

# Spatial distribution and partitioning of organophosphates pesticide in water and sediment from Sarno River and Estuary, Southern Italy

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**Abstract** The organophosphates pesticide (OPP) pollution in the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea) were estimated. Nine selected OPPs (diazinon, dimethoate, malathion, chlorpyrifos, dichlorvos, fenitrothion, methidathion, tolclofos-methyl, azinphos-methyl) were determined in the water dissolved phase (DP), suspended particulate matter (SPM) and sediment samples. Total OPP concentrations ranged from 5.58 to 39.25 ng L<sup>-1</sup> in water (as the sum of the DP and SPM) and from 0.19 to 3.98 ng g<sup>-1</sup> in sediment samples. Contaminant discharges of OPPs into the sea were calculated in about 48,064.08 g year<sup>-1</sup>, showing that this river should account as one of the main contribution sources of OPPs to the Tyrrhenian Sea.

**Keywords** Sarno River · Organophosphate pesticides · River outflow · Contaminant transport processes · Contaminant loads · Temporal trend

## Introduction

Defined as “the most polluted river in Europe,” the Sarno River originates in south-western Italy and has a watershed of about 715 km<sup>2</sup>. It flows through the Sarno flatland, is delimited in the west by Mt. Vesuvius and in the east by the

Lattari Mountains, and reaches the sea in the Gulf of Naples (Tyrrhenian Sea), flowing through the city of Pompei (Fig. 1). The Sarno watershed collects water from two important effluents, the Cavaiola and Solofrana torrents.

The Sarno flatland is one of the most fertile in Italy due to the high quality of the soil, constituted by layers of volcanic and alluvial origins. The high population density, the massive use of fertilisers and pesticides in agriculture (Sarno flatland ranks 2nd in Italy for pesticide consumption) and the industrial development represent the main causes of pollution of the Sarno River (Arienzo et al. 2001). The main agricultural activity is based on tomato production in the San Marzano area. In terms of industrial development, Solofra, a city on the Solofrana River, has a long-standing tradition in leather tannery that currently counts about 400 productive units and 3500 workers. The pharmaceutical industry is represented principally by Novartis Pharma, whose plant is located at exactly 200 m from the river mouth and covers an area of about 201,000 m<sup>2</sup>. This plant is one of the largest facilities of Novartis Pharma and one of the most important in the world. Another source of environmental pollution can be attributed to urban agglomerations and their wastewaters. Regarding the sewer system of the 39 towns of the Sarno area basin (with a population of about 1,300,635 and an average density of 1.818 inhabitants km<sup>-2</sup>), the wastewater collection and treatment in the area is inadequate. Nineteen of the 39 towns collect between 0 and 33 % of the wastewater generated, 7 towns between 34 and 66 %, and only 13 have a net which collects between 67 and 100 % of it. However, at present, the administrations are trying to recover this heavily impacted area by means of investment policies aimed to improve the wastewater treatment systems (De Pippo et al. 2006; Anno 2007).

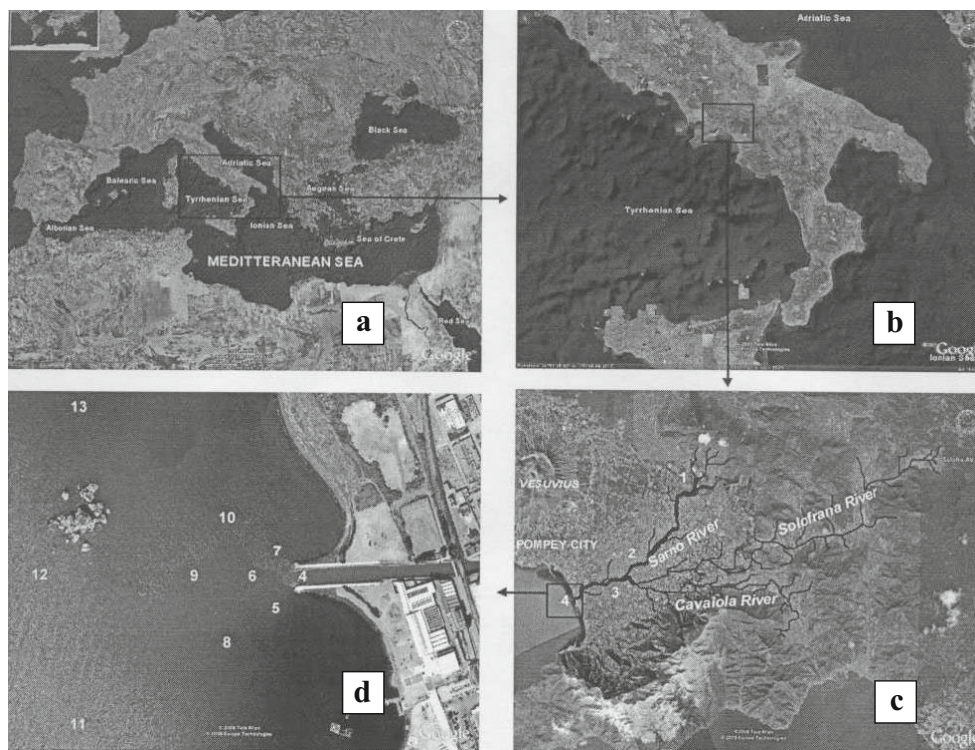
This study is part of a large project aimed to contribute to the knowledge of the pollution affecting the Sarno River and

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



its environmental impact on the Gulf of Naples. The objective 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 contamination caused by the organophosphate pesticides drained into the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea).

Organophosphates pesticides (OPPs), acting as cholinesterase inhibitors, are extensively used in agriculture all over the world. In place of organochlorine pesticides, OPP began to be very popular because they are cheap and readily available, have a wide range of efficacy, are able to combat a large number of pest species, and have a shorter environmental half-life than their organochlorine predecessors. 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 and are still the most popular pesticides and their usage is still growing, because their reliability, wide range of applications and prices. (Zulin et al. 2002; Ma et al. 2009; Tankiewicz et al. 2011; Sappamrer and Hongsibsong 2014).

OPPs have been recognized as harmful for both environment and human health when present above certain levels: they can influence body glucose homeostasis through several mechanisms including physiological stress, 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). While high-level exposure to OPPs can lead to death in the short term, many studies have suggested that chronic low-level exposure can also have serious health consequences such as neurological disorders, brain anomalies and compromised cognitive development especially for infants and children (Wang et al. 2009; Ophir et al. 2014; Epstein 2014). 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. 2014). 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 and industrial wastewater, runoff from non-point sources, and direct dumping of wastes (Vryzas et al. 2009; Tankiewicz et al. 2010; Poulhier et al. 2014). Water could constitute a direct measure of the degree of aquatic environment. Sediments are natural sinks and environmental reservoirs for OPPs in the aquatic environment, and they offer an irreplaceable aid in reconstructing the input and pollution of OPPs. OPPs can represent the group of compound posing the highest risk to ecosystem and may be a source of contaminants to aquatic biota. Thus, the assessment of OPPs in coastal environments is of great 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; Kuzmanović et al. 2014; Poulhier et al. 2014; Dzul-Caamal et al. 2014). Nevertheless, few studies evaluated the

pollution from organophosphate pesticides in surface waters compared to organochlorine pesticides (Zulin et al. 2002).

## Materials and methods

### Sampling

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

Precleaned 2.5-L glass amber bottles were deployed closed with a homemade device as described previously (IOC 1984; Gómez-Gutiérrez et al. 2006). This device consists in a stainless steel cage holding the sampling bottle, which is submerged sealed with a PTFE stopper that can be remotely opened at the desired sampling depth (in this case, at about 0.5-m depth). In each sampling point, 2.5 L of water (one amber bottle) 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 fibre filter (47 mm×0.7 µm; Whatman, Maidstone, UK). Filters (suspended particulate matter (SPM)) were kept in the dark at -20 °C until analysis. Dissolved phase refers to the fraction of contaminants passing through the filter. This includes the compounds that are both truly dissolved as well as those associated with colloidal organic matter. These filtrates were kept in the dark at 4 °C and extracted within the same day of sampling (3–6 h from sampling).

Surface sediment (0–5 cm) samples were collected 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.

### OPPs extraction and analyses

#### *Suspended particulate phase*

SPM content was gravimetrically determined, after drying the filter in an air-heated oven (55 °C until constant weight) and equilibrated at room temperature in a desiccator. Filters were spiked for recovery calculations with a solution of 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 Na<sub>2</sub>SO<sub>4</sub> (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. Finally, the column was eluted with 12 mL of ethyl acetate (fraction III) containing more polar compounds.

#### *Dissolved phase*

The dissolved phase (DP) was spiked with a surrogate solution of 1,3-dimethyl-2-nitrobenzene achieving a final concentration in water of 5 ng L<sup>-1</sup>. Two litres of previously filtered water (DP) were preconcentrated by solid-phase extraction (SPE) using a 100-mg polymeric phase cartridge Strata XTM from Phenomenex (Torrance, CA, USA). After eluting with 10 mL 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.

#### *Sediment*

Sediments were oven-dried at 60 °C and sieved at 250 µm. Five-gram aliquots were spiked with the surrogate mixture (2 ng of 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 extract were concentrated and fractionated as the water samples.

#### *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<sup>-1</sup> at constant flow mode. The hydrogen and air had a flow rate of 4 and 60 mL min<sup>-1</sup>, respectively. The make-up gas (nitrogen) had a flow rate of 3 mL min<sup>-1</sup>, 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<sup>-1</sup> (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 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)

( $r^2 > 0.97$ ). Triphenyl phosphate was used as 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, dichlorvos, fenitrothion, methidathion, tolclofos-methyl, azinphos-methyl.

The surrogate averaged recoveries in the dissolved phase were  $95.8 \pm 3.9$  % for 1,3-dimethyl-2-nitrobenzene. In the SPM and sediment samples, recoveries for 1,3-dimethyl-2-nitrobenzene were  $90.2 \pm 6.2$  and  $88.4 \pm 7.3$  %, respectively. Resulting data for OPP 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  $1.00 \text{ ng L}^{-1}$  (malathion) in the dissolved phase. In the particulate phase, the values ranged from 0.30 to  $1.50 \text{ ng L}^{-1}$  and from 0.15 to  $0.8 \text{ ng g}^{-1}$  in the sediment.

#### Statistical analysis and calculation of the pollutant inputs

Data analysis was performed with the statistical software SPSS, version 14.01 for Windows (SPSS Inc., Chicago, IL, USA). All data 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 ( $F_{\text{annual}}$ ) 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 ( $C_{\text{aw}}$ ) was calculated for the available data, which was corrected by the total water discharge in the sampled period. The equations used were the following:

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

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

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).  $Q_{\text{T}}$  represents the total river discharge for the period considered (February–November 2008), calculated by adding the monthly averaged water flow. River flow data was collected from the register of the Autorità di Bacino del Sarno to <http://www.autoritabacinosarno.it> (Campania 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 grams per day.

## Results and discussions

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

As shown in Table 1, excluding the river source, in which no detectable concentrations of OPPs were encountered, the concentrations of total OPPs obtained in the DP ranged from 5.3 (site 1) to  $34.1 \text{ ng L}^{-1}$  (site 5) with a mean value of  $12.7 \text{ ng L}^{-1}$ . In detail, they ranged from 0.32 to  $2.01 \text{ ng L}^{-1}$  with a mean value of  $0.64 \text{ ng L}^{-1}$  for diazinon, from 1.77 to  $6.23 \text{ ng L}^{-1}$  for dimethoate, from 1.75 to  $5.14 \text{ ng L}^{-1}$  for malathion, from 0.87 to  $9.10 \text{ ng L}^{-1}$  for chlorpyrifos, from 0.75 to  $1.54 \text{ ng L}^{-1}$  for dichlorvos, from 1.51 to  $4.79 \text{ ng L}^{-1}$  for fenitrothion, from 0.50 to  $2.31 \text{ ng L}^{-1}$  for methidathion, from 1.51 to  $2.13 \text{ ng L}^{-1}$  for tolclofos-methyl and from 0.51 to  $1.12 \text{ ng L}^{-1}$  for azinphos-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 Sarno River and Estuary ( $5.3$ – $34.1 \text{ ng L}^{-1}$ ) were much higher than those found in the Yongding River (China), by Yao et al. (Yao et al. 2001); in the North Sea (Germany), by Mai et al. (2013); in the Litani River (Lebanon), by Kouzayha et al. (2013); in the Suquia River (Argentina), by Bonansea et al. (2013); and in Portugal, in the Guadiana River, by Palma et al. (2009, 2014), but lower than those reported in the Atoya River (Nicaragua), by Castillo et al. (2000); in the Kalamas River (Greece), by Lambropoulou et al. (2002); in the Ebro River (Spain), by Claver et al. (2006), Terrado et al. (2007) and Navarro et al. (2010); in the Llobregat River (Spain), by Terrado et al. (2009), Ricart et al. (2010) and Masiá et al. (2014); in China, by Gao et al. (2009); in the San Joaquin River (California), by Ensminger et al. (2011); in the Babolrood River (Iran), by Fadaei et al. (2012); in the Santa Maria River (California), by Phillips et al. (2012); in the Shahrood River (Iran), by Karyab et al. (2013); in the Guadalquivir River (Spain), by Masiá et al. (2013) and Robles-Molina et al. (2014); and in South Korea, by Cho et al. (2014). Based on these results, the levels of OPPs in the dissolved phase in the Sarno River and Estuary are comparable to those found in Japan, Tama River, by Nakamura et al. (2005); in the Ebro River (Spain), by Gómez-Gutiérrez et al. (2006); in Iran by Berijani et al. (2006); in the Mar Menor (Spain), by Moreno-Gonzales et al. (2013); and in the Jucar River (Spain), by Belenguer et al. (2014).

The compositional profiles of OPPs in the dissolved phase indicate that chlorpyrifos was abundant in all sampling sites,

**Table 1** Description of the sampling sites and concentration (ng L<sup>-1</sup>) of organophosphate pesticides in the water samples (as the sum of the DP and SPM) of the Sarno River and the continental shelf, Southern Italy

Sampling location	Organophosphate pesticides										Total					
	Site Characteristics	Site Location	Campaigns	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methidathion	Tolclofos-methyl	Azinphos-methyl	DP + SPM	DP	SPM	SPM
1 (river water)	Sarno River Source	40° 48' 54.03" N 14° 36' 45.36" E	May Aug Nov Feb	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND	ND ND ND ND
2 (river water)	Upstream Alveo Comune	40° 46' 42.73" N 14° 34' 00.48" E	May Aug Nov Feb	0.33 0.63 0.37 0.35	1.81 2.47 1.88 1.83	1.98 2.31 1.82 1.77	2.22 3.22 1.82 1.87	0.81 1.43 ND ND	1.55 1.78 1.63 1.76	0.84 1.07 ND ND	0.57 0.55 0.55 0.54	10.11 13.46 8.07 8.12	9.61 12.66 7.62 7.53	0.50 0.80 0.45 0.59	219.17 93.44 54.95 92.97	
3 (river water)	After Alveo Comune	40° 46' 00.34" N 14° 33' 10.68" E	May Aug Nov Feb	0.58 1.12 0.53 0.54	2.45 3.80 2.33 2.35	2.25 3.31 2.16 2.17	3.20 6.82 2.98 3.35	0.83 1.42 0.75 0.79	1.76 2.85 1.67 1.68	0.99 1.19 0.93 0.94	0.69 0.70 0.66 0.66	12.75 24.38 16.52 16.52	11.93 20.70 15.31 15.31	0.82 3.68 1.21 1.21	18.83 77.70 36.25 37.74	
4 (river water)	Sarno River Mouth	40° 43' 42.62" N 14° 28' 07.89" E	May Aug Nov Feb	0.70 1.41 0.63 0.61	2.76 4.58 2.59 2.55	2.49 3.91 2.35 2.32	4.14 9.23 3.78 3.98	0.94 1.01 0.98 0.96	2.01 3.47 1.87 1.84	1.14 1.56 1.05 1.03	0.77 0.89 0.72 0.71	16.52 30.03 13.97 15.70	15.31 24.87 12.82 12.58	1.21 5.16 1.15 3.12	36.25 37.74 14.83 57.93	
5 (sea water)	River mouth At 50 m south	40° 43' 40.11" N 14° 28' 06.45" E	May Aug Nov Feb	0.97 2.01 0.90 0.83	3.53 6.23 3.32 3.16	3.06 5.14 2.90 2.77	5.13 12.16 4.94 4.87	1.18 1.31 1.10 1.05	2.62 4.79 2.46 2.33	1.49 2.31 1.39 1.31	1.91 4.20 1.82 1.74	20.67 39.27 19.73 18.92	19.84 34.12 18.73 17.69	0.83 5.15 1.01 1.23	12.47 9.41 10.09 13.92	
6 (sea water)	River mouth At 50 m central	40° 43' 42.46" N 14° 28' 05.03" E	May Aug Nov Feb	0.62 1.36 0.61 0.82	2.58 4.47 2.55 2.60	2.34 3.81 2.32 2.35	3.15 7.46 3.21 3.80	0.97 1.41 0.81 0.76	1.87 3.39 1.85 1.88	1.04 1.49 1.03 1.05	0.72 0.86 0.71 0.72	13.29 27.87 13.09 17.91	12.76 24.58 12.45 17.46	0.53 3.29 0.64 0.45	12.36 20.43 5.07 13.42	
7 (sea water)	River mouth At 50 m north	40° 43' 45.09" N 14° 28' 05.17" E	May Aug Nov Feb	0.82 1.60 0.79 0.65	3.12 5.15 3.03 2.68	2.75 4.32 2.68 2.41	4.03 8.29 4.13 3.49	1.17 1.54 1.35 0.86	2.30 3.93 2.23 1.94	1.30 1.80 1.26 1.08	1.73 2.13 1.68 1.53	29.78 17.98 17.27 15.38	17.46 28.67 17.27 14.67	0.45 1.11 0.71 0.71	9.11 6.13 6.96 7.79	
8 (sea water)	River Mouth At 150 m south	40° 43' 35.68" N 14° 28' 02.94" E	May Aug Nov Feb	0.66 1.22 0.65 0.59	2.68 4.12 2.66 2.51	2.42 3.54 2.40 2.28	3.24 5.96 3.25 3.20	1.15 1.15 1.06 0.90	1.95 3.10 1.93 1.81	1.10 1.32 1.08 1.01	1.53 1.67 1.52 ND	15.48 22.85 14.79 13.00	15.02 22.24 14.79 12.28	0.44 0.61 0.50 0.72	5.49 6.46 8.26 7.81	
9 (sea water)	River Mouth At 150 m central	40° 43' 42.25" N 14° 27' 59.97" E	May Aug Nov	0.41 0.51 0.39	1.93 2.13 1.89	1.88 2.06 1.85	1.98 2.59 1.95	ND 0.86 ND	1.85 1.51 1.53	0.79 0.82 0.76	ND ND ND	9.43 11.08 8.93	8.91 10.31 8.38	0.52 0.77 0.55	8.25 5.95 6.09	

Table 1 (continued)

Sampling location		Organophosphate pesticides											Total			
Site number (identification)	Site Characteristics	Site Location	Campaigns	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methidathion	Tolelofos-methyl	Azinphos-methyl	DP + SPM	DP	SPM	SPM (ng.g <sup>-1</sup> )
10 (sea water)	River mouth At 150 m north	40° 43' 49.26" N 14° 27' 59.82" E	Feb	0.38	1.87	1.83	1.88	ND	ND	0.50	ND	0.56	7.02	6.49	0.53	6.61
			May	0.45	2.09	1.98	2.14	ND	1.97	0.83	ND	0.60	10.06	9.66	0.40	6.19
			Aug	0.68	2.63	2.42	3.38	1.05	1.91	0.93	1.51	0.58	15.09	14.39	0.70	4.79
11 (sea water)	River mouth At 500 m south	40° 43' 30.31" N 14° 27' 58.93" E	Nov	0.41	1.99	1.90	1.99	ND	1.64	0.77	ND	0.58	9.28	8.84	0.44	5.01
			Feb	0.40	1.97	1.89	1.99	ND	ND	0.76	ND	0.57	7.58	7.14	0.44	4.96
			May	0.40	1.92	1.86	1.83	ND	1.53	0.76	ND	0.57	8.87	8.49	0.38	5.83
12 (sea water)	River mouth At 500 m central	40° 43' 42.29" N 14° 27' 46.41" E	Aug	0.50	2.15	2.06	2.34	0.91	1.52	0.85	ND	0.63	10.96	10.47	0.49	5.24
			Nov	0.37	1.88	1.82	1.83	ND	ND	ND	0.55	6.45	5.99	0.46	10.25	
			Feb	0.37	1.86	1.81	1.80	ND	ND	ND	0.55	6.39	5.93	0.46	5.60	
13 (sea water)	River mouth At 500 m north	40° 43' 57.85" N 14° 27' 48.68" E	May	0.36	1.81	1.79	1.64	ND	1.57	ND	ND	0.54	7.71	7.31	0.40	6.43
			Aug	0.39	1.86	1.83	1.79	ND	1.53	0.76	ND	0.56	8.72	8.26	0.46	5.05
			Nov	0.35	1.78	1.76	1.56	ND	ND	ND	0.53	5.98	5.61	0.37	7.64	
			Feb	0.32	1.78	1.77	1.35	ND	ND	ND	0.51	5.73	5.40	0.33	2.14	
			May	0.32	1.80	1.77	1.33	ND	1.51	ND	0.51	7.24	6.86	0.37	5.42	
			Aug	0.33	1.97	1.77	1.43	ND	1.68	ND	0.52	7.70	7.35	0.35	3.81	
			Nov	0.34	1.77	1.75	1.21	ND	ND	ND	0.56	5.63	5.30	0.32	7.41	
			Feb	0.34	1.77	1.76	1.18	ND	ND	ND	0.52	5.57	5.27	0.31	5.06	

ND not detectable

**Table 2** Concentration ranges and mean value of organophosphate pesticides in the water from recent studies of different rivers, estuaries and coasts in the world (ng L<sup>-1</sup>)

Area	References	Organophosphates pesticides										
		Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methodathion	Tolclofos-methyl	Azinphos-methyl		
<b>Asia</b>												
Yongding River, China	Yao et al. (2001)		ND	ND								
Tama River, Japan	Nakamura et al. (2005)	8.1			13.2					8.8		
Tehran, Iran	Berijani et al. (2006)	21.8		ND	17.7							ND
Songhuajiang River, China	Gao et al. (2009)		1.3–180	0.8–1070								
Liaohu River, China	Gao et al. (2009)		1.3–480	0.8–180								
Haihe River, China	Gao et al. (2009)		1.3–220	10–130								
Yellow River, China	Gao et al. (2009)		1.3–2660	10–1290								
Yangtze River, China	Gao et al. (2009)		1.3–16	0.8–540								
Huaihe River, China	Gao et al. (2009)		1.3–280	0.8–229								
Pearl River, China	Gao et al. (2009)		1.3–28.8	0.8–216								
Babolrood River, Iran	Fadaei et al. (2012)	4970–768910		4590–503580								
Shahrood River, Iran	Karyab et al. (2013)	4120		2200								
Major Rivers in Korea, South Korea	Cho et al. (2014)				1.34–10.9	45–147						
<b>America</b>												
Atoya River, Nicaragua	Castilho et al. (2000)			346								
San Joaquin River, California	Ensminger et al. (2011)	ND–912	ND–190	ND	ND–79							ND
Santa Maria River, California	Phillips et al. (2012)	ND–66.3	ND–80.7	ND–2930	ND–1874	ND–8.3						
Suquia River, Argentina	Bonasea et al. (2013)				ND–7.1							
<b>Europe</b>												
Guadiana River, Portugal	Palma et al. (2009)	0.68–9.47	0.05–2.8	1.23–3.34								
Guadalquivir River, Spain	Masiá et al. (2013)	1.18–456.72	2.7–69.26		0.67–14.8							
North Sea, Germany	Mai et al. (2013)	ND–0.046	ND–0.045	ND								
Guadiana River, Portugal	Palma et al. (2014)	0.54–4.25	0.50–14.81	ND						ND		ND–0.039
Guadalquivir River, Spain	Robles-Molina (2014)	234.5	5166.9									
<b>Mediterranean sea</b>												
This study <sup>a</sup>		0.32–2.01	1.77–6.23	1.75–5.14	1.18–12.16	0.75–1.54	1.51–4.79	0.50–2.31	3.17–4.20			0.51–1.12
Kalamas River, Greece	Lambropoulou et al. (2002)	40–250										
Ebro River, Spain	Claver et al. (2006)				15–312							
Ebro River, Spain	Gómez-Gutiérrez et al. (2006)	0.2–1.7		ND						ND–42.5		
Ebro River, Spain	Terrado et al. (2007)	0.04–44								14–680		
Llobregat River, Spain	Terrado et al. (2009)	5.0–376			5.0–1085							
Ebro River, Spain	Navarro et al. (2010)	5–256	16–259	46–60	10–71					13–29		

Table 2 (continued)

Area	References	Organophosphates pesticides									
		Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methidathion	Tolclofos-methyl	Azinphos-methyl	
Llobregat and Anoia River, Spain	Ricart et al. (2010)	0.83–785	0.65–87.8	ND			0.9–3.43				
Litani River, Lebanon	Kouzayha et al. (2013)	2.8–9.7			0.00–7.1						
Mar Menor, Spain	Moreno-Gonzalez et al. (2013)	ND–5.4			ND–45.8						
Jucar River, Spain	Belenguier et al. (2014)	0.44–11.94	1.64	8.75–12.62	2.23–36.23			12.63–28.64			
Llobregat River, Spain	Masiá et al. (2014)	0.47–35.77	5.08–71.91	3.01–320.35	0.22–13.65		35–47.39				

ND not detectable

<sup>a</sup> DP + SPM

representing on average over 19.7 % of all OPPs. In addition, dimethoate, malathion and fenitrothion were present in high concentrations, accounting respectively for 22.1 % (range 17.5–33.7 %), 20.8 % (range 15.1–33.4 %) and 15.8 % (range 12.9–23.4 %) of total OPPs. Tolclofos-methyl and methidathion were present in medium concentrations, accounting respectively for 9.1 % (range 6.2–10.5 %) and 7.8 % (range 5.7–10.7 %) of total OPPs. Diazinon, azinphos-methyl and dichlorvos were present in low concentrations, accounting respectively for only 5.1 % (range 3.4–6.5 %), 6.1 % (range 3.3–10.5 %) and 6.8 % (range 3.8–11.3 %) of total OPPs. 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 2011; ISPRA 2013; Van Dinh et al. 2014). It is especially used as a substitute of other organophosphate pesticides (such as azinphos-methyl, azinphos-ethyl, chlorfenvinphos, diazinon, ethion, fenitrothion, fenthion, omethoate, and parathion-methyl and parathion-ethyl) banned by EU (Regulation EC No 2009/1107 of the European Parliament and of the Council of 21 2009) (Terrado et al. 2009; Masiá et al. 2014).

In the SPM, chlorpyrifos and tolclofos-methyl were the only OPPs detected. The cumulative concentrations on dry weight (dw) ranged from 0.31 ng L<sup>-1</sup> (2.14 ng g<sup>-1</sup>) in site 13 to 5.16 ng L<sup>-1</sup> (219.17 ng g<sup>-1</sup>) in site 4 (mean value of 0.99 ng L<sup>-1</sup>) (Table 1). Chlorpyrifos was still abundant in all sampling sites, accounting for 95.1 % of  $\sum$ OPP in SPMs, while the proportion of tolclofos-methyl decreased to 4.89 %. 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.

The total OPP concentrations in sediments are illustrated in Table 3. Also in sediment samples, chlorpyrifos and tolclofos-methyl were the only OPPs detected. Results range from 0.19 (site 13) to 3.98 ng g<sup>-1</sup> (site 5) with a mean value of 1.72 ng g<sup>-1</sup>. Chlorpyrifos was still abundant in all sampling sites, accounting for 75.9 % of  $\sum$ OPP. Compared with other polluted rivers, estuaries and coasts in the world (Table 4), the concentrations of OPPs in the sediment samples from the Samo River and Estuary (0.19–3.98 ng g<sup>-1</sup>) were much higher than those found in the in the Arc River-Berre Lagoon (France), by Kanzari et al. (2012); in the Huveaune River (France), by Kanzari et al. (2014); and in Guan River (China), by He et al. (2014), but lower than those reported in the Portuguese River (Portugal), by Villaverde et al. (2008); in the Guadalquivir River (Spain), by Masiá et al. (2013); and in the Llobregat River (Spain), Masiá et al. (2014). Based on these results, the levels of OPPs in the sediment samples in the



**Table 3** Description of the sampling sites and concentration of organophosphate pesticides in the sediment samples (ng g<sup>-1</sup> dw) of the Samo River and the continental shelf Southern Italy

Sampling location			Organophosphates pesticides													Total
Site number (identification)	Site Characteristics	Site Location	Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methidathion	Tolclofos-methyl	Azinphos-methyl	Total				
1 (river water)	Samo River Source	40° 48' 54.03" N 14° 36' 45.36" E	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND				
2 (river water)	Upstream Alveo Comune	40° 46' 42.73" N 14° 34' 00.48" E	ND	ND	ND	0.71	ND	ND	ND	0.92	ND	1.63				
3 (river water)	After Alveo Comune	40° 46' 00.34" N 14° 33' 10.68" E	ND	ND	ND	1.29	ND	ND	ND	1.07	ND	2.36				
4 (river water)	Samo River Mouth	40° 43' 42.62" N 14° 28' 07.89" E	ND	ND	ND	1.81	ND	ND	ND	1.19	ND	3.01				
5 (sea water)	River Mouth At 50 m south	40° 43' 40.11" N 14° 28' 06.45" E	ND	ND	ND	2.60	ND	ND	ND	1.39	ND	3.98				
6 (sea water)	River mouth At 50 m central	40° 43' 42.46" N 14° 28' 05.03" E	ND	ND	ND	2.10	ND	ND	ND	1.27	ND	3.37				
7 (sea water)	River mouth At 50 m north	40° 43' 45.09" N 14° 28' 05.17" E	ND	ND	ND	0.87	ND	ND	ND	0.96	ND	1.83				
8 (sea water)	River mouth At 150 m south	40° 43' 35.68" N 14° 28' 02.94" E	ND	ND	ND	0.64	ND	ND	ND	0.90	ND	1.54				
9 (sea water)	River mouth At 150 m central	40° 43' 42.25" N 14° 27' 59.97" E	ND	ND	ND	0.58	ND	ND	ND	0.89	ND	1.47				
10 (sea water)	River mouth At 150 m north	40° 43' 49.26" N 14° 27' 59.82" E	ND	ND	ND	0.49	ND	ND	ND	ND	ND	0.49				
11 (sea water)	River mouth At 500 m south	40° 43' 30.31" N 14° 27' 58.93" E	ND	ND	ND	0.39	ND	ND	ND	ND	ND	0.39				
12 (sea water)	River Mouth At 500 m central	40° 43' 42.29" N 14° 27' 46.41" E	ND	ND	ND	0.33	ND	ND	ND	ND	ND	0.33				
13 (sea water)	River mouth At 500 m north	40° 43' 57.85" N 14° 27' 48.68" E	ND	ND	ND	0.19	ND	ND	ND	ND	ND	0.19				

**Table 4** Concentration ranges and mean value of organophosphate pesticides in the sediments from recent studies of different rivers, estuaries and coasts in the world (ng g<sup>-1</sup> dw)

Area	References	Organophosphate pesticides										
		Diazinon	Dimethoate	Malathion	Chlorpyrifos	Dichlorvos	Fenitrothion	Methidathion	Tolclofos-methyl	Azinphos-methyl		
Asia												
Guan River, China	He et al. (2014)	0.0–2.18 (OPP sum)										
Portuguese Rivers	Villaverde et al. (2008)	11.5–19.2							17.0–55.0			
Arc River, France	Kanzari et al. (2012)				0.01 (0.01–0.02)							
Guadalquivir River, Spain	Masia et al. (2013)	0.2–175.5			0.7–15.9							
Mediterranean sea												
This study		ND	ND	ND	0.19–2.60	ND	ND	ND	ND	ND	0.89–1.39	ND
Llobregat and Anoia River, Spain	Ricart et al. (2010)	0.09–1.29	ND	ND					1.51–3			
Huveaune River, France	Kanzari et al. (2014)				ND							
Llobregat River, Spain	Masia et al. (2014)	0.04–2.53			0.39–130.97							

ND not detectable

Sarno River and Estuary are comparable to those found in the Llobregat and Anoia River (Spain), by Ricart et al. (2010).

OPP seasonal and spatial distribution in the water DP, SPM and sediment samples

Chlorpyrifos and tolclofos-methyl were the only OPPs detected in SPM and sediment samples, 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). The cumulative concentrations of these compounds in DP, SPM and sediment samples of the Sarno River and Estuary show that the concentration ratios in DP samples to those in SPM (ng L<sup>-1</sup>) were >1 in most sampling sites (average 4.05; range 0.82–11.70; SD ± 0.33). These results lead us to consider that the total amount of chlorpyrifos and tolclofos-methyl in DP samples was more abundant than in SPM samples for each site and season. With some exception, the total amount of chlorpyrifos and tolclofos-methyl in water bodies (DP and SPM samples) was more abundant than their corresponding sediment samples. In fact, the ratio of the concentration of chlorpyrifos and tolclofos-methyl in sediment samples to that in the corresponding water bodies (DP and SPM samples) was <1 in most sampling sites and for each season. These results show that higher levels of chlorpyrifos and tolclofos-methyl were found in DP than SPM samples and sediment samples, which are an indication of fresh inputs of these pesticides in the Sarno. In addition, higher levels of chlorpyrifos and tolclofos-methyl detected in water bodies (DP samples and SPM) than in their corresponding samples of sediments indicate that the processes of gravitational sedimentation and suspension are mainly in this area with the subsequent transfer of chlorpyrifos and tolclofos-methyl between water bodies and sediments. This is also confirmed that chlorpyrifos and tolclofos-methyl found in DP samples generally reflected a similar quantitative pattern detected in SPM and sediment samples.

These results are also confirmed by the partition coefficient ( $K_p$ ), defined as the ratio of the concentration of a chemical associated with DP to that in the SPM ( $K_p = C_{DP}/C_{SPM}$ ). The partition coefficients showed a decreasing trend in the chlorpyrifos and tolclofos-methyl partitioning from DP to SPM ( $C_{DP}/C_{SPM}$  mean value of 3.24), and to sediments ( $C_{SPM}/C_{Sediment}$  mean value of 59.3). Regarding the chlorpyrifos, the partition coefficients showed a decreasing trend in the chlorpyrifos concentrations from DP to SPMs (chlorpyrifos<sub>DP</sub>/chlorpyrifos<sub>SPM</sub> ratio mean value of 3.55 ± 0.21; range 1.80–8.77) and from SPMs to sediments (chlorpyrifos<sub>SPM</sub>/chlorpyrifos<sub>Sediment</sub> ratio mean value of 146.62 ± 0.15; range 16.21–647.37). Also, the concentrations of tolclofos-methyl in DP, SPM and sediment samples showed a decreasing trend from DP to SPM and to

sediment samples ( $\text{tolclofos-methyl}_{DP}/\text{tolclofos-methyl}_{SPM}$  and  $\text{tolclofos-methyl}_{SPM}/\text{tolclofos-methyl}_{Sediment}$  ratio mean values of 1.10 and 20.88, respectively).

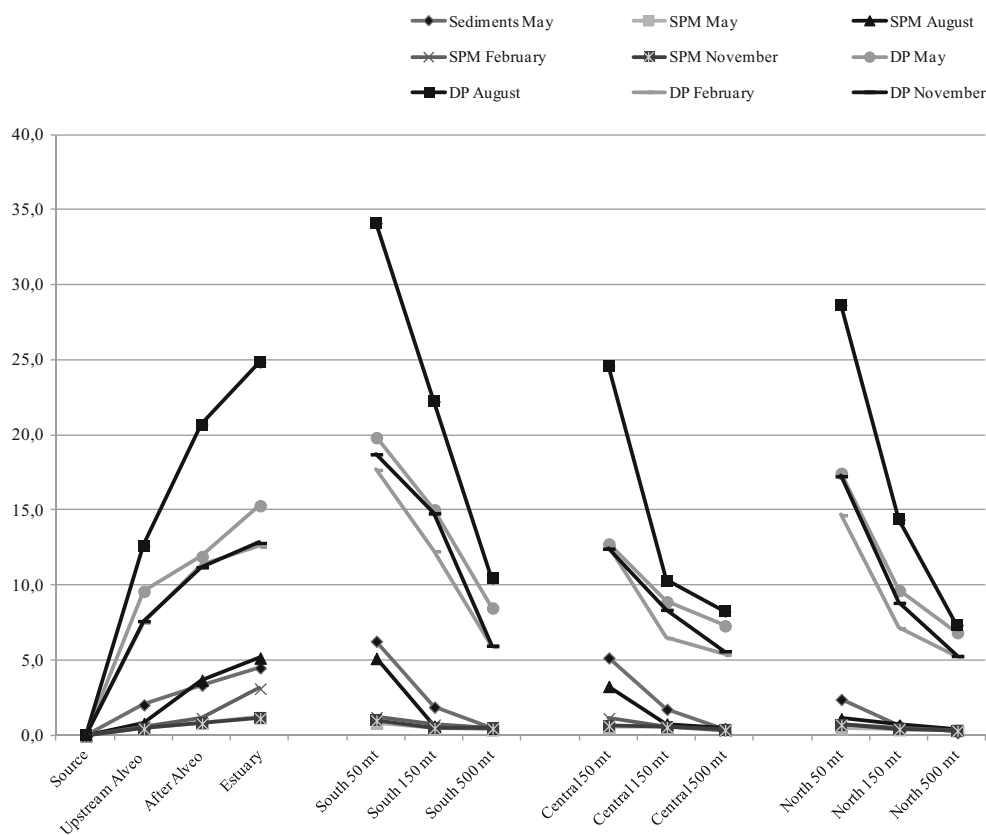
The spatial distribution of OPPs in DP, SPM and sediment samples from the Sarno River and its estuary were studied by comparing the concentrations of  $\Sigma$ OPP in different sampling sites in dry and rainy seasons, respectively. The results, summarized in Fig. 2, show a similar trend. Indeed, the OPP contamination levels in the Sarno increase clearly from location 1 to 4. In general, the upland part of the river was less contaminated by OPPs. Where the river flows through the flatland and the different urban agglomerations, the total OPPs concentrations increased to  $9.80 \text{ ng L}^{-1}$  (DP + SPM mean values of four seasons) at location 2 (upstream Alveo Comune). The total OPP concentrations then increased to  $15.40 \text{ ng L}^{-1}$  (DP + SPM mean values of four seasons) at location 3 (after Alveo Comune). This increase in total OPP concentrations resulted from the inflow from the Alveo Comune ( $30\text{--}50 \text{ m}^3 \text{ s}^{-1}$ ), which carries the discharge of another industrial district. In the lower part of the Sarno (location 4, Estuary), the OPP concentrations increased again, reaching  $19.05 \text{ ng L}^{-1}$  (Figs. 1 and 2). The OPP loading into the Tyrrhenian Sea occur through various transport pathways including storm water runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, atmospheric deposition, and dredged material disposal. The

total OPP load contributions to the Tyrrhenian Sea from the Sarno River are calculated in about  $48,064.08 \text{ g year}^{-1}$ . In the Tyrrhenian Sea, around the Sarno plume, total OPP concentrations range in general from very low in offshore areas to very high in the vicinity of the river outflows (Figs. 1 and 2). At 50 m of the river outflow, the total OPP concentrations were close to those of the Sarno Estuary (Fig. 2). The concentrations at the sampling sites then decreased at 150 m and more at 500 m of the river outflows. Moreover, at the central estuary, the total OPP concentrations were close to those at the southern estuary, decreasing northward (Fig. 2). These results allow us to conclude that although some of the OPP loads from the Sarno inputs are headed northwards, most of them move into the Tyrrhenian Sea southward.

### Eco-toxicity assessment of OPPs in the Sarno River and Estuary

Many countries have developed Environmental Quality Standards (EQS) for priority substances and certain other pollutants in inland surface waters and coastal waters. Guidelines derived in one region will not be relevant for all regions, because, for example, biochemical reaction rates and biological activity increase exponentially with

**Fig. 2** Spatial and temporal concentration of organophosphates pesticides in the water dissolved phase (DP,  $\text{ng L}^{-1}$ ), the suspended particulate matter (SPM,  $\text{ng L}^{-1}$ ) and the sediments ( $\text{ng g}^{-1} \text{ dw}$ ) of the Sarno River and the continental shelf, Southern Italy



temperature (Van Dinh et al. 2014). Regionally developed EQS may be less relevant in other regions with different contaminant mixtures. The concentrations of OPPs found in the water of the Sarno 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 of the European Parliament and of the Council of 16 2008), our data show that the mean concentrations of chlorpyrifos (3.42  $\text{ng L}^{-1}$ ) in the Sarno River and its estuary were lower than the EQS value of 30  $\text{ng L}^{-1}$  showing that the ecological integrity of the river watercourse is possibly at risk. The OPP levels observed do not seem to cause immediate biological effects on the sedimentary environment in the Sarno River and its estuary, but the sustainable use of pesticides and their substitution by compounds with more favourable physicochemical 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 river from further contamination.

## Conclusions

This study is the first to document a comprehensive analysis of OPP levels in the Sarno 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, which is part of the Mediterranean Sea. The results show that higher levels of OPPs were found in DP samples than SPM and sediment samples, which are an indication of 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. The results show that these areas are the main contribution sources of OPPs into the Tyrrhenian Sea and, although some of the OPPs from the Sarno River inputs move northwards, the majority of them moves into the Tyrrhenian Sea southward. In relation to the eco-toxicological assessment, the concentrations of most OPPs in the water and sediments from the Sarno River and its estuary were lower than guideline values, but the Sarno waters should be continuously monitored since OPPs may cause potential damage to aquatic biota animals

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