Persistent and Emerging Organic Pollutants in the Marine Coastal Environment of the Gulf of Milazzo (Southern Italy): Human Health Risk Assessment

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The Gulf of Milazzo (north-eastern Sicily) has been recognized as Italian Site of National Interest (SNI; areas characterized by high level of contamination with potential effects on human health) in 2005 because of its high level of pollution. In this study we measured the concentration of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), and polyBrominated diphenyl ether (PBDE) in seawater and sediments sampled from the Gulf of Milazzo in order to assess (i) the environmental status of contamination, and (ii) cancer and non-cancer human health risk potentially due to dermal absorption from contaminated seawater and/or ingestion of contaminated fish. Particularly, POPs content in pelagic and demersal fish of different size classes (small, medium, and large) were estimated, starting from the measured seawater and sediments concentrations, using the KABAM model. In particular, Monte Carlo simulation techniques were applied to address uncertainty in assessment of the risk and to provide quantitative estimates of probability of exposition. Ingestion of contaminated pelagic and demersal fish was the dominant pathway of exposition with high probability of significant cancer risk (Ingestion Cancer Risk $>10^{-4}$) and significant non-cancer risk (Hazard Index $>1$). No human health risks emerged to be associated to dermal adsorption from contaminated seawater. Benzo(a)pyrene show the highest Ingestion Cancer Risk with respect to the other PAHs, while the highest Hazard Index for non-cancerogenic molecules was estimated for the PBDE47 congener.

Keywords: human health risk, KABAM, polycyclic aromatic hydrocarbons, organochlorine pesticides, polybrominated diphenyl ether, bio-accumulation factor, risk assessment

INTRODUCTION

Persistent organic pollutants (POPs) are organic compounds with a worldwide occurrence in the marine environment because of their resistance to environmental degradation. The high lipophilicity makes them capable to bioaccumulate in large quantities in tissues of marine organisms. The polycyclic aromatics hydrocarbons (PAHs) are a mixture of aromatic compounds of great environmental concern released both by natural sources (pyrolysis, incomplete combustion...
of organic matter) and anthropogenic activities (industrial processes, combustion of wood and fossil fuels, motor vehicles, incinerators, oil plants and oil spills). Several researches indicate that high environmental PAHs concentrations are related to increasing incidence of cancer and mutagenic events for exposed organisms (Ramesh et al., 2012). As a consequence, several high molecular weight PAHs have been classified as recognized (class 1), probable (class 2A), or possible (class 2B) human carcinogens (International Agency for Research on Cancer [IARC], 1987).

On the other side, the intensifications of agricultural activities has led to increased concentration in the environment of pesticides, a group of POPs belonging to organochlorines compounds (OC). Organochlorines are commonly classified as endocrine disrupting chemicals (EDCs) and are reported to increase the risk of hormone-related cancers by interfering with the endocrine metabolism (Wolff et al., 1993; Sohail et al., 2004). Moreover, epidemiological studies demonstrated a positive correlation between high levels of OCs and incidence of hypertension, cardiovascular diseases and other health-related issues in humans (Subramaniam and Solomon, 2006; Jayaraj et al., 2016). Finally, Polybrominated diphenyl ethers (PBDEs) are a group of emerging ubiquitous POPs used as flame-retardants during the production of textiles, paints, furnitures, electronic circuit boards and plastics. Toxicological studies on laboratory animals demonstrated that PBDEs exposure is positively correlated with thyroid homeostasis disruption, neurotoxic effects, reproductive disorders and cancer (Linares et al., 2015). As recommended by the Marine Strategy Framework Directive (MSFD) (2008/105/CE; Descriptor D8), monitoring studies are needed to assess the environmental risk due to traditional and emerging contaminants and their possible adverse effects on wildlife and human health. The Gulf of Milazzo, located in northern Sicily (southern Italy), has been recognized as Site of National Interest (SNI) in 2005 because of its high level of pollution due to the intensive industrial activities started in the 1950. High arsenic concentrations were recorded in seawater (La Pera et al., 2008) while high concentrations of zinc, lead, cobalt, and copper were recorded in sediments (Pepe et al., 2010). In this paper, we report POPs concentration in seawater and sediments of the Gulf of Milazzo in order to assess the human health risk due to the presence of these contaminants. In particular, we evaluate human cancer and non-cancer risk due to POPs in seawater through two ways of exposure: direct contact by skin during summer activities and by ingestion of contaminated fish. Monte Carlo simulation techniques were run to verify the probability distribution of risk indices, useful for a better assessment of pathways of exposition.

**MATERIALS AND METHODS**

**Sampling Strategy**

Seawater stations (n = 16) were sampled in the Gulf of Milazzo, during two oceanographic cruises: Cisas I Milazzo (July–August, 2017) and Cisas II Milazzo (April, 2018) aboard R/V Luigi Sanzo, at three different depths of the water column (surface, intermediate, and bottom) with 10 L “Niskin” bottles. Sediment samples (n = 8) were collected using a box-corer. The sampling stations are shown in Figure 1. Analyses on sediment samples were carried out on samples collected from the superficial 5 cm depth. Seawater samples were preserved in dark glass bottles, previously cleaned with acetone and rinsed with Milli-Q. All the samples were stored at −20°C, until the analysis. During each survey, hydrological parameters (temperature, salinity, dissolved oxygen, fluorescence, and pH) were measured along the water column (more details are reported in the Supplementary Material). The hydrology study showed evidence of a stratified system with a mixed layer depth (MLD) of about 15 m and an evident thermocline, at about 20 m of depth (Supplementary Material). We measured the contaminants only in surface waters.

**Chemical Materials**

All reagents used, methanol (CH$_3$OH), methylene chloride (CH$_2$Cl$_2$), n-hexane (n-C$_6$H$_{14}$), ethyl acetate (C$_4$H$_8$O$_2$), purchased by VWR were pure and pesticides free. The solid phase disk C18 was Empore disk C18 of 50 mm. The PAHs mix standard containing naphthalene (Nap), acenaphthylene (Acn), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaPy), indeno(1,2,3-cd)pyrene (InP), dibenzo(a,h)anthracene (DahA), and Benzo(g,h,i)perylene (BghiP), with a concentration of 100 µg/ml per each congeners, get by Dr. Ehrenstorfer GmbH (PAH-MIX9), was used to calibrate the instrument. The internal standard was a mix of four deuterated PAHs (PAH Mix 25), and a mix of three more deuterated PAHs (PAH Mix77 get by Dr. Ehrenstorfer GmbH) was used to check the recovery. A mix of PBDE (28, 47, 99, 100, 153, 154, and 209) was prepared ad hoc by LabStandard (Italy). Two mixes of OCPs, one containing Alachlor, Aldrin, Dieldrin, Endrin, Isodrin, DDE, DDD, DDT (Σ isomers), Endosulfan (Σ isomers), with a concentration of 100 mg/l each one; and the other containing Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclohexane (Σ isomers), Pentachlorobenzene with

![Figure 1](https://via.placeholder.com/150)
a concentration of 100 mg/l each-one, were prepared ad hoc by LabStandard (Italy).

Chemical Analysis

Seawater Analysis

USEPA Method 525.1, EPA 8270D e EPA 8081 was run to extract and analyze POPs from seawater. Particularly, the extraction of POPs from seawater was carried out, according to US EPA Method 525.1, using a solid phase disk bakerbond speedisk C18 of 50 mm and an apparatus of six extractors coupled with a vacuum system. 1 L of seawater sample was poured onto the disk previously cleaned with 10 ml of CH₂Cl₂, conditioned with 20 ml of CH₃OH and 20 ml of distilled water (with 0.5% of CH₂OH). The elution was run by (i) drying the disk, venting air for at least 10 min with a vacuum pump; (ii) pouring 10 ml of n-Hexane (containing internals standard) was spilled inside the test tube and recovered for GC/MS. Analysis was carried out using a GC/MS Triple Quadrapole (by Thermo Fisher GC Trace 1310 coupled with a TSQ8000 mass spectrometry and Triplus RSH autosampler). The GC was equipped with a DB-5 ms capillary column (30 m × 0.25 mm, 0.25 μm) and with a PTV injector set in large volume mode. PAHs, OCPs and PBDE were determined in SRM Mode as reported in the Thermo Scientific application note 52389.

Sediment Analysis

USEPA Method 3545, EPA 8270D, EPA 8081 was used to extract and analyze POPs from sediments. Synthetically, 2 g of dry, sieved and homogenized sediment, spiked with surrogate standards, was extracted by Accelerated Solvent Extraction (ASE 200, DIONEX, Thermo Scientific) using a hexane/acetone (80:20 v/v) mixture. The clean up was run using SPE Silica Gel and SPE Florisil to PAH and OCPs, respectively. The final extracts were analyzed by Gas Chromatography (GC-MS ISQ; Thermo Finnigan) with Mass Spectrometric detection in Selective Ion Monitoring (SIM) mode for PAH with a limit of detection estimated as 1 μg/kg for each PAH and by Gas Chromatography with mass spectrometric Ion-Trap with tandem mode (GC-Ion Trap Polaris; Thermo Finnigan) in MSN mode for OCPs with a limit of detection estimated as 0.25 μg/kg.

Total Organic Carbon in Sediments

Total organic carbon was determined by a Thermo Electron Flash EA 1112 coupled to a Thermo Electron Delta V Advantage mass spectrometer. Analysis was carried out after elimination of all of the carbonate present in the samples (ca. 10–15 mg of bulk sediment samples were de-carbonated using HCl 1 M in silver cups for 24 h at ambient temperature and then dried in an oven at 60°C). An internal standard (urea with C = 20%, N = 46%) was run every six samples. The detection limit for TOC measurements was established at 0.05%, considering chromatogram peak > 500 mV and correspondingly determining the sample weight.

Quality Control

Laboratory quality control procedures for PAHs, OCPs and PBDEs both in seawater and sediments included analyses of blanks, spiked samples and reference materials for sediments. The recovery measured on artificial seawater spiked with a final concentration of 100 ng/l per each contaminant was between 75 and 115%. A mix of deuterated PAH with a final concentration of 10 ng/l was added before the extraction to monitor the recovery percentage (PAH deuterated MIX) in each seawater sample. The reproducibility measured by three consecutive extractions was less than 20%.

The reference material used for quality control, on sediment analyses, was SRM 1941b-NIST.

The recoveries for each analyte of PAHs ranged between 94 and 107%, the reproducibility was about 10% for all substances, and the accuracy was estimated greater than 10% for each single analysis. The SRM 1941b-NIST reference material was also used to measure the accuracy of total organic carbon percentage (TOC%) in sediment. The accuracy and reproducibility were about 5 and 0.4%, respectively.

Human Health Risk Assessment

The human health risk for resident population was assessed hypothesizing two routes of contaminant exposure:

1) Dermal adsorption during summer activities (e.g., swimming).
2) Ingestion of contaminated fishes.

Dermal Cancer and Hazard Risk

Dermal Hazard Risk (DHR) and Dermal Cancer Risk (DCR) were assessed according to US EPA protocol, Risk Assessment Guidance for Superfund: part E (RAGS, E), following the equations 1–5:

\[
\text{Dose Adsorbed (DA)}_{\text{event}} = \frac{2 \times FA \times Kp \times Cw \times \sqrt{6 \times t_{\text{event}} \times t_{\text{event}}}}{\pi} \quad (1)
\]

\[
\text{Dermal Adsorbed Dose (DAD)} = \frac{DA_{\text{event}} \times EV \times ED \times EF \times SA}{BW \times AT} \quad (2)
\]

\[
\text{Dermal Cancer Risk (DCR)} = \text{DAD} \times SFo/\text{ABS}_{\text{Gl}} \quad (3)
\]

\[
\text{Hazard Quotient Dermal (HQ)} = \text{DAD}/(\text{RfDo} \times \text{ABS}_{\text{Gl}}) \quad (4)
\]

\[
\text{Hazard Index (HI)} = \Sigma HQD \quad (5)
\]

where FA is the fraction of the adsorbed water, \( K_p \) is dermal permeability coefficient calculated per each compound (cm/h) as function of \( K_{ow} \) and molecular weight, \( C_w \) is pollutant.
concentration in surface water (ng/l), \( t \) event is lag time per event
(h/event), \( t_e \) event is the duration of the event (h/event), EV is the
frequency of the event (events/day), ED is the exposure duration
(years), EF is the frequency of exposure (days/year), SA is the skin
surface area (cm\(^2\)), BW is the body weight (kg), AT is the average
lifespan (years, \( AT = ED \) for not cancer risk), SFo is Cancer
Slope Factor oral (mg/kg/day), RfDo is oral Reference Dose
(mg/kg/day), and \( ABS_{GI} \) is the fraction of contaminant absorbed
in the gastro-intestinal tract. The values of these parameters are
shown in Table 1. The combined DCR associated to all congeners
of PAH was calculated as Benzo(a)pyrene TEQ (Eq. 6)

\[
\text{BaPy}_{-\text{TEQ}} = \sum C_i \cdot TEF_i \quad (6)
\]

where TEFi is Toxicity Effect Factor and Ci is the concentration of
each congener in seawater (ng/l). The combined DCR associated
to all POPs was calculated as the sum of each carcinogenic
compound that can injury the same target organ.

**Contaminant Concentrations in Fish Tissues**

Contaminant concentrations in fish were simulated using the
model KABAM (\( K_{ow} \) based Aquatic Bioaccumulation Model)
following Arnot and Gobas (2004), who parameterized a
bioaccumulation model in aquatic ecosystems using the octanol-
water partition coefficient (\( K_{ow} \)) to estimate uptake and
elimination constants through respiration and diet of organisms
in different trophic levels. We used the model to estimate the
concentration of contaminants in edible tissues of pelagic and
demersal fish of 3 size classes, small fish (SF, 10–100 g), medium
fish (MF, 100–1,000 g), and large fish (LF, −1,000 g), starting from
the contaminant concentrations in seawater column and in pore
waters, respectively. Contaminant concentrations in seawater
and sediments were calculated as the average of concentrations
measured in all samples during the two surveys. We used values
corresponding at half of detection limit for not quantifiable
measures. We used the sediment/liquid partition coefficients
(K\(d = K_{oc} \cdot K_{ow} = C_{sediment}/C_{pore \text{ water}} \)) to estimate contaminant
concentrations in pore waters starting from concentrations
measured in sediment samples. Time to steady-state (Tss) for
each compound was calculated using Kow as follows:

\[
\text{Tss(days)} = \left( 0.00654 \cdot K_{ow} + 55, 31 \right)/24 \quad (7)
\]

Contaminant concentrations in fish were measured at 2-year
life for each compound with Tss greater than 730 days
(2 years). Furthermore, we set the KABAM model (ecosystem
input paragraph) according to the diet and habitat of the fish.

**Ingestion Cancer and Hazard Risk**

The Average Daily potential Dose (ADD) was calculated as follows:

\[
\text{ADD} = C_{fish} \times IR \times EF \times ED/(BW \times AT) \quad (8)
\]

where \( C_{fish} \) is the estimated concentration of contaminant in fish
tissue, IR is the Ingestion Rate (gr/days); EF is the Exposure
Frequency (days/years); ED is the Exposure Duration (years); BW
is the Body Weight (kg) and AT is the average lifespan (years,
\( AT = ED \) for not cancer risk). The values of these parameters
are shown in Table 1. The Ingestion Cancer Risk (ICR) was
calculated multiplying the ADD by the Cancer Slope Factor oral
(CSF) of each contaminant:

\[
\text{ICR} = \text{ADD} \times \text{CSF}_{o}/\text{ABS}_{GI} \quad (9)
\]

The combined ICR associated to all POPs was calculated as the
sum of each compound that can injury the same organ. The
Hazard Quotient risk (HQ) regarding non-cancerogenic health
issues was calculated dividing the ADD by the Reference Dose
oral (RfDo) of each contaminant:

\[
\text{HQ} = \text{ADD}/(\text{RfDo} \times \text{ABS}_{GI}) \quad (10)
\]

\[
\text{HI} = \sum \text{HQ} \quad (11)
\]

**Statistical Analysis**

Monte Carlo simulation techniques with 5,000 iterations were
applied to estimate variability and uncertainty in risk assessment.
The repeated sampling was based on probability distributions of
contaminant concentrations in water and fish. The procedure
was performed by R 3.6.1 (R Core Team, 2019). Differences
of contaminant contribution for the ingestion cancer risk were
tested by a non-parametric test (Kruskal–Wallis test) and by
pairwise comparison. The level of significance was set at \( p < 0.05 \).

**RESULTS AND DISCUSSION**

**Occurrence of Contaminants in the Study Area**

The concentrations of PAHs, OCPs, and PBDEs in seawater
and superficial sediments of the Gulf of Milazzo are shown in
Table 2. Higher concentrations of low molecular weight
PAHs (sum of congeners 4, 5 and 6 rings) were more abundant in sediments. Alachlor is the most concentrated OCPs in seawater (average 2.84 ng/l) followed by DDE (average 1.06 ng/l), while PBDE47 is the most concentrated PBDEs (3.58 ng/l). Contaminant concentrations in seawater samples are lower than the maximum admissible concentrations (MAC) set by the Italian Regulations n.172/2015 (application of the European Directive 2013/39/EU, 2008/105/CE, and 2000/60/CE) except for Benzo(ghi)Perylene and \( \Sigma \) PBDE that exceeds the threshold limits in 13 and 5 sampling stations, respectively. Depending on PAHs contamination, seawater could be classified as: micro-polluted, \( \Sigma \) PAHs 10–50 ng/l; lightly-polluted, \( \Sigma \) PAHs 50–250 ng/l; moderately polluted, \( \Sigma \) PAHs 250–1,000 ng/l and heavily polluted, \( \Sigma \) PAHs > 1,000 ng/l according to Chen (2008). The concentrations of \( \Sigma \) PAHs in seawater
TABLE 1 | Variables used for risks determination.

| Variable (symbol)                  | Unit       | Value (dermal absorption) | Value (ingestion rate) | References                        |
|------------------------------------|------------|---------------------------|------------------------|-----------------------------------|
| Fraction absorbed water (FA)       | Unitless   | Chemical specific         |                        | Environmental Protection Agency [EPA], 2004 |
| Dermal permeability coefficient (Kp) | cm/h       | Chemical specific         |                        | Environmental Protection Agency [EPA], 2004 |
| Lag time per event (tau event)     | h/event    | Chemical specific         |                        | Environmental Protection Agency [EPA], 2004 |
| Event duration (tevent)            | h/event    | 0.33                      |                        |                                   |
| Event frequency (Ev)               | Event/day  | 3                         | 1                      |                                   |
| Exposure duration (ED)             | Year       | 30                        | 30                     |                                   |
| Exposure frequency (EF)            | Days/year  | 90                        | 104                    |                                   |
| Surface area (SA)                  | cm²        | 18,000                    |                        |                                   |
| Body weight (BW)                   | kg         | 70                        | 70                     |                                   |
| Averaging time (AT)                | Year       | 70/30                     | 70/30                  |                                   |
| Cancer Oral slope factor (CSfo)    | (mg/kg-day) | 1                         | Chemical specific      | Health Canada [HC] (2007a,b); IRIS (2007) |
| Absorption fraction (ABSgj)        | Unitless   | Chemical specific         |                        | Environmental Protection Agency [EPA], 2004 |
| Oral reference dose (RDj)          | mg/kg-day  | 170                       |                        | INFAN                             |

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ranged from 1.6 to 70.3 ng/l, showing that the site could be classified as micro-polluted/light-polluted by PAHs. Particularly, light-polluted seawaters were found in the stations MZ13 (ΣPAHs = 59.2 ng/l) and MZ43 (ΣPAHs = 70.3 ng/l). PAHs concentrations in sediments (26.94–862.0 µg/kg), are much higher than organochlorine pesticides (2.50–3.72 µg/kg) and PBDE concentrations (0.93–3.72 µg/kg). Hexachlorobenzene (HCB) is the most concentrated organochlorine pesticide in sediments followed by DDD and DDT, while the same concentrations were found for PBDE congeners. Contaminant concentrations in superficial sediments are lower than the maximum admissible concentrations (MAC) set by the European Directive 2013/39/EU, except for Fluoranthene concentrations in 2 sampling stations (MZ13 and MZ33), Benzo(b)fluoranthene in 1 sampling station (MZ13), Benzo(k)fluoranthene in 1 sampling station (MZ13) and Benzo(a)pyrene in 1 sampling station (MZ13). Total PAH concentrations, sediments may be classified according to Soclo et al. (2000) as highly contaminated with PAHs > 500 µg/kg, moderately contaminated with PAHs > 250, and slightly contaminated with PAHs < 250 µg/kg. Our data demonstrate that the superficial sediment samples of the Gulf of Milazzo cover the entire range of contamination. Particularly, high PAHs contamination was found in the stations MZ13 (ΣPAHs = 861 µg/kg) and MZ33 (ΣPAHs = 544 µg/kg). Relatively low values of organic chlorinated pesticides (OCPs) concentrations were found in seawaters and superficial sediment samples suggesting a reduced level of this class of contaminant contribution from agricultural activities in the study area. A comparison of PAHs concentrations in sediments from other industrialized marine sites is shown in Table 3. No sufficient data on OCP and PBDE concentrations in the Mediterranean Sea are available in literature for robust and statistically significant comparisons. This work offers one of the first complete datasets of these classes of contaminants in seawater and sediments from highly contaminated industrial areas.

PAHs Source Identification

The identification of the PAHs source was assessed calculating Fluo/Fluo + Pyr and Ant/Ant + Phe ratios per each sample. Fluo/Fluo + Pyr <0.40 show a petroleum contamination, between 0.40 than 0.50 a liquid fossil fuel (vehicle and crude oil) combustion and >0.50 are characteristic of grass, wood, or coal combustion; Ant/Ant + Pyr <0.1 petroleum and >0.1 pyrogenic sources (Yunker et al., 2002; He et al., 2014; Soliman et al., 2014; Ya et al., 2014). Fluo/Fluo + Pyr and Ant/Ant + Pyr show mean value of 0.41(±0.14) and 0.28(±0.14) in seawater and 0.54(±0.07) and 0.21(±0.2) in sediment. These results suggest both petroleum contamination and pyrogenic source due to refinery activities/marine traffic and thermopower plant.

Health Risk Assessment

Cancer Risk Assessment

The Dermal Cancer Risk (DCR) due to dermal absorption of all contaminants in surface seawater (ΣDCR) for each sampling station ranged from 4.8·10^{-7} to 6.0·10^{-6}. These values are shown in the distribution map (Figure 2), using inverse distance weighting (IDW) and setting a buffer with a fixed distance of 1 km from sampling station, in order to identify the most dangerous area. The average values of DCR for each contaminant ranged from 10^{-13} to 10^{-7} (Table 4). The cancer risk due to fish ingestion ranged from 10^{-13} to 5.0·10^{-4} (Table 4). We estimated the combined cancer risk for different organs supposing additive carcinogenic effects of contaminants with the same target. The information about the target organs of each contaminant was checked using IRIS database. The combined DCR per target organs ranged from 7.0·10^{-9} for breast cancer to 9.4·10^{-7} for lung cancer, while the combined ICR per target organs ranged from 1.7·10^{-7} for breast cancer to 5·10^{-4} for gastro-intestinal cancer (Table 5). The target organ with the highest potential to develop a carcinogenic event is the gastro-intestinal tract (followed by liver, skin, lung, and breast) because of the higher ICR associated with BaPy (2.7·10^{-4}, Table 4). The risks here analyzed are compared with the acceptable risk levels proposed by the international agencies. The US EPA assumed acceptable risk level in a range from 10^{-6} to 10^{-4} (Environmental Protection Agency [EPA], 1991). No remediation measures are required when the cancer risk falls lower than the acceptable range.
### TABLE 2 | Range and mean contaminant concentrations in seawater and sediment.

| Contaminant | Water | Sediment |
|-------------|-------|----------|
|             | Average (ng/l) | Range (ng/l) | MAC (ng/l) | d.l. (ng/l) | Average (µg/kg) | Range (µg/kg) | MAC (µg/kg) | d.l. (µg/kg) |
| PAH         |       |          |           |            |                |                |             |             |
| Napthalene  | 6.43  | 0.10–37.72 | 130000.00 | 0.20       | 1.28           | 0.50–2.88      | 35.00       | 1.00        |
| Acenaphthylene | 0.12 | 0.10–0.17  | 0.20       | 1.39       | 0.50–4.63      | 1.00          |
| Acenaphthene | 0.47  | 0.10–1.20  | 0.20       | 4.49       | 0.50–13.80     | 1.00          |
| Fluorene    | 1.52  | 0.10–3.46  | 0.20       | 3.41       | 0.50–17.40     | 1.00          |
| Phenanthrene | 5.13 | 0.10–12.90 | 0.20       | 20.50      | 1.78–73.60     | 1.00          |
| Anthracene  | 0.74  | 0.10–5.66  | 100.00     | 8.52       | 0.50–19.8      | 24.00         |
| Fluoranthene | 1.18 | 0.10–4.82  | 120.00     | 45.34      | 4.63–177.00    | 110.00        |
| Pyrene      | 2.75  | 0.10–14.10 | 0.20       | 38.21      | 4.28–149.00    | 1.00          |
| Benzo(a)anthracene | 0.63 | 0.10–3.18  | 0.20       | 20.22      | 0.50–84.10     | 1.00          |
| Chrysene    | 0.68  | 0.10–3.35  | 0.20       | 22.09      | 0.47–99.70     | 1.00          |
| Benzo(b)fluoranthene | 0.15 | 0.10–1.53  | 17.00      | 14.10      | 0.50–79.10     | 40.00         |
| Benzo(k)fluoranthene | 0.16 | 0.10–1.99  | 17.00      | 5.80       | 0.50–33.70     | 20.00         |
| Benzo(a)pyrene | 0.16 | 0.10–1.82  | 27.00      | 11.18      | 0.50–60.40     | 30.00         |
| Indeno(123)pyrene | 0.21 | 0.10–3.07  | 0.20       | 12.79      | 0.88–50.90     | 70.00         |
| Dibenzo(ah)anthracene | 0.21 | 0.10–3.03  | 0.20       | 2.59       | 0.50–10.30     | 55.00         |
| Benzo(ghi)perylene | 1.18 | 0.10–4.50  | 0.82       | 12.34      | 1.03–41.30     | 1.00          |
| OCP         |       |          |           |            |                |                |             |             |
| Alachlor    | 2.84  | 0.25–13.00 | 700.00    | 0.50       | 0.13           | 0.13–0.13      | 0.25        |
| Aldrin      | 0.09  | 0.02–0.50  | 5.00       | 0.13       | 0.13–0.13      | 0.25          |
| Isodrin     | 0.03  | 0.03–0.03  | 0.05       | 0.13       | 0.13–0.13      | 0.25          |
| Dieldrin    | 0.06  | 0.03–0.85  | 0.05       | 0.13       | 0.13–0.13      | 0.25          |
| Endrin      | 0.03  | 0.03–0.03  | 0.05       | 0.13       | 0.13–0.13      | 0.25          |
| Endosulfan  | 0.03  | 0.03–0.03  | 4          | 0.05       | 0.13           | 0.13–0.13      | 0.25        |
| Hexachlorobutadiene | 0.01 | 0.01–0.10  | 600.00    | 0.02       | nd             | nd            |
| HexachlorocycloHexane | 0.06 | 0.03–0.13  | 20.00     | 0.13       | 0.13–0.13      | 0.25          |
| Hexachlorobenzene | 0.14 | 0.01–0.62  | 50.00     | 0.35       | 0.10–1.50      | 0.25          |
| DDE         | 1.06  | 0.15–4.86  | 25.00      | 0.16       | 0.13–0.34      | 1.80          |
| DDD         | 0.19  | 0.15–0.59  | 0.30       | 0.25       | 0.25–0.25      | 0.80          |
| DOTop       | 0.19  | 0.15–0.89  | 0.30       | 0.25       | 0.25–0.25      | 1.00          |
| DOTpp`      | 0.16  | 0.15–0.55  | 10.00      | 0.25       | 0.25–0.27      | 1.00          |
| ΣOCPs       | 4.52  | 0.24–20.82 | 2.71      | 2.5–3.72   |                |               |
| PBDE        |       |          |           |            |                |                |             |             |
| PBDE28      | 0.03  | 0.03–0.03  | 4          | 0.05       | 0.10           | 0.10–0.10      | 0.20        |
| PBDE47      | 3.58  | 0.03–21.8  | 0.05       | 0.11       | 0.10–0.20      | 0.20          |
| PBDE99      | 0.03  | 0.03–0.03  | 0.05       | 0.10       | 0.10–0.10      | 0.20          |
| PBDE100     | 0.03  | 0.03–0.03  | 0.05       | 0.10       | 0.10–0.10      | 0.20          |
| PBDE153     | 0.03  | 0.03–0.03  | 0.05       | 0.10       | 0.10–0.10      | 0.20          |
| PBDE154     | 0.03  | 0.03–0.03  | 0.05       | 0.10       | 0.10–0.10      | 0.20          |
| PBDE209     | 0.05  | 0.05–0.05  | 0.10       | 0.41       | 0.18–0.79      | 0.50          |
| ΣPBDEs      | 3.70  | 0.15–21.8  | 1.02      | 0.78–1.39  |                |               |
| TOC (%)     | 0.80  | 0.11–3.73  |            |            |                |               |

MAC, Maximum Admissible Concentrations set by European Directive 2013/39. d.l., detection limit; nd, not determined; the minimum value was set, arbitrarily, for the risk assessment study half of d.l.

within this range. The US EPA assumes the unconditionally acceptable risk level below $10^{-6}$ (Environmental Protection Agency [EPA], 2004) while a risk greater than $10^{-4}$ requires protective measures to mitigate the risk. All the DCRs here found were under the USEPA acceptable range ($10^{-6}–10^{-4}$). We recorded ICRs above the upper bound of the USEPA acceptable range ($10^{-4}$) due to the ingestion of demersal medium and large fishes and pelagic large fishes (Tables 4, 5), suggesting a significant risk to develop cancer for the resident population. The probabilistic distributions of Dermal Cancer Risk (DCR) and Ingestion Cancer Risks (ICR) for small (SF), medium (MF), large (LF) pelagic, and demersal fish were obtained from Monte Carlo simulations (Figures in Supplementary Material). The descriptive statistical values (including 5th percentile, 25th
The hazard index (HI) for the sum of all POPs are given in Table 6 and the ingestion of contaminated fishes (IHQ) and area. The hazard quotients calculated for the dermal adsorption of the sum of contaminants found in the study the non-carcinogenic health risk through ingestion and dermal absorption (2004; WHO, 2010). Hazard Index (HI) were applied to evaluate exert hemato-, cardio-, renal-, neuro-, immuno-, reproductive toxic effects in laboratory animals and humans (Ramesh et al., 2004; WHO, 2010). Hazard Index (HI) were applied to evaluate the non-carcinogenic health risk through ingestion and dermal adsorption of the sum of contaminants found in the study area. The hazard quotients calculated for the dermal adsorption (DHQ) and the ingestion of contaminated fishes (IHQ) and hazard index (HI) for the sum of all POPs are given in Table 6.

We found HQ values less than 1 for all the measured POPs due to ingestion and dermal adsorption, which indicated little or no potential adverse effects on local residents’ health through ingestion and/or dermal absorption of a single contaminant. The exception is represented by the HQ of PBDE47 due to the ingestion of pelagic and demersal large fishes (IHQ = 2.47 and 2.49, respectively; Table 6). According to Table 6, the HIs due to the ingestion of pelagic and demersal medium-large fishes are above the unity, indicating potential adverse effects on local resident’s health due to the ingestion of a mix of pollutants from contaminated commercial fishes. Thus, it can be concluded that the mix of pollutants can cause harmful non-carcinogenic health effects in the resident population of Milazzo. The HQs and HI due to dermal absorption of all contaminants are negligible. The HI values are shown in a distribution map (Figure 3) using inverse distance weighting (IDW). The probabilistic distributions of Dermal Hazard Risk (DHR) and the Ingestion Hazard Risks (IHR) for small (SF), medium (MF), large (LF) pelagic and demersal fishes were obtained from Monte Carlo simulations (Figures in Supplementary Material). The descriptive statistical values (5th percentile, 25th percentile, median, 75th percentile and 95th percentile) are reported in Table 8.

Table 7. Integration of variability can lead to a more realistic evaluation of risk estimation, that could be affected by data scarcity, parameter variability and model limitations (Chen et al., 2015; Qu et al., 2015). According to the guideline established by United States Environmental Protection Agency [US EPA] (1991), the unconditionally acceptable risk level is below $10^{-6}$ and the acceptable risk levels range from $10^{-6}$ to $10^{-4}$. All the simulated statistical values of DCR and ICR of PBDE of pelagic and demersal fish were lower than $10^{-6}$. On the contrary, the density distributions of ICR due to PAHs exposure from ingestion of pelagic and demersal fish estimated the unacceptable risk level ($10^{-4}$) in correspondence with the 93th percentile for medium pelagic fishes, the 80th percentile for large pelagic fishes, the 85th percentile for small demersal fishes, the 65th percentile for medium demersal fishes, and 38th percentile for large demersal fishes. This means that the probability to exceed the unacceptable threshold is 7, 20, 15, 35, and 62%, respectively. About 5% of ICR due to exposure to OCPs for large pelagic fish, 8% for medium demersal fish and 22% for large demersal fish is above the unacceptable risk level ($10^{-4}$).

### Non-cancer Risk Assessment

Hazard Quotients (HQ) were applied for the evaluation of non-carcinogenic health risk through ingestion and dermal adsorption of single contaminant. It is well known that POPs exert hemato-, cardio-, renal-, neuro-, immuno-, reproductive effects in laboratory animals and humans (Ramesh et al., 2004; WHO, 2010). Hazard Index (HI) were applied to evaluate the non-carcinogenic health risk through ingestion and dermal adsorption of the sum of contaminants found in the study area. The hazard quotients calculated for the dermal adsorption (DHQ) and the ingestion of contaminated fishes (IHQ) and hazard index (HI) for the sum of all POPs are given in Table 6.

![Dermal Cancer Risk (ΣDCR) distribution in the study area.](image_url)
### TABLE 4 | Mean Ingestion Cancer Risk (ICR) for small (SF), medium (MF), large (LF) pelagic, and demersal fish and mean Dermal Cancer Risk (DCR).

| Contaminant        | Target organ | DCR | ICR SF | ICR MF | ICR LF |
|--------------------|--------------|-----|--------|--------|--------|
|                    |              |     | Pelagic | Demersal | Pelagic | Demersal | Pelagic | Demersal |
| PAHs               |              |     |        |         |        |        |        |         |
| Naphthalene        | Generic      | 3.72E-09 | 2.2E-08 | 2.3E-08 | 2.2E-08 | 2.3E-08 |
| Phenanthrene       | Generic      | 2.6E-10 | 4.4E-09 | 1.2E-08 | 4.9E-09 | 1.4E-08 |
| Antracene          | Generic      | 2.97E-09 | 5.2E-08 | 3.3E-07 | 5.7E-08 | 3.7E-07 |
| Fluoranthene       | Generic      | 1.46E-10 | 3.5E-09 | 3.5E-08 | 5.0E-09 | 5.8E-08 |
| Benzo(a)anthracene | Skin         | 3.41E-08 | 1.4E-06 | 8.8E-06 | 2.9E-06 | 2.1E-05 |
| Chrysenes          | Skin         | 4.49E-10 | 1.5E-08 | 9.3E-08 | 3.1E-08 | 2.2E-07 |
| Benzo(a)pyrene     | Skin         | 3.4E-09 | 1.3E-08 | 2.1E-07 | 3.1E-08 | 5.5E-08 |
| Indeno (123) pyrene| Skin, Lung   | 7.54E-08 | 3.3E-07 | 2.8E-06 | 7.8E-07 | 7.4E-06 |
| Dibenzo[a]anthracene| Lung       | 3.3E-07 | 8.8E-07 | 1.2E-07 | 7.8E-07 | 3.4E-05 |
| Benzo(a)pyrene     | Gastrointestinal tract | 7.33E-07 | 1.6E-05 | 7.4E-05 | 3.6E-05 | 1.9E-04 |
| PAHs               |              |     |        |         |        |        |        |         |
| OCPs               |              |     |        |         |        |        |        |         |
| HexaCycloHexane(a + b) | Liver  | 5.76E-08 | 3.3E-08 | 1.9E-07 | 3.4E-08 | 2.0E-07 |
| HexaCycloBenzene   | Liver        | 6.1E-09 | 6.0E-07 | 1.0E-06 | 1.2E-06 | 2.1E-06 |
| Aldrin             | Liver        | 2.12E-07 | 6.2E-06 | 1.1E-05 | 1.5E-05 | 2.9E-05 |
| Dieldrin           | Liver        | 8.65E-10 | 7.0E-08 | 1.1E-07 | 7.1E-08 | 1.1E-07 |
| Alachlor           | Gastrointestinal tract | 3.78E-10 | 6.6E-10 | 1.3E-09 | 6.7E-10 | 1.3E-09 |
| DDE                | Liver        | 5.46E-08 | 1.5E-06 | 4.6E-05 | 3.5E-06 | 3.8E-06 |
| DDD                | Liver        | 3.9E-09 | 1.8E-07 | 2.4E-07 | 4.0E-07 | 5.5E-07 |
| DDTop              | Liver        | 1.33E-08 | 6.4E-08 | 1.2E-07 | 1.4E-07 | 2.9E-07 |
| DDTmp              | Liver        | 1.31E-08 | 5.7E-08 | 1.2E-07 | 1.2E-07 | 2.7E-07 |
| OCPs               |              |     |        |         |        |        |        |         |
| PBDEs              |              |     |        |         |        |        |        |         |
| PBDE28             | Liver        | 3.77E-13 | 3.6E-11 | 6.5E-11 | 6.2E-11 | 1.2E-10 |
| PBDE47             | Liver        | 7.82E-11 | 1.2E-08 | 1.2E-08 | 2.7E-08 | 2.8E-08 |
| PBDE99             | Liver        | 1.16E-12 | 1.8E-11 | 6.3E-11 | 3.9E-11 | 1.5E-10 |
| PBDE100            | Liver        | 1.16E-12 | 1.8E-11 | 6.3E-11 | 3.9E-11 | 1.5E-10 |
| PBDE153            | Liver        | 2.03E-12 | 4.5E-13 | 8.2E-12 | 5.5E-13 | 1.3E-11 |
| PBDE154            | Liver        | 2.03E-12 | 4.5E-13 | 8.2E-12 | 5.5E-13 | 1.3E-11 |
| PBDE209            | Liver        | 4.06E-12 | 9.0E-13 | 1.6E-11 | 1.1E-12 | 2.6E-11 |
| PBDE               |              |     |        |         |        |        |        |         |

In bold: significant cancer risks.

### TABLE 5 | Combined Ingestion Cancer Risk for small (SF), medium (MF), large (LF) demersal-pelagic fishes, and Combined Dermal Cancer Risk calculated for the target organ of each carcinogenic contaminant.

| Target organ         | ICR (demersal fish) | ICR (pelagic fish) | DCR |
|----------------------|---------------------|--------------------|-----|
|                      | SF                  | MF                | LF  | SF  | MF | LF |
| Breast               | 1.7E-07             | 4.5E-07           | 1.2E-06 | 8.7E-06 | 2.0E-05 | 5.5E-05 | 7.9E-09 |
| Gastrointestinal     | 7.4E-05             | 1.9E-04           | 5.0E-04 | 1.7E-07 | 3.2E-07 | 7.3E-07 | 7.9E-07 |
| Generic              | 3.0E-06             | 6.8E-06           | 1.5E-05 | 2.1E-05 | 4.8E-05 | 1.3E-04 | 2.1E-08 |
| Liver                | 1.5E-05             | 3.6E-05           | 9.6E-05 | 4.3E-07 | 8.0E-07 | 1.8E-06 | 3.6E-07 |
| Lung                 | 9.0E-06             | 2.3E-05           | 5.7E-06 | 1.8E-06 | 3.8E-06 | 9.3E-06 | 9.5E-07 |
| Skin                 | 1.2E-05             | 2.8E-05           | 6.8E-05 | 2.7E-06 | 6.0E-06 | 1.5E-05 | 1.1E-07 |

In bold: significant cancer risks.

**Contribution of Different Pathways**

It is noteworthy that food ingestion is the main pathway of contaminants exposure for humans when compared with other routes such as inhalation, dermal contact and drinking water (Lioy et al., 1988; Butler et al., 1993). Studies conducted on human exposure to BaPy revealed that the range and magnitude of dietary exposures (2–500 ng/day) were larger for inhalation and dermal contact (Lioy et al., 1988). Diet makes a substantial
In Table 6, we present the Ingestion Hazard Quotient (IHQ) for small (SF), medium (MF), and large (LF) pelagic and demersal fishes, Dermal Hazard Quotient (DHQ), and Hazard Index (HI) as the sum of the HQs.

| Contaminant | DHQ Pelagic | DHQ Demersal | IHQ SF Pelagic | IHQ SF Demersal | IHQ MF Pelagic | IHQ MF Demersal | IHQ LF Pelagic | IHQ LF Demersal |
|-------------|-------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|
| PAHs        |             |              |                |                |                |                |                |                |
| Naphthalene | 3.62E-06    | 2.11E-05     | 2.19E-05       | 2.13E-05       | 2.21E-05       | 2.16E-05       | 2.24E-05       | 2.16E-05       |
| Acenaphthene| 1.71E-07    | 1.96E-06     | 4.37E-06       | 2.01E-06       | 4.54E-06       | 2.16E-05       | 4.76E-06       | 2.12E-06       |
| Fluorene    | 1.30E-06    | 1.81E-05     | 2.04E-05       | 1.90E-05       | 2.16E-05       | 2.16E-05       | 2.37E-05       | 2.09E-05       |
| Antracene   | 1.01E-07    | 1.77E-06     | 1.11E-05       | 1.93E-06       | 1.26E-05       | 2.17E-06       | 1.44E-05       | 2.17E-06       |
| Fluoranthene| 3.72E-06    | 8.77E-05     | 8.96E-04       | 1.27E-04       | 1.48E-03       | 2.21E-04       | 2.50E-03       | 2.21E-04       |
| Pyrene      | 8.90E-06    | 1.67E-04     | 5.94E-04       | 2.08E-04       | 8.09E-04       | 2.99E-04       | 1.14E-03       | 2.99E-04       |
| Benzo(a)pyrene | 2.49E-04 | 5.26E-03     | 4.23E-02       | 1.22E-02       | 1.12E-01       | 3.24E-02       | 2.89E-01       | 3.24E-02       |
| Benzo(a)pyreneTEQ | 7.82E-04 | 3.20E-02 | 7.93E-02 | 1.80E-02 | 2.08E-01 | 1.30E-01 | 5.36E-01 |
| OCPs        |             |              |                |                |                |                |                |                |
| HexaClCycloHexane(a+b) | 2.67E-06 | 1.54E-06 | 8.86E-06 | 1.57E-06 | 9.17E-06 | 1.63E-06 | 9.53E-06 |
| HexaClBenzene | 1.11E-05 | 1.10E-03 | 1.85E-03 | 2.14E-03 | 3.84E-03 | 5.00E-03 | 8.91E-03 |
| Aldrin      | 9.70E-04   | 3.36E-02     | 6.08E-02       | 8.09E-02       | 1.55E-01       | 2.19E-01       | 4.16E-01       | 2.19E-01       |
| Dieldrin    | 2.52E-06   | 2.03E-04     | 3.25E-04       | 2.07E-04       | 3.22E-04       | 2.14E-04       | 3.42E-04       | 2.14E-04       |
| Endrin      | 3.16E-07   | 1.34E-05     | 3.47E-05       | 1.37E-05       | 3.56E-05       | 1.41E-05       | 3.67E-05       | 1.41E-05       |
| Endosulfan  | 1.56E-08   | 8.39E-07     | 4.87E-06       | 8.57E-07       | 5.04E-06       | 8.92E-07       | 5.23E-06       | 8.92E-07       |
| Alachlor    | 1.58E-06   | 2.76E-06     | 5.31E-06       | 2.80E-06       | 5.39E-06       | 2.86E-06       | 5.50E-06       | 2.86E-06       |
| DDE         | 1.25E-03   | 3.97E-02     | 4.24E-02       | 9.55E-02       | 1.03E-01       | 2.59E-01       | 2.78E-01       | 2.59E-01       |
| DDD         | 1.04E-03   | 5.73E-02     | 7.72E-02       | 1.28E-01       | 1.80E-01       | 3.35E-01       | 4.66E-01       | 3.35E-01       |
| DDTop       | 1.83E-04   | 2.69E-03     | 5.17E-03       | 5.78E-03       | 1.20E-02       | 1.41E-02       | 2.90E-02       | 1.41E-02       |
| DDTop'      | 1.81E-04   | 2.31E-03     | 4.74E-03       | 4.99E-03       | 1.11E-02       | 1.22E-02       | 2.67E-02       | 1.22E-02       |
| PBDEs       |             |              |                |                |                |                |                |                |
| PBDE28      | 1.26E-05   | 8.50E-03     | 2.18E-03       | 9.80E-03       | 4.00E-03       | 9.90E-04       | 8.33E-03       | 9.90E-04       |
| PBDE47      | 2.61E-03   | 3.87E-01     | 3.89E-01       | 9.14E-01       | 9.19E-01       | 2.47E+00       | 2.49E+00       | 2.47E+00       |
| PBDE99      | 3.87E-05   | 1.76E-03     | 6.28E-03       | 3.85E-03       | 1.50E-02       | 9.42E-03       | 3.60E-02       | 9.42E-03       |
| PBDE100     | 3.87E-05   | 1.78E-03     | 6.28E-03       | 3.85E-03       | 1.50E-02       | 9.42E-03       | 3.60E-02       | 9.42E-03       |
| PBDE153     | 3.39E-05   | 1.11E-04     | 2.04E-03       | 1.37E-04       | 3.30E-03       | 2.05E-04       | 4.68E-03       | 2.05E-04       |
| PBDE154     | 3.39E-05   | 1.11E-04     | 2.04E-03       | 1.37E-04       | 3.30E-03       | 2.05E-04       | 4.68E-03       | 2.05E-04       |
| HI          | 7.45E-03   | 5.65E-01     | 7.23E-01       | 1.27E+00       | 1.75E+00       | 3.50E+00       | 4.63E+00       | 3.50E+00       |

In bold: significant risks.

Contribution of Different Contaminants

Statistically significant differences (KW test, p = 0.002) between contaminant contribution for the ICRs were evidenced. Particularly, higher PAHs contribution was recorded concerning OCPs and PBDEs because of their higher concentrations in seawater and sediments of the study area. BaPy has the highest ICR with respect to the other PAH congeners that exceed the upper bound of EPA acceptable range ($2.7 \times 10^{-4}$ for the ingestion of large demersal fishes, Table 3). BaPy is the most known and studied member of PAHs because of its highest carcinogenic
TABLE 7 | Monte Carlo simulation, probabilistic distribution of DCR and ICR, statistical values (percentiles).

|       | 5%   | 25%  | 50%  | 75%  | 95%  |
|-------|------|------|------|------|------|
| **DCR** |      |      |      |      |      |
| PAHs  | 8.9E-9 | 8.5E-8 | 1.7E-7 | 7.2E-7 | 2.7E-6 |
| OCPs  | 8.6E-9 | 8.3E-8 | 2.6E-7 | 6.2E-7 | 1.5E-6 |
| **ICR pelagic fishes** |      |      |      |      |      |
| SF    |      |      |      |      |      |
| PAHs  | 4.3E-7 | 1.7E-6 | 4.9E-6 | 1.4E-5 | 6.2E-5 |
| OCPs  | 1.0E-6 | 2.5E-6 | 4.9E-6 | 9.6E-6 | 2.4E-5 |
| PBDEs | 8.0E-10 | 2.5E-9 | 5.7E-9 | 1.3E-8 | 3.9E-8 |
| MF    |      |      |      |      |      |
| PAHs  | 9.4E-7 | 4.2E-6 | 1.2E-5 | 3.2E-5 | 1.4E-4 |
| OCPs  | 2.6E-6 | 6.2E-6 | 1.2E-5 | 2.3E-5 | 5.6E-5 |
| PBDEs | 1.9E-9 | 6.4E-9 | 1.4E-8 | 3.1E-8 | 9.6E-8 |
| LF    |      |      |      |      |      |
| PAHs  | 2.0E-6 | 9.6E-6 | 2.6E-5 | 7.5E-5 | 3.7E-4 |
| OCPs  | 1.8E-5 | 3.1E-5 | 4.3E-5 | 6.1E-5 | 1.0E-4 |
| PBDEs | 1.2E-8 | 2.8E-8 | 5.1E-8 | 9.1E-8 | 2.2E-7 |
| **ICR demersal fishes** |      |      |      |      |      |
| SF    |      |      |      |      |      |
| PAHs  | 1.9E-6 | 8.5E-6 | 2.3E-6 | 6.6E-5 | 2.9E-4 |
| OCPs  | 1.2E-6 | 3.3E-6 | 6.2E-6 | 1.2E-5 | 2.9E-5 |
| PBDEs | 8.0E-10 | 2.6E-9 | 5.7E-9 | 1.3E-8 | 4.3E-8 |
| MF    |      |      |      |      |      |
| PAHs  | 4.8E-6 | 2.2E-5 | 6.3E-5 | 1.7E-4 | 7.4E-4 |
| OCPs  | 5.5E-6 | 1.3E-5 | 2.6E-5 | 4.9E-5 | 1.2E-4 |
| PBDEs | 1.9E-9 | 6.3E-9 | 1.4E-8 | 3.0E-8 | 9.7E-8 |
| LF    |      |      |      |      |      |
| PAHs  | 1.4E-5 | 6.1E-5 | 1.7E-4 | 4.6E-4 | 2.1E-3 |
| OCPs  | 1.0E-5 | 2.5E-5 | 4.8E-5 | 9.0E-5 | 2.7E-4 |
| PBDEs | 1.2E-8 | 2.8E-8 | 5.1E-8 | 9.1E-8 | 2.2E-7 |

*In bold: significant risks.*

potential (Howard and Fazio, 1980). A lot of epidemiological studies confirm the strong relationship between the ingestion of highly contaminated food with BaPy and risk for gastrointestinal cancer, particularly stomach, esophagus (Ward et al., 1997) and colorectal cancer (Schiffman and Felton, 1990; Muscat and Wynder, 1994; Sinha et al., 1999). BaPy concentration higher than the MAC set by the Directive 2013/39/EU here found in sediment of the sampling station MZ13 located near the industrial pole (where both thermopower plant and refinery plant are present), suggest a significant anthropogenic input of this contaminant in the study area with a relevant health risk for local populations. Although a not statistically significant level, the higher mean contribution of OCPs was found for non-cancerogenic health issues with respect to PAHs and PBDEs contributions (Table 5). OCPs, such as Endosulphan and Lindane (γ-hexachlorocyclohexane), are well known to exert neurotoxic effects inhibiting the calcium ion influx and Ca- and Mg-ATPase and causing release of neurotransmitters (Mathew, 2012). Moreover, epidemiological studies have shown that exposure to OCPs is strongly associated with type 2 diabetes (Lee et al., 2006) and Parkinson’s disease (Steenland et al., 2014). As shown in Table 5, the HI associated to OCPs and due to the ingestion of large demersal fishes is higher than 1 suggest that local population could experience these pathologies after a long-time exposure of OCPs. As shown in Table 2, all the OCPs concentrations in seawater and sediment samples are lower than the MAC set by the Directive 2013/39/EU. This study evidence that the threshold limits imposed by legislation could not be sufficiently protective against a long-time exposure of a mix of highly toxic contaminants. Although the OCPs has the highest mean contribution, the highest HI was reported for PBDE47 (HI = 2.5; Table 5). PBDE-47 is an emerging contaminant diffuse worldwide in the marine environment at constant increasing concentrations (Hites et al., 2004; Schecter et al., 2007) although its use has been banned in many countries. In spite of these concern, limited information on the PBDE47 toxicity is available. Exposure of neonatal mice to PBDE47 is reported to exert neurodevelopment toxicity causing behavioral alterations, learning and memory deficits and dysfunctions in the cholinergic system in adult stage (Eriksson et al., 2001, 2002; Branchi et al., 2003). PBDE47 exceed the MAC set by the Directive 2013/39/EU in seawater column of 5 sampling stations, suggesting relevant contamination of this pollutant in the study area.

Uncertainty
As reported in the Basic Information about the Integrated Risk Information System (IRIS), Cancer Oral slop factor (CSFo), and Reference Dose (RfDo) are parameters estimated with uncertainty due to limitations of the data used and could represent an uncertainty factor for risk assessment. Fixed exposure factors, commonly used in risk assessment, may not be adequately accurate in reproducing reality because of their variability due to different life stages and/or different environmental condition. Finally, the cancer risks per target organs here calculated are probably underestimated for the lack of information about carcinogenic action of every single PAH on human. For example, we established a specific carcinogenic
**TABLE 8** | Monte Carlo simulation, probabilistic distribution of DHR and IHR, statistical values (percentiles).

|          | 5%      | 25%     | 50%     | 75%     | 95%     |
|----------|---------|---------|---------|---------|---------|
| **DHR**  |         |         |         |         |         |
| PAHs     | 2.7E-7  | 2.7E-5  | 2.4E-4  | 9.8E-4  | 3.7E-3  |
| OCPs     | 6.6E-5  | 6.4E-4  | 2.0E-3  | 4.7E-3  | 1.2E-2  |
| **IHQ pelagic fish** |         |         |         |         |         |
| SF       |         |         |         |         |         |
| PAHs     | 4.5E-4  | 1.8E-3  | 5.2E-3  | 1.4E-2  | 6.6E-2  |
| OCPs     | 1.8E-2  | 4.5E-2  | 8.6E-2  | 1.7E-1  | 4.3E-1  |
| PBDEs    | 2.7E-2  | 8.2E-2  | 1.9E-1  | 4.3E-1  | 2.7E-1  |
| MF       |         |         |         |         |         |
| PAHs     | 1.0E-3  | 4.4E-3  | 1.2E-2  | 4.3E-1  | 1.5E-1  |
| OCPs     | 4.6E-2  | 1.1E-1  | 2.2E-1  | 4.1E-1  | 2.6E-1  |
| PBDEs    | 6.4E-2  | 2.1E-1  | 4.6E-1  | 1.0     | 3.2     |
| LF       |         |         |         |         |         |
| PAHs     | 2.2E-3  | 1.0E-2  | 2.7E-2  | 7.9E-2  | 3.9E-1  |
| OCPs     | 3.3E-1  | 5.6E-1  | 7.7E-1  | 1.1     | 1.8     |
| PBDEs    | 3.9E-1  | 9.3E-1  | 1.7     | 3.0     | 7.2     |
| **IHQ demersal fish** |         |         |         |         |         |
| SF       |         |         |         |         |         |
| PAHs     | 2.1E-3  | 9.0E-3  | 2.4E-2  | 6.9E-2  | 3.1E-1  |
| OCPs     | 1.1E-1  | 2.9E-1  | 5.6E-1  | 1.1     | 2.6     |
| PBDEs    | 2.7E-2  | 8.8E-2  | 1.9E-1  | 4.3E-1  | 1.4     |
| MF       |         |         |         |         |         |
| PAHs     | 5.1E-3  | 2.3E-2  | 6.7E-2  | 1.8E-1  | 7.9E-1  |
| OCPs     | 5.5E-1  | 1.4     | 2.6     | 5.0     | 12.6    |
| PBDEs    | 6.6E-2  | 2.1E-1  | 4.6E-1  | 1.0     | 3.2     |
| LF       |         |         |         |         |         |
| PAHs     | 1.5E-2  | 6.4E-2  | 1.8E-1  | 4.9E-1  | 2.2     |
| OCPs     | 2.3E-1  | 5.8E-1  | 1.1     | 2.1     | 5.3     |
| PBDEs    | 4.0E-1  | 9.3E-1  | 1.7     | 3.0     | 7.3     |

*In bold: significant risks.*

action of BaP in the gastro-intestinal tract based on IRIS database, excluding other target organs for the carcinogenic action of this compound for lack of evidence in humans. However, several studies with experimental animals suggest that oral, intratracheal and subcutaneous injection of BaP led to carcinogenic events in multiple sites (IARC, 2010). Furthermore, BaP has been proven to induce breast tumors in animal through genotoxic activities implied in p53 mutations (Morris and Seifler, 1992). This information suggests that the carcinogenic action of BaP could affect other organs and not exclusively the gastro-intestinal tract. Moreover, uncertainty is not considered in the models applied to mixtures of compounds thus possibly affecting their mobility, partitions and health impacts.

**CONCLUSION**

The study investigated, for the first time, persistent and emerging pollutants in seawater and sediments of the Gulf of Milazzo. The concentration of BghiP, PBDE in seawater samples and BbF, BkF, BaP in sediment samples higher than MAC show a low quality of this marine environment.

The human health risk was calculated through cancer and non-cancer risk indices. These indices provide only point estimates giving little information about uncertainty and variability surrounding the risk impact. Therefore, Monte Carlo simulation was necessary to provide complete information on the likelihood of the various risk levels. The cancer risk assessment shows higher risks for resident population through the ingestion of large demersal fish, especially gastro-intestinal cancer caused by BaP. Negligible cancer risks were associated with dermal adsorption of contaminants from seawater. The non-cancer risk assessment (HI) shows significant risks for resident population to develop health issues due to the ingestion of large demersal fish contaminated by mixture of the analyzed pollutants. OCPs and especially PBDE47 represent the major contribution for non-cancer risk. The present study might provide, assuming permanent environmental conditions, useful information on human exposure to POPs in Milazzo bay and will be useful for strategies focused on risks mitigation. Particular attention should be done to reduce BaPy emission from refinery plant, thermopower plant and maritime transport. The use of other less toxic flame retardants than PBDE47 for the production of plastic and fiber materials is also recommended.

**DATA AVAILABILITY STATEMENT**

All datasets generated for this study are included in the article/Supplementary Material.

**AUTHOR CONTRIBUTIONS**

FD'A led the conception and design of the manuscript. AB led the conception and writing of the manuscript. MD led the sampling
strategy. EQ carried out the statistical analysis and developed the risk map. SG carried out the chemical analysis on sediment samples. FP carried out the interpretation of oceanographic data. NS carried out the total organic carbon analysis on sediment samples. GB led the oceanographic survey. GA and GD contributed to carry out the chemical analysis on seawater samples and to review the manuscript. All authors contributed to the article and approved the submitted version.

**FUNDING**

The CISAS project is a multidisciplinary project on environment/health relationships funded by the Italian Ministry of Education, Universities and Research (MIUR) and approved by the Interministerial Committee for Economic Planning (CIPE) – body of the Italian Government – with Resolution n. 105/2015 of 23 December 2015.

**ACKNOWLEDGMENTS**

The authors thank the project of the National Research Council of Italy (CNR) titled "International Center of Advanced Study in Environment, Ecosystem and Human Health (CISAS).”

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2020.00117/full#supplementary-material

**REFERENCES**

Alebic-Juretic, A. (2011). Polycyclic aromatic hydrocarbons in marine sediments from the Rijeka Bay area, Northern Adriatic, Croatia, 1998-2006. Mar. Poll. Bull. 62, 863-869. doi: 10.1016/j.marpolbul.2011.01.035

Branchi, I., Capone, F., Alleva, E., and Costa, L. G. (2003). Polybrominated diphenyl ethers: neurobehavioral effects following developmental exposure. Neurotoxicology 24, 449-462. doi: 10.1016/s0161-813x(03)00020-2

Antizar-Ladislao, B. (2009). Polycyclic aromatic hydrocarbons, polychlorinated biphenyls, phthalates and organotins in northern Atlantic Spain’s coastal marine sediments. J. Environ. Monit. 11, 85–91. doi: 10.1039/b808668k

Arnot, J. A., and Gobas, F. A. (2004). A food web bioaccumulation model for organic chemicals in aquatic ecosystems. Environ. Toxicol. Chem. 23, 2343–2355.

Asia, L., Mazouz, S., Gualiano, M., Doumenq, P., and Gilbert Mille, G. (2009). Occurrence and distribution of hydrocarbons in surface sediments from Marseille Bay (France). Mar. Pollut. Bull. 58, 443–451. doi: 10.1016/j.marpolbul.2008.11.022

Baumd, P., Budzinski, H., and Garrigues, P. (1998). PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms. Mar. Pollut. Bull. 36, 577–586. doi: 10.1016/s0025-326x(98)00014-9

Beckman, S. O., Thuvander, A., and Andersson, C. (1998). Preview of PAHs in Food: Potential Health Effects and Contents in Food, Report 8. Upscala: Swedish National Food Administration.

Butler, J. P., Post, G. B., Liow, P. I., Waldman, J. M., and Greenberg, A. (1993). Assessment of carcinogenic risk from personal exposure to benzo(a)pyrene in the total human environmental exposure study (THEES). J. Air Waste Manage. Assoc. 43, 970–977. doi: 10.1080/1073161x.1993.10467179

Chen, S., Chen, B., and Fath, B. D. (2015). Assessing the cumulative environmental impact of hydropower construction on river systems based on energy network model. Renew. Sustain. Energy Rev. 42, 78–92. doi: 10.1016/j.rser.2014.10.017

Chen, Y. (2008).

Eriksson, P., Jakobsson, E., and Fredriksson, A. (2001). Brominated flame retardants: a novel class of developmental neurotoxicants in our environment? Environ. Health Perspect. 109, 903–908. doi: 10.1289/ehp.01109903

Eriksson, P., Viberg, H., Jakobsson, E., Orn, U., and Fredriksson, A. (2002). A brominated flame retardant, 2,2',4,4',5-pentabromodiphenyl ether: uptake, retention, and induction of neurobehavioral alterations in mice during a critical phase of neonatal brain development. Toxicol. Sci. 67, 98–103. doi: 10.1093/toxicolsci/nfj018

He, X., Pang, Y., Song, X., Chen, B., Feng, Z., and Ma, Y. (2014). Distribution, sources and ecological risk assessment of PAHs in surface sediments from Guan River Estuary, China. Mar. Pollut. Bull. 80, 52–58. doi: 10.1016/j.marpolbul.2014.01.051

Health Canada [HC] (2007a). Federal Contaminated Site Risk Assessment in Canada. Part I: Guidance on Human Health Preliminary Quantitative Risk Assessment. Version 2.0. Ottawa: Health Canada.

Health Canada [HC] (2007b). Federal Contaminated Site Risk Assessment in Canada. Part II: Health Canada Toxicological Reference Values (TRVs). Version 2.0. Ottawa: Health Canada.

Hites, R. A., Foran, J. A., Carpenter, D. O., Hamilton, M. S., Knuth, B. A., and Schaefer, S. J. (2004). Global assessment of organic contaminants in farmed salmon. Science 303, 226–229. doi: 10.1126/science.1091447

Howard, J. W., and Fazio, T. (1980). Analytical methodology and reported findings of polycyclic aromatic hydrocarbons in foods. Ass. Offic. Anal. Chem. 63, 1077–1104. doi: 10.1093/jaoac/63.5.1077

IARC (2010). Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monogr. Eval. Carcinog. Risks Hum. 92, 1–853.

ICRAM (2006). Progetto Preliminare di Bonifica Della Rada di Augusta Incluso nel Sito di Bonifica di Interesse Nazionale di Priolo. Fase I e II. Elaborazione Definitiva # Bol-Pr-SI-PR-Rada di Augusta-93.22.

International Agency for Research on Cancer [IARC] (1987). Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs. Lyon: International Agency for Research on Cancer, 1–42.

IRIS (2007). US EPA. Integrated Risk Information System. Online. IRIS Advanced Search. Available online at: https://cfpub.epa.gov/ncea/iris/search/index.cfm

Jayaraj, R., Megha, P., and Sreedeep, P. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interscience. Toxicol. 9, 90–100. doi: 10.1515/intox-2016-0012

Ju, T., Ge, W., Jiang, T., and Chai, C. (2016). Polybrominated diphenyl ethers in dissolved and suspended phases of seawater and in surface sediment from Jiaozhou Bay, North China. Sci. Total Environ. 55, 571–578. doi: 10.1016/j.scitotenv.2016.03.013

Khairy, M., Kolb, M., Mostafa, A., Fiky, A., and Bahadir, M. (2009). Risk assessment of polycyclic aromatic hydrocarbons in a Mediterranean semi-enclosed basin affected by human activities (Abu Qir Bay, Egypt). J. Hazard. Mater. 170, 389–397. doi: 10.1016/j.jhazmat.2009.04.084

La Pera, L., Di Bella, G., Rando, R., Lo Turco, V., and Dugo, G. (2008). Speciation of inorganic arsenic in coastal seawater from Ionian and Tyrrenhenian Seas (Sicily,
Italy) using derivative anodic stripping chronopotentiometry. *Environ. Monit. Assess.* 145, 119–126. doi: 10.1007/s10661-007-0021-8

Lee, J. Y., Kim, Y. P., Kang, C. H., Ghim, Y. S., and Kaneyasu, N. (2006). Temporal trend and long-range transport of particulate PAHs at Gosan in Northeast Asia between 2001 and 2004. *J. Geophys. Res.* 111:D11303. doi: 10.1029/2005JD006537

Linares, V., Bellès, M., and Domingo, J. L. (2015). Human exposure to PBDE and critical evaluation of health hazards. *Arch. Toxicol.* 89, 335–356. doi: 10.1007/s00204-015-1457-1

Lioy, P. L., Waldman, J. M., and Greenberg, A. (1988). The Total Human Environmental Exposure Study (THEES) to benzo(a)pyrene: comparison of the inhalation and food pathways. *Arch. Environ. Health* 43, 304–312. doi: 10.1080/00039898.1988.10545954

Liu, Y., Zheng, G. J., Yu, H., Martin, M., Richardson, B., Lam, M., et al. (2005). Polychlorinated biphenyl ethers (PBDEs) in sediments and mussel tissues from Hong Kong marine waters. *Mar. Pollut. Bull.* 50, 1173–1184. doi: 10.1016/j.marpolbul.2005.04.025

Magi, E., Bianco, R., Ianni, C., and Di Carro, M. (2002). Distribution of polychlorinated aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environ. Pollut.* 119, 91–98. doi: 10.1016/s0269-7491(01)00321-9

Mathew, L. L. (2012). Organochloride Pesticide Toxicity. Drugs, Diseases and Procedures. Medscape References.

Moon, H.-B., Kannan, K., Lee, S.-J., and Choi, M. (2007). Polybrominated diphenyl ethers (PBDEs) in sediment and bivalve waters from Korean coastal waters. *Chemosphere* 66, 243–251. doi: 10.1016/j.chemosphere.2006.05.025

Morris, J. J., and Seifert, E. (1992). The role of aromatic Hydrocarbons in the genesis of breast cancer. *Med. Hypotheses* 38, 177–184. doi: 10.1016/0306-9877(92)90090-y

Muscat, J. E., and Wynder, E. L. (1994). The consumption of well-done red meat and the risk of colorectal cancer. *Am. J. Publ. Health* 84, 856–858. doi: 10.2105/ajph.84.5.856

Pepe, F., Scopelliti, G., Di Leonardo, R., and Ferruzza, G. (2010). Granulometry, mineralogy and trace elements of marine sediments from the Gulf of Milazzo (NE Sicily): evaluation of anthropogenic impact. *Italian J. Geol.* 129, 385–394.

Phillips, D. H. (1999). Polychlorinated aromatic hydrocarbons in the diet. *Mutat. Res.* 443, 139–147.

Qiu, Y. W., Zhang, G.-Q., Liu, G., Guo, L.-L., Li, X.-D., and Wai, O. (2009). Polychlorinated aromatic hydrocarbons (PAHs) in the water column and sediment core of Deep Bay, South China. *Estuar. Coast. Shelf Sci.* 83, 60–66. doi: 10.1016/j.ecss.2009.03.018

Qu, C., Li, B., Wu, H., Wang, S., and Giesy, J. P. (2015). Multi-pathway assessment of human health risk posed by polychlorinated aromatic hydrocarbons. *Environ. Geochim.* Health 37, 587–601. doi: 10.1007/s10653-014-9675-7

R Core Team (2019). *R: A language and Environment for Statistical Computing*. Vienna: R Foundation for Statistical Computing. Available online at: https://www.R-project.org/

Ramesh, A., Hood, D., Guo, Z., and Loganathan, B. (2012). “Global environmental distribution and human health effects of polychlorinated aromatic hydrocarbons,” in *Global Contamination Trends of Persistent Organic Chemicals*, 1st Edn, eds B. G. Loganathan and P. Kwan-Sing Lam (Boca Raton, FL: CRC Press).

Ramesh, A., Walker, S. A., Hood, D. B., Gullen, M. D., Schneider, K., and Weyand, E. H. (2004). Bioavailability and risk assessment of orally ingested polychlorinated aromatic hydrocarbons. *Int. J. Toxicol.* 23, 301–333. doi: 10.1080/10915810490517063

Schechter, A., Johnson-Welsh, S., Tung, K. C., Harris, T. R., Papke, O., and Rosen, R. (2007). Polychlorinated diphenyl ether (PBDE) levels in livers of U.S. human fetuses and newborns. *J. Toxicol. Environ. Health A* 70, 1–6. doi: 10.1080/15287390600748369

Schiffman, M., and Felton, J. S. (1990). Fried foods and the risk of colon cancer. *Am. J. Epidemiol.* 131, 376–378. doi: 10.1093/oxfordjournals.aje.a115508

Sinha, R., Chow, W. H., Kullerlov, M., Denoble, J., Butler, J., Garcia-Closas, M., et al. (1999). Well-done, grilled red meat increases the risk of colorectal adenomas. *Cancer Res.* 59, 4320–4324.

Socol, H. H., Garrigues, P. H., and Ewald, M. (2000). Origin of polychlorinated aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) Areas. *Mar. Pollut. Bull.* 40, 387–396.

Sohail, E., Waseem, A., Chae, W. L., Jong, J. L., and Imitiaz, H. (2004). Endocrine disrupting pesticides: a leading cause of cancer among rural people in Pakistan. *Exp. Oncol.* 26, 98–105.

Soliman, Y. S., Al-Ansari, E., and Wade, T. (2014). Concentration, composition and sources of PAHs in the coastal sediments of the exclusive economic zone (EEZ) of Qatar, Arabian Gulf. *Mar. Pollut. Bull.* 85, 542–548.

Steenland, K., Mora, A. M., Barr, D. B., Juncos, I., Roman, N., and Wesseling, C. (2014). Organochlorine chemicals and neurodegeneration among elderly subjects in Costa Rica. *Environ. Res.* 134, 205–209.

Subramaniam, K., and Solomon, R. D. (2006). Organochlorine pesticides BHC and DDE in human blood in and around Madurai, India. *Indian J. Clin. Biochem.* 21, 169–172.

United States Environmental Protection Agency [US EPA] (1991). *Risk Assessment Guidance for Superfund (RAGS), Vol. I: Human Health Evaluation Manual (HHEM), Part B, Development of Risk-Based Preliminary Remediation Goals*, Publication 9285.7-01B, NTIS PB92-963331. Washington, DC: Office of Solid Waste and Emergency Response.

Ward, M. H., Sinha, R., Heineman, E. F., Rothman, N., Markin, R., Weisenburger, D. D., et al. (1997). Risk of adenocarcinoma of the stomach and esophagus with meat cooking method and doneness preference. *Int. J. Cancer* 71, 14–19.

WHO (2010). *Some Non-Heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 92. Lyon: International Agency for Research on Cancer.

Wolff, M. S., Toniolo, P. G., Lee, E. W., Rivera, M., and Dubin, N. (1993). Blood levels of organochlorine residues and risk of breast cancer. *J. Natl. Cancer Inst.* 89, 468–462.

Yau, M., Wang, X.-H., Wu, Y., Ye, C., and Li, Y.-Y. (2014). Enrichment and partitioning of polychlorinated aromatic hydrocarbons in the sea surface microlayer and subsurface water along the coast of Xiamen Island, China. *Mar. Pollut. Bull.* 78, 110–117.

Yunker, M., Macdonald, R., Vingarzan, R., Mitchell, R., Goyette, and Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organ. Geochem.* 33, 489–515.

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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