Polychlorinated biphenyls and organochlorine pesticides in water and sediment from Volturno River, Southern Italy: occurrence, distribution and risk assessment

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Abstract

Background: To assess the Volturno River pollution and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea) caused by Polychlorinated biphenyls (PCBs) and Organochlorine pesticides (OCPs), 32 PCBs and Aldrin, α-BHC, β-BHC, δ-BHC, γ-BHC (lindane), 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, endrin, heptachlor, heptachlor epoxide (isomer B) and methoxychlor have been selected and were analyzed in three different phases: dissolved phase (DP), suspended particulate matter (SPM) and sediments. PCBs and OCPs were extracted using an SPE column for the DP and glass fiber filter for SPM and sediment samples. Cleaned extracts were analyzed by gas chromatography with electron capture detector (ECD) and mass spectrometry (MS) detector for PCBs and OCPs, respectively.

Results: Pollutants discharges of PCBs and OCPs into the sea were calculated in about 106.9 kg year$^{-1}$ (87.1 kg year$^{-1}$ of PCBs and 19.7 kg year$^{-1}$ of OCPs), showing that this river could be a major source of PCBs and OCPs pollution to the Central Mediterranean Sea. Total concentrations of PCBs ranged from 4.1 to 48.0 ng L$^{-1}$ in water (sum of DP and SPM) and from 4.3 to 64.3 ng g$^{-1}$ in sediment samples. The concentrations of total organochlorine pesticides (OCPs) obtained in water (sum of DP and SPM) ranged from 0.93 to 8.66 ng L$^{-1}$ and from 0.52 to 9.89 ng g$^{-1}$ in sediment samples. Principal component analysis shows that all PCB compounds are more likely to come from surface runoff than an atmospheric deposition.

Conclusion: The data show that higher levels of PCBs and OCPs were found in sediment samples than in DP and SPM samples, which are an indication of no fresh inputs of these compounds. Based on our results, unintentionally produced PCBs by industrial processes (and other processes) were considered to be the main sources of PCBs in Volturno River and Estuary sediments. Considering the Sediment Quality Guidelines (SQGs), the Ecological Risk Index (ERI), the Risk Quotient (RQ) and the USEPA Environmental Quality Standards (EQS), the Volturno River and its Estuary would be considered an area in which the integrity is possibly at risk.

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Highlights

- PCBs and OCPs discharged into the Mediterranean Sea were 87.1 and 19.7 kg y⁻¹, respectively.
- High chlorinated CB were predominant compounds and DDTs and HCHs were dominant OCPs.
- PCBs are more likely to come from surface runoff than atmospheric deposition.
- The ecological integrity of the Volturno River and estuary is possibly at risk.

Background

The Mediterranean Sea is one of the most polluted water basins in the world because of its highly developed tourism, maritime traffic that crosses its waters and densely populated coasts [1, 2]. The Mediterranean Sea covers 1% of the world’s marine areas and almost completely landlocked on the sea, its waters have a very low renewal rate that makes them excessively sensitive to pollution. Pollution reaches the Mediterranean Sea mainly through its main river systems such as the Ebro, the Nile and the Tiber which transport considerable quantities of agricultural and industrial wastes [3–5]. Among the several rivers that flow into the Mediterranean Sea, there is also the Volturno River.

The Volturno River is the most relevant watercourse in Southern Italy because of its length and its water flow. It rises in the Abruzzese Apennines near Alfedena and flows southeast as far as its junction with the Calore River near Caiazzo. It then turns southwest, past Capua, to enter the Tyrrhenian Sea (Central Mediterranean Sea) at Castel Volturno, northwest of Naples. The river is 109 miles (175 km) long and has a drainage basin of 2100 square miles (5450 square km). In the past, many people have settled along the Volturno River banks and its waters have promoted the development of a great aquatic and terrestrial biodiversity. Because of that, the area surrounding the Volturno River, has been called “Campania Felix”. This name refers to a land full of culture and traditions, with a mild climate and fertile soil thanks to the presence of some rivers. It was also strategically perfect for commerce and agriculture has always been the main source of income in the area for the production of vegetables and fruits. In the last decade, illegal disposal of toxic waste caused a trend reversal and this area has renamed as “Land of Fire” (Fig. 1). This name is due to the presence of numerous illegal landfills along the roads and in the open countryside. Every time these landfills are filled, fires are set to dispose of them [6, 7]. In the past decade,
many studies have focused on the potential of illegal waste augmented mortality rate in some cities included in this area due to the development of various neoplastic diseases. The manuscripts mentioned and the interest of the media have created important issues due to the high amount of pollutants generated by the illegal combustion and percolation of liquid waste through the soil, which can contaminate all environmental compartments: air, water, and soil eventually entering the trophic chain and affecting animal and vegetable [8].

PCBs appear as artificial organic compounds formed by a biphenyl with variable numbers of chlorine atoms alternating on two benzene rings composed of six carbons. These compounds could have 10 homologues and 209 congeners recognized on the basis of the number and position of the chlorine atoms. These contaminants are lipophilic chemicals commonly used in electronics manufacture, as vehicles for pesticides, and in building materials [9]. The global production of PCBs has been estimated to be over 1.3 million tons [10, 11]. Because of their toxicity and danger to human health, the use of PCBs was banned in the U.S. and in most industrialized countries since 1970s.

Organochlorine pesticides (OCPs) are widely used organic pollutants, which caused widespread concern around the world due to their resistance to environmental decay. They belong to the group of chlorinated hydrocarbon derivatives, which have vast application in the chemical industry and in agriculture [12]. The production and usage of these pesticides were stopped or restricted in the 1970s and 1980s in developed countries; however, most OCPs, especially dichlorodiphenyltrichloroethane (DDTs) and hexachlorocyclohexanes (HCHs), are still used in some developing countries in agriculture due to their high efficiency, low cost, and broad-spectrum pest-killing efficacy [9, 13].

The marine environment, as confirmed by many studies, seems to be one of the primary places for the accumulation of PCB and OCP [14, 15]. It is believed that water and sediment are probably the main means of assessing the degree of marine pollution. Due to their high persistence and limited mobility, sediments represent fundamental wells and environmental reservoirs for establishing the temporal order of PCBs and OCPs [16]. United Nations Environment Program [17] has considered the Mediterranean Sea as one of the water basin for the monitoring because it represents a regionally based assessment of sources, of environmental levels, of transport pathways and of effects of persistent toxic substances in the environment [17]. Moreover, the Barcelona Convention for the Protection of the Mediterranean Sea, including the Mediterranean Action Plan (MAP) and the Mediterranean Marine Pollution Monitoring and Research Program (MED POL), has encouraged the implementation of monitoring programs for evaluating the health status of this water body [18]. As is evident from the above, it is crucial to consider the role played by the Volturno River in keeping Mediterranean Sea “clean”.

This study is part of a wider project that aims to assess the pollution of the Volturno River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea). In particular, the project aims to assess the pollution of water and sediments of the Volturno River and the estuary, trying to identify the different organic and inorganic chemicals present and the possible origin of these substances (industrial, agricultural and household waste). To the best of our knowledge, no previous studies report the load of PCBs and OCPs into the Central Mediterranean Sea from Volturno River. The main objectives of the present study are (i) to assess the PCBs and OCPs pollution of the Volturno River; (ii) to estimate the PCBs and OCPs input into the Central Mediterranean Sea (Tyrrhenian Sea) from Volturno River; (iii) to evaluate the spatial distributions and temporal trends of PCBs and OCPs concentrations in the Volturno River and its estuary; (iv) to assess the PCBs and OCPs risk in this area of the Central Mediterranean Sea and (v) to provide a guide in policy formulation toward the restoration of the river and to create a starting point about a future study on the pollution of this area.

Materials and methods
Study area
The Volturno River is one of the most important rivers in southern Italy (Fig. 1), with an annual flow rate of 82.1 m³/s. A large quantity of pollutants are discharged from factories, sewage and agricultural discharges and they are introduced into the Volturno River [19, 20]. The Volturno River originates in Molise, and it receives the input of many tributaries, including the Calore river, which is also very polluted, increases the concentrations of contaminants in the Volturno River. In the lower part of the basin, the Volturno river flows through the cities of Capua and Castelvolturno before flowing into the Tyrrhenian Sea.

Sampling
Four intensive sampling campaigns have been conducted in the summer, autumn, winter and spring of 2017–2018 to assess the seasonal variations of the Volturno flow. In each campaign, one location at the river mouth and nine points in the continental shelf around the Volturno mouth were sampled (Fig. 1). In each sampling point, 2.5 L of water and surface sediment were collected and transported refrigerated (4 °C) to the laboratory.
Pre-cleaned 2.5 L glass amber bottles were deployed closed with a home-made device as described previously [3, 21, 22]. This device consists in a stainless steel cage holding the sampling bottle, which is submerged sealed with a PTFE stopper that can be remotely opened at the desired sampling depth (in this case at about 0.5 m depth). In each sampling point, 2.5 L of water (one amber bottle) was collected and transported refrigerated (4 °C) to the laboratory. Water samples were filtered through a previously kiln-fired (400 °C overnight) GF/F glass fibre filter (47 mm previously kiln-fired (400 °C overnight) GF/F glass fibre filter (47 mm × 0.7 μm; Whatman, Maidstone, UK). Filters (suspended particulate matter SPM) were kept in the dark at −20 °C until analysis. Dissolved phase refers to the fraction of contaminans passing through the filter. This includes the compounds that are both truly dissolved as well as those associated with colloidal organic matter. These filtrates were kept in the dark at 4 °C and extracted within the same day of sampling (3–6 h from sampling).

Surface sediment (0–5 cm) samples were collected using a grab sampler (Van Veen Bodemhappe 2 L capacity) and put in aluminium containers. The sediments were transported refrigerated to the laboratory and kept at −20 °C before analysis.

Extraction and analyses

**Suspended particulate phase**

Suspended particulate phase (SPM) content was gravimetrically determined, after drying the filter in an air-heated oven (55 °C until constant weight) and equilibrated at room temperature in a desiccator. Filters were spiked for recovery calculations with a solution of PCB International Union of Pure and Applied Chemistry (IUPAC) #65 and PCB IUPAC #166 with 2 ng for each PCB. Filters were extracted three times by sonication with 10 mL of dichloromethane/methanol (1:1) (Carlo Erba, Milano, Italy) for 15 min. The pooled recovered extracts were dried on anhydrous Na₂SO₄ (Carlo Erba), concentrated to 0.5 mL under vacuum and solvent exchanged to hexane (Carlo Erba). Extract fractionation was carried out by open column chromatography (3 g of neutral alumina Carlo Erba, deactivated with 3% (w/w) Milli-Q water), and the OCPs were eluted with 5.5 mL of hexane (Merck) in fraction I (PCBs and p,p′-DDE) and 6 mL of hexane/ethyl acetate (9:1) (Merck) in fraction II (p,p′-DDD and p,p′-DDT). Finally, the column was eluted with 12 mL of ethyl acetate (fraction III) containing more polar compounds.

**Dissolved phase**

The dissolved phase (DP) was spiked with a surrogate solution of PCB IUPAC #65 and PCB IUPAC #166, achieving a final concentration in water of 5 ng L⁻¹. Two litres of previously filtered water (DP) were preconcentrated by solid-phase extraction (SPE) using a 100 mg polymeric phase cartridge Strata XTM from Phenomenex (Torrance, CA, USA). After eluting with 10 mL ethyl acetate/hexane (1:1), the extract was rotaevaporated to roughly 0.5 mL. The sample was fractionated using an alumina open column chromatography as indicated above for the particulate phase.

**Sediment**

Sediments were oven dried at 60 °C and sieved at 250 μm. Five-gram aliquots were spiked with the surrogate mixture (2 ng of PCB IUPAC #65 and PCB IUPAC #166) and extracted three times by sonication using 15 mL of DCM/methanol (1:1) for 15 min. After centrifuging, the organic extract was concentrated and fractionated as the water samples.

**Analytical determination of PCBs and OCPs**

Cleaned extracts of fractions I and II were analyzed by GC electron capture detector (ECD) using a GC 17A Shimadzu (Kyoto, Japan) equipped with an AOC-20i Shimadzu (Kyoto, Japan) autosampler. Samples were injected in the split mode at 230 °C, and the detector was held at 310 °C. Helium (1.93 mL min⁻¹ at 150 °C) and nitrogen (50 mL min⁻¹) were used as carrier and make-up gases. Chromatographic separation was achieved using a 50 m × 0.25 mm ID × 0.25 μm CPSil8 CB column. Identification of PCBs was carried out by comparing retention times with standards. The presence of OCPs was confirmed by means of GC–MS using a GC–MS 2010 Plus Shimadzu (Kyoto, Japan) working in the electron impact mode and operating at 70 eV. The transfer line and ion source temperatures were held at 240 and 200 °C, respectively. Compound identification was carried out by comparing retention times with standards and using the characteristic ions and their ratio for each target analyte, confirming for the higher concentrated samples, the identification of target analytes in full-scan mode. The concentrations were calculated from the calibration curves for the PCBs (C-SCA-06 PCB Congeners Mix #6; AccuStandard, Inc., CT 06513, USA) and OCPs (M-8080 Organochlorine Pesticides; AccuStandard, Inc., CT 06513, USA) (r² > 0.97). PCB IUPAC #30 (2,4,6- trichlorobiphenyl) and PCB IUPAC #204 (2,2′,3,4,4′,5,6,6′- octachlorobiphenyl) were used as an internal standard to compensate for the sensitivity variation of the ECD detector, and triphenylamine of the MS detector.

In each sample of DP, SPM and sediment, the concentration of following 32 selected PCBs were measured: IUPAC PCB numbers 8, 28, 37, 44, 49, 52, 60, 66, 70, 74, 77, 82, 87, 99, 101, 105, 114, 118, 126, 128, 138, 153, 156, 158, 166, 169, 170, 179, 180, 183, 187 and 189. In each
sample of DP, SPM and sediment, the concentration of following OCPs was measured: aldrin, α-BHC, β-BHC, δ-BHC, γ-BHC (lindane), 4,4′-DDD, 4,4′-DDE, 4,4′- DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, endrin, heptachlor, heptachlor epoxide (isomer B) and methoxchlor.

Quality assurance and quality control
The data quality of OCPs and PCBs was assured through the analysis of solvent blanks, procedural blanks, internal standards, and detection limits, as well as certified reference materials. All reagents used during the analysis were exposed to the same extraction procedures and run to check for interfering substances. Certified reference materials and blank samples were run between for every ten samples, in the same way as samples. The surrogate standards used were PCB #65 and PCB #166, that were added to all samples prior to extraction to quantify procedural recoveries. Method Detection Limit (MDL) and Instrument Detection Limit (IDL) were calculated as follows: MDL were determined as the average blank values plus three times the standard deviation and it ranged from 0.005 to 0.050 ng L⁻¹ for individual PCBs and OCPs in the particulate phase. In the dissolved phase, the values ranged from 0.005 to 0.100 ng L⁻¹ and from 0.0002 to 0.0050 ng g⁻¹ in the sediment; IDL was calculated as a signal to noise ratio because lowest calibration level produced a signal that distinguishable from a blank at a 3 S/N ratio.

If the concentration of any analyte in a sample was below its MDL/IDL, this compound was considered as not detected in the sample (below the limit of detection, < LOD).

The surrogate averaged recoveries in the dissolved phase were 95.8±7.0% for PCB #65 and 95.7±5.2% for PCB #166. In the SPM samples, recoveries were 95.4±4.3% for PCB #65 and 95.2±5.8% for PCB #166. Finally, in the sediment samples, the averaged recoveries were the following: 96.8±7.2% for PCB #65 and 93.1±4.1% for PCB #166. Resulting data for PCB and OCP pesticides were corrected for surrogate recoveries.

Statistical analysis and calculation of the pollutant inputs
Statistical analyses were conducted with SPSS, version 22.0 statistic software package (IBM-SPSS Inc., Chicago, IL, USA). All means are arithmetic unless otherwise noted. Statistical significance was defined as p ≤ 0.05.

The method used to estimate the annual contaminant discharges (F annual) was based on the UNEP guidelines (UNEP/MAP 2004) and has been widely accepted [23–25]. A flow-averaged mean concentration (C aw) was calculated for the available data, which was corrected by the total water discharge in the sampled period. The equations used were the following:

\[
C_{aw} = \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \tag{1}
\]

\[
F_{\text{annual}} = C_{aw} Q_T \tag{2}
\]

where \(C_i\) and \(Q_i\) are the instantaneous concentration and the daily averaged water flow discharge, respectively, for each sampling event (flow discharge, section and bed elevation of river mouth were measured by manual probes). \(Q_T\) represents the total river discharge for the period considered (November 2017–July 2018), calculated by adding the monthly averaged water flow. River flow data was collected from the register of the Autorità di Bacino Nazionale dei Fiumi Liri-Gargliano e Volturno [26].

Principal component analysis (PCA) was applied to the correlation matrix with Varimax rotation and Kaiser Normalization for PCB concentrations in the water and sediments to identify the possible sources.

Calculation of toxicity equivalent (TEQ) of Dioxin-Like PCBs
Some PCBs are called dioxin-like PCBs because they have a similar chemical structure to dioxins and furans. In fact, 12 PCB congeners (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) defined as dioxin-like-PCBs (DL-PCBs) have been selected, because they have been defined as hazardous to the environment and human health [27, 28]. Therefore, the toxicity equivalent (TEQ), established by the World Health Organization (WHO 2005), was calculated by summing the multiplication of congener concentrations with congener-specific Toxic Equivalency Factors (TEFs) [29]. TEFs are an essential part of the Toxic Equivalent (TEQ) concept and have evolved for dioxins/dioxin-like compounds over the last two and half decades.

The TEF values are 0.0001 for PCB 77; 0.0003 for PCB 81; 0.00003 for PCB 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189; 0.03 for PCB 169 and 0.1 for PCB 126. The TEQ values were calculated using the measured DL-PCB concentrations in sediment samples and WHO 2005 TEF values for human and mammals [29]. The TEQ maximum tolerable US EPA value is 0.7 pg WHO-TEQ/kg body weight.

The calculation was carried out using:

\[
\Sigma \text{TEQ} = \Sigma C_i \times \text{TEF}_i
\]

where \(C_i\) was the concentration (nanograms per gram) of DL-PCBs. The TEQ in this study was used to determine whether the PCB levels in the studied sediments could pose any significant threat to humans or the environment.
| Site Number identification | Site characteristics | Site location | ΣPCBs | Dissolved Phase (ng L$^{-1}$) | Particulate phase (ng L$^{-1}$) (ng g$^{-1}$ dry wt) | Sediments (ng g$^{-1}$ dry wt) |
|---------------------------|----------------------|---------------|-------|-------------------------------|------------------------------------------------|---------------------|
| 1 (river water)           | Volturno River Source | 40°48'54.03"N 14°36'45.36"E | 7.48  | 10.2  | 8.04  | 5.23  | 170 (2091.6) | 11.3 (1157.1) | 32.2 (2843.7) | 42.8 (2170.8) | 64.4 |
| 2 (sea water)             | River Mouth at 500mt North | 40°46'42.73"N 14°34'00.48"E | 6.71  | 7.70  | 6.56  | 4.68  | 2.71 (293.5) | 2.94 (1567.0) | 9.47 (305.2)  | 22.2 (190.0)   | 29.2 |
| 3 (sea water)             | River Mouth at 500mt Central | 40°46'00.34"N 14°33'10.68"E | 6.80  | 6.29  | 6.84  | 4.76  | 5.2 (1269.8) | 7.74 (2735.9) | 10.8 (3481.2) | 6.85 (2300.7) | 18.4 |
| 4 (sea water)             | River Mouth at 500mt South | 40°43'42.62"N 14°28'07.89"E | 7.72  | 9.37  | 7.77  | 5.02  | 8.76 (858.1) | 5.34 (4995.5) | 26.9 (780.7)  | 30.6 (286.7)  | 51.2 |
| 5 (sea water)             | River Mouth at 1000mt North | 40°43'40.11"N 14°28'06.45"E | 6.21  | 6.86  | 5.81  | 3.94  | 1.74 (235.0) | 2.31 (160.8)  | 6.55 (495.8)  | 8.08 (79.8)  | 22.1 |
| 6 (sea water)             | River Mouth at 1000mt Central | 40°43'42.46"N 14°28'05.03"E | 6.35  | 5.85  | 6.71  | 3.74  | 3.87 (1356.3) | 4.79 (1593.9) | 4.27 (1479.6) | 2.66 (870.5)  | 10.3 |
| 7 (sea water)             | River Mouth at 1000mt South | 40°43'45.09"N 14°28'05.17"E | 6.90  | 8.88  | 6.74  | 4.73  | 5.75 (660.5) | 4.28 (291.4)  | 17.4 (664.7)  | 11.5 (966.6)  | 30.7 |
| 8 (sea water)             | River Mouth at 1500mt North | 40°43'56.88"N 14°28'02.94"E | 5.07  | 5.55  | 4.84  | 2.41  | 1.49 (1488)  | 0.71 (42.5)   | 2.71 (946.1)  | 3.76 (1185.2) | 9.2  |
| 9 (sea water)             | River Mouth at 1500mt Central | 40°43'42.25"N 14°27'59.97"E | 4.92  | 5.89  | 5.00  | 2.28  | 2.71 (8772)  | 2.75 (922.3)  | 1.82 (652.9)  | 1.78 (609.0)  | 4.3  |
| 10 (sea water)            | River Mouth at 1500mt South | 40°43'49.38"N 14°27'59.82"E | 5.93  | 7.48  | 5.62  | 3.96  | 3.32 (11785) | 2.94 (245.1)  | 5.06 (131.0)  | 7.54 (2654.9) | 25.9 |
Results and discussions
PCBs in the water dissolved phase suspended particulate matter and sediment samples
The concentrations of total PCBs, as shown in Table 1, obtained in the DP ranged from 2.28 ng L\(^{-1}\) (site 9) to 10.0 ng L\(^{-1}\) (site 1) with a mean value of 6.07 ± 1.67 ng L\(^{-1}\). In Fig. 2a, is reported the compositional profiles of PCBs in the DP; data show that tetra, penta and hexa-CBs were abundant in all sampling sites, indicating on average over 84% of ΣPCBs. Hepta-CB were present in low concentrations, accounting for only 7% of total PCBs. The dominance of high CBs (tetra, penta and hexa) in the water could be explained because PCBs are semi-volatile persistent contaminants and their solubility and volatility reduce as the number of chlorine atoms increases [30, 31].

In the SPM, the PCBs concentrations on dry weight (dw) ranged from 0.71 ng L\(^{-1}\) (42.5 ng g\(^{-1}\)) in site 8 to 42.8 ng L\(^{-1}\) (2170.8 ng g\(^{-1}\)) in site 1 (mean value of 8.82 ± 9.6 ng L\(^{-1}\)) Table 1. PCBs most abundant in almost all sampling sites were tetra, penta, and hexa-CB accounting for 33, 31, 19% of ΣPCBs in SPMs, probably because higher chlorinated PCBs are mainly adsorbed by the particulate matter due to their low hydrophilic properties, in fact also the proportion of hepta-CBs increased to 8.02% compared to DP (Fig. 2a).

In Table 1, are also reported the values of the total PCBs concentrations in sediments; in particular, they range from 4.3 ng g\(^{-1}\) (site 9) to 64.4 ng g\(^{-1}\) (site 1) (mean value of 26.5 ± 18.8 ng g\(^{-1}\)) Table 1. Tetra and penta-CBs were abundant in sediments at each site, accounting, for 26 and 35% of ΣPCBs, respectively (Fig. 2a). The proportion of hepta-PCBs increased to 12% (4% more than that in SPM samples). In addition, the proportion of di-+ tri-PCBs decreased in sediments samples (2.8%) compared to SPM (7.6%) and DP (8.1%) samples. These results could indicate that lower chlorinated PCBs are progressively transported from the sediment due to their relatively high water solubility and easier degradation. Infact, higher chlorinated PCBs levels increased in the sediments due to their low degradation and vaporization rates, high liposolubility, and easy partitioning to particles with rich organic carbon.

Sediments tend to be a sink for these organic pollutants and are a measure of their concentrations over times, therefore, the higher chlorinated PCBs are most probably to be associated with the sediment or particulate adsorption phase than the lower chlorinated PCBs [32].

The concentrations of PCBs in the Volturno River have been analysed and compared with the concentrations found in other rivers and estuary in the world, to understand the degree of contamination due to these pollutants. As showed in Table 2, PCBs in samples from the Volturno River were similar to those found in the Hangzhou Bay, China [33], in the Chenab River, Pakistan [34], in the Portuguese coast, Portugal [35] and in Chenab River, Pakistan, by [36]. The concentrations were higher than those presented in the Tokyo Bay, Japan [37], in the Chao River, China [38], in the Haizhou Bay, China [27], in the Daliao River Estuary, China [39], in the Shuangtzaizi Estuary, China [9], in the Chaohu Lake, China [28], in the Yellow River, China [11], in the China Sea, China [40], in
Table 2 Concentration ranges and mean value of PCBs in the water dissolved phase (DP), the suspended particulate matter (SPM) and the sediments from recent studies of different rivers, estuaries and coasts in the world

| Area                              | References                  | N. of PCBs | DP (ng L\(^{-1}\)) Range | Mean | SPM (ng L\(^{-1}\)) Range | Mean | Sediments (ng g\(^{-1}\)) Range | Mean |
|-----------------------------------|-----------------------------|------------|---------------------------|------|---------------------------|------|-------------------------------|------|
| PCBs                              |                             |            |                           |      |                           |      |                               |      |
| Tokyo Bay, Japan                  | Kobayashi et al. [37]       | 209        | 0.04–0.64                 | 0.096| 0.05–0.58                 | 0.15 | 2.7–110                       | 39.0 |
| Bengal Bay, India                 | Chakraborty et al. [76]     | 19         |                           |      |                           |      |                               |      |
| Yangtze Estuary, China            | Gao et al. [19]             | 28         |                           |      |                           |      |                               |      |
| Chao River, China                 | Yu et al. [38]              | 12         |                           |      |                           |      |                               |      |
| Haizhou Bay, China                | Zhang et al. [27]           | 22         |                           |      |                           |      |                               |      |
| Daliao River Estuary, China       | Men et al. [39]             | 41         | 5.51–40.28                | 16.91| 6.78–66.55                | 21.81| 0.83–72.9                     | 1.77 |
| Shuangtaizi Estuary, China        | Yuan et al. [9]             | 28         |                           |      |                           |      |                               |      |
| Chaohu Lake, China                | He et al. [28]              | 34         |                           |      |                           |      |                               |      |
| Yellow River, China               | Gao et al. [11]             | 12         |                           |      |                           |      |                               |      |
| Hangzhou Bay, China               | Adeleye et al. [33]         | 9          |                           |      |                           |      |                               |      |
| China Sea, China                  | Kaiser et al. [40]          | 24         |                           |      |                           |      |                               |      |
| Chenab River, Pakistan            | Mahmood et al. [36]         | 32         | 0.21–27.5                 | 5.72 |                           |      | 0.83–59.4                     | 13.9 |
| Ravi River, Pakistan              | Syed et al. [49]            | 31         |                           |      |                           |      | 4.6–424.3                    | 49.0 |
| Chenab River, Pakistan            | Eqani et al. [34]           | 7          | 1.1–8.5                   | 2.8  |                           |      |                               |      |
| Congo River Basin, Congo          | Verhaert et al. [41]        | 33         |                           |      |                           |      |                               |      |
| Congo River Basin, Congo          | Mwanamoki et al. [42]       | 12         |                           |      |                           |      |                               |      |
| Umgeni River, South Africa        | Gakuba et al. [50]          | 8          | 6.91–21.69                |      |                           |      | 102.60–427.8                 | 1.77 |
| Msunduzu River, South Africa      | Adeyinka [51]               | 8          |                           |      |                           |      | 3617–5041.6                  | 2163.4|
| Sea Lots, Trinidad and Tobago     | Mohammed et al. [52]        | 136        |                           |      |                           |      | 62–601                        | 6.49–141.68|
| Panama Canal and California Coast, USA | Menzies et al. [53]     | 19         | ND-18,450                 | 1164.0|                           |      | 62–601                        | 6.49–141.68|
| Bedford Harbor, USA               | Subedi et al. [54]          | 136        |                           |      |                           |      | 2800.0–109,000               | 50.7 |
| Chiacago Ship Canal, USA          | Peverly et al. [55]         | 209        |                           |      |                           |      | 690–5000                     |      |
| Midway Atoll, Hawaii              | Ge et al. [55]              | 28         |                           |      |                           |      | 2.6–148.8                    |      |
| Portuguese coast, Portugal        | Ferreira et al. [35]        | 17         |                           |      |                           |      | 4.2–30.1                     |      |
| Portuguese Coastal area, Portugal | Carvalho et al. [57]        | 7          |                           |      |                           |      | 4366.8                       |      |
| Moscow River, Russia              | Eremina et al. [48]         | 9          | ND–180.7                  |      |                           |      | 03–466.8                     |      |
| Someșu Mic River, Romania         | Barhoumi et al. [61]        | 20         |                           |      |                           |      | 274–252.72                   |      |
| Rhone River, France               | Mourier et al. [58]         | 7          |                           |      |                           |      | 115–417.1                    |      |
| Huveaune River, France            | Kanzari et al. [59]         | 7          |                           |      |                           |      | 28–435.0                     | 148.0|
| Durance River and Berre Lagoon, France | Kanzari et al. [60]     | 7          |                           |      |                           |      | 003–514.4                    |      |
| Izmir Bay, Turkey                 | Pazi et al. [43]            | 20         |                           |      |                           |      | 021–31.95                    |      |
| Egyptian Coast, Egypt             | Barakat et al. [83]         | 96         |                           |      |                           |      | 229–377.0                    | 32.2 |


Table 2 (continued)

| Area                        | References             | N. of PCBs | DP (ng L⁻¹) | SPM (ng L⁻¹) | Sediments (ng g⁻¹) | DP + SPM (ng L⁻¹) |
|-----------------------------|------------------------|------------|--------------|---------------|-------------------|------------------|
| Nador Lagoon, Marocco       | Giuliani et al. [44]   | 127        |              |               | 2.50–207          | 9.17             |
| Tripoli Harbor, Lebanon     | Merhaby et al. [62]    | 28         |              |               | 17.81–301.95      |                  |
| Morava River, Czech Republic| Kukucka et al. [45]    | 12         |              |               | 0.17–0.98         |                  |
| Plitvice Lakes, Croatia     | Dvorscak et al. [46]   | 17         |              |               | 0.07–1.78         |                  |
| River Po, Italy             | Viganò et al. [63]     | 14         |              |               | 48.6–335.0        |                  |
| Adriatic Sea, Italy         | Combi et al. [47]      | 28         |              |               | ND-90             |                  |
| Mar Piccolo coast, Italy    | Bellucci et al. [64]   | 32         |              |               | 82.9–1045.0       |                  |
| This study                  |                        | 32         | 2.28–10.0    | 0.71–42.8     | 4.37–64.4         | 4.07–48.04       |

Range | Mean | Range | Mean | Range | Mean | Range | Mean | Range | Mean |
-----------|------|-------|------|-------|------|-------|------|-------|------|
2.28–10.0 | 6.07 | 0.71–42.8 | 8.82 | 4.37–64.4 | 26.5 | 4.07–48.04 | 14.9 |
OCPs in the water dissolved phase suspended particulate matter and sediment samples

The concentrations obtained for total OCPs in the DP samples ranged from 0.45 ng L\(^{-1}\) (site 9) to 6.98 ng L\(^{-1}\) (site 1) (mean value of 1.51 ± 1.20 ng L\(^{-1}\)) Table 3. In particular, as shown in Fig. 2b they ranged from ND to 0.89 ng L\(^{-1}\) (mean value of 0.36 ng L\(^{-1}\)) for hexachlorocyclohexanes (α-BHC, β-BHC, δ-BHC, γ-BHC), from ND to 1.34 ng L\(^{-1}\) (mean value of 0.38 ng L\(^{-1}\)) for dichlorodiphenyltrichloroethane and its degradates (4,4′-DDD, 4,4′-DDE, 4,4′-DDT and methoxychlor) and from 0.10 to 4.65 ng L\(^{-1}\) (mean value of 0.77 ng L\(^{-1}\)) for cyclodienes (aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, endrin, heptachlor and heptachlor epoxide). In DP samples, the HCHs/DDTs ratio was > 1 at most sites (mean 1.20 ± 1.07; range ND-3.91), and the DDTs/cyclodienes ratio was < 1 at most sites (mean 0.69 ± 0.65; range ND-2.95). The HCHs/cyclodienes ratio varied within a range of ND-3.07 (mean value of 0.71 ± 0.58).

The OCPs concentrations in the SPM samples, ranged from 0.08 ng L\(^{-1}\) (29.1 ng g\(^{-1}\) dw) in site 9 to 5.67 ng L\(^{-1}\) (287.6 ng g\(^{-1}\) dw) in site 1 (mean value of 1.01 ± 1.05 ng L\(^{-1}\)) Table 3. The HCHs ranged from ND to 0.96 ng L\(^{-1}\) (mean 0.33 ng L\(^{-1}\)), the DDTs from ND to 0.95 ng L\(^{-1}\) (mean 0.20 ngL\(^{-1}\)), and the cyclodienes from ND to 3.75 ng L\(^{-1}\) (mean 0.47 ngL\(^{-1}\)), as shown in Fig. 2b. The HCHs/DDTs ratio was > 1 at most sites with an average of 17.8, while the HCHs/cyclodienes and DDTs/cyclodienes ratios were < 1 at most sites (mean 1.88 and 2.27, respectively).

The total OCPs concentrations in sediments Table 3 ranged from 0.52 ng g\(^{-1}\) (site 8) to 9.89 ng g\(^{-1}\) (site 1) (mean value of 2.69 ± 2.78 ng g\(^{-1}\)). The HCHs ranged from 0.05 to 1.34 ng g\(^{-1}\) (mean 0.32 ng g\(^{-1}\)), the DDTs from 0.10 to 5.22 (mean 1.16 ng g\(^{-1}\)) and the cyclodienes from 0.13 to 3.32 ng g\(^{-1}\) (mean 1.20 ng g\(^{-1}\)) (Fig. 2b). The cyclodienes and DDTs concentrations were similar but they prevailed than those of HCHs. Infact, the DDTs/cyclodienes ratio was < 1 at most sites (mean 0.63), such as the HCHs/DDTs and HCHs/cyclodienes ratios (means 0.37 and 0.24, respectively). Therefore, the concentrations of cyclodienes in sediment, SPM and DP samples of the Volturno River and Estuary were higher than those of HCHs, while DDT were similar in the DP samples compared to HCHs concentrations but were lower than those of HCHs in SPM and were higher in sediment samples. Therefore, abundant concentrations of DDTs and HCHs could be justified due to extensive use in agricultural and to a large amount of municipal waste [30, 49]. In detail, the average compositions of HCHs were the following: in DP, α-HCH = 11%, β-HCH = 66%, γ-HCH = 39% and δ-HCH = 4%; in SPM, α-HCH = 9%, β-HCH = 51%, γ-HCH = 36% and δ-HCH = 2%; and in sediments, α-HCH = 10%, β-HCH = 29%, γ-HCH = 49% and δ-HCH = 9%. Among the HCH isomers analyzed, β-HCH was the highest in all the sites, which was attributed to its high environmental stability and low volatility [65]. There is also a possibility of α-HCH and γ-HCH transforming to β-HCH isomer, therefore, making it the most predominant contaminant [66]. A similar trend for β-HCH has also been reported by [67] and [68]. The low levels of lindane (γ-HCH) were attributed to its restricted use, and transformation to β-HCH, with its presence also signifying past use of the pesticide α-HCH gave the lowest concentration among the isomers probably due to its high vapor pressure [69].

It is also very important to evaluate the biodegradation of DDT in its metabolites in the riverine ecosystem. DDT biodegraded into DDE under aerobic conditions via dehydrochlorination and oxidation process, and into DDD involving reductive dechlorination under anaerobic conditions [49]. To ascertain whether the reported levels of DDT in the present study were due to current or past application, the ratio of p,p′-DDT to its metabolites p,p′-DDE and p,p′-DDD was applied. A ratio of > 0.5 suggested aged use and a ratio of < 0.5 indicated fresh input [70]. The mean values of (DDD + DDE)/DDT ratio in DP, SPM and sediment samples of the Volturno River and its estuary were 13.8, 14.8 and 16.8, respectively. These results suggest that most of the DDTs in the Volturno River were derived from historical discharge (Fig. 3), due to their capability to remain in the agricultural soil for a long time and re-mobilize through evaporation and runoff [71]. DDT has been banned from agricultural use and restricted for public health purpose under the Stockholm convention. The present study, therefore, gives an indication of the restricted use of DDT for agricultural.
Table 3 Description of the sampling sites and concentration of OCPs in the water dissolved phase (DP), the suspended particulate matter (SPM) and the sediments of the Volturno River, Southern Italy

| Sampling Location | Site number and identification | Site characteristics | Site Location | ΣOCPs (ng L⁻¹) | Particulate Phase (ng L⁻¹) (ng g⁻¹ dry wt) | Sediments (ng g⁻¹ dry wt) |
|-------------------|--------------------------------|----------------------|---------------|---------------|------------------------------------------|--------------------------|
|                   |                                |                      | 1 (river water) Volturno River Source 40°48′54.03″N 14°36′45.36″E | 4.25 6.98 3.75 1.95 | 2.11 (259.7) 1.68 (172.6) 405 (3573) 5.67 (2876) | 9.89 |
|                   |                                |                      | 2 (sea water) River Mouth at 500mt North 40°46′42.73″N 14°43′40.00″E | 1.57 1.98 2.12 1.10 | 0.55 (60.2) 0.57 (307.7) 1.53 (495) 1.80 (153) | 3.50 |
|                   |                                |                      | 3 (sea water) River Mouth at 500mt Central 40°46′00.34″N 14°33′10.68″E | 0.95 1.55 1.96 0.88 | 0.93 (236.4) 0.41 (144.9) 0.85 (2738) 0.65 (2198) | 1.35 |
|                   |                                |                      | 4 (sea water) River Mouth at 500mt South 40°43′42.62″N 14°28′07.89″E | 1.64 2.47 2.25 1.90 | 1.51 (148.7) 0.73 (686.6) 1.67 (484) 2.35 (220) | 4.32 |
|                   |                                |                      | 5 (sea water) River Mouth at 1000mt North 40°43′40.11″N 14°28′06.45″E | 0.97 1.08 1.96 0.99 | 0.48 (64.5) 0.55 (38.5) 0.98 (746) 0.99 (882) | 1.41 |
|                   |                                |                      | 6 (sea water) River Mouth at 1000mt Central 40°43′42.46″N 14°28′05.03″E | 0.87 1.22 1.23 0.51 | 0.68 (2380) 0.10 (343) 0.77 (2685) 0.50 (1652) | 1.15 |
|                   |                                |                      | 7 (sea water) River Mouth at 1000mt South 40°43′45.09″N 14°28′05.17″E | 1.02 1.99 0.66 1.16 | 0.10 (115.2) 0.29 (203) 0.75 (375) 0.98 (821) | 2.13 |
|                   |                                |                      | 8 (sea water) River Mouth at 1500mt North 40°43′35.68″N 14°28′02.94″E | 0.60 0.95 0.91 0.73 | 0.43 (43.3) 0.35 (213) 0.73 (2555) 0.57 (1819) | 1.26 |
|                   |                                |                      | 9 (sea water) River Mouth at 1500mt Central 40°43′42.25″N 14°27′59.97″E | 0.61 0.93 0.88 0.45 | 0.40 (131.5) 0.08 (291) 0.44 (1597) 0.48 (1655) | 0.52 |
|                   |                                |                      | 10 (sea water) River Mouth at 1500mt South 40°43′49.26″N 14°27′59.82″E | 0.92 1.10 0.52 0.80 | 0.58 (207.0) 0.10 (895) 0.57 (149) 0.66 (2332) | 1.37 |
With regard to the cyclodiene pesticides and their metabolites, endosulfan sulfate was the cyclodiene pesticides with the highest levels in water samples (sum of DP and SPM), accounting for 11.3% of ΣOCPs. Endosulfan has still been used in agricultural activities in Italy. It was established that heptachlor is metabolised to heptachlor epoxide. The mean values of heptachlor/heptachlor epoxide ratio in the aquatic environment of the Volturno were 0.17, respectively. This present trend where the degradation product was higher than the parent compound gives an indication of no fresh inputs of this pesticide in the water body [72].

Compared with other polluted rivers in the world Table 4, OCPs in samples from the Volturno River were close to those found in the Plitvice Lakes, Croatia [46], in the Arc River, France [16] and in the Izmir Bay, Turkey by [43]. The concentrations were much higher than those presented in the Yangtze River, China [73], in the Yangtze River, China [74], in the China Sea, China [40], in the Congo River Basin, Congo [42], in the Gulf of Batabanò, Cuba [75] and in the Durance River and Berre Lagoon, France [60]; but lower than those found in the Bengal Bay, India [76], in the Pearl River Delta, China [77], in the Poyang Lake, China [78], in the Hangzhou Bay, China [33], in the Hangzhou Bay, China [79], in the Awash River Basin, Ethiopia [80], in the Nairobi River, Kenya [69], in the Sea Lots, Trinidad and Tobago [52], in the Jaguariibe River, Brazil [81], in the Portuguese Coastal Area, Portugal [57], in the Moscow River, Russia [48], in the Candarli Gulf, Turkey [82], in the Egyptian Coast, Egypt [83], in the River Po, Italy [63], in the Northern coast of Cyprus [84] and in the Someşu Mic River, Romania [61].

Spatial and seasonal distribution of PCBs and OCPs in the water DP, SPM and sediment samples

The concentrations of total PCBs in DP, SPM and sediment samples of the Volturno River (Table 1, Fig. 2a) showed that the total amount of PCBs in sediment samples was more abundant than their corresponding waterbodies (DP and SPM samples). Infact, the ratio of the concentration of ΣPCBs in sediment samples to that in the corresponding waterbodies (DP and SPM samples) was > 1 in most sampling sites. Moreover, the high chlorinated congener (hepta-CB) concentrations decreased from sediment samples to SPMs and more to DPs (Fig. 4), while less chlorinated PCBs (di- + tri-CBs) showed a reverse trend with an increase of concentrations from sediment samples to SPMs and DPs.

In Italy, the use and sale of PCBs have been banned, but despite these compounds were released into the environment due to anthropogenic activities such as illegal incineration of waste, materials treated with pentachlorophenol or substances containing chlorine. In addition, PCBs were once widely used as dielectric and coolant fluids in electrical appliances such as transformers and capacitors. PCBs were also used as pesticide extenders, heat exchange fluids, and flame retardants [85, 86].
Table 4 Concentration ranges and mean value of OCPs in the water dissolved phase (DP), the suspended particulate matter (SPM) and the sediments from recent studies of different rivers, estuaries and coasts in the world

| Area                    | References                  | N. of OCPs | DP (ng L\(^{-1}\)) | SPM (ng L\(^{-1}\)) | Sediments (ng g\(^{-1}\)) | DP + SPM (ng L\(^{-1}\)) |
|-------------------------|-----------------------------|------------|---------------------|----------------------|--------------------------|--------------------------|
|                         |                             |            | Range               | Mean                 | Range                   | Mean                     | Range                   | Mean |
| OCPs                    |                             |            |                     |                      |                         |                          |                         |      |
| Asia                    |                             |            |                     |                      |                          |                          |                          |      |
| Bengal Bay, India       | Chakraborty et al. [76]     | 2          | 2–245               | 47                   |                          |                          |                          |      |
| Pearl River Delta, China| Huang et al. [77]           | 8          | 14.8–87.8           |                      |                          |                          |                          |      |
| Yangtze River, China    | Zhou et al. [74]            | 12         |                      |                      |                          |                          |                          |      |
| Yangtze River, China    | Li et al. [100]             | 19         |                      |                      |                          |                          |                          |      |
| Chao River, China       | Yu et al. [38]              | 24         |                      |                      |                          |                          |                          |      |
| Huaihe River, China     | Meng et al. [101]           | 6          | 1.48–32.65          |                      |                          |                          |                          |      |
| Shuangtaizi Estuary, China| Yuan et al. [9]             | 18         |                      |                      |                          |                          |                          |      |
| Yangtze River, China    | Lin et al. [73]             | 8          | 0.31–1.63           | 0.92                 |                          |                          |                          |      |
| Poyang Lake, China      | Zhi et al. [78]             | 20         | 20.65–115           |                      |                          |                          |                          |      |
| Hangzhou Bay, China     | Adeleye et al. [33]         | 8          |                      |                      |                          |                          |                          |      |
| Hangzhou Bay, China     | Li et al. [79]              | 10         | 1.35–26.36          | 9.39                 | 2.52–27.99               |                          |                          |      |
| China Sea, China        | Kaiser et al. [40]          | 4          |                      |                      |                          |                          |                          |      |
| Africa                  |                             |            |                     |                      |                          |                          |                          |      |
| Congo River Basin, Congo| Mwanamoki et al. [42]       | 5          |                      |                      |                          |                          |                          |      |
| Awash River Basin, Ethiopia| Diriba et al. [80]         | 16         | 6.63–206.13         | 76.43                |                          |                          |                          |      |
| Nairobi River, Kenya    | Ndunda et al. [102]         | 17         | ND–39.7             |                      |                          |                          |                          |      |
| America                 |                             |            |                     |                      |                          |                          |                          |      |
| Sea Lots, Trinidad and Tobago| Mohammed et al. [52]       | 29         | 44.5–145            |                      |                          |                          |                          |      |
| Gulf of Batabanò, Cuba  | Alonso-Hernández et al. [75]| 5          | 0.029–0.374         |                      |                          |                          |                          |      |
| Jaguaribe River, Brazil| Oliveira et al. [81]        | 8          | 5.09–154.43         |                      |                          |                          |                          |      |
| Europe                  |                             |            |                     |                      |                          |                          |                          |      |
| Arc River, France       | Kanzari et al. [16]         | 15         | 0.02–7.15           |                      |                          |                          |                          |      |
| Portuguese Coastal Area, Portugal| Carvalho et al. [57]    | 12         | 0.08–26             |                      |                          |                          |                          |      |
| Moscow River, Russia    | Eremina et al. [48]         | 11         | ND–51.1             |                      |                          |                          |                          |      |
| Someșu Mic River, Romania| Barhoumi et al. [61]       | 11         | 1.00–39.24          |                      |                          |                          |                          |      |
| Mediterranean sea        |                             |            |                     |                      |                          |                          |                          |      |
| Candarli Gulf, Turkey   | Pazi et al. [82]            | 9          | 10.2–57.3           |                      |                          |                          |                          |      |
| Izmir Bay, Turkey       | Pazi et al. [43]            | 9          | 0.12–11.35          |                      |                          |                          |                          |      |
| Calanque National Park coastlines, France| Syakti et al. [103]| 18         | 1.2–190.6           |                      |                          |                          |                          |      |
| Durance River and Berre Lagoon, France| Kanzari et al. [60]| 11         | 0.07–2.11           |                      |                          |                          |                          |      |
Table 4 (continued)

| Area                        | References                  | N. of OCPs | DP (ng L\(^{-1}\)) | SPM (ng L\(^{-1}\)) | Sediments (ng g\(^{-1}\)) | DP + SPM (ng L\(^{-1}\)) |
|-----------------------------|-----------------------------|------------|---------------------|-----------------------|-----------------------------|--------------------------|
|                             |                             |            | Range               | Mean                  | Range                       | Mean                     |
| Egyptian Coast, Egypt       | Barakat et al. [83]         | 14         | 0.27–83.4           | 0.027–83.4            |                             |                          |
| River Po, Italy             | Viganò et al. [63]          | 6          | 7.5–68.2            | 7.5–68.2              |                             |                          |
| Northern coast of Cyprus    | Kucuksezgin et al. [84]     | 9          | 2.78–306.4          | 2.78–306.4            | 508                         |                          |
| Plitvice Lakes, Croatia     | Dvorscak et al. [46]        | 11         | 0.30–5.86           | 0.30–5.86             |                             |                          |
| This study                  |                             | 16         | 0.45–6.9            | 0.08–5.7              | 0.52–9.8                    | 0.9–8.6                  |

Note: The table continues with similar data entries for different areas.
The partition coefficients, $K_P = \frac{C_{SPM}}{C_{DP}}$, showed a decreasing trend in the HCHs partitioning from sediments to SPM (HCH$_{SPM}$/HCH$_{Sediment}$ mean value of 3.12) and to DPs (HCH$_{DP}$/HCH$_{Sediment}$ mean value of 3.47). Regarding the DDTs, the partition coefficients showed a decreasing trend in the DDTs concentrations from sediments to SPMs (DDT$_{SPM}$/DDT$_{Sediment}$ mean value of 0.4; range 0.05–0.64) and from SPMs to DPs (DDT$_{SPM}$/DDT$_{DP}$ mean value of 2.47). Also, the concentrations of cyclodienes in DP, SPM and sediment samples showed a decreasing trend from sediments to SPMs and DPs (cyclodienes$_{SPM}$/cyclodienes$_{Sediment}$ and cyclodienes$_{DP}$/cyclodienes$_{Sediment}$ ratio mean values of 0.55 and 3.48, respectively). These results showed that higher levels of OCPs were found in sediment samples than in DP and SPM samples (Fig. 4), which were an indication of no fresh inputs of these pesticides in the Volturno. Moreover, the higher levels of the OCPs found in sediments than in their corresponding waterbodies (DP and SPM samples) indicated that the gravitational sedimentation and suspension processes were mainly in this area with subsequent transfer of the OCPs, particularly more polar, from sediments to waterbodies.

The spatial distribution of PCBs and OCPs in DP, SPM and sediment samples from the Volturno River was studied by comparing the concentrations of ΣPCBs and ΣOCPs in different sampling sites in dry and rainy seasons, respectively. The results, summarized in Fig. 5a and b, showed a similar trend. Indeed, the PCBs and OCPs contamination levels in the Volturno decreased clearly from location 1 to 4. The total PCBs concentrations decreased from 33.2 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 1 (River Mouth) to 13.1 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 2 (500mt) to 10.9 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 3 (1000mt) and 9.2 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 4 (1500mt); while OCPs concentrations decreased from 7.61 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 1 (River Mouth) to 2.83 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 2 (500mt) to 1.81 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 3 (1000mt) and 1.24 ng L$^{-1}$ (DP+SPM mean values of four seasons) at site 4 (1500mt). In the Tyrrhenian Sea, around the mouth of the Volturno, PCBs and OCPs concentrations range were general from higher in the vicinity of the river outflows to lower in offshore areas (Fig. 5a and b). The results suggest that the pollutants in the aqueous phase were diluted as they were discharged from the river to the sea through the estuary. Particularly, at the Volturno mouth the contaminants load move into the Tyrrhenian sea southward (Fig. 5a and b).

The PCBs and OCPs load into the Tyrrhenian Sea occurred through various transport pathways including stormwater runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, atmospheric deposition and dredged material disposal. The total PCBs and OCPs load contributions to the Tyrrhenian Sea from the Volturno River were calculated in about 106.89 kg year$^{-1}$ (87.1 kg year$^{-1}$of PCBs and 19.7 kg year$^{-1}$ of OCPs).

**Qualitative analysis for PCBs sources**

The concentration of PCBs in Volturno River Mouth (33.2 ng L$^{-1}$, DP+SPM mean values of four seasons) was abnormally higher than those from other sites, suggesting direct PCBs inputs from the river. Potential sources of PCBs in the Volturno River were due in part to equipment/utilities in use (e.g., old transformers and capacitors), waste incineration, accidental fires, and atmospheric deposition [75]. The Volturno River flows through an intensely polluted area of the Campania Region, renamed as “Land of Fires”. Since 1980, waste management in this area has been characterized by the
waste crisis. This waste crisis has resulted in the widely documented illegal disposal of urban, toxic and industrial wastes. The environmental impacts of illegal waste disposal led to the deterioration of land, as well as ground and surface water, also impacting air quality.

To analyze the pollution of PCBs affecting the Volturno River and its estuary, principal component analysis [87, 88] has been conducted on sediment different datasets. In each analysis, six groups of PCBs (Di-PCB, Tri-PCB, Tetra-PCB, Penta-PCB, Hexa-PCB and Hepta-PCB) have been taken into account. In general, we can observe that all PCB compounds are more likely to come from surface runoff than an atmospheric deposition.

Most variables have positive correlations, we could expect that the first component might be considered as an average of PCB. Looking at the result of PCA, we can observe that the first three principal components explain 52.1% (PC1), 17% (PC2) and 13% (PC3) of the total variance, respectively (Fig. 6a and b). All the variables contribute to the definition of the first principal component with very dissimilar intensity. So, the first component was mostly composed of high chlorinated congeners,
including Tetra-PCB, Penta-PCB and Hexa-PCB, which could be conveyed into the river by surface runoff after rain events, and accumulated in the estuary. The second component was composed of chlorinated congeners, such as Di-PCB, Tri-PCB, and, indicating atmospheric deposition and microbial degradation [89]. Many studies [90] have shown that PCB concentration levels in the lower atmosphere near the water are sustained by Tri-PCB volatilized from the upper water layer. In addition, the dechlorination of highly chlorinated congeners with anaerobic microbe can occur in the sediments, which contributes to the high proportion of light PCBs. By contrast, the third component (PC3) accounted for 22.59% and was composed of high chlorinated congeners, such as Hepta-PCB, and, indicating a point source deposition industrial discharges along the course of the Volturno River through the “Land of Fires”. Therefore, the conclusions of PCA added credence to the view that light chlorinated congeners are derived from atmospheric deposition and microbial degradation. As for highly chlorinated congeners, the existence of a single major source in the Volturno River is possibly related to the point source (e.g., intense use of heat transfer and hydraulic fluids and solvent extenders in ship painting) but above all derived from erosion of contaminated soils transported to the River by surface runoff, after rain events [10, 89].

**Toxicity equivalency quantity of dioxin-like PCB**

In this study, eight DL-PCBs (PCB 77, 105, 114, 118, 126, 156, 169, and 189) were identified in all sediment samples. To quantify the potential toxicity of DL-PCBs in sediment samples from the Volturno River, the TEQ method was adopted to estimate the human exposure and health risk via dietary intake of the dioxin-like congeners, which accounted for an average of 24.3% of the total PCBs concentration. The TEQs of the DL-PCBs from the sediment samples ranged from 0.002 to 0.33 ng/g with an average level of 0.07 ng/g. Although the TEQs for the sediment samples were very low, the toxicities of the PCBs in the water ecosystem of the Volturno River could adversely affect the ecological environment and human health through biomagnification.

**Risk assessment**

To assess the PCBs and OCPs risk in water samples from Volturno River and estuary, all data were compared with Environmental Quality Standards (EQS) for priority substances and certain other pollutants in inland surface waters and coastal waters [91]. Even if PCBs were banned by Regulation (EC) No. 850/2004 (European Parliament and Council 2004), many EQS were mentioned for PCBs. In detail, the concentrations of ΣPCBs found in the water of the Volturno River and its estuary as the sum of the DP and SPM were at the limit than the criterion continuous concentration (CCC) for water quality recommended by USEPA (14.0 and 30.0 ng L$^{-1}$ for freshwater and saltwater, respectively). Regarding the OCPs, although compliance with European EQS in surface waters is checked using an annual average of monthly whole water (DP + SPM) concentrations [92] our data show that the mean concentrations of HCHs (0.79 ng L$^{-1}$) DDTs (0.55 ng L$^{-1}$) and Σaldrin, dieldrin and endrin (0.50 ng L$^{-1}$) in the Volturno River were lower than the EQS value of 20.0, 25.0 and 10.0 ng L$^{-1}$, respectively.
In this work have been used the sediment quality guidelines (SQGs) for aquatic environments to evaluate the risk caused by PCBs and OCPs contained in the sediments from Volturno River [93, 94]. Two sets of SQGs, that are defined as: (i) effect range low (ERL)/effect range median (ERM) and ii) the threshold effect level (TEL)/probable effect level (PEL), were used. ERLs and TELs represent chemical concentrations below which the probability of toxicity and other effects are rare. Differently, the ERM and PELs represent mid-range above which adverse effects would occur frequently. As reported in Table 5, the SQGs only refer to ΣPCBs, γ-HCH (lindane), dieldrin, 4,4-DDD, 4,4-DDE, 4,4-DDT and ΣDDT.

In the Volturno River, the total PCBs concentrations in sediment samples were significantly lower than PEL and ERM values Table 5, while 60% and 50% of samples showed levels above TEL and ERL values, respectively. Regarding the OCPs, all analyzed samples showed concentrations below PEL and ERM values; while only 10% of samples showed detected levels of DDD above the TEL values. Regarding ERL value, a high percentage of samples (70%) showed levels above for dieldrin and 10% of samples for DDT.

To assess the ecological risk associated with PCBs and OCPs in the aquatic environment, two indices have also been calculated: The Ecological Risk Index (ERI), proposed by Hakanson [95], to estimate the degree of pollution of PCBs in the river environment; and the Risk Quotient (RQ) method (WHO 2001) [96] for the OCPs pollution. According to the toxicity of PCBs:

\[
RI = \sum E_{ri}^i
\]

\[
E_{ri}^i = T_{ri}^i C_{i n}^i
\]

where RI was determined like the sum of all risk factors for the total PCBs, RI was equal to \(E_{ri}^i\), \(E_{ri}^i\) is the monomial potential ecological risk factor, \(T_{ri}^i\) was the toxic-response factor for PCBs which for these substances was equal to 40, according to the standardization developed by Hakanson [95]. \(C_{i n}^i\) was the contamination factor. \(C_{i 0}^i\) was PCBs concentration in sediment and \(C_{i n}^i\) was an established value equal to 10 µg/kg. Hakanson categories the potential ecological risk factors of a particular contaminant into following categories: \(E_{ri}^i < 40\) indicates low potential ecological risk, \(40–79\) \(E_{ri}^i\) values represented moderate potential ecological risk, \(80–159\) \(E_{ri}^i\) values represented considerable potential ecological risk, \(160–319\) \(E_{ri}^i\) values represented high potential ecological risk and \(E_{ri}^i > 320\) for very high potential ecological risk.

Regarding OCPs ecological risk, the risk quotient (RQ) was calculated by the following formula:

\[
RQ = \frac{C_{i n}}{PNEC}
\]

where \(C\) was the measured concentration and PNEC was the predicted no-effect concentrations for a particular OCPs. The PNEC data were acquired from ECOTOX database (www.epa.gov/eco tox) and by some papers [97, 98]. The classification of ecological risks was different according to various assessment standards and management purposes. Generally, if the value of RQ < 1 negative effects could be expected due to the presence of the pollutant in the water. On the other hand, if RQ < 0.1 the environmental risk is low. If RQ ranged between 0.1 and 1, it indicated medium risk [99]. The potential ecological risk factors of PCBs for each sampling site in the sediment of the Volturno River were high at River Mouth and 500mt south, while in the other sites the risk values varied

Table 5 A comparison of the TEL, PEL, ERL and ERM guideline values (µg Kg\(^{-1}\)) for PCBs and OCPs and data found in the Volturno River and Estuary, South Italy

|          | TEL Samples percentage over the TEL | PEL Samples percentage over the PEL | ERL Samples percentage over the ERL | ERM Samples percentage over the ERM |
|----------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| PCBs     |                                     |                                     |                                     |                                     |
| Total PCBs | 21.6 60                              | 198 0                               | 22.7 50                             | 180 0                               |
| OCPs     |                                     |                                     |                                     |                                     |
| γ-HCH (lindane) | 0.32 0                              | 0.99 0                              | –                                   | –                                   |
| Dieldrin | 0.72 0                               | 4.3 0                               | 0.02 70                             | 8 0                                 |
| 4,4-DDD | 1.22 10                              | 7.81 0                              | 2 0                                 | 20 0                                |
| 4,4-DDE | 2.07 0                               | 3.74 0                              | 2.2 0                               | 27 0                                |
| 4,4-DDT | 1.19 0                               | 4.77 0                              | 1 10                                | 7 0                                 |
| Total DDT | 3.89 0                               | 51.7 0                              | 1.58 10                             | 46.1 0                              |
from considerable to low. Based on these results, the ecosystem risk of PCBs in the sediments from the Volturno River was medium. Regarding the OCPs, all analyzed samples showed ratio between C and PNEC for the individual OCPs was calculated and also this ratio showed a RQ < 1 for most of the analytes, except DDT and dieldrin that showed a RQ >1. These results indicate that adverse effects on the biota would rarely be observed.

Conclusions
This study is the first one to document provided very useful information for the evaluation of trace PCB and OCP levels in the Volturno River and its input into the Tyrrhenian Sea (Central Mediterranean Sea). The results show that higher levels of PCBs and OCPs were found in sediment samples than in DP and SPM samples, which are an indication of no fresh inputs of these compounds. Moreover, higher levels of PCBs and OCPs found in sediment samples than in their corresponding water bodies (DP and SPM samples) indicate that gravitational sedimentation and suspension processes are mainly in this area with subsequent transfer of the PCBs and OCPs, particularly more polar, from sediment to water bodies. Based on our results, unintentionally produced PCBs by industrial processes (and other processes) were considered to be the main sources of PCBs in Volturno River and Estuary sediments. In relation to the risk assessment, the concentrations of most PCBs were at the limit than the criterion continuous concentration (CCC) for water quality recommended by USEPA for freshwater (14 ng L⁻¹), but they are lower than (CCC) for saltwater (30 ng L⁻¹).

Moreover, the potential risk factors of PCBs for each sampling site in the sediment of the Volturno River were high at River Mouth and 500mt south, and relatively low in the other sites. The concentrations of OCPs, however, in the water and sediment from the Volturno River and its estuary were lower than guideline values and the ratio of C to PNEC showed an RQ < 1 for most analytes.

In conclusion, the PCBs and OCPs levels observed do not seem to cause immediate biological effects on the sedimentary environment in the Volturno River and its estuary but must be kept under control to evaluate possible influences that could have on potential negative impacts on aquatic ecosystems. These results enhance our knowledge on the Volturno River water and sediment quality and on its environmental impact on the Central Mediterranean Sea to become a useful assessment tool for the administrations and to create a starting point about a future study on the pollution of this area.

Abbreviations
PCB: Polychlorinated biphenyls; OCP: Organochlorine pesticides; DP: Dissolved Phase; SPM: Suspended particulate matter; DDT: Dichlorodiphenyltrichloroethane; HCH: Hexachlorocyclohexanes; MAP: Mediterranean Action Plan; MED POL: Mediterranean Marine Pollution; DCM: Dichloromethane; PCA: Principal component analysis; DL-PCB: Dioxin Like Polychlorinated biphenyls; TEQ: Toxicity Equivalency Quantity; WHO: World Health Organization; TEF: Toxic Equivalency Factors; EQS: Environmental Quality Standards; CCC: Criterion Continuous Concentration; SQG: Sediment Quality Guidelines; ERL: effect range low; ERM: Effect range median; TEL: Threshold effect level; PEL: Probable effect level.

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Authors’ contributions
PM, AN and MT designed the research; PM, ED, FD and DPP organized and carried out samplings and laboratory analyzes; PS, PM and ED analyzed the data and performed the statistical analysis. All authors read and approved the final manuscript.

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The authors declare that they have no competing interests.

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