



Polychlorinated biphenyls and organochlorine pesticides in Tiber River and Estuary: Occurrence, distribution and ecological risk



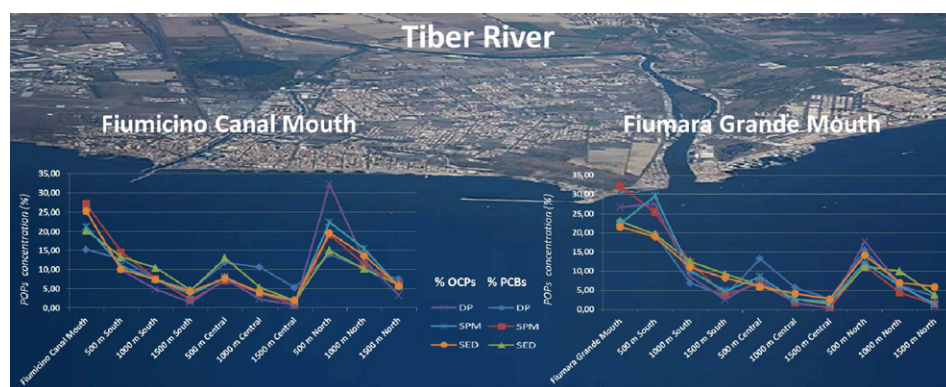
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HIGHLIGHTS

- DDTs and HCHs were the most detected among OCPs, while high chlorinated CB emerged as predominant compounds among PCBs.
- OCPs in sediment samples came from DDTs used in the past times, while in water samples from new use of lindane.
- OCPs and PCBs levels were higher in Fiumicino Canal than in Fiumara Grande.
- TEQ_{PCB} concentrations of 8 detected DL-PCBs were mainly affected by PCB 126.
- TEQ_{PCB} suggest potentially carcinogenic risk of DL-PCBs exposure in Tiber River and Estuary.

GRAPHICAL ABSTRACT



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ABSTRACT

The polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) pollution in the Tiber River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea) were estimated. 32 PCBs and 17 OCPs (aldrin, α -BHC, β -BHC, δ -BHC, lindane, p,p'-DDD, p,p'-DDE, p,p'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, methoxychlor) were determined in the water dissolved phase (DP), suspended particulate matter (SPM) and sediment samples. Total concentrations of PCBs ranged from 0.54 to 74.75 ng L⁻¹ in water (sum of DP and SPM) and from 3.73 to 79.30 ng g⁻¹ dry weigh in sediment samples; while the concentrations of total OCPs collected in water (sum of DP and SPM) ranged from 0.07 to 7.04 ng L⁻¹ and from 0.66 to 10.02 ng g⁻¹ dry weigh in sediment samples. Contaminant discharges into the sea were calculated in about 227.08 kg year⁻¹ for PCBs and 24.91 kg year⁻¹ for OCPs, showing that this river should account as one of the main contribution sources of PCBs and OCPs to the Tyrrhenian Sea. The \sum TEQ_{PCB} from the sediment samples ranged from 0.0006 to 0.37 ng g⁻¹ with an average level of 0.13 ng g⁻¹. Based on Sediments Quality Guidelines, biological adverse effects on aquatic ecosystem were rare to occasional for PCB and OCP levels in Tiber water system.

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1. Introduction

Persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are xenobiotic

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compounds with great chemical stability. Due to their difficult degradation, bioaccumulative effect, ecotoxicity and carcinogenic properties, these man-made chemicals have become a critical world concern (Ge et al., 2013; Zhi et al., 2015; Lin et al., 2015). The United Nations Environment Programme identified twelve POPs, including PCBs and OCPs, listed in the Stockholm Convention to be forbidden and restricted worldwide. The OCPs or pesticide POPs identified in the convention include aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. Nine new POPs, including hexachlorocyclohexane, chlordecone, lindane, pentachlorobenzene, pentachlorophenol and endosulfan, were added to the convention (Chung and Chen, 2001; Xu et al., 2013; Li et al., 2014; UNEP, 2015).

PCBs were used extensively in the past as electrical insulating materials, due their characteristics of low electrical conductivity and high resistance to heat and thermal degradation (Bigus et al., 2014; Yuan et al., 2015; Omar and Mahmoud, in press). The global production of PCBs has been estimated to be over 1.3 million tons (Gao et al., 2013). Technical mixtures of PCB congeners were manufactured and sold under several trade names such as Aroclor (USA), Phenoclor (France), Clophen (Germany), Kanechlor (Japan) and Fenchlor (Italy) (Scarpato et al., 2010; Dodoo et al., 2012).

OCPs were extensively applied worldwide as pesticide in agriculture and health sector for several decades (Zehra et al., 2015; Zhi et al., 2015; Oliveira et al., 2016). The production and usage of these pesticides were stopped or restricted in the 1970s and 1980s in developed countries; however, most OCPs, especially DDTs and HCHs, are still used in some developing countries in agriculture due to their high efficiency, low cost, and broad-spectrum pest-killing efficacy (Bigus et al., 2014; Yuan et al., 2015).

POPs could persist in the environment, bioaccumulate through the food chain and affect human health and environment (Miglioranza et al., 2013; Bettinetti et al., 2016). Their fate and distribution have been intensively investigated in marine and freshwater ecosystem (Barakat et al., 2013; Verhaert et al., 2013; Merhaby et al., 2015). The water systems drain via catchment all the earth surface and large rivers are usually the final receptacle of pollutants, including organic compounds. Estuaries are one of the main zones receiving freshwater runoff before discharging into marine systems (Menzies et al., 2013; Couderc et al., 2015). POP behavior in marine and freshwater ecosystems depends on several factors such as physicochemical properties, water and sediment movement and size fraction (Bigus et al., 2014; Mwanamoki et al., 2014; Lin et al., 2015). POPs are absorbed onto particulate matter and accumulate in sediments according to their high hydrophobicity and molecular mass (Čonka et al., 2014; Mourier et al., 2014; Li et al., 2016). Sediments, the primary reservoir for hydrophobic contaminants, offer an irreplaceable aid in reconstructing the historical inputs of these pollutants (Kanzari et al., 2014; Wu et al., in press; Yuan et al., 2015). Hence, the investigation of PCBs and OCPs in aquatic environments is the primary source of information about the anthropogenic impact on the environment and concentrations serve as indicator of contaminant load (Alonso-Hernández et al., 2015; Oliveira et al., 2016).

In the Mediterranean basin, the occurrence of these contaminants become of a great importance after the Barcelona Convention approval, that promoted the Mediterranean Action Plan (MAP) and its environmental assessment programmes (Programme for Pollution Monitoring and Research in the Mediterranean Sea—MED POL) (Scarpato et al., 2010). Following these monitoring programmes, many studies have been performed in order to determinate the environmental contamination levels along the Mediterranean coasts (Syakti et al., 2013; Moreno-González et al., 2013; Kanzari et al., 2014). In Italy, recent studies (Viganò et al., 2015; Bellucci et al., 2016; Bettinetti et al., 2016; Combi et al., 2016) showed higher levels of POPs due to industrial and agricultural activities presently developed in the different region.

Indeed, we chose the Tiber River, the second largest watercourse in Italy. The Tiber River crosses densely populated urban area of Rome, the largest agricultural district in Europe and the most populated city

of Italy, with a population of about 2,863,322 residents (ISTAT, 2010; ISTAT, 2014), before flowing into the Tyrrhenian Sea (Central Mediterranean Sea). Due to different anthropogenic activities developed in the basin, Tiber River discharge is an important source of contamination to the adjacent coastal environment. Nevertheless, there is a lack of information in recent literature on PCBs and OCPs pollution in the Tiber River and its Estuary; indeed, to the best of our knowledge, only one past research has been focused on the occurrence of PCB contamination in samples of water and sediments collected in 1976–1977 from the coastal area of the Tiber (Puccetti and Leoni, 1980).

This study is part of a large project aimed to contribute to the knowledge of the pollution affecting the Tiber River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea). The aim of this project is to assess the pollution due to effluents from local industries, agriculture and the urban impact by identifying 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 Tiber River and its environmental impact on the Central Mediterranean Sea.

2. Materials and methods

2.1. Study area and sampling

The Tiber River rises in the Apennine Mountains (Central Italy) and, with a length of 409 km, it flows through six regions of Central Italy before flowing into the Tyrrhenian Sea (Central Mediterranean Sea). The water volume, with an annual mean flow rate of $230 \text{ m}^3 \text{ s}^{-1}$, is widely used for irrigation, hydropower and industrial water (di Lascio et al., 2013; Patrolecco et al., 2015). The hydrology of the basin is highly influenced by the intense rainfall at the upstream part that causes frequent floods in the downstream areas (Fiseha et al., 2014). The Tiber River basin represents one of the largest agricultural area in Italy and it is strongly affected by inputs of agricultural pollutants used in fruit and vegetables (such as cereals and potatoes) crops and vineyards, olive and tobacco and to a less extent by industrial activities, such as those related to the steel mills, chemical plants and paper factories.

In order to assess temporal trends of pollutants, four sampling campaigns were conducted in August 2014, November 2014, February 2015 and May 2015. In each campaign were sampled 21 location: three locations were sampled before and after the fork in the river, in order to have a proper idea of the evolution of the contamination downriver. In addition, nine points were sampled in the continental shelf around the Tiber artificial mouth (Fiumicino canal) and other nine points in the continental shelf around the Tiber natural mouth (Fiumara Grande) to assess the environmental impact of the Tiber River on the Mediterranean Sea. Three points were sampled 500 m from the Tiber River mouths, another three points 1000 m away and, finally, another three points 1500 m from the river mouths (Fig. 1).

Precleaned 2.5 L glass amber bottles were deployed closed with a homemade device (Gómez-Gutiérrez et al., 2006; Montuori et al., 2014). In each sampling point 2.5 L of water (one amber bottles) were collected and transported refrigerated ($4 \text{ }^\circ\text{C}$) to the laboratory. Surface sediment (0–5 cm) samples were collected by using a grab sampler (Van Veen Bodemhappe 2 litre capacity) and put in aluminum containers. The sediments were transported refrigerated to the laboratory and kept at $-20 \text{ }^\circ\text{C}$ before analysis.

2.2. Extraction and cleanup of PCBs and OCPs

The method used for extraction and cleanup has been published previously (Montuori et al., 2014). Briefly, water samples were filtered through a previously kiln-fired ($400 \text{ }^\circ\text{C}$ overnight) GF/F glass fiber filter ($47 \text{ mm} \times 0.7 \text{ }\mu\text{m}$; Whatman, Maidstone, UK). Filters (suspended particulate matter, SPM) were kept in the dark at $-20 \text{ }^\circ\text{C}$ until analysis. Dissolved phases (fraction of contaminants

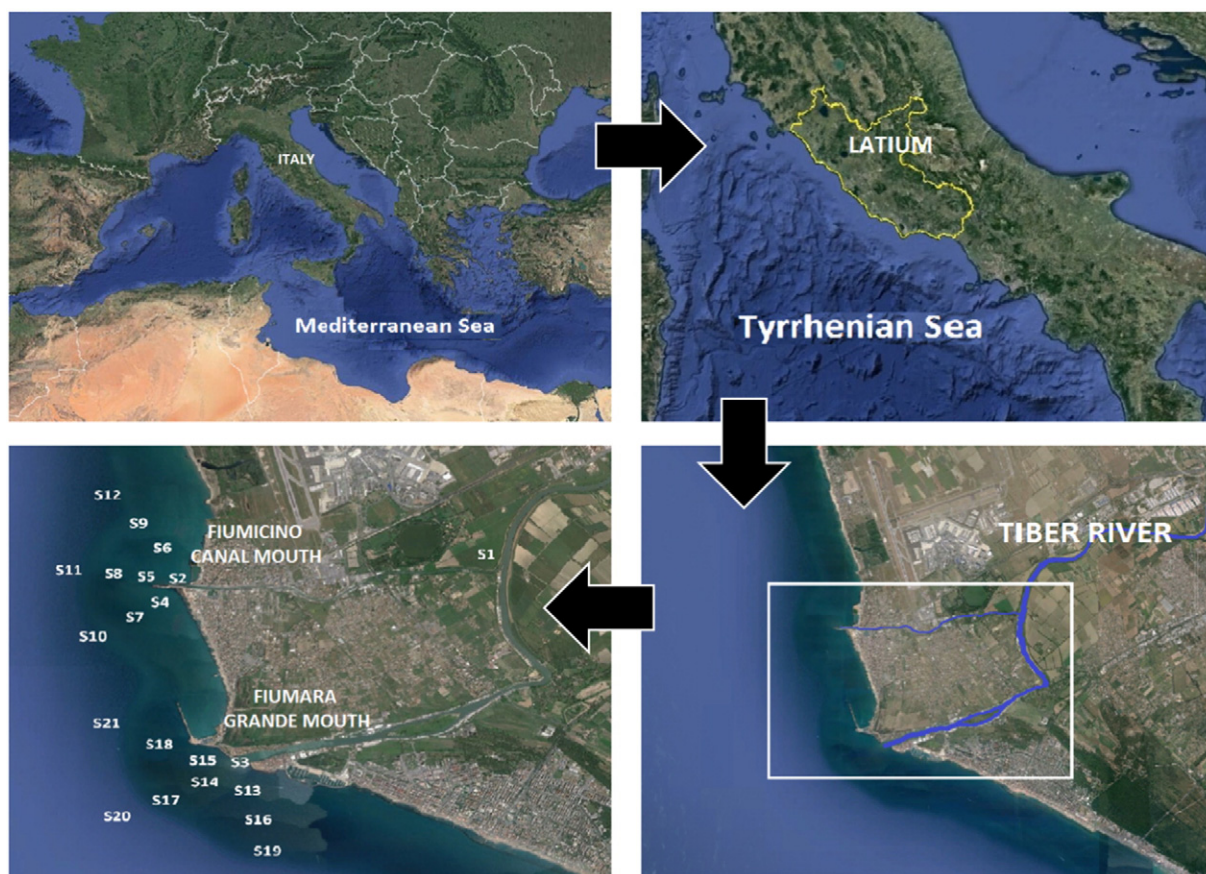


Fig. 1. Map of the study areas and sampling sites in the Tiber River and Estuary, Central Italy.
Source: Google Earth.

passing through the filter) were kept in the dark at 4 °C and extracted within the same day of sampling (3–6 h from sampling). Filters were spiked for recovery calculations with 2 ng of a surrogate standard solution, PCB 65 (2,3,5,6-tetrachlorobiphenyl) and PCB 166 (2,3,4,4,5,6-hexachlorobiphenyl). Spiked filters were extracted three times by sonication with 10 mL of dichloromethane/methanol (1:1 v/v) (Carlo Erba, Milano, Italy) for 15 min. The 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 OCPs and PCBs were eluted with 5.5 mL of hexane (Merck) in fraction I and 6 mL of hexane/ethyl acetate (9:1 v/v) (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 (Montuori et al., 2014). The two surrogate standards (PCB 65 and PCB 166) were eluted in fraction I.

The dissolved phase (DP) was spiked with a surrogate solution of PCB 65 (2,3,5,6-tetrachlorobiphenyl) and PCB 166 (2,3,4,4,5,6-hexachlorobiphenyl), achieving a final concentration in water of 5 ng L⁻¹. Two liters 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 v/v), the extract was rotaevaporated to roughly 0.5 mL. The sample was fractionated using an alumina open column chromatography as indicated for the particulate phase (Montuori et al., 2014).

Wet sediment samples were weighed, dried for 24 h at 60 °C, cooled in a desiccator, and weighed again. Dry sediment samples were then ground with a mortar and sieved at 250 μm. Five-gram aliquots were spiked with the surrogate mixture (2 ng of PCB 65 and PCB 166) and

extracted three times by sonication using 15 mL of DCM/methanol (1:1 v/v) for 15 min. After centrifuging, the organic extract was concentrated and fractionated as the water samples (Montuori et al., 2014).

2.3. 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.

The analytes were identified by comparison of the retention times of the peaks detected in each replicate with the peaks obtained on the calibration curves. The quantification of the POPs was based on the area obtained for each analyte in the samples, according to the mass/area ratio obtained for the internal standard and on the response factor obtained from the calibration curve. Confirmatory analysis of selected PCBs and OCPs peaks was accomplished by GC/MS analysis (GC-MS 2010Plus Shimadzu), applied with a 50 m capillary column (Varian, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25 μm). The injector temperature was 250 °C. Helium was used as the carrier gas. The mass spectrometer was operated at an electron impact (EI) energy of 70 eV and the target compounds were monitored in the selected ion monitoring (SIM) mode. The standard solution of composite PCBs included 32 congeners (CBs 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) (C-SCA-06 PCB Congeners Mix #6; AccuStandard, Inc., CT 06513, USA). The calibration curve showed that R varied from 0.981 to 0.999. The mixed OCPs standard solution containing aldrin, α -BHC, β BHC, δ -BHC, γ -BHC (lindane), p,p'-DDD, p,p'-DDE, p,p'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide (isomer B) and methoxychlor (M-8080 Organochlorine Pesticides; AccuStandard, Inc., CT 06513, USA) ($r^2 > 0.97$). PCB 30 (2,4,6-trichlorobiphenyl) and PCB 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 concentrations 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 concentrations of following OCPs were measured: aldrin, α -BHC, β BHC, δ -BHC, γ -BHC (lindane), p,p'-DDD, p,p'-DDE, p,p'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide (isomer B) and methoxychlor.

2.4. Quality assurance and quality control

Recoveries were determined for all samples by spiking with surrogate standards prior to extraction. The surrogate averaged recoveries in the dissolved phase were $91.7 \pm 9.8\%$ for PCB 65 (2,3,5,6-tetrachlorobiphenyl) and $95.1 \pm 3.2\%$ for PCB 166 (2,3,4,4,5,6-hexachlorobiphenyl). In the SPM samples, recoveries were $89.2 \pm 6.1\%$ for PCB 65 and $91.1 \pm 6.8\%$ for PCB 166. Finally, in the sediment samples, the averaged recoveries were the following: $88.6 \pm 5.5\%$ for PCB 65 and $89.7 \pm 3.9\%$ for PCB 166. Resulting data for PCB and OCPs were corrected for surrogate recoveries. Laboratory blanks were under quantitation limits for all compounds. The limit of detection (LOD) and limit of quantification (LOQ) were calculated as having signal-to-noise ratios of above 3 and 10, respectively, by five replicate analyses. In the dissolved phase, LODs ranged from 0.004 to 0.110 ng L⁻¹ for individual PCBs and OCPs; while, in SPM and sediment samples, from 0.005 to 0.044 ng L⁻¹ and from 0.0002 to 0.0044 ng g⁻¹ respectively. The quantification limits (LOQ) was in the range of 0.008 ng L⁻¹–0.15 ng L⁻¹ in dissolved water samples, 0.01–0.09 ng L⁻¹ in SPM samples and 0.008 to 0.09 ng g⁻¹ in sediment samples.

2.5. 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 was presented as the mean \pm 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). Q_T represents the total river discharge for the period considered (August 2014–May 2015), calculated by adding the monthly

averaged water flow. River flow data was collected from the register of the Autorità di Bacino del Tevere to <http://www.abtevere.it> (Lazio Government for the Environment). Furthermore, to study the temporal contaminant discharge variation, C_i and Q_i were considered for each campaign and expressed as kg year⁻¹.

2.6. Calculation of toxicity equivalent (TEQ) of dioxin-like PCBs

PCBs have a spatial structure that is similar to dioxins and furans and appear to pose similar risks to both animals and humans. Indeed, 12 PCB congeners (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) can be defined as dioxin-like-PCBs (DL-PCBs) and are generally considered to have potentially negative health effects (Zhang et al., 2013; He et al., 2016). Therefore, the toxicity equivalent (TEQ), established by the World Health Organization Van den Berg et al. (2006), was an estimate of the toxicity levels of dioxin-like PCBs (DL-PCBs), where each DL-PCB congener has a toxicity equivalence factor (TEF). The procedure involves assigning individual TEFs to dioxin-like PCB congeners in terms of their relative toxicity to 2,3,7,8-TCDD. 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 total toxic equivalent for PCBs ($\sum \text{TEQ}_{\text{PCB}}$) was calculated using the measured DL-PCB concentrations in sediment samples and WHO 2005 TEF values for human and mammals (Van den Berg et al., 2006). The calculation was carried out using:

$$\sum \text{TEQ}_{\text{PCB}} = \sum C_i \times \text{TEF}_i$$

where C_i was the concentration (nanograms per gram) of DL-PCBs. The TEQ_{PCB} 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 (Zhang et al., 2013).

3. Results and discussion

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

Table 1 shows that total PCB levels, defined as the sum of 32 individual congener concentrations, in the DP ranged from 0.19 ng L⁻¹ (site 20) to 6.82 ng L⁻¹ (site 1) with a mean value of 2.03 ± 1.62 ng L⁻¹. The compositional profiles of PCBs in the dissolved phase are illustrated in Fig. 2a, which indicates that tetra- and penta-CBs were abundant in all sampling sites, accounting for 39% and 29% of \sum PCBs, respectively. The proportion of less chlorinated CB (di- + tri-CBs) accounted for 18% of total PCBs, probably due to inputs into the river by atmospheric deposition, directly or followed by runoff. In fact, these congeners exhibit higher mobility in the atmosphere and aquatic environment (Gao et al., 2013; Men et al., 2014). Among congeners, PCB 28 dominated with 11.4% of the total PCB followed by PCB 66 (9.6%) and PCB 60 (8.8%). From the eight DL-PCBs studied, PCB 77 was the dominant, accounting for 3.4% of total PCB concentrations; following by PCB 118 (3.1%).

In the SPM, the PCB concentrations (as the sum of 32 kinds of PCBs) on dry weight (dw) ranged from 0.18 ng L⁻¹ (7.02 ng g⁻¹) in site 20 to 73.28 ng L⁻¹ (190.77 ng g⁻¹) in site 1 (mean value of 10.98 \pm 15.23 ng L⁻¹) (Table 1). The most abundant PCB congeners in SPM samples were PCB 180 and 189, accounting for 15% of the total PCBs. Hepta-, penta- and hexa-CBs were abundant in all sampling sites, accounting for 38, 21 and 20% of \sum PCBs, respectively (Fig. 2b). The proportion of hepta-CBs was increased probably because of the partitioning to the particulate matter due to their hydrophobicity (Yuan et al., 2015).

The total concentrations of 32 PCBs ($\sum_{32} \text{PCBs}$) in sediments are reported in Table 1. The results range from 3.73 ng g⁻¹ dw (site 20) to 79.30 ng g⁻¹ dw (site 1) with a mean value of 33.98 ± 21.96 ng g⁻¹ dw. Among individual PCB, in sediments two DL-PCBs (PCB 169 and

Table 1

Description of the sampling sites and concentrations of PCBs in the water dissolved phase (DP), suspended particulate matter (SPM) and sediments of the Tiber River and the continental shelf, Central Italy.

Sampling location			\sum PCBs								
Site number identification	Site characteristics	Site location	DP (ng L ⁻¹)				SPM (ng L ⁻¹) (ng g ⁻¹ dry wt.)				Sediment (ng g ⁻¹ dry wt.)
			May	Aug	Nov	Feb	May	Aug	Nov	Feb	May
1 (river water)	Upstream Tiber River fork	41°46'40.65"N 12°16'45.62"E	6.06	6.82	2.67	1.82	18.99 (37.44)	9.21 (22.54)	33.91 (384.29)	73.28 (190.77)	79.30
2 (river water)	Tiber River Mouth Fiumicino Canal	41°46'17.34"N 12°13'06.37"E	4.19	6.37	2.32	1.52	14.27 (31.51)	4.91 (12.49)	48.25 (475.06)	65.26 (119.04)	73.81
3 (river water)	Tiber River Mouth Fiumara Grande	41°44'24.50"N 12°13'58.73"E	4.21	5.72	2.05	1.53	10.32 (35.65)	3.38 (11.31)	33.03 (438.61)	48.47 (287.33)	62.06
4 (sea water)	River Mouth Fiumicino Canal at 500 m South	41°46'01.74"N 12°12'56.67"E	3.69	5.15	1.90	1.38	3.13 (18.31)	3.12 (14.91)	37.98 (704.09)	27.49 (293.85)	48.46
5 (sea water)	River Mouth Fiumicino Canal at 500 m Central	41°46'17.84"N 12°12'44.76"E	3.45	4.75	1.73	1.34	1.39 (17.27)	1.38 (7.02)	20.28 (413.24)	11.82 (309.09)	47.43
6 (sea water)	River Mouth Fiumicino Canal at 500 m North	41°46'31.73"N 12°12'53.50"E	3.81	5.79	2.27	1.44	7.25 (20.04)	5.94 (67.74)	38.96 (504.09)	41.62 (617.63)	54.92
7 (sea water)	River Mouth Fiumicino Canal at 1000 m South	41°45'47.87"N 12°12'53.50"E	2.05	3.03	1.12	0.84	1.28 (29.20)	1.28 (13.87)	21.21 (348.66)	13.76 (502.21)	38.16
8 (sea water)	River Mouth Fiumicino Canal at 1000 m Central	41°46'17.30"N 12°12'20.34"E	2.76	4.42	1.42	1.42	1.03 (9.61)	1.12 (47.28)	10.31 (111.63)	6.60 (180.62)	19.42
9 (sea water)	River Mouth Fiumicino Canal at 1000 m North	41°46'46.51"N 12°12'41.74"E	2.93	4.21	1.60	1.08	3.10 (13.88)	2.11 (8.92)	28.98 (685.44)	20.99 (289.20)	37.03
10 (sea water)	River Mouth Fiumicino Canal at 1500 m South	41°45'33.77"N 12°12'40.43"E	1.20	1.97	0.73	0.47	1.55 (19.31)	1.53 (21.80)	5.07 (176.01)	2.07 (105.06)	16.84
11 (sea water)	River Mouth Fiumicino Canal at 1500 m Central	41°46'16.33"N 12°12'01.41"E	1.40	2.18	0.86	0.57	0.73 (0.99)	0.84 (7.94)	1.53 (45.27)	1.15 (13.96)	6.79
12 (sea water)	River Mouth Fiumicino Canal at 1500 m North	41°46'58.36"N 12°12'29.55"E	2.04	3.13	1.17	0.77	1.99 (19.28)	2.99 (14.84)	16.89 (246.19)	9.17 (262.15)	22.19
13 (sea water)	River Mouth Fiumara Grande at 500 m South	41°44'08.68"N 12°14'07.38"E	3.18	5.03	1.91	1.41	8.85 (26.22)	4.19 (75.13)	29.71 (240.17)	32.57 (694.07)	52.83
14 (sea water)	River Mouth Fiumara Grande at 500 m Central	41°44'14.43"N 12°13'40.05"E	2.37	3.31	1.23	0.90	1.31 (5.96)	1.03 (7.79)	10.93 (123.89)	6.90 (24.05)	17.07
15 (sea water)	River Mouth Fiumara Grande at 500 m North	41°44'27.27"N 12°13'36.50"E	2.69	3.83	1.44	1.10	1.84 (20.89)	1.08 (9.03)	8.39 (116.77)	22.16 (334.84)	30.21
16 (sea water)	River Mouth Fiumara Grande at 1000 m South	41°43'52.67"N 12°14'13.37"E	1.23	1.67	0.64	0.52	4.64 (27.86)	1.37 (3.55)	17.60 (254.41)	13.04 (234.08)	33.82
17 (sea water)	River Mouth Fiumara Grande at 1000 m Central	41°44'06.84"N 12°13'20.15"E	1.03	1.37	0.56	0.40	0.26 (0.38)	0.19 (2.86)	3.35 (57.00)	1.35 (52.55)	7.32
18 (sea water)	River Mouth Fiumara Grande at 1000 m North	41°44'28.80"N 12°13'12.00"E	1.17	1.45	0.53	0.48	0.84 (37.41)	0.73 (13.63)	5.38 (117.93)	5.99 (139.16)	26.91
19 (sea water)	River Mouth Fiumara Grande at 1500 m South	41°43'38.09"N 12°14'18.04"E	0.65	0.85	0.35	0.26	0.49 (9.40)	0.51 (11.50)	3.15 (139.56)	6.86 (88.05)	25.10
20 (sea water)	River Mouth Fiumara Grande at 1500 m Central	41°43'59.84"N 12°13'01.01"E	0.44	0.56	0.41	0.19	0.18 (7.02)	0.16 (2.18)	0.69 (8.32)	0.47 (19.05)	3.73
21 (sea water)	River Mouth Fiumara Grande at 1500 m North	41°44'32.41"N 12°12'52.76"E	0.62	0.84	0.32	0.25	0.24 (6.58)	0.14 (2.44)	0.52 (14.33)	3.08 (74.03)	10.21

PCB 114) were dominant with 16.2% and 9.7% of total PCBs, respectively. Penta- and epta-CBs were abundant in sediments at each site, accounting, respectively, for 28 and 34% of \sum PCBs (Fig. 2c). The proportion of di- + tri-CBs decrease in sediment samples (1%) compared to SPM (6%) and DP (18%) samples. A possible explanation is that higher chlorinated PCBs could accumulate in the sediment due to their low water solubility, degradation and vapor pressure. Indeed, their water solubility and biodegradability decreases with an increase of number of chlorine atoms and, consequently, the higher chlorinated PCBs are more likely to be associated with the sediment or particulate adsorption phase than the lower chlorinated PCBs (Omar and Mahmoud, in press).

The concentrations of total PCBs in DP, SPM and sediment samples of the Tiber River and Estuary (Table 1, Fig. 2) show that 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 compared to that in the corresponding waterbodies (DP and SPM samples) was > 1 in most sampling sites and for all seasons. Moreover, the high chlorinated congener (hexa- and hepta-CB) concentrations decrease from sediment samples to SPMs and more to DPs (Fig. 2), while less chlorinated PCBs (di- + tri-CBs) showed a reverse trend with an increase of concentrations from sediment samples to SPMs and more to DPs. Globally, the PCBs

compositional pattern in the Tiber River and its Estuary suggested that significant sources of these congeners were possibly from various industrial processes, including steel manufacturing (Syed et al., 2014). The Tiber River flows through large industrial cities in central Italy, with steel mills, chemical plants and paper mills; large agricultural areas and densely populated urban area. Indeed, even if PCBs are no longer produced and used in Italy, they are still contained in many industrial applications and household materials and they can reach surface waters in industrialized and urbanized areas (Bettinetti et al., 2011). As a consequence, the Tiber River receives various industrial wastewater, municipal effluents via direct disposal of huge amount of incompletely treated domestic sewage and pollutants produced by agriculture.

To understand the magnitude of PCBs contamination, the concentrations found in the Tiber River and Estuary were comparable with those from other rivers, estuaries and coasts in the world (Table 2). PCBs levels in samples from the Tiber River were similar to those found in the Chenab River, Pakistan (Mahmood et al., 2014; Eqani et al., 2015) and in Hangzhou Bay, China (Adeleye et al., 2016). The concentrations were higher than those presented in the Portuguese coast, by Ferreira et al. (2003), in the Morava River, Czech Republic (Kukučka et al., 2015), in the Adriatic Sea, Italy (Combi et al., 2016), in the Nador Lagoon,

Morocco (Giuliani et al., 2015) and in the Haizhou Bay, China (Zhang et al., 2014); but lower than those found along the coastlines of “Calanque National Park”, France (Syakti et al., 2013), in the Rhone River, France (Mourier et al., 2014), in the Po River, Italy (Viganò et al., 2015), in the Mar. Piccolo coast (Bellucci et al., 2016), in the Moscow River, Russia (Eremina et al., 2016) and in the Durance River and the Berre Lagoon, France (Kanzari et al., 2015) (Table 2).

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

The total OCPs concentration obtained in the DP ranged from 0.009 ng L⁻¹ (site 20) to 5.53 ng L⁻¹ (site 1) (mean value of 0.91 ±

1.17 ng L⁻¹) (Table 3). In detail (Fig. 3a), they ranged from 0.003 to 1.37 ng L⁻¹ (mean value of 0.21 ng L⁻¹) for hexachlorocyclohexanes (α -BHC, β -BHC, δ -BHC, γ -BHC), from 0.004 to 1.78 ng L⁻¹ for dichlorodiphenyltrichloroethane and its degradates (p,p'-DDD, p,p'-DDE, p,p'-DDT and methoxychlor) and from 0.001 to 2.42 ng L⁻¹ for cyclodienes (aldrin, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor and heptachlor epoxide). In DP samples, the HCHs/DDTs ratio was <1 at all sites (mean 0.83 ± 1.14; range 0.12–9.52), and the DDTs/cyclodiene ratio was >1 at most sites (mean 1.04 ± 0.88; range 0.06–5.41). The HCHs/cyclodiene ratio varied within a range of 0.08–2.92 (mean value of 0.66 ± 0.55).

In the SPM samples, the OCPs concentrations ranged from 0.04 ng L⁻¹ (1.10 ng g⁻¹ dw) in site 21 to 4.71 ng L⁻¹ (12.27 ng g⁻¹

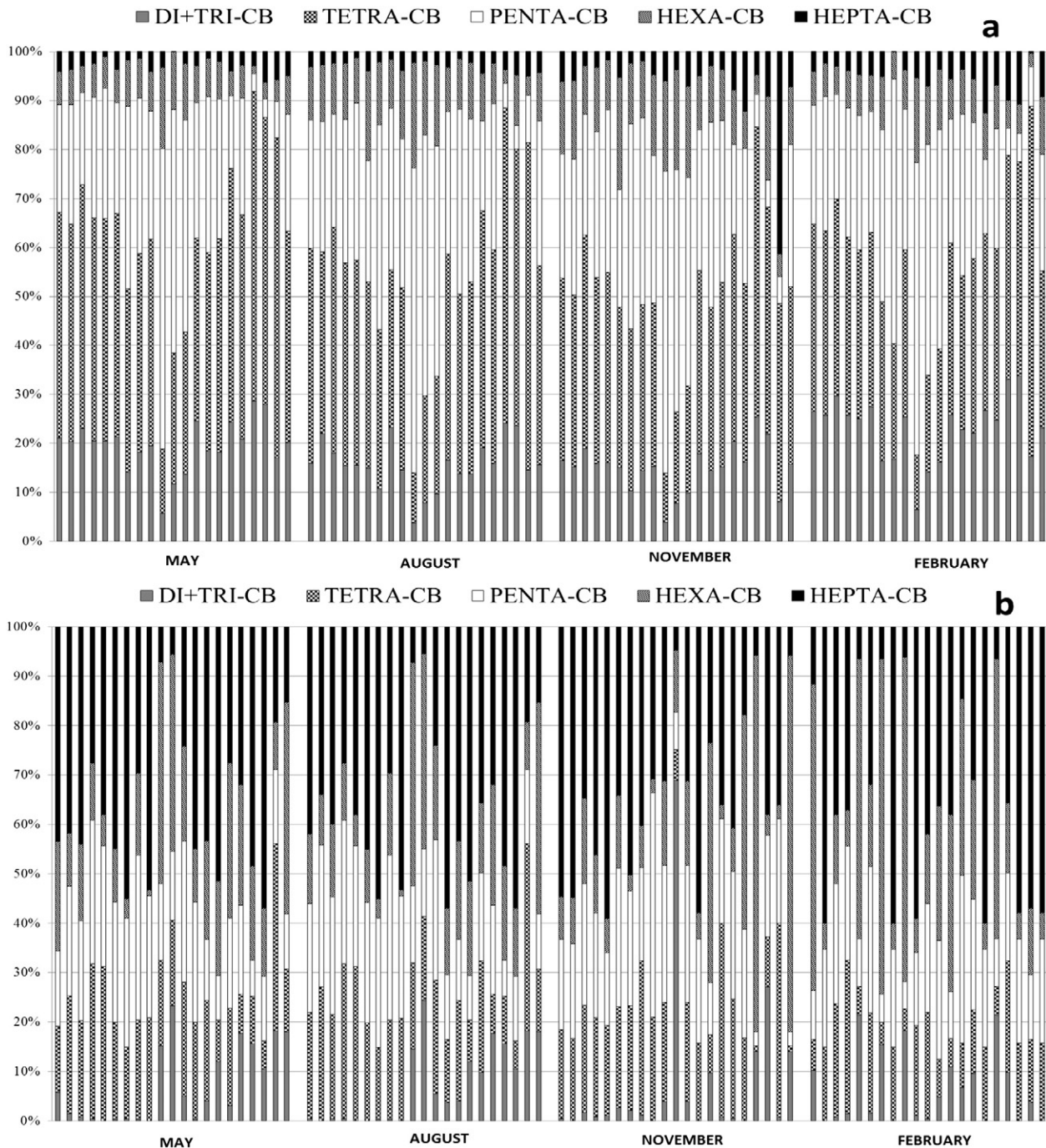


Fig. 2. Composition pattern of total PCBs in water dissolved phase (DP; a), the suspended particulate matter (SPM; b) and sediments (c) of the Tiber River and the continental shelf, Central Italy.

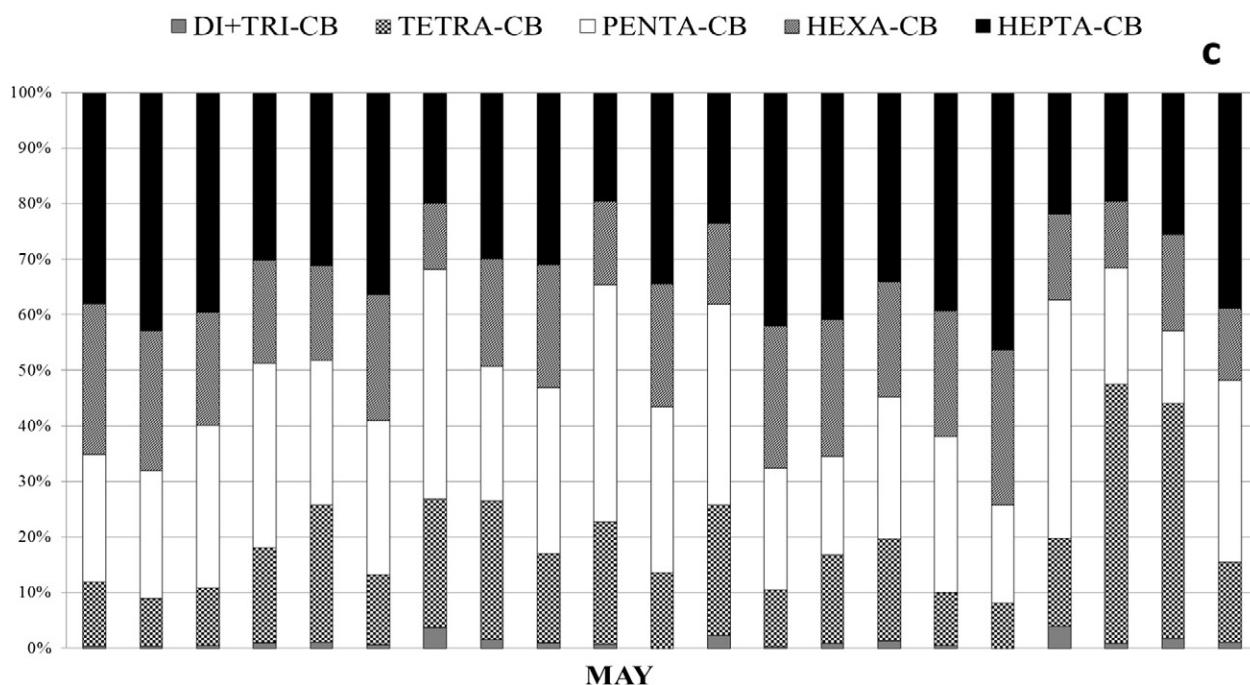


Fig. 2 (continued).

dw) in site 1 (mean $0.78 \pm 0.87 \text{ ng L}^{-1}$) (Table 3). The HCHs ranged from 0.014 to 1.20 ng L^{-1} (mean 0.23 ng L^{-1}), the DDTs from 0.003 to 1.95 ng L^{-1} and the cyclodienes from 0.008 to 1.55 ng L^{-1} (Fig. 3b). The HCHs/DDTs ratio was >1 at most sites with an average of 2.23, such as the HCHs/cyclodienes and DDTs/cyclodienes ratios (mean 1.24 and 1.04, respectively). On the contrary to results in the DP samples, the SPM samples contain prevailing concentrations of the HCHs than the DDTs and cyclodienes.

The total OCPs concentration in sediments (Table 3) ranged from $0.66 \text{ ng g}^{-1} \text{ dw}$ (site 11) to $10.02 \text{ ng g}^{-1} \text{ dw}$ (site 1) (mean value of $3.26 \pm 2.52 \text{ ng g}^{-1} \text{ dw}$). The HCHs ranged from 0.07 to $1.71 \text{ ng g}^{-1} \text{ dw}$ (mean 0.49 ng g^{-1}), the DDTs from 0.28 to $3.86 \text{ ng g}^{-1} \text{ dw}$ and the cyclodienes from 0.18 to $4.45 \text{ ng g}^{-1} \text{ dw}$ (Fig. 3c). The DDTs concentrations prevailed than those of cyclodienes and HCHs. In fact, the DDTs/cyclodienes ratio was >1 at most sites (mean 1.72), while the HCHs/DDTs and HCHs/cyclodienes ratios (means 0.28 and 0.43, respectively).

Compared with other polluted rivers in the world (Table 2), OCPs in samples from the Tiber River were close to those found in the Arc River, France (Kanzari et al., 2012), in the Yangtze River, China (Lin et al., 2015) and in the Izmir Bay, Turkey, by Pazi et al. (2011). The concentrations were much higher than those presented in the Gulf of Batabanó, Cuba (Alonso-Hernández et al., 2015) and in the Durance River and Berre Lagoon, France (Kanzari et al., 2015); but lower than those found in the Portuguese coast, by Carvalho et al. (2009), in the Candarli Gulf, Turkey (Pazi et al., 2012), along the coastlines of “Calanque National Park”, France (Syakti et al., 2013), in the Po River, Italy (Viganò et al., 2015), in the Northern coast of Cyprus (Kucuksezgin et al., 2016), in the Moscow River, Russia (Eremina et al., 2016), in Egyptian Coast, by Barakat et al. (2013) and in the Jaguaribe River, Brazil (Oliveira et al., 2016).

The concentrations of DDTs in DP, SPM and sediment samples of the Tiber River and Estuary were higher than those of cyclodienes. Also DDTs concentrations in sediment and DP samples were higher than HCHs concentrations, but similar in the SPM samples. Therefore, DDTs and HCHs were the most dominant OCPs probably due to extensively use in agricultural and to a large amount of municipal waste (Syed et al., 2014; Wu et al., 2015a; Lin et al., 2016). In addition, the partition coefficients (K_p , defined as the ratio of the concentration of a chemical associated with SPM to that in the DP: $K_p = C_{\text{SPM}}/C_{\text{DP}}$) showed a

decreasing trend in the HCHs partitioning from sediments to SPM ($\text{HCHs}_{\text{SPM}}/\text{HCHs}_{\text{Sediment}}$ mean value of 0.58 ± 0.34 ; range 0.13–1.30) and from SPMs to DPs ($\text{HCHs}_{\text{SPM}}/\text{HCHs}_{\text{DP}}$ mean value of 3.53). Regarding the DDTs, the partition coefficients showed a decreasing trend in the DDTs concentrations from sediments to SPMs ($\text{DDTs}_{\text{SPM}}/\text{DDTs}_{\text{Sediment}}$ mean value of 0.09 ± 0.08 ; range 0.01–0.26) and from SPMs to DPs ($\text{DDTs}_{\text{SPM}}/\text{DDTs}_{\text{DP}}$ mean value of 2.16). Also, the concentrations of cyclodienes in DP, SPM and sediment samples showed a decreasing trend from sediments to SPMs and DPs ($\text{cyclodienes}_{\text{SPM}}/\text{cyclodienes}_{\text{Sediment}}$ and $\text{cyclodienes}_{\text{SPM}}/\text{cyclodienes}_{\text{DP}}$ ratio mean values of 0.17 and 2.20, respectively). These results show that higher levels of OCPs were found in sediment samples than in DP and SPM samples (Fig. 3), which are an indication of no fresh inputs of these pesticides in the Tiber.

In detail, with regard the compositions of HCHs (Fig. S1 in the Supplementary material), the dominance of γ -HCH in the water samples suggest that lindane was recently used in the Tiber River Basin; while the high β -HCH concentrations in sediments samples were mainly derived from historical large agricultural use. Indeed, β -HCH was the most stable of the HCH isomers due to its high resistant to microbial degradation and because α -HCH and γ -HCH could be transformed into β -HCH in the environment (Carvalho et al., 2009; Kanzari et al., 2012; Li et al., 2016).

Regarding DDT, in the riverine ecosystem the biodegradation into its metabolites cannot be neglected. DDT biodegraded into DDE under aerobic conditions via dehydrochlorination and oxidation process, and into DDD involving reductive dechlorination under anaerobic conditions (Syed et al., 2014). In the Tiber ecosystem, the prevalence of DDE over DDD suggest that DDT were degraded to DDE under aerobic conditions (Wu et al., 2015a, in press; Oliveira et al., 2016). According to previous studies, the $(\text{DDD} + \text{DDE})/\text{DDT}$ ratio can be used to examine if the DDT input was old or recent (Mohammed et al., 2011; Li et al., 2016). A ratio of 0.5 suggested aged use and a ratio of <0.5 indicated fresh input. The mean values of $(\text{DDD} + \text{DDE})/\text{DDT}$ ratio in DP, SPM and sediment samples of the Tiber River and its estuary were 5.76, 3.75 and 4.32, respectively. These results suggest that most of the DDTs in the Tiber River and Estuary were derived from historical discharge, due to their capability to remain in the agricultural soil for a long time and re-mobilize through evaporation and runoff (Miglioranza et al., 2013;

Table 2
Concentration ranges and mean value of PCBs and OCPs in water, suspended particulate matter (SPM) and sediments from recent studies of different rivers, estuaries and coasts in the world.

Area	References	No.	DP (ng L ⁻¹)		SPM (ng L ⁻¹)		Sediments (ng g ⁻¹)	
			Range	Mean	Range	Mean	Range	Mean
<i>PCBs</i>								
<i>Asia</i>								
Tokyo Bay, Japan	Kobayashi et al. (2010)	209	0.04–0.64	0.096	0.05–0.58	0.15	2.7–110	39.0
Yangtze Estuary, China	Gao et al. (2013)	28					1.86–148.22	24.85
Chenab River, Pakistan	Mahmood et al. (2014)	32	0.21–27.5	5.72			0.83–59.4	13.9
Ravi River, Pakistan	Syed et al. (2014)	31					4.6–424.3	49.0
Bohai Sea, China	Men et al. (2014)	41	5.51–40.28	16.91	6.78–66.55	21.81	0.83–7.29	1.77
Chao River, China	Yu et al. (2014)	12					0.004–0.036	
Haizhou Bay, China	Zhang et al. (2014)	22					1.33–6.27	4.0
Shuangtaizi Estuary, China	Yuan et al. (2015)	28					1.83–36.68	10.53
Chaohu Lake, China	He et al. (2016)	34					0.007–3.99	0.67
Chenab River, Pakistan	Eqani et al. (2015)	7	1.1–8.5	2.8				
Yellow River, China	Gao et al. (2015)	12					0.001–0.010	0.0025
Hangzhou Bay, China	Adeleye et al. (2016)	9					0.60–63.00	
<i>Africa</i>								
Congo River Basin, Congo	Verhaert et al. (2013)	33					ND–1.4	
Congo River Basin, Congo	Mwanamoki et al. (2014)	12					0.07–0.99	
Umgeni River, South Africa	Gakuba et al. (2015)	8	6.91–21.69				102.60–427.80	
<i>America</i>								
Sea Lots, Trinidad and Tobago	Mohammed et al. (2011)	136					62.0–601.0	
Panama Canal and California Coast, USA.	Menzies et al. (2013)	19	ND–18,450.0	1164.0				
Midway Atoll, Hawaii	Ge et al. (2013)	28					2.6–148.8	50.7
Bedford Harbor, USA	Subedi et al. (2014)	136					2800.0–109,000.0	
Chicago Ship Canal, USA	Peverly et al. (2015)	209					69.0–5000.0	
<i>Europe</i>								
Portuguese coast, Portugal	Ferreira et al. (2003)	17			4.2–30.1			
Portuguese Coastal area, Portugal	Carvalho et al. (2009)	7					0.3–466.8	
Moscow River, Russia	Eremina et al. (2016)	9	ND–180.7					
<i>Mediterranean Sea</i>								
Tiber River Estuary, Italy	Puccetti and Leoni (1980)		9.0–1000.0	297.0			28.0–770.0	
Izmir Bay, Turkey	Pazi et al. (2011)	20					0.21–31.95	
Calanque National Park coastlines, France	Syakti et al. (2013)	7					9.1–226.9	84.3
Egyptian Coast, Egypt	Barakat et al. (2013)	96					2.29–377.0	32.2
Rhone River, France	Mourier et al. (2014)	7					11.5–417.1	
Huveaune River, France	Kanzari et al. (2014)	7					2.8–435.0	148.0
Nador Lagoon, Morocco	Giuliani et al. (2015)	127					2.50–20.7	9.17
Tripoli Harbor, Lebanon	Merhaby et al. (2015)	28					17.81–301.95	
Morava River, Czech Republic	Kukučka et al. (2015)	12					0.17–0.98	
Durance River and Berre Lagoon, France	Kanzari et al. (2015)	7					0.03–514.4	
River Po, Italy	Viganò et al. (2015)	14					48.6–335.0	
Adriatic Sea, Italy	Combi et al. (2016)	28					ND–9.0	
Mar Piccolo coast, Italy	Bellucci et al. (2016)	32					82.9–1045.0	
<i>This study</i>		32	0.19–6.82	2.03	0.18–73.28	10.98	3.73–79.30	33.98
<i>OCPs</i>								
<i>Asia</i>								
Yangtze River, China	Zhou et al. (2014)	12					0.17–5.0	2.09
Yangtze River, China	Li et al. (2014)	19					0.4–82.1	
Chao River, China	Yu et al. (2014)	24					0.81–16.85	
Huaihe River, China	Meng et al. (2014)	6					1.48–32.65	9.60
Shuangtaizi Estuary, China	Yuan et al. (2015)	18					0.02–14.57	5.65
Pearl River Delta, China	Huang et al. (2015)	8	14.8–87.8					
Yangtze River, China	Lin et al. (2015)	8	0.31–1.63	0.92				
Jiulong River, China	Wu et al. (in press)	25	39.3–94.4	60.0				
Poyang Lake, China	Zhi et al. (2015)	20	20.65–115					
Hangzhou Bay, China	Adeleye et al. (2016)	8					0.60–24.50	
Hangzhou Bay, China	Li et al. (2016)	10	1.35–26.36	9.39	2.52–27.99			
<i>Africa</i>								
Congo River Basin, Congo	Mwanamoki et al. (2014)	5					0.61–3.33	
<i>America</i>								
Sea Lots, Trinidad and Tobago	Mohammed et al. (2011)	29					44.5–145.0	
Gulf of Batabanó, Cuba	Alonso-Hernández et al. (2015)	5					0.029–0.374	
Jaguaribe River, Brazil	Oliveira et al. (2016)	8					5.09–154.43	
<i>Europe</i>								
Portuguese Coastal area, Portugal	Carvalho et al. (2009)	12					0.08–26.0	
Arc River, France	Kanzari et al. (2012)	15					0.02–7.15	
Moscow River, Russia	Eremina et al. (2016)	11	ND–51.1					
<i>Mediterranean Sea</i>								
Izmir Bay, Turkey	Pazi et al. (2011)	9					0.12–11.35	
Candarli Gulf, Turkey	Pazi et al. (2012)	9					10.2–57.3	34.0
Calanque National Park coastlines, France	Syakti et al. (2013)	18					1.2–190.6	
Egyptian Coast, Egypt	Barakat et al. (2013)	14					0.27–83.4	
Durance River and Berre Lagoon, France	Kanzari et al. (2015)	11					0.07–2.11	

Table 2 (continued)

Area	References	No.	DP (ng L ⁻¹)		SPM (ng L ⁻¹)		Sediments (ng g ⁻¹)	
			Range	Mean	Range	Mean	Range	Mean
River Po. Italy	Viganò et al. (2015)	6					7.5–68.2	
Northern coast of Cyprus	Kucuksezgin et al. (2016)	9					2.78–306.4	50.8
This study		17	0.009–5.53	0.91	0.04–4.71	0.78	0.66–10.02	3.26

ND: not detectable.

Wu et al., in press). Although the agricultural use of DDT in Italy was stopped in 1978, it is estimated that Italy was one of the ten largest purchasers of DDTs in the world, with an use in agricultural of approximately 4.6×10^5 tons (Li and Macdonald, 2005). Also in the field of public health, DDT was widely used for eradicating Italian malaria-vector species (*Anopheles labranchiae*) in the Tiber River Delta (Soper et al., 1947).

Among the other OCPs analyzed, endosulfan II was the most detected OCP in the Tiber water, while heptachlor epoxide in sediment samples (Fig. S2 in the Supplementary material). Endosulfan was a mixture of two diastereoisomers (endosulfan I and endosulfan II) present in different ratio in the technical mixture (Karadeniz and

Yenisoy-Karakaş, 2015). Endosulfan I could be degraded more rapidly than endosulfan II, thus the higher concentration of endosulfan II suggested that there was no new input of endosulfan in recent years. In addition, the two isomers could be converted to endosulfan sulfate by oxidative degradation. In this study, this compound was the dominant fraction of endosulfan in the sediment samples, that could originate from its parent isomers, indicating historical use of the pesticide (Miglioranza et al., 2013). Regarding heptachlor, that has generally been used as insecticides in agricultural and in urban (lawns, gardens, and termite/grasshopper control) settings; it has been metabolized to heptachlor epoxide by photolysis or epoxidation. The ratio of

Table 3

Description of the sampling sites and concentrations of OCPs in the water dissolved phase (DP), suspended particulate matter (SPM) and sediments of the Tiber River and the continental shelf, Central Italy.

Sampling location			Σ OCPs								
Site number identification	Site characteristics	Site location	DP (ng L ⁻¹)				SPM (ng L ⁻¹) (ng g ⁻¹ dry wt.)				Sediment (ng g ⁻¹ dry wt.)
			May	Aug	Nov	Feb	May	Aug	Nov	Feb	May
1 (river water)	Upstream Tiber River fork	41°46'40.65"N 12°16'45.62"E	4.54	5.53	3.43	1.11	2.49 (4.91)	1.24 (3.02)	3.46 (39.23)	4.71 (12.27)	10.02
2 (river water)	Tiber River Mouth Fiumicino Canal	41°46'17.34"N 12°13'06.37"E	3.68	2.93	2.22	0.40	1.45 (3.19)	0.56 (1.45)	2.02 (19.86)	3.22 (5.87)	8.14
3 (river water)	Tiber River Mouth Fiumara Grande	41°44'24.50"N 12°13'58.73"E	2.70	2.40	1.00	0.59	0.92 (3.19)	0.48 (1.60)	0.89 (11.91)	1.99 (11.80)	5.68
4 (sea water)	River Mouth Fiumicino Canal at 500 m South	41°46'01.74"N 12°12'56.67"E	1.20	1.38	0.69	0.35	0.98 (5.75)	0.40 (1.90)	0.93 (17.34)	1.45 (15.47)	3.25
5 (sea water)	River Mouth Fiumicino Canal at 500 m Central	41°46'17.84"N 12°12'44.76"E	0.88	1.16	0.56	0.18	0.40 (4.93)	0.27 (1.38)	0.88 (18.04)	1.17 (30.71)	2.52
6 (sea water)	River Mouth Fiumicino Canal at 500 m North	41°46'31.73"N 12°12'53.50"E	3.58	4.46	2.32	1.43	1.48 (4.09)	0.99 (11.29)	2.04 (26.35)	3.15 (46.74)	6.33
7 (sea water)	River Mouth Fiumicino Canal at 1000 m South	41°45'47.87"N 12°12'53.50"E	0.56	0.78	0.28	0.14	0.34 (7.72)	0.25 (2.68)	0.75 (12.40)	1.91 (43.50)	2.38
8 (sea water)	River Mouth Fiumicino Canal at 1000 m Central	41°46'17.30"N 12°12'20.34"E	0.25	0.32	0.13	0.14	0.22 (2.05)	0.34 (15.59)	0.30 (3.30)	0.47 (12.78)	1.31
9 (sea water)	River Mouth Fiumicino Canal at 1000 m North	41°46'46.51"N 12°12'41.74"E	1.25	1.65	0.78	0.90	1.01 (4.52)	0.95 (2.72)	1.32 (31.42)	1.99 (27.55)	4.39
10 (sea water)	River Mouth Fiumicino Canal at 1500 m South	41°45'33.77"N 12°12'40.43"E	0.19	0.17	0.09	0.09	0.25 (3.15)	0.33 (4.69)	0.32 (11.04)	0.32 (16.07)	1.38
11 (sea water)	River Mouth Fiumicino Canal at 1500 m Central	41°46'16.33"N 12°12'01.41"E	0.06	0.10	0.04	0.09	0.12 (0.16)	0.17 (1.79)	0.13 (3.91)	0.14 (1.70)	0.66
12 (sea water)	River Mouth Fiumicino Canal at 1500 m North	41°46'58.36"N 12°12'29.55"E	0.39	0.45	0.21	0.15	0.50 (4.87)	0.22 (1.64)	0.51 (7.44)	0.67 (19.16)	1.86
13 (sea water)	River Mouth Fiumara Grande at 500 m South	41°44'08.68"N 12°14'07.38"E	1.93	2.62	1.52	0.82	1.09 (3.24)	0.70 (12.56)	1.69 (13.66)	2.16 (46.00)	5.00
14 (sea water)	River Mouth Fiumara Grande at 500 m Central	41°44'14.43"N 12°13'40.05"E	0.59	0.65	0.29	0.38	0.39 (1.78)	0.28 (1.70)	0.37 (4.19)	0.58 (2.04)	1.56
15 (sea water)	River Mouth Fiumara Grande at 500 m North	41°44'27.27"N 12°13'36.50"E	1.50	1.74	1.09	0.14	0.44 (5.04)	0.21 (1.02)	0.66 (9.21)	1.01 (15.22)	3.73
16 (sea water)	River Mouth Fiumara Grande at 1000 m South	41°43'52.67"N 12°14'13.37"E	0.59	0.69	0.46	0.41	0.42 (2.50)	0.32 (0.82)	0.49 (7.03)	0.72 (12.85)	2.89
17 (sea water)	River Mouth Fiumara Grande at 1000 m Central	41°44'06.84"N 12°13'20.15"E	0.12	0.16	0.05	0.09	0.07 (0.10)	0.09 (0.94)	0.14 (2.41)	0.21 (8.14)	1.11
18 (sea water)	River Mouth Fiumara Grande at 1000 m North	41°44'28.80"N 12°13'12.00"E	0.62	0.57	0.34	0.08	0.19 (8.62)	0.10 (1.71)	0.33 (7.28)	0.55 (12.85)	1.85
19 (sea water)	River Mouth Fiumara Grande at 1500 m South	41°43'38.09"N 12°14'18.04"E	0.22	0.24	0.08	0.12	0.16 (2.99)	0.17 (3.92)	0.20 (8.78)	0.40 (5.08)	2.17
20 (sea water)	River Mouth Fiumara Grande at 1500 m Central	41°43'59.84"N 12°13'01.01"E	0.02	0.03	0.01	0.01	0.07 (2.68)	0.13 (1.54)	0.06 (0.69)	0.13 (5.17)	0.71
21 (sea water)	River Mouth Fiumara Grande at 1500 m North	41°44'32.41"N 12°12'52.76"E	0.08	0.08	0.03	0.03	0.04 (1.10)	0.04 (0.46)	0.06 (1.74)	0.12 (2.99)	1.57

heptachlor/heptachlor epoxide in sediments samples of Tiber River and Estuary was generally lower than 1, indicating historical use (Parween et al., 2014). Instead aldrin was detected in lower concentrations at all locations compared to dieldrin, suggesting no fresh usage. Finally, the concentration of endrin was lower at many locations during all the seasons in relation to its degradation product endrin aldehyde. The content of endrin and its breakdown product endrin aldehyde was due to persistence and degradation of aldrin, dieldrin, and isodrin in the environment (Kuranchie-Mensah et al., 2012; Kanzari et al., 2015). Indeed, the mean value of aldrin/dieldrin and endrin/endrin aldehyde ratio in the Tiber waterbody is 0.44 and 0.90, respectively. The predominance of degradation compound also indicating historical use of these pollutants

in the area (Kuranchie-Mensah et al., 2012; Miglioranza et al., 2013; Montuori et al., 2014).

3.3. Spatial and seasonal distribution of PCBs and OCPs

The spatial distribution of PCBs and OCPs in DP, SPM and sediment samples from the Tiber River and its Estuary were studied by comparing the concentrations of \sum PCBs and \sum OCPs in different sampling sites in dry and rainy seasons, respectively. The results showed that the PCBs and OCPs contamination levels in the Tiber decrease from location 1 to 2 and 3 (Figs. 4 and 5). This decrease in total concentrations is due to the splitting of the river in its two mouths, before flowing into the

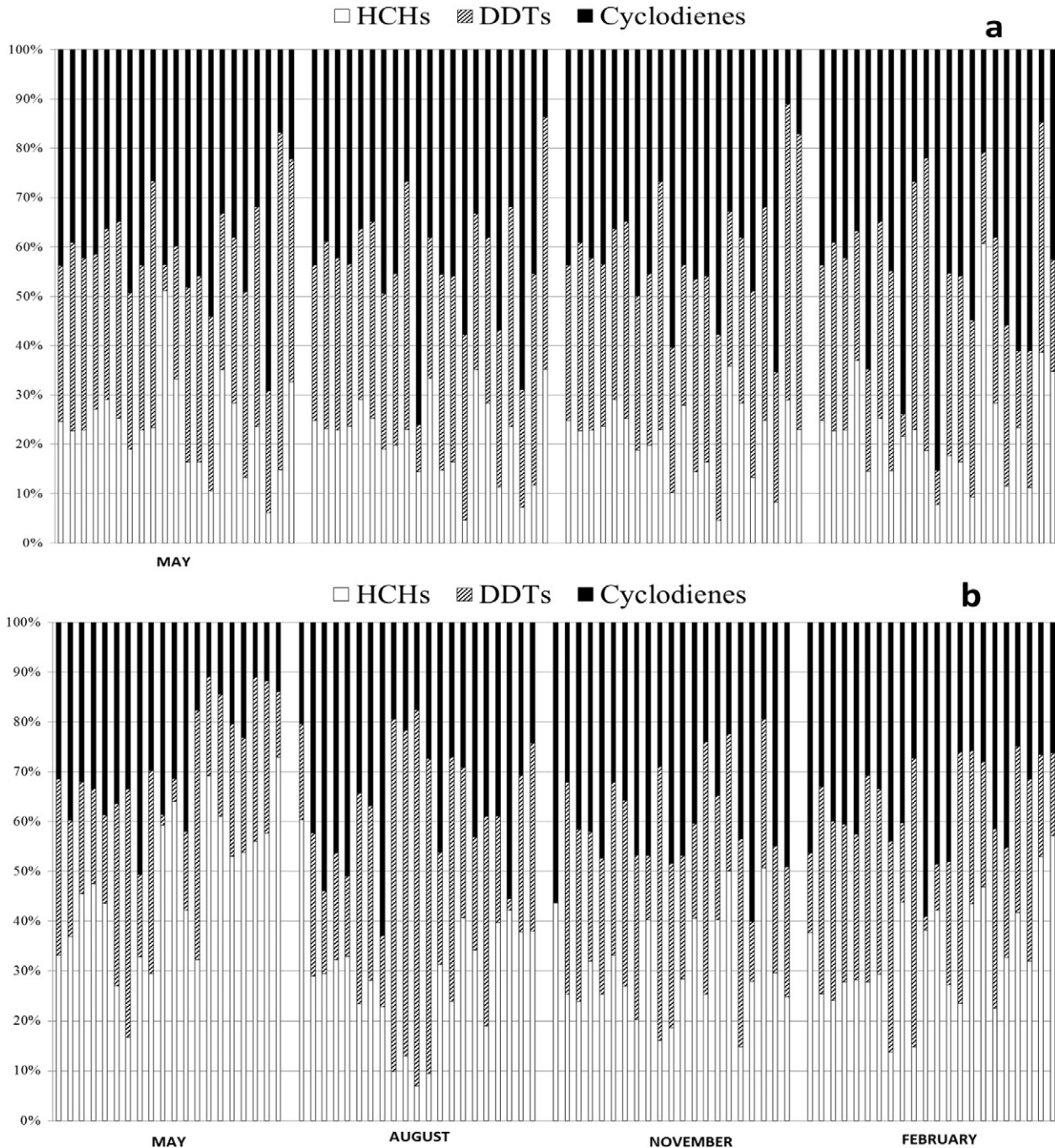


Fig. 3. Composition pattern of total OCPs in water dissolved phase (DP; a), the suspended particulate matter (SPM; b) and sediments (c) of the Tiber River and the continental shelf, Central Italy.

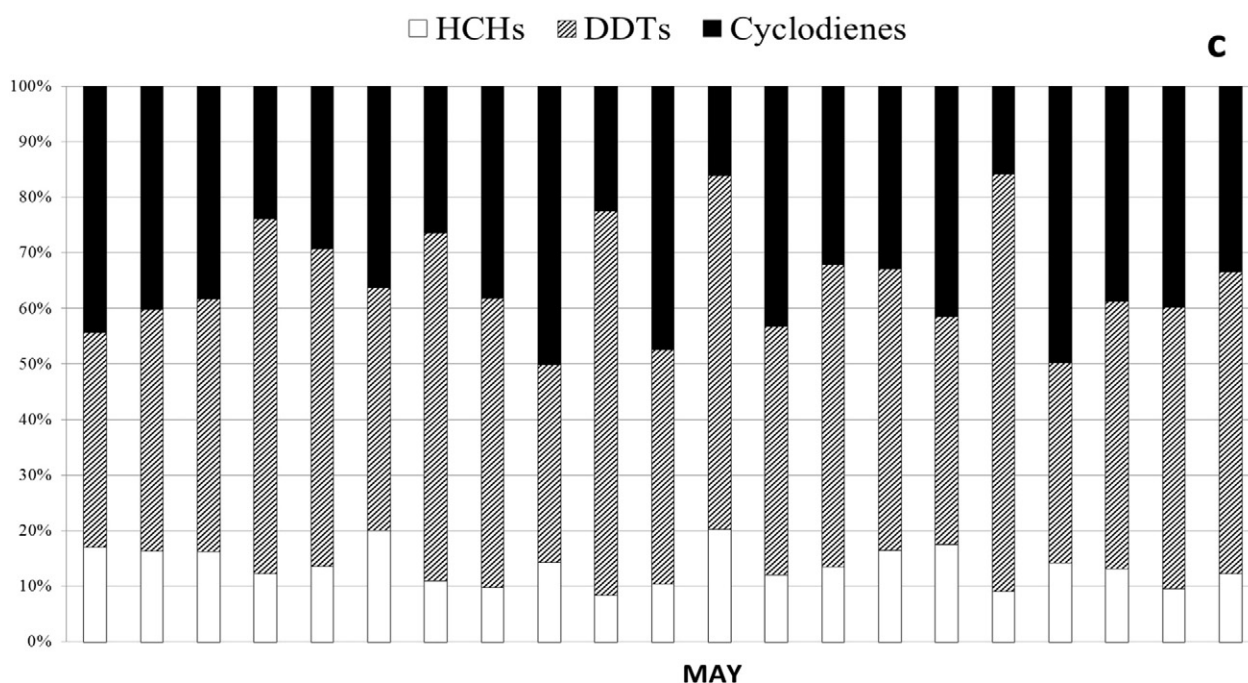


Fig. 3 (continued).

Tyrrhenian Sea. In detail, the total PCBs concentration decreased from 37.13 ng L^{-1} (DP + SPM mean values of four seasons) at site 1 to 36.08 ng L^{-1} (DP + SPM mean values of four seasons) at site 2 and to 26.53 ng L^{-1} (DP + SPM mean values of four seasons) at site 3; while OCPs concentrations decreased from 6.63 ng L^{-1} (DP + SPM mean values of four seasons) at site 1 to 4.12 ng L^{-1} (DP + SPM mean values of four seasons) at site 2 and to 2.74 ng L^{-1} (DP + SPM mean values of four seasons) at site 3. Moreover, the POPs pollution levels in the estuary and the adjacent coastal area gradually decreased from the vicinity of the river outflows to offshore areas (Figs. 4 and 5). The results suggest that these pollutants in the waterbodies were diluted as they were discharged from the river to the sea through the estuary. Particularly, at the Fiumicino mouth the contaminants loads move into the Tyrrhenian Sea northward (Figs. 4a and 5a). On the contrary, at the Fiumara Grande mouth the contaminants loads move into the Tyrrhenian Sea (Figs. 4b and 5b).

In order to estimate the huge input of PCBs and OCPs drained into the Tiber River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea), the total load of these pollutants was calculated. The total PCBs and OCPs loads contribution to the Tyrrhenian Sea from the Tiber River is calculated in about $227.08 \text{ kg year}^{-1}$ for PCBs and $24.91 \text{ kg year}^{-1}$ for OCPs. This high load of selected POPs was probably due to the re-suspension of sediment contaminated long ago (Bettinetti et al., 2011). In the DP samples, the total concentrations of POPs were significantly low especially during the wet season (February), owing to the hydrological conditions, which caused dilution effects owing to high-rainfall events. In contrast, in SPM samples the concentrations were lowest in all sampling sites during the dry season. These results were closely related to the flow variation, that decrease during the dry season and consequently cause a stagnation of SPM that determined the transfer of these pollutants from DP to SPM.

3.4. TEQs of dioxin-like PCBs

In this study, eight DL-PCBs (PCB 77, 105, 114, 118, 126, 156, 169, and 189) were identified in all sediment samples. In order to quantify the potential toxicity of DL-PCBs in sediment samples from the Tiber River and Estuary, the TEQ_{PCB} 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 31.5% of the total PCBs concentration. The $\sum \text{TEQ}_{\text{PCB}}$ from the sediment samples ranged from 0.0006 to 0.37 ng g^{-1} with an average level of 0.13 ng g^{-1} . The highest $\sum \text{TEQ}_{\text{PCB}}$ levels were found at site 1 (Fig. S3 in the Supplementary material). Although PCB-114 showed concentration higher than others PCB-DL, PCB-126 and PCB-169 contributed for 99.8% to TEQ_{PCB} , due to their higher TEF. The average level of $\sum \text{TEQ}_{\text{PCB}}$ found in sediment samples of the Tiber River and its Estuary was lower than in the sediments from Masan Bay, Korea (Moon et al., 2009); but was similar to those found in the sediments of Ravi River, Pakistan (Syed et al., 2014). The results showed that TEQ_{PCB} values of the Tiber River and its Estuary were in a medium level, suggesting that the toxicity of the PCBs in the water ecosystem could adversely affect the ecological environment and human health through biomagnification.

3.5. Evaluation of ecotoxicological risk

To assess the ecotoxicological risk of PCBs and OCPs in water samples from Tiber 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 (USEPA, 2010). 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 $\sum \text{PCBs}$ found in the water of the Tiber River and its Estuary were lower 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). According to the Directive 2008/105/EC 2008, we compared the concentrations found with European EQS in surface waters using the annual average of monthly whole water (DP + SPM) concentrations in order to assess OCP ecotoxicological risk. Our data showed that the mean concentrations of HCHs (0.44 ng L^{-1}) DDTs (0.61 ng L^{-1}) and \sum aldrin, dieldrin and endrin (0.22 ng L^{-1}) in the Tiber River and its Estuary were lower than the EQS value of 20.0 , 25.0 and 10.0 ng L^{-1} , respectively, showing that the ecological risk is low.

In order to estimate the ecological risk caused by PCBs and OCPs detected in the sediments from Tiber River and its Estuary, the sediment quality guidelines (SQGs) for aquatic environments have been used (Long et al., 1995; MacDonald et al., 1996). In particular, two sets of

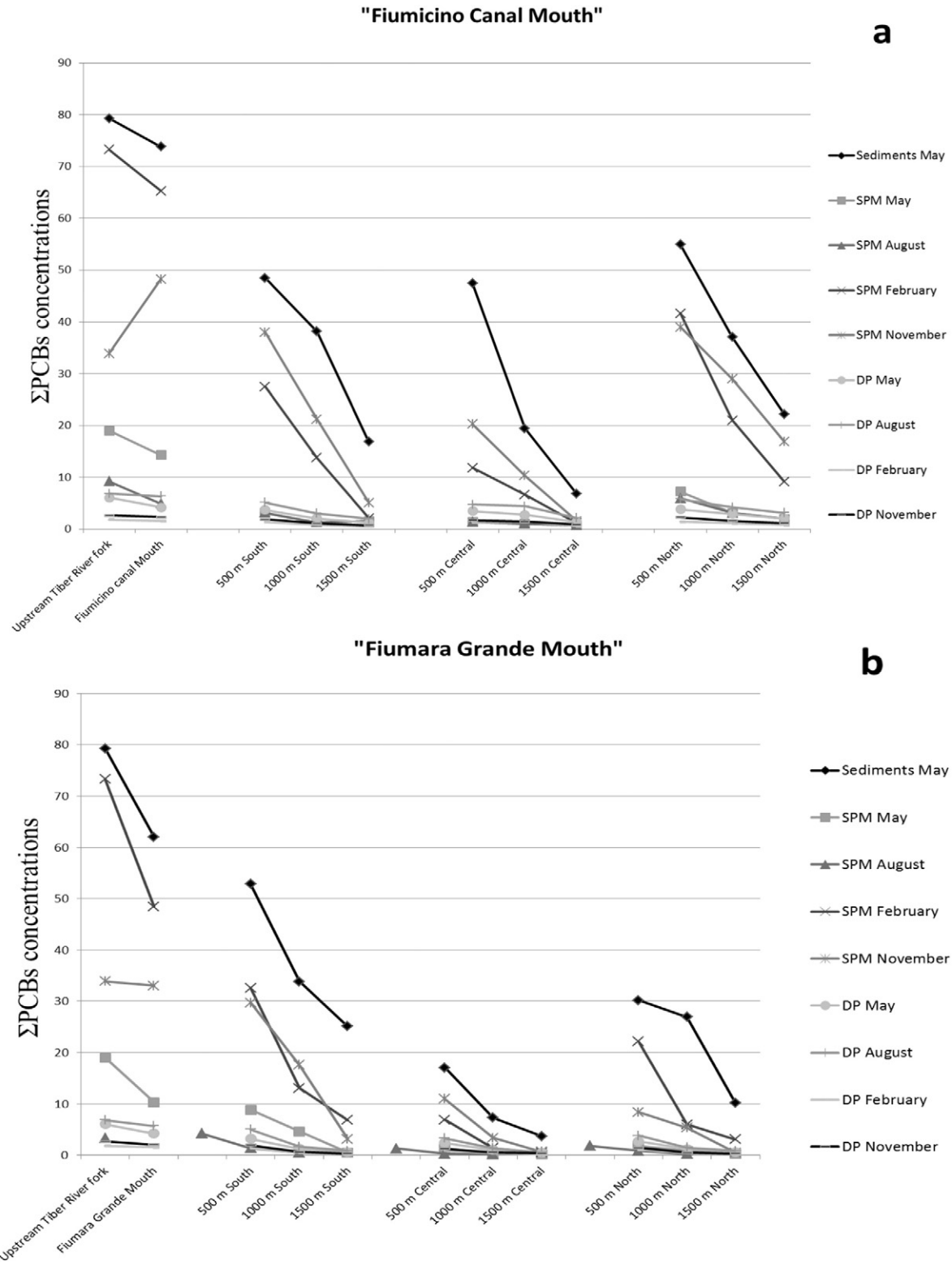


Fig. 4. Spatial and temporal concentration of PCBs in the water dissolved phase (DP, ng L^{-1}), suspended particulate matter (SPM, ng L^{-1}) and sediments (ng g^{-1} dry wt) in the Tiber River Estuary (Fiumicino Canal mouth, a; Fiumara Grande mouth, b).

SQGs were used: i) effect range low (ERL)/effect range median (ERM) and ii) the threshold effect level (TEL)/probable effect level (PEL). As reported in the Table 4, the SQGs refer only to Σ PCBs, γ -HCH (lindane), dieldrin, p,p'-DDD, p,p'-DDE, p,p'-DDT and Σ DDT.

In the Tiber River and its Estuary, the total PCB concentrations in sediment samples were significantly lower than PEL and ERM values (Table 4), while 66.7% and 61.9% of samples showed levels above TEL and ERL

values, respectively. These results indicated that certain sites showed PCBs levels that occasionally cause biological impairment, nevertheless the ecosystem risk of the Tiber River and Estuary was low.

Regarding the OCPs, all analyzed samples showed concentrations below PEL and ERM values; while only 4.8% of samples showed detected levels of lindane above the TEL values (Table 4). Regarding ERL value, a high percentage of samples (76.2%) showed levels above for dieldrin

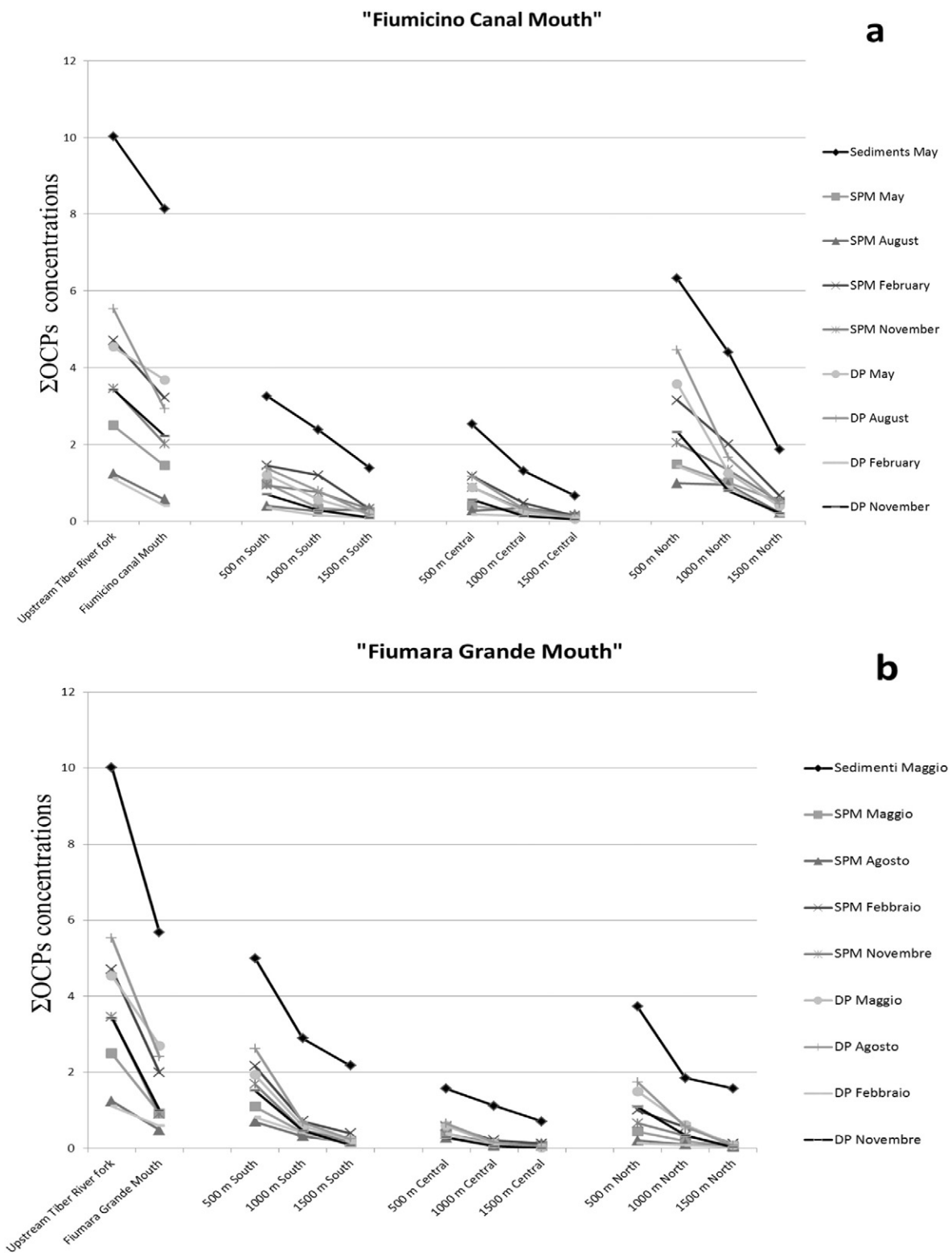


Fig. 5. Spatial and temporal concentration of OCPs in the water dissolved phase (DP, ng L^{-1}), suspended particulate matter (SPM, ng L^{-1}) and sediments (ng g^{-1} dry wt) in the Tiber River Estuary (Fiumicino Canal mouth, a; Fiumara Grande mouth, b).

and 33.3% of samples for total DDT, which indicate that adverse effects to the biota would rarely be observed.

4. Conclusions

This present paper is the first study on the evolution of trace PCBs and OCPs contamination level in the Tiber 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 compared to DP and SPM samples, suggesting no fresh inputs of these compounds. The ecotoxicological assessment showed that the concentrations of most PCBs and OCPs in the water and sediments from the Tiber River and its estuary were lower than guideline values, revealing that the ecosystem risk of the Tiber River and Estuary was

Table 4A comparison of the TEL, PEL, ERL and ERM guideline values ($\mu\text{g Kg}^{-1}$) for PCBs and OCPs and data found in the Tiber River and the continental shelf, Central Italy.

	TEL ^a	Sample percentage over the TEL	PEL ^a	Sample percentage over the PEL	ERL ^b	Sample percentage over the ERL	ERM ^b	Sample percentage over the ERM
PCBs								
Total PCBs	21.6	66.7	189	0	22.7	61.9	180	0
OCPs								
γ -HCH (lindane)	0.32	4.8	0.99	0	–	–	–	–
Dieldrin	0.72	0	4.3	0	0.02	76.2	8	0
4,4-DDD	1.22	0	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	0	7	0
Total DDT	3.89	0	51.7	0	1.58	33.3	46.1	0

^a MacDonald et al. (1996).^b Long et al. (1995).

low. A possible ecological risk about DL-PCBs contamination was pointed out by the toxic equivalent concentrations (TEQ_{PCB}). Therefore, the Tiber waters should be continuously monitored since POPs may still pose some risks to aquatic ecosystems.

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Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.07.089>.

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