

Spatial distribution and partitioning of polychlorinated biphenyl and organochlorine pesticide in water and sediment from Sarno River and Estuary, Southern Italy

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Abstract The Sarno River is nicknamed “the most polluted river in Europe”. The main goal of this study is to enhance our knowledge on the Sarno River water and sediment quality and on its environmental impact on the gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea) in order to become a useful assessment tool for the regional administrations. For these reasons, 32 selected polychlorinated biphenyls (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, endrin aldehyde, heptachlor, heptachlor epoxide (isomer B) and methoxychlor were determined in the water dissolved phase (DP), suspended particulate matter (SPM) and sediments. Total concentrations of PCBs ranged from 1.4 to 24.9 ng L⁻¹ in water (sum of DP and SPM) and from 1.01 to 42.54 ng g⁻¹ in sediment samples. The concentrations of total organochlorine pesticides (OCPs) obtained in water (sum of DP and SPM) ranged from 0.54 to 7.32 ng L⁻¹ and from 0.08 to 5.99 ng g⁻¹ in sediment samples. Contaminant discharges of PCBs and OCPs into the sea were calculated in about 1,247 g day⁻¹ (948 g day⁻¹ of PCBs and 326 g day⁻¹ of OCPs), showing that this river should account as one of the main contribution sources of PCBs and OCPs to the Tyrrhenian Sea.

Keywords Sarno River · Polychlorinated biphenyls · Organochlorine pesticides · River outflow · Contaminant transport processes · Temporal trends

Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are organic compounds in which the hydrogen atoms of the molecule are replaced, in whole or in part, by chlorine atoms. PCBs and OCPs are xenobiotic compounds of anthropogenic origin and are classified as persistent organic pollutants (POPs) (Buccini 2003; El-Shahawi et al. 2010).

PCBs were used extensively in the past as electrical insulating materials. The mixtures of PCBs have also been used in a wide range of applications, such as fluids for capacitors and transformers, as heat-conductive liquids in machinery, as lubricants and cutting oils and as additives in paints. The total amount of PCBs produced worldwide is estimated at 1.5 million tons (Ivanov and Sandell 1992; Rantanen 1992). OCPs were used on a large scale in agriculture, forestry and public health. In agriculture, they act as insecticides, acaricides and fumigants to control pests in orchards, vegetable, grain, cotton and tobacco fields and vineyards. In the field of public health, they have played a decisive role in eradicating certain parasitic diseases such as malaria. Based on the statistics of 1993, North America was the predominant pesticides (especially hexachlorocyclohexane (HCH), DDT and other OCPs) application region, followed by Western Europe (Loqanathan and Kannan 1994). The consumption of pesticides in developed countries (e.g. Euro-American) was significantly more than that in other countries (Wang et al. 2005).

In the past decades, many studies have focused on the potential of PCBs and OCPs to cause adverse effects to the environmental and human health (El-Shahawi et al. 2010).

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The low water solubility and high lipid solubility, which increase with the number of chlorine atoms, make these compounds to bioaccumulate in fatty tissues. Recently, there has been concern about the hormone-like effects on the endocrine and reproductive systems of wildlife and humans of PCBs and many OCPs because of their lipophilicity and tendency to accumulate in food chains and bodies (Amaral Mendes 2002). Today, these chemicals are collectively termed endocrine-disrupting chemicals (EDCs), endocrine disruptors or environmental estrogens. Several regional and global treaties and/or initiatives have been negotiated for developing risk management measures to reduce the exposure of humans and the ecosystem to these toxic substances (Buccini 2003; Zhang et al. 2005). Among these treaties, the Stockholm Convention on POPs, which came into effect on 17 May 2004, is the most important milestone. Twelve POPs, consisting primarily of PCBs and OCPs, were initially listed in the Stockholm Convention to be eliminated or their production and use to be restricted. The OCPs or pesticide POPs identified in the convention include aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. At the fourth meeting of the Conference of the Parties (COP4), the depositary communicated the adoption of the amendment to annexes A (elimination), B (restriction) and C (unintentional production) of the Stockholm Convention that is entered into force on 26 August 2010. Nine new POPs, including hexachlorocyclohexane, chlordecone, lindane and pentachlorobenzene, were added to the convention (Tsai 2010).

PCBs and OCPs are very stable compounds that resist photolytic, biological and chemical degradation and that thus persist in the environment with long half lives (Loqanathan and Kannan 1994). As confirmed by numerous studies, the marine environment appears to be one of the primary locations for the accumulation of PCBs and OCPs (Chen et al. 2010; Gómez-Gutiérrez et al. 2006; Guan et al. 2009). They are carried from terrestrial sources through various pathways, such as atmospheric and river transports. The input pathways of PCBs and OCPs into river environments include discharge of domestic sewage and industrial wastewater, runoff from non-point sources and direct dumping of wastes into the river (Walling and Webb 1985; Steen et al. 2001; Wang et al. 2005). Water could constitute a direct measure of the degree of marine pollution. Sediments are natural sinks and environmental reservoirs for PCBs and OCPs in the aquatic environment, and they offer an irreplaceable aid in reconstructing the historical inputs of PCBs and OCPs. Due to the high persistence and low mobility, PCBs and OCPs can accumulate and remain in the sediment for very long periods of time and may be a source of contaminants to aquatic biota. Therefore, the study of PCBs and OCPs into the marine environment is of great concern (Guan et al. 2009; Kanzari et al. 2012; Syakti et al. 2011).

Nicknamed “the most polluted river in Europe”, the Sarno River originates in south-western Italy and has a watershed of

about 715 km². It flows through the Sarno flatland, delimited in the west by Mt. Vesuvius and in the east by the Lattari Mountains, and reaches the sea at the Gulf of Naples (Tyrrhenian Sea), flowing through Pompeii City (Fig. 1). The Sarno watershed collects water from two important effluents, the Cavaiola and Solofrana torrents (Alveo Comune). The Sarno flatland is one of the most fertile in Italy due to the high quality of the soil, constituted by layers with volcanic and alluvial origins. The high human presence, the massive use of fertilisers and pesticides in agriculture and the development of industry represent the main causes of pollution in the Sarno River (Arienzo et al. 2001). Agriculture is focused on tomato production in the San Marzano area. In terms of industry, Solofra, a city around the Solofrana River, boasts an ancient tradition in the leather industry that currently counts for about 400 productive units and 3,500 workers. Another source of environmental pollution can be attributed to urban agglomerations and their wastewaters. Regarding the sewer system of the 39 towns of the Sarno area basin (with a population of about 1,300,635 and an average density of 1,818 inhabitants/km²), the wastewater collection and treatment in the area are inappropriate (De Pippo et al. 2006; ISTAT 2011).

This paper is part of a large project which has the objective of enhancing the knowledge on the Sarno River pollution and its environmental impact in the Gulf of Naples in order to become a useful assessment tool for the regional administrations. This project try to assess the pollution derived from the local industry, the agriculture and the urban impact through the determination of several groups of organic and inorganic chemical and some indicators of microbial pollution in water and sediments. This paper reports the results about the pollution by PCBs and OCPs in the Sarno River and its environmental impact on the Gulf of Naples.

Materials and methods

Sampling

Considering the seasonal variations of the Sarno flow, sampling campaigns have been conducted on the winter, spring, summer and autumn of 2008 considering four locations, at the sources, just before and after the junction with Alveo Comune and at the river mouth, and further nine points in the continental and sea shelf around the Sarno mouth (Fig. 1).

Precleaned 2.5-L glass amber bottles were deployed closed with a home-made device as described previously (IOC 1984; Gómez-Gutiérrez et al. 2006). 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)

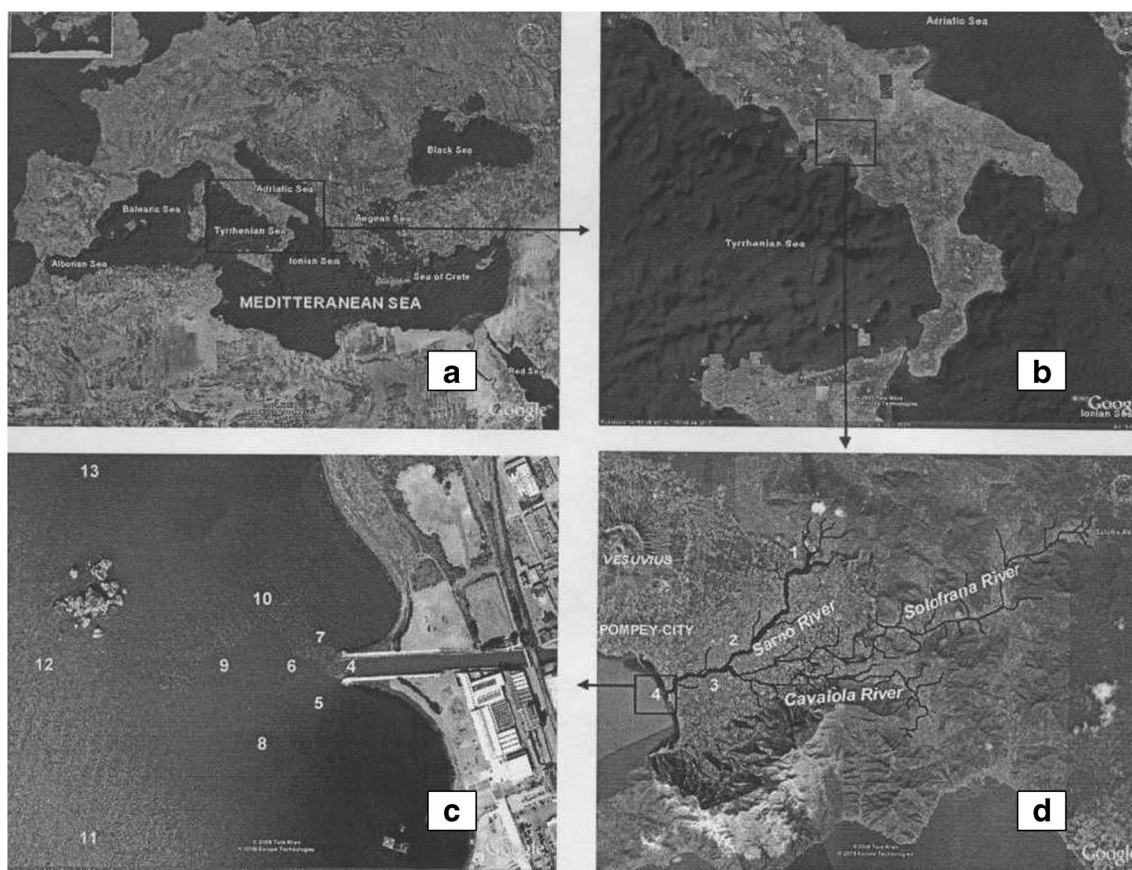


Fig. 1 Map of the study areas and sampling sites in the Sarno River and Estuary, Southern Italy (from Google Earth). **a** Mediterranean Sea. **b** Southern Italy. **c** Sarno River. **d** Sarno Estuary

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 of PCBs and OCPs

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. Spiked 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 for PCBs CP7482 (Varian, CA 92630, USA) with a temperature programme of 150 °C (1 min) to 200 °C at 30 °C min⁻¹ (2 min), to 270 °C at 2 °C min⁻¹ (1 min) and then to 310 °C at 20 °C min⁻¹ (1 min), holding it for 10 min. 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 2010Plus 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 SPM, DP 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 SPM, DP 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, endrin aldehyde, heptachlor, heptachlor epoxide (isomer B) and methoxychlor.

The surrogate averaged recoveries in the dissolved phase were 93.1 ± 7.3 % for PCB #65 and 92.7 ± 4.6 % for PCB #166. In the SPM samples, recoveries were 91.5 ± 4.1 % for PCB #65 and 90.6 ± 6.8 % for PCB #166. Finally, in the sediment samples, the averaged recoveries were the following: 90.9 ± 7.3 % for PCB #65 and 87.7 ± 5.9 % for PCB #166. Resulting data for PCB and OCP pesticides were corrected for surrogate recoveries. Procedural blanks were processed in the same manner as real samples and evaluated with each set of water samples. Limits of detection (LODs) were calculated as the average blank value plus three times the standard deviation of the blanks and ranged from 0.005 to 0.044 ng L⁻¹ for individual PCBs and OCPs in the particulate phase. In the dissolved phase, the values ranged from 0.004 to 0.110 ng L⁻¹ and from 0.0002 to 0.0044 ng g⁻¹ in the sediment.

Statistical analysis and calculation of the pollutant inputs

Data analysis was performed with the statistical software SPSS, version 14.01, for Windows (SPSS, Inc., Chicago, IL, USA). All data were presented as the mean ± SD. The level of significance was set at $p \leq 0.05$.

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 (Walling and Webb 1985; HELCOM 1993; Steen et al. 2001). 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:

$$C_{\text{aw}} = \frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \quad (1)$$

$$F_{\text{annual}} = C_{\text{aw}} Q_T \quad (2)$$

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), and Q_T represents the total river discharge for the period considered (February 4–November 4), calculated by adding the monthly averaged water flow. River flow data were collected from the register of the Autorità di Bacino del Sarno to Campania Government for the Environment (<http://www.autoritabacinosarno.it>). Furthermore, to study the temporal

contaminant discharge variation, C_i and Q_i were considered for each campaign and expressed in grams per day.

Results and discussions

PCBs in the water dissolved phase, suspended particulate matter and sediment samples

As shown in Table 1, the concentrations of total PCBs obtained in the DP ranged from 1.00 ng L^{-1} (site 1) to 5.20 ng L^{-1} (site 4) with a mean value of 3.04 ng L^{-1} . The compositional profiles of PCBs in the dissolved phase are illustrated in Fig. 2a, which indicates that tetra-, penta- and hexa-PCBs were abundant in all sampling sites, representing on average over 84 % of all PCBs. In addition, the di- + tri-CBs and hepta-CBs were present in low concentrations, accounting, respectively, for only 7 % (range 5–10 %) and 9 % (range 5–16 %) of total PCBs. The prevalence of tetra-, penta- and hexa-PCBs in the water could be explained by the higher concentrations of these congeners contained in liquids for machinery rather than by their water solubility (Lin et al. 2006).

In the SPM, the PCB concentrations on dry weight (dw) ranged from 0.41 ng L^{-1} (74.5 ng g^{-1}) in site 1 to 19.99 ng L^{-1} (276.8 ng g^{-1}) in site 3 (mean value of 9.1 ng L^{-1}) (Table 1). Tetra-, penta- and hexa-PCBs were abundant in all sampling sites, accounting for 30, 41 and 28 % of \sum PCBs in SPMs, respectively (Fig. 2a). Although tetra-, penta- and hexa-PCBs were still abundant in SPMs, the proportion of hepta-CBs increased to 14 %, much above than in dissolved samples, where it was 9 %, probably because the higher chlorinated PCBs are preferentially sorbed by the particulate matter due to their low hydrophilicity (Falconer and Bidleman 1994; Gedik and Imamoğlu 2011; Lugo-Ibarra et al. 2011; You et al. 2011). As the most recent studies reported PCB concentrations in the water as the sum of the DP and SPM, it is difficult to make a proper comparison between the concentrations of organochlorine compounds in SPM samples found in this study and those from other polluted aquatic environments (Table 2).

The total PCB concentrations in sediments are illustrated in Table 1. The results range from 1.01 ng g^{-1} (site 1) to 42.54 ng g^{-1} (site 3) with a mean value of 23.54 ng g^{-1} . Penta- and hexa-PCBs were abundant in sediments at each site, accounting, respectively, for 37 and 25 % of \sum PCBs (Fig. 2a). The proportion of tetra-PCBs decrease to 15 % in sediments, 10 % less than that in SPM samples, while the proportion of hepta-PCBs increased to 20 % (6 % more than that in SPM samples). Also, the proportion of di- + tri-PCBs decrease in sediments samples (1.5 %) compared to SPM (3 %) and DP (5 %) samples. These results could be explained that lower chlorinated PCBs are gradually carried away from the sediment due to their relatively high water solubility and

easier degradation. Indeed, higher chlorinated PCBs could easily reach the sediment due to their low water solubility, more refractory behaviour and low vapour pressure. Because the PCB vapour pressure decreases generally with an increase in the degree of chlorination, the higher chlorinated PCBs are more likely to be associated with the sediment or particulate adsorption phase than the lower chlorinated PCBs (Lin et al. 2006; Chen et al. 2010).

OCPs in the water dissolved phase, suspended particulate matter and sediment samples

The total OCP concentrations obtained in the DP ranged from 0.44 ng L^{-1} (site 1) to 3.52 ng L^{-1} (site 4) (mean value of 1.12 ng L^{-1}) (Table 3). In detail (Fig. 2b), they ranged from 0.006 to 0.85 ng L^{-1} (mean value of 0.24 ng L^{-1}) for hexachlorocyclohexanes (α -BHC, β -BHC, δ -BHC, γ -BHC), from 0.23 to 1.18 ng L^{-1} for dichlorodiphenyltrichloroethane and its degradates (4,4'-DDD, 4,4'-DDE, 4,4'-DDT and methoxy-chlor) and from 0.14 to 1.49 ng L^{-1} for cyclodienes (aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, endrin, endrin aldehyde, heptachlor and heptachlor epoxide). In DP samples, the HCHs/DDTs ratio was <1 at all sites (mean 0.46 ± 0.14 ; range 0.25 – 0.71), and the DDTs/cyclodiene ratio was >1 at most sites (mean 1.22 ± 0.26 ; range 0.79 – 1.64). The HCHs/cyclodiene ratio varied within a range of 0.37 – 0.56 (mean value of 0.52 ± 0.05).

In the SPM samples, the concentrations OCPs ranged from 0.10 ng L^{-1} ($18.8 \text{ ng g}^{-1} \text{ dw}$) in site 1 to 4.267 ng L^{-1} ($129.08 \text{ ng g}^{-1} \text{ dw}$) in site 4 (mean 0.99 ng L^{-1}) (in Table 1). The HCHs ranged from 0.02 to 1.22 ng L^{-1} (mean 0.23 ng L^{-1}), the DDTs from 0.04 to 1.17 ng L^{-1} and the cyclodienes from 0.048 to 1.87 ng L^{-1} (Fig. 2b). The HCHs/DDTs ratio (52 samples) showed an average of 1.04, while the HCHs/cyclodienes and DDTs/cyclodienes ratios were <1 at most sites (mean 0.66 and 0.62, respectively). On the contrary to that found in the DP samples, the SPM samples contain prevailing concentrations of the cyclodienes than the DDTs.

The total OCP concentrations in sediments (Table 1) ranged from 0.08 ng g^{-1} (site 1) to 5.99 ng g^{-1} (site 4) (mean value of 2.47 ng g^{-1}). The HCHs ranged from 0.018 to 1.47 ng g^{-1} (mean 0.608 ng g^{-1}), the DDTs from 0.027 to 2.09 ng g^{-1} and the cyclodienes from 0.04 to 2.42 ng g^{-1} (Fig. 2b). The cyclodiene concentrations (13 samples) prevailed than those of DDTs and HCHs, and DDT concentrations prevailed than those of HCHs. In fact, the DDTs/cyclodienes ratio was <1 at most sites (mean 0.86), such as the HCHs/DDTs and HCHs/cyclodienes ratios (means 0.69 and 0.60, respectively). Therefore, the concentrations of cyclodienes in sediment, SPM and DP samples of the Samo River and Estuary were higher than those of HCHs. Also, the DDT concentrations were higher than those of HCHs in sediment and DP samples, but similar in the SPM samples.

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 Samo River and the continental shelf, Southern Italy

Site number	identification	Sampling location	Site location	Σ PCBs														
				DP (ng L ⁻¹)						SPM (ng L ⁻¹) (ng g ⁻¹ dry wt)						Sediments (ng g ⁻¹ dry wt)		
				May	Aug	Nov	Feb	May	Aug	Nov	Feb	May	Aug	Nov	Feb	May		
1	(river water)	Samo River source	40°48'54.03"N 14°36'45.36"E	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.4 (74.5)	1.0 (137.9)	1.0 (159.8)	1.0 (154.9)	1.0
2	(river water)	Upstream Alveo Comune	40°46'42.73"N 14°34'00.48"E	3.6	2.7	4.1	3.4	7.5 (326.2)	5.9 (68.4)	14.2 (226.0)	10.1 (122.9)	26.3						
3	(river water)	After Alveo Comune	40°46'00.34"N 14°33'10.68"E	3.6	2.9	5.0	4.0	10.0 (304.6)	7.8 (121.8)	20.0 (276.8)	13.9 (250.3)	42.5						
4	(river water)	Samo River mouth	40°43'42.62"N 14°28'07.89"E	3.7	2.6	5.2	4.0	10.5 (316.9)	7.5 (54.8)	19.1 (354.3)	13.4 (173.1)	36.0						
5	(sea water)	River mouth at 50 m south	40°43'40.11"N 14°28'06.45"E	3.7	2.8	5.1	3.9	9.0 (136.3)	6.8 (12.5)	17.2 (195.8)	12.1 (122.5)	37.1						
6	(sea water)	River mouth at 50 m central	40°43'42.46"N 14°28'05.03"E	3.4	2.4	3.5	3.3	8.9 (206.8)	6.7 (41.9)	16.6 (194.5)	11.8 (93.3)	30.8						
7	(sea water)	River mouth at 50 m north	40°43'45.09"N 14°28'05.17"E	3.0	2.0	3.0	3.1	8.3 (166.8)	6.4 (35.2)	15.5 (170.7)	11.1 (108.2)	28.0						
8	(sea water)	River mouth at 150 m south	40°43'35.68"N 14°28'02.94"E	4.1	2.8	4.4	3.6	9.7 (121.3)	6.7 (71.4)	16.8 (182.5)	11.7 (194.6)	24.2						
9	(sea water)	River mouth at 150 m central	40°43'42.25"N 14°27'59.97"E	3.9	2.5	3.9	3.6	8.8 (138.7)	7.2 (56.3)	18.1 (230.0)	12.8 (140.7)	22.2						
10	(sea water)	River mouth at 150 m north	40°43'49.26"N 14°27'59.82"E	3.6	2.4	3.6	3.1	7.3 (114.5)	5.7 (39.6)	13.4 (146.9)	9.6 (113.9)	18.8						
11	(sea water)	River mouth at 500 m south	40°43'30.31"N 14°27'58.93"E	3.2	2.0	2.5	2.7	6.8 (104.8)	5.3 (56.7)	7.5 (90.8)	8.9 (196.8)	23.4						
12	(sea water)	River mouth at 500 m central	40°43'42.29"N 14°27'46.41"E	3.1	2.1	2.5	2.4	4.3 (69.1)	3.7 (40.2)	12.4 (80.7)	5.6 (114.8)	10.4						
13	(sea water)	River mouth at 500 m north	40°43'57.85"N 14°27'48.68"E	2.6	1.6	2.0	2.1	3.5 (52.4)	3.2 (34.2)	5.9 (96.8)	4.6 (105.1)	5.3						

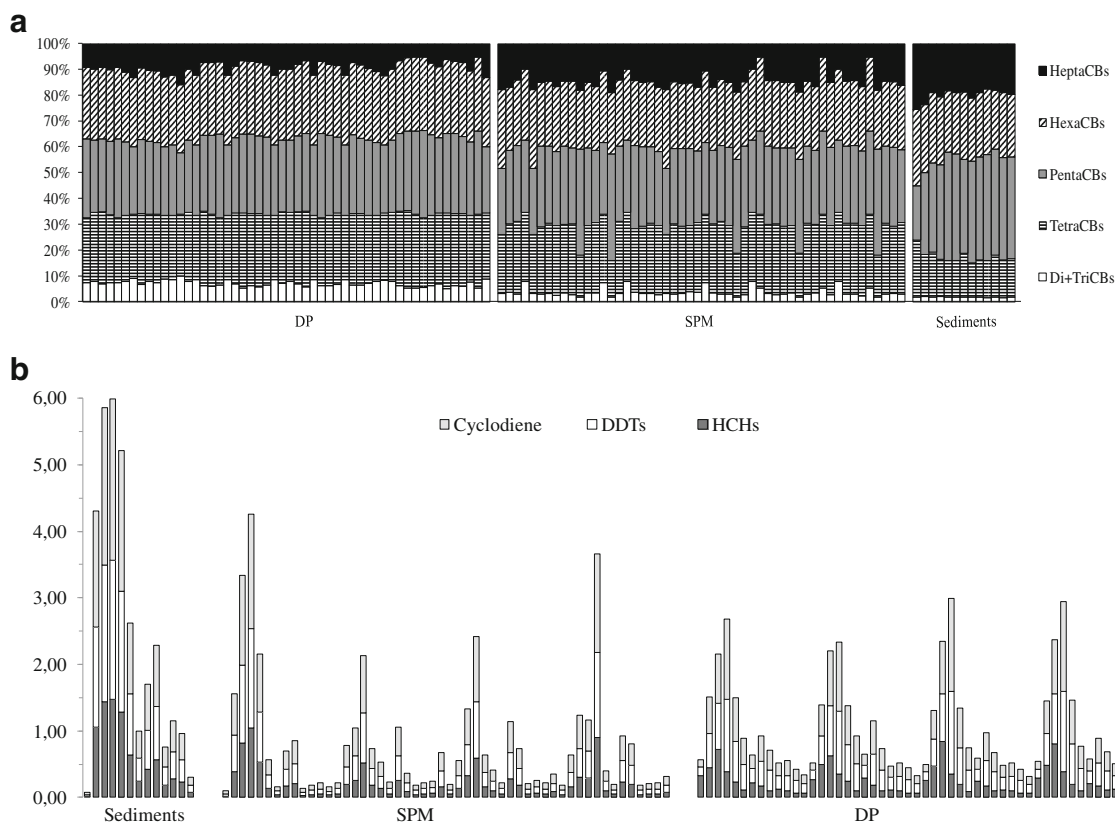


Fig. 2 **a** Relative abundance of di- + tri-, tetra-, penta-, hexa- and hepta-PCBs in water dissolved phase (DP) samples, suspended particulate matter (SPM) and sediments of the Sarno, Southern Italy. **b** Concentration of HCHs (α -BHC, β -BHC, δ -BHC and γ -BHC), DDTs ($\alpha,4'$ -DDD, $4,4'$ -DDE, $4,4'$ -DDT and methoxychlor) and cyclodiene

(aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulphate, endrin, endrin aldehyde, heptachlor and heptachlor epoxide) in the water DP (in nanograms per litre), the SPM (in nanograms per litre) and the sediments (in nanograms per gram dry wt) of the Sarno River and the continental shelf, Southern Italy

The average compositions of HCHs were the following: in DP, α -HCH=26.4 %, β -HCH=34.8 %, γ -HCH=22.3 % and δ -HCH=16.4 %; in SPM, α -HCH=22.9 %, β -HCH=32.8 %, γ -HCH=13.1 % and δ -HCH=31.1 %; and in sediments, α -HCH=21.3 %, β -HCH=36.4 %, γ -HCH=15.4 % and δ -HCH=26.8 %. β -HCH was the dominant HCH isomer in both sediments and settling particles, which indicated that residues of HCHs were mainly from the large usage in the history (Carvalho et al. 2009; Yang et al. 2010; Kanzari et al. 2012). The DDT residues can be biodegraded to DDE via oxidative dehydrochlorination, and DDD involving reductive dechlorination of DDT (Mohn and Tiedje 1992). The DDT/(DDD + DDE) ratio can be used to examine whether the DDT input is old or recent (Mohn and Tiedje 1992; Tan et al. 2009; Mohammed et al. 2011). The mean values of DDT/(DDD + DDE) ratio in SPM and sediment samples of the Sarno River and its estuary were 0.29 and 0.47, respectively. These results suggest that most of the DDTs in the Sarno River and Estuary were derived from historical discharge. However, among the 52 DP samples, 22 had DDT/(DDD + DDE) ratios of >1, implying a possible new DDT input to the aquatic environment of the Sarno. Indeed, the ratios of DDT/(DDD + DDE) in DP samples ranged from 0.35 to 2.91 (mean 1.13 ± 0.76). The

mean values of aldrin in DP, SPM and sediment samples of the Sarno River and Estuary were 0.05 ng L^{-1} and 0.04 and 0.08 ng g^{-1} , respectively. It was established that heptachlor is metabolised to heptachlor epoxide, endrin is subjected to some photolytic degradation to endrin aldehyde and ketone, isodrin is metabolically converted to endrin, and aldrin is converted to its enoxide analogue (Kuranchie-Mensah et al. 2011). The mean values of endrin/endrin aldehyde and heptachlor/heptachlor epoxide ratio in the aquatic environment of the Sarno were 0.28 and 0.48, respectively. This present trend where the degradation products are higher than the parent compounds gives an indication of no fresh inputs of this pesticide in the waterbody (Yang et al. 2010; Kuranchie-Mensah et al. 2011).

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 Sarno River and Estuary (Table 1, Fig. 3) show that the \sum PCB concentration ratios in DP samples to those in SPM (in nanograms per litre) were <1 in most sampling sites (average 0.44; range 0.19–2.45; SD ± 0.33). These results lead

Table 2 Concentration ranges and mean value of PCBs and 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	No. of PCBs	No. of OCPs	DP (ng L ⁻¹)		SPM (ng L ⁻¹)		Sediments (ng g ⁻¹)	
				Range	Mean	Range	Mean	Range	Mean
Asia									
Tokyo Bay, Japan	Kobayashi et al. (2010)	209		0.04–0.64 0.12–1.1*	0.096 0.25*	0.05–0.58 14–97 ng g ⁻¹	0.15 34 ng g ⁻¹	2.7–110	39
Yangtze River Delta, China	Zhang et al. (2011)	38		1.23–16.6*	3.36*				
Songhua River, China	You et al. (2011)	84		1.1–14*	6.8*			0.26–9.7	294
Gwangyang Bay, South Korea	Hong et al. (2011)	78			2.99*				
Pearl River Delta, China	Guan et al. (2009)	20		0.12–1.47					
USA									
Ship Chanel, Houston	Lakshmanan et al. (2010)	209		0.47–69.2*				1.4–108	26
Sea Lots, Port of Spain	Mohammed et al. (2011)	136						62–601	
Europe									
Arc River-Berre Lagoon, France	Kanzari et al. (2012)	7						0.3–466.8	
Mediterranean Sea									
This study		32		1.00–5.20 1.41–24.9*	3.04 12.14*	0.41–19.99	9.10	1.01–42.54	23.53
Mersin Bay, Turkey	Gedik and Imamoğlu (2011)	41						0.61–1.04	
Ghar ElMelh Lagoon, Tunisia	Ameur et al. (2011)	20						ND–3.98	
Marseille, France	Syakti et al. (2011)	7						9.1–226.9	
Izmir Bay, Eastern Aegean Sea	Pazir et al. (2011)	20						0.21–31.95	
Asia									
Peacock River, China	Chen et al. (2011)		12	ND–195*				1.36–24.6	
Pearl River Delta, China	Guan et al. (2009)		21	2.57–41.2*					
Daliao River Estuary, China	Tan et al. (2009)		19	3.7–30.1		4.6–52.6		2.1–213.6	
USA									
Sea Lots, Port of Spain	Mohammed et al. (2011)		29					44.5–145	
Colorado River, Mexico	Lugo-Ibarra et al. (2011)		20					1.3–47.4	
Europe									
Arc River-Berre Lagoon, France	Kanzari et al. (2012)		15					0.02–7.15	
Portuguese Coastal Area	Carvalho et al. (2009)		12					0.08–26	
Mediterranean Sea									
This study			17	0.44–3.52 0.54–7.32*	1.12 1.91*	0.10–4.26	0.81	0.08–5.99	2.48
Marseille, France	Syakti et al. (2011)		18					1.2–190.6	
Izmir Bay, Eastern Aegean Sea	Pazir et al. (2011)		9					0.12–11.35	

ND not detectable

* DP+SPM

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 Samo River and the continental shelf, Southern Italy

Site number	Identification	Sampling location	Site characteristics	Site location	Σ OCPs													
					DP (ng L ⁻¹)						SPM (ng L ⁻¹) (ng g ⁻¹ dry wt)						Sediments (ng g ⁻¹ dry wt)	
					May	Aug	Nov	Feb	May	Aug	Nov	Feb	May	Aug	Nov	Feb	May	
1	(river water)	Samo River source	40°48'54.03"N 14°36'45.36"E	0.44	0.45	0.46	0.45	0.10	(18.80)	0.22	(30.61)	0.18	(27.50)	0.19	(30.78)	0.08		
2	(river water)	Upstream Alveo Comune	40°46'42.73"N 14°34'00.48"E	1.47	1.25	1.34	1.17	1.56	(179.22)	0.78	(90.60)	0.64	(77.67)	0.56	(88.15)	4.30		
3	(river water)	After Alveo Comune	40°46'00.34"N 14°33'10.68"E	1.95	2.14	2.11	2.05	3.34	(77.06)	1.04	(21.99)	1.24	(98.09)	1.33	(96.04)	5.85		
4	(river water)	Samo River mouth	40°43'42.62"N 14°28'07.89"E	3.07	2.68	3.40	3.52	4.26	(129.02)	2.13	(15.55)	1.17	(15.10)	2.42	(44.96)	5.99		
5	(sea water)	River mouth at 50 m south	40°43'40.11"N 14°28'06.45"E	1.74	1.55	1.74	1.58	2.15	(32.40)	0.74	(1.35)	3.66	(36.90)	0.64	(7.24)	5.21		
6	(sea water)	River mouth at 50 m central	40°43'42.46"N 14°28'05.03"E	1.10	1.16	0.96	0.92	0.56	(13.13)	0.53	(3.31)	0.40	(3.19)	0.41	(4.76)	2.62		
7	(sea water)	River mouth at 50 m north	40°43'45.09"N 14°28'05.17"E	0.62	0.56	0.57	0.56	0.16	(3.25)	0.23	(1.28)	0.19	(1.90)	0.22	(2.41)	0.99		
8	(sea water)	River mouth at 150 m south	40°43'35.68"N 14°28'02.94"E	1.05	1.33	1.01	1.12	0.70	(8.78)	1.06	(11.18)	0.93	(15.43)	1.14	(12.39)	1.70		
9	(sea water)	River mouth at 150 m central	40°43'42.25"N 14°27'59.97"E	0.87	0.91	0.84	0.83	0.85	(13.41)	0.36	(2.83)	0.80	(8.81)	0.73	(9.28)	2.29		
10	(sea water)	River mouth at 150 m north	40°43'49.26"N 14°27'59.82"E	0.59	0.57	0.60	0.57	0.13	(2.10)	0.19	(1.31)	0.18	(2.11)	0.21	(2.33)	0.76		
11	(sea water)	River mouth at 500 m south	40°43'30.31"N 14°27'58.93"E	0.67	0.63	0.64	0.63	0.18	(2.81)	0.22	(2.37)	0.21	(4.59)	0.26	(3.15)	1.16		
12	(sea water)	River mouth at 500 m central	40°43'42.29"N 14°27'46.41"E	0.56	0.59	0.58	0.56	0.22	(3.47)	0.24	(2.62)	0.22	(4.42)	0.22	(1.40)	0.96		
13	(sea water)	River mouth at 500 m north	40°43'57.85"N 14°27'48.68"E	0.48	0.47	0.46	0.47	0.16	(2.31)	0.67	(7.22)	0.31	(7.26)	0.35	(5.74)	0.31		

us to consider that the total amount of PCBs in SPM samples was more abundant than in DP samples for each site and season. With some exception, the total amount of PCBs in sediment samples was more abundant than their corresponding waterbodies (DP and SPM samples). In fact, the ratio of the concentration of \sum PCBs in sediment samples to that in the corresponding waterbodies (DP and SPM samples) was >1 in most sampling sites and for each season. Moreover, the high chlorinated congener (hepta-CB) concentrations decrease from sediment samples to SPMs and more to DPs (Fig. 2a), while low chlorinated PCBs (di- + tri-CBs) showed a reverse trend with an increase of concentrations from sediment samples to SPMs and more to DPs. The observed pattern of accumulation in sediments may, therefore, be explained by the lower chlorinated PCBs been more readily released from sediments because of their higher water solubility, vapour pressure and biodegradability (Lin et al. 2006; Chen et al. 2010).

The partition coefficients, $K_p = C_{SPM}/C_{DB}$, showed a decreasing trend in the HCHs partitioning from sediments to SPM ($HCH_{SPM}/HCH_{Sediment}$ mean value of 0.60) and to DPs ($HCH_{SPM}/HCH_{Sediment}$ mean value of 0.67). The concentrations of HCHs in SPM and DP samples were similar (HCH_{SPM}/HCH_{DP} ratio mean value of 0.91 ± 0.54 ; range 0.36–2.93). Regarding the DDTs, the partition coefficients showed a decreasing trend in the DDT concentrations from sediments to SPMs ($HCH_{SPM}/HCH_{Sediment}$ ratio mean value of 0.28 ± 0.21 ; range 0.09–1.70) and from SPMs to DPs (HCH_{SPM}/HCH_{DP} ratio mean value of 0.42 ± 0.30 ; range 0.12–1.56). 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 0.53 and 0.82, respectively). These results show that higher levels of the OCPs were found in sediment samples than in DP and SPM samples (Fig. 2b), which are an indication of no fresh inputs of these pesticides in the Sarno (Yang et al. 2010; Kuranchie-Mensah et al. 2011). Moreover, the higher levels of the OCPs found in sediments than in their corresponding waterbodies (DP and SPM samples) indicate that the gravitational sedimentation and suspension processes are mainly in this area with subsequent transfer of the OCPs, particularly more polar, from sediments to waterbodies. This is also confirmed that OCPs found in sediments were the same as those detected in DP and SPM samples and generally reflected a similar pattern (Fig. 2b).

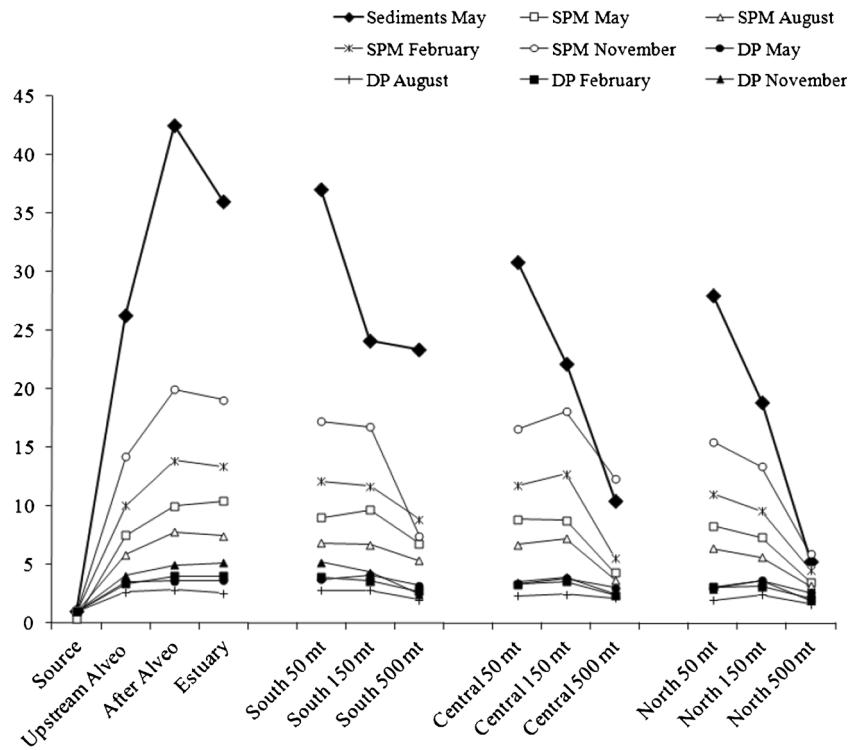
The spatial distribution of PCBs and OCPs in DP, SPM and sediment samples from the Sarno River and its estuary was studied by comparing the concentrations of \sum PCBs and \sum OCPs in different sampling sites in dry and rainy seasons, respectively. The results summarized in Fig. 3 (PCBs) and Fig. 4 (OCPs) show a similar trend. Indeed, the PCB and OCP contamination levels in the Sarno increase clearly from

locations 1 to 4. In general, the upland part of the river was less contaminated by PCBs and OCPs. Where the river flows through the flatland and the different urban agglomerations, the total PCB and OCP concentrations increase, respectively, to 6.42 and 1.09 $ng L^{-1}$ (DP + SPM mean values of four seasons) at location 2 (upstream Alveo Comune). The total PCB and OCP concentrations then increased, respectively, to 8.39 and 1.90 $ng L^{-1}$ (DP + SPM mean values of four seasons) at location 3 (after Alveo Comune). This increase in total PCB and OCP concentrations resulted from the inflow from the Alveo Comune ($30\text{--}50 m^3 s^{-1}$), which carries the discharge of another industrial district. In the lower part of the Sarno (location 4, estuary), the PCB and OCP concentrations increased again, reaching, respectively, 9.32 and 2.82 $ng L^{-1}$ (Fig. 1, Table 3). The PCBs and OCPs loading into the Tyrrhenian Sea occur through various transport pathways including storm water runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, atmospheric deposition and dredged material disposal. The total PCB and OCP load contributions to the Tyrrhenian Sea from the Sarno River are calculated in about $1,247 g day^{-1}$ ($948 g day^{-1}$ of PCBs and $326 g day^{-1}$ of OCPs). In the Tyrrhenian Sea, around the Sarno plume, total PCB and OCP concentrations range in general from very low in offshore areas to very high in the vicinity of the river outflows (Fig. 1, Table 3). At 50 m of the river outflow, the total PCB and OCP concentrations were close to those of the Sarno Estuary. The concentrations at the sampling sites then decreased at 150 m and more at 500 m of the river outflows. Moreover, at the central estuary, the total PCB and OCP concentrations were close to those at the southern estuary, decreasing northward (Figs. 3 and 4). These results allow us to conclude that although some of the PCB and OCP loads from the Sarno inputs are headed northwards, most of them move into the Tyrrhenian Sea southward.

Eco-toxicity assessment of PCBs and OCPs in the Sarno River and Estuary

Many countries have developed Environmental Quality Standards (EQS) for priority substances and certain other pollutants in inland surface waters and coastal waters. Guidelines derived in one region will not be relevant for all regions, because, for example, biochemical reaction rates and biological activity increase exponentially with temperature (Chapman 2004; Sánchez-Avila et al. 2010). Also, the in situ communities can vary between different regions. Regionally developed EQS may be less relevant in other regions with different contaminant mixtures. Although many EQS were mentioned for PCBs, these substances were banned by Regulation (EC) No. 850/2004 (European Parliament and Council 2004), except in items that were already in use at the time. The concentrations of PCBs found in the water of the

Fig. 3 Spatial and temporal concentration of total PCBs in the water dissolved phase (*DP*, in nanograms per litre), the suspended particulate matter (*SPM*, in nanograms per litre) and the sediments (in nanograms per gram dry wt) of the Sarno River and the continental shelf, Southern Italy

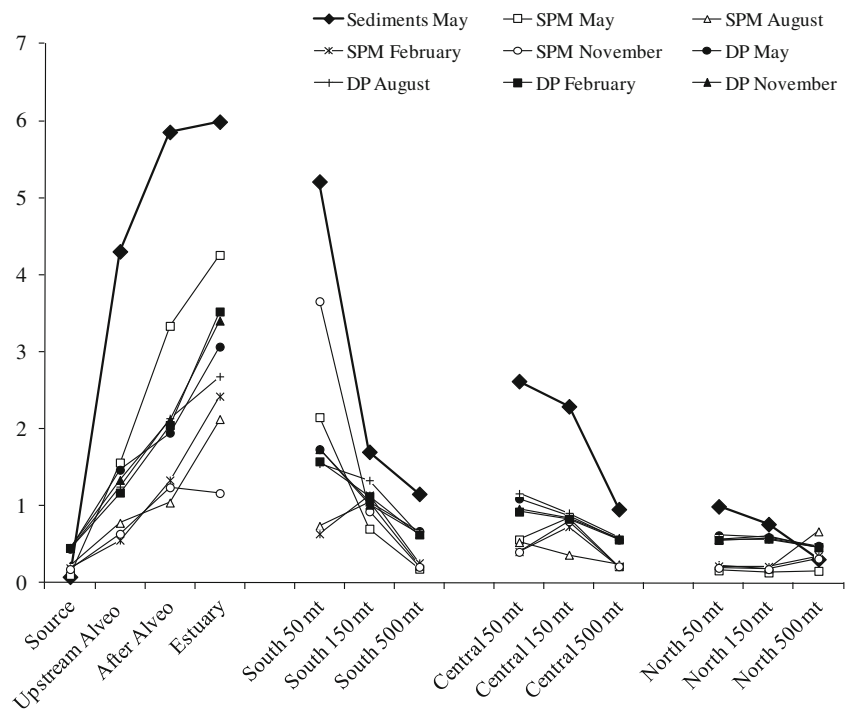


Sarno River and its estuary as the sum of the DP and SPM were significantly lower than the criterion continuous concentration (CCC) (2002) for water quality recommended by US EPA Agency (30 ng L^{-1} as ΣPCBs). The Sarno waters should be continuously monitored since PCBs may cause potential damage to aquatic biota animals (Walling and Webb 1985; Steen et al. 2001). The US EPA (2002) recommends against

human consumption of organisms from waters with ΣPCB concentrations higher than 0.06 ng L^{-1} , a value based on the bioaccumulation of these substances in fish and a carcinogenicity of 10^{-6} risk. This ΣPCB limit was exceeded in all samples of the Sarno River and its estuary ($1.4\text{--}24.9 \text{ ng L}^{-1}$).

Although compliance with EC EQS in surface waters is checked using an annual average of monthly whole water

Fig. 4 Spatial and temporal concentration of total OCPs in the water dissolved phase (*DP*, in nanograms per litre), the suspended particulate matter (*SPM*, in nanograms per litre) and the sediments (in nanograms per gram dry wt) of the Sarno River and the continental shelf, Southern Italy



(dissolved + SPM) concentrations (European Union 2010), our data show that the mean concentrations of HCHs (0.11 ng L^{-1}); DDTs (0.16 ng L^{-1}); Σ aldrin, dieldrin, endrin and isodrin (0.090 ng L^{-1}); and endosulfan (0.091 ng L^{-1}) in the Sarno River and its estuary were higher than the EQS value of 0.02, 0.025, 0.01 and 0.038 ng L^{-1} , respectively, showing that the ecological integrity of the river watercourse is possibly at risk.

In order to assess whether PCBs and OCPs in the Sarno River and its estuary will cause toxic effects, we compared the PCB and OCP levels in sediment against effect-based guideline values such as the effect range-low (ER-L), effect range-median (ER-M) and apparent effect threshold values developed by the US Natural Oceanic and Atmospheric Administration (Long et al. 1995; De Deckere et al. 2011). Sediment quality guidelines have not been determined for chlorinated pesticides other than DDT. ER-L and ER-M values are useful in assessing sediment quality and provide qualitative guidelines on what needs to be done to effectively protect the aquatic environment. In the Sarno River and its estuary, the total PCB concentrations in sediment samples ($1.0\text{--}42.5 \text{ ng g}^{-1}$, mean $23.5 \text{ ng g}^{-1} \pm 12.3$) were higher than ER-L value (22.7 ng g^{-1}) and were significantly lower than the ER-M value (180 ng g^{-1}). Regarding the DDTs, the concentrations in these sediment samples were lower than their respective ER-L values (1.58 ng g^{-1}) and ER-M values (46.1 ng g^{-1}).

Conclusions

This study is the first to document a comprehensive analysis of PCB and OCP levels in the Sarno River and its estuary; it has provided very useful information for the evaluation of trace PCB and OCP levels in this river and its input into the Tyrrhenian Sea, which is part of the 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 waterbodies (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 waterbodies. This confirms also that PCBs and OCPs found in sediment samples were the same as those detected in DP and SPM samples and generally reflected a similar pattern. The results show that these areas are the main contribution sources of PCBs and OCPs into the Tyrrhenian Sea, and although some of the PCBs and OCPs from the Sarno River inputs move northwards, the majority of them move into the Tyrrhenian Sea southward. In relation to the ecotoxicological assessment, the concentrations of most PCBs

and OCPs in the water and sediments from the Sarno River and its estuary were lower than guideline values. In conclusion, the PCB and OCP levels observed do not seem to cause immediate biological effects on the sedimentary environment in the Sarno River and its estuary.

Highlights

- Σ PCB concentrations ranged from 1.4 to 24.9 ng L^{-1} in water (sum of DP and SPM).
- Σ PCB concentrations ranged from 1.01 to 42.54 ng g^{-1} in sediment samples.
- OCP concentrations in water (sum of DP and SPM) ranged from 0.54 to 7.32 ng L^{-1} .
- OCP ranged from 0.08 to 5.99 ng g^{-1} in sediment samples.
- Contaminant discharges in the sea were 948 g day^{-1} of PCBs and 326 g day^{-1} of OCPs.

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