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Estimates of Tiber River organophosphate pesticide loads to the Tyrrhenian Sea and ecological risk



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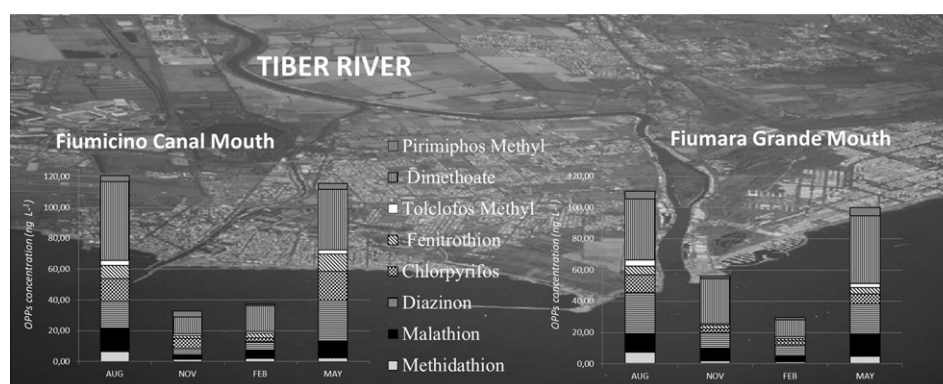
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HIGHLIGHTS

- Spatial and temporal distribution of 8 organophosphate pesticides in Tiber River and Estuary were assessed.
- Concentrations were seasonally highly variable.
- All organophosphate pesticides concentrations complied with the Environmental Quality Standards.
- No organophosphate pesticides presented a Risk Quotient higher than unit when using mean values.

GRAPHICAL ABSTRACT



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ABSTRACT

The organophosphate pesticides pollution in the Tiber River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea) were estimated. Eight selected organophosphate pesticides (diazinon, dimethoate, malathion, chlorpyrifos, pirimiphos-methyl, fenitrothion, methidathion, tolclofos-methyl) were determined in the water dissolved phase, suspended particulate matter and sediment samples collected from 21 sites in different seasons. Total organophosphate pesticides concentrations ranged from 0.40 to 224.48 ng L⁻¹ in water (as the sum of the water dissolved phase and suspended particulate matter) and from 1.42 to 68.46 ng g⁻¹ in sediment samples. Contaminant discharges of organophosphate pesticides into the sea were calculated in about 545.36 kg year⁻¹ showing that this river should be consider as one of the main contribution sources of organophosphate pesticides to the Tyrrhenian Sea. In relation to the eco-toxicological assessment, the concentrations of most OPPs in the water and sediments from the Tiber River and its estuary were lower than guideline values.

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1. Introduction

During the last decades organophosphate pesticides (OPPs) gained popularity worldwide compared to organochlorine pesticides.

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Organochlorine pesticides are persistent and damaging to the environment (Tankiewicz et al., 2011; Zheng et al., 2016; Yu et al., 2016), instead the OPPs break down more rapidly in the environment, have a milder impact and are safer and less persistent. It is estimated that OPPs are worth nearly 40% of the global market and that they are expected to maintain dominance for some time into the future. They are the most popular pesticides and their usage is still growing, mainly because of their low cost, reliability, wide spectrum of applications, multi-pest control capability and lack of pest resistance (Ma et al., 2009; Dujaković et al., 2010; Li et al., 2010; Sapbamrer and Hongsibsong, 2014).

The widespread application of the OPPs has been questioned as a potential risk to human health: they can influence body glucose homeostasis through several mechanisms including physiological stress, allergies and nausea, adverse physiologic effects, oxidative stress, inhibition of paraoxonase, nitrosative stress, pancreatitis, inhibition of cholinesterase, stimulation of the adrenal gland, and disturbance in the metabolism of liver tryptophan (Badrane et al., 2014). Other risks of organophosphate exposure include serious health consequences such as neurobehavioral and cognitive abnormalities, teratogenicity, endocrine modulation, immunotoxicity and compromised cognitive development especially for infants and children reproductive effects, spontaneous abortions, and fetal death. In fact the use of many organophosphate insecticides has been restricted by the Environmental Protection Agency (EPA) of the United States of America in order to prevent health risks (Wang et al., 2009; Epstein, 2014; Ophir et al., 2014; Yu et al., 2016).

As confirmed by numerous studies, the aquatic environment appears to be one of the primary locations for OPPs (Wang et al., 2009; González-Curbelo et al., 2013; Sangchan et al., 2014; Masiá et al., 2015). They are carried from terrestrial sources through various pathways, such as atmospheric and river transports. The input pathways of OPPs into aquatic environment include discharge of agricultural sewage, runoff from non-point sources, and direct dumping of wastes (Vryzas et al., 2009; Tankiewicz et al., 2010; Thomatou et al., 2013; Poulier et al., 2014; Mamta et al., 2015). OPPs represent nowadays the group of compound posing the highest risk for the ecosystem. They are source of contaminants to aquatic biota, because a large portion of the pesticides used in watersheds is rushed into river system and carried into the estuaries. Thus, the assessment of OPPs in aquatic environments is of primary importance as these areas could receive considerable amounts of pollutant inputs from land-based sources through coastal discharges, which could potentially threaten the biological resources (De Lorenzo et al., 2001; Poulier et al., 2014; Dzul-Caamal et al., 2014; Kuzmanović et al., 2015). Nevertheless, few studies evaluated the pollution from organophosphate pesticides in surface waters compared to organochlorine pesticides (Zulin et al., 2002; Fadaei et al., 2012; Assoumani et al., 2013).

Indeed, we chose the Tiber River, the second biggest river in Italy, and its estuary as a case for total OPP pollution and risk evaluation. The Tiber River is the most polluted river among the twenty longest river in Italy (Legambiente, 2006). The Tiber Valley, with a catchment area of 17,375 km², is one of the most fertile in Italy thanks to the high quality of the soil and Mediterranean climate. A large portion of the Tiber Valley is devoted to agricultural use which might result in water quality deterioration because of the input of pesticides and fertilizers. In an attempt to estimate the risk organisms and humans could face when exposed to pesticides, the ecological risk assessment of this river is carried out.

Ecological risk assessment is a technique applied to evaluate the undesirable impacts caused by the environmental pollutants in an ecological system; in particular, the Risk Quotient (RQ) is one general assessment approach to characterize ecological risk from OPPs in waters. RQ of selected pesticides is calculated using the ratio of the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) (Palma et al., 2014).

This study is part of a large project aimed at contributing to the knowledge of the pollution affecting the Tiber River and its environmental impact on the Tyrrhenian Sea. The purpose 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 data on the distribution pattern and potential impact of OPPs in Tiber River system and its estuary and assesses the ecological risk to human health risk.

2. Materials and methods

2.1. Study area

The Tiber River rises in the Apennine Mountains (Central Italy) and, with a length of 409 km, passes through the city of Rome before flowing into the Tyrrhenian Sea by two mouths, Fiumara Grande and Fiumicino Canal, with an annual mean flow rate of 230 m³ s⁻¹. Rome, a city rich in history with 2,863,322 inhabitants, has an ancient agricultural tradition that is still the main resource for the socio-economic development. Indeed, with 37,000 ha of Utilized Agricultural Surface (SAU), Rome is the largest agricultural district in Europe (Minissi and Lombi, 1997; ISTAT, 2014). The climate of the area is characterized by Mediterranean climate with warm and dry summers (from July to August) and relatively wet and mild winters. The rainy season is from autumn to spring. 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).

2.2. Pesticides investigated

The last Italian agriculture census (Italian Statistical Institute, 2010, ISTAT) reports that the main crops in the Tiber River basin are fruit and vegetables (such as cereals and potatoes), vineyards, olive and tobacco. The intensive agricultural activities might result in water quality deterioration due to the usage of pesticides and fertilizers. In particular, the most widely used pesticides in the Tiber flatland are organophosphate pesticides, such as chlorpyrifos and dimethoate, with 62.50 and 72.27 t annual sold (database of the National Agricultural Information System, 2012, SIAN), which are consistent with the main crops of the area. With the exception of chlorpyrifos and dimethoate, in this study the others OPPs investigated (diazinon, malathion, pirimiphos-methyl, fenitrothion, methidathion and tolclofos-methyl) were selected according to the last Italian agriculture census by ISTAT (2010) and the current EU regulations, such as the Water Framework Directive (WFD) (EC, 2000). Also, the current literature was considered to select the pesticides to be monitored (Bonansea et al., 2013; Kanzari et al., 2014; Cruzeiro et al., 2015; Ccancapa et al., 2016; Zheng et al., 2016). Therefore, the distribution pattern and potential impact of the following OPPs in Tiber River system and its estuary were investigated: diazinon, dimethoate, malathion, chlorpyrifos, pirimiphos-methyl, fenitrothion, methidathion and tolclofos-methyl.

2.3. Sampling

Considering the seasonal variations of the Tiber flow and in the attempt to assess temporal trends of pollutants, four intensive sampling campaigns have been conducted in the summer, autumn, winter and spring of 2014–2015. In each campaign 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 (Fig. 1). In addition, nine points 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) were sampled in each campaign to assess the environmental impact of the Tiber River on the Tyrrhenian Sea (Fig. 1). Three points were sampled 500 m from the

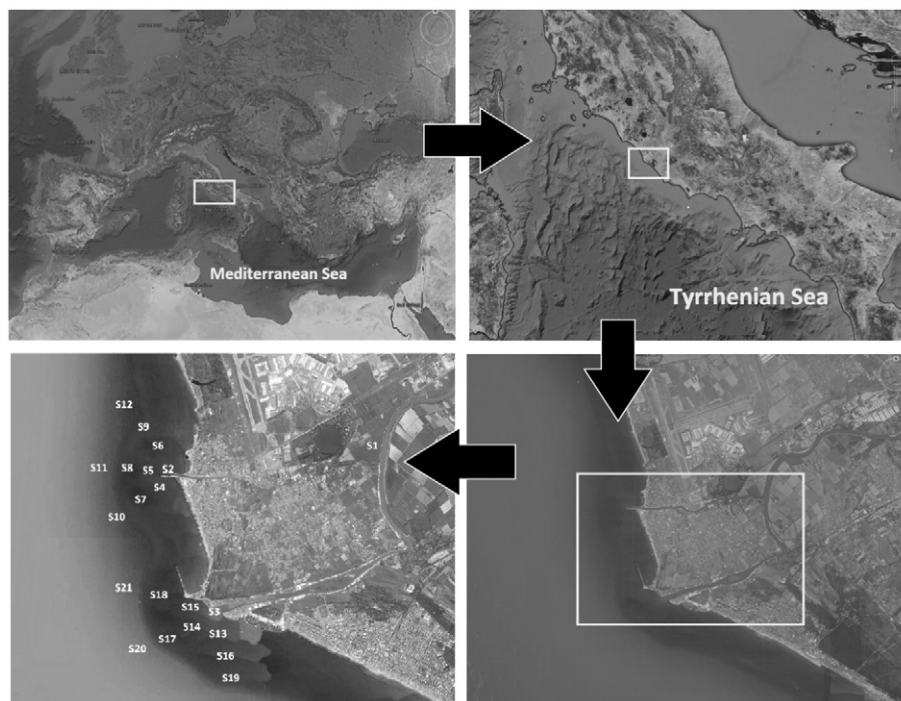


Fig. 1. Map of the study area and sampling sites in the Tiber River and Estuary, Central Italy.

Tiber River mouths, another three points 1000 m away and, finally, another three points 1500 m from the river mouths.

Precleaned 2.5 L glass amber bottles were deployed closed with a homemade device (IOC, 1984; Gómez-Gutiérrez et al., 2006; Montuori et al., 2015). 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 bottles) were collected and transported refrigerated (4 °C) to the laboratory. Water samples were filtered through a previously kiln-fired (400 °C overnight) GF/F glass fiber 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 by 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.

2.4. OPPs extraction and analyses

2.4.1. Suspended particulate phase

Suspended particulate phase (SPM) content was gravimetrically determined (filter weight), after drying the filter in an air-heated oven (55 °C until constant weight) and equilibrated at room temperature in a desiccators (Montuori et al., 2015). Filters were spiked for recovery calculations with a solution of 1,3-Dimethyl-2-nitrobenzene. 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 compounds

were eluted with 5.5 ml of hexane (Merck) in fraction I and 6 mL of hexane:ethyl acetate (9:1) (Merck) in fraction II. Lastly, the column was eluted with 12 mL of ethyl acetate (fraction III) containing more polar compounds.

2.4.2. Dissolved phase

The dissolved phase (DP) was spiked with a surrogate solution of 1,3-Dimethyl-2-nitrobenzene achieving a final concentration in water of 5 ng L⁻¹. Two liters of previously filtered water (DP, dissolved phase) 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 ethylacetate-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 (Montuori et al., 2015).

2.4.3. Sediment

Sediments were oven dried at 60 °C and sieved at 250 μm. 5 g aliquots were spiked with the surrogate mixture (2 ng of 1,3-Dimethyl-2-nitrobenzene) and extracted three times by sonication using 15 mL of DCM/methanol (1:1) for 15 min. After centrifuging, the organic extracts concentrated and fractionated as the water samples (Montuori et al., 2015).

2.4.4. Analytical determination of OPPs

Cleaned extracts of fractions II and III were analyzed by GC-NPD using a GC-2014 Shimadzu (Kyoto, Japan) equipped with a AOC-20i Shimadzu (Kyoto, Japan) autosampler. Samples were injected in the splitless mode at 250 °C and the detector was held at 280 °C. Helium gas was used as a carrier with a flow rate of 25 cm/s at constant flow mode. The hydrogen and air had a flow rate of 4 and 60 mL/min, respectively. The make-up gas (nitrogen) had a flow rate of 3 mL/min, and the detector temperature was 330 °C. Chromatographic separation was achieved by using a 30 m × 0.25 mm ID × 0.25 μm Rxi-17 column for pesticides and herbicides (Restek, Bellefonte, PA 16823) with a temperature program of 40 °C (1 min) to 280 °C at 8 °C min⁻¹ (30 min), holding it for 15 min. The presence of OPPs was confirmed by means of GC-MS using a GC-MS 2010Plus Shimadzu (Kyoto, Japan) working

Table 1Description of the sampling sites and concentration (ng L⁻¹) of organophosphate pesticides in the water samples (as the sum of the DP and SPM) of the Tiber River and the continental shelf, Central Italy.

Sampling location			Organophosphate pesticides									Total			
Site number identification	Site characteristics	Site location	Campaigns	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Pirimiphos methyl	Fenitrothion	Methidathion	Tolclofos methyl	DP + SPM	DP	SPM	SPM (ng g ⁻¹)
1 (river water)	Upstream Tiber River fork	41°46'40.65"N 12°16'45.62"E	Aug	42.10	88.74	32.27	21.83	8.27	12.81	11.75	6.70	224.48	204.37	19.88	49.19
			Nov	15.95	33.61	12.22	4.48	3.18	4.85	4.45	2.02	80.77	77.41	1.91	38.08
			Feb	12.64	26.65	9.69	3.55	2.13	3.85	3.53	1.72	63.76	60.63	0.82	6.21
			May	34.72	73.18	26.61	16.76	6.84	10.57	9.69	5.23	183.60	168.54	14.87	29.67
2 (river water)	Tiber River mouth Fiumicino Canal	41°46'17.34"N 12°13'06.37"E	Aug	18.06	51.09	14.84	14.35	3.78	8.59	6.39	3.41	120.52	107.79	12.27	32.41
			Nov	3.96	10.92	3.17	6.57	3.90	1.84	1.37	1.01	32.74	25.75	5.78	66.00
			Feb	5.98	16.92	4.91	2.44	0.93	2.84	2.12	1.07	37.21	35.25	0.56	2.78
			May	26.64	39.37	10.64	18.79	3.57	11.35	2.42	2.61	115.40	104.81	9.93	22.26
3 (river water)	Tiber River mouth Fiumara Grande	41°44'24.50"N 12°13'58.73"E	Aug	26.32	38.82	11.76	11.34	5.17	5.62	7.20	4.25	110.47	102.76	7.61	25.81
			Nov	10.29	29.18	7.79	2.21	1.42	2.34	1.70	0.89	55.82	53.80	0.91	20.33
			Feb	7.41	10.94	3.31	2.63	1.46	1.58	1.03	1.04	29.40	27.36	0.61	8.60
			May	19.31	43.47	14.09	6.54	5.19	3.97	4.50	2.86	99.95	93.66	4.74	21.73
4 (sea water)	River mouth Fiumicino Canal at 500 m south	41°46'01.74"N 12°12'56.67"E	Aug	5.08	11.36	5.18	7.41	1.41	0.93	1.93	2.47	35.76	27.72	6.89	38.33
			Nov	3.67	3.62	1.65	0.45	0.87	0.63	2.64	0.93	14.46	14.10	ND	6.75
			Feb	4.71	6.81	1.74	0.48	0.47	0.92	0.65	ND	15.77	15.43	ND	4.60
			May	18.41	22.89	6.32	2.66	1.36	2.26	ND	1.47	55.37	52.18	1.38	16.54
5 (sea water)	River mouth Fiumicino Canal at 500 m central	41°46'17.84"N 12°12'44.76"E	Aug	7.08	12.41	1.14	6.01	0.31	0.72	1.34	0.84	29.85	25.21	3.69	23.33
			Nov	1.57	1.48	1.03	0.84	0.28	0.82	ND	ND	6.02	5.76	ND	5.61
			Feb	1.80	4.08	1.07	0.99	0.27	0.67	1.44	ND	10.33	10.06	ND	7.02
			May	2.41	7.87	ND	1.21	0.24	0.94	1.18	0.98	14.84	12.35	1.05	26.62
6 (sea water)	River mouth Fiumicino Canal at 500 m north	41°46'31.73"N 12°12'53.50"E	Aug	11.56	37.69	9.12	14.59	4.59	5.19	3.20	1.96	87.91	76.04	10.45	135.43
			Nov	2.88	9.24	2.24	3.61	2.19	1.27	1.79	ND	23.21	22.37	0.37	12.82
			Feb	3.33	13.86	2.63	1.90	1.15	1.50	0.92	0.97	26.26	24.67	0.44	12.63
			May	14.22	16.36	11.22	6.21	1.83	6.39	1.93	1.89	60.04	55.33	2.97	13.01
7 (sea water)	River mouth Fiumicino Canal at 1000 m South	41°45'47.87"N 12°12'53.50"E	Aug	12.78	8.97	1.31	2.21	1.54	3.65	4.93	ND	35.39	33.89	1.28	23.23
			Nov	1.88	1.12	ND	2.42	1.52	0.67	0.66	ND	8.26	8.12	ND	3.02
			Feb	1.09	2.52	ND	1.12	0.57	0.83	ND	ND	6.13	5.84	ND	11.30
			May	1.92	7.21	2.91	1.43	1.04	1.81	ND	ND	16.32	15.42	0.79	33.12
8 (sea water)	River mouth Fiumicino Canal at 1000 m central	41°46'17.30"N 12°12'20.34"E	Aug	2.21	7.66	ND	0.47	0.28	0.63	0.66	0.95	12.86	11.68	ND	53.46
			Nov	0.55	2.38	ND	0.27	0.22	ND	0.92	ND	4.34	4.08	ND	0.58
			Feb	0.78	2.70	ND	0.22	0.23	ND	0.63	ND	4.55	4.32	ND	1.87
			May	1.23	0.44	1.18	0.21	0.61	0.61	ND	ND	4.28	4.04	ND	6.98
9 (sea water)	River mouth Fiumicino Canal at 1000 m north	41°46'46.51"N 12°12'41.74"E	Aug	8.85	22.71	4.20	3.83	1.10	1.07	1.11	1.99	44.85	41.05	2.79	10.92
			Nov	6.82	5.73	1.13	1.49	0.85	0.61	0.67	ND	17.30	17.06	ND	8.03
			Feb	1.21	7.87	1.35	0.59	0.76	0.65	ND	ND	12.43	12.24	ND	3.39
			May	9.88	11.08	3.09	2.85	0.82	2.81	0.81	0.93	32.28	30.17	0.81	8.87
10 (sea water)	River mouth Fiumicino Canal at 1500 m south	41°45'33.77"N 12°12'40.43"E	Aug	1.26	5.19	ND	0.25	0.22	ND	0.69	ND	7.61	7.13	ND	2.31
			Nov	0.26	0.81	1.11	0.21	0.31	ND	ND	ND	2.70	2.68	ND	0.93
			Feb	0.63	1.17	ND	1.21	ND	ND	ND	ND	3.01	2.98	ND	2.02

(continued on next page)

Table 1 (continued)

Sampling location			Organophosphate pesticides										Total			
Site number identification	Site characteristics	Site location	Campaigns	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Pirimiphos methyl	Fenitrothion	Methidathion	Tolclofos methyl	DP + SPM	DP	SPM	SPM (ng g ⁻¹)	
11 (sea water)	River mouth Fiumicino Canal at 1500 m central	41°46'16.33"N 12°12'01.41"E	May	2.64	3.31	1.71	0.27	0.22	ND	ND	ND	8.15	7.84	ND	1.62	
			Aug	0.22	3.18	ND	0.22	ND	ND	ND	ND	ND	3.62	3.40	ND	1.16
			Nov	ND	0.40	ND	ND	ND	ND	ND	ND	ND	0.40	0.40	ND	0.14
			Feb	ND	1.08	ND	0.20	ND	ND	ND	ND	ND	1.28	1.08	ND	0.08
			May	ND	1.25	ND	ND	ND	ND	ND	ND	ND	1.25	1.25	ND	0.06
12 (sea water)	River mouth Fiumicino Canal at 1500 m north	41°46'58.36"N 12°12'29.55"E	Aug	1.08	9.66	1.19	1.94	0.27	0.66	0.73	ND	15.53	14.29	0.93	11.27	
			Nov	0.33	1.80	ND	0.97	0.37	ND	ND	ND	ND	3.47	3.45	ND	0.58
			Feb	0.91	0.90	ND	ND	ND	ND	ND	ND	ND	1.81	1.81	ND	2.22
			May	8.26	6.33	1.08	0.22	ND	1.19	ND	ND	ND	17.08	16.79	ND	2.73
			Aug	14.53	27.92	10.75	7.44	2.22	3.40	4.07	3.00	3.00	73.32	68.20	4.80	91.79
13 (sea water)	River mouth Fiumara Grande at 500 m south	41°44'08.68"N 12°14'07.38"E	Nov	7.72	16.92	3.70	1.61	0.56	1.86	1.02	ND	33.40	32.79	ND	6.67	
			Feb	4.32	8.31	1.20	1.92	1.06	1.07	1.21	0.94	0.94	20.02	19.22	0.44	17.13
			May	9.17	32.95	16.68	7.59	3.62	1.99	2.15	2.26	2.26	76.42	72.00	3.28	13.07
			Aug	4.77	8.36	2.66	1.39	0.97	1.19	0.73	ND	ND	20.08	19.62	0.32	6.65
			Nov	1.54	2.75	ND	1.46	0.32	0.66	0.62	ND	ND	7.34	7.20	ND	1.81
14 (sea water)	River mouth Fiumara Grande at 500 m central	41°44'14.43"N 12°13'40.05"E	Feb	1.61	2.81	ND	0.47	0.33	0.69	ND	ND	5.90	5.75	ND	0.76	
			May	3.78	6.62	3.11	1.10	1.52	0.72	0.92	ND	17.78	16.67	0.78	5.68	
			Aug	10.52	12.28	6.27	2.20	3.76	0.69	2.33	1.10	1.10	39.16	36.58	1.28	12.30
			Nov	8.91	8.14	2.12	0.41	0.26	0.97	0.79	ND	ND	21.59	21.42	ND	3.62
			Feb	2.92	4.21	2.15	1.19	0.56	0.71	0.80	ND	ND	12.53	12.19	ND	7.00
15 (sea water)	River mouth Fiumara Grande at 500 m north	41°44'27.27"N 12°13'36.50"E	May	6.65	10.78	ND	2.68	1.67	1.04	1.15	1.74	25.70	23.49	1.24	25.10	
			Aug	2.36	2.93	1.09	3.35	1.67	0.84	1.19	1.48	1.48	14.90	11.52	1.54	6.77
			Nov	1.98	10.92	1.36	0.75	0.22	0.61	ND	ND	ND	15.84	15.31	ND	7.42
			Feb	1.79	2.97	ND	0.77	0.42	0.88	0.97	ND	ND	7.81	7.48	ND	7.46
			May	3.72	2.58	5.97	2.07	0.68	0.74	1.05	1.22	1.22	18.03	15.59	1.20	10.63
16 (sea water)	River mouth Fiumara Grande at 1000 m south	41°43'52.67"N 12°14'13.37"E	Aug	1.35	5.55	1.93	0.22	0.28	0.62	ND	ND	9.95	9.70	ND	2.05	
			Nov	0.69	11.25	ND	0.42	0.29	ND	ND	ND	ND	12.65	12.62	ND	0.60
			Feb	0.47	1.93	ND	0.38	0.24	0.66	ND	ND	ND	3.69	3.66	ND	1.17
			May	0.91	3.74	1.62	0.38	0.36	0.66	0.67	ND	ND	8.34	8.21	ND	0.35
			Aug	7.49	8.08	3.45	1.30	1.33	0.63	1.19	1.18	1.18	24.66	22.11	0.97	30.54
17 (sea water)	River mouth Fiumara Grande at 1000 m central	41°44'06.84"N 12°13'20.15"E	Nov	4.07	3.17	ND	1.22	0.27	ND	0.61	ND	9.34	9.00	ND	5.51	
			Feb	2.90	3.13	ND	0.26	0.23	0.61	ND	ND	7.14	6.81	ND	4.82	
			May	20.36	8.28	4.03	0.25	0.28	0.95	ND	ND	ND	34.15	33.40	ND	39.42
			Aug	1.47	4.09	3.79	0.71	0.35	ND	0.97	ND	ND	11.38	10.67	0.70	18.70
			Nov	0.62	1.45	ND	0.53	ND	ND	ND	ND	ND	2.60	2.59	ND	1.68
18 (sea water)	River mouth Fiumara Grande at 1000 m north	41°44'28.80"N 12°13'12.00"E	Feb	0.72	1.43	ND	ND	ND	ND	ND	ND	2.15	2.14	ND	0.64	
			May	1.25	2.37	2.21	1.13	0.23	ND	ND	ND	ND	7.19	6.83	ND	10.05
			Aug	0.22	1.33	1.09	0.23	ND	ND	ND	ND	ND	2.87	2.86	ND	0.98
			Nov	0.23	0.79	ND	ND	ND	ND	ND	ND	ND	1.02	1.02	ND	0.05
			Feb	0.66	0.55	ND	ND	ND	ND	ND	ND	ND	1.21	1.20	ND	0.23
19 (sea water)	River mouth Fiumara Grande at 1500 m south	41°43'38.09"N 12°14'18.04"E	May	0.25	0.31	ND	ND	ND	ND	ND	ND	0.56	0.55	ND	2.00	
			Aug	3.36	3.67	1.36	ND	0.51	ND	1.24	ND	ND	10.14	10.13	ND	8.64
			Nov	1.23	2.37	ND	0.99	ND	ND	ND	ND	ND	4.59	4.58	ND	0.54
			Feb	1.04	1.71	ND	ND	ND	ND	ND	ND	ND	2.75	2.72	ND	1.43
			May	3.66	1.09	1.18	0.95	ND	ND	ND	ND	ND	6.88	6.63	ND	10.70

ND: not detectable.

DP: water dissolved phase.

SPM: suspended particulate matter.

Table 2Concentration ranges and mean value of organophosphate pesticides in the water (ng L^{-1}) and in sediments (ng g^{-1} dw) from recent studies of different rivers, estuaries and coasts in the world.

Area	References	Organophosphate pesticides							
		Diazinon	Dimethoate	Malathion	Chlorpyrifos	Pirimiphos methyl	Fenitrothion	Methidathion	Tolclofos methyl
Asia									
Yongding River, China	Yao et al. (2001)			ND ^a			ND ^a		
Tama River, Japan	Nakamura and Daishima (2005)	8.1 ^a					8.8 ^a	12 ^a	
Tehran, Iran	Berijani et al. (2006)	21.8 ^a		ND ^a	17.7 ^a				
Songhuajiang River, China			1.3–180 ^a	0.8–1070 ^a					
Liaohe River, China			1.3–480 ^a	0.8–180 ^a					
Haihe River, China			1.3–220 ^a	10–130 ^a					
Yellow River, China	Gao et al. (2009)		1.3–2660 ^a	10–1290 ^a					
Yangtse River, China			1.3–16 ^a	0.8–540 ^a					
Huaihe River, China			1.3–280 ^a	0.8–229 ^a					
Pearl River, China			1.3–28.8 ^a	0.8–216 ^a					
Zhujiang River, China	Li et al. (2010)	ND ^a		ND ^a	ND ^a	ND ^a	ND ^a		
Babolrood River, Iran	Fadaei et al. (2012)	4970–768,910 ^a		4590–503,580 ^a					
Shahrood River, Iran	Karyab et al. (2013)	4120 ^a		2200 ^a					
Guan River, China	He et al. (2014)	0.0–2.18 (OPPs sum) ^b							
Major rivers, South Korea	Cho et al. (2014)				1.34–10.9 ^a				
Tighra Reservoir, India	Mamta et al. (2015)	0–16.2 ^a		0.68–36.24 ^a	0–12.27 ^a				
Kurose River, Japan	Kaonga et al. (2015)						ND–370.0 ^a		
Africa									
Zio River, Togo	Mawussi et al. (2014)	ND ^a ND ^b	ND ^a ND ^b	ND ^a ND ^b	ND ^a 0.82–26.93 ^b	ND ^a ND ^b	ND ^a ND ^b		
America									
Atoya River, Nicaragua	Castilho et al. (2000)			346					
San Joaquin River, California	Ensminger et al. (2011)	ND–912 ^a	ND–190 ^a	ND ^a	ND–79 ^a				
Santa Maria River, California	Phillips et al. (2012)	ND–66.3 ^a	ND–80.7 ^a	ND–2930 ^a	ND–1874 ^a				
Suquia River, Argentina	Bonanse et al. (2013)				ND–7.1 ^a				
Lake Zumpango, Mexico	Dzul-Caamal et al. (2014)	4.1 ^a 110.0 ^b			25.2 ^a 5120.0 ^b				

(continued on next page)

Table 2 (continued)

Area	References	Organophosphate pesticides							
		Diazinon	Dimethoate	Malathion	Chlorpyrifos	Pirimiphos methyl	Fenitrothion	Methidathion	Tolclofos methyl
Europe									
Portuguese rivers	Villaverde et al. (2008)	11.5–19.2 ^b					17.0–55.0 ^b		
Guadiana River, Portugal	Palma et al. (2009)	0.68–9.47 ^a	0.05–2.8 ^a	1.23–3.34 ^a					
Arc River, France	Kanzari et al. (2012)				0.01 (0.01–0.02) ^b				
Guadalquivir River, Spain	Masiá et al. (2013)	1.18–456.72 ^a 0.2–175.5 ^b	2.7–69.26 ^a		0.67–14.8 ^a 0.7–15.9 ^b				
North Sea, Germany	Mai et al. (2013)	ND–0.046 ^a	ND–0.045 ^a	ND ^a					
Amvrakia Lake, Greece	Thomatou et al. (2013)	ND–52.6 ^a	ND–68.5 ^a	ND–10.9 ^a	ND–29.2 ^a		ND–48.4 ^a	ND–20.8 ^a	
Guadiana River, Portugal	Palma et al. (2014)	0.54–4.25 ^a	0.50–14.81 ^a	ND ^a			ND ^a		
Guadalquivir River, Spain	Robles-Molina et al. (2014)	234.5 ^a	5166.9 ^a						
Ria Formosa Lagoon, Portugal	Cruzeiro et al. (2015)	26.8–139.2 ^a	7.2–202.1 ^a	6.0–13.1 ^a	15.6–22.0 ^a		5.3 ^a		
Mediterranean Sea									
Kalamas River, Greece	Lambropoulou et al. (2002)	40–250 ^a							
Damietta Canal, Egypt	Abdel-Halim et al. (2006)	705,000.0 ^a 279.0 ^b		466,000.0 ^a 5.12 ^b	139,000.0 ^a 303.8 ^b	23,300.0 ^a ND ^b			
Ebro River, Spain	Claver et al. (2006)		78.0–182.0 ^a		15–312 ^a				
Ebro River, Spain	Gómez-Gutiérrez et al. (2006)	0.2–1.7 ^a					ND–42.5 ^a		
Ebro River, Spain	Terrado et al. (2007)	0.04–44 ^a		ND ^a			14–680 ^a		
Llobregat River, Spain	Terrado et al. (2009)	5.0–376 ^a			5.0–1085 ^a				
Ebro River, Spain	Navarro et al. (2010)	5–256 ^a	16–259 ^a	46–60 ^a	10–71 ^a		13–29 ^a		
Llobregat and Anoia River, Spain	Ricart et al. (2010)	0.83–785 ^a 0.09–1.29 ^b	0.65–87.8 ^a ND ^b	ND ^a ND ^b			0.9–3.43 ^a 1.51–3.0 ^b		
Litani River, Lebanon	Kouzayha et al. (2013)	2.8–9.7 ^a			0.00–7.1 ^a				
Mar Menor, Spain	Moreno-González et al. (2013)	ND–5.4 ^a			ND–45.8 ^a				
Jucar River, Spain	Belenguer et al. (2014)	0.44–11.94 ^a	1.64 ^a	8.75–12.62 ^a	2.23–36.23 ^a				12.63–28.64 ^a
Huveaune River, France	Kanzari et al. (2014)				ND ^b				
Llobregat River, Spain	Masiá et al. (2015)	0.47–35.77 ^a 0.04–2.53 ^b	5.08–71.91 ^a	3.01–320.35 ^a	0.22–13.65 ^a 0.39–130.97 ^b		35–47.39 ^a		
Berre Lagoon, France	Kanzari et al. (2015)				ND ^b				
Asopos River, Greece	Charalampous et al. (2015)			0.01–0.04 ^a					
Lake Vistonis basin, Greece	Papadakis et al. (2015)		376.0 ^a		419.0 ^a	ND ^a			
Turia and Jucar rivers, Spain	Ccancapa et al. (2016)	6.57–37.00 ^a ND ^b	6.15–97.39 ^a ND ^b	ND ^a ND ^b	6.07–30.75 ^a 4.51–55.95 ^b		0.63–17.96 ^a		0.27–7.76 ^a
	DP + SPM	0.22–42.10 (6.22 ± 7.97)	0.31–88.74 (11.35 ± 15.7)	1.03–32.27 (5.32 ± 6.28)	0.20–21.83 (3.01 ± 4.47)	0.22–8.27 (1.41 ± 1.67)	0.61–12.81 (2.24 ± 2.77)	0.61–11.75 (2.13 ± 2.31)	0.84–6.70 (1.97 ± 1.37)
This study (mean + Sd)	Sediment	0.18–0.54 (0.35 ± 0.18)	ND	ND	0.26–32.85 (6.75 ± 8.67)	0.18–8.69 (2.38 ± 2.39)	ND	ND	0.28–26.37 (5.63 ± 6.53)

ND: not detectable.

^a Water.^b Sediment.

Table 3Description of the sampling sites and concentration of organophosphate pesticides in the sediment samples (ng g^{-1} dw) samples of the Tiber River and the continental shelf, Central Italy.

Sampling location			Organophosphate pesticides								
Site number identification	Site characteristics	Site location	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Pirimiphos methyl	Fenitrothion	Methidathion	Tolclofos methyl	Total
1 (river water)	Upstream Tiber River fork	41°46'40.65"N 12°16'45.62"E	0.54	ND	ND	32.85	8.69	ND	ND	26.37	68.46
2 (river water)	Tiber River mouth Fiumicino Canal	41°46'17.34"N 12°13'06.37"E	ND	ND	ND	9.92	3.19	ND	ND	15.78	28.89
3 (river water)	Tiber River mouth Fiumara Grande	41°44'24.50"N 12°13'58.73"E	0.49	ND	ND	25.55	6.36	ND	ND	13.09	45.49
4 (sea water)	River mouth Fiumicino Canal at 500 m south	41°46'01.74"N 12°12'56.67"E	0.21	ND	ND	3.34	3.67	ND	ND	5.14	12.36
5 (sea water)	River mouth Fiumicino Canal at 500 m central	41°46'17.84"N 12°12'44.76"E	ND	ND	ND	1.23	1.54	ND	ND	1.95	4.72
6 (sea water)	River mouth Fiumicino Canal at 500 m north	41°46'31.73"N 12°12'53.50"E	0.18	ND	ND	7.76	5.18	ND	ND	4.48	17.60
7 (sea water)	River mouth Fiumicino Canal at 1000 m south	41°45'47.87"N 12°12'53.50"E	ND	ND	ND	1.51	1.08	ND	ND	3.53	6.12
8 (sea water)	River mouth Fiumicino Canal at 1000 m central	41°46'17.30"N 12°12'20.34"E	ND	ND	ND	0.67	0.43	ND	ND	1.82	2.91
9 (sea water)	River mouth Fiumicino Canal at 1000 m north	41°46'46.51"N 12°12'41.74"E	ND	ND	ND	1.22	2.85	ND	ND	5.92	9.99
10 (sea water)	River mouth Fiumicino Canal at 1500 m south	41°45'33.77"N 12°12'40.43"E	ND	ND	ND	0.55	0.49	ND	ND	0.54	1.59
11 (sea water)	River mouth Fiumicino Canal at 1500 m central	41°46'16.33"N 12°12'01.41"E	ND	ND	ND	0.26	1.16	ND	ND	ND	1.42
12 (sea water)	River mouth Fiumicino Canal at 1500 m north	41°46'58.36"N 12°12'29.55"E	ND	ND	ND	0.72	2.02	ND	ND	1.82	4.56
13 (sea water)	River mouth Fiumara Grande at 500 m south	41°44'08.68"N 12°14'07.38"E	0.37	ND	ND	14.32	2.47	ND	ND	8.10	25.26
14 (sea water)	River mouth Fiumara Grande at 500 m central	41°44'14.43"N 12°13'40.05"E	ND	ND	ND	11.32	0.38	ND	ND	2.93	14.63
15 (sea water)	River mouth Fiumara Grande at 500 m north	41°44'27.27"N 12°13'36.50"E	0.29	ND	ND	9.94	6.19	ND	ND	9.68	26.10
16 (sea water)	River mouth Fiumara Grande at 1000 m south	41°43'52.67"N 12°14'13.37"E	ND	ND	ND	9.19	1.09	ND	ND	2.60	12.88
17 (sea water)	River mouth Fiumara Grande at 1000 m central	41°44'06.84"N 12°13'20.15"E	ND	ND	ND	2.51	0.18	ND	ND	0.48	3.17
18 (sea water)	River mouth Fiumara Grande at 1000 m north	41°44'28.80"N 12°13'12.00"E	ND	ND	ND	3.33	0.25	ND	ND	1.94	5.52
19 (sea water)	River mouth Fiumara Grande at 1500 m south	41°43'38.09"N 12°14'18.04"E	ND	ND	ND	3.73	1.36	ND	ND	0.49	5.58
20 (sea water)	River mouth Fiumara Grande at 1500 m central	41°43'59.84"N 12°13'01.01"E	ND	ND	ND	1.17	0.21	ND	ND	0.28	1.66
21 (sea water)	River mouth Fiumara Grande at 1500 m north	41°44'32.41"N 12°12'52.76"E	ND	ND	ND	0.63	1.11	ND	ND	ND	1.74

ND: not detectable.

in the electron impact mode and operating at 70 eV. 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 OPPs (AccuStandard Inc., CT 06513, USA) ($r^2 > 0.99$). Triphenyl phosphate was used as an internal standard to compensate for the sensitivity variation of the NPD detector, and triphenylamine of the MS detector. In each sample of SPM, DP and sediment the concentration of following OPPs were measured: diazinon, dimethoate, malathion, chlorpyrifos, pirimiphos-methyl, fenitrothion, methidathion and tolclofos-methyl.

The surrogate averaged recoveries in the dissolved phase were $96.6 \pm 7.8\%$ for 1,3-Dimethyl-2-nitrobenzene. In the SPM and sediment samples, recoveries for 1,3-Dimethyl-2-nitrobenzene were $92.3 \pm 5.3\%$ and $91.5 \pm 8.8\%$, respectively. Resulting data for OPPs 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 0.20 (chlorpyrifos) to 1.00 ng L^{-1} (malathion) in the dissolved phase. In the particulate phase the values ranged from 0.30 to 1.50 ng L^{-1} and from 0.15 to 0.8 ng g^{-1} in the sediment.

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 were presented as the mean \pm standard deviation (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 water flow, calculated by means of a daily averaged water flow, respectively for each sampling event. Q_T represents the total water flow for the period considered (August 2014–May 2015), calculated by adding the monthly

averaged water flow (Gómez-Gutiérrez et al., 2006; Montuori et al., 2015). 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} .

Principal component analysis (PCA) is a multivariate statistical method that allows developing a smaller number of artificial variables (called principal components) from a typically large number of variables in which there is some redundancy. In this case, redundancy means that some of the variables are correlated with one another, possibly because they are measuring the same construct. For this reason, it is possible to reduce the observed variables into a smaller number of principal components that will account for most of the variance in the observed variables. Technically, a principal component can be defined as a linear combination of optimally-weighted observed variables. PCA, performed using SPAD (Système Portable pour l'Analyse des Données), summarizes the variables as a set of new orthogonal variables called principal components and displays the pattern of similarity of the observations (sampling sites) and of the variables as points. In the PCA, when concentrations were below the LOD, a value of half the LOD was used.

2.6. Risk assessment

The risk assessment was performed on the basis of the Risk Quotient Index (RQ) (Vryzas et al., 2009; Thomatou et al., 2013). The risk quotient of a single pesticide was calculated by using the following equation:

$$RQ = \frac{MEC}{PNEC} \quad (3)$$

where, MEC is the mean or maximum concentration of pesticides detected in the water samples and PNEC is the predicted no-effect concentration. The mean and maximum detected concentrations were, respectively, used as measured mean and maximum environmental concentrations (MECs) for the general case (RQ_m) and the worst case (RQ_{ex}) scenarios, respectively (Thomatou et al., 2013). PNEC can be calculated for acute or chronic toxicity, by dividing the lowest short-term $L(E)C_{50}$ or long-term No-Observed Effect Concentration (NOEC) values respectively by an assessment factor (AF). The AF is an arbitrary factor to consider the inherent uncertainty in the obtained laboratory toxicity data (Palma et al., 2014; Papadakis et al., 2015; Zheng et al., 2016). Thus, we determined the ecological risk of each pesticide for the ecosystem in each water sample, as well as the ecological risk of the water sample, using the maximum and the mean detected concentrations of the pesticides. If the value of RQ index is higher than one ($RQ > 1$), harmful effects could be expected due to the presence of the pollutant in water. On the contrary, if the value of RQ index is less than zero point one ($RQ < 0.1$), the environmental risk is low. The intermediate situation in which the RQ index is between 0.1 and 1 ($0.1 < RQ < 1$) involves medium risk (Palma et al., 2014).

3. Results and discussions

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

As shown in Table 1, the concentrations of total OPPs obtained in the dissolved phase (DP) ranged from 0.40 (site 11) to 204.37 (site 1) ng L^{-1} with a mean value of $26.15 \pm 36.01 \text{ ng L}^{-1}$. In detail, they ranged from 0.22 to 41.36 ng L^{-1} with a mean value of $6.12 \pm 7.84 \text{ ng L}^{-1}$ for diazinon, from 0.31 to 88.74 ng L^{-1} for dimethoate, from 1.03 to 32.22 ng L^{-1} for malathion, from 0.20 to 12.15 ng L^{-1} for

chlorpyrifos, from 0.23 to 6.09 ng L^{-1} for pirimiphos-methyl, from 0.60 to 12.66 ng L^{-1} for fenitrothion, from 0.61 to 11.73 ng L^{-1} for methidathion and from 0.80 to 2.47 ng L^{-1} for tolclofos-methyl.

Compared with other polluted rivers, estuaries and coasts in the world (Table 2), the concentrations of total OPPs in the dissolved phase from the Tiber River and Estuary ($0.40\text{--}204.37 \text{ ng L}^{-1}$) were much higher than those found in the Tama River (Japan), by Nakamura and Daishima (2005), in the Tighra Reservoir (India), by Mamta et al. (2015), in the Suquia River (Argentina), by Bonansea et al. (2013) in the Guadiana River (Portugal), by Palma et al. (2014) and in Greece, in the Asopos River by Charalampous et al. (2015); but lower than those reported in the China, by Gao et al. (2009), in the Llobregat River (Spain), by Terrado et al. (2009), in the Santa Maria River, (California), by Phillips et al. (2012) and in the Guadalquivir River (Spain), by Robles-Molina et al. (2014). Based on these results, the levels of OPPs in the dissolved phase in the Tiber River and Estuary are comparable to those found in Portugal and Spain (Cruzeiro et al., 2015; Masiá et al., 2015; Ccancapa et al., 2016).

The compositional profiles of OPPs in the dissolved phase indicate that dimethoate was abundant in all sampling sites, representing on average over 43.4% of all OPPs. Dimethoate, one of the most used insecticides in agriculture, has a relatively high mobility because of its high solubility and low stability; indeed it was not detected in SPM and sediment samples (SIAN, 2012; Palma et al., 2014; Poulier et al., 2014; Sangchan et al., 2014). In addition, diazinon and malathion were present in high concentrations, accounting respectively for 22.6% and 13.3% of total OPPs. These compounds have historically been used for pest control on a wide variety of crops (Thomatou et al., 2013; Ryberg and Gilliom, 2015). Fenitrothion, chlorpyrifos, methidathion and pirimiphos-methyl were present in medium/low concentrations, accounting respectively for 5.8%, 5.7%, 4.9% and 3.4% of total OPPs. Toluofos-methyl was present in very low concentrations, representing only 0.9% of total OPPs.

In the suspended particulate matter (SPM), chlorpyrifos, pirimiphos-methyl, tolclofos-methyl and diazinon were the only OPPs detected. The cumulative concentrations on dry weight (dw) ranged from 0.32 ng L^{-1} (6.65 ng g^{-1}) in site 14 to 19.88 ng L^{-1} (49.19 ng g^{-1}) in site 1 (mean value of $3.53 \pm 4.60 \text{ ng L}^{-1}$) (Table 1). Chlorpyrifos was the most abundant in all sampling sites, accounting for 73.7% of \sum OPPs in SPMs. The prevalence of chlorpyrifos, one of the most used pesticides worldwide, could be explained by the higher concentrations of this compound utilized in agriculture, representing the best selling insecticide in the area (Claver et al., 2006; Eaton et al., 2008; Angioni et al., 2011; SIAN, 2012; ISPRA, 2014; Dinh Van et al., 2014; Papadakis et al., 2015). It is especially used as substitute of other organophosphate pesticides (such as azinphos-methyl, azinphos-ethyl, chlorfenvinphos, diazinon, ethion, fenitrothion, fenthion, omethoate, parathion-methyl and parathion-ethyl) banned by EU (Regulation EC No 2009/1107) (Terrado et al., 2009; Masiá et al., 2015). Many studies, and in particular the most recent, reported concentrations of OPPs found in the water as the sum of the DP and SPM, and not separately. Therefore, it is difficult to make a proper comparison between the concentrations of OPPs in SPM samples found in this study and those from other polluted aquatic environments.

As shown in Table 3, the concentrations of total OPPs obtained in the sediment samples ranged from 1.42 (site 11) to 68.46 (site 1) ng L^{-1} with a mean value of $14.32 \pm 16.91 \text{ ng L}^{-1}$. Also in sediment samples, chlorpyrifos, pirimiphos-methyl, tolclofos-methyl and diazinon were the only OPPs detected, probably because these compounds are considered pseudo-persistent organic pollutants, due to their extensive usage and continuous introduction into the environment (Barceló and Hennion, 1997; Bonansea et al., 2013; Li et al., 2014).

Compared with other polluted rivers, estuaries and coasts in the world (Table 2), the concentrations of OPPs in the sediment samples from the Tiber River and Estuary ($1.42\text{--}68.46 \text{ ng g}^{-1}$) were much higher than those found in the Anoia River (Spain), by Ricart et al.

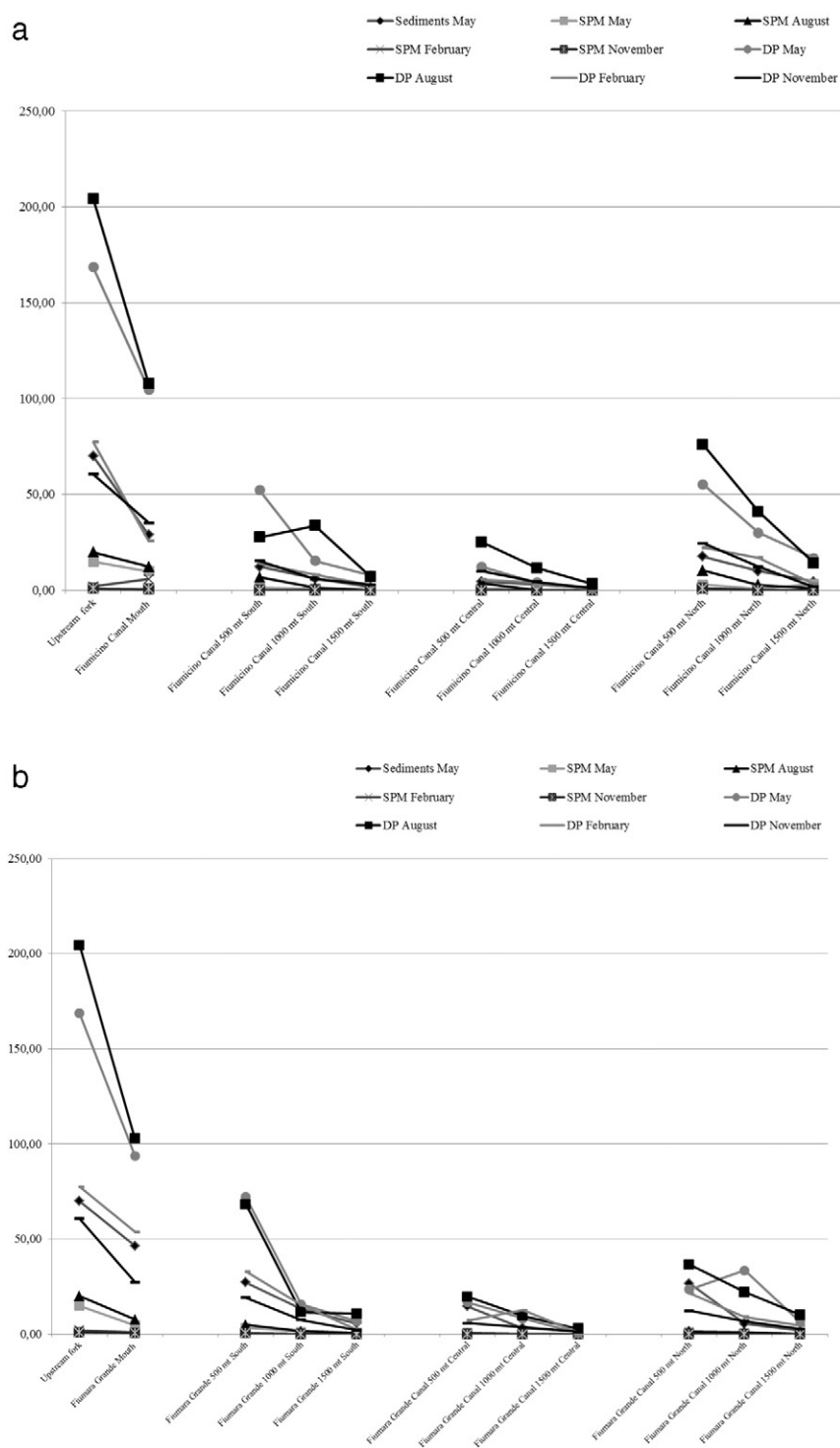


Fig. 2. a. Spatial and temporal concentration of organophosphate pesticides in the water dissolved phase (DP, ng L^{-1}), the suspended particulate matter (SPM, ng L^{-1}) and the sediments (ng g^{-1} dry wt) of the Fiumicino Canal mouth and the continental shelf, Central Italy. b. Spatial and temporal concentration of organophosphate pesticides in the water dissolved phase (DP, ng L^{-1}), the suspended particulate matter (SPM, ng L^{-1}) and the sediments (ng g^{-1} dry wt) of the Fiumara Grande mouth and the continental shelf, Central Italy.

(2010) and in the Arc River–Berre Lagoon (France), by Kanzari et al. (2012); but lower than those reported in the Lake Zumpango (Mexico), by Dzul-Caamal et al. (2014), in the Guadalquivir River (Spain), by Masiá et al. (2013) and in the Llobregat River (Spain), by Masiá et al. (2015). Based on these results, the levels of OPPs in the sediment samples in the Tiber River and Estuary are comparable to those found in the Portuguese River (Portugal), by Villaverde et al. (2008) and in Spain (Turia and Jucar rivers), by Ccancappa et al. (2016).

Nevertheless, Europe, Asia, America and Africa are extremely different regions, both culturally and geographically, but the studies analyzed show minimal differences between developed and developing countries in the use of pesticides, possibly due to globalization. In particular, the rivers of the Mediterranean area present similar concentrations and types of pesticides, probably because there are similar cultivations in all the Mediterranean (Villaverde et al., 2008; Masiá et al., 2015; Ccancappa et al., 2016).

3.2. OPPs distribution between water DP, SPM and sediment samples

Chlorpyrifos, pirimiphos-methyl, tolclofos-methyl and diazinon were the only OPPs detected in SPM samples. The cumulative concentration ratios of these pesticides in DP samples to those in SPM (ng L^{-1}) were >1 in most sampling sites (average 8.80; range 1.21–25.02; $\text{SD} \pm 6.73$). These results lead us to consider that the total amount of selected OPPs in DP samples was more abundant than in SPM samples for each site and season. With some exception, the amount of these pesticides in sediment samples was more abundant than their corresponding water bodies (DP and SPM samples). In fact, the ratio of the concentration of these pesticides in water bodies (DP and SPM samples) compared to that in the corresponding sediment samples was <1 in most sampling sites and for each season. These results show that higher levels of these pesticides, found in sediment samples than DP and SPM samples, are indicators of no fresh inputs of these pesticides in the Tiber. In addition, the higher levels of these pesticides detected in sediments samples compared to the ones detected in their corresponding water bodies (DP samples and SPM), indicate that the processes of gravitational sedimentation and suspension are mainly in this area with the subsequent transfer of these pesticides between sediments and water bodies. This is also confirmed that OPPs found in water bodies, generally reflected a similar quantitative pattern detected in sediment samples.

3.3. Spatial and seasonal distribution of OPPs

The spatial distribution of OPPs concentrations is useful aid to assess the possible source of enrichment and to identify hotspots with high OPPs concentration. The spatial distribution of selected pesticides in DP, SPM and sediment samples from the Tiber River and its estuary were studied by comparing the concentrations of OPPs in different sampling sites in dry and rainy seasons, respectively. The results, summarized in Fig. 2a and b, show a similar trend. Indeed, the OPPs contamination levels in the Tiber decrease clearly from locations 1 to 2 and 3. The total OPPs concentrations decreased to 138.15 ng L^{-1} (DP + SPM mean values of four seasons) at location 1 (Upstream Tiber River fork) to 76.47 ng L^{-1} (DP + SPM mean values of four seasons) at location 2 (Tiber River Mouth Fiumicino Canal) and to 73.91 ng L^{-1} (DP + SPM mean values of four seasons) at location 3 (Tiber River Mouth Fiumara Grande). This decrease in total OPPs concentrations is due to the splitting of the river in its two mouths, before flowing into the Tyrrhenian Sea (Fig. 2a and b). In the Tyrrhenian Sea, around the two mouths of the Tiber, OPPs concentrations range in general from very high in the vicinity of the river outflows to very low in offshore areas (Fig. 2a and b). At 500 m of river outflow, the concentration of OPPs was close to those of the Tiber mouths (Fig. 2a and b). The concentrations at the sampling sites then decreased at 1000 m and more at 1500 m of the river outflows. Particularly, at the Fiumicino mouth the OPPs loads move

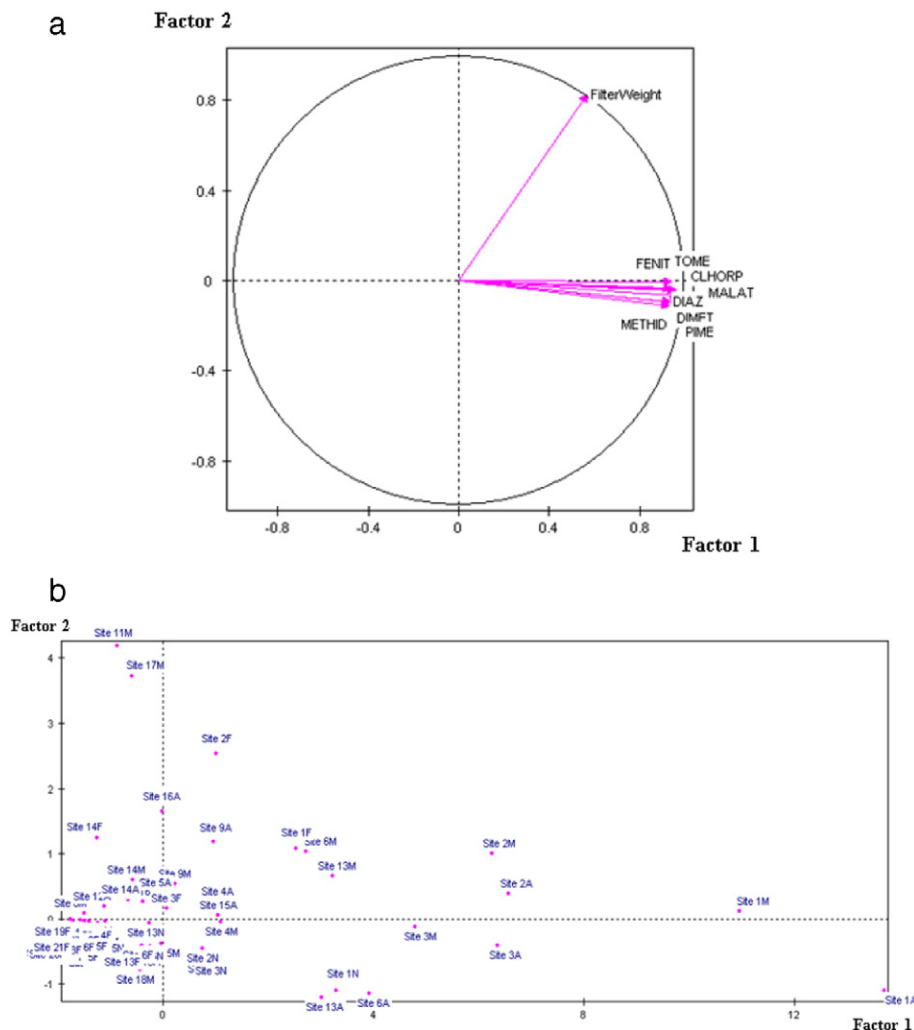


Fig. 3. a. Principal component analysis (PCA) of the data of the Tiber River. Loading plot for the first and second principal component (PC). b. Score plot for the first and second principal component (PC) of the organophosphate pesticides in water samples (as the sum of the water dissolved phase and the suspended particulate matter) from the Tiber River.

Table 4

Ecotoxicity endpoints^a for fish, aquatic invertebrates and algae, related PNEC values ($\mu\text{g L}^{-1}$) and Risk Quotient (MEC/PNEC) for organophosphate pesticides detected in the Tiber River and Estuary.

OPPs	Fish	Aquatic invertebrates	Algae	Critical concentration	Assessment factor	PNEC	RQ _m	RQ _{ex}
Diazinon	700	0.6	10,000	NOEC: 0.56	10	0.056	0.052	0.7518
Dimethoate	400	40.0	32,000	NOEC: 40.0	10	4.0	0.0015	0.0222
Malathion	91.0	0.06	1200	NOEC: 0.06	10	0.006	0.4850	5.3781
Chlorpyrifos	0.14	4.6	43	NOEC: 0.14	10	0.014	0.0874	1.5593
Pirimiphos-methyl	23.0	0.08	1000 (EC ₅₀)	NOEC: 0.08	50	0.0016	0.4914	5.1688
Fenitrothion	88.0	0.087	100	NOEC: 0.087	10	0.0087	0.1103	1.4726
Methodathion	6.1	0.66	22,000	NOEC: 0.66	50	0.0132	0.0903	0.8904

MEC: mean or maximum values; NOEC: no-observed effect concentration values; PNEC: predicted no-effect concentration; RQ_m: Risk Quotient based on mean values; RQ_{ex}: Risk Quotient based on maximum values.

^a Thomatou et al. (2013) and Palma et al. (2014).

into the Tyrrhenian Sea northward (Fig. 2). On the contrary, at the Fiumara Grande mouth the OPPs loads move into the Tyrrhenian Sea southward (Fig. 2b).

The OPPs inputs mainly occurred in the final part of the river by diffuse surface or subsurface hydrological pathways, including storm water runoff, tributary inflow, or due to industrial effluent discharge, atmospheric deposition and bad agricultural practices. The total load of OPPs released by Tiber River to the Tyrrhenian Sea was estimated to be at $545.36 \text{ kg year}^{-1}$. This high load of pesticides, even in periods of low pesticide concentration, could have impact on the biota and marine ecosystems (Cancapà et al., 2016). The occurrence of OPPs in surface waters is typically a consequence of seasonal agriculture practice with episodic peaks correlating with meteorological and hydrological events. The highest levels of pesticide residues are in accordance with the pesticide application events. (Thomatou et al., 2013; Köck-Schulmeyer et al., 2014). Lower concentrations were observed during the autumn and winter months because of dilution effects owing to high-rainfall events and the increased degradation of pesticides after their application (Schäfer et al., 2011; Thomatou et al., 2013).

The PCA was also employed to conduct quantitative assessment. PCA was conducted for the eight OPPs in 21 water samples of four sampling campaigns (Fig. 3a and b). The eigenvalues and the cumulative proportions of the explained variance suggest that it is reasonable to retain the first two PCs. In fact, the first 2 PCs explain up to 70.5% of the total variability. The plot of the first two PCs against each other (Fig. 3) enhances visual interpretation. First of all, the first component (Factor 1) could be interpreted as the concentration of OPPs detected while the second component (Factor 2) is linked to the filter weight. In fact when all loadings are positive, as the case of the first component, the PC is a weighted average of the variables therefore a measure of overall pollution rate; likewise, the positive and negative coefficients in the second component may be regarded the weight of each OPP. Moreover, Fig. 3 shows that the filter weights are substantially independent from the concentrations of OPPs detected. The highest filter weights were found in February, which is attributable to the wet season floods. This suggests that part of these suspended materials could come from the remobilization of polluted sediments. In the score plot (Fig. 3b), the data are distributed in a limited region of space spanned by the two factor well-defined axes. Since OPPs have higher positive loadings, samples loaded with these compounds are distributed along a straight diagonal line drawn from the axes origin through the right upper quadrant, tending towards the Factor 1 axis. These samples correspond to waters collected in the Tiber River in the period May–August, following application period. Their presence and trends could be more associated to their agricultural application and weather conditions. This is in part due to the physicochemical properties because they are more associated with the dissolved than with the particulate phase and are less persistent in the environment. The same occurs in the lower left quadrant where the data points correspond to the contribution by OPPs detected in autumn and winter, with negative loadings for Factor 1 (right quadrant) and positive loadings for Factor 2 (lower quadrant).

3.4. Eco-toxicity and risk assessment of OPPs in the Tiber River and Estuary

Many countries have developed Environmental Quality Standards (EQS) for priority substances and 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 (Belenguer et al., 2014; Dinh Van et al., 2014; Cancapà et al., 2016). Regionally developed EQS may be less relevant in other regions with different contaminant mixtures. The concentrations of OPPs found in the water of the Tiber River and its estuary as the sum of the DP and SPM were significantly lower than the Criterion Continuous Concentration (CCC) for water quality recommended by US-EPA Agency (0.041, 0.17, and $0.1 \mu\text{g L}^{-1}$ respectively for chlorpyrifos, diazinon and malathion) (USEPA, 2010).

Although compliance with EC-EQS in surface waters is checked using an annual average of monthly whole water (DP + SPM) concentrations (Directive 2008/105/EC, 2008), our data show that the mean concentrations of chlorpyrifos (3.01 ng L^{-1}) in the Tiber River and its estuary were lower than the EQS value of 30 ng L^{-1} showing that the ecological integrity of the river watercourse is possibly at risk.

In order to evaluate negative impact of OPPs on Tiber River ecosystem, an environmental risk assessment was performed employing the NOEC values obtained from chronic toxicity tests for producing the corresponding PNECs. Table 4 reported the results obtained for all the detected compounds exhibiting low to high risk at either average or extreme conditions, as calculated from their corresponding mean and maximum concentrations. No OPPs presented RQ_m higher than unit when using mean MECs. Malathion, chlorpyrifos, pirimiphos-methyl and fenitrothion would be present in some samples at levels that are representatively high risk (RQ_{ex} > 1) using maximum MEC values. Medium risk (RQ_{ex} between 0.1 and 1) was associated with diazinon and methidathion in few case. Finally, dimethoate exhibited no risk. However, considering the large mass loads for these pesticides in the river, potential negative impacts on aquatic ecosystems should not be neglected at the current situations.

In the long term, this high aquatic risk caused by pesticides may lead to changes in the fish and invertebrate communities, following a decrease of the most sensitive species and an increase of the most resistant ones, with a consequent loss of biodiversity (Palma et al., 2014; Kuzmanović et al., 2015; Zheng et al., 2016). The application of the RQ method in the present study showed that although all pesticide concentrations complied with the EQS, the potential risk associated with the pesticides should not be neglected. Therefore the sustainable use of pesticides and their substitution by compounds with more favourable physico-chemical properties and lower toxicity, taking into account both abiotic and biotic factors, must be considered as important mitigation measures to reduce inputs into surface water and to protect the aquatic ecosystem from further contamination.

4. Conclusions

This study is the first documenting a comprehensive analysis of OPPs levels in the Tiber River and its estuary; it has provided very useful information for the evaluation of trace OPPs levels in this river and its input into the Tyrrhenian Sea (Mediterranean Sea). The results show that higher levels of OPPs were found in sediment than DP samples and SPM samples, which are indicators of no fresh inputs of these compounds. Moreover, the higher levels of OPPs found in water bodies than in their corresponding sediment samples indicate that the gravitational sedimentation and suspension processes are mainly in this area with subsequent transfer of OPPs particularly less polar, from water bodies to sediments. In relation to the eco-toxicological assessment, the concentrations of most OPPs in the water and sediments from the Tiber River and its estuary were lower than guideline values. Nevertheless, we suggest that the Tiber waters should be continuously monitored since OPPs may cause potential damage to aquatic biota animals.

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