Occurrence, origin and potential ecological risk of dissolved polycyclic aromatic hydrocarbons and organochlorines in surface waters of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea)

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ABSTRACT

We investigated the occurrence, origin, and potential ecological risk of dissolved polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs) and organochlorine pesticides (OCPs) in 27 surface water samples collected from a highly anthropized and industrialized area in the Gulf of Gabès (Tunisia, Southern Mediterranean Sea) in October–November 2017. The results demonstrated a wide range of concentrations (ng L^{-1}) with the following decreasing order: $\Sigma16$ PAHs (17.6–71.2) > $\Sigma20$ PCBs (2.9–33.7) > $\Sigma6$ DDTs (1.1–12.1) > $\Sigma4$ HCHs (1.1–14.8). Selected diagnostic ratios indicated a mixture of both pyrolytic and petrogenic sources of PAHs, with a predominance of petrogenic sources. PCB compositions showed distinct contamination signatures for tetra- to hepta-chlorinated PCBs, characteristic of contamination by commercial (Aroclor) PCB mixtures. The dominant OCP congeners were γ-HCH, 2,4′-DDD and 2,4′-DDE, reflecting past use of Lindane and DDTs in the study area. Agricultural, industrial and domestic activities, as well as atmospheric transport are identified as potential sources of PAHs, PCBs and OCPs in surface waters of the Gulf of Gabès. Toxic equivalents (TEQs) suggested a low carcinogenic potential for PAHs in seawater samples (mean of 0.14 ng TEQ L^{-1}). Evaluation of risk coefficients revealed low risk for PAHs and PCBs, and moderate to severe risk for OCPs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are widespread in the environment (e.g. water, particulate matter, sediment, soil and organisms) and have been a focus of attention due to their persistence nature, bioaccumulation, toxicity, carcinogenicity and long range transport (Lee et al., 2016; Miraji et al., 2021; Nguyen et al., 2014;

Nyarko et al., 2011). They are a serious threat to both ecosystems and human health. As a consequence, many of these compounds are listed as priority pollutants by international organizations (Ashraf, 2017; Guo et al., 2019; Jones and de Voogt, 1999; Muir and Howard, 2006). PCBs and OCPs have been widely used for industrial and agricultural purposes, while PAHs are accidental byproducts of combustion. Therefore, they can be used as chemical tracers for their possible sources (Lin et al., 2013). These pollutants can enter the ocean by various vectors including

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rivers, effluents, runoff and the atmosphere (Barhoumi et al., 2018; Moreno-González et al., 2013; Tolosa et al., 1997). In marine waters, they can undergo diverse processes, such as adsorption onto particles and subsequent sinking to sediments, adsorption on/absorption in biota, and accumulation into the food chains (Jamieson et al., 2017; Luo et al., 2014; Ma et al., 2015). Generally, their fate in the environment is strongly influenced by their physical–chemical properties (Mackay et al., 1992). Due to their hydrophobicity, PAHs, PCBs and OCPs have a tendency to partitioning between the dissolved phase of seawater/coastal waters and particles/sediment (Mhadhbi et al., 2019; Rabodonirina et al., 2015; Zhang et al., 2013). When sediment resuspension occurs due to changes in hydrodynamic processes such as waves, tides and currents, trawling and ship traffic, deposited contaminants in sediments may be again reintroduced to the overlying water, thus causing a secondary contamination (Zhao et al., 2021). In the dissolved state, these compounds may be subjected to quite strong dynamics, i.e., exchange with the atmosphere (deposition, volatilization), photodegradation, interactions with dissolved and particulate organic matter, or transport with water masses. In addition, from their dissolved form, they may bioconcentrate in a variety of micro- and macro-organisms via respiration or passive diffusion (Dachs et al., 2002; Dachs and Méjanelle, 2010; Daewel et al., 2020; Duran and Cravo-Laureau, 2016; Montuori et al., 2014; Salvadó et al., 2019). Therefore, the knowledge of the distribution of dissolved PAHs, PCBs and OCPs is an essential step to better understand and quantify their global budget and their potential impact on a marine environment.

The Mediterranean Sea, a semi-closed aquatic ecosystem, is particularly vulnerable to chemical pollution due mainly to the long history of industrialization of its basin, its high population density, and its natural characteristics (such as large watersheds, high continental inputs, intense and extreme meteorological events, thermohaline circulation) (The MerMex Group, 2011). As consequence, a multitude of chemical pollutants derived from urban, agricultural and industrial activities find their way into the Mediterranean waters (Campillo et al., 2019; Gómez-Gutiérrez et al., 2007; Köck-Schulmeyer et al., 2021; Sánchez-Avila et al., 2012). The Gulf of Gabès (Southeastern Tunisia) is one particular ecoregion of interest within the Mediterranean Sea basin due to its hydrodynamics, biogeochemical and biological features (Ayata et al., 2018; D'Ortenzio and d'Alcalà, 2009). It is one of the most productive areas of the Mediterranean, characterized by hydrodynamics driven by tides and low bathymetry (Béjaoui et al., 2019; Hattab et al., 2013). While the Gulf of Gabès contributes approximately 40% of the national fish production in Tunisia (DGPA, 2015), the coastal zone of the Gulf of Gabès is subjected to high anthropogenic pressures due to numerous industrial and agricultural activities within the zone. The latter are mainly concentrated in great coastal urban centers (Gabès and Sfax cities), which host fishing and commercial harbours, phosphoric acid production plants, municipal landfills, and various industries (Fourati et al., 2018; Nedia et al., 2011; Zaghden et al., 2007). Despite its ecological and biogeochemical importance within the Mediterranean Sea, and at the same time, its high level of anthropogenic pressure, the Gulf of Gabès remains very poorly documented in terms of concentrations of organic pollutants in the dissolved phase of seawater, in particular organochlorine (OCs) compounds such as PCBs and OCPs. In this context, the objectives of this work were i) to describe the spatial distribution of dissolved PAHs, PCBs and OCPs (concentrations, molecular patterns) in surface coastal waters of the Ghannouch-Gabès area (Gulf of Gabès, Tunisia) and compare this distribution with that of core physico-chemical and biogeochemical parameters, ii) to assess the main origins/sources of these organic contaminants, and iii) to determine their potential ecological risk. To our knowledge, this work is the first to provide together levels of dissolved PAHs, PCBs and OCPs in coastal marine waters of Tunisia.

2. Material and methods

2.1. Study area

The Gulf of Gabès is located in the Southeastern part of Tunisia (Southern Mediterranean Sea), and spreads over 400 km of coastline (more than 50% of the Tunisian coastline) between the city of Chebba in the North and the Tunisian-Libyan border in the South (Fig. 1). The Gulf of Gabès, which accounts for ~30% of the Tunisian coastal waters, is characterized by a wide continental shelf, shallow waters (isobaths 50-m deep are reached 110-km offshore), high amplitude (up to 2-m) tides, and hydrodynamics driven by tides and anticyclonic winds (Béjaoui et al., 2019; Zayen et al., 2020). The Gulf of Gabès hosts coastal cities, such as Sfax and Gabès, with concentrated industrial, harbour and agriculture activities. The Ghannouch-Gabès area in the central part of the Gulf, holds one of the biggest industrial zones in Tunisia. This industrial complex includes the Ghannouch commercial harbour, the phosphoric acid industry of the Tunisian Chemical Group, the Gabès Fluorine Chemical Industry, a thermal power plant, petrochemical infrastructures, as well as industries related to agribusiness, building materials, energy production and textiles (El Zrelli et al., 2015, 2018; Fourati et al., 2018). The phosphoric acid industry of the Ghannouch industrial complex has been discharging the phosphogypsum, an acidic by-product of phomanufacturing, into the Gabès coastal waters over the past several decades. The solid phosphogypsum issued from the production of phosphoric acid, diluted with seawater to form gypsum water, is conveyed by several pipes to the South of the Ghannouch commercial harbour where the gypsum water mixes with the cooling water discharged by all the chemical industry units, and finally ends up at sea through a unique canal (Darmoul et al., 1980). Between 1000 and 13,000 t of phosphogypsum is released daily this way into the sea (Béjaoui et al., 2004; El Zrelli et al., 2015). In addition to this phosphogypsum discharges, several wadis carry a variety of urban, industrial and agricultural wastes to marine waters.

2.2. Sampling and in situ measurements

Samples were collected at 27 stations in the Ghannouch-Gabès coastal area during the MERITE cruise from 30 October to 3 November 2017. Stations were distributed along coastal-offshore transects (also corresponding to North-South transects), i.e., S1–S3, S20 in front of El Melah wadi (Northern Ghannouch), S4–S6, S21 in front of El Demna wadi (Northern Ghannouch), S7–S12, S23 in front of Ghannouch industrial complex/commercial harbour and phosphogypsum effluent outlet, S13–S15 in front of fishing harbour and Gabès wadi, and S16–S18, S27 in front of Mersit wadi (Southern Gabès). Also, S19 was positioned as the north most station, S22 close to the Ghannouch industrial complex, in front of Ettine wadi/fluorine discharges, S24 and S25 between the Ghannouch industrial complex and the fishing harbour, and S26 in front of Griaa wadi (Fig. 1, Table S1). Stations S1–S18 (>5-m depth) were sampled on board the vessel "*Rahma*" on 30 October (S1–S6), 1 November (S7–S12) and 3 November (S13–S18). The most coastal stations S19–S27 (<5-m depth) were sampled on board a zodiac-type vessel on 31 October (S23–S27) and 2 November (S19–S22). Stations S1–S11 and S16 were sampled at high tide, while stations S12–S15 and S17–S27 were sampled at low tide. Sunny weather and very calm sea conditions prevailed during the cruise, except during the sampling of stations S13–S18 (3 November) for which windy weather and rough sea conditions were encountered (Fig. 1, Table S1).

At each station, seawater samples for the analyses of dissolved organic pollutants (PAHs, PCBs and OCPs) and other biogeochemical parameters were collected at ~0.5-m depth using a LIMNOS water sampler (Hydro-Bios) equipped with two Schott® glass bottles of 1-L volume each. This sampler allowed the bottles to go down in water closed and thus avoid the sampling of the surface microlayer. The glass bottles were rinsed several times with sea water before filling. Once
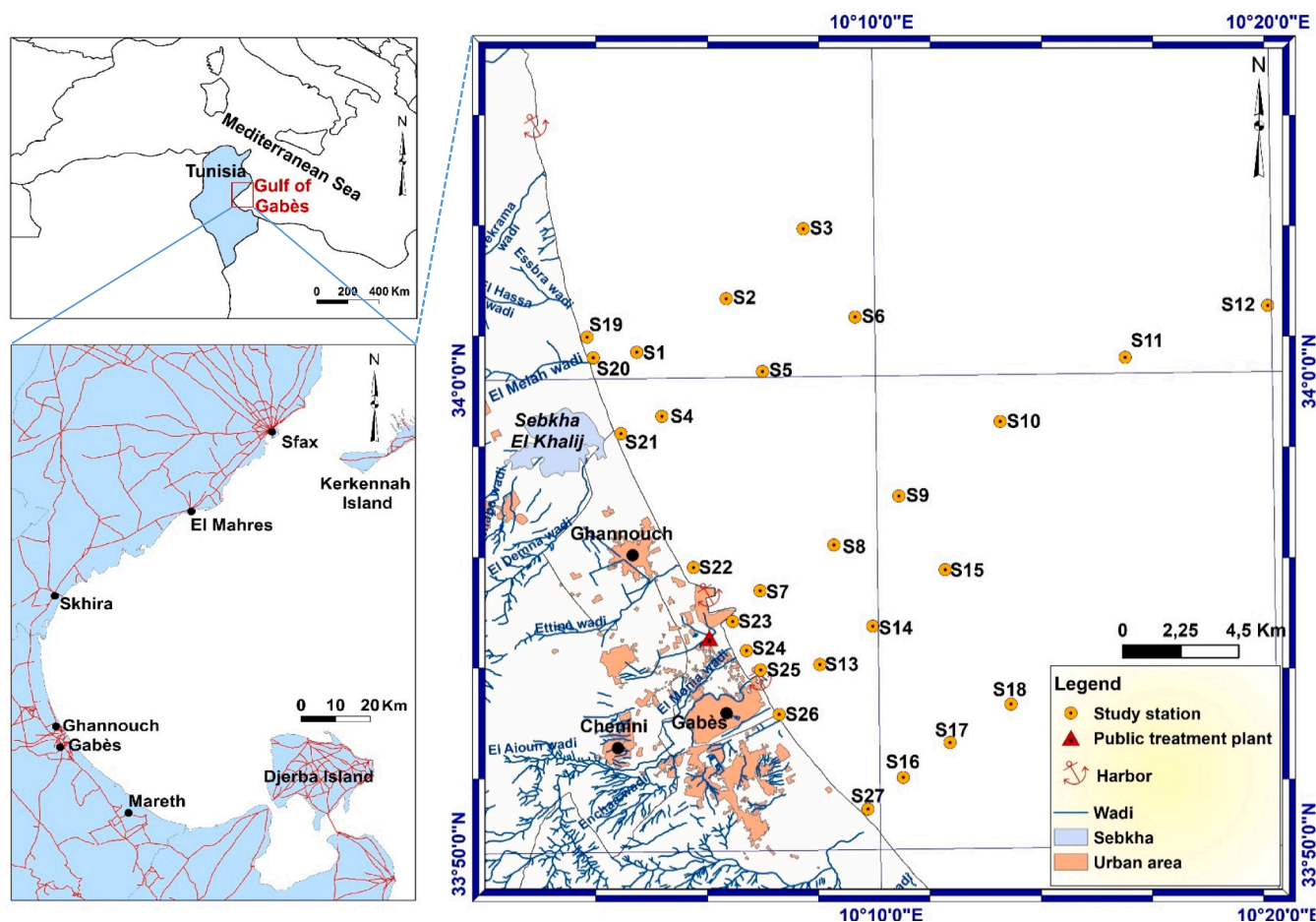
Fig. 1. Location of the study stations in the Ghannouch-Gabès coastal area in the Gulf of Gabès (Tunisia, Southern Mediterranean Sea). The detailed characteristics of the stations are given in Table 1.

filled, they were unscrewed from the sampler, closed with their Teflon lined caps, and stored in the dark at 4 °C. Before sampling, the glass bottles were extensively washed with 1 M hydrochloric acid (HCl) and ultrapure (resistivity 18.2 MΩ cm) water, and baked at 450 °C for 6 h.

Besides sampling, in situ profiles of temperature, salinity, concentration of total chlorophyll *a* (TChl*a*) and turbidity were conducted in the water column (from 0.5-m depth to the bottom) using a 19 *plus* SBE conductivity-temperature-depth (CTD) profiler (SeaBird Electronics, Inc.) equipped with a WETStar Chl*a* fluorometer (WETLabs, Inc.) and a STM turbidity meter (Seapoint, Inc.). Moreover, a Tripod multiparameter probe (Aqualabo) was deployed in surface waters (at ~0.5-m depth) for the measurement of temperature, salinity, pH, dissolved oxygen (O_2) concentration and redox potential (redox). Sensors were calibrated just before the cruise according to manufacturer's procedures.

2.3. Filtration of samples

Once in the laboratory, seawater samples were immediately filtered under a low vacuum (<50 mmHg) through pre-baked (450 °C, 6 h) GF/F (~0.7 μm) glass fiber filters (25- or 47-mm diameter, Whatman) using glassware filtration systems. For dissolved organic pollutants (PAHs, PCBs, OCPs), 1 L of sample was filtered through 47-mm diameter GF/F filters. Filtered samples were stored in 2.5 L glass bottles with 50 mL of dichloromethane (CH_2Cl_2) at 4 °C in the dark before solvent extraction.

For the determination of the concentrations of suspended particulate matter (SPM), particulate organic carbon and nitrogen (POC and PON), as well as $\delta^{13}C$ and $\delta^{15}N$ isotopic ratios, between 250 and 1100 mL of sample were filtered with pre-weighted 25-mm diameter GF/F filters

(the same filter was used for SPM, POC, PON, $\delta^{13}C$ and $\delta^{15}N$ analyses). After seawater filtration, filters were rinsed with ultrapure water to remove salts, and then were dried at 60 °C for 24 h and stored in aluminum foil until analysis.

2.4. Analytical procedures for PAHs, PCBs and OCPs

The analyzed compounds included 16 PAHs, 20 PCB congeners and 10 OCPs (Text S1, Table S2). The targeted PAHs were naphthalene (Nap), acenaphthylene (Acy), acenaphtene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP), and indeno[1,2,3-*cd*]pyrene (IcdP). The 20 PCBs congeners were PCB 8, 18, 28, 52, 44, 66, 77, 101, 105, 118, 126, 128, 138, 153, 170, 180, 195, 206, 187 and 209. The 10 OCPs were four hexachlorocyclohexanes (α-HCH, β-HCH, γ-HCH, δ-HCH), as well as two dichlorodiphenyltrichloroethanes (2,4′-DDT, 4,4′-DDT) and their metabolites, dichlorodiphenyldichloroethylenes (2,4′-DDE and 4,4′-DDE) and dichlorodiphenyldichloroethanes (2,4′-DDD and 4,4′-DDD). Details on analytical procedures for the determination of dissolved PAHs, PCBs and OCPs including chemicals, extraction/cleanup and instrumental analysis are presented in Text S1. Briefly, water samples (dissolved phase) were spiked with a multi standard mixture containing surrogate standards for PAHs, PCBs and OCPs, and extracted by liquid–liquid extraction (LLE). The extracts were then purified using silica-alumina columns, internal standards were added before the analysis which was subsequently performed using gas

chromatography coupled with a mass spectrometer (GC–MS) and an electron capture detector (GC-ECD) (Text S1, Table S2).

2.5. Quality assurance/quality control

All data were guaranteed through the implementation of strict QA/QC procedures. Before use, all glassware was intensively cleaned and baked at 450 °C for 6 h. All the material that could not be baked was washed with 1 M HCl, ultrapure water, *n*-hexane:acetone mixture 1:1 (v/v) and then dried at room temperature. Procedural blanks (to determine the contamination introduced during extraction and cleanup) were processed in the same way as the real samples and were included with each batch of 5 samples. Most of the analytes were not detected in blanks, except Nap, Acy, Ace, Flu, Phe, Ant, Flt, Pyr, BaA and Chr. Their amounts were not significant relative to that of the water samples (<7%). The recoveries of target compounds were checked using standard mixtures spiked in ultrapure water (50 ng for PAHs, 20 ng for PCBs and 30 ng for OCPs). They ranged from 63 to 114% (mean of 87%), 7 to 117% (mean of 85%) and 20 to 115% (mean of 79%) for PAHs, PCBs and OCPs, respectively (Table S2). The surrogate standard (added to perform the quantification) recoveries ranged from 69 to 92% and from 66 to 84% for PAHs and OCs, respectively (Table S3). Method detection limits (MDLs) defined as mean blank value $+3 \times$ standard deviation (SD) ranged from 0.04 to 2.66 ng L^{-1}, 0.03 to 0.42 ng L^{-1} and 0.10 to 0.40 ng L^{-1} for PAHs, PCBs and OCPs, respectively (Table S2). For compounds that were not detected in blanks, instrument detection limits (IDLs), determined as a signal-to-noise ratio (S/N) of 3, were substituted. If the concentration of a given compound in a sample was below its MDL/IDL, thus this compound was considered as not detected in the sample, and was assumed zero. All data reported here were blank corrected.

2.6. Data handling and risk assessment

The low molecular weight (LMW) PAHs (Nap, Acy, Ace, Flu, Phe, Ant) are petrogenic (non-combustion processes) origin while the high molecular weight (HMW) PAHs (Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, BghiP, IcdP) are rather associated with incomplete pyrogenic processes origin. In addition, two molecular PAH ratios, i.e., Flt/(Flt + Pyr) and Ant/(Ant + Phe) were used to identify the possible PAH sources (petrogenic versus pyrogenic) (Table S4). According to their degree of chlorination, the 20 PCBs can be classified into 9 groups: di-(PCB-8), tri- (PCB-18 and -28), tetra- (PCB-52, -44, -66 and -77), penta- (PCB-101, -105, -118 and -126), hexa- (PCB-128, -138 and -153), hepta- (PCB-170 and -180), octa- (PCB-195), nona- (PCB-206) and deca-PCBs (PCB-187 and -209). Among the 20 PCB congeners targeted, seven PCBs (PCB-28, -52, -101, -118, -138, -153, and -180), are named indicators PCBs (Σ7 IN-PCBs). Among the 10 targeted OCPs, Σ4 HCHs represent the sum of α-, β-, γ- and δ-HCH and Σ6 DDTs represent the sum of 2,4′-DDT, 4,4′-DDT, 2,4′-DDE, 4,4′-DDE, 2,4′-DDD and 4,4′-DDD. Two ratios, (DDE + DDD)/ ΣDDTs and DDD/DDE, were used to determine the recent/historical character of DDT contamination and to determine the type of biodegradation mechanism (aerobic or anaerobic) to which DDT is subjected in the study area (Table S4), respectively.

To estimate the environmental risk posed by PAHs in the study aquatic system, toxicity equivalents (TEQs) was calculated using Toxicity Equivalent Factors (TEFs) (Nisbet and LaGoy, 1992), as follows:

$$TEQs = TEF \times PAH \text{ concentration}$$

The risk quotients of negligible concentrations $RQ_{(NCs)}$ and maximum permissible concentrations $RQ_{(MPCs)}$ (Cao et al., 2010) were calculated as follows:

$$RQ_{(NCs)} = C_{PAHs}/C_{(NCs)}$$

$$RQ_{(MPCs)} = C_{PAHs}/C_{(MPCs)}$$

Finally, the risk of PAHs on benthic species endemic in the water column ($\sum$RQs) was calculated by the sum of RQs for individual PAHs, as follows:

$$RQ_{\Sigma PAHs(NCs)} = \sum_{i=1}^{16} RQi \left(RQ_{(NCs)} \geq 1 \right)$$

$$RQ_{\Sigma PAHs(MPCs)} = \sum_{i=1}^{16} RQi \left(RQ_{(MPCs)} \geq 1 \right)$$

The interpretation of the risk classification of individual PAHs and ΣPAHs are as follows (Cao et al., 2010). In principle, $RQ_{(MPCs)} > 1$ indicates that contamination by the single PAH is sever, whereas an $RQ_{(NCs)} < 1$ indicates that a single PAHs is probably of negligible concern. In the case of $RQ_{(NCs)} > 1$ and $RQ_{(MPCs)} < 1$, contamination of the single PAH might be considered moderate. For $RQ_{\Sigma PAHs}$, $RQ_{\Sigma PAHs (MPCs)} < 1$ indicates PAH contamination is low-level, while $RQ_{\Sigma PAHs(NCs)} > 800$ would indicate severe PAH contamination. If $RQ_{\Sigma PAHs(NCs)} \geq 1$ or <800 and $\sum RQ_{(MPCs)} > 1$, it likely indicates moderate PAH contamination.

Regarding OCP and PCBs, the risk assessment was estimated similarly using the following equations:

$$RQ = C_{TCs}/C_{QV}$$

$$RQ_{CCCs} = C_{TCs}/C_{QV\ (CCCs)}$$

$$RQ_{CMCs} = C_{TCs}/C_{QV\ (CMCs)}$$

where, C_{TCs} is the concentration of targeted contaminants, C_{QV}, is the corresponding quality values of certain OCPs and PCBs, RQ_{CCCs} is the risk quotient for continuous criteria concentrations (CCCs), whereas RQ_{CMCs} is the risk quotient for maximum criteria concentrations (CMCs) (United States Environmental Protection Agency (USEPA), 2006).

2.7. Other analyses

After 24 h in the desiccator, 25-mm GF/F filters were reweighed by the same balance that was used for pre-weighting. The SPM concentration was then calculated as the difference between filter weight before and after sample filtration, normalized to the filtration volume (Neukermans et al., 2012). POC and PON concentrations, and $\delta^{13}C$ and $\delta^{15}N$ stable isotopic ratios were determined by high combustion method with mass spectrometer (Raimbault et al., 2008). Measurements of fluorescent dissolved organic matter (FDOM) at 254-nm excitation wavelength and 360-nm emission wavelength were performed on unfiltered (raw) seawater samples (~500 mL) with a UV EnviroFlu-HC fluorometer (TriOS Optical sensors) (Tedetti et al., 2010). Here, fluorescence data are provided in relative unit (RU).

2.8. Statistics

Statistical analyses, including Pearson correlations and a principal component analysis (PCA) based on Spearman's rank order correlation matrix, were performed using XLSTAT 2013.5.01. Colour maps of physico-chemical parameters and pollutant concentrations were carried out using Ocean Data View (ODV) software version 4.6.5 (http://odv.awi.de). The spatial interpolation/gridding of data was conducted using Data-Interpolating Variational Analysis (DIVA) (Barth et al., 2010; Troupin et al., 2012).

3. Results

3.1. Spatial distribution of physico-chemical and biogeochemical parameters

The spatial distribution of temperature, salinity, pH, FDOM, O₂ concentration, and redox potential in surface waters in the study area (at

~0.5-m depth) is shown Fig. 2. Temperature did not display any strong variability (from 21.48 °C at S4 to 23.43 °C at S22), nor any clear trend relative to the phosphogypsum effluent outlet (S23, Fig. 2a). However, salinity, pH, FDOM and O_2 concentration exhibited a distribution pattern related to the effluent. Indeed, the most coastal stations, particularly stations S23, S24 and S25 (the three stations located between the two harbours and directly under the influence of the effluent) presented the highest salinity values (40.11–40.95), the lowest pH values (7.49–7.82), the highest FDOM values (1089–1410 RU), and the highest O_2 concentrations (9.6–10.6 mg L^{-1}) (Fig. 2b–e). Stations S22 and S26, situated North and South of these 3 stations, respectively, also

showed higher values of FDOM (634–824 RU), O_2 concentration (8.6–9.8 mg L^{-1}), and lower values of pH (8.17–8.29) relative to the other stations. In contrast, the lowest values of salinity (<39.40), FDOM (<600 RU), O_2 concentration (<8.0 mg L^{-1}), and the highest values of pH (>8.30) were encountered mostly in the Northern and offshore sites (S1–S11) (Figs. 2b–e). Redox potential displayed the lowest values (<200 mV) along the transect in front of Ghannouch commercial harbour/phosphogypsum discharges (S7, S8, S10, S11), whereas the highest values (>260 mV) were found in the Southern part (S13–S18) (Fig. 2f).

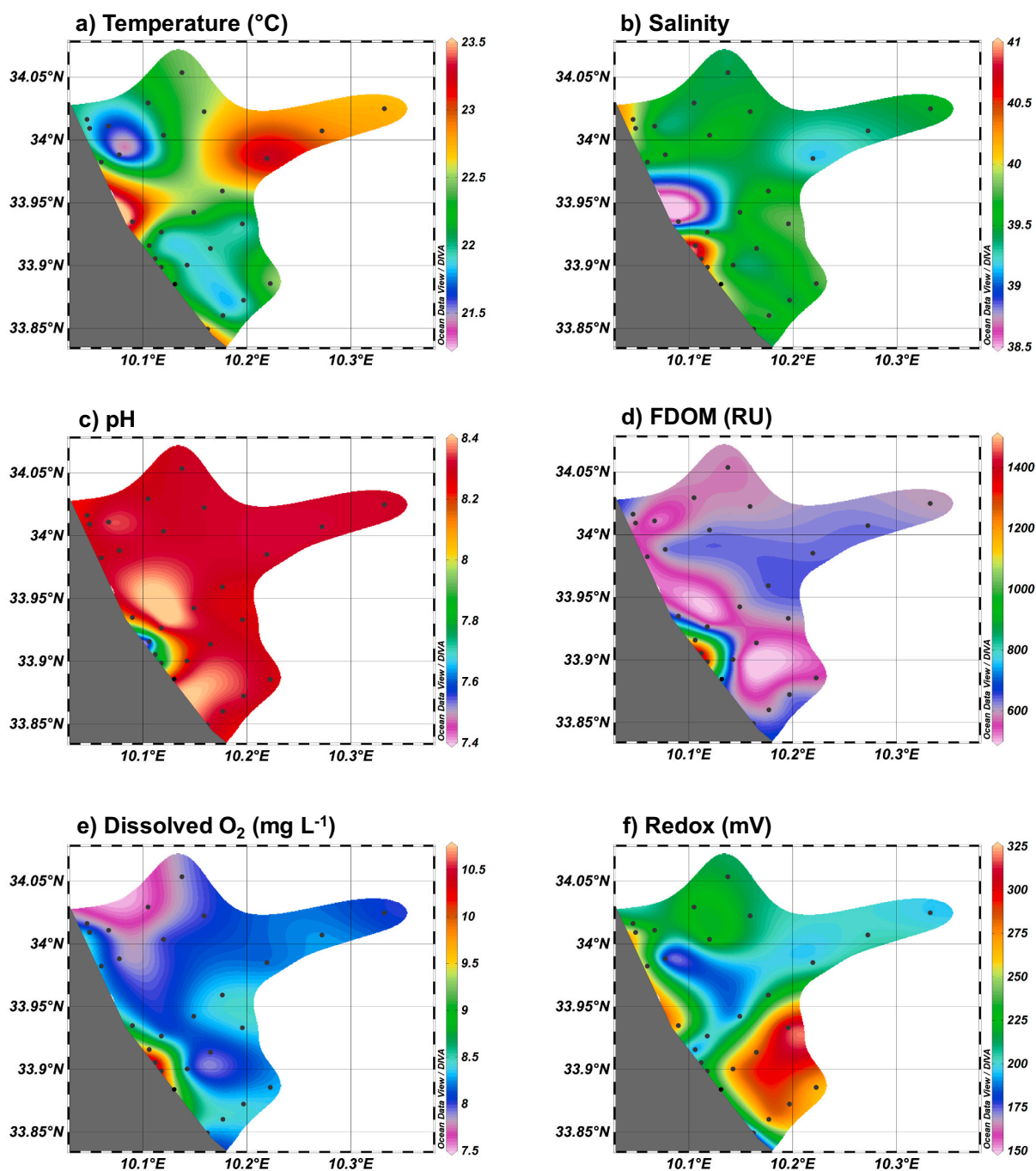The coastal stations S23–S25 were also characterized by the highest

Fig. 2. Spatial distribution of a) temperature, b) salinity, c) pH, d) fluorescent dissolved organic matter (FDOM) at 254-nm excitation wavelength and 360-nm emission wavelength (in relative unit, RU), e) dissolved oxygen (O_2) concentration, and f) redox potential in coastal surface waters (at ~0.5-m depth) of the Gulf of Gabès. Spatial interpolation was made using Data-Interpolating Variational Analysis (DIVA) method from Ocean Data View (ODV) software version 4.6.5. http://odv.awi.de.

POC and PON concentrations (73.2–89.6 μM and 8.9–10.9 μM, respectively), the highest SPM values (15.0–16.8 mg L^{-1}), and the lowest δ^{15}N values (−1.2–1.9‰) (Table S5). On the other side, the lowest concentrations of POC, PON and SPM were recorded in the Northern and offshore sites (S3, S4, S8, S11) (Table S5). Also, salinity, FDOM, O$_2$ concentration, POC, PON and SPM concentrations were positively (linearly) correlated to each other (r = 0.65–0.97, n = 15, p < 0.0001–0.009), while these latter were all negatively correlated to pH (r = −0.70–0.93, n = 15, p < 0.0001–0.004). Turbidity and TChl$a$ concentration, albeit not measured in stations S19–S27, showed higher values in the Southern stations (S13–S18) than in the Northern ones (Table S5). Overall, these results highlight coast-offshore and South-North gradients of the different physico-chemical and biogeochemical parameters, with a substantial influence of the phosphogypsum effluent outlet on the local biogeochemistry.

3.2. Spatial distribution of total dissolved PAHs, PCBs and OCPs

The spatial distribution of concentrations of Σ16 PAHs (sum of 16 compounds), Σ20 PCBs (sum of 20 congeners) and Σ10 OCPs (sum of 10 compounds) in surface waters (at ~0.5-m depth) is provided Fig. 3. Detailed information about individual compounds is given in Table S6. Concentration of Σ16 PAHs was the highest in the vicinity of Ghannouch industrial complex: at stations S8 and S9 (62.7–71.2 ng L^{-1}), in front of Ghannouch harbour/phosphogypsum discharges, at station S22 (64.9 ng L^{-1}), in front of Ettine wadi/fluorine discharges, at stations S4, S19, S20 (40.5–59.8 ng L^{-1}), Northern Ghannouch, and at station S24 (46.1 ng L^{-1}), between Ghannouch and Gabès harbours (Fig. 3a, Table 1). Concentration of Σ20 PCBs showed a quite different distribution with the highest values found off Ghannouch-Gabès area (at S9: 33.7 ng L^{-1} and S11: 31.4 ng L^{-1}), Northern Ghannouch (at S1: 22.1 ng L^{-1}), and in

front of fishing harbour and Gabès wadi (at S13: 28.3 ng L^{-1}) (Fig. 3b, Table 1).

For OCPs, concentration of Σ4 HCHs displayed a distribution pattern relatively similar to that of PAHs, with the highest values observed around the Ghannouch industrial complex and Northern Ghannouch: at stations S8 (14.8 ng L^{-1}), S22 (9.4 ng L^{-1}), S19 and S20 (6.4–7.0 ng L^{-1}) (Fig. 3c, Table 1). Interestingly, Σ16 PAH and Σ4 HCH concentrations were positively correlated (r = 0.72, n = 27, p < 0.001). The highest concentration of Σ6 DDTs observed was in Northern Ghannouch (at S4–S6 and S19: 11.3–13.2 ng L^{-1}), and in front of phosphogypsum discharges (at S8: 12.0 ng L^{-1}), as well as Southern Gabès, in front of Griaa wadi (at S26: 10.9 ng L^{-1}) and in front of Mersit wadi (at S16: 11.7 ng L^{-1}) (Fig. 3d, Table 1). It appeared that the spatial distributions of PAHs, PCBs, HCHs and DDTs were relatively different from those of the physical and physico-chemical parameters described above (i.e., salinity, pH, FDOM, O$_2$ concentration and redox potential) because the contaminant concentrations exhibited less pronounced coast-offshore gradients, and were less driven by the phosphogypsum effluent outlet. PAHs and OCPs (particularly HCHs) nonetheless seemed to show more similarities with physico-chemical parameters than PCBs, especially regarding their higher concentrations in the Ghannouch/effluent zone.

3.3. Molecular distribution of dissolved PAHs, PCBs and OCPs

Among the 16 PAHs targeted in this study, four were not detected in the samples: BaP, DahA, IcdP, and BghiP (Fig. 4a). The most abundant PAHs were Nap (on average 63% of total PAHs, ranging from 27% at S7 to 82% at S19) followed by Phe (on average 12%, ranging from 7% at S8, S19, S22 to 25% at S4), and Flt (on average 7%, ranging from 1% at S8, S22 to 36% at S7), while other compounds only accounted for 0–5% on average of total PAHs (Fig. 4a). With respect to size, the concentrations
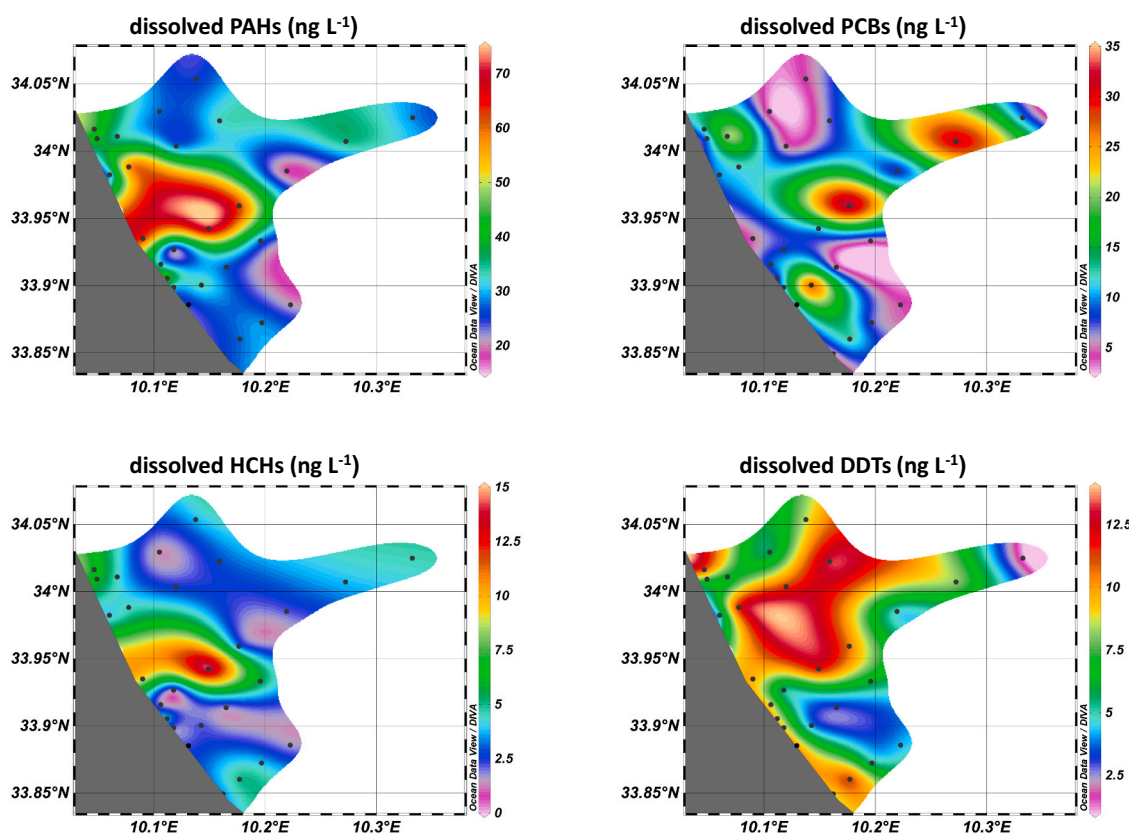

Fig. 3. Spatial distribution of concentrations of total dissolved a) PAHs (sum of 16 compounds), b) PCBs (sum of 20 congeners), c) HCHs (sum of 4 compounds), and d) DDTs (sum of 6 compounds) (in ng L^{-1}) in coastal surface waters (at ~0.5-m depth) of the Gulf of Gabès. Spatial interpolation was made using Data-Interpolating Variational Analysis (DIVA) method from Ocean Data View (ODV) software version 4.6.5. http://odv.awi.de.

Table 1
Total concentrations of dissolved PAHs, PCBs, OCPs, HCHs, DDTs and associated ratios from seawater samples collected at ~0.5-m depth in coastal area of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea).

Stations	PAHs			OCs				
	Σ16 PAHs (ng L^{-1})	Flt/(Flt + Pyr)	Ant/(Ant + Phe)	Σ20 PCBs (ng L^{-1})	Σ10 OCPs (ng L^{-1})	Σ4 HCHs (ng L^{-1})	Σ6 DDTs (ng L^{-1})	DDD/DDE
S1	32.7	0.71	0.01	22.0	11.0	4.3	6.6	0.77
S2	27.7	0.43	*nd*	2.9	6.8	1.3	5.5	1.21
S3	25.0	0.43	*nd*	4.3	12.7	4.1	8.6	0.78
S4	59.8	0.79	0.02	11.6	16.6	4.5	12.1	1.48
S5	27.1	0.50	*nd*	4.6	13.9	2.6	11.3	0.80
S6	32.8	0.73	0.04	6.9	16.1	2.9	13.2	0.69
S7	19.5	0.90	0.16	8.1	6.0	1.1	4.9	3.74
S8	71.2	0.49	0.21	11.2	26.7	14.8	12.0	0.71
S9	62.7	0.47	0.15	33.6	13.5	3.0	10.5	0.64
S10	17.6	0.40	*nd*	7.3	6.7	2.2	4.6	0.63
S11	35.3	0.54	0.05	31.4	12.3	4.0	8.2	0.21
S12	28.3	0.52	0.04	9.6	5.6	4.5	1.1	*nd*
S13	33.5	0.55	0.03	28.3	6.1	2.3	3.8	2.24
S14	26.8	0.44	0.06	4.3	5.3	2.3	2.9	2.38
S15	27.5	0.51	0.03	4.7	11.8	5.6	6.2	*nd*
S16	27.4	0.49	0.03	13.3	16.7	5.1	11.7	1.13
S17	29.0	0.55	0.03	6.7	8.9	3.8	5.0	3.41
S18	20.6	0.48	*nd*	4.6	5.9	1.6	4.3	3.25
S19	45.0	0.53	*nd*	12.7	18.5	7.0	11.5	1.13
S20	40.5	*nd*	0.02	8.5	13.7	6.4	7.3	0.85
S21	27.7	0.81	0.08	10.1	8.2	3.9	4.3	0.57
S22	64.9	0.48	0.18	4.6	19.0	9.4	9.7	0.31
S23	30.9	0.61	0.15	9.4	10.4	1.5	8.9	0.87
S24	46.1	0.43	0.12	6.9	13.7	4.6	9.1	2.93
S25	28.1	0.73	0.04	10.7	10.7	1.5	9.2	0.57
S26	22.9	0.72	0.04	7.6	13.3	2.3	10.9	0.77
S27	25.3	0.47	0.02	4.8	12.3	3.6	8.7	0.42
Min	17.6	0.40	0.01	2.9	5.3	1.1	1.1	0.21
Max	71.2	0.90	0.21	33.6	26.7	14.8	13.2	3.74
Mean	34.7	0.56	0.07	10.8	11.9	4.1	7.9	1.30
Median	28.3	0.51	0.04	8.1	12.3	3.8	8.6	0.80

nd: not determined.

of LMW-PAHs in surface waters of the Gulf of Gabès ranged from 15.8 to 62.4 ng L^{-1} and for HMW-PAHs, the range was 1.4 to 23.3 ng L^{-1}. The Flt/(Flt + Pyr) ratio was 0.56 on average and ranging in values from 0.40 (S10) to 0.90 (S7), while the Ant/(Ant + Phe) ratio was 0.07 on average with values ranging from 0.01 (S1) to 0.21 (S8) (Table 1).

Of the 20 targeted PCB congeners, 11 were not detected in the samples. These were PCB-8, -44, -66, -77, -105, -126, -170, -187, -195, -206, and -209 (Fig. 4b). The relative abundance of the 9 congeners detected was highly variable from station to station. PCB-180 alone accounted for 27% of the PCBs on average, with minimal contribution of 1% (at S10) and maximal contribution of 71% (at S26). PCB-18 and -52 were also detected in large amounts. The two congeners represented 18 and 19% of PCBs on average, respectively, with minimal values of 0% (at S3 and S26 for PCB-18, and at S12, S14 and S15 for PCB-52) and maximal values of 41% (at S20 for PCB-52) or 59% (at S14 for PCB-18) (Fig. 4b). PCB-101, -28 and -153 displayed lower mean relative abundances representing 14, 10 and 6% (respectively) while the sum of the remaining congeners (PCB-118, -128, -138) only depicted 6% of total PCBs (Fig. 4b).

Among OCPs of interest, 2,4′-DDT, 4,4′-DDT and 4,4′-DDD were not at all detected. 2,4′-DDD and 2,4′-DDE compounds were major species, with average contributions to total OCPs of 31 and 28%, respectively, minimal contributions of 0% (at S12, S15) and 4% (at S7, S18), respectively, and maximal contributions of 64% (at S7) and 51% (at S11), respectively (Fig. 4c). They were followed by γ-HCH, which represented on average 19% with minimal and maximal values of 4% (at S11, S14) and 51% (at S12), respectively. The sum of the remaining compounds (α-HCH, β-HCH, δ-HCH, 4,4′-DDE) accounted on average for 22% of total OCPs (Fig. 4c). The DDD/DDE ratio was quite variable, ranging from 0.21 (S11) to 3.74 (S7), with mean and median values of 1.30 and 0.80, respectively (Table 1). Since 2,4′-DDT and 4,4′-DDT were not detected, the (DDE + DDD)/ΣDDTs ratios were all equal to 1 (data

not reported in Table 1).

3.4. PCA classification of stations

Spearman PCA was applied on various parameters including salinity, pH, O$_2$ concentration, FDOM, as well as concentrations of Σ16 PAHs, Σ20 PCBs and Σ10 OCPs (Fig. 5). The first principal component (PC1), which explained 39% of total variability within samples, mainly received the contribution of variables salinity, pH, FDOM and in a lesser extent O$_2$ concentration and Σ10 OCPs. The second principal component (PC2) accounted for 21% of total variability within samples and was mostly related to variables Σ16 PAHs, Σ20 PCBs, followed by O$_2$ concentration and Σ10 OCPs. PCA allowed the discrimination of different groups of stations. Group n°1 (S2, S3, S5, S7, S10, S12, S14, S17, S18, S21 and S27) is rather characterized by high values of pH, low values of salinity, O$_2$ concentration and FDOM, and low concentrations of total dissolved PAHs, PCBs and OCPs. Group n°2 (S1, S6 and S11) is depicted by quite high values of pH, low values of salinity, O$_2$ concentration and FDOM, and high concentrations of total dissolved PAHs, PCBs and OCPs. Group n°3 (S4, S8, S9, S13, S16, S19, S20, S22) is defined by lower values of pH, higher values of salinity, O$_2$ concentration and FDOM, and high concentrations of total dissolved PAHs, PCBs and OCPs. Finally, group n°4 is characterized by roughly low values of pH, high values of salinity, O$_2$ concentration and FDOM, and low concentrations of total dissolved PAHs, PCBs and OCPs (Fig. 5).

4. Discussion

4.1. Concentration levels

The concentrations of total dissolved (Σ16) PAHs (17.6–71.2 ng L^{-1}) recorded here in the surface waters of the Ghannouch-Gabès area
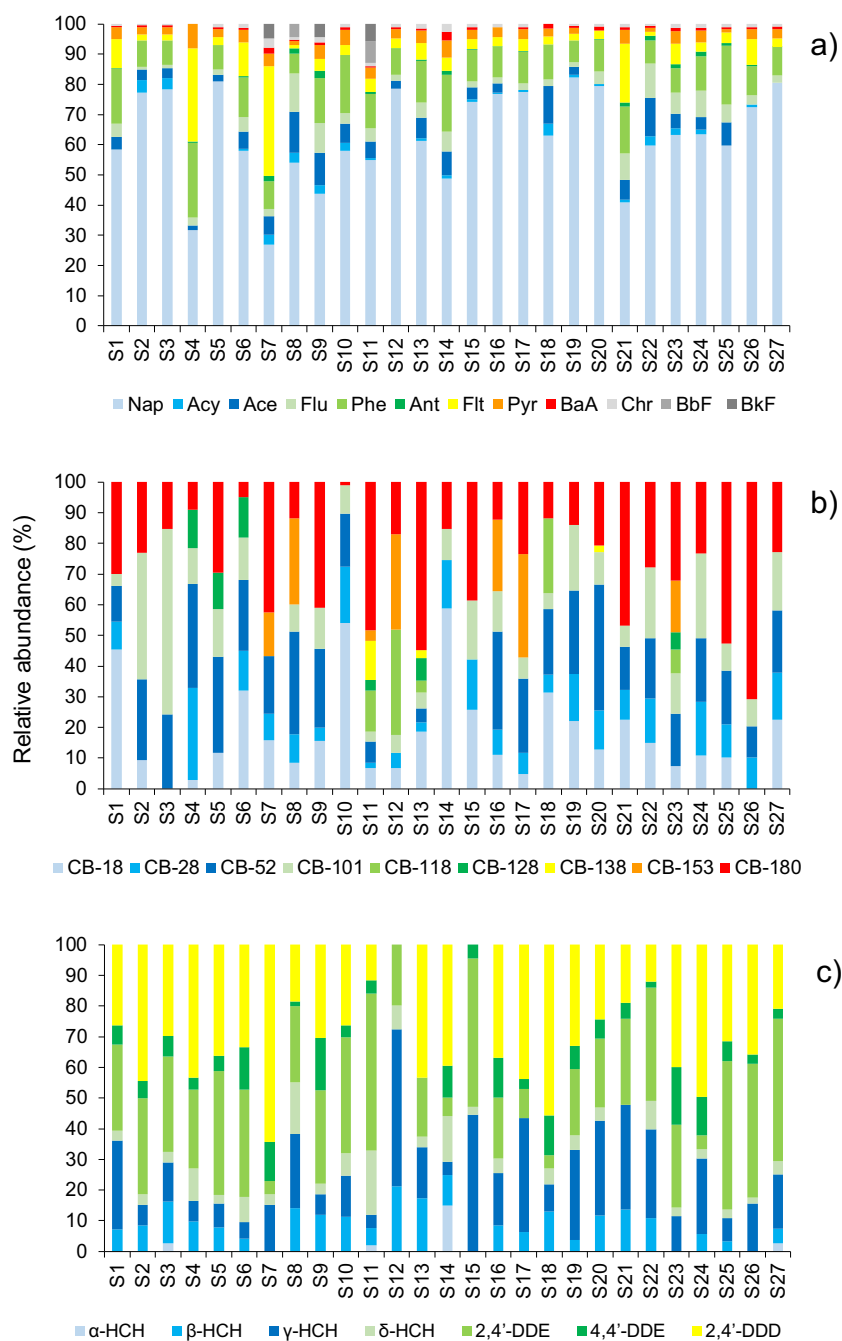
Fig. 4. Relative abundance (in %) of a) 12 PAHs, b) 9 PCBs congeners, and c) 7 OCPs in each station.

(Fig. 3a, Table 1) were of the same order of magnitude but were lower than those recently measured in the neighboring area by Fourati et al. (2018) (i.e., 9–198 ng L^{-1}; Table S7). This difference may be due to the fact that this latter study targeted more compounds (Σ29 PAHs) including alkylated compounds, which are recognized to account for a large part of the pool of dissolved PAHs in natural waters (Guigue et al., 2014; Wang et al., 1999). Also, dissolved PAH concentrations were in the lower range of those reported in coastal Bohai Bay, China (48–607 ng L^{-1} for Σ16 PAHs) (Tong et al., 2019), various coastal areas of the Southern, Northern and Northwestern Mediterranean Sea, such as the Gulf of Tunis, Tunisia (139–1008 ng L^{-1} for Σ24 PAHs) (Mzoughi and Chouba, 2011), the Marseilles coastal area, France (1.9–151 ng L^{-1} for Σ17 PAHs) (Guigue et al., 2011, 2014) and the Alexandria coast, Egypt (13–120 ng L^{-1} for Σ7 PAHs) (El Nemr and Abd-Allah, 2003), but were higher than those observed in the Open Western and Eastern

Mediterranean Sea (0.16–9 ng L^{-1} for Σ19 PAHs) (Berrojalbiz et al., 2011), the Northwest Atlantic coast of the Iberian Peninsula (9.3 ± 0.6 ng L^{-1} for Σ16 PAHs) (Rocha and Rocha, 2021), the European Atlantic coastline, Portugal (8.3–9.5 ng L^{-1} for Σ16 PAHs) (Rocha et al., 2021) and Barcelona, Spain and Banyuls-sur-Mer, France (0.4–8.6 ng L^{-1} for Σ15 PAHs) (Garcia-Flor et al., 2005) (Table S7).

The concentrations of total dissolved (Σ20) PCBs (2.9–33.6 ng L^{-1}) we determined here in the Gulf of Gabès (Fig. 3b, Table 1) were in most cases higher than those recorded in other environments, such as the Open Baltic Sea (0.02 ± 0.01 ng L^{-1} for Σ7 PCBs) (Cornelissen et al., 2008) and the Tokyo Bay, Japan (0.04–0.6 ng L^{-1} for Σ209 PCBs) (Kobayashi et al., 2010). However, they were of the same order of magnitude than those recorded in the Singapore's northeastern and southwestern coastlines (0.22–20.41 ng L^{-1} for Σ8 PCBs) (Basheer et al., 2003), and they were lower than those found in the Daya Bay, China
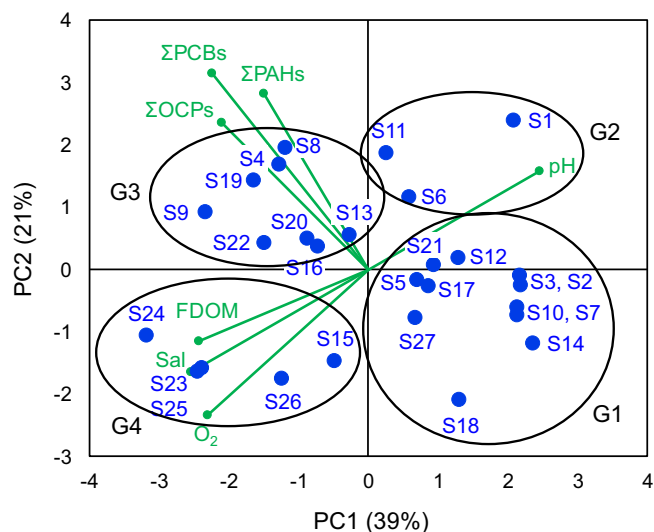
Fig. 5. Principal component analysis (PCA), based on the Spearman's correlation matrix, applied on various parameters measured in coastal surface waters (at ~0.5-m depth) of the Gulf of Gabès, i.e., salinity (Sal), pH, dissolved oxygen concentration (O_2), fluorescent dissolved organic matter (FDOM), and concentrations of total dissolved PAHs (ΣPAHs), PCBs (ΣPCBs) and OCPs (ΣOCPs). Projection of variables (green lines) and samples (blue circles) on the first factorial plane (PC1 versus PC2). Four groups of stations have been highlighted (G1–G4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(91.1–1355.3 ng L^{-1} for Σ12 PCBs) (Zhou et al., 2001), and the Panama Canal and California Coast, USA (*bdl*–18,450 ng L^{-1} for Σ19 PCBs) (Menzies et al., 2013) (Table S7). Urbanization, human activities and particularly, intense industrialization in this area may explain the higher PCB concentrations compared to the other environments.

The concentrations of total dissolved (Σ10) OCPs (5.3–26.7 ng L^{-1}) found here (Fig. 3c and d, Table 1) were in the same range than those measured in Hangzhou Bay, China (1.3–26 ng L^{-1} for Σ10 OCPs) (Li et al., 2016) and Singapore's northeastern and southwestern coastlines (4.9–22 ng L^{-1} for Σ12 OCPs) (Basheer et al., 2003), but lower than that recorded in Jinzhou Bay, China (4.2–136.8 ng L^{-1} for Σ19 OCPs) (Yao et al., 2013) (Table S7). Large differences in pesticide concentrations in global surface waters may be explained mainly by differences in agricultural activities, given the strong connection between OCPs and agriculture (Montory et al., 2017). Although all these comparisons should be taken with caution due to the different number of compounds analyzed, the tendency that emerges is that the concentrations we measured in this work in the Ghannouch-Gabès area (Southern Gulf of Gabès) were in the mid-range of those reported in other coastal environments (Table S7).

4.2. Sources/origins

Compositional profiles for PAHs in water samples are illustrated in Fig. 4a. LMW-PAHs were abundant at all sampling sites, representing on average > 80% of Σ16 PAHs; HMW-PAHs, on the other hand, were present in low concentrations and contributions to Σ16 PAHs. This is typical for surface waters because of the relatively high solubility of LMW-PAHs (log K_{ow} is 3–5 for LMW and 5–7 for HMW) (Moeckel et al., 2014; Shen et al., 2021).

The evaluation of PAH sources by sampling site was achieved by considering published indicators (Table 1) and the analysis of bivariate cross plots, which reflect characteristic PAHs ratios (Fig. S1). Because PAHs naturally partitioned between dissolved and particulate water phases in line with their molecular weight/hydrophobicity, the dominance of the LMW compounds in the present samples (especially Nap

and Phe), which are much more soluble than the HMW ones, cannot be used as an origin/source criterion. For that, isomeric compound ratios, Ant/(Ant + Phe) and Flt/(Flt + Pyr) are more reliable, although they might be affected by weathering processes between the emission points and the sampling area (Katsoyiannis and Breivik, 2014). According to Table 1 and Table S4, PAHs were found to be both pyrolytic and petrogenic origin, with a predominance of petrogenic sources (63% of the stations had a ratio of Flt/(Flt + Pyr) between 0.4 and 0.5, and 89% of the stations had a ratio of Ant/(Ant + Phe) < 0.1) (Ravindra et al., 2006; Soclo et al., 2000; Yunker et al., 2002). The plot of isomeric ratios, Ant/(Ant + Phe) versus Flt/(Flt + Pyr) (Fig. S1), confirm the presence of the last referred sources in surface waters. This reflects the multitude of sources of PAHs in this anthropized coastal area of the Gulf of Gabès through the utilization of petroleum products and incomplete combustion of fossil fuels and biomass (Stogiannidis and Laane, 2015). Petrogenic PAHs could be introduced via accidental oil spills, discharges from routine ship and harbour activities/operations, and urban runoff, while pyrogenic PAHs may enter via exhausts and residues issued from the combustion related to the various urban, industrial and agriculture activities occurring in this region. Moreover, PAHs, particularly LMW-PAHs prevailing in this study, can reach surface waters of the Gulf of Gabès via atmospheric transport over long distances from the Gabès city and other areas. Interestingly, the stations located either in front of (S7–S9, S23) or close to (S22, S24) Ghannouch industrial complex/ commercial harbour and phosphogypsum effluent outlet (Fig. 1, Table S1) presented dissolved PAHs mainly of pyrogenic (combustion) origin, as seen from their Ant/(Ant + Phe) (0.12–0.21) and Flu/(Flu + Pyr) ratios (0.43 and 0.90) (Table 1, Table S4). Moreover, these stations (S7–S9, S22–S24) were marked by higher concentrations of total dissolved PAHs (19.5–71.2 ng L^{-1}; mean and median: 49 and 56 ng L^{-1}) compared to the other stations (17.6–59.8 ng L^{-1}; mean and median: 31 and 28 ng L^{-1}). This could be the sign of a specific PAH fingerprint due to the whole Ghannouch industrial complex activity.

The dissolved phase was mostly enriched by PCBs displaying a low degree of chlorination, i.e., tri- (CB-18, CB-28; 28% of total PCBs on average), tetra- (CB-52; 19% of total PCBs on average), penta- (CB-101; 19% of total PCBs on average), and hexaCBs (CB-153; 19% of total PCBs on average) (Table 1, Fig. 4b), which is in agreement with previous observations and may be explained by their higher solubility in water compared to PCBs of higher degree of chlorination (Li et al., 2016; Montuori et al., 2020; Moret et al., 2005). Less chlorinated PCBs are more amenable to long range atmospheric transport than heavier ones (Wania and MacKay, 1995). This suggests that atmospheric transport could be the most important PCB source in the studied region. Furthermore, Tri-CBs, which are mainly used as an insulating liquid for transformer oils and power capacitors (Tang et al., 2020), can leaked into the soil and end up in surface waters via surface runoff and land use (Duan et al., 2013). Surprisingly, CB-180 which is a heptachloro-congener, characterized by a higher number of chlorine atoms (and thus a lower solubility in water), was one of the most abundant PCBs in our samples (27% of total PCBs on average). Generally, CB-180 is not detected or detected at very low levels in the dissolved phase of natural waters (Montuori et al., 2020; Moret et al., 2005; Rabodonirina et al., 2015). Indicator PCBs were detected in the surface waters of the Gulf of Gabès with detection frequency varied from 19 to 100%, and concentrations ranged from 1.8 to 28.4 ng L^{-1}. The levels of Σ7 IN-PCBs were strongly correlated with total PCBs (Σ20 PCBs) (Pearson $r = 0.97$, $p <$ 0.0001) and a conversion factor of 4 can be used to estimate total PCB concentrations (Σ209 PCBs) from 7 IN-PCBs (i.e., Σ209 PCBs = 4 × 7 IN-PCBs). Similar conversion factor was applied by previous studies for sediment and road dust (Anh et al., 2019; Hoai et al., 2010). PCBs are used in industry as a heat exchanger liquid in transformers and capacitors, and as additives in paints, carbonless copy papers and plastics. As in numerous other countries, equipment containing PCBs have been widely used in Tunisia from the 1970s to late 1980s (an import ban of those equipment being occurred in 1986). Generally, sources of PCBs in

marine environment are wastes of electrical transformers, oil spillage, and any historical use of PCB (Mitra et al., 2019). Recently, PCBs have been recorded in Tunisian (Bizerte) coastal areas: in surface sediments, mussels, fishes and atmospheric particles (Barhoumi et al., 2014a, 2014b, 2014c; Barhoumi et al., 2018; Ben Ameur et al., 2013). In these compartments (sediments, fishes, atmosphere), the presence of tetra-chloro-, pentachloro-, hexachloro- and even heptachloro-congeners was consistent with a contribution of commercial (Aroclor) PCB mixtures (Takasuga et al., 2006). In the same way, our PCB molecular distribution may reflect the influence of commercial PCB mixtures.

Various approaches based on the ratio of parent DDTs and their metabolites have been used to assess whether the DDT contamination in a given area can be considered recent, and whether the degradation of DDTs occurred rather under aerobic or anaerobic condition (Hitch and Day, 1992; Hong et al., 2003; Lee et al., 2001; Liu et al., 2008) (Table S4). Here, since parent DDTs were not detected at all in our samples, the ratios $(DDE + DDD)/\Sigma DDTs$ were always equal to 1. This point outs the historical/ancient character of the DDT contamination in the Gulf of Gabès. Moreover, more than half of stations displayed DDD/DDE ratio < 1 (Table 1), which suggests that DDT was rather bio-transformated into DDE under aerobic conditions (Galanopoulou et al., 2005; Mostafa et al., 2007). This is in accordance with the oxidizing conditions prevailing in surface waters of the Gulf of Gabès, as indicated by O_2 concentrations and redox values (Table S5). Therefore, our results indicate that DTTs origin from historical load since only their metabolites have been detected. Prior to their ban in Tunisia early 1984s (APEK, 2005), DDTs were largely used as pesticides in agriculture in the environment of the Gulf of Gabès, thus the current flux may come from places where they have remained via runoff and wadis or the sediment resuspension. The highest DDT concentrations measured at stations S4 (12.1 ng L^{-1}), S5 (11.35 ng L^{-1}), S6 (13.23 ng L^{-1}) and S19 (11.5 ng L^{-1}) located in front of El Demna and El Melah wadis (Northern Ghannouch), and station S16 (11.66 ng L^{-1}) located in front of Mersit wadi (Southern Gabès), may confirms the last statement. In addition, anti-fouling paints used in boat maintenance could be another source of DDTs in surface water of the Gulf of Gabès, evidenced by the high DDT concentration measured at station S8 (11.97 ng L^{-1}) located in front of Ghannouch harbour/phosphogypsum discharges.

HCHs usually have two formulations: technical-grade (predominantly constituted by α-HCH) and lindane (>99% γ-HCH) (Iwata et al., 1993). The isomer ratio α-/γ-HCH can be used as an indicator of the HCH sources, i.e., technical HCH has α-HCH/γ-HCH ratios ranging between 3 and 7, whereas those of lindane are <1.0 or close to 1.0 (Willett et al., 1998). α-HCH was found in only three sites, in the Gulf of Gabès, whereas γ-HCH was detected at all sites (Table S6), thus yielding ratios lower than technical HCHs. This reflects the fact that HCHs were predominantly of lindane origin. Lindane was usually used in agriculture for seed treatment for beans, barley and wheat, as well as a lesser degree as a pharmaceutical to treat lice and scabies (Barhoumi et al., 2016). Given their high vapour pressure (Shunthirasingham et al., 2010), γ-HCH was probably entered the Gulf via atmospheric transport. Additionally, high detection frequency (85%) of β-HCH was observed, suggested that HCHs were applied in these areas in the past and had degraded, because β-HCH is more stable than other HCH isomers and accumulates in the environment over time (Malik et al., 2009). Direct discharges, surface runoff from surrounding agricultural soils, along with long-range transport may account for the HCHs pollution in this area.

As shown in Fig. 4c, DDTs and HCHs displayed different patterns. This could indicate different types of human activities (agriculture) prevailed in the area, as well as different input sources, e.g., wet and dry deposition sources, surface runoff, and atmospheric transport. DDT and HCH patterns could be also influenced by the physico-chemical properties of isomer compounds along with environmental conditions. In addition, redox potential, topography, and hydrodynamic condition together with other factors play important roles in controlling the

distribution and fate of DDTs and HCHs (Su et al., 2006).

4.3. Potential influence of the industrial effluent and ecological risk assessment

Our results show a significant influence of the phosphogypsum effluent on the local physico-chemistry and biogeochemistry, with the highest values of salinity, FDOM, O_2, SPM, POC, PON, and the lowest values of pH observed in the most coastal stations located between the Ghannouch and Gabès harbours (S23–S25; Fig. 1), and the opposite pattern (i.e., the lowest values of salinity, FDOM, O_2, SPM, POC, PON, and the highest values of pH) found in the Northern and offshore sites, leading to marked coast-offshore and South-North gradients (Fig. 2, Table S5). Hence, the influence of the phosphogypsum effluent mostly appeared South of the Ghannouch industrial complex, in the inter-harbour (Ghannouch-Gabès) zone. These observations are in accordance with recent works, which pointed out a substantial effect of the Ghannouch phosphogypsum effluent on seawater or surface sediment chemistry, with lower pH values and higher concentrations in various major, trace and metal elements in stations situated close to/South of the discharge outlet, and in the inter-harbour area (El Kateb et al., 2018; El Zrelli et al., 2015, 2018). The fact that the phosphogypsum followed a North to South direction, and accumulate in the area between Ghannouch and Gabès harbours is consistent with results from Zayen et al. (2020), who reported, during our sampling period and in our sampling area, the occurrence of a tidally-averaged coastal current flowing from the North to the South, very likely in relation with wind and the regional current. Dissolved organic contaminants (PAHs, PCBs and OCPs) did not closely follow the spatial distribution of salinity, FDOM, O_2, SPM, POC and PON (Fig. 3), neither were correlated to these parameters as seen from the PCA (Fig. 5). They displayed less marked coast-offshore and North-South gradients (particularly for PCBs and DDTs), although PAHs and HCHs presented higher concentrations in the Ghannouch/effluent zone (Fig. 3). This was due to the fact that dissolved PAHs, PCBs and OCPs in coastal surface waters of the Gulf of Gabès very likely originated from various sources including probably the phosphogypsum effluent but also many others as industrial effluents, wadis, runoffs, sediment resuspension, and the atmosphere with aerosol deposition and gas exchanges (Barhoumi et al., 2018; Fourati et al., 2018; Zouch et al., 2018).

Concentrations of the targeted PAH, PCB and OCP molecules in surface waters of the Gulf of Gabès were generally low. As a consequence of their environmental persistence, bioaccumulation and toxicity, the continued exposure to these POPs can pose adverse effects to animals and human health, even at very low levels (Kim et al., 2018). Therefore, the potential risk of those chemicals on aquatic organisms was evaluated. TEFs were applied here to quantify the current mixture of PAHs carcinogenicity in seawater samples (Table 2). The results show that in terms of total TEQs$_{\sum PAHs}$, the measured values were found in the range between 0.04 and 0.51 ng TEQ L^{-1} (mean of 0.14 ng TEQ L^{-1}) which were lower than the threshold values established for BaP in water, suggesting that at the ongoing concentrations the evaluated mixture does not seem able to start carcinogenic responses in aquatic organisms (Abdel-Shafy and Mansour, 2016). TEQs$_{\sum PAHs}$ observed in surface waters of the Gulf of Gabès is comparable to that found in the Atlantic Iberian northwest coastline (Rocha and Rocha, 2021).

It is also important to evaluate if the measured concentrations of PAHs pose ecological risks. As shown in Table 2, RQ$_{(MPCs)}$ of individual PAHs in waters from the study area were all <1, indicating relatively low ecosystem risk (Cao et al., 2010). RQ$_{(NCs)}$ of Chr was <1 indicating almost no risk to the ecosystem, whereas RQ$_{(NCs)}$ of the other PAHs was >1 in at least 7% of samples indicating moderate risks. Concerning the mix of the twelve PAHs (RQ$_{\Sigma PAHs}$), as the value of RQ$_{\Sigma PAHs(NCs)}$ are ≥1 or <800 and those of RQ$_{\Sigma PAHs(MPCs)}$ are ≈0, it is concluded that, overall, the analyzed PAHs have a low risk to aquatic organisms.

Regarding organochlorines, it can be seen that all RQ$_{CMCs}$ values for individual OCPs were <1 and RQ$_{CCCs}$ > 1 suggesting that risk from

Table 2

Toxic equivalence quantities (TEQs) and mean values of RQ$_{(NCs)}$ and RQ$_{(MPCs)}$ of PAHs from seawater samples collected at ~0.5-m depth in coastal area of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea).

PAHs	TEQs (ng L^{-1})				RQs for PAHs								
	TEFs	Min	Max	Mean	NECs	Min	Max	Mean	RQ$_{(NCs)}$ > 1*	MPCs	Min	Max	Mean
Nap	0.001	0.005	0.039	0.021	12	0.436	3.236	1.776	93	1200	0.004	0.032	0.018
Acy	0.001	0.000	0.002	0.001	0.7	0.000	3.469	0.741	30	70	0.000	0.035	0.007
Ace	0.001	0.000	0.010	0.002	0.7	0.000	13.770	2.830	81	70	0.000	0.138	0.028
Flu	0.001	0.000	0.009	0.002	0.7	0.332	12.960	2.708	56	70	0.003	0.130	0.027
Phe	0.001	0.002	0.015	0.004	3	0.592	4.949	1.389	59	300	0.006	0.050	0.014
Ant	0.001	0.000	0.002	0.001	0.7	0.000	2.304	0.409	15	70	0.000	0.023	0.004
Flt	0.01	0.005	0.185	0.028	3	0.154	6.159	0.766	19	300	0.002	0.062	0.008
Pyr	0.001	0.000	0.005	0.001	0.7	0.000	6.849	1.654	81	70	0.000	0.069	0.017
BaA	0.1	0.000	0.078	0.027	0.1	0.000	7.771	2.655	89	10	0.000	0.078	0.027
Chr	0.01	0.000	0.011	0.004	3.4	0.000	0.311	0.104	0	340	0.000	0.003	0.001
BbF	0.1	0.000	0.310	0.030	0.1	0.000	31.000	2.082	7	10	0.000	0.310	0.021
BkF	0.1	0.000	0.277	0.029	0.4	0.000	6.926	0.531	11	40	0.000	0.069	0.005
TEQs$_{\sum PAHs}$		0.040	0.510	0.137	RQ$_{\sum PAHs(NCs)}$	6.550	73.170	17.646		RQ$_{\sum PAHs(MPCs)}$	0.070	0.730	0.176

Percent of stations with RQ$_{(NCs)}$ of PAHs > 1.

measured OCPs is moderate to severe, however, RQ$_{CCCs}$ for PCBs are <1 indicating a low risk (Table 3).

5. Conclusion

The results obtained in this study provided the first detailed analysis of dissolved PAH and OCs (including PCBs and OCPs) distributions in surface water collected from 27 stations in the Gulf of Gabès (Tunisia). PAH levels were lower than those found in other coastal waters around the world, while OC levels were moderated. The tendency that emerges is that the concentrations we measured in this work in the Ghannouch-Gabès area (Southern Gulf of Gabès) were in the mid-range of those reported in other coastal environments. They displayed less marked coast-offshore and North-South gradients (particularly for PCBs and DDTs), although PAHs and HCHs presented higher concentrations in the Ghannouch/effluent zone. Risk assessment based on toxic equivalents (TEQs) indicated that DDTs could induce the highest risks for benthic organisms, whereas ecological risks from PAHs and PCBs were potentially lower. This work provides baseline information for further studies about this Gulf. Since PAHs and OCs levels were only studied in autumn, more studies throughout the whole year with increasing samples sizes are needed to fully understand the levels of PAHs and OCs and the ecological risk assessment of this area.

CRediT authorship contribution statement

Hatem Zaghden: Conceptualization, Investigation, Methodology, Data curation, Writing – original draft, Writing – review & editing. **Badreddine Barhoumi:** Conceptualization, Investigation, Methodology, Data curation, Writing – original draft, Writing – review & editing. **Lobna Jlaiel:** Methodology, Data curation. **Catherine Guigue:** Writing – review & editing. **Lassaad Chouba:** Conceptualization, Data curation. **Soufiane Touil:** Supervision. **Sami Sayadi:** Supervision. **Marc Tedetti:** Conceptualization, Investigation, Methodology, Data curation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hatem Zaghdena reports financial support was provided by French

Table 3

Mean values of RQ (CCCs) and RQ (CMCs) for OCPs and PCBs from seawater samples collected at ~0.5-m depth in coastal area of the Gulf of Gabès (Tunisia, Southern Mediterranean Sea).

	γ-HCH	DDEs	DDDs	PCBs
CMCs (ng L^{-1})	950	1100	1100	–
CCCs (ng L^{-1})	–	1	1	4
MEC*	2.286	4.295	3.568	10.771
RQ$_{CMCs}$	0.002	0.004	0.003	–
RQ$_{CCCs}$	–	4.295	3.568	0.769

* Average measured concentration for OCPs and PCBs in this study (ng L^{-1}).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.113737.

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