found to be in concordance with the required standards fixed by the Tunisian guidelines for industrial discharges in the maritime field (Table 5). These results led to deduce that the industrial wastes discharged from the coastal industrial complex of Ghannouche-Gabes, in particular the PG wastes from the GCT, represent the most contributing factors to the degradation of seawater quality in the central coastal area of GG. PG wastes are well known to contain various components of environmental concern including trace metals, acid residual impurities, fluorides, sulfate ions, organic matter and natural radioelements (Rutherford et al., 1994; Papastefanou et al., 2006; El Afifi et al., 2009; Tayibi et al., 2009; Pérez-López et al., 2010).

Due to their continuous daily discharge in the coastal area since decades, there has been mostly a cumulative effect of PG on the quality status of the marine environment. In fact, nearly 14,400 tons of untreated dry PG wastes ($\sim 30.10^3$ t/day of humid PG) are estimated to be daily discharged from the GCT into GG marine environment (El Zrelli et al., 2017). This has contributed to many environmental issues that led most environmentalists to conclude that the PG wastes are the main polluting factor behind the continuous degradation of marine life and habitats in the central coastal area of GG, since the establishment of the coastal industrial complex in 1972 (Darmoul et al., 1980; Darmoul, 1988; Kharroubi et al., 2012; El Zrelli et al., 2015, 2017; Rabaoui et al., 2014, 2015, 2017). Based on the results obtained herein, the ICF industrial wastes seem also to accentuate the degradation of the marine environment quality in GG, since the seawater parameters (mainly F, pH, Temperature and Cr) are above the Tunisian standard levels (Table 4). In addition, these latter findings are evidently confirmed by the spatial distributions of F and P, the main elements discharged by the GCT and ICF factories respectively, which highlighted a clear degradation pattern of the seawater quality from the northern and/or southern sectors to the central sector which hosts the industrial complex including these two latter factories (Fig. 3).

Moreover, based on the results of the seawater parameters considered herein, the domestic (wastewater) discharge sources (i.e. at Ennaten Wadi and Gabes Wadi) were not found to represent threats to the seawater quality and the marine environment in the central coastal area of GG (Table 5). In addition, the industrial discharges sources seem to exert a much heavier negative effect on the marine environment of GG, compared to the domestic discharge sources.

Among the several authors having carried out studies on the impacts of marine pollution in the central part of GG, Darmoul and Vitiello (1980) were the first to mention the serious potential of PG catastrophic risks in the central part of GG. Their experiment on the acute toxicity of

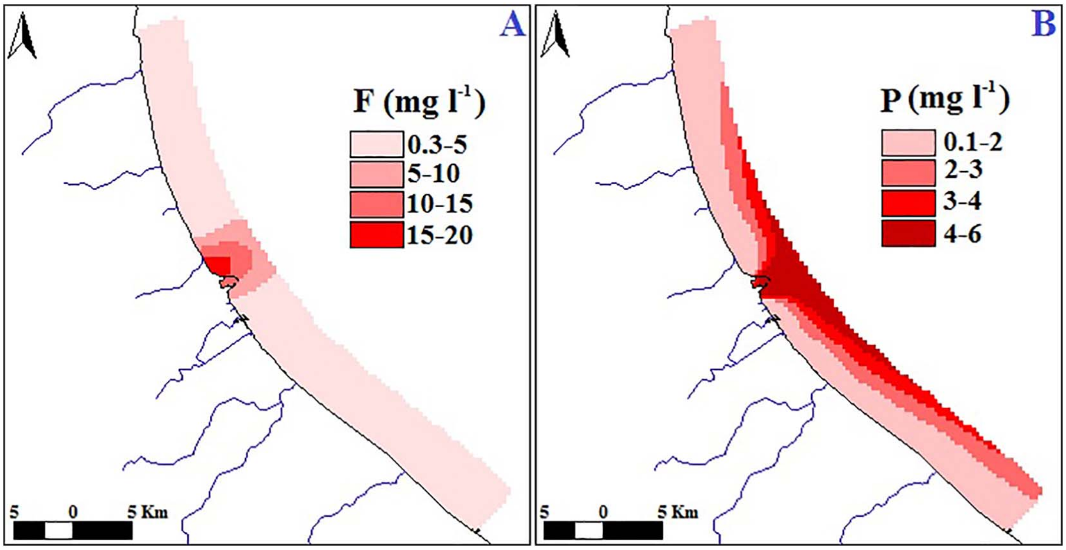

Fig. 3. Spatial distribution of fluorine (F; A) and phosphorus (P; B) concentrations in the surface seawater of the central coastal area of Gabes Gulf.

PG releases on some benthic organisms (*Sphaeroma serratum*, *Cymodoce truncata*, *Nassa corniculum*, *Ruditapes decussatus* and *Mytilus galloprovincialis*) showed that PG is short-term toxic for all species, at 16 to 18 °C and with fairly high PG levels (24 to 43 $g{\cdot}L^{-1}$ during 48 h and 14 to 28 $g{\cdot}L^{-1}$ at 96 h). This toxicity is directly related to pH and PG fluoride content which act in synergy with other PG components (phosphorus, organic matter and trace elements). After six years of pollution monitoring (1976–1981), Darmoul (1988) concluded that PG is the main polluting source which is responsible of chemical seawater contamination, accentuation of *Posidonia oceanica* degradation and fluorine contamination of some marine species. Nowadays, toxicity is obvious and the pollution impacts are manifested by the installation of a wide azoic zone of several hectares, in the inter-harbor zone, as shown in Appendix I.

It is worth mentioning that during the sampling period, several dead organisms (birds, sea turtles, fish and shellfish species) were observed with relatively higher abundances in the inter-harbor beach area (Chatt Essalam Beach) which is the most affected area by PG wastes (Fig. 4). More than 40 species most likely affected by the industrial releases were identified during this work. Among these latter, 10 species (*Caretta caretta*, *Phalacrocorax carbo*, *Chroicocephalus genei*, *Larus michahellis*, *Atherina boyeri*, *Sardina pilchardus*, *Sepia officinalis*, *Rhizostoma pulmo*, *Belone belone* and *Liza aurata*) seem to be the most affected by marine pollution, based on the frequent number of observations of washed individuals along the beach of Chat Essalam.

In addition, several skeleton-deformed individuals of the two fish species *Belone belone* and *Liza aurata* are often found along the central coast of GG (Fig. 5). Several authors reported similar observations and attribute these anomalies either to the high metallic (Dethlefsen, 1989; Messaoudi et al., 2009a, 2009b) or radioactive pollution of the marine environment (Trapeznikov et al., 1994; Bogutskaya et al., 2011). Therefore, in the case of the central part of GG, PG metallic and radioactive pollutants can act separately and/or synergistically to cause these fish skeletal malformations. Indeed, 14,400 t of dry phosphogypsum (which is known to be a radio-chemical waste) are daily released into the open sea without any treatment (El Zrelli et al., 2017).

Summarizing, the present work dealt with studying the seawater in GG through the assessment of its quality status and the identification of the local pollution sources. The pollution index method highlighted that there is an increasing gradient of seawater quality degradation approaching the industrial complex of Gabes (either from north or from south). Furthermore, the comparison of seawater quality close to industrial and domestic discharge sources with the Tunisian standards highlighted that the major polluting effects are exerted by industrial sources and not by domestic ones. For instance, GCT and ICF wastes appeared to decrease the pH and increase the seawater temperature close to their discharge sources as well as to enrich the marine environment with fluorine and cadmium (only for GCT). The Pollution Index results indicated that phosphogypsum wastes (dumped by GCT) represent the main and heaviest pollution source which degrades the marine environment quality in the central coastal area of GG. The ICF wastes seem also to accentuate this degradation process. In addition, the environmental effects of industrial discharge sources on the GG seawater quality are heavier than those of domestic discharge sources. Based on these findings, it is recommended to stop dumping phosphogypsum discharges directly in the central coastal area of GG and to adopt very strict rigorous surveillance/control protocols of the industrial and domestic discharges in the local marine environment. The Tunisian authorities have fixed standard levels for these wastes (NT 106-02, 1989), but it appeared from this study that these regulations are not respected in some industries and that the industrial wastes are not in compliance with these standards, due most likely to the absence of any treatment process of wastes preceding their dumping into the marine environment. Treating the industrial and domestic wastes must be compulsory before discharging them into the marine environment, in order to keep the environment safe not only for marine life but also for humans because many hazardous pollutants can be accumulated by marine species and biomagnified in food chains to end in humans leading to serious health risks. The results of the present study confirm that phosphogypsum wastes represent the major degradation factor of marine environment in GG. Therefore, the first step toward the remediation of the local degraded habitats and the protection of marine life must be the prevention of dumping phosphogypsum wastes directly in the marine environment. Once these phosphogypsum wastes are stopped, the coastal ecosystems in the central area of GG are most likely able to establish their auto-remediation. Within this context, it is worth noting that because of some social strikes in 2012, throwing phosphogypsum wastes in the coastal area of GG was prevented for three continuous months, during which an obvious improvement of the coastal habitat quality was observed. This improvement includes the re-apparition of some species which disappeared since long time from the inter-harbor zone (area between the port of Gabes and that of Ghannouch), change of the seawater color from brown to turquoise and change of the bottom sediment color from black to clear white. Besides, during these three months of phosphogypsum waste prevention, the flowering process of *P. oceanica* seagrass was observed. Note that the phenomenon of

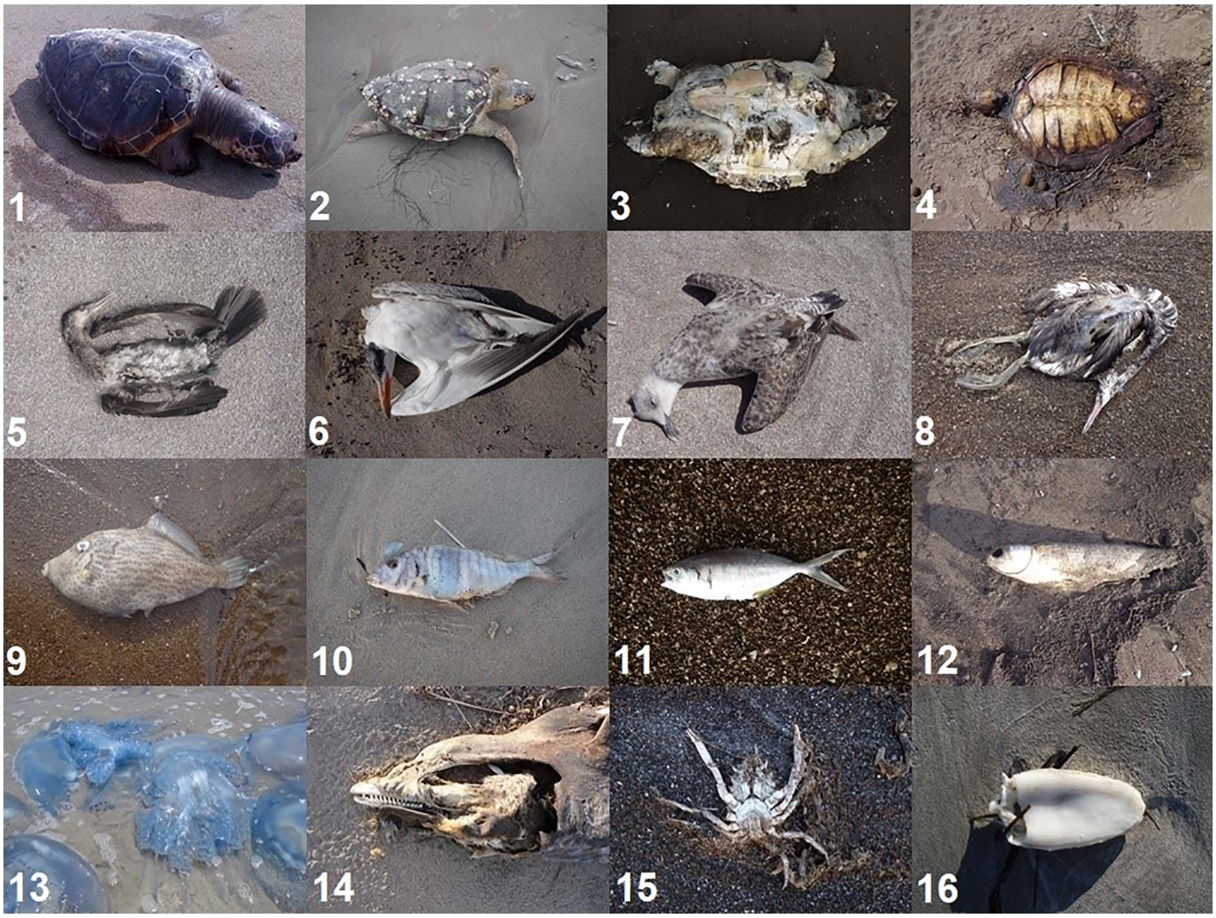

Fig. 4. Photographs of dead organisms/species encountered frequently in the inter-harbor area (Chat Essalam area). 1, 2, 3, and 4: *Caretta caretta*; 5: *Phalacrocorax carbo*; 6: *Hydroprogne caspia*; 7: *Larus argentatus*; 8: *Podiceps cristatus*; 9: *Baliste cabri*; 10: *Lithognathus mormyrus*; 11: *Pomatomus saltatrix*: 12: *Liza saliens*; 13: *Rhizostoma pulmo*; 14: *Tursiops truncatus*; 15: *Maja crispata*; 16: *Sepia officinalis.*

Fig. 5. Skeleton-deformed individuals of *Belone belone* (upper panel) and *Liza aurata* (lower panel) observed along the central coastal area of Gabes Gulf.

P. oceanica flowering has been rarely observed in the central area of GG since 1972. All these observations show clearly that the ecological equilibrium of the coastal ecosystem in central GG can be achieved by only preventing the phosphogypsum wastes in the marine environment.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2017.12.012.

Acknowledgments

This work is dedicated to the memory of Nader Chkiwa (28.04.1986/08.08.2017), the ex-president of the "Association de la Protection de l'Oasis de Chatt Sidi Abd Essalam". The authors would like to thank all those who helped in field sampling, laboratory analyses and providing useful data for the realization of this work. We are also grateful to the reviewer who helped to improve the quality of the manuscript.

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