

Estimation of Polycyclic Aromatic Hydrocarbons pollution, risk assessment and loads into Mediterranean Sea from Volturno River, Southern Italy.

Paolo Montuori (✉ pmontuor@unina.it)

Università degli Studi di Napoli Federico II Dipartimento di Sanità Pubblica <https://orcid.org/0000-0002-8745-232X>

Elvira De Rosa

University of Naples Federico II: Università degli Studi di Napoli Federico II

Fabiana Di Duca

University of Naples Federico II: Università degli Studi di Napoli Federico II

Donatella Paola Provisiero

University of Naples Federico II: Università degli Studi di Napoli Federico II

Pasquale Samacchiaro

University of Rome: Università degli Studi di Roma La Sapienza

Antonio Nardone

University of Naples Federico II: Università degli Studi di Napoli Federico II

Maria Triassi

University of Naples Federico II: Università degli Studi di Napoli Federico II

Research

Keywords: Polycyclic aromatic hydrocarbons, Volturno River, Composite indicator, Contaminant loads, Risk assessment

Posted Date: November 9th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-103107/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

Background: This study reports the data on the contamination caused by polycyclic aromatic hydrocarbons (PAHs) drained into the Volturno River and its environmental impact on the Tyrrhenian Sea (Central Mediterranean Sea). One of the key aims of this study is to use the PAHs as indicators of pollution, by identifying the main sources from which these pollutants originate. Also, the ecosystem health risk and the seasonal and spatial distribution of PAHs in samples of water and sediment was assessed. The 16 PAHs identified by the USEPA as priority pollutants were determined in the water dissolved phase, suspended particulate matter and sediments collected from 10 sites in four seasons.

Results: A multidimensional statistical approach was used to identify three pollution composite indicators. Contaminant discharges of PAHs into the sea were calculated in about 3.158,2 kg/year showing that this river should account as one of the main contribution sources of PAHs to the Tyrrhenian Sea. Total concentrations of PAHs varied in ranges 434.8 to 872.1 ng g⁻¹ and 256.7 to 1686.3 ng L⁻¹ in sediment samples and in water (total of water dissolved phase and suspended particulate matter), respectively.

Conclusion: The statistical results indicated that the PAHs mainly had a pyrolytic source and the rainy season was the most polluted time. The toxic equivalent concentration (TEQ) of carcinogenic PAHs was 130.3 to 302.1 ngTEQ g⁻¹, implying that the Volturno River basin presents a definite carcinogenic risk.

1. Background

Polycyclic aromatic hydrocarbons (PAHs) are a common class of environmental pollutants [1, 2]. PAHs distribution and source in the environment have attracted much attention because of their persistent, toxic, genotoxic and carcinogenic qualities as a potential hazard for human health. [3, 4, 5].

PAHs are produced by natural processes and anthropogenic activities and 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. Based on their specific characteristics, PAHs origin can be divided into three classes [6, 7, 8]. The first class originates from pyrolytic sources, including fossil fuels combustion, gasoline or diesel fueled vehicles, combustion-based waste disposal and metallurgical coke production, petroleum, asphalt, coal tar pitch and carbon black cracking. The second class comes from petrogenic sources, which include crude oil and petrochemicals such as diesel fuel, kerosene, gasoline and lubricating oil. Lastly, PAHs is derived also from natural processes such as diagenesis (short-term degradation of biogenic precursors). All of the aforementioned sources (i.e. pyrolytic, petrogenic and diagenetic) bring about distinctive PAHs patterns. At large, combustion products are mainly composed of elements with four or more condensed aromatic rings, marking them as relatively high molecular weight (HMW), whereas low molecular weight compounds (LMW) - such as those with bi- and tricyclic aromatic rings - are more represented in fossil fuels, which are also dominated by alkylated derivatives [9, 10, 11]. Through chemical analysis and specific compound ratios, recognizing the generating processes of the sample is achievable [12, 13].

Since 1980, waste management in Campania region has been characterized by crisis. This waste crisis in the Campania Region has resulted in the widely documented illegal disposal of urban, toxic and industrial wastes [14, 15]. In recent years, the Campania region was involved in some environmental emergencies: illegal dumping and burning of toxic waste. These events caused a trend reversal and this area has renamed as "Land of Fire" (Fig. 1). In many cases, the piled of waste, illegally dumped in the countryside or by the roadside, are set on fire, releasing smoke full of toxic substances and many PAHs are generated [14, 16]. The environmental impacts of illegal waste disposal led to the deterioration of land, as well as ground and surface water, also impacting air quality. In this regard, Senior and Mazza in the journal *The Lancet Oncology* used the term "Triangle of Death" for the first time referring to this eastern area of the Campania Region [17].

The "Land of Fires" is crossed by the Volturno River (Fig. 1), which is the longest river in Southern Italy because of its length and its water flow; it runs for 175 km to the mouth in Castel Volturno, where it flows in Central Mediterranean Sea [18, 19].

The input pathways of PAHs into aquatic environment include discharge of industrial wastewater and domestic sewage, runoff from non-point sources, atmospheric deposition, and direct dumping of wastes. Water could constitute a direct measure of the degree of aquatic environment. Sediments are natural sinks and environmental reservoirs for PAHs in the aquatic environment and they offer an irreplaceable aid in reconstructing the input and pollution of PAHs. Due to the high persistence, PAHs can accumulate and remain in the sediment for very long periods of time and may be a source of contaminants to aquatic biota. Therefore, PAHs pollution in coastal and estuarine areas became object of studies since they are exposed to a large amount of terrestrial drainage pollution, which could possibly pose a substantial danger to the biological resources [20, 21].

This study goal is reporting data concerning PAHs drainage contamination into the Volturno River and its impact on the Tyrrhenian Sea (Central Mediterranean Sea). Also, the ecosystem health risk and the PAHs spatial and seasonal distribution in samples of water and sediment was assessed in this water body. One of the key aims of this study is to assess the PAHs as indicators of pollution, by identifying the main sources from which these pollutants originate. To the best of our knowledge, no previous studies estimate the PAHs input into the Central Mediterranean Sea from Volturno River.

2. Materials And Methods

2.1. Sampling

In this paper, four sampling campaigns were conducted in the summer, autumn, winter and spring of 2017–2018, with the purpose of to assess changing trends of the contaminant in time. Every campaign consisted of 10 locations sampling: one location was sampled at the river mouth in order to have a proper

idea of the evolution of the pollution downriver and nine points were sampled in the continental shelf around the Volturno mouth in order to estimate the impact of the Volturno River pollution on the Mediterranean Sea environment. The first three sites to undergo sampling were 500mt away from the Volturno Estuary, further sampling was executed on three locations 1000mt away from the river mouth and, lastly, the final three samples were gathered 1500mt away (Fig. 1). Sampling coordinates are stated in Table 1.

Table 1

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

Sampling Location			ΣPAHs								
Site Number Identification	Site Characteristics	Site Location	Dissolved Phase (ng L ⁻¹)				Particulate Phase (ng L ⁻¹) (ng g ⁻¹ dry wt)				Sediments (ng g ⁻¹ dry wt)
			Apr	Jul	Nov	Feb	Apr	Jul	Nov	Feb	Apr
1 (river water)	Volturno River Source	40°48'54.03' 'N 14°36'45.36' 'E	919.8	1429.1	865.1	318.1	401.1 (49334.1)	257.1 (26324.6)	243.8 (21499.3)	444.9 (155032)	872.1
2 (sea water)	River Mouth at 500mt North	40°46'42.73' 'N 14°34'00.48' 'E	604.0	987.5	571.1	197.8	332.3 (35892.9)	221.8 (118021.2)	183.3 (5907.4)	381.0 (3253.1)	637.2
3 (sea water)	River Mouth at 500mt Central	40°46'00.34' 'N 14°33'10.68' 'E	726.9	1020.9	708.8	329.4	372.3 (94015.7)	225.1 (79558.8)	214.5 (68758.0)	400.9 (134546)	777.5
4 (sea water)	River Mouth at 500mt South	40°43'42.62' 'N 14°28'07.89' 'E	783.3	1246.2	813.3	332.4	387.9 (38000.5)	241.8 (226017.2)	225.0 (6516.6)	417.2 (3902.2)	822.2
5 (sea water)	River Mouth at 1000mt North	40°43'40.11' 'N 14°28'06.45' 'E	496.6	797.4	436.2	120.8	243.9 (32792.5)	194.3 (13512.9)	167.2 (12661.5)	267.7 (2644.7)	514.1
6 (sea water)	River Mouth at 1000mt Central	40°43'42.46' 'N 14°28'05.03' 'E	627.3	923.6	548.9	248.1	328.7 (114934.8)	214.7 (71336)	193.2 (67336.9)	361.1 (118028)	686.5
7 (sea water)	River Mouth at 1000mt South	40°43'45.09' 'N 14°28'05.17' 'E	602.7	1111.2	611.5	262.1	361.7 (41484.5)	218.7 (14888.4)	185.7 (9221.1)	351.7 (2946.8)	640.1
8 (sea water)	River Mouth at 1500mt North	40°43'35.68' 'N 14°28'02.94' 'E	375.4	612.4	295.2	64.3	204.2 (20348.5)	179.0 (10706.3)	149.3 (7564.9)	192.3 (60683.0)	434.8
9 (sea water)	River Mouth at 1500mt Central	40°43'42.25' 'N 14°27'59.97' 'E	482.8	831.7	445.3	174.9	268.6 (86952.9)	197.9 (66193.6)	169.5 (60767.3)	269.1 (91871)	560.4
10 (sea water)	River Mouth at 1500mt South	40°43'49.26' 'N 14°27'59.82' 'E	545.8	911.9	519.5	206.0	275.0 (97525.2)	194.1 (16159.0)	173.1 (4485.7)	277.9 (97859.7)	646.3

In each sampling site two amber bottles of water (consisting of 2.5 litres) were collected and brought back to the laboratory while refrigerated (4 °C). Samples of surface sediment (0–5 cm) were gathered through a grab sampler (Van Veen Bodemhappe 2 L capacity) and conserved in aluminum box. Sediments samples were refrigerated all through transfer to the laboratory and preserved at -20 °C until analysis.

2.2. Sample cleanup and analysis

The procedure employed for extraction and cleanup has been published before and opportunely modified [22]. Water samples were shortly filtered through a GF/F glass fiber filter (47 mm x 0.7 µm; Whatman, Maidstone, UK) which had been previously kiln-fired at 400 °C overnight. Filters (suspended particulate matter, SPM) were preserved at -20 °C in the dark until analysis. The portion of pollutants passing through the filter (DP, dissolved phase) was extracted in the same day of sampling (3–6 h from sampling) after being conserved at 4 °C in the darkness.

The dissolved phase was examined by liquid-liquid extraction procedure. One 2 L separatory funnel was loaded with water sample and was spiked with a surrogate solution of benzo[a]pyrene-*d*₁₂ and indeno[1,2,3-cd] pyrene-*d*₁₂ in methanol obtaining a final concentration in water of 10 ng L⁻¹. Have been added 50 mL of dichloromethane (VWR, Radnor, Pennsylvania, USA) to the 2 L separatory funnel and it was extracted the sample by stirring the funnel for 3 minutes with periodic venting to discharge excess pressure. The organic layer was left to rest to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers was more than one-third the volume of the solvent layer, has been added a few mL of saturated sodium chloride solution, has been shaken and waited a few minutes. At the end of the last filtration the sample has been connected to the rotary evaporator and concentrate to 2 mL. The extract has been transferred to a 4 mL vial and evaporate until dry under a gentle nitrogen flow. To continue by adding 0.5 mL of hexane with internal standard chrysene-*d*₁₂.

Sediments were oven dried at 60 °C and sieved at 250 µm. Then, 5 g of sediment were spiked with the surrogate mixture (10 ng of benzo[a]pyrene-*d*₁₂ and indeno[1,2,3-cd] pyrene-*d*₁₂) and extracted three times by sonication using 15 mL of dichloromethane/methanol (1:1) (VWR) for 15 min. After centrifuging, the organic extract has been analyzed in the same way than the water samples.

2.3. Instrumental analysis

PAHs were quantified by GC-MS QP2010 Plus Shimadzu (Kyoto, Japan), equipped with a AOC-20i Shimadzu (Kyoto, Japan) autosampler, operating in the electron impact mode at 70 eV. A Rxi 5Sil MS capillary column (5% phenyl 95% dimethylpolysiloxane) (30 m, 0.25 mm ID and 0.10 µm of film thickness) was used. The column temperature was programmed as follows: first, heated to 60 °C and held for 2 min; ramped to 200 at 25 °C min⁻¹; then ramped to 270 at 10 °C min⁻¹ and held for 6 min; and finally ramped to 310 at 25 °C min⁻¹ and held for 10 min. Helium was used as carrier gas. The injection port temperature was 300 °C and it was operated in pulsed splitless mode. Acquisition was carried out in the single ion monitoring mode (SIM) using two characteristic ions for each target analyte. Target analytes were identified and verified by comparing retention times of the samples 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) and were quantified using the internal using the characteristic ions and their ratio for each target analyte.

The concentration was calculated from the calibration curves for the 16 PAHs (Dr. Ehrenstorfer GmbH, Augsburg, Germany) (*r*² > 0.98). Crisene-*d*₁₂ 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) [23] as priority pollutants were measured: naphthalene (Nap), acenaphthylene (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 (InP). Moreover, perylene (Per), not included in this list, also were monitored. Total PAHs concentration were calculated as the sum of the concentrations of the 16 PAHs compounds (ΣPAHs) selected by the USEPA as priority pollutants.

2.4. 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 mean surrogate recoveries in the dissolved phase were 92.8 ± 5.2% for benzo[a]pyrene-*d*₁₂ and 99.6 ± 4.5% for indeno[1,2,3-cd] pyrene-*d*₁₂. In the SPM samples, recoveries were 99.3 ± 4.1% for benzo[a]pyrene-*d*₁₂ and 98.6 ± 3.6% for indeno[1,2,3-cd] pyrene-*d*₁₂. Finally, in the sediment samples the averaged recoveries were the following: 99.6 ± 3.9% for benzo[a]pyrene-*d*₁₂ and 98.1 ± 3.7% for indeno[1,2,3-cd] pyrene-*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 and sediment 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) was in the range of 0.02 ng L⁻¹ – 0.15 ng L⁻¹ in dissolved water samples, 0.06–0.3 ng L⁻¹ in SPM samples and 0.03 to 0.2 ng g⁻¹ in sediment samples. Reported concentrations were corrected by surrogate recoveries.

2.5. Statistical analysis and calculation of PAHs inputs

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

The method used to estimate the annual contaminant discharges (*F*_{annual}) was based on the UNEP guidelines [24] and has been widely accepted [25–27]. 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:

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

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

where C_i and Q_i are the instantaneous concentration and water flow discharge, calculated by means of a daily averaged water flow, respectively for each sampling event. Q_T represents the total river discharge for the period considered (November 2017 – July 2018), calculated by adding the monthly averaged water flow [28, 29, 30]. River flow data was collected from the register of the Autorità di Bacino Nazionale dei Fiumi Liri-Garigliano e Volturno to <http://www.ildistrettoidrograficodellappenninomeridionale.it> (Abruzzo, Basilicata, Calabria, Campania, Lazio, Molise, Puglia 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.

Principal component analysis (PCA) is a useful technique that allows to reduce the dimensionality of a data set (sample) by finding a new set of variables, smaller than the original set of variables, that nonetheless retains most of the sample's information [31, 32], like the sample's variation, originated from the correlations between the initial variables. It tries to preserve the essential parts that have more variation of the data and remove the non-essential parts with fewer variation. These new variables, called principal components (PCs), are not correlated, and are ordered by the fraction of the entirety of the information each retains. There are three main methods used in order to determine the optimal number of components [33, 34, 35] in a principal component model (Amount of explained variance, Cattell's scree test and Kaiser's eigenvalue greater than 1.0 rule). In order to enhance the interpretation of the results of the PCA, it is possible to rotate the axes to reduce the dimensions or cover the maximum variation. Rotation is done so that the first axis contains as much variation as possible, the second axis contains as much of the remaining variation and so on. Change of coordinates used in principal component analysis (PCA) is known as Varimax rotation. It maximizes the sum of the variances of the squared loadings as all the coefficients will be either large or near zero, with few intermediate values. The goal is to associate each variable to at most one factor. The interpretation of the results of the PCA will be simplified. In order to analyse in depth the pollution of PAHs affecting the Volturno River and its environmental impact on the Tyrrhenian Sea, principal component analysis has been conducted on a dataset obtained on dissolved phase and suspended particulate matter. In each analysis, 17 PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b) fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Indeno(1,2,3,c,d)pyrene, Dibenz(a,h)anthracene and Perylene) have been taken into account.

3. Results And Discussion

3.1. PAHs concentrations in water dissolved phase

The concentrations in the water dissolved phase (DP) of total PAHs detected at 10 locations of the Volturno River and its Estuary, during the four campaigns, ranged from 64.3 (site 8) to 1429.1 (site 1) ng L^{-1} with a mean value of $602.6 \pm 319.3 \text{ ng L}^{-1}$ (Table 1). These values ranged from 3.44 to 174.4 ng L^{-1} with a mean value of $58.4 \pm 39.5 \text{ ng L}^{-1}$ for 2-ring PAHs (Nap), from 19.9 to 805.1 ng L^{-1} for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 12.7 to 244.1 ng L^{-1} for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 9.48 to 151.1 ng L^{-1} for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 17.6 to 74.6 ng L^{-1} for 6-ring PAHs (BghiP, InP). The compositional profiles of PAH in the dissolved phase, which indicate that 2- and 3-ring PAHs were abundant in all sampling sites, representing on average over 62% of all PAHs. In addition, the suspected carcinogenic 5–6-ring PAHs was present in low concentrations, accounting for only 17% of total PAHs. The prevalence of low molecular weight PAHs (2–3-ring) in the water could be explained by their high water solubility and relatively high vapor pressures [36, 37, 38]. Compared with the water of polluted rivers in other parts of the world (Table 2), the concentration of Σ PAHs in the the Volturno River dissolved phase ($64.3\text{-}1429.1 \text{ ng L}^{-1}$) was much higher than those found in the Xijiang River, China by Deng et al. [39], in the Yellow River (China) by Li et al. [40], in the Songhua River (China) by Ma et al. [41], in the Wyre River, England by Moeckel et al. [42], in the Elbe and Weser Rivers, Germany by Siemers et al. [43], in the Marseilles coastal area, France by Guigue et al. [44] and in the Tiber River (Italy) by Patrolecco et al. [45] and Montuori et al. [22]; these levels were however lower than those found in the Daliao River, China by et al. [46], in the Yellow River (China) by Zhao et al. [47], in the Songhua River (China) by Zhao et al. [48], in the Daliao River estuary (China) by Zheng et al. [49], in the Gomti River, India by Malik et al. [50], in the Cauca River, Colombia by Sarria-Villa et al. [8], in the Almendares River, Cuba by Santana et al. [51] and in the Buffalo River estuary, South Africa by Adeniji et al. [52]. Based on these results, the levels of PAHs in the dissolved phase in the Volturno River are comparable to those found in the Henan Reach of Yellow River, China by Sun et al. [53], in the Gulf of Tunis, Tunisia by Mzoughi and Chouba [54], in the Danube River, Hungary by Nagy et al. [55] and in the Sarno River by Montuori and Triassi [22].

Table 2

Concentration ranges and mean value of PAHs in the water dissolved phase (DP), suspended particulate matter (SPM) and sediments from recent studies of different rivers, estuaries and coasts in the world.

Area	References	Number PAHs	Range Σ PAHs	Mean Σ PAHs
Water (ng L ⁻¹)				
Xijiang River, China	Deng et al. [39]	15	21.7–138.0	-
Yellow River, China	Li et al. [40]	15	179.0-369.0	248.2
Daliao River, China	Guo et al. [46]	18	570.2-2318.6	-
Henan Reach of Yellow River, China	Sun et al. [53]	16	144.3–2361.0	662.0
Songhua River, China	Ma et al. [41]	15	14.0-161.0	33.9
Yellow River, China	Zhao et al. [47]	16	548.0-2598.0	1375.0
Songhua River, China	Zhao et al. [48]	16	163.5-2746.2	934.6
Daliao River estuary, China	Zheng et al. [49]	16	71.1-4255.4	748.8
Gomti River, India	Malik et al. [50]	16	60-84210.0	10330.0
Cauca River, Colombia	Sarria-Villa et al. [8]	12	52.1-12888.2	2344.5
Almendares River, Cuba	Santana et al. [51]	14	836.0-15811.0	2512.0
Buffalo River Estuary, South Africa	Adeniji et al. [52]	16	ND-24910	-
Gulf of Tunis, Tunisia	Mzoughi and Chouba [54]	22	139.2-1008.3	-
Wyre River, England	Moeckel et al. [42]	28	2.7–20.0	-
Elbe and Weser Rivers, Germany	Siemers et al. [43]	16	10.0–40.0	-
Marseilles coastal area, France	Guigue et al. [44]	32	8.1–405.0	-
Danube River, Hungary	Nagy et al. [55]	16	25.0-1208.0	122.6
Tiber River, Italy	Patrolecco et al. [45]	6	23.9–72.0	43.4
Tiber River, Italy	Montuori et al. [30]	17	1.75-607.48	90.46
Sarno River, Italy	Montuori and Triassi [22]	17	12.4-2321.1	739
SPM (ng L ⁻¹)				
Xijiang River, China	Deng et al. [39]	15	1.4–58.1	29.8
Yellow River, China	Li et al. [40]	13	54.0-155.0*	-
Daliao River, China	Guo et al. [46]	18	151.0-28483.8	-
Henan Reach of Yellow River, China	Sun et al. [53]	16	506.6-10510.0*	4100.0*
Songhua River, China	Ma et al. [41]	15	9.21–83.1	26.4
Yellow River, China	Zhao et al. [47]	16	1502.0-11562.0*	5591.0*
Daliao River estuary, China	Zheng et al. [49]	16	1969.9-11612.2	4015.7
Gulf of Mexico, Mexico	Adhikari et al. [21]	43	0.9-7.0	3.2
Gulf of Tunis, Tunisia	Mzoughi and Chouba [54]	22	909.9-8222.4*	-
Tiber River, Italy	Patrolecco et al. [45]	6	37.6–353.0	
Tiber River, Italy	Montuori et al. [30]	17	4.53-473.39	111.51
Sarno River, Italy	Montuori and Triassi [22]	17	6.1-778.9	-
Sediment (ng g ⁻¹)				
East China Sea, China	Zhao et al. [62]	16	57.5-364.5	166.2
Yellow River, China	Li et al. [40]	13	31.0-133.0	76.8
Daliao River, China	Guo et al. [46]	18	102.9-3419.2	-

* ng/g

ND: not detectable

Area	References	Number PAHs	Range Σ PAHs	Mean Σ PAHs
Henan Reach of Yellow River, China	Sun et al. [53]	16	16.4–1358.0	182.0
Yellow River, China	Zhao et al. [47]	16	181.0-1583.0	810.0
Bohai Bay, China	Li et al. [58]	16	24.6-280.6	79.3
Yellow River Estuary, China	Liu et al. [63]	15	89.5–208.0	140.5
Erjien River, Taiwan	Wang et al. [59]	16	22.0-28622.0	737.0
Caspian sea coast, India	Yancheshmeh et al. [68]	23	1294.0-9009.0	3228.0
Baffin Bay, Canada	Foster et al. [69]	66	341.0-2693.0	-
Cocó and Ceará Rivers, Brazil	Cavalcante et al. [70]	17	3.0-2234.8	-
Ibirité Reservoir, Brazil	Mozeto et al. [64]	16	79.8-219.9	129.5
Tampa Bay, Florida	Lewis and Russell [65]	16	1.7-147.9	18.0
Bahia Blanca Estuary, Argentina	Oliva et al. [10]	17	19.7-30054.5	1798.5
Gulf of Mexico, Mexico	Adhikari et al. [21]	43	70–162	120
Cauca River, Colombia	Sarria-Villa et al. [8]	12	ND-3739.0	1028.0
Buffalo River Estuary, South Africa	Adeniji et al. [52]	16	ND-7792	-
Yellow Sea, China	Li et al. [58]	16	148.3-907.5	548.6
Ammer River, Germany	Liu et al. [9]	16	112.0-22900.0	8770.0
Portimão Harbor, Portugal	Bebianno et al. [71]	16	218.0-1690.0	-
Danube River, Hungary	Nagy et al. [55]	16	8.3-1202.5	170.0
Gulf of Tunis, Tunisia	Mzoughi and Chouba [54]	22	363.3-7026.4	-
Durance River, France	Kanzari et al. [73]	16	57.0-1528.0	-
Huveaune River, France	Kanzari et al. [72]	16	571.7-4234.9	1966.00
Iberian coast, Spain	León et al. [74]	13	5.3-2627.4	-
Ría de Arousa, Spain	Peréz-Fernández et al. [6]	35	45.0-7901.0	-
Marano and Grado Lagoon, Italy	Acquavita et al. [60]	16	50.0-1026.0	-
Italian Marine Protected Areas, Italy	Perra et al. [66]	16	0.7–1550.0	155.3
Gulf of Trieste, Italy	Bajt [75]	16	214.0-4416.0	-
Priolo Bay, Italy	Di Leonardo et al. [61]	18	56.4-847.1	-
Tiber River, Italy	Patrolecco et al. [45]	6	157.8-271.6	215.2
Tiber River, Italy	Minissi et al. [67]	13	4.5-652.2	-
Tiber River, Italy	Montuori et al. [30]	17	36.21–545.60	155.26
Sarno River, Italy	Montuori and Triassi [22]	17	5.5-678.6	266.9
<i>This study</i>	<i>DP</i>	17	64.3-1429.1	602.6 ± 319.3
	<i>SPM</i>		143.3-444.9	264.7 ± 83.3
	<i>Sediment</i>		434.8-872.1	659.1 ± 136.9
<i>* ng/g</i>				
<i>ND: not detectable</i>				

3.2. PAHs concentrations in suspended particulate matter

The concentrations of PAHs in the suspended particulate matter (SPM) samples range from 149.3 ng L⁻¹ in site 8 to 444.9 ng L⁻¹ in site 1 (mean value of 264.7 ± 83.3 ng L⁻¹), as shown in Table 1. The concentrations of PAHs detected ranged from 4.05 to 38.9 ng L⁻¹ with a mean value of 15.1 ± 8.1 ng L⁻¹ for 2-ring PAHs (Nap), from 51.8 to 154.1 ng L⁻¹ for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 39.6 to 181.0 ng L⁻¹ for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 26.5 to 103.1 ng L⁻¹ for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 17.8 to 66.6 ng L⁻¹ for 6-ring PAHs (BghiP, InP). The compositional profiles of PAHs in SPMs show that 4-, 5-, 6-ring PAHs were abundant at most sampling sites, accounting for 25%, 20%, and 12% of Σ PAHs in SPMs, respectively.

The proportion of high molecular weight PAHs increased to 57%, much above than in dissolved samples, where it was 38%. The results indicated that high molecular weight PAHs were preferentially sorbed by the particulate matter due to its high hydrophobicity and hardly biodegraded, in agreement with the PAHs partition theory [45, 54, 47]. 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 of high-ring compounds in their SPM partitioning (average value of 0.80, 0.96 and 1.00 respectively for 4-, 5-, 6-ring PAHs).

Compared with other polluted rivers in the world (Table 2), PAHs in SPMs from the Volturno River were much higher than those detected in the Xijiang River and Yellow River, China by Deng et al. [39] and Li et al. [40] respectively, in the Henan Reach of Yellow River (China) by Sun et al. [53], in the Songhua River (China) by Ma et al. [41], in the Yellow River (China) by Zhao et al. [47], in the Gulf of Mexico, Mexico by Adhikari et al. [21] and in the Gulf of Tunis, Tunisia by Mzoughi and Chouba [54], but lower than those found in the Daliao River estuary, China by Guo et al and Zheng et al. [46, 49] respectively and in the Sarno River by Montuori and Triassi [22].

3.3. PAHs concentrations in sediments

The concentrations of total PAHs in sediment samples are illustrated in Table 1. Results range from 434.8 (site 8) to 872.1 (site 1) ng g^{-1} with a mean value of $659.1 \pm 136.9 \text{ ng g}^{-1}$. The concentrations detected ranged from 5.29 to 73.7 ng g^{-1} with a mean value of $24.1 \pm 27.5 \text{ ng g}^{-1}$ for 2-ring PAHs (Nap), from 42.9 to 186.3 ng g^{-1} for 3-ring PAHs (Acy, Ace, Flu, Phe, An), from 61.7 to 199.7 ng g^{-1} for 4-ring PAHs (Fl, Pyr, BaA, Chr), from 262.7 to 507.1 ng g^{-1} for 5-ring PAHs (BbF, BkF, BaP, DahA) and from 17.5 to 133.2 ng g^{-1} for 6-ring PAHs (BghiP, InP). As to the compositional profiles of PAH in sediments at each sampling sites, 4- and 5-ring PAHs were abundant at most sites, accounting for 37% and 40% of Σ PAHs in sediments, respectively. Low molecular weight PAHs were gradually decrease by dilution 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 behavior; thus, they were more resistant to degradation [56, 57, 38].

In comparison with polluted rivers in other parts of the world (Table 2), the concentration of Σ PAHs in the samples of sediment from the Volturno River and its Estuary ($434.8\text{--}872.1 \text{ ng g}^{-1}$) was similar to those found in the Yellow River and Yellow Sea, China by Zhao et al. [47] and Li et al. [58] respectively, in the Erjien River, Taiwan by Wang et al. [59], in the Marano and Grado Lagoon and Priolo Bay, Italy by Acquavita et al. [60] and Di Leonardo et al. [61] respectively. The concentration of Σ PAHs in the samples of sediment from the Volturno River and its river mouth was greater than the concentration found in the East China Sea, China by Zhao et al. [62], in the Yellow River and in the Henan Reach of Yellow River, China by Li et al. [40] and Sun et al. [53] respectively, in the Yangtze River Estuary (China) by Liu et al. [63], in the Bohai Bay (China) by Li et al. [57], in the Ibirité Reservoir, Brazil by Mozeto et al. [64], in the Tampa Bay, Florida by Lewis and Russel [65], in the Gulf of Mexico, Mexico by Adhikari et al. [21], in the Danube River, Hungary by Nagy et al. [55] and in Italy, in the Italian Marine Protected Areas by Perra et al. [66], in the Tiber River by Patrolecco et al. [45], Minissi et al. [67] and Montuori et al. [30], and in the Sarno River by Montuori and Triassi [22]. The concentration of Σ PAHs in the samples of sediment from the Volturno River and river mouth was inferior than the concentration found in the Daliao River, China by Guo et al. [46], in the Caspian sea coast, India by Yancheshmeh et al. [68], in the Baffin Bay, Canada by Foster et al. [69], in the Cocó and Ceará Rivers, Brazil by Cavalcante et al. [70], in the Bahia Blanca Estuary, Argentina by Oliva et al. [10], in the Cauca River, Colombia by Sarria-Villa et al. [8], in the Buffalo River Estuary, South Africa by Adeniji et al. [52], in the Ammer River, Germany by Liu et al. [9], in the Portimão Harbor, Portugal by Bebianno et al. [71], in the Gulf of Tunis, Tunisia by Mzoughi and Chouba [54], in Durance River and Huveaune River, France by Kanzari et al. [72, 73] and in the Iberian coast and Ría de Arousa, Spain by Leòn et al. [74] and Peréz-Fernández et al. [6] respectively and in the Gulf of Trieste, Italy by Bajt [75]. The low concentrations of PAHs in sediments may be due to the high content of sand and low TOC contents ($1.1\text{--}9.5 \text{ mg g}^{-1}$, mean 5.1). Figure 2 showed the relationship between %TOC with the Σ PAHs in the sediment samples. As results showed, a positive linear regression exists between total PAH concentration and TOC data in sediments ($r = 0.97$, $p < 0.01$) as indicated by many other studies [46, 53, 8].

3.4. PAHs seasonal and spatial distribution in DP, SPM and sediment samples

The concentrations of total PAHs in DP, SPM and sediment samples of the Volturno River at different sampling sites are illustrated in Table 1. The results show that the ratio of the concentration of Σ PAHs in DP samples to that in SPM was higher than one in all sites (average 2.5; $\text{SD} \pm 1.5$). 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. These data were also confirmed by the analysis of the ratio of the individual PAHs, and it was possible to observe the same trend obtained from the reports of the sums.

Even the total amount of PAHs in SPM samples was more abundant than in sediment samples for each sampling site. In fact, 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 (average 0.014; range 0.006–0.022; $\text{SD} \pm 0.006$). In particular, the results indicate that PAHs concentrations in DP were low during the wet season floods (February) and high during the dry season (July). The seasonal variation of PAHs concentrations was depending to the hydrological conditions, which could cause dilution ratio variations. Therefore, a high river flow rate resulted in a higher dilution ratio in the wet season floods caused a decrease in the PAHs concentration in both the Volturno River and its estuary. In July, the concentrations of total PAHs in SPM samples were lowest in all sampling sites. The results could be explained by the flow decrease during the dry season that a greater stagnation of SPM determining 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 Volturno were related to a variation in the flow during rainy and dry seasons. Therefore, high concentration of PAHs in SPMs but moderate in sediment indicated that the contamination of PAHs in Volturno River and Estuary might be caused by fresh input of PAHs.

In order to evaluate the huge input of PAHs drained from storm water runoff, tributary inflow, wastewater treatment plant and industrial effluent discharge, agricultural runoff, atmospheric deposition, dredged material disposal, the total load of PAHs into the Tyrrhenian Sea was calculated. The total PAHs loads contribution to the Tyrrhenian Sea from the Volturno River is calculated in about 3.158,2 kg/year.

The spatial distribution of PAHs in DP, SPM and sediment samples from the Volturno River and its estuary were studied by comparing the concentrations of ΣPAHs in different sampling sites in dry and rainy seasons, respectively (Fig. 3). Indeed, the level of contamination of PAHs in the water clearly decrease from location 1 to 4. The total PAHs concentrations decreased to 1219.8 ng L⁻¹ (DP + SPM mean values of four seasons) at location 1 (Volturno River Mouth) to 993.8 ng L⁻¹ (DP + SPM mean values of four seasons) at location 2 (500 m from the Mouth) to 823.0 ng L⁻¹ (DP + SPM mean values of four seasons) at location 3 (1000 m from the Mouth) and to 668.0 ng L⁻¹ (DP + SPM mean values of four seasons) at location 4 (1500 m from the Mouth). In the Tyrrhenian Sea, PAHs concentrations range in general from very high in the vicinity of the river outflows to very low in offshore areas (Fig. 3). At 500 m of river outflow, the concentration of PAHs were close to those of the Volturno mouth (Fig. 3). The concentrations at the sampling sites then decreased at 1000m and more at 1500m of the river outflows. Particularly, at the Volturno mouth the PAHs loads move into the Tyrrhenian sea southward (Fig. 3). As can be seen from the data obtained, the trend concentrations shows a decreasing movement from the mouth towards 1500m at sea. This can depend both on the flow of the river which varies according to the season, and on the diluting effect of the sea.

3.5. Source identification

To investigate the origin of PAHs and identify separately petrogenic from pyrolytic inputs, chemical profiling and different diagnostic ratios on isomeric relations were used: An/(An + Phe), Fl/(Fl + Pyr), BaA/(BaA + Chr) and InP/(InP + BghiP) [13, 76]. The first group is from pyrolytic sources, which includes combustion of fossil fuels, vehicles using gasoline or diesel fuel, waste incineration and coke production, carbon black, coal tar pitch, asphalt and petroleum cracking. The second group is from petrogenic sources, which include crude oil and petrochemicals (gasoline, diesel fuel, kerosene and lubricating oil). Finally, apart from pyrolytic or petrogenic source, PAHs can be formed during diagenetic processes, i.e. the formation of sediments from organic material [6]. 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 [9, 10, 11].

The ratio study reflected a prevailing pattern of pyrolytic inputs of PAHs in the Volturno River and its estuary. In fact, the results showed that An/(An + Phe) ratio was 0.1 in DP, SPM and sediments (mean 0.42, 0.40 and 0.47, respectively), which attributed the origin of PAHs to pyrogenic sources. Furthermore, Fl/(Fl + Pyr) ratios can distinguish petroleum input from combustion processes and discriminate among such sources [13, 77]. For Fl/(Fl + Pyr), low ratios (< 0.40) indicate petroleum, intermediate ratios (0.40–0.50) of liquid fossil fuel combustion, whereas ratios > 0.50 are characteristic of grass, wood, or coal combustion. In the Volturno River and Estuary, ratio Fl/(Fl + Pyr) 0.5 was found to water, particulate matter and sediments, indicating a variable impact urban traffic emissions and from biomass burning (Fig. 4a). Ratio BaA/(BaA + Chr) 0.35 was found in water and in sediments, which suggests vehicular emissions; and similar behavior it is observed for ratio InP/(InP + BghiP) 0.35, which indicates combustion sources (Fig. 4b). Finally, the LMW/HMW ratio was relatively low (< 1 for most sites), suggesting a pyrolytic origin of PAHs at these sites (mean 0.85; range 0.09–2.99).

These results, obtained by different molecular ratios, were correlated with the specific pollution conditions in the Volturno River. The Volturno flatland is a heavy industrial area, with many heavily polluting factories. In additions in the Campania Region has resulted in the widely documented illegal disposal of urban, toxic and industrial wastes. The industrial wastes enriched with combustion-derived PAHs are directly discharged into the Volturno River. Although none of the industries present in the the Volturno River area exceed the legal limits in terms of emissions to the atmosphere or industrial discharges as reported by the Piano Regione Campania, the emission of atmospheric particles from factories, could cause serious air pollution over time, and the particulate-associated PAHs may transport and deposit into the river over time. 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. About that, no other rivers in the area adjacent to that of the Volturno River has been considered with regard to the evaluation of the PAHs and for this reason valid comparisons can't currently be made. However, some rivers have been taken into consideration for the evaluation of the PAHs, even if they are at greater distances from Volturno River [22, 78, 30].

The Volturno flatland is a heavy industrial area, with many heavily polluting factories. In additions in the Campania Region has resulted in the widely documented illegal disposal of urban, toxic and industrial wastes. The industrial wastes enriched with combustion-derived PAHs are directly discharged into the Volturno River. The emission of atmospheric particles from factories, 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, Per is also produced by in situ degradation of biogenic precursors [12, 76, 6]. Indeed, Per is probably the most important diagenetic PAHs encountered in sedimentary environments and, thus, a high abundance of Per relative to other PAHs can indicate an important natural origin of the compound. Per has been frequently associated with inputs from rivers and estuaries [12, 68, 79]. In fact, it has been suggested that concentrations of Per above 10% of the total penta-aromatic isomers indicate a probable diagenetic input, whereas those in which Per accounts for less than 10% indicate a probable pyrolytic origin of the compound. In the present study, the concentrations of Per detected in all sediment samples were very low (range 4.3–15.5 ng g⁻¹) and contributed less than 2% to the penta-aromatic isomers, indicating a pyrolytic origin of these compounds.

3.6. A composite indicator for water pollution

In order to formalize a Water Pollution Composite Indicator (WP-CI) we analysis at the same time Dissolved phase (DP) and Suspended Particulate phase (SPM) samples collected from 10 sites ("Sou1", "500N2", "1000N3", "1500N4", "500C5", "1000C6", "1500C7", "500S8", "1000S9", "1500S10") during the months of April, July, November and February. The correlation matrix points out sets of correlated variables and only the first seven highest eigenvalue are larger than one. However, the first two components explain the 60,0% (32,6% and 27,4%, respectively) of the total variance. The PCA for this dataset pointed out a clear distinction of the pollution of the two phases and allowed us to define two SCIs (Specific Composite Indicator). In fact, the first factor is characterized by the presence of PAHs belonging to SPM and we named it "SPM-Composite Indicator"; the second factor is defined by the PAHs of the DP; the

second factor is called “DP - Composite Indicator”. Looking at the plot of the first two principal components, and making a correlation between sites and seasons we observe that the pollution from SPM is higher in February, in the sites 500N2, 1000C6, 1500C7, 1000S9, however DP pollution is higher in July at sites 1500C7 e 1500S10 (Fig. 5a and 5b). For each SCI is possible to rank the 40 statistical units and finally it is possible to observe the final ranking based on the WP-CI (Table 3). The site that has a lower rate of global pollution in all seasons of the year is the 4, followed by 3 and then 7. However, just in reference to site 7 there is an irregular behavior of the two parties. In fact, while in November both SPM and DP appear to have a low level of pollution, in other seasons the two components have contrasting behavior. The most polluted months are February and April especially for the SPM component, on the contrary, the least polluted months are July and November, in particular for the SPM component. The month of February, instead, has a tendency to lower pollution for the DP, on the contrary, July and April are the months most polluted. Based on these results, it can be confirmed that the load and relocate of PAHs between different phases in each sampling site of the Volturno were related to a variation in the flow during rainy and dry seasons.

Table 3

Rankings based on SCIs and WP-CI according to these thresholds, (1): normalized score > 0:60, (2): normalized score > 0:30 and < 0:60, (3): normalized score < 0:30.

	High Pollution												
	-												+
SPM Specific Composite Indicator	07-apr	10-apr	06-apr	05-apr	09-feb	06-feb	02-feb	01-apr	09-apr	05-feb	08-apr	08-feb	01-feb
DP Specific Composite Indicator	10-apr	09-apr	05-apr	01-apr	07-jul	02-jul	10-jul	08-apr	06-jul	05-jul	09-jul	01-jul	08-jul
WP Composite Indicator	07-apr	09-jul	06-apr	01-jul	10-apr	05-feb	08-jul	05-apr	08-feb	01-feb	01-apr	09-apr	08-apr

	Medium Pollution													
	-												+	
SPM Specific Composite Indicator	02-jul	05-jul	08-nov	05-nov	01-nov	02-apr	03-apr	06-jul	09-jul	01-jul	08-jul	03-feb	10-feb	07-feb
DP Specific Composite Indicator	10-nov	06-nov	08-feb	01-feb	02-nov	09-nov	04-jul	05-nov	02-apr	06-apr	07-apr	03-jul	08-nov	01-nov
WP Composite Indicator	03-feb	05-nov	10-feb	07-feb	10-jul	08-nov	02-apr	02-jul	01-nov	05-jul	09-feb	02-feb	06-feb	06-jul

	Low Pollution												
	-												+
SPM Specific Composite Indicator	04-jul	04-nov	03-nov	07-nov	10-nov	03-jul	07-jul	04-apr	04-feb	02-nov	09-nov	10-jul	06-nov
DP Specific Composite Indicator	04-feb	03-feb	07-feb	04-nov	10-feb	02-feb	04-apr	09-feb	06-feb	03-nov	07-nov	03-apr	05-feb
WP Composite Indicator	04-nov	03-nov	07-nov	04-feb	04-jul	04-apr	10-nov	03-jul	02-nov	09-nov	06-nov	07-jul	03-apr

3.7. Risk assessment

To evaluate the potential adverse effects caused by PAHs in the Volturno River were used the sediment quality guidelines (SQGs) values developed by [80] and by [81]. Sediment quality guidelines (SQGs) are an important tool for the assessment of contamination in marine and estuarine sediments. Two sets of SQGs, including the ERL/ERM and the TEL/PEL values, were applied in this study to assess the toxic effects of individual PAHs in sediments. These sets are defined as: i) effect range low (ERL)/effect range median (ERM) and ii) the threshold effect level (TEL)/probable effect level (PEL). ERLs and TELs represent chemical concentrations below which the probability of toxicity and other effects are rare. Differently, the ERMs and PELs represent mid-range above which adverse effects would occur frequently. ERLs-ERMs and TELs-PELs represent a possible-effects range, within which negative effects would occasionally occur [61, 82]. In the Volturno River, not all PAHs concentrations in sediment samples were below the TEL and ERL values, but the concentrations were significantly lower than the PEL and ERM values (Table 4).

Table 4

A comparison of the TEL, PEL, ERL and ERM guideline values ($\mu\text{g Kg}^{-1}$) for polycyclic aromatic hydrocarbons and data found in the Voltorno River, Southern Italy.

	PAHs																
	Nap	Acy	Ace	Flu	Phe	An	Fl	Pyr	BaA	Chr	BbF	BkF	BaP	DahA	BghiP	InP	Σ PAHs
TEL ^a	34.6	5.87	6.71	21.2	86.7	46.9	113	153	74.8	108	-	-	88.8	6.22	-	-	1684
Samples percentage over the TEL	30	100	100	30	0	0	0	0	0	0			80	100			0
PEL ^a	391	128	88.9	144	544	245	1494	1398	693	846	-	-	763	135	-	-	16770
Samples percentage over the PEL	0	0	0	0	0	0	0	0	0	0			0	10			0
ERL ^b	160	44	16	19	240	85	600	665	261	384	-	-	430	63.4	-	-	4022
Samples percentage over the ERL	0	0	70	30	0	0	0	0	0	0			0	100			0
ERM ^b	2100	640	500	540	1500	1100	5100	2600	1600	2800	-	-	1600	260	-	-	44792
Samples percentage over the ERM	0	0	0	0	0	0	0	0	0	0			0	0			0
^a MacDonald et al. [81].																	
^b Long et al. [80].																	

In relation to the individual compounds, the mean concentrations of detected PAHs were lower than their respective PEL values, while TEL values were exceeded for Acy, Ace and DahA for all samples, for Nap and Flu in 30%, and for BaP 80%, suggesting that adverse effects might occasionally occur. The concentrations of individual PAHs do not exceed their respective ERM values, but the ERL values exceeded for Flu in 30%, Ace in 70% and DahA for all samples. The results indicated that in certain sites PAHs may have been found and the environmental integrity was at risk of PAHs in the sediments from the Voltorno River and Estuary.

Although compliance with EC-EQS (European Commission - Environmental Quality Standards) in surface waters is checked using an annual average of monthly whole water (DP + SPM) concentrations (Directive 2008/105/EC, 2008) [83], our data showed that the mean values of BaP and BkF + BbF concentration in the Voltorno River (63.9 and 41.2 ng L^{-1} , respectively) were higher than the EQS values (50 and 30 ng L^{-1} , respectively), and mean value of BghiP + InP values (67.4 ng L^{-1}) was significantly higher than the EQS value of 2 ng L^{-1} , showing that the environmental integrity of the river watercourse was at risk. Also RQ (Risk Quotient), the ratio between the Measured Environmental Concentration (MEC) and the Predicted No Effect Concentrations (PNECs), has been calculated. OSPAR Commission, the mechanism by which 15 Governments and the EU cooperate to protect the marine environment of the North-East Atlantic, established a list of PNECs for several substances, including PAHs. In particular, in OSPAR Agreement 2014-05, in Table 2, Sect. 5, PNECs values were reported for single PAHs. According to these values, we calculated ratio between single MEC and PNEC for single PAHs. As result, we obtained, both for water (sum of DP + SPM) and sediment, an RQ > 1 for most compounds, confirming that the environmental integrity of the river watercourse was at risk.

4. Conclusions

This research is part of a larger project which brings forth fundamental data on the frequency, distribution and likely sources of PAHs in the Voltorno River and its input into the Tyrrhenian Sea (Central Mediterranean Sea), Southern Italy. Low molecular weight PAHs were abundantly present in water samples, while in sediment samples the predominant class were high molecular weight PAHs. The concentration levels of PAHs in DP, SPM and sediment phases were remarkably different amongst sampling sites. Contaminant discharges of PAHs into the sea showed that this river should account as one of the main contribution sources of PAHs to the Central Mediterranean Sea. A Water Pollution Composite Indicator (WP-CI) and individual diagnostic PAHs ratio revealed that the main PAHs source was pyrolytic and suggested that the majority of this pollution derived for the most part from vehicle traffic and combustion processes. Regarding the risk assessment, even if the concentration of many single PAHs in a number of stations were above ERL and/or TEL (and below ERM and/or PEL), which would on occasion yield negative environmental consequences, the EC-EQS (European Commission - Environmental Quality Standards) and the RQ (Risk Quotient) indicated that the integrity of this area is possibly at risk. Thus, the Voltorno River waters should be continuously kept under monitor as PAHs could lead to negative consequences on its aquatic ecosystems and organisms.

Abbreviations

PAHs: Polycyclic aromatic hydrocarbons; HMW: high molecular weight; LMW: low molecular weight; SPM: suspended particulate matter; DP: dissolved phase; SIM: single ion monitoring mode; USEPA: US Environmental Protection Agency; Nap: naphthalene; Acy: acenaphthylene; Ace: acenaphthene; Flu: fluorene; Phe: phenanthrene; An: anthracene; Fl: fluoranthene; Pyr: pyrene; BaA: benzo[a]anthracene; Chr: chrysene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BaP: benzo[a]pyrene; DahA: dibenzo[a,h]anthracene; BghiP: benzo[ghi]perylene; InP: indeno[1,2,3-cd]pyrene; Per: perylene; LOD: limit of detection; LOQ: limit of quantification; PCA: Principal component analysis; TOC: total organic carbon; WP-CI: Water Pollution Composite Indicator; SQGs: sediment quality guidelines; ERL: effect range low; ERM: Effect range median; TEL: Threshold effect level; PEL: Probable effect level; EQS: Environmental Quality Standards; RQ: Risk Quotient; MEC: Measured Environmental Concentration; PNECs: Predicted No Effect Concentrations; OSPAR: [Protection of the Marine Environment of the North-East Atlantic](#).

Declarations

Acknowledgements

Not applicable

Authors' contributions

P.M., A.N. and M.T. designed the research; P.M., E.D., F.D. and D.P.P. organized and carried out samplings and laboratory analyzes; P.S., P.M. and E.D. analyzed the data and performed the statistical analysis. All authors have discussed results and co-written the manuscript.

Funding

This study received no funds.

Availability of data and materials

The datasets obtained and analyzed in the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

References

1. Qin N, He W, Kong XZ, Liu WX, He QS, Yang B, Ouyang HL, Wang QM, Xu FL (2013) Ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the water from a large Chinese lake based on multiple indicators. *Ecol Indic* 24:599–608. <https://doi.org/10.1016/j.ecolind.2012.08.019>
2. Duodu GO, Ogogo KN, Mummullage S, Harden F, Goonetilleke A, Ayoko GA (2017) Source apportionment and risk assessment of PAHs in Brisbane River sediment, Australia. *Ecol Indic* 73:784–799. <https://doi.org/10.1016/j.chemosphere.2005.12.027>
3. Yu W, Liu R, Xu F, Shen Z (2015) Environmental risk assessments and spatial variations of polycyclic aromatic hydrocarbons in surface sediments in Yangtze River Estuary. *China Mar Pollut Bull* 100:507–515. <https://doi.org/10.1016/j.marpolbul.2015.09.004>
4. Wang D, Wang Y, Singh VP, Zhu J, Jiang L, Zenga D, Liu D, Zeng X, Wua J, Wang L, Zeng C (2018) Ecological and health risk assessment of PAHs, OCPs, and PCBs in Taihu Lake basin. *Ecol Indic* 92:171–180. <https://doi.org/10.1016/j.ecolind.2017.06.038>
5. Egres G, Hatje V, Miranda DA, Gallucci F, Barrosa F (2019) Functional response of tropical estuarine benthic assemblages to perturbation by Polycyclic Aromatic Hydrocarbons. *Ecol Indic* 96:229–240. <https://doi.org/10.1016/j.ecolind.2018.08.062>
6. Pérez-Fernández B, Viñas L, Franco M, Bargiela J (2015) PAHs in the Ría de Arousa (NW Spain): A consideration of PAHs sources and abundance. *Mar Pollut Bull* 95:155–165. <https://doi.org/10.1016/j.marpolbul.2015.04.028>
7. Singare PU (2015) Studies on polycyclic aromatic hydrocarbons in surface sediments of Mithi River near Mumbai, India: Assessment of sources, toxicity risk and biological impact. *Mar Pollut Bull* 101:232–242. <https://doi.org/10.1016/j.marpolbul.2015.09.057>
8. Sarria-Villa R, Ocampo-Duque W, Páez M, Schuhmacher M (2016) Presence of PAHs in water and sediments of the Colombian Cauca River during heavy rain episodes, and implications for risk assessment. *Sci Total Environ* 540:455–465. <https://doi.org/10.1016/j.scitotenv.2015.07.020>

9. Liu Y, Beckingham B, Ruegner H, Li Z, Ma L, Schwientek M, Xie H, Zhao J, Grathwohl P (2013) Comparison of sedimentary PAHs in the rivers of Ammer (Germany) and Liangtan (China): differences between early- and newly-industrialized countries. *Environ Sci Technol* 47:701–709. <https://doi.org/10.1021/es3031566>
10. Oliva AL, Quintas PY, La Colla NS, Arias AH, Marcovecchio JE (2015) Distribution, Sources, and Potential Ecotoxicological Risk of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Bahía Blanca Estuary, Argentina. *Arch Environ Contam Toxicol* 69:163–172. <https://doi.org/10.1007/s00244-015-0169-0>
11. Wu Y, Wang X, Li Y, Ya M, Luo H, Hong H (2015) Polybrominated diphenyl ethers, organochlorine pesticides, and polycyclic aromatic hydrocarbons in water from the Jiulong River Estuary, China: levels, distributions, influencing factors, and risk assessment. *Environ Sci Pollut Res* 24:8933–8945. <https://doi.org/10.1007/s11356-015-4782-2>
12. Baumard P, Budzinski H, Michon Q, Garrigues P, Burgeot T, Bellocq J (1998) Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuar Coast Shelf Sci* 47:77–90. <https://doi.org/10.1006/ecss.1998.0337>
13. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515. [https://doi.org/10.1016/S0146-6380\(02\)00002-5](https://doi.org/10.1016/S0146-6380(02)00002-5)
14. Legambiente. Rapporto Ecomafia - I numeri e le storie della criminalità ambientale Legambiente: Roma, Italy, 2007. Available at: http://www.amblav.it/download/0417_ecomafia_introduzione.pdf. (Accessed 31 March 2020)
15. D'Alisa G, Armiero M, De Rosa SP (2014) Political ecology: Rethink Campania's toxic-waste scandal. *Nature* 509:427. <http://doi.org/10.1038/509427d>
16. Esposito F, Nardone A, Fasano E, Scognamiglio G, Esposito D, Agrelli D, Ottaiano L, Fagnano M, Adamo P, Beccaloni E, Vanni F, Cirillo T (2018) A systematic risk characterization related to the dietary exposure of the population to potentially toxic elements through the ingestion of fruit and vegetables from a potentially contaminated area. A case study: the issue of the “Land of Fires” area in Campania region, Italy. *Environ Pollut* 243:1781–1790. <https://doi.org/10.1016/j.envpol.2018.09.058>
17. Senior K, Mazza A (2004) Italian “Triangle of death” linked to waste crisis. *The Lancet Oncol* 5:525–527. [https://doi.org/10.1016/S1470-2045\(04\)01561-X](https://doi.org/10.1016/S1470-2045(04)01561-X)
18. Isidori M, Lavorgna M, Nardelli A, Parrella A (2004) Integrated environmental assessment of Volturno River in South Italy. *Sci Total Environ* 327:123–134. <https://doi.org/10.1016/j.scitotenv.2004.01.021>
19. Triassi M, Nardone A, Giovinetti MC, De Rosa E, Canzanella S, Sarnacchiaro P, Montuori P (2019) Ecological risk and estimates of organophosphate pesticides loads into the Central Mediterranean Sea from Volturno River, the river of the “Land of Fires” area, southern Italy. *Sci Total Environ* 678:741–754. <https://doi.org/10.1016/j.scitotenv.2019.04.202>
20. Moreno M, Semprucci F, Vezzulli L, Balsamo M, Fabiano M, Albertelli G (2011) The use of nematodes in assessing ecological quality status in the Mediterranean coastal ecosystems. *Ecol Indic* 11:328–336. <https://doi.org/10.1016/j.ecolind.2010.05.011>
21. Adhikari PL, Mait K, Bam W (2019) Fate of particle-bound polycyclic aromatic hydrocarbons in the river influenced continental margin of the northern Gulf of Mexico. *Mar Pollut Bull* 141:350–362. <https://doi.org/10.1021/es960233j>
22. Montuori P, Triassi M (2012) Polycyclic aromatic hydrocarbons loads into the Mediterranean Sea: estimate of Sarno River inputs. *Mar Pollut Bull* 64:512–520. <https://doi.org/10.1016/j.marpolbul.2012.01.003>
23. USEPA (2012) (US Environmental Protection Agency). Regional screening levels for chemical contaminants at superfund sites. Regional Screening Table. User's Guide. Available at 31/03/2020 to: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2713671/>
24. UNEP/MAP (2004) Guidelines for river (including estuaries) pollution monitoring programme for the Mediterranean Region. MAP Technical Reports Series No. 151. UNEP/MAP, Athens
25. Walling DE, Webb BW (1985) Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. *Mar Pollut Bull* 16:488–492. [https://doi.org/10.1016/0025-326X\(85\)90382-0](https://doi.org/10.1016/0025-326X(85)90382-0)
26. HELCOM (1993) Second Baltic Sea Pollution Load Compilation. Baltic Sea Environment Proceedings No. 45, Baltic Marine Environment Protection Commission. Helsinki, Finland
27. Steen RJCA, van der Baart M, Hiep B, van Hattum WP, Cono WP, Brinkman UAT (2001) Gross fluxes and estuarine behaviour of pesticides in the Scheldt estuary (1995–1997). *Environ Pollut* 115:65–79. [https://doi.org/10.1016/S0269-7491\(01\)00085-9](https://doi.org/10.1016/S0269-7491(01)00085-9)
28. Gómez-Gutiérrez AI, Jover E, Bodineau L, Albaigés J, Bayona JM (2006) Organic contaminant loads into the Western Mediterranean Sea: estimate of Ebro River inputs. *Chemosphere* 65:224–236. <https://doi.org/10.1016/j.chemosphere.2006.02.058>
29. Montuori P, Aurino S, Nardone A, Cirillo T, Triassi M (2015) Spatial distribution and partitioning of organophosphates pesticide in water and sediment from Sarno River and Estuary, Southern Italy. *Environ. Sci. Pollut. Res. Int.* 22:8629–8642. <https://link.springer.com/article/10.1007%2Fs11356-014-4016-z>
30. Montuori P, Aurino S, Garzonio F, Sarnacchiaro P, Polichetti S, Nardone A, Triassi M (2016) Estimates of Tiber River organophosphate pesticide loads to the Tyrrhenian Sea and ecological risk. *Sci Total Environ* 559:218–231. <https://doi.org/10.1016/j.scitotenv.2016.03.156>
31. Pearson K (1901) On lines and planes of closest fit to systems of points in space. *Philosophical Magazine, Series 6, vol. 2, no. 11*, pp. 559–572
32. Hotelling H (1933) Analysis of a Complex of Statistical Variables Into Principal Components. *J Educ Psychol* 24:417–441 and 498–520. <https://doi.org/10.1037/h0071325>. pages .
33. Guttman L (1954) Some necessary conditions for common factor analysis. *Psychometrika* 19:149–161
34. Kaiser HF (1960) The application of electronic computers to factor analysis. *Educ Psychol Measur* 20:141–151. doi.org/10.1177/001316446002000116
35. Yeomans KA, Golder PA (1982) The Guttman-Kaiser Criterion as a Predictor of the Number of Common Factors. *J Roy Stat Soc* 31:221–229. <https://doi.org/10.2307/2987988>

36. Kim L, Jeon HJ, Kim YC, Yang SH, Choi H, Kim TO, Lee SE (2019) Monitoring polycyclic aromatic hydrocarbon concentrations and distributions in rice paddy soils from Gyeonggi-do, Ulsan, and Pohang. *Appl Biol Chem* 62:18–26. <https://doi.org/10.1186/s13765-019-0423-7>
37. Edokpayi JN, Odiyo JO, Popoola OE, Msagati TAM (2016) Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Sediments and Wastewater Effluents in Vhembe District, South Africa. *Int J Environ Res Public Health* 13:387–399. <https://doi.org/10.3390/ijerph13040387>
38. Zakaria MP, Mahat AA (2006) Distribution of polycyclic aromatic hydrocarbon (PAHs) in sediments in the Langat Estuary. *Agris.fao.org*
39. Deng H, Peng P, Huang W, Song J (2006) Distribution and loadings of polycyclic aromatic hydrocarbons in the Xijiang River in Guangdong. *South China Chemosphere* 64:1401–1411. <https://doi.org/10.1016/j.chemosphere.2005.12.027>
40. Li G, Xia X, Yang Z, Wang R, Voulvoulis N (2006) Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River. *China Environ Pollut* 144:985–993. <https://doi.org/10.1016/j.envpol.2006.01.047>
41. Ma WL, Liu LY, Qi H, Zhang ZF, Song WW, Shen JM, Chen ZL, Ren NQ, Grabuski J, Li YF (2013) Polycyclic aromatic hydrocarbons in water, sediment and soil of the Songhua River Basin, China. *Environ Monit Assess* 185:8399–8409. <https://doi.org/10.1007/s10661-013-3182-7>
42. Moeckel C, Monteith DT, Llewellyn NR, Henrys PA, Pereira MG (2013) Relationship between the concentrations of dissolved organic matter and polycyclic aromatic hydrocarbons in a typical U.K. upland stream. *Environ Sci Technol* 48:130–138. <https://doi.org/10.1021/es403707q>
43. Siemers AK, Mänz JS, Palm WU, Ruck WK (2015) Development and application of a simultaneous SPE-method for polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, heterocyclic PAHs (NSO-HET) and phenols in aqueous samples from German Rivers and the North Sea. *Chemosphere* 122:105–114. <https://doi.org/10.1016/j.chemosphere.2014.11.022>
44. Guigue C, Tedetti M, Ferretto N, Garcia N, Méjanelle L, Goutx M (2014) Spatial and seasonal variabilities of dissolved hydrocarbons in surface waters from the Northwestern Mediterranean Sea: results from one year intensive sampling. *Sci Total Environ* 466–467:650–662. <https://doi.org/10.1016/j.scitotenv.2013.07.082>
45. Patrolecco L, Ademollo N, Capri S, Pagnotta R, Polesello S (2010) Occurrence of priority hazardous PAHs in water, suspended particulate matter, sediment and common eels (*Anguilla anguilla*) in the urban stretch of the River Tiber (Italy). *Chemosphere* 81:1386–1392. <https://doi.org/10.1016/j.chemosphere.2010.09.027>
46. Guo W, He M, Yang Z, Lin C, Quan X, Men B (2009) Distribution, partitioning and sources of polycyclic aromatic hydrocarbons in Daliao River water system in dry season China. *J Hazard Mater* 164:1379–1385. <https://doi.org/10.1016/j.jhazmat.2008.09.083>
47. Zhao X, Qiu H, Zhao Y, Shen J, Chen Z, Chen J (2015) Distribution of polycyclic aromatic hydrocarbons in surface water from the upper reach of the Yellow River, Northwestern China. *Environ Sci Pollut Res Int* 22:6950–6956. <https://doi.org/10.1007/s11356-014-3846-z>
48. Zhao X, Ding J, You H (2014) Spatial distribution and temporal trends of polycyclic aromatic hydrocarbons (PAHs) in water and sediment from Songhua River. *China Environ Geochem Health* 36:131–143. <https://dx.doi.org/10.1007/s10653-013-9524-0>
49. Zheng B, Wang L, Lei K, Nan B (2016) Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area. *China Chemosphere* 149:91–100. <https://doi.org/10.1016/j.chemosphere.2016.01.039>
50. Malik A, Verma P, Singh AK, Singh KP (2011) Distribution of polycyclic aromatic hydrocarbons in water and bed sediments of the Gomti River, India. *Environ Monit Assess* 172:529–545. <https://doi.org/10.1007/s10661-010-1352-4>
51. Santana JL, Massone CG, Valdés M, Vazquez R, Lima LA, Olivares-Rieumont S (2015) Occurrence and Source Appraisal of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Waters of the Almendares River, Cuba. *Arch Environ Contam Toxicol* 69:143–152. <https://doi.org/10.1016/j.envpol.2016.04.011>
52. Adeniji AO, Okoh OO, Okoh AI (2019) Levels of Polycyclic Aromatic Hydrocarbons in the Water and Sediment of Buffalo River Estuary, South Africa and Their Health Risk Assessment. *Arch Environ Con Tox* 76:657–669. <https://doi.org/10.1007/s00244-019-00617-w>
53. Sun JH, Wang GL, Chai Y, Zhang G, Li J, Feng J (2009) Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicol Environ Saf* 72:1614–1624. <https://doi.org/10.1016/j.ecoenv.2008.05.010>
54. Mzoughi N, Chouba L (2011) Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *J Environ Monit* 13:689–698. <http://dx.doi.org/10.1039/c0em00616e>
55. Nagy AS, Szabó J, Vass I (2014) Occurrence and distribution of polycyclic aromatic hydrocarbons in surface water and sediments of the Danube River and its tributaries. *Hungary J Environ Sci Health A Tox Hazard Subst Environ Eng* 49:1134–1141. <https://doi.org/10.1080/10934529.2014.897155>
56. Abdel-Shafy HI, Mansour MSM (2016) A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt J Pet* 25:107–123. <https://doi.org/10.1016/j.ejpe.2015.03.011>
57. Liu Z, He L, Lu Y, Su J, Song H, Zeng X, Yu Z (2015) Distribution, source, and ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the Hun River, northeast China. *Environ Monit Assess* 187:290–300. <https://doi.org/10.1007/s10661-015-4525-3>
58. Li J, Dong H, Zhang D, Han B, Zhu C, Liu S, Liu X, Ma Q, Li X (2015) Sources and ecological risk assessment of PAHs in surface sediments from Bohai Sea and northern part of the Yellow Sea, China. *Mar Pollut Bull* 96:485–490. <https://doi.org/10.1016/j.marpolbul.2015.05.002>
59. Wang YB, Liu CW, Kao YH, Jang CS (2015) Characterization and risk assessment of PAH-contaminated river sediment by using advanced multivariate methods. *Sci Total Environ* 524–525:63–73. <https://doi.org/10.1016/j.scitotenv.2015.04.019>
60. Acquavita A, Falomo J, Predonzani S, Tamberlich F, Bettoso N, Mattassi G (2014) The PAH level, distribution and composition in surface sediments from a Mediterranean lagoon: The Marano and Grado Lagoon (Northern Adriatic Sea, Italy). *Mar Pollut Bull* 81:234–241. <https://doi.org/10.1016/j.marpolbul.2014.01.041>

61. Di Leonardo R, Mazzola A, Tramati CD, Vaccaro A, Vizzini S (2014) Highly contaminated areas as sources of pollution for adjoining ecosystems: The case of Augusta Bay (Central Mediterranean). *Mar Pollut Bull* 89:417–426. <https://doi.org/10.1016/j.marpolbul.2014.10.023>
62. Zhao X, Jin H, Ji Z, Li D, Kaw HY, Chen J, Xie Z, Zhang T (2020) PAES and PAHs in the surface sediments of the East China Sea: Occurrence, distribution and influence factors. *Sci Total Environ* 703:134763. <https://doi.org/10.1016/j.scitotenv.2019.134763>
63. Liu B, Liu Y, Bu Q, Cao H, Zhang H, Liu C, He X, Yun M (2020) Polycyclic Aromatic Hydrocarbons in Surface Water from Wuhai and Lingwu Sections of the Yellow River: Concentrations, Sources, and Ecological Risk. *Environmental Behavior and Effects of Pollutants in Water*. Article ID 8458257:8 pages. <https://doi.org/10.1155/2020/8458257>
64. Mozeto AA, Yamada TM, De Moraes CR, Do Nascimento MRL, Fadini PS, Torres RJ, Sueitt AP, De Faria BM (2014) Assessment of organic and inorganic contaminants in sediments of an urban tropical eutrophic reservoir. *Environ Monit Assess* 186:815–834. <https://doi.org/10.1007/s10661-013-3419-5>
65. Lewis MA, Russell MJ (2015) Contaminant profiles for surface water, sediment, flora and fauna associated with the mangrove fringe along middle and lower eastern Tampa Bay. *Mar Pollut Bull* 95:273–282. <https://doi.org/10.1016/j.marpolbul.2015.04.001>
66. Perra G, Pozo K, Guerranti C, Lazzeri D, Volpi V, Corsolini S, Focardi S (2011) Levels and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) in superficial sediment from 15 Italian marine protected areas (MPA). *Mar Pollut Bull* 62:874–877. <https://doi.org/10.1016/j.marpolbul.2011.01.023>
67. Minissi S, Caccese D, Passafiume F, Grella A, Eleonora C, Rizzoni M (1998) Mutagenicity (micronucleus test in *Vicia faba* root tips), polycyclic aromatic hydrocarbons and heavy metal content of sediments collected in Tiber river and its tributaries within the urban area of Rome. *Mutat Res* 420:77–84. [https://doi.org/10.1016/S1383-5718\(98\)00142-9](https://doi.org/10.1016/S1383-5718(98)00142-9)
68. Yancheshmeh RA, Bakhtiari AR, Mortazavi S, Savabieasfahani M (2014) Sediment PAH: contrasting levels in the Caspian Sea and Anzali Wetland. *Mar Pollut Bull* 84:391–400. <https://doi.org/10.1016/j.marpolbul.2014.05.001>
69. Foster KL, Stern GA, Carrie J, Bailey JN, Outridge PM, Sanei H, Macdonald RW (2015) Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay, Eastern Canadian Arctic. *Sci Total Environ* 506–507:430–443. <https://doi.org/10.1016/j.scitotenv.2014.11.002>
70. Cavalcante RM, Sousa FW, Nascimento RF, Silveira ER, Freire GS (2009) The impact of urbanization on tropical mangroves (Fortaleza, Brazil): evidence from PAH distribution in sediments. *J Environ Manage* 91:328–335. <https://doi.org/10.1016/j.jenvman.2009.08.020>
71. Bebianno MJ, Pereira CG, Rey F, Cravo A, Duarte D, D'Errico G, Regoli F (2015) Integrated approach to assess ecosystem health in harbor areas. *Sci Total Environ* 514:92–107. <https://doi.org/10.1016/j.scitotenv.2015.01.050>
72. Kanzari F, Syakti AD, Asia L, Malleret L, Piram A, Mille G, Doumenq P (2014) Distributions and sources of persistent organic pollutants (aliphatic hydrocarbons, PAHs, PCBs and pesticides) in surface sediments of an industrialized urban river (Huveaune). *France Sci Total Environ* 478:141–151. <https://doi.org/10.1016/j.scitotenv.2014.01.065>
73. Kanzari F, Asia L, Syakti AD, Piram A, Malleret L, Mille G, Doumenq P (2015) Distribution and risk assessment of hydrocarbons (aliphatic and PAHs), polychlorinated biphenyls (PCBs), and pesticides in surface sediments from an agricultural river (Durance) and an industrialized urban lagoon (Berre lagoon), France. *Environ Monit Assess* 187:591–603. <https://link.springer.com/article/10.1007%2Fs10661-015-4823-9>
74. León VM, García I, Martínez-Gómez C, Campillo JA, Benedicto J (2014) Heterogeneous distribution of polycyclic aromatic hydrocarbons in surface sediments and red mullet along the Spanish Mediterranean coast. *Mar Pollut Bull* 87:352–363. <https://doi.org/10.1016/j.marpolbul.2014.07.049>
75. Bajt O (2014) Aliphatic and polycyclic aromatic hydrocarbons in Gulf of Trieste sediments (northern Adriatic): potential impacts of maritime traffic. *Bull Environ Contam Toxicol* 93:299–305. <https://doi.org/10.1007/s00128-014-1321-7>
76. Tobiszewski M, Namiesnik J (2012) Review – PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162:110–119. <https://doi.org/10.1016/j.envpol.2011.10.025>
77. Ekpo BO, Oyo-Ita OE, Oros DR, Simoneit BR, Niger SE, Delta (2012) Distributions and sources of polycyclic aromatic hydrocarbons in surface sediments from the Cross River estuary. *Nigeria Environ Monit Assess* 184:1037–1047. <https://doi.org/10.1007/s10661-011-2019-5>
78. Arienzo M, Albanese S, Lima A, Cannetelli C, Aliberti F, Cicotti F, Qi S, De Vivo B (2015) Assessment of the concentrations of polycyclic aromatic hydrocarbons and organochlorine pesticides in soils from the Sarno River basin, Italy, and ecotoxicological survey by *Daphnia magna*. *Environ Monit Assess* 187: 52 <https://doi.org/10.1007/s10661-015-4272-5>
79. Wakeham SG, Canuel EA (2015) Biogenic polycyclic aromatic hydrocarbons in sediments of the San Joaquin River in California (USA), and current paradigms on their formation. *Environ Sci Pollut Res Int* 23:10426–10442. <http://dx.doi.org/10.1007/s11356-015-5402-x>
80. Long ER, MacDonald DD, Smith SL, Calder ED (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ Manage* 19:81–97
81. MacDonald DD, Carr RS, Calder FD, Long ER (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5:253–278
82. Adeleye AO, Jin H, Di Y, Li D, Chen J, Ye Y (2016) Distribution and ecological risk of organic pollutants in the sediments and seafood of Yangtze Estuary and Hangzhou Bay, East China Sea. *Sci Total Environ* 541:1540–1548. <https://doi.org/10.1016/j.scitotenv.2015.09.124>
83. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council. *Off J Eur Union* 348:84–97

Figures

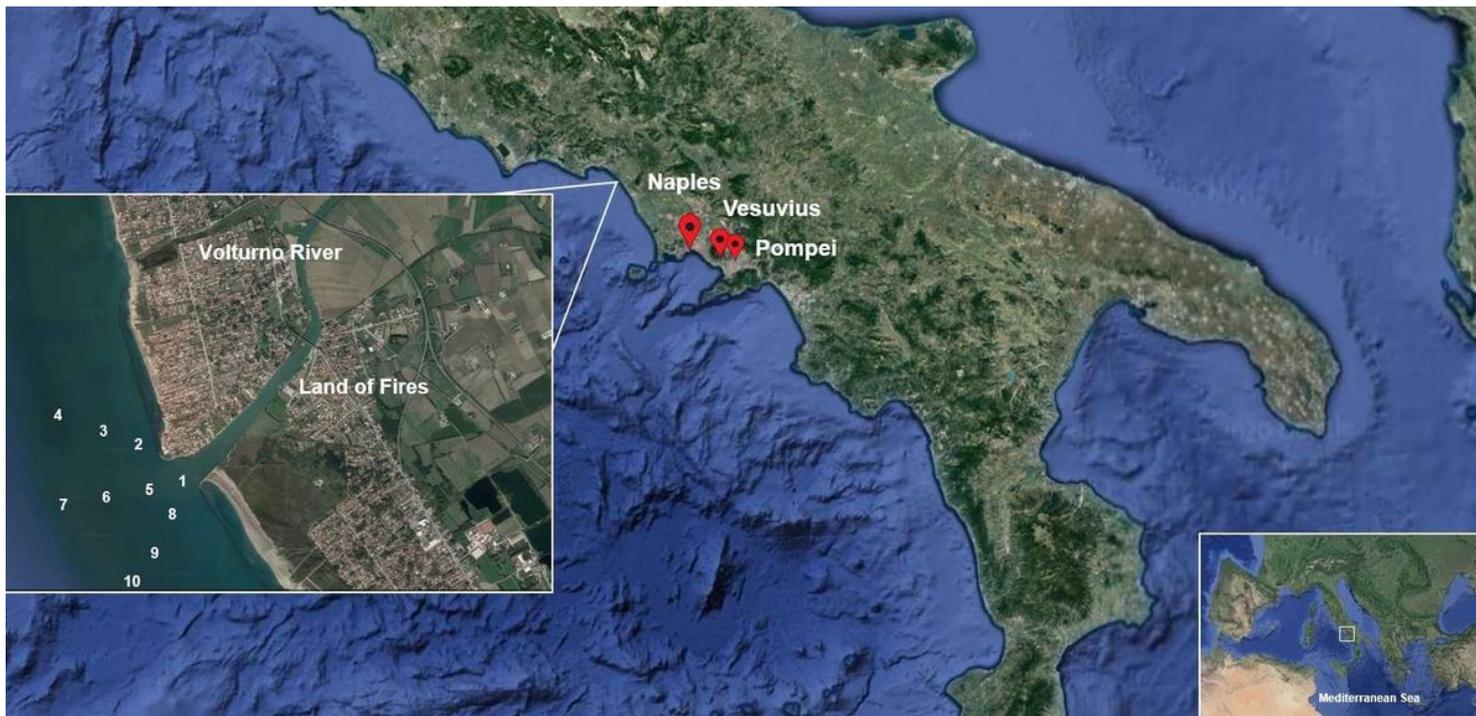


Figure 1

Map of the study area and sampling sites in the Volturno River and Estuary, Southern Italy.

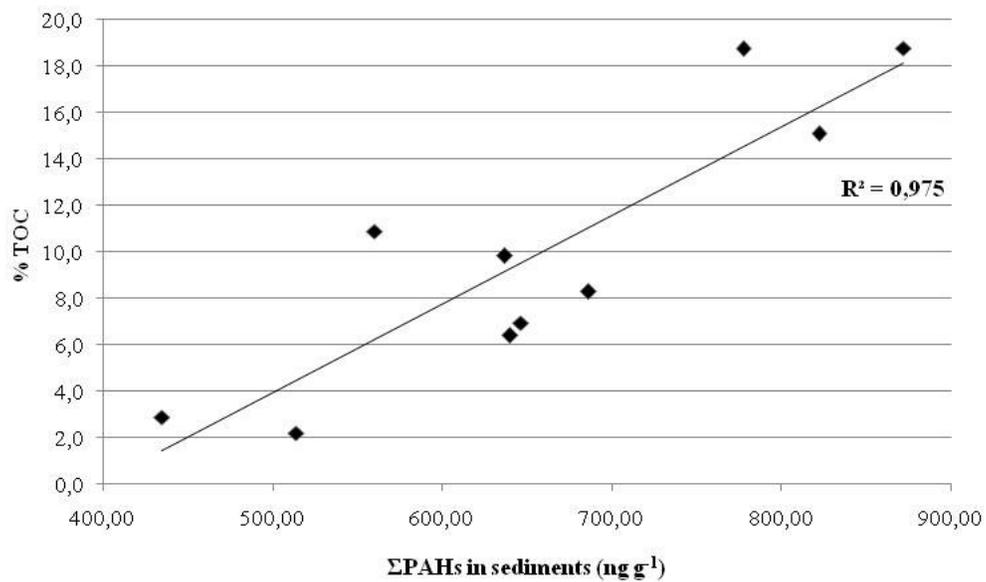


Figure 2

Relationship between TOC (%) and ΣPAHs in the sediment samples of the Volturno River.

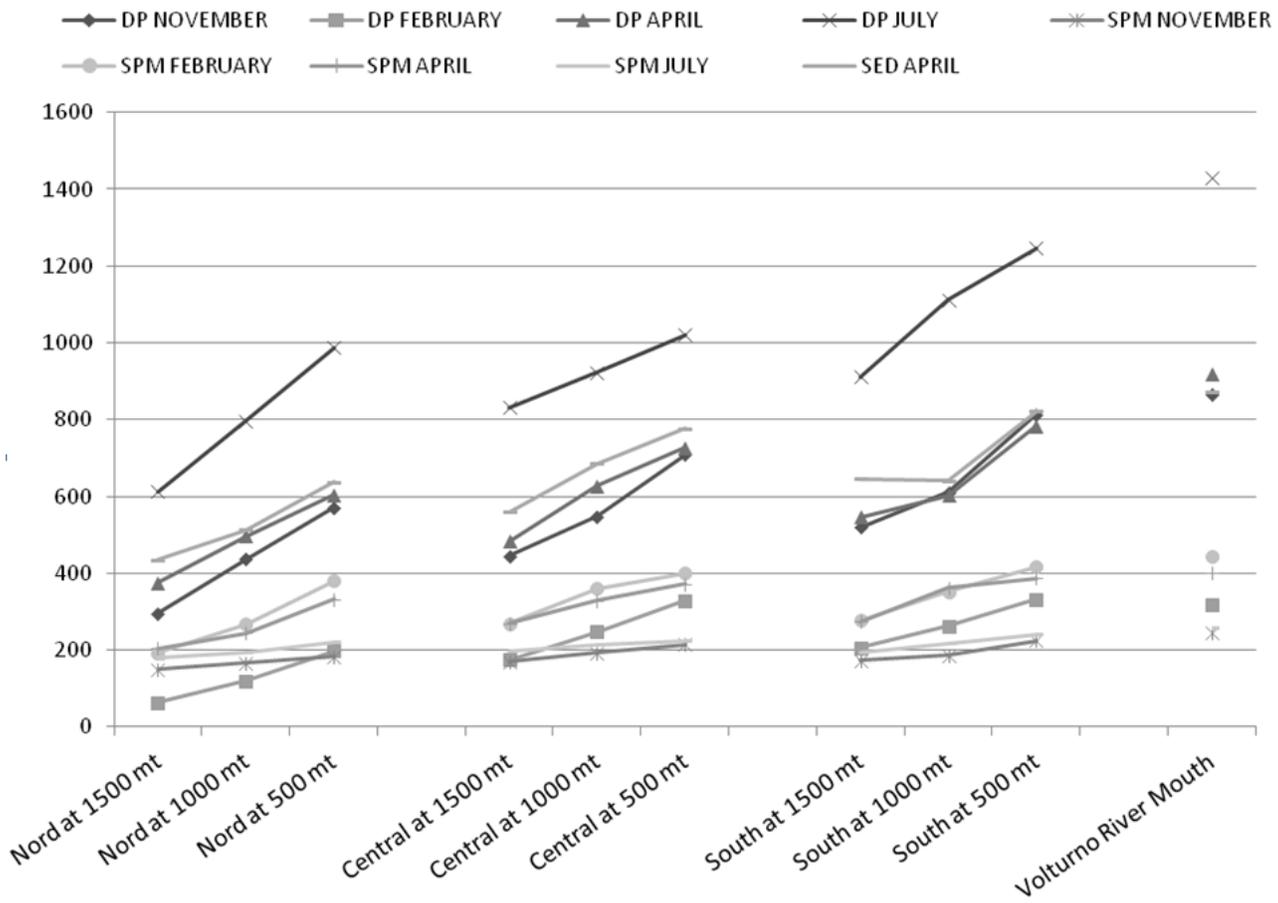


Figure 3 Spatial and temporal concentration of PAHs in the water dissolved phase (DP, ng L⁻¹), suspended particulate matter (SPM, ng L⁻¹) and sediments (ng g⁻¹ dry wt) of the Volturno River and Estuary, Southern Italy.

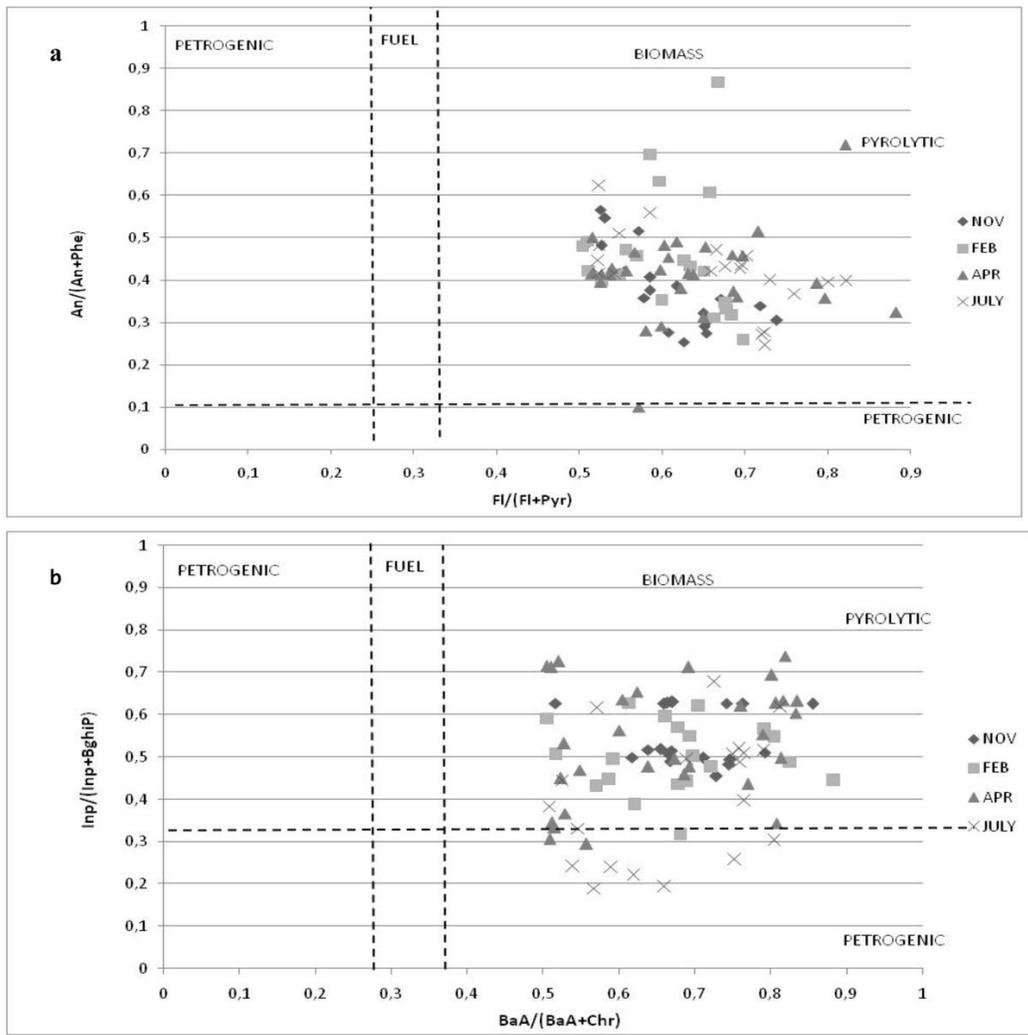


Figure 4
 a) Cross plots of the values of FI/(FI + Pyr) versus An/(An + Phe) and b) BaA/(BaA + Chr) versus InP/(InP+ BghiP) for all samples data of the Volturno River and its Estuary.

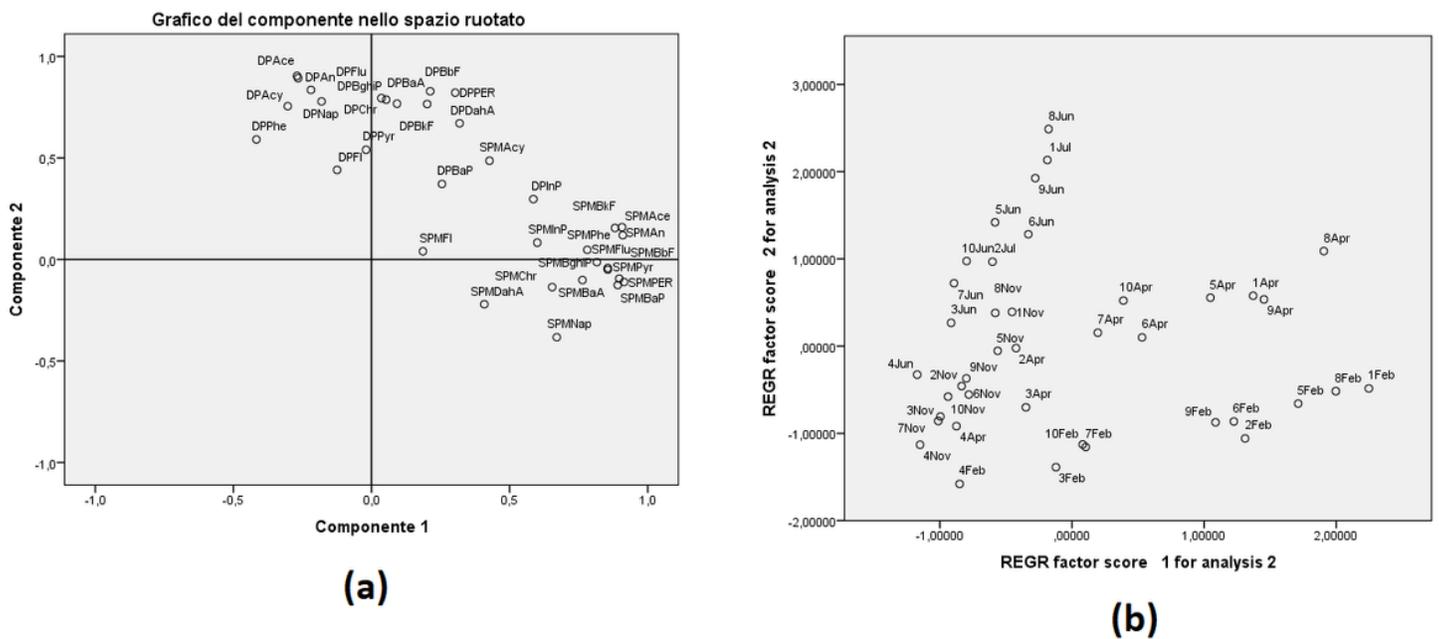


Figure 5
 Page 18/19

a) Principal Component Analysis of the DP & SPM data of the Volturno River. Score plot for the first and second principal component. b) Principal Component Analysis of the DP & SPM data of the Volturno River. Loading plot for the first and second principal component.