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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, endo-sulfan 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 Mediterranian 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,
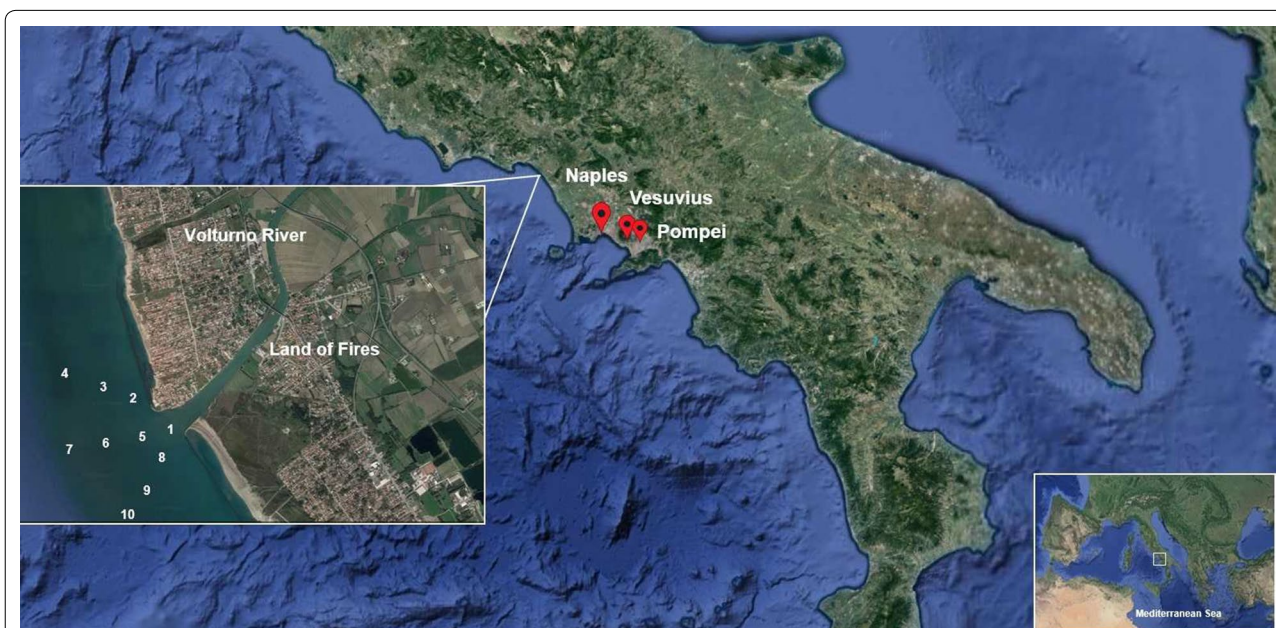

Fig. 1 Map of the study areas and sampling sites in the Volturno River and Estuary, Southern Italy Source: Google Earth

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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 vegetables [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 × 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 contaminants 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 Na_2SO_4 (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) ($r^2 > 0.97$). 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

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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 methoxychlor.

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 $p \leq 0.05$.

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:

$$C_{\mathrm{aw}} = \frac{\sum_{\mathrm{i}=1}^{n} C_i Q_i}{\sum_{\mathrm{i}=1}^{n} Q_i} \tag{1}$$

$$F_{\mathrm{annual}} = C_{aw} Q_{\mathrm{T}} \tag{2}$$

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-Garigliano 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, 156, 157, 167 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:

$$\Sigma \mathrm{TEQ} = \Sigma \mathrm{C_i} \times \mathrm{TEF_i}$$

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.

Table 1 Description of the sampling sites and concentration of PCBs in the water dissolved phase (DP), the suspended particulate matter (SPM) and the sediments of the Volturno River, Southern Italy

Sampling location			ΣPCBs									
Site Number identification	Site characteristics	Site location	Dissolved Phase (ng L^{-1})				Particulate phase (ng L^{-1}) (ng g^{-1} dry wt)				Sediments (ng g^{-1} dry wt)
			Apr	Jul	Nov	Feb	Apr	Jul	Nov	Feb	Apr
1 (river water)	Volturno River Source	40°48′54.03″N 14°36′45.36″E	7.48	10.2	8.04	5.23	17.0 (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 (864.7)	11.5 (96.6)	30.7
8 (sea water)	River Mouth at 1500mt North	40°43′35.68″N 14°28′02.94″E	5.07	5.55	4.84	2.41	1.49 (148.8)	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 (877.2)	2.75 (922.3)	1.82 (652.9)	1.78 (609.0)	4.3
10 (sea water)	River Mouth at 1500mt South	40°43′49.26″N 14°27′59.82″E	5.93	7.48	5.62	3.96	3.32 (1178.5)	2.94 (245.1)	5.06 (131.0)	7.54 (2654.9)	25.9

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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
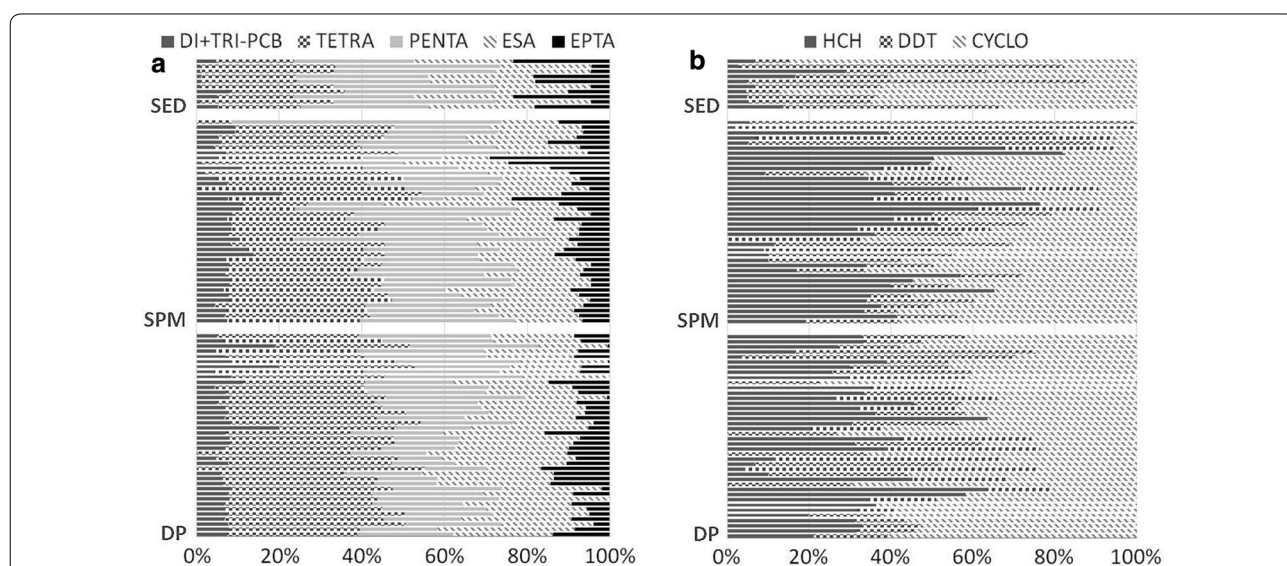

Fig. 2 Composition pattern of total PCBs (**a**) and OCPs (**b**) in the water dissolved phase (DP), in the suspended particulate matter (SPM) and in the sediments of the Volturno River and Estuary, Southern Italy

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	DP (ng L⁻¹) Mean	SPM (ng L⁻¹) Range	SPM (ng L⁻¹) Mean	Sediments (ng g⁻¹) Range	Sediments (ng g⁻¹) Mean	DP + SPM (ng L⁻¹) Range	DP + SPM (ng L⁻¹) 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							39–233	115.2
Yangtze Estuary, China	Gao et al. [19]	28					1.86–148.22	24.85		
Chao River, China	Yu et al. [38]	12					0.004–0.036			
Haizhou Bay, China	Zhang et al. [27]	22					1.33–6.27	4.0		
Daliao River Estuary, China	Men et al. [39]	41	5.51–40.28	16.91	6.78–66.55	21.81	0.83–7.29	1.77		
Shuangtzaizi Estuary, China	Yuan et al. [9]	28					1.83–36.68	10.53		
Chaohu Lake, China	He et al. [28]	34					0.07–3.99	0.67		
Yellow River, China	Gao et al. [11]	12					0.001–0.010	0.0025		
Hangzhou Bay, China	Adeleye et al. [33]	9					0.60–63.00			
China Sea, China	Kaiser et al. [40]	24					ND–0.12			
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					ND–1.4			
Congo River Basin, Congo	Mwanamoki et al. [42]	12					0.07–0.99			
Umgeni River, South Africa	Gakuba et al. [50]	8	6.91–21.69				102.60–427.80			
Msunduzi River, South Africa	Adeyinka [51]	8					361.7–5041.6	2163.4	6.49–141.68	36.7
Sea Lots, Trinidad and Tobago	Mohammed et al. [52]	136					62–601			
Panama Canal and California Coast, USA	Menzies et al. [53]	19	ND–18,450	1164.0			62–601			
Bedford Harbor, USA	Subedi et al. [54]	136					2800.0–109,000			
Chiacago Ship Canal, USA	Peverly et al. [55]	209					69.0–5000			
Midway Atoll, Hawaii	Ge et al. [55]	28			4.2–30.1		2.6–148.8	50.7		
Portuguese coast, Portugal	Ferreira et al. [35]	17								
Portuguese Coastal area, Portugal	Carvalho et al. [57]	7					0.3–466.8			
Moscow River, Russia	Eremina et al. [48]	9	ND–180.7							
Someşu Mic River, Romania	Barhoumi et al. [61]	20					2.74–252.72			
Rhone River, France	Mourier et al. [58]	7					11.5–417.1			
Huveaune River, France	Kanzari et al. [59]	7					2.8–435.0	148.0		
Durance River and Berre Lagoon, France	Kanzari et al. [60]	7					0.03–514.4			
Izmir Bay, Turkey	Pazi et al. [43]	20					0.21–31.95			
Egyptian Coast, Egypt	Barakat et al. [83]	96					2.29–377.0	32.2		

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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})	
			Range	Mean	Range	Mean	Range	Mean	Range	Mean
Nador Lagoon, Marocco	Giuliani et al. [44]	127					2.50–20.7	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–9.0			
Mar Piccolo coast, Italy	Bellucci et al. [64]	32					82.9–1045.0			
This study		32	2.28–10.0	6.07	0.71–42.8	8.82	4.37–64.4	26.5	4.07–48.04	14.9

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the Congo River Basin, Congo [41], in the Congo River Basin, Congo [42], in the Izmir Bay, Turkey [43], in the Nador Lagoon, Marocco [44], in the Morava River, Czech Republic [45], in the Plitvice Lake, Croazia [46], and in the Adriatic Sea, Italia [47]; but lower than those found in Moscow River, Russia [48], in the Yangtze Estuary, China [10], in the Ravi River, Pakistan [49], in the Umgeni River, South Africa [50], in the Msunduzi River, South Africa [51], in the Sea Lots, Trinidad and Tobago [52], in the Panama Canal and California Coast, USA [53], in the Bedford Harbor, USA [54], in the Chiacago Ship Canal, USA [55], in the Midway Atoll, Hawaii [56], in the Portuguese Coastal area, Portugal [57], in the Rhone River, France [58], in the Huveaune River, France [59], in the Durance River and Berre Lagoon, France [60], in the Someşu Mic River, Romania [61], in the Tripoli Harbor, Lebanon [62], in the River Po, Italy [63], and in Mar Piccolo coast, Italia [64].

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/cyclodiene ratio was < 1 at most sites (mean 0.69 ± 0.65; range ND-2.95). The HCHs/cyclodiene 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			ΣOCPs								
			Dissolved Phase (ng L^{-1})				Particulate Phase (ng L^{-1}) (ng g^{-1} dry wt)				Sediments (ng g^{-1} dry wt)
Site number identification	Site characteristics	Site Location	Apr	Jul	Nov	Feb	Apr	Jul	Nov	Feb	Apr
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)	4.05 (357.3)	5.67 (287.6)	9.89
2 (sea water)	River Mouth at 500mt North	40°46′42.73″N 14°34′00.48″E	1.57	1.98	2.12	1.10	0.55 (60.2)	0.57 (307.7)	1.53 (49.5)	1.80 (15.3)	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 (273.8)	0.65 (219.8)	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 (48.4)	2.35 (22.0)	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 (74.6)	0.99 (9.82)	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 (238.0)	0.10 (34.3)	0.77 (268.5)	0.50 (165.2)	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	1.00 (115.2)	0.29 (20.3)	0.75 (37.5)	0.98 (8.21)	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 (21.3)	0.73 (255.5)	0.57 (181.9)	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 (29.1)	0.44 (159.7)	0.48 (165.5)	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 (8.95)	0.57 (14.9)	0.66 (233.2)	1.37

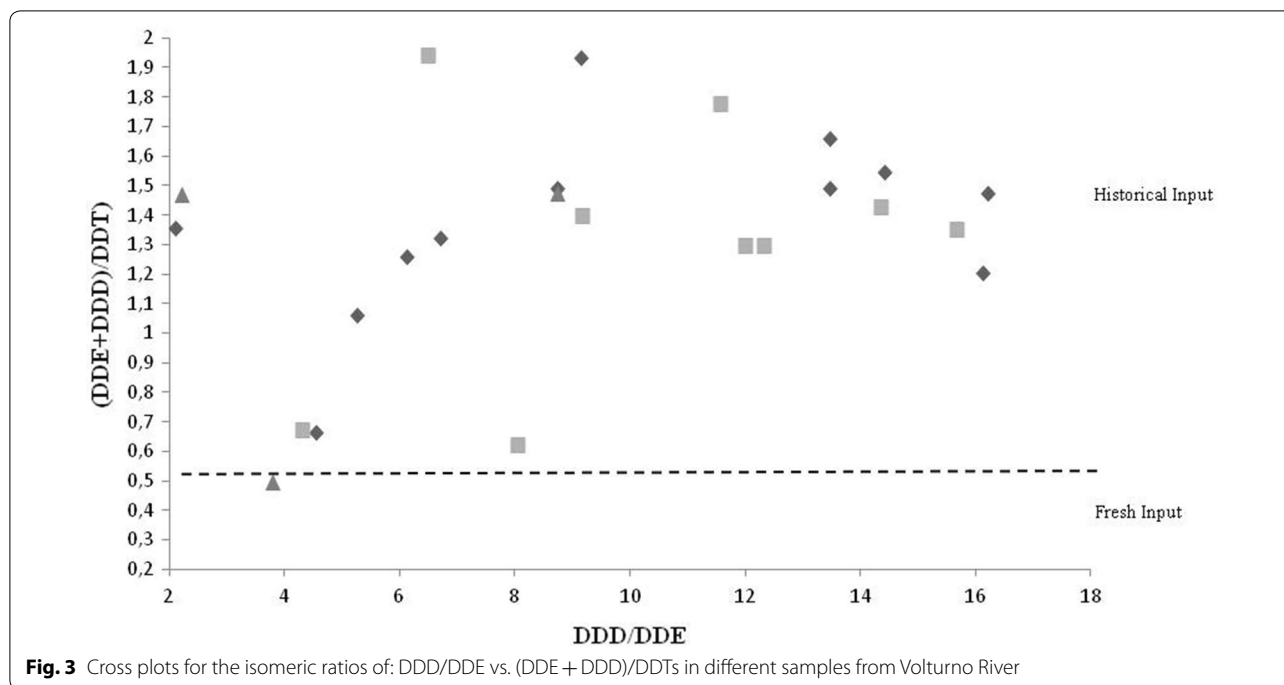Montuori *et al. Environ Sci Eur*   (2020) 32:123

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Fig. 3 Cross plots for the isomeric ratios of: DDD/DDE vs. (DDE + DDD)/DDTs in different samples from Volturno River

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 Jaguaribe 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) Range	DP Mean	SPM (ng L⁻¹) Range	SPM Mean	Sediments (ng g⁻¹) Range	Sediments Mean	DP + SPM (ng L⁻¹) Range	DP + SPM Mean
OCPs										
Asia										
Bengal Bay, India	Chakraborty et al. [76]		2–245	47						
Pearl River Delta, China	Huang et al. [77]	8	14.8–87.8							
Yangtze River, China	Zhou et al. [74]	12					0.17–5.0	2.09		
Yangtze River, China	Li et al. [100]	19					0.4–82.1			
Chao River, China	Yu et al. [38]	24					0.81–16.85			
Huaihe River, China	Meng et al. [101]	6					1.48–32.65			
Shuangtaizi Estuary, China	Yuan et al. [9]	18					0.02–14.57	5.65		
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					0.60–24.50			
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					ND–0.82			
Africa										
Congo River Basin, Congo	Mwanamoki et al. [42]	5					0.61–3.33			
Awash River Basin, Ethiopia	Dirbaba et al. [80]	16					6.63–206.13	76.43		
Nairobi River, Kenya	Ndunda et al. [102]	17	ND–39.7				0.01–41.9			
America										
Sea Lots, Trinidad and Tobago	Mohammed et al. [52]	29					44.5–145			
Gulf of Batabanò, Cuba	Alonso-Hernandez 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			

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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	Range	Mean	Range	Mean
Egyptian Coast, Egypt	Barakat et al. [83]	14					0.27–83.4			
River Po, Italy	Viganò et al. [63]	6					7.5–68.2			
Northern coast of Cyprus	Kucuksezgin et al. [84]	9					2.78–306.4	50.8		
Plitvice Lakes, Croatia	Dvorscak et al. [46]	11					0.30–5.86			
This study		16	0.45–6.9	1.5	0.08–5.7	1.0	0.52–9.8	2.7	0.9–8.6	2.5
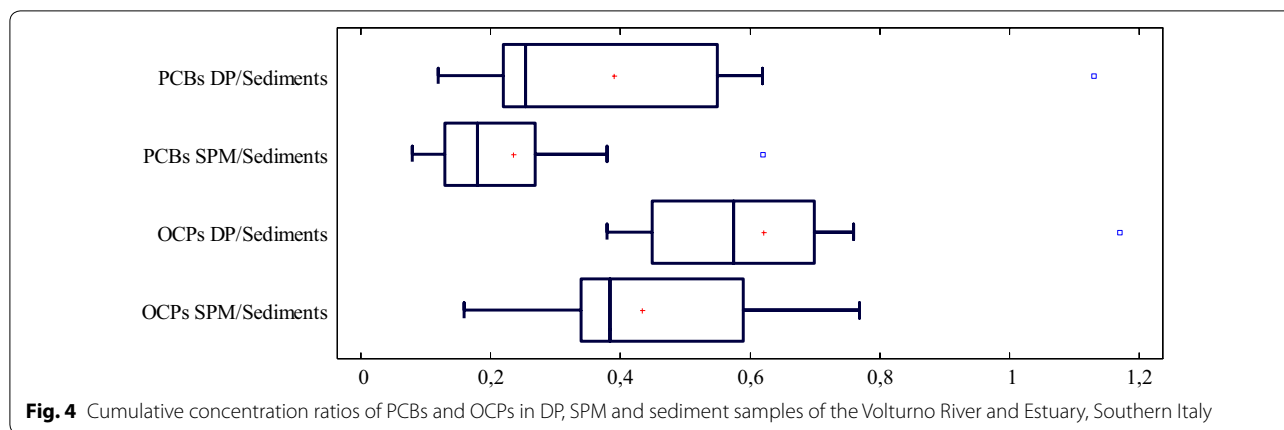
Fig. 4 Cumulative concentration ratios of PCBs and OCPs in DP, SPM and sediment samples of the Volturno River and Estuary, Southern Italy

The partition coefficients, $KP = C_{SPM}/C_{DP}$, showed a decreasing trend in the HCHs partitioning from sediments to SPM ($HCHs_{SPM}/HCHs_{Sediment}$ mean value of 3.12) and to DPs ($HCHs_{DP}/HCHs_{Sediment}$ mean value of 3.47). Regarding the DDTs, the partition coefficients showed a decreasing trend in the DDTs concentrations from sediments to SPMs ($DDTs_{SPM}/DDTs_{Sediment}$ mean value of 0.4; range 0.05–0.64) and from SPMs to DPs ($DDTs_{SPM}/DDTs_{DP}$ 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 ngL^{-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 Mounth (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
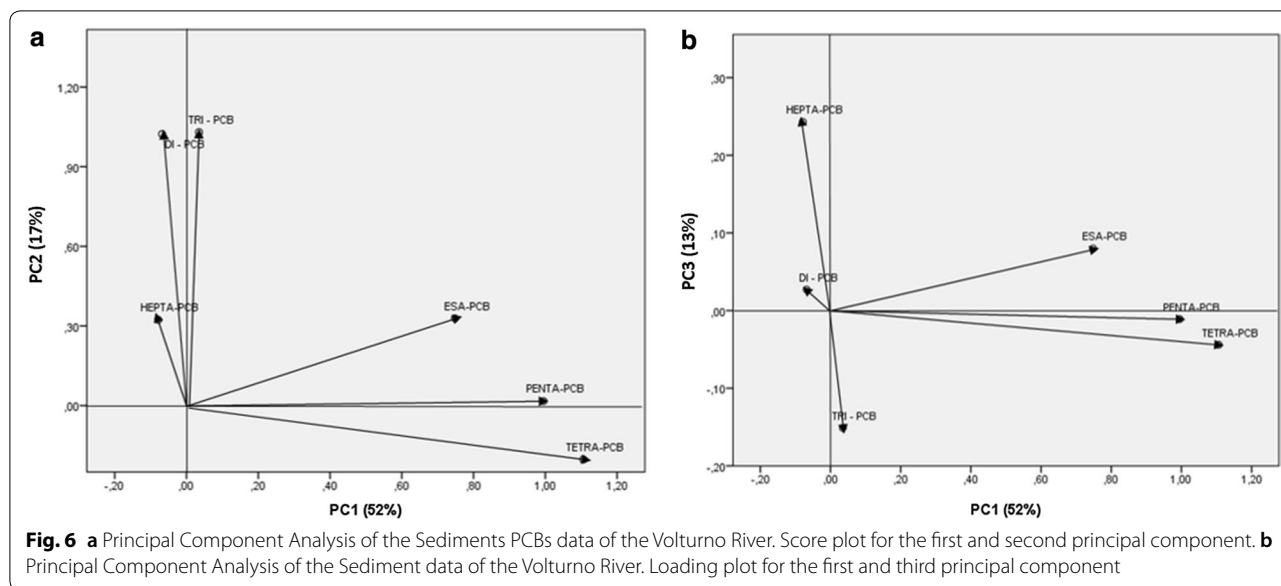
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Fig. 5 a and **b** Spatial and temporal concentration of PCBs and OCPs in the water dissolved phase (DP, ng L^{-1}), suspended particulate matter (SPM, ng L^{-1}) and sediments (ng g^{-1} dry wt) of the Volturno River and Estuary, Southern Italy
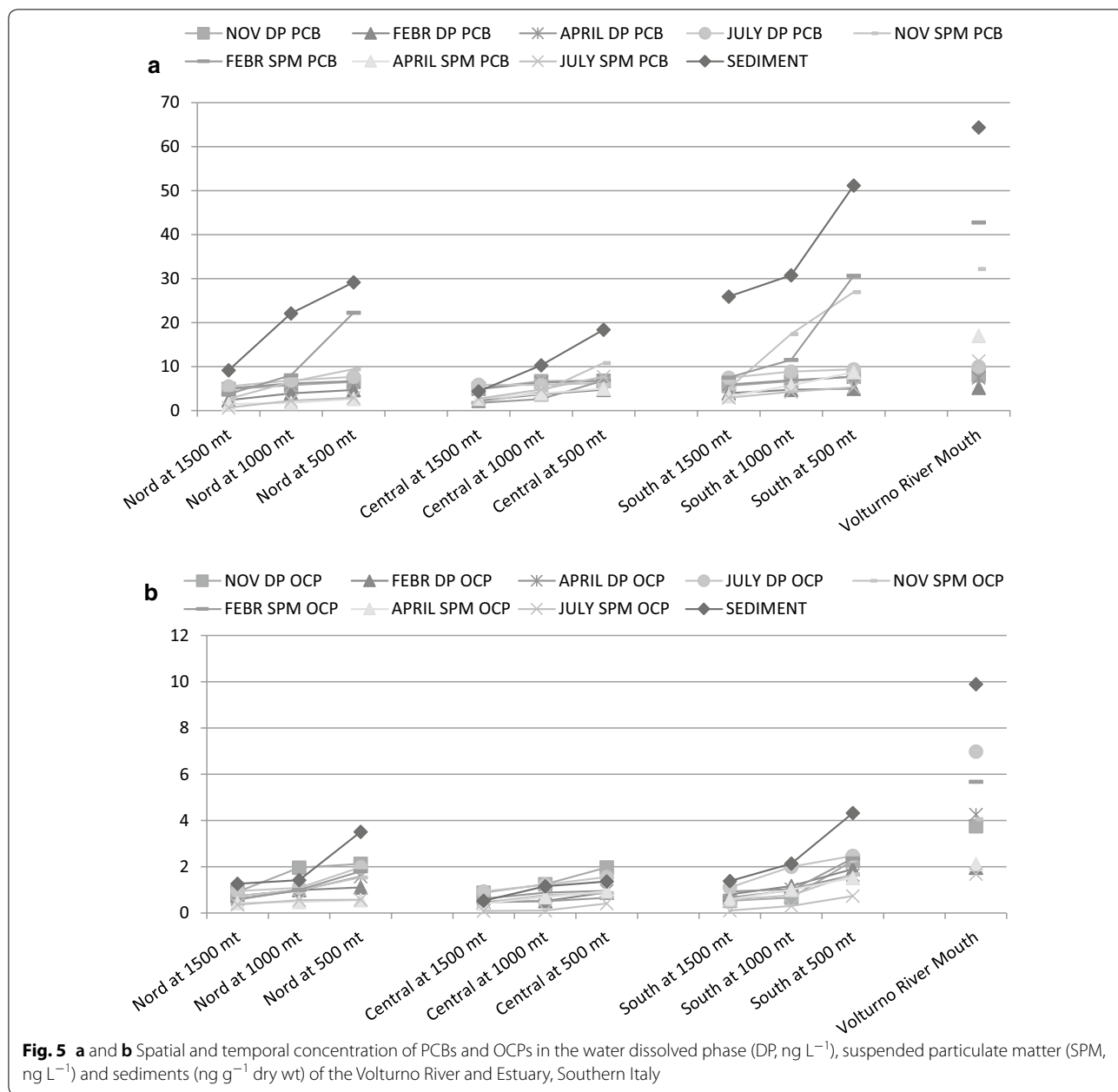
crisis. This waste crisis has resulted in the widely documented illegal disposal of urban, toxic and industrial wastes. The environmental impacts of illegal waste disposal led to the deterioration of land, as well as ground and surface water, also impacting air quality.

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,

Fig. 6 **a** Principal Component Analysis of the Sediments PCBs data of the Volturno River. Score plot for the first and second principal component. **b** Principal Component Analysis of the Sediment data of the Volturno River. Loading plot for the first and third principal component

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, dieldrinand 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 ERMs 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:

$$\mathrm{RI} = \sum E_r^i$$

$$E_r^i = T_r^i C_f^i$$

$$C_f^i = C_0^i / C_n^i$$

where RI was determined like the sum of all risk factors for the total PCBs, RI was equal to E_r^i. E_r^i is the monomial potential ecological risk factor, T_r^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_f^i was the contamination factor, C_0^i was PCBs concentration in sediment and C_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: $E_r^i < 40$ indicates low potential ecological risk, 40–79 E_r^i values represented moderate potential ecological risk, 80–159 E_r^i values represented considerable potential ecological risk, 160–319 E_r^i values represented high potential ecological risk and $E_r^i > 320$ for very high potential ecological risk.

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

$$\mathrm{RQ} = \frac{C}{\mathrm{PNEC}}$$

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/ecotox) 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	189	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	374	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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References
1. De Flora S, Bagnasco M, Zanacchi P (1991) Genotoxic, carcinogenic and teratogenic hazards in the marine environment, with special reference to the Mediterranean Sea. Mutat Res Gen Tox En. 258:285–320. https://doi.org/10.1016/0165-1110(91)90013-L
2. Danovaro R (2003) Pollution threats in the Mediterranean Sea: an overview. J Chem Ecol 19:15–32. https://doi.org/10.1080/0275754031000081467
3. Gómez-Gutiérrez AI, Jover E, Bodineau L, Albaigés J, Bayona JM (2006) Organic contaminant loads into the Western Mediterranean Sea: estimate of Ebro river inputs. Chemosphere 65:224–236. https://doi.org/10.1016/j.chemosphere.2006.02.058
4. Dahshan H, Megahed AM, Abd-Elall AMM, Abd-El-Kader MA, Nabawy E, Elbana MH (2016) Monitoring of pesticides water pollution The Egyptian River Nile. J Environ Health Sci Eng 14:15. https://link.springer.com/content/pdf/10.1186/s40201-016-0259-6
5. Montuori P, Aurino S, Garzonio F, Triassi M (2016) Polychlorinated biphenyls and organochlorine pesticides in Tiber River and Estuary: occurrence, distribution and ecological risk. Sci Total Environ. 571:1001–1016. https://doi.org/10.1016/j.scitotenv.2016.07.089
6. Legambiente (2006) Monitoraggio sull'illegalità e sullo stato di salute dei fiumi italiani. 08/05/2020 to: http://www.legambiente.it/contenuti/dossier/fiumi-e-legalit%C3%A0

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7. Esposito F, Nardone A, Fasano E, Scognamiglio G, Esposito D, Agrelli D, Ottaiano L, Fagnano M, Adamo P, Beccaloni E, Vanni F, Cirillo T (2018) A systematic risk characterization related to the dietary exposure of the population to potentially toxic elements through the ingestion of fruit and vegetables from a potentially contaminated area. A case study: the issue of the "Land of Fires" area in Campania region, Italy. Environ Pollut. 243:1781–1790. https://doi.org/10.1016/j.envpol.2018.09.058

8. Senior K, Mazza A (2004) Italian "Triangle of death" linked to waste crisis. Lancet. Oncol. 5:525–527. https://doi.org/10.1016/s1470-2045(04)01561-x

9. Yuan X, Yang X, Na G, Zhang A, Mao Y, Liu G, Wang L, Li X (2015) Polychlorinated biphenyls and organochlorine pesticides in surface sediments from the sand flats of Shuangtaizi Estuary, China: levels, distribution, and possible sources. Environ Sci Pollut Res. 22:14337–14348. https://doi.org/10.1007/s11356-015-4688-z

10. Gao S, Chen J, Shen Z, Liu H, Che Y (2013) Seasonal and spatial distributions and possible sources of polychlorinated biphenyls in surface sediments of Yangtze Estuary, China. Chemosphere 91:809–816. https://doi.org/10.1016/j.chemosphere.2013.01.085

11. Gao L, Huang H, Liu L, Li C, Zhou X, Xia D (2015) Polychlorinated dibenzo-p-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in sediments from the Yellow and Yangtze Rivers, China. Environ Sci Pollut Res. 22:19804–19813. https://doi.org/10.1007/s11356-015-5175-2

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

13. Unyimadu JP, Osibanjo O, Babayemi JO (2019) Concentration and distribution of organochlorine pesticides in sediments of the Niger River, Nigeria. J. Health Pollut. 9:190606. https://doi.org/10.5696/2156-9614-9.22.190606

14. Chen MY, Yu M, Luo XJ, Chen SJ, Mai BX (2010) The factors controlling the partitioning of polybrominated diphenyl ethers and polychlorinated biphenyls in the water-column of the Pearl River Estuary in South China. Mar Pollut Bull 62:29–35. https://doi.org/10.1016/j.marpolbul.2010.09.018

15. Guan YF, Wang JZ, Ni HG, Zeng EY (2009) Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: assessment of mass loading, input source and environmental fate. Environ Pollut 157:618–624. https://doi.org/10.1016/j.envpol.2008.08.011

16. Kanzari F, Syakti AD, Asia L, Malleret L, Mille G, Jamoussi B, Abderrabba M, Doumenq P (2012) Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine, and organophosphorous pesticides in surface sediments from the Arc river and the Berre lagoon, France. Environ Sci Pollut Res. 19:559–576. https://doi.org/10.1016/j.marpolbul.2018.10.039

17. UNEP/MAP (2004) Guidelines for river (including estuaries) pollution monitoring programme for the Mediterranean Region. MAP Technical Reports Series No. 151. UNEP/MAP, Athens

18. Karydis M, Kitsiou D (2012) Eutrophication and environmental policy in the Mediterranean Sea: a review. Environ Monit Assess. 184:4931–4984. https://doi.org/10.1007/s10661-011-2313-2

19. Isidori M, Lavorgna M, Nardelli A, Parrella A (2004) Integrated environmental assessment of Volturno River in South Italy. Sci Total Environ 327:123–134. https://doi.org/10.1016/j.scitotenv.2004.01.021

20. Triassi M, Nardone A, Giovinetti MC, De Rosa E, Canzanella S, Sarnacchiaro P, Montuori P (2019) Ecological risk and estimates of organophosphate pesticides loads into the Central Mediterranean Sea from Volturno River, the river of the "Land of Fires" area, southern Italy. Sci Total Environ 678:741–754. https://doi.org/10.1016/j.scitotenv.2019.04.202

21. IOC (1984) Manual for monitoring oil and dissolved/dispersed petroleum hydrocarbons in marine waters and on beaches. Manuals and Guides No 13 UNESCO, Paris. 08/05/2020. https://www.jodc.go.jp/jodcweb/info/ioc_doc/Manual/060618eb

22. Montuori P, Cirillo T, Fasano E, Nardone A, Esposito F, Triassi M (2014) Spatial distribution and partitioning of polychlorinated biphenyl and organochlorine pesticide in water and sediment from Sarno River and

23. Walling DE, Webb BW (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Mar Pollut Bull 16:488–492. https://doi.org/10.1016/0025-326X(85)90382-0

24. HELCOM (1993) Second Baltic Sea Pollution Load Compilation Balt Sea Environ Proc No 45 Baltic Marine Environment Protection Commission. Helsinki, Finland

25. Steen RJCA, van der Baart M, Hiep B, van Hattum WP, Cono WP, Brinkman UAT (2001) Gross fluxes and estuarine behaviour of pesticides in the Scheldt estuary (1995–1997). Environ Pollut 115:65–79. https://doi.org/10.1016/S0269-7491(01)00085-9

26. Piano di gestione acque ciclo 2015-2021 Distretto Idrografico dell'Appennino Meridionale Autorità di Bacino Nazionale dei Fiumi Liri-Garigliano e Volturno, Regione Abruzzo, Regione Basilicata, Regione Calabria, Regione Campania, Regione Lazio, Regione Molise, Regione Puglia. http://www.ildistrettoidrograficodellappenninomeridionale.it/, Accessed 20 April 2020

27. Zhang R, Zhang F, Zhang T, Yan H, Shao W, Zhou L, Tong H (2014) Historical sediment record and distribution of polychlorinated biphenyls (PCBs) in sediments from tidal flats of Haizhou Bay, China. Mar Pollut Bull. 89:487–493. https://doi.org/10.1016/j.marpolbul.2014.09.001

28. He W, Bai ZL, Liu WX, Kong XZ, Yang B, Yang C, Jørgensen SE, Xu FL (2016) Occurrence, spatial distribution, sources, and risks of polychlorinated biphenyls and heavy metals in surface sediments from a large eutrophic Chinese lake (Lake Chaohu). Environ Sci Pollut Res. 23:10335–10348. https://doi.org/10.1007/s11356-015-6001-6

29. Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, TuomistoJ Tysklind M, Walker N, Peterson RE (2006) The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci 93:223–241. https://doi.org/10.1093/toxsci/kfl055

30. Lin T, Nizzetto L, Guo Z, Li Y, Li J, Zhang G (2016) DDTs and HCHs in sediment cores from the coastal East China Sea. Sci Total Environ 539:388–394. https://doi.org/10.1016/j.scitotenv.2015.09.010

31. Čonka K, Chovancová J, Stachová Sejáková Z, Dömötörová M, Fabišiková A, Drobná B, Kočan A (2014) PCDDs, PCDFs, PCBs and OCPs in sediments from selected areas in the Slovak Republic. Chemosphere 98:37–43. https://doi.org/10.1016/j.chemosphere.2013.09.068

32. Omar WA, Mahmoud HM (2016) Risk assessment of polychlorinated biphenyls (PCBs) and trace metals in River Nile up- and downstream of a densely populated area. Environ Geochem Health 39:125–137. https://doi.org/10.1007/s10653-016-9814-4

33. Adeleye AO, Jin H, Di Y, Li D, Chen J, Ye Y (2016) Distribution and ecological risk of organic pollutants in the sediments and seafood of Yangtze Estuary and Hangzhou Bay, East China Sea. Sci Total Environ. 541:1540–1548. https://doi.org/10.1016/j.scitotenv.2015.09.124

34. Eqani SA, Cincinelli A, Mehmood A, Malik RN, Zhang G (2015) Occurrence, bioaccumulation and risk assessment of dioxin-like PCBs along the Chenab river, Pakistan. Environ Pollut. 206:688–695. https://doi.org/10.1016/j.envpol.2015.08.045

35. Ferreira AM, Martins M, Vale C (2003) Influence of diffuse sources on levels and distribution of polychlorinated biphenyls in the Guadiana River estuary, Portugal. Mar Chem. 83:175–184. https://doi.org/10.1016/S0304-4203(03)00111-7

36. Mahmood A, Malik RN, Li J, Zhang G (2014) Levels, distribution profile, and risk assessment of polychlorinated biphenyls (PCBs) in water and sediment from two tributaries of the River Chenab, Pakistan. Environ Sci Pollut Res. 21:7847–7855. https://doi.org/10.1007/s11356-014-2730-1

37. Kobayashi J, Serizawa S, Sakurai T, Imaizumi Y, Suzuki N, Horiguchi T (2010) Spatial distribution and partitioning of polychlorinated biphenyls in Tokyo Bay, Japan. J Environ Monit. 12:838–845. https://doi.org/10.1039/B925541A

38. Yu Y, Li Y, Shen Z, Yang Z, Mo L, Kong Y, Lou I (2014) Occurrence and possible sources of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) along the Chao River, China. Chemosphere 114:136–143. https://doi.org/10.1016/j.chemosphere.2014.03.095

39. Men B, He M, Tan L, Lin C (2014) Distributions of polychlorinated biphenyls in the Daliao River estuary of Liaodong Bay, Bohai Sea (China). Mar Pollut Bull 78:77–84. https://doi.org/10.1016/j.marpolbul.2013.11.005

Estuary, southern Italy. Environ Sci Pollut Res 21:5023–5035. https://doi.org/10.1007/s11356-013-2419-x

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40. Kaiser D, Schulz-Bull DE, Waniek JJ (2018) Polycyclic and organochlorine hydrocarbons in sediments of the northern South China Sea. Mar Pollut Bull 137:668–676. https://doi.org/10.1016/j.marpolbul.2018.10.039

41. Verhaert V, Covaci A, Bouillon S, Abrantes K, Musibono D, Bervoets L, Verheyen E, Blust R (2013) Baseline levels and trophic transfer of persistent organic pollutants in sediments and biota from the Congo River Basin (DR Congo). Environ Int 59:290–302. https://doi.org/10.1016/j.envint.2013.05.015

42. Mwanamoki PM, Devarajan N, Thevenon F, Birane N, de Alencastro LF, Grandjean D, Mpiana PT, Prabakar K, Mubedi JI, Kabele CG, Wildi W, Poté J (2014) Trace metals and persistent organic pollutants in sediments from river-reservoir systems in Democratic Republic of Congo (DRC): spatial distribution and potential ecotoxicological effects. Chemosphere 111:485–492. https://doi.org/10.1016/j.chemosphere.2014.04.083

43. Pazi I, Kucuksezgin F, Gonul LT (2011) Distribution and sources of organochlorinated contaminants in sediments from Izmir Bay (Eastern Aegean Sea). Mar Pollut Bull 62:1115–1119. https://doi.org/10.1016/j.marpolbul.2011.03.016

44. Giuliani S, Piazza R, El Moumni B, Polo FP, Vecchiato M, Romano S, Zambon S, Frignani M, Bellucci LG (2015) Recognizing different impacts of human and natural sources on the spatial distribution and temporal trends of PAHs and PCBs (including PCB-11) in sediments of the Nador Lagoon (Morocco). Sci Total Environ 526:346–357. https://doi.org/10.1016/j.scitotenv.2015.04.057

45. Kukučka P, Audy O, Kohoutek J, Holt E, Kalábová T, Holoubek I, Klánová J (2015) Source identification, spatio-temporal distribution and ecological risk of persistent organic pollutants in sediments from the upper Danube catchment. Chemosphere 138:777–783. https://doi.org/10.1016/j.chemosphere.2015.08.001

46. Dvorscak M, Fingler S, Mendaš G, Stipičević S, Vasilić Ž, Drevenkar V (2019) Distribution of organochlorine pesticide and polychlorinated biphenyl residues in lake sediment cores from the Plitvice Lakes National Park (Croatia). Arch Environ Contam Toxicol 77:537–548. https://doi.org/10.1007/s00244-019-00668-z

47. Combi T, Miserocchi S, Langone L, Guerra R (2016) Polychlorinated biphenyls (PCBs) in sediments from the western Adriatic Sea: sources, historical trends and inventories. Sci Total Environ 562:580–587. https://doi.org/10.1016/j.scitotenv.2016.04.086

48. Eremina N, Paschke A, Mazlova EA, Schüürmann G (2016) Distribution of polychlorinated biphenyls, phthalic acid esters, polycyclic aromatic hydrocarbons and organochlorine substances in the Moscow River, Russia. Environ Pollut. 210:409–418. https://doi.org/10.1016/j.envpol.2015.11.034

49. Syed JH, Malik RN, Li J, Chaemfa C, Zhang G, Jones KC (2014) Status, distribution and ecological risk of organochlorines (OCs) in the surface sediments from the Ravi River, Pakistan. Sci Total Environ. 472:204–211. https://doi.org/10.1016/j.scitotenv.2013.10.109

50. Gakuba E, Moodley B, Ndungu P, Birungi G (2015) Occurrence and significance of polychlorinated biphenyls in water, sediment pore water and surface sediments of Umgeni River, KwaZulu-Natal, South Africa. Environ Monit Ass. 187:568. https://doi.org/10.1007/s10661-015-4790-1

51. Adeyinka GC, Moodley B, Birungi G, Ndungu P (2018) Quantitative analyses of selected polychlorinated biphenyl (PCB) congeners in water, soil, and sediment during winter and spring seasons from Msunduzi River, South Africa. Environ Monit Assess. 190:621. https://doi.org/10.1007/s10661-018-6993-8

52. Mohammed A, Peterman P, Echols K, Feltz K, Tegerdine G, Manoo A, Maraj D, Agard J, Orazio C (2011) Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in harbor sediments from Sea Lots, Port-of-Spain, Trinidad and Tobago. Mar Pollut Bull 62:1324–1332. https://doi.org/10.1016/j.marpolbul.2011.03.043

53. Menzies R, Soares Quinete N, Gardinali P, Seba D (2013) Baseline occurrence of organochlorine pesticides and other xenobiotics in the marine environment: caribbean and Pacific collections. Mar Pollut Bull 70:289–295. https://doi.org/10.1016/j.marpolbul.2013.03.003

54. Subedi B, Yun S, Jayaraman S, Bergen BJ, Kannan K (2014) Retrospective monitoring of persistent organic pollutants, including PCBs, PBDEs, and polycyclic musks in blue mussels (Mytilus edulis) and sediments from New Bedford Harbor, Massachusetts, USA: 1991–2005. Environ Monit Assess 186:5273–5284. https://doi.org/10.1007/s10661-014-3776-8

55. Peverly AA, O'Sullivan C, Liu LY, Venier M, Martinez A, Hornbuckle KC, Hites RA (2015) Chicago's Sanitary and Ship Canal sediment: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, brominated flame retardants, and organophosphate esters. Chemosphere 134:380–386. https://doi.org/10.1016/j.chemosphere.2015.04.065

56. Ge J, Woodward LA, Li QX, Wang J (2013) Distribution, sources and risk assessment of polychlorinated biphenyls in soils from the Midway Atoll, North Pacific Ocean. Plos One 8:71521. https://doi.org/10.1371/journal.pone.0071521

57. Carvalho PN, Rodrigues PN, Basto MC, Vasconcelos MT (2009) Organochlorine pesticides levels in Portuguese coastal areas. Chemosphere 75:595–600. https://doi.org/10.1016/j.chemosphere.2009.01.060

58. Mourier B, Desmet M, Van Metre PC, Mahler BJ, Perrodin Y, Roux G, Bedell JP, Lefèvre I, Babut M (2014) Historical records, sources, and spatial trends of PCBs along the Rhône River (France). Sci Total Environ 476–477:568–576. https://doi.org/10.1016/j.scitotenv.2014.01.026

59. Kanzari F, Syakti AD, Asia L, Malleret L, Piram A, Mille G, Doumenq P (2014) Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune), France. Sci. Total Environ. 478:141–151. https://doi.org/10.1016/j.scitotenv.2014.01.065

60. Kanzari F, Asia L, Syakti AD, Piram A, Malleret L, Mille G, Doumenq P (2015) Distribution and risk assessment of hydrocarbons (aliphatic and PAHs), polychlorinated biphenyls (PCBs), and pesticides in surface sediments from an agricultural river (Durance) and an industrialized urban lagoon (Berre lagoon), France. Environ Monit Ass. 187:591. https://doi.org/10.1007/s10661-015-4823-9

61. Barhoumi B, Beldean-Galea MS, Al-Rawabdeh AM, Roba C, Martonos IM, Balc R, Kahlaoui M, Touil S, Tedetti M, Driss MR, Baciu C (2019) Occurrence, distribution and ecological risk of trace metals and organic pollutants in surface sediments from a Southeastern European river (Someşu Mic River, Romania). Sci Total Environ 660:660–676. https://doi.org/10.1016/j.scitotenv.2018.12.428

62. Merhaby D, Net S, Halwani J, Ouddane B (2015) Organic pollution in surficial sediments of Tripoli harbour, Lebanon. Mar Pollut Bull. 93:284–293. https://doi.org/10.1016/j.marpolbul.2015.01.004

63. Viganò L, Mascolo G, Roscioli C (2015) Emerging and priority contaminants with endocrine active potentials in sediments and fish from the River Po (Italy). Environ Sci Pollut Res 22:14050–14066. https://doi.org/10.1007/s11356-015-4388-8

64. Bellucci LG, Cassin D, Giuliani S, Botter M, Zonta R (2016) Sediment pollution and dynamic in the Mar Piccolo of Taranto (southern Italy): insights from bottom sediment traps and surficial sediments. Environ Sci Pollut Res Int 23:12554–12565. https://doi.org/10.1007/s11356-016-6738-6

65. Kinyamu JK, Kanja LW, Skaare JU, Maitho TE (1998) Organochlorine pesticides residues in milk of urban mothers in Kenya. Bull Environ Contam Toxicol. 60:732–738. https://doi.org/10.1007/s001289900687

66. Willet KL, Ulrich RA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol 32:2197–2207. https://doi.org/10.1021/es9708530

67. Doong R, Lee S, Lee C, Sun Y, Wu S (2008) Characterization and composition of heavy metals and persistent organic pollutants in water and estuarine sediments from Gao-ping River, Taiwan. Mar Pollut Bull. 57:846–857. https://doi.org/10.1016/j.marpolbul.2007.12.015

68. Salem MS, Khaled A, Nemr AE (2013) Assessment of pesticides and polychlorinated biphenyls in sediments of the Egyptian Mediterranean coast, Egypt. J Aquat Res. 39:141–152. https://doi.org/10.1016/j.ejar.2013.11.001

69. Nunda EN, Madadi VO, Wandiga SO (2018) Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment. Environ Sci Pollut Res 25:34510–34518. https://doi.org/10.1007/s11356-018-3398-8

70. Wasswa J, Kiremire BT, Nkedi-Kizza T, Mbabazi J, Ssebugere P (2011) Organochlorine pesticides residues in sediments from the Uganda side of Lake Victoria. Chemosphere 82:130–136. https://doi.org/10.1016/j.chemosphere.2010.09.010

71. Wu Y, Wang X, Li Y, Ya M, Luo H, Hong H (2015) Polybrominated diphenyl ethers, organochlorine pesticides, and polycyclic aromatic hydrocarbons in water from the Jiulong River Estuary, China: levels,

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distributions, influencing factors, and risk assessment. Environ Sci Pollut Res. 24:8933–8945. https://doi.org/10.1007/s11356-015-4782-2

72. Kuranchie-Mensah H, Atiemo SM, Palm LM, Blankson-Arthur S, Tutu AO, Fosu P (2011) Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana. Chemosphere 86:286–292. https://doi.org/10.1016/j.chemosphere.2011.10.031

73. Lin T, Guo Z, Li Y, Nizzetto L, Ma C, Chen Y (2015) Air-seawater exchange of organochlorine pesticides along the sediment plume of a large contaminated river. Environ Sci Technol 49:5354–5362. https://doi.org/10.1021/es505084j

74. Zhou S, Yang H, Zhang A, Li YF, Liu W (2014) Distribution of organochlorine pesticides in sediments from Yangtze River Estuary and the adjacent East China Sea: implication of transport, sources and trends. Chemosphere 114:26–34. https://doi.org/10.1016/j.chemosphere.2014.03.100

75. Alonso-Hernández CM, Tolosa I, Mesa-Albernas M, Díaz-Asencio M, Corcho-Alvarado JA, Sánchez-Cabeza JA (2015) Historical trends of organochlorine pesticides in a sediment core from the Gulf of Batabanó, Cuba. Chemosphere 137:95–100. https://doi.org/10.1016/j.chemosphere.2015.05.044

76. Chakraborty P, Khuman SN, Selvaraj S, Sampath S, Devi NL, Bang JJ, Katsoyiannis A (2016) Polychlorinated biphenyls and organochlorine pesticides in River Brahmaputra from the outer Himalayan Range and River Hooghly emptying into the Bay of Bengal: occurrence, sources and ecotoxicological risk assessment. Environ Pollut 219:998–1006. https://doi.org/10.1016/j.envpol.2016.06.067

77. Huang S, He S, Xu H, Wu P, Jiang R, Zhu F, Luan T, Ouyang G (2015) Monitoring of persistent organic pollutants in seawater of the Pearl River Estuary with rapid on-site active SPME sampling technique. Environ Pollut 200:149–158. https://doi.org/10.1016/j.envpol.2015.02.016

78. Zhi H, Zhao Z, Zhang L (2015) The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake, the largest freshwater lake in China. Chemosphere 119:1134–1140. https://doi.org/10.1016/j.chemosphere.2014.09.054

79. Li W, YangH Jiang X, Liu Q, Sun Y, Zhou J (2016) Residues and distribution of organochlorine pesticides in water and suspended particulate matter from Hangzhou Bay, East China Sea. Bull Environ Contam Toxicol. 96:295–302. https://doi.org/10.1007/s00128-016-1739-1

80. Dirbaba NB, Li S, Wu H, Yan X, Wang J (2018) Organochlorine pesticides, polybrominated diphenyl ethers and polychlorinated biphenyls in surficial sediments of the Awash River Basin, Ethiopia. Plos One 13(10):e0205026. https://doi.org/10.1371/journal.pone.0205026

81. Oliveira AH, Cavalcante RM, Duaví WC, Fernandes GM, Nascimento RF, Queiroz ME, Mendonça KV (2016) The legacy of organochlorine pesticide usage in a tropical semi-arid region (Jaguaribe River, Ceará, Brazil): implications of the influence of sediment parameters on occurrence, distribution and fate. Sci Total Environ 542:254–263. https://doi.org/10.1016/j.scitotenv.2015.10.058

82. Pazi I, Kucuksezgin F, Gonul LT (2012) Occurrence and distribution of organochlorine residues in surface sediments of the Candarli Gulf (Eastern Aegean). Mar Pollut Bull 64:2839–2843. https://doi.org/10.1016/j.marpolbul.2012.09.008

83. Barakat AO, Mostafa A, Wade TL, Sweet ST, El Sayed NB (2013) Distribution and ecological risk of organochlorine pesticides and polychlorinated biphenyls in sediments from the Mediterranean coastal environment of Egypt. Chemosphere 93:545–554. https://doi.org/10.1016/j.chemosphere.2013.06.050

84. Kucuksezgin F, Pazi I, Gonul LT, Duman M (2016) Organochlorine compounds in surface sediments from the northern coast of Cyprus, Eastern Mediterranean: levels, possible sources and potential risk. Mar Pollut Bull 109:591–596. https://doi.org/10.1016/j.marpolbul.2016.05.034

85. Safe SH (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. Crit Rev Toxicol 24:87–149. https://doi.org/10.3109/10408449409049308

86. Davis JA, Hetzel F, Oram JJ, McKee LJ (2007) Polychlorinated biphenyls (PCBs) in San Francisco Bay. Environ Res 105:67–86. https://doi.org/10.1016/j.envres.2007.01.013

87. Pearson K (1901) On lines and planes of closest fit to systems of points in space. Philosophical Magazine, Series 6, vol. 2, no. 11, pp 559–572. https://doi.org/10.1080/14786440109462720

88. Hotelling H (1993) Analysis of a complex of statistical variables into principal components, J Educational Psychol. 24: 417–441 and 498–520

89. Zhong T, Niu X, Li X, Zhang D, Zou L, Yao S (2020) Distribution, composition profiles, source identification and potential risk assessment of Polychlorinated Biphenyls (PCBs) and Dechlorane Plus (DP) in sediments from Liaohe Estuary. Reg Stud Mar Sci 36:101291. https://doi.org/10.1016/j.rsma.2020.101291

90. Gioia R, Nizzetto L, Lohmann R, Dachs J, Temme C, Jones KCJ (2008) Polychlorinated biphenyls (PCBs) in air and seawater of the Atlantic Ocean: sources, trends and processes. Environ Sci Technol. 42:1416–1422. https://doi.org/10.1021/es071432d

91. USEPA (2010) National Recommended Water Quality Criteria, United States Environmental Protection Agency. 13/05/2020. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

92. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. Off J Eur Union 348, 84-97.

93. Long ER, MacDonald DD, Smith SL, Calder ED (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage. 19:81–97. https://doi.org/10.1007/BF02472006

94. MacDonald DD, Carr RS, Calder FD, Long ER (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5:253–278. https://doi.org/10.1007/BF00118995

95. Hakanson L (1980) An ecological risk index for aquatic pollution control-A sedimentological approach. Water Res. 14:9751001. https://www.researchgate.net/publication/235936664

96. WHO (2001) Water quality: guidelines, standards and health. IWA, London

97. Di Lorenzo T, Cifoni M, Fiasca B, Di Cioccio A, Galassi DMP (2018) Ecological risk assessment of pesticide mixtures in the alluvial aquifers of central Italy: toward more realistic scenarios for risk mitigation. Sci Total Environ 644:161–172. https://doi.org/10.1016/j.scitotenv.2018.06.345

98. Cui S, Fu Q, Guo L, Li YF, Li TX, Ma WL, Wan M, Li WL (2016) Spatial–temporal variation, possible source and ecological risk of PCBs in sediments from Songhua River, China: effects of PCB elimination policy and reverse management framework. Mar Pollut Bull 106:109–118. https://doi.org/10.1016/j.marpolbul.2016.03.018

99. Peng X, Ou W, Wang C, Wang Z, Huang Q, Jin J, Tan J (2014) Occurrence and ecological potential of pharmaceuticals and personal care products in groundwater and reservoirs in the vicinity of municipal landfills in China. Sci Total Environ 490:889–898. https://doi.org/10.1016/j.scitotenv.2014.05.068

100. Li Y, Niu J, Shen Z, Zhang C, Wang Z, He T (2014) Spatial and seasonal distribution of organochlorine pesticides in the sediments of the Yangtze Estuary. Chemosphere 114:233–240. https://doi.org/10.1016/j.chemosphere.2014.04.112

101. Meng J, Wang T, Wang P, Giesy JP, Lu Y (2014) Perfluoroalkyl substances and organochlorine pesticides in sediments from Huaihe watershed in China. J Environ Sci 26:2198–2206. https://doi.org/10.1016/j.jes.2014.09.002

102. Ndunda EN, Madadi VO, Wandiga SO (2018) Organochlorine pesticide residues in sediment and water from Nairobi River, Kenya: levels, distribution, and ecological risk assessment. Environ Sci Pollut Res 25:34510–34518. https://doi.org/10.1007/s11356-018-3398-8

103. Syakti AD, Asia L, Kanzari F, Umasangadji H, Malleret L, Ternois Y, Mille G, Doumenq P (2012) Distribution of organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) in marine sediments directly exposed to wastewater from Cortiou, Marseille. Environ Sci Pollut Res 19:1524–1535. https://doi.org/10.1007/s11356-011-0640-z

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