



Polycyclic aromatic hydrocarbons loads into the Mediterranean Sea: Estimate of Sarno River inputs

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ABSTRACT

The polycyclic aromatic hydrocarbons (PAHs) pollution in the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea) were estimated. The 16 PAHs identified by the USEPA as priority pollutants and perylene were determined in the water dissolved phase (DP), suspended particulate matter (SPM) and sediments. Total PAHs concentrations ranged from 23.1 to 2670.4 ng L⁻¹ in water (sum of DP and SPM) and from 5.3 to 678.6 ng g⁻¹ in sediment samples. Source analysis revealed that PAHs mainly came from combustion process. Contaminant discharges of PAHs into the sea were calculated in about 8530 g d⁻¹ showing that this river should account as one of the main contribution sources of PAHs to the Tyrrhenian Sea.

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1. Introduction

Defined as "the most polluted river in Europe", the Sarno River originates in south-western Italy and has a watershed of about 715 km². It flows through the Sarno flatland, 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 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 m². 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/km²), 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; Legambiente, 2001; Novartis Pharma, 2002; ISTAT, 2007).

This study is part of a large project aimed to contribute to the knowledge of the pollution affecting the Sarno River and 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 polycyclic aromatic hydrocarbons (PAHs) drained into the Sarno River and its environmental impact on the Gulf of Naples (Tyrrhenian Sea, Central Mediterranean Sea).

Polycyclic aromatic hydrocarbons (PAHs) are a well known group of environmental pollutants (Baek et al., 1991; Dominguez et al., 2010). The evidence of their genotoxicity and carcinogenicity for animal species is already available, and epidemiological studies have demonstrated a correlation between PAHs exposure and cancer incidence for various human tissues (Brender et al., 2003; Brody and Rudel, 2003). PAHs are produced by both natural and anthropogenic processes and can be introduced into the environment through various routes. Anthropogenic inputs can originate from incomplete combustion, oil spills, domestic and industrial wastewater discharges, as well as atmospheric fallout of vehicle exhaust and industrial stack emission. In the aquatic media, PAHs can be degraded by photooxidation in the water surface (Guitart

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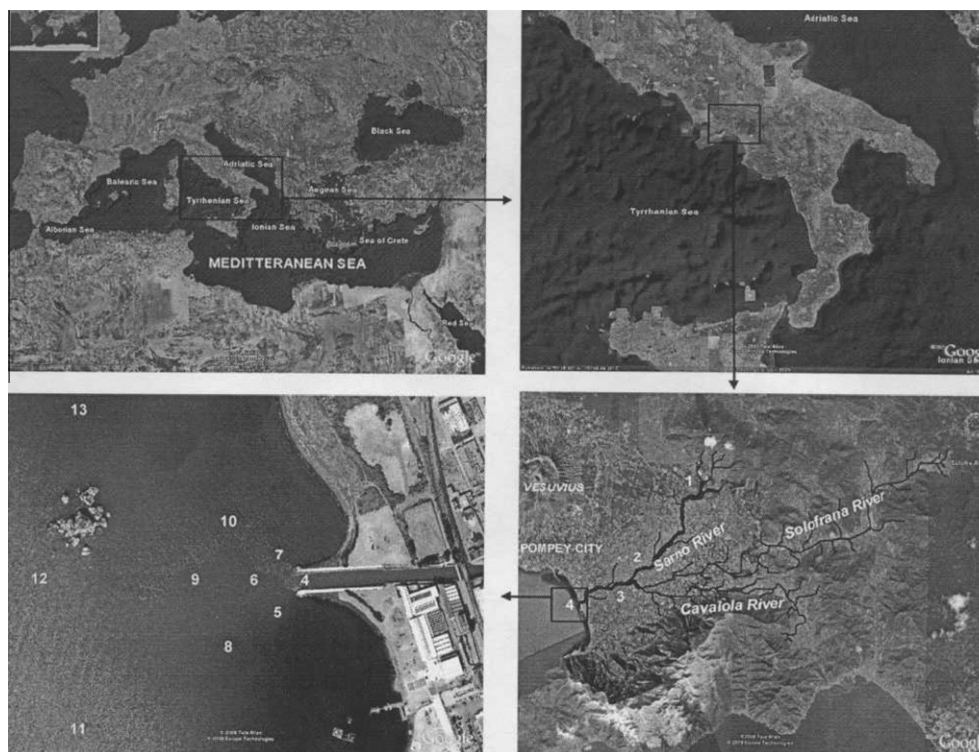


Fig. 1. Map of the study areas and sampling sites in the Sarno River and Estuary, Southern Italy (from Google earth).

et al., 2007), and by microbial action in the water column and in sediments (Cerniglia and Heitkamp, 1989). Thus, the assessment of PAHs 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.

2. Materials and methods

2.1. Sampling points and sample collection

Considering the seasonal variations of the Sarno flow, four intensive sampling campaigns have been conducted in the winter, spring, summer and autumn of 2008. In each campaign four locations were sampled (near the source of the Sarno River, just before and after the junction with Alveo Comune and at the river mouth) in order to have a proper idea of the evolution of the contamination along the river (Fig. 1). Also nine points in the continental shelf around the Sarno mouth were sampled in each campaign to assess the environmental impact of the Sarno River on the Gulf of Naples (Fig. 1). Three points were sampled 50 m from the Sarno River mouth, another three points 150 m away and, finally, another three points 500 m from the river mouth.

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 bottles) were collected and transported refrigerated 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 (0–20 cm) samples were collected by using a grab sampler (Van Veen Bodemhappe 2 L) and put in aluminium containers. The sediments were transported refrigerated to the laboratory and kept at –20 °C before analysis. In each sampling point were collected 2 L of water and an adequate quantity of surface sediment.

2.2. PAHs extraction and analyses

2.2.1. Suspended particulate phase

SPM content was determined by gravimetry, 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 with the surrogate (10 ng of anthracene-*d*₁₀, pyrene-*d*₁₀ and perylene-*d*₁₂) and extracted three times by sonication with 10 mL of dichloromethane-methanol (1:1) (Carlo Erba, Milano, Italy) for 15 min. The recovered extracts were combined and dried with anhydrous sodium sulphate (Carlo Erba). Then they were concentrated in a rotary evaporator to 0.5 mL 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). Three fractions were collected: fraction I with 5.5 mL of hexane (Carlo Erba), fraction II with 6 mL of hexane:ethylacetate (9:1) (Carlo Erba) and, finally, fraction III with 12 mL of ethylacetate (fraction III or F3). PAHs were eluted in fraction II, while fractions I and III contained other organic pollutants which were also determined in the samples.

2.2.2. Dissolved phase

The dissolved phase was spiked with a surrogate solution of deuterated pyrene, anthracene and perylene in methanol achieving

a final concentration in water of 10 ng L^{-1} . Two litres 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.

2.2.3. Sediment

Sediments were oven dried at $60 \text{ }^\circ\text{C}$ and sieved at $250 \text{ }\mu\text{m}$. Then, 5 g of sediment were spiked with the surrogate mixture (10 ng of anthracene- d_{10} , pyrene- d_{10} and perylene- d_{12}) 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 in the same way than the water samples. The total organic carbon (TOC) of sediment samples was determined by TOC analyzer (TOC-V_{CPH}, Shimadzu Corp., Japan).

2.2.4. Analytical determination of PAHs

Cleaned extracts of fractions II were analysed on a GC-MS QP5050A Shimadzu (Kyoto, Japan) working in the electron impact mode at 70 eV. A SPB 20 chromatographic column (20% diphenyl 80% dimethylpolysiloxane) (60 m, 0.25 mm ID and $0.25 \text{ }\mu\text{m}$ of film thickness) was used. The initial oven temperature was temperature programmed at $50 \text{ }^\circ\text{C}$ (2 min) to $250 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$, holding for 30 min. The MS transfer line and ion source were kept at $250 \text{ }^\circ\text{C}$. Acquisition was carried out in the single ion monitoring mode (SIM) using two characteristic ions for each target analyte. Compound identification was carried out by comparing retention times with standards and using the characteristic ions and their ratio for each target analyte. Furthermore, for the higher concentrated samples, the identification of target analytes was confirmed in full-scan mode (m/z range from 60 to 350). The concentration were calculated from the calibration curves for the 17 PAHs (Dr. Ehrenstorfer GmbH, Augsburg, Germany) ($r^2 > 0.98$). Triphenylamine was used as internal standard to compensate for the sensitivity variation of the MS detector. In each sample the concentration of following sixteen selected PAHs monitored by the US Environmental Protection Agency (USEPA) as priority pollutants were measured: naphthalene (Nap), acenaphthalene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (InD). Moreover, perylene, not included in this list, also were monitored. Total PAHs concentration were calculated as the sum of the concentrations of the 16 PAHs compounds (\sum PAHs) selected by the USEPA as priority pollutants.

2.3. Quality assurance and quality control

The limit of detection (LOD) and limit of quantification (LOQ) were calculated as having signal-to-noise ratios of above 3 and 10, respectively, by five replicate analyses. The surrogate averaged recoveries in the dissolved phase were $88.2 \pm 4.9\%$ for anthracene- d_{10} , $94.6 \pm 8.2\%$ for pyrene- d_{10} and $97.1 \pm 9.6\%$ for perylene- d_{12} . In the SPM samples, recoveries were $82.8 \pm 6.9\%$ for anthracene- d_{10} , $93.1 \pm 9.7\%$ for pyrene- d_{10} and $98.8 \pm 10.1\%$ for perylene- d_{12} . Finally, in the sediment samples the averaged recoveries were the following: $84.8 \pm 7.8\%$ for anthracene- d_{10} , $91.1 \pm 8.5\%$ for pyrene- d_{10} and $102 \pm 11.8\%$ for perylene- d_{12} . Blank assays were carried out and used for the calculation of LODs and LOQs. In the dissolved phase, LODs ranged from 0.01 ng L^{-1} for

pyrene to 0.1 ng L^{-1} for indeno(1,2,3-cd)pyrene while, in SPM (1 L) and sediments (5 g) samples, from 0.03 to 0.2 ng L^{-1} and from 0.01 to 0.15 ng g^{-1} respectively. The quantification limits (LOQ) ranged from 0.02 ng L^{-1} for pyrene to 0.15 ng L^{-1} for indeno(1,2,3-cd)pyrene in dissolved water samples, from 0.06 to 0.3 ng L^{-1} in SPM samples and from 0.03 to 0.2 ng g^{-1} in sediments samples. The reported results were corrected for surrogates recoveries.

2.4. Statistical analysis and calculation of PAHs inputs

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

The method used to estimate the annual contaminant discharges (F_{annual}) was based on the UNEP guidelines (UNEP/MAP, 2004b) and has been widely accepted (Walling and Webb, 1985; HELCOM, 1993; Steen et al., 2001). A flow-averaged mean concentration (C_{aw}) was calculated for the available data, which was corrected by the total water discharge in the sampled period. The equations used were the following:

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

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

where C_i and Q_i are the instantaneous concentration and the daily averaged water flow discharge, respectively for each sampling event (flow discharge, section and bed elevation of river mouth were measured by manual probes). Q_T represents the total river discharge for the period considered (February 04–November 04), 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 g d^{-1} .

3. Results

3.1. PAHs concentrations in water dissolved phase

As shown in Table 1, the concentrations of total PAHs obtained in the dissolved phase (DP) ranged from 12.4 (site 1) to 2321.1 (site 8) ng L^{-1} with a mean value of 739 ng L^{-1} . In detail, they ranged from 0.9 to 175.2 ng L^{-1} with a mean value of 65.2 ng L^{-1} for 2-ring PAHs (Nap), from 0.6 to 149.1 ng L^{-1} for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 0.5 to 181.8 ng L^{-1} for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 0.4 to 156.1 ng L^{-1} for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 0.5 to 127.2 ng L^{-1} for 6-ring PAHs (BghiP, InD). The compositional profiles of PAH in the dissolved phase are illustrated in Fig. 2, which indicates that 2- and 3-ring PAHs were abundant in all sampling sites, representing on average over 58% of all PAHs. In addition, the suspected carcinogenic 5–6-ring PAHs was present in low concentrations, accounting for only 11% of total PAHs. The prevalence of low molecular weight PAHs (2–3-ring) in the water could be explained by their high water solubility (Mackay et al., 1992).

Compared with other polluted rivers in the world (Fig. 3), the concentrations of \sum PAHs in the dissolved phase from the Sarno River (12.4 – 1105.9 ng L^{-1}) were much higher than those found in the Gaoping River (Taiwan) by Doong and Lin (2004), in the Middle and Lower Yellow River (China) by Li et al. (2006), in the Qiantang

Table 1

Description of the sampling sites and concentration of PAHs in the water dissolved phase (DP), the suspended particulate matter (SPM) and the sediments of the Sarno River and the continental shelf, Southern Italy.

Sampling location	Site characteristics	Site location	Σ PAHs								Sediments (ng g ⁻¹ dry wt.)
			Dissolved phase (ng L ⁻¹)				Particulate phase (ng L ⁻¹) (ng g ⁻¹ dry wt.)				
			May	August	November	February	May	August	November	February	
1 (River water)	Sarno River Source	40°48'54.03"N 14°36'45.36"E	21	27	12	23	10 (1783)	6 (833)	11 (1637)	9 (1435)	6
2 (River water)	Upstream Alveo Comune	40°46'42.73"N 14°34'00.48"E	433	461	242	378	116 (16325)	82 (9504)	170 (15841)	75 (11925)	100
3 (River water)	After Alveo Comune	40°46'00.34"N 14°33'10.68"E	893	905	396	751	223 (5159)	106 (2240)	234 (12331)	208 (9612)	205
4 (River water)	Sarno River Mouth	40°43'42.62"N 14°28'07.89"E	945	1105	530	916	372 (8662)	253 (1848)	454 (5879)	360 (6672)	352
5 (Sea water)	River Mouth at 50mt South	40°43'40.11"N 14°28'06.45"E	1159	1851	599	1126	526 (7919)	247 (1952)	635 (6409)	493 (5607)	446
6 (Sea water)	River Mouth at 50mt Central	40°43'42.46"N 14°28'05.03"E	1591	2321	871	1336	549 (10374)	229 (1430)	580 (4601)	543 (6374)	502
7 (Sea water)	River Mouth at 50mt North	40°43'45.09"N 14°28'05.17"E	482	527	327	378	185 (3708)	88 (985)	223 (2173)	171 (1885)	180
8 (Sea water)	River Mouth at 150mt South	40°43'35.68"N 14°28'02.94"E	1815	2096	809	1477	668 (8339)	257 (2724)	735 (12938)	667 (7252)	651
9 (Sea water)	River Mouth at 150mt Central	40°43'42.25"N 14°27'59.97"E	1977	2165	820	1528	694 (10943)	357 (2768)	779 (8092)	691 (8780)	679
10 (Sea water)	River Mouth at 150mt North	40°43'49.26"N 14°27'59.82"E	616	819	438	503	173 (2706)	43 (304)	180 (2137)	148 (1627)	162
11 (Sea water)	River Mouth at 500mt South	40°43'30.31"N 14°27'58.93"E	319	366	188	275	75 (1148)	37 (388)	87 (1921)	68 (828)	66
12 (Sea water)	River Mouth at 500mt Central	40°43'42.29"N 14°27'46.41"E	241	333	178	231	69 (1101)	46 (502)	82 (1674)	61 (399)	87
13 (Sea water)	River Mouth at 500mt North	40°43'57.85"N 14°27'48.68"E	220	211	77	147	49 (729)	25 (271)	59 (1356)	35 (571)	40

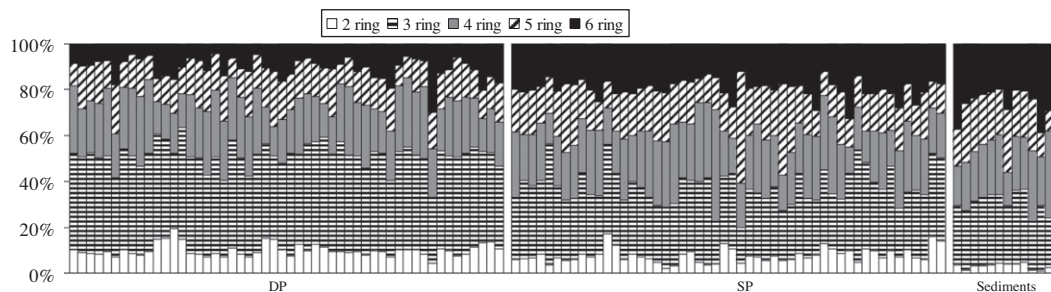


Fig. 2. Relative abundance of 2-, 3-, 4-, 5-, 6-ring PAHs in water dissolved phase (DP) samples, suspended particulate matter (SPM) and sediments of the Sarno, Southern Italy.

River (China) by [Chen et al. \(2007\)](#), in the Xijiang River (China) by [Deng et al. \(2006\)](#), in the Lower Brisbane River (Australia) by [Shaw et al. \(2004\)](#), in the Susqueahanna River (USA) by [Ko et al. \(2007\)](#), in the Mississippi River (USA) by [Mitra and Bianchi, 2003](#) and in the Elbe River (Hamburg, Germany) by [Götz et al. \(1998\)](#); these levels were however lower than those found in China in the Daliao River watershed ([Guo et al., 2009](#)) and in the Wuhan Section of Yangtze ([Feng et al., 2007](#)). Based on these results, the levels of PAHs in the dissolved phase in the Sarno River are comparable to those found in China in the Heman Reach of the Yellow River, by [Sun et al. \(2009\)](#), in the Tianjing River by [Shi et al. \(2005\)](#) and in the Tonghui River by [Zhang et al. \(2004a,b\)](#). As shown in [Fig. 3](#), the concentrations of Σ PAHs in the water-dissolved phase from the continental shelf of the Sarno River (77.2–2321.1 ng L⁻¹) were much higher than those found in the Mediterranean Sea by [Maldonado et al. \(1999\)](#), [Bihari et al. \(2006\)](#), [Manoli et al. \(2000\)](#), [El Nembr and Abd-Allah, 2003](#) and [Manodori et al. \(2005\)](#), but lower than those reported in the seawater around England and Wales by [Law et al. \(1997\)](#).

3.2. PAHs concentrations in water suspended particulate matter

The concentrations of PAHs in the suspended particulate matter (SPM) samples range from 6.1 ng L⁻¹ (833.1 ng g⁻¹ dry weight) in site 1 to 778.9 ng L⁻¹ (8091.9 ng g⁻¹ dry weight) in site 9 (mean value of 254.9 ng L⁻¹), as shown in [Table 1](#). The concentrations of PAHs detected ranged from 0.4 to 69.2 ng L⁻¹ with a mean value of 18.2 ng L⁻¹ for 2-ring PAHs (Nap), from 0.3 to 200.4 ng L⁻¹ for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 0.4 to 71.8 ng L⁻¹ for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 0.4 to 128.2 ng L⁻¹ for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 0.4 to 72.9 ng L⁻¹ for 6-ring PAHs (BghiP, InD). The compositional profiles of PAHs in SPMs are illustrated in [Fig. 2](#); this figure shows that 2-, 3-, 4-ring PAHs were abundant at most sampling sites, accounting for 8%, 31%, and 25% of Σ PAHs in SPMs, respectively. Although low molecular weight PAHs were still abundant in SPMs, the proportion of high molecular weight PAHs increased to 36%, much above than in dissolved samples, where it was 19%. The results indicated that high molecular weight PAHs were

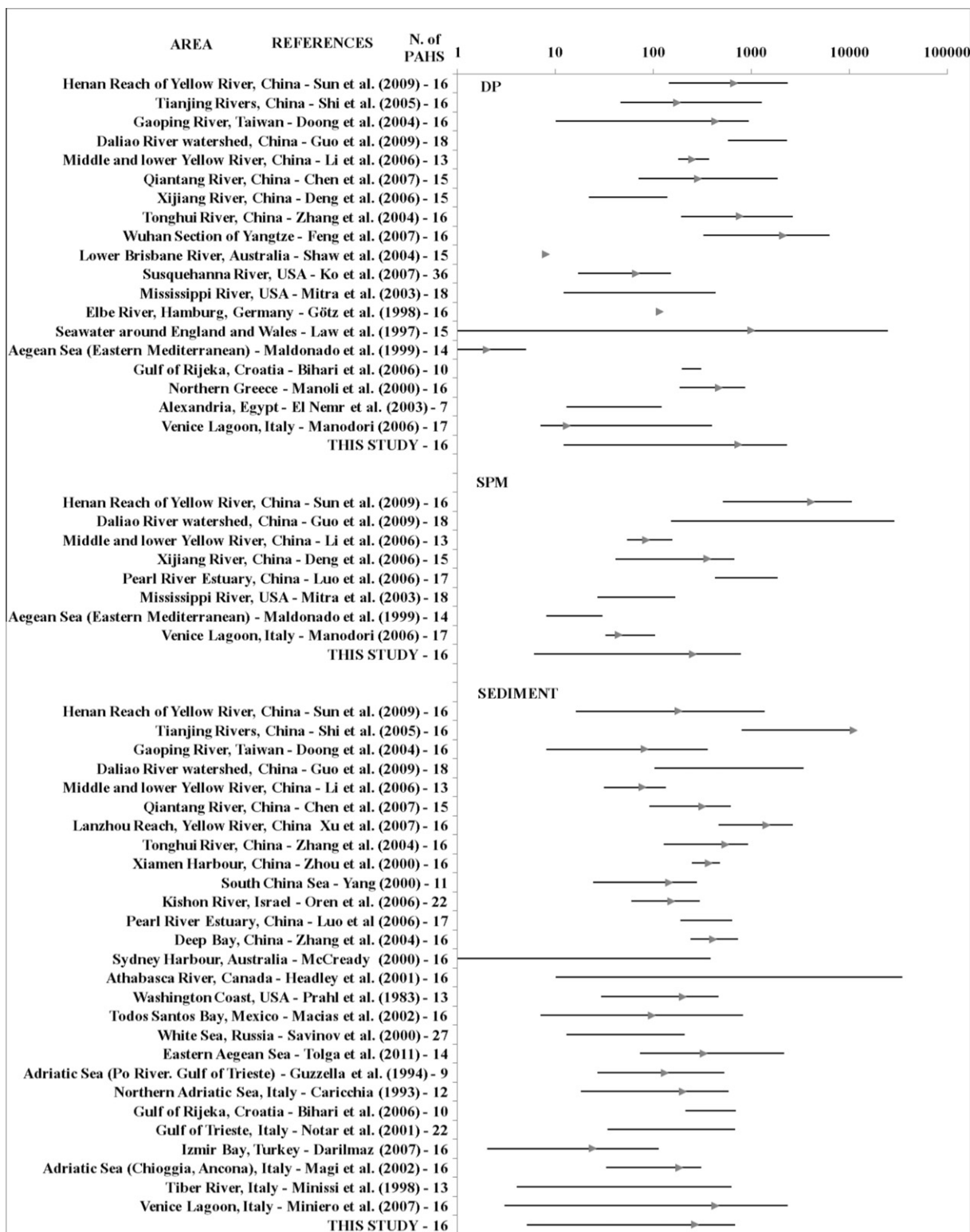


Fig. 3. Concentration ranges and mean value (▶) of PAHs in water dissolved phase (DP, ng L⁻¹), water suspended particulate matter (SPM, ng L⁻¹) and sediment (ng g⁻¹ dry wt.) from different rivers, estuaries and coasts in the world.

preferentially sorbed by the particulate matter due to its high hydrophobicity, in agreement with the PAHs partition theory (Mackay et al., 1992; Zhou et al., 2000). In fact, the partition coefficients (K_p , defined as the ratio of the concentration of a chemical associated with SPM to that in the DP: $K_p = C_{SPM}/C_{DP}$) showed an increasing trend in their SPM partitioning from

low-ring compounds to high-ring compounds (average value of 0.77, 0.73, 1.04, 1.24 and 1.31 respectively for 2-, 3-, 4-, 5-, 6-ring PAHs).

Compared with other polluted rivers in the world (Fig. 3), PAHs in SPMs from the Sarno River were in the medium range. Fig. 3 shows that concentrations of \sum PAHs in SPMs from the Sarno River

were close to those found in the Xijiang River, China (Deng et al., 2006). The concentrations were much higher than those presented in the Middle and Lower Yellow River, China (Li et al., 2006) and in the Mississippi River, USA (Mitra and Bianchi, 2003), but lower than those found in China in the Henan Reach of the Yellow River (Sun et al., 2009), in the Tianjing River, (Shi et al., 2005) and in the Daliao River watershed (Guo et al., 2009). Σ PAHs in SPMs from the continental shelf of the Sarno River (25.1–779.6 ng L⁻¹) were much higher than those found in the Aegean Sea (Maldonado et al., 1999) and in the Venice Lagoon (Manodori et al., 2005), but lower than those found in China in the Pearl River Estuary (Luo et al., 2006).

3.3. PAHs concentrations in sediment

The concentrations of total PAHs in sediment samples are illustrated in Table 1. Results range from 5.2 (site 1) to 678.6 (site 9) ng g⁻¹ with a mean value of 266.9 ng g⁻¹. The concentrations detected ranged from 0.2 to 31.6 ng g⁻¹ with a mean value of 9.7 ng g⁻¹ for 2-ring PAHs (Nap), from 0.2 to 46.3 ng g⁻¹ for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 0.3 to 47.2 ng g⁻¹ for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 0.2 to 46.6 ng g⁻¹ for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 0.5 to 46.7 ng g⁻¹ for 6-ring PAHs (BghiP, InD). As to the compositional profiles of PAH in sediments at each sampling sites, 3- and 4-ring PAHs were abundant at most sites, accounting for 27% and 23% of Σ PAHs in sediments, respectively (Fig. 2). The proportion of high molecular weight PAHs increased to 47% in sediments, 12% more than in SPM samples. Low molecular weight PAHs are gradually carried away from the environment due to their relatively high water solubility and easier degradation. Therefore, high molecular weight PAHs could easily reach the sediment due to their low vapour pressure, low water solubility and more refractory behaviour.

Compared with other polluted rivers in the world (Fig. 3), the concentrations of Σ PAHs in sediment samples from the Sarno River (5.6–352.4 ng g⁻¹) were close to those found in China in the Daliao River watershed (Guo et al., 2009) and in the Qiantang River (Chen et al., 2007). Values slightly higher than those found in the Sarno were found in the Tiber River (Italy) by Minissi et al. (1998) and in the Tonghui River (China) by Zhang et al. (2004a,b), while much higher concentrations were encountered in the Tianjing River (China) by Shi et al. (2005), in the Lanzhou Reach of Yellow River (China) by Xu et al. (2007), in the Zhujiang River (China) by Mai et al. (2002), in the Susqueahanna River (USA) by Ko et al. (2007) and in the Athabasca River (Canada) by Headley et al. (2001). The concentrations of Σ PAHs in sediment samples from the Sarno were higher than those found in the Heman Reach of Yellow River, China (Sun et al., 2009), in the Gaoping River, Taiwan (Doong and Lin, 2004), in the Middle and Lower Yellow River, China (Li et al., 2006), and in the Kishon River, Israel (Oren et al., 2006). Σ PAHs in sediment samples from the continental shelf of the Sarno River (40.3–678.6 ng g⁻¹) were close to those found in the Pearl River Estuary (China) by Luo et al. (2006), in the Deep Bay, China (Zhang et al., 2004a,b), in the Gulf of Rijeka, Croatia (Bihari et al., 2006) and in the Gulf of Trieste, Italy (Notar et al., 2001). The concentrations of Σ PAHs in sediment samples from the continental shelf of the Sarno River were higher than those found in Xiamen Harbour, China (Zhou et al., 2000), in the South China Sea (Yang, 2000), in Sydney Harbour, Australia (McCready et al., 2000), along the Washington Coast, USA (Prah and Carpenter, 1983), in Todos Santos Bay, Mexico (Macias-Zamora et al., 2002), in the White Sea, Russia (Savinov et al., 2000), in Izmir Bay, Turkey (Darilmaz and Kucuksezgin, 2007), in the Eastern Aegean Sea, Turkey (Tolga Gonul and Kucuksezgin, 2011) and in the Adriatic Sea, Italy (Guzzella and De Paolis, 1994; Caricchia et al., 1993; Magi et al., 2002). The concentrations of Σ PAHs in sediment samples from the continental shelf of the Sarno

River were lower than those found in the Venice Lagoon by Manodori et al. (2005).

4. Discussion

4.1. Relationship between PAHs in the water dissolved phase, suspended particulate matter and sediment samples in different seasons

The concentrations of total PAHs in DP, SPM and sediment samples of the Sarno at different sampling sites are illustrated in Table 1 and Fig. 4. The results show that the ratio of the concentration of Σ PAHs in SPM samples (expressed in ng L⁻¹) to that in DP (ng L⁻¹) was less than one in all sites (average 0.384; range 0.005–0.993; SD \pm 0.237). These results lead us to consider that the total amount of PAHs in DP samples was more abundant than in SPM samples for each site and season. With the exception of August, even the total amount of PAHs in SPM samples was more abundant than in sediment samples for each sampling site and season. In fact, with the exception of August (1.181), the ratio of the concentration of Σ PAHs in sediment samples (ng g⁻¹) to that in the SPM samples (expressed in ng g⁻¹) was less than 1 in all sampling sites and for each season (average 0.179; range 0.002–1.181; SD \pm 0.119).

These results indicate that PAHs concentrations in DP were low during the flooding event (February) and high during the dry season (August). The seasonal variation of PAHs concentrations was attributed to the variation of hydrological conditions, which could cause dilution ratio variations. Therefore, a high river flow rate resulted in a higher dilution ratio in the flooding season that led to a decrease in the PAHs concentration in both the Sarno River and its estuary. In August, instead, the concentrations of Σ PAHs in SPM samples were lowest in all sampling sites. The results could be explained by the fact that the decrease of the flow during the dry season induces the mobilization of a smaller amount of SPM and PAHs; in addition, a greater stagnation of SPM due to a reduced flow during the dry season can presumably determine the transfer of the more polar PAHs from SPM to DP. Based on these results, it can be concluded that the load and relocate of PAHs between different phases in each sampling site of the Sarno were related to a variation in the flow of water during rainy and dry seasons.

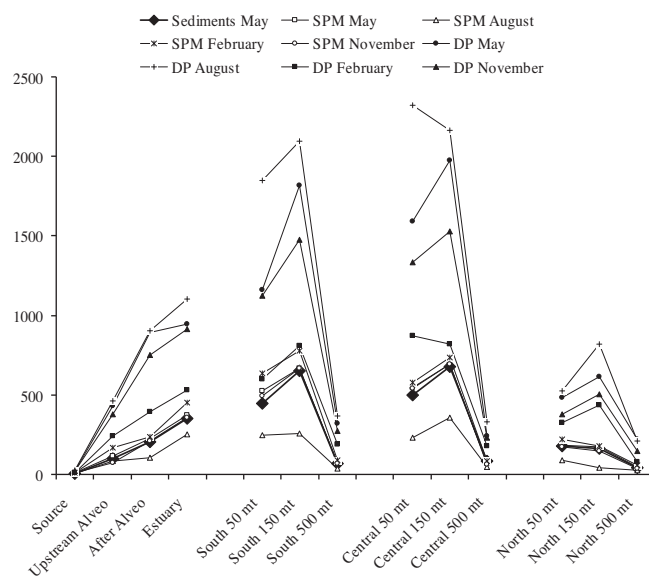


Fig. 4. Spatial and temporal concentration of total PAHs in water dissolved phase (DP, ng L⁻¹), water suspended particulate matter (SPM, ng L⁻¹) and sediment (ng g⁻¹ dry wt.) samples of the Sarno, Southern Italy.

The concentrations of Σ PAHs in sediments were below 180 ng g^{-1} in most sampling sites of the Sarno and were relatively lower than those present in other rivers and coasts. The low concentrations of PAHs in sediments may be due to the high sand and low TOC contents ($0.68\text{--}12.59 \text{ mg g}^{-1}$, mean 4.61). It was believed that the environmental fate and behaviour of hydrophobic organic compounds was ultimately determined by the physico-chemical properties of each compound and sediment. In fact, a positive linear regression exists between total PAH concentration and TOC data in sediments ($r = 0.89$, $p < 0.01$) as indicated by many other studies (El Nemr et al., 2007; Feng et al., 2007; Liu et al., 2008; Sun et al., 2009).

4.2. Spatial distribution of PAHs and loads into the Tyrrhenian Sea

The spatial distribution of PAHs in DP, SPM and sediment samples from the Sarno River and its estuary were studied by comparing the concentrations of Σ PAHs in different sampling sites in dry and rainy seasons, respectively. The results are summarized in Fig. 4. The level of contamination of PAHs in the water clearly increases from location 1–4. In general, the upland part of the Sarno River was less contaminated by PAHs. Where the river flows through the Sarno flatland and through different urban agglomerations, the concentration of total PAHs increased to 489 ng L^{-1} (DP + SPM mean value of four seasons) at location 2 (Upstream Alveo Comune). The concentration then increased to 929 ng L^{-1} (DP + SPM mean value of four seasons) at location 3 (after Alveo Comune). This increase in total PAHs 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 River (location 4, Sarno Estuary), the concentration increased again, reaching 1234 ng L^{-1} (Figs. 1 and 4 and Table 1). Although compliance with EC-EQS in surface waters is checked using an annual average of monthly whole water (dissolved + SPM) concentrations (European Commission, 2009; Common Implementation Strategy for the Water Framework Directive, 2005), our data show that the mean BaP concentration in the River Sarno (63.9 ng L^{-1}) was higher than the EQS value of 50 ng L^{-1} , whereas the BkF + BbF and BghiP + InD values, of 98.1 and 126.8 ng L^{-1} , respectively, were significantly higher than those set by the EQS (30 and 2 ng L^{-1} , respectively), showing that the ecological integrity of the river watercourse is possibly at risk.

The PAHs loading into the Tyrrhenian Sea occurs 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 PAHs loads contribution to the Tyrrhenian Sea from the Sarno River is calculated in about 8530 g d^{-1} . Although PAHs input from other transport pathways are possible (e.g., acute events such as oil spills), these are generally infrequent and rarely visible in monitoring data. Storm water runoff is a major transport pathway for PAHs into the bay, especially during the rainy season when the river water flow is highest.

In the Tyrrhenian Sea, around the Sarno plume, total PAH concentrations range in general from very low in offshore areas to very high in the vicinity of the river outflows (Figs. 1 and 4 and Table 1). As shown in Fig. 4, relatively high concentrations of total PAHs were detected from sampling sites at 150 m of river outflows. At 50 m of river outflow, the concentration of total PAHs were close to those of the Sarno estuary. The concentrations at the sampling sites then increased at 150 m and decreased at 500 m of river outflows. The higher PAHs concentrations found at 150 m may be due to coagulation processes related to river water and sea water mix. The increased concentrations of PAHs found in sediment samples at 150 m suggest that the stagnation of SPM and the gravitational sedimentation and/or coagulation are mainly in this area. Simi-

larly, high concentrations of PAHs found in the DP samples taken at 150 m can be explained by a greater stagnation of SPM in this area with subsequent transfer of the more polar PAHs from SPM to DP. Certainly, the river-water discharge and SPM load, the primary biomass production, the wind fetch and currents also contribute to increase PAHs concentrations at these sampling sites. Moreover, Fig. 4 shows that the concentration of total PAHs at the central estuary were close to those at the southern estuary, decreasing northward. These results allow us to conclude that although some of the PAHs loads from the Sarno inputs are headed northwards, most of them move into the Tyrrhenian Sea southward.

4.3. Source of PAHs in the Sarno

PAHs can derive from anthropogenic inputs and can be the result of the incomplete combustion of organic matter (pyrolytic) and the discharge of crude oil-related material (petrogenic). The pyrogenic origin includes combustion of fossil fuels, waste incineration and coke production, carbon black, coal tar pitch, asphalt and petroleum cracking (McCready et al., 2000). Spillage of fossil fuels can be accidental or intentional (e.g., deballasting water discharges). PAHs can also originate from natural processes such as short-term diagenetic degradation of biogenic precursors (diagenesis). Direct PAH biosynthesis by organisms such as bacteria, fungus, and algae has not yet been clarified. Each source (i.e. pyrolytic, petrogenic and diagenetic) gives rise to typical PAH patterns. In general, combustion products are dominated by relatively high molecular weight (HMW) compounds with four or more condensed aromatic rings, whereas bi- and tricyclic aromatic compounds (LMW) are more abundant in fossil fuels, which are, moreover, dominated by alkylated derivatives (Prah and Carpenter, 1983). Diagenetic PAHs are represented by some characteristic species (e.g., perylene). Using chemical profiling and particular compound ratios, it is possible to recognize the processes that generate these compounds (Budzinski et al., 1997; Yunker et al., 2002; De Luca et al., 2004). The ratios of phenanthrene to anthracene (Phe/An) and fluoranthene to pyrene (Flu/Pyr) have been used to assess the contribution of petroleum or combustion sources of PAHs in coastal environments. A Phe/An ratio lower than 10 and a Flu/Pyr ratio higher than 1 have been shown in most cases, strongly supporting the pyrogenic origin of PAHs (Baumard et al., 1998). In addition to this, when the ratio of chrysene to benzo[a]anthracene (Chr/BaA) is lower than 0.1 it is usually an indication of a pyrolytic origin, while a fluorene to fluorene + pyrene (Flu/(Flu + Pyr)) ratio below 0.5 is typical of a petrogenic source. However, difficulties exist in identifying these origins due to the possible co-existence of several sources.

The ratio study reflected a prevailing pattern of pyrolytic inputs of PAHs in the Sarno River and its estuary. In fact, the results showed that the Phe/An ratio was <10 at all sites (mean 1.73; range 0.43–4.14), and Flu/Pyr was >1 at most sites (mean 1.21; range 0.65–4.01). Chr/BaA and Flu/(Flu + Pyr) varied within a range of 0.12–2.39 (mean 0.91) and 0.29–1.44 (mean 0.78), respectively. Thus, the LMW/HMW ratio was relatively low (<1 for most sites), suggesting a pyrolytic origin of PAHs at these sites (mean 0.88; range 0.19–3.99). These results, obtained by different molecular ratios, were correlated with the specific pollution conditions in the Sarno flatland. The Sarno flatland is a heavy industrial area, with many heavily polluting factories. The industrial wastes enriched with combustion-derived PAHs are directly discharged into the Sarno River. The emission of atmospheric particles from factories and from the whole Naples urban area also cause serious air pollution, and the particulate-associated PAHs may transport and deposit into the river. In addition to these inputs, some other sources such as the roads on both sides of the river and along

the coast, the runoff containing street dust, and municipal wastewater, result in the pattern of pyrolytic origins of PAHs contamination in the area.

In addition to pyrolytic and petrogenic sources, perylene is also produced by in situ degradation of biogenic precursors (Venkatesan, 1988; Baumard et al., 1998). Indeed, perylene is probably the most important diagenetic PAH encountered in sedimentary environments and, thus, a high abundance of perylene relative to other PAHs can indicate an important natural origin of the compound. The highest concentrations of perylene were observed at location 3 (After Alveo Comune) and between the Sarno and its estuaries. The clearly seaward-decreasing trends of perylene concentrations suggest that perylene originates mainly from terrestrial inputs. Perylene has been frequently associated with inputs from rivers and estuaries (LaFlamme and Hites, 1978; Baumard et al., 1998). In fact, it has been suggested that concentrations of perylene above 10% of the total penta-aromatic isomers indicate a probable diagenetic input, whereas those in which perylene accounts for less than 10% indicate a probable pyrolytic origin of the compound. In the present study perylene was studied in all sediment samples, and concentrations of this compound ranged from 0.12 to 30.3 ng g⁻¹. The concentrations of perylene relative to the penta-aromatic isomers indicated that the relative abundance of some of them was lower than 10%, indicating a pyrolytic origin of the compounds that could reach the river from different sources in this area.

4.4. Eco-toxicity assessment of PAHs in sediment

In order to assess whether PAH in the Sarno River and its estuary will cause toxic effects, we compared the PAHs levels in sediment against effects-based guideline values such as the effect range-low (ER-L), effect range-median (ER-M) and apparent effects threshold values developed by the US Natural Oceanic and Atmospheric Administration (Long et al., 1995; Witt, 1995). ER-L and ER-M values are useful in assessing sediment quality and provide qualitative guidelines on what needs to be done to effectively protect the aquatic environment (Kim et al., 1999; Mai et al., 2002). In the Sarno, the total PAH concentrations in sediment samples were below the ER-L value (4000 ng g⁻¹) and significantly lower than the ER-M (44,792 ng g⁻¹). In relation to the individual compounds, also the mean concentrations of Acy, Ace, Fle, An and Dah were lower than their respective ER-L values (44, 16, 19, 85 and 63 ng g⁻¹) and ER-M values (640, 500, 540, 1100 and 260 ng g⁻¹). The concentrations of other PAHs in these sediment samples were lower than their respective ER-L and ER-M values. Apart from this, several individual PAHs such as BbF and BkF do not have a lowest safe value. In the Sarno River and its estuary, some of these PAHs were also detected at many sampling sites.

5. Conclusions

This study is the first to document a comprehensive analysis of PAHs in the Sarno River and its estuary; it has provided very useful information for the evaluation of trace PAHs and probable sources of PAHs in this river and its input into the Tyrrhenian Sea, which is part of the Mediterranean Sea. The results show that PAH concentrations in DP, SPM and sediment phases varied significantly among sampling locations. Two- and three-ring PAHs were abundant in water samples, whereas, high-ring PAHs were major species in sediment samples. In SPM samples, more kinds of PAHs were detected including low- and high-ring PAHs. Source analysis revealed that PAHs derive mainly from combustion processes. The results show that these areas are the main contribution sources of PAHs into the Tyrrhenian Sea and, although some of the PAHs from the Sarno River inputs move northwards, the majority of it moves

into the Tyrrhenian Sea southward. In relation to the eco-toxicological assessment, the concentrations of most PAHs in the sediments from the Sarno River and its estuary were much lower than guideline values regarding the effect range-low (ER-L) and effect range-median (ER-M). In conclusion, PAHs do not seem to cause immediate biological effects on the sedimentary environment in the Sarno River and its estuary.

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