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RESEARCH ARTICLE

Chemical characterisation of PM_{10} from ship emissions: a study on samples from hydrofoil exhaust stacks

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Abstract

A chemical characterization of PM_{10} collected at hydrofoil exhaust stacks was performed conducting two on-board measuring campaigns, with the aim of assessing the ship emission impact on PM_{10} collected in the coastal area of Naples (Southern Italy) and providing information about the characteristics of this important PM emission source.

Samples were analysed determining the contribution of different chemical parameters to PM_{10}'s mass, which consisted of polycyclic aromatic hydrocarbons (PAHs) ($0.10 \pm 0.12\%$), total carbon ($61.9\% \pm 20.0\%$, with 40.4% of organic carbon, OC, and 21.5% of elemental carbon, EC) and elemental fraction ($0.44\% \pm 1.00\%$). Differences in terms of composition and chemical parameter profiles were observed between samples collected during offshore navigation (Off) and samples collected during shunting operations (SO), the latter of higher concern on a local scale. For SO samples, lower contributions of OC and EC were observed (39.7% and 19.6% respectively) compared to Off samples (41.5% and 24.2%), and an increase in terms of elements (from 0.32 to 0.51%) and PAHs (from 0.06 to 0.12%) concentrations was observed. In addition, enrichment factors (EFs) for some elements such as V, Zn, Cd, Cu, Ag and Hg as well as PAHs profile varied significantly between SO and Off. Data presented here were compared with data on chemical composition of PM_{10} sampled in a tunnel, in a background site and in an urban site in the city of Naples. Results indicated that shipping activities contributed significantly to the emission of V and, in some extent, Zn and Cd; in addition, PAH profiles indicated a greater contribution to urban PM_{10} from vehicular traffic than shipping emissions. These results can significantly contribute to the correct evaluation of the influence of shipping emission on PM_{10} generation in urban coastal areas and can be a useful reference for similar studies. The coastal area of Naples is an important example of the coexistence of residential, touristic and natural areas with pollutants emission sources including, among the others, shipping emissions. In this and similar contexts, it is important to distinguish the contribution of each emission source to clearly define environmental control policies.

Keywords Shipping emissions · Sources identification · Chemical characterization · Coastal area · Harbours · Urban area

Introduction

The impact of emissions (CO_2, NO_x, SO_x and OC and EC, PM_{10}, $PM_{2.5}$ and PAHs) from the maritime transport sector on public health and air quality is currently intensely studied, on both local (coastal areas and their surroundings)

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and global scale (Corbett et al. 2007; Toscano and Murena 2019). In particular, the presence of harbours near to urban areas seriously affects environmental quality (air, water and sediments) due to many factors as induced road traffic, oil combustion, direct ship emissions during manoeuvring and hoteling phases (Monaco et al., 2017). These factors can determine primary emission of PM_{10} and $PM_{2.5}$ and contribute to their secondary production, causing the formation of up to 50–55% of $PM_{2.5}$ and PM_{10} measured in the harbour's proximities and up to 9–12% and 11–15% of urban $PM_{2.5}$ and PM_{10}, respectively (Perez et al. 2016).

Previous studies indicate that shipping emissions of atmospheric pollutants are strongly influenced by ship category (passengers, cruise and non-cruise and commercial), navigation phase (hoteling, manoeuvring, offshore navigation) and type of port. For example, Toscano and Murena (2019) reported that annual PM_{10} emissions due to cruise range between 2 t/y and 94 t/y (in Copenhagen and Barcelona ports, respectively), while emissions due to commercial ships range between 1 t/y and 1836 t/y (Koge and Tanijin ports, respectively). The Italian ports show significant PM_{10} emission rates, with values of 10 t/y due to cruise ships and 68 t/y due to commercial ships for the port of Genoa and values of 26 t/y and 135 t/y for the port of Venice (cruise and commercial ships, respectively). Published data for the port of Naples showed an emission rate of 11 t/y due to emissions from cruise ships during hoteling in port (Murena et al. 2018).

The annual bulletin published by the "Autorità di Sistema Portuale del Mar Tirreno Centrale" (https://adsptirrenocentrale.it/statistiche/traffico-passeggeri/traffico-locale) attribute a volume of 2,908,208 passengers in the 2020 and 6,897,027 passengers in the 2019 (the difference can be attributed to COVID-19 pandemic) to the hydrofoils travelling in the Gulf of Naples. These values are very high considering that for the same years (2020 and 2019 respectively), there were 28,176 and 1,454,023 passengers due to cruises. As considered in Walsh and Bows (2012), the relative contributions of small ships to emission factors may be bigger due to their large numbers. Finally, it is important to note that there are periods of the year (fall and winter) when the number of cruises is reduced, and hydrofoils represent the most used means of navigation.

The chemical composition of ambient PM has also been analysed using PMF to determine the specific contribution of shipping emissions (Gregoris et al. 2016; Manousakas et al. 2017; Masiol et al. 2014; Matthias et al. 2010; Yau et al. 2013). These studies clearly assessed the direct contribution of shipping emission and harbour activities on local concentrations of PM (primary contribution) (Cesari et al. 2014; Contini et al. 2015; Donateo et al. 2014; Ledoux et al. 2018; Merico et al. 2016; Prati et al. 2015; Romagnoli et al. 2017); furthermore, Pey et al. (2013) and Viana et al. (2009) also demonstrated the contribution of shipping emissions to secondary PM formation (aged contribution), characterized mainly by secondary inorganic aerosol and OC/EC ratio.

To clearly assess the contribution of shipping emission to urban PM, the chemical composition and chemical fingerprint of these emissions are required; this information can be obtained by directly sampling PM at stack exhausts, to avoid contamination from other sources. Only few such studies have been reported to date.

Moldanova et al. (2013) performed two measurement campaigns on a carrier ship and on a cargo/passenger ship travelling in the Baltic Sea, determining the PM_{10} chemical composition; Popovicheva et al. (2012) and Moldanova et al. (2009) reported data on PM chemical composition, whereas Fridell et al. (2008), Cooper (2001) and Cooper (2003) showed data on PMs concentration and size distribution.

The coastal area of Naples is an important example of the coexistence of residential, touristic and natural areas with pollutants emission sources including, among the others, shipping emissions. In this and similar contexts, it is important to distinguish the contribution of each emission source to clearly define environmental control policies. Studies that characterize the chemical properties of specific PM sources are necessary to meet this need.

To provide more data on the chemical composition of PM from ship exhaust, we carried out on-board measurements, directly sampling PM_{10} at the exhaust stacks of a hydrofoil travelling in the Gulf of Naples, during shunting operations and offshore navigation.

The collected samples were analysed to determine the elemental, EC/OC and PAHs composition of PM_{10}. The chemical data were further evaluated to investigate correlations among chemical parameters and to assess differences among samples collected during different navigation phases.

Materials and methods

Site description and sampling method

Living in front of an extended hilly area, the coastal strip of Naples, Southern Italy (Fig. 1) is characterized by great heterogeneity: within about 15 kms, different harbours (commercial and passenger) are present, for a total of 75 moorings. The most important harbours are Angioino Pier and the Maritime Station (for the mooring of large cruise ships and for the connection with the major islands such as Sardinia and Sicily). In addition, the Beverello Pier (that serves the connection of Naples with the smaller islands of Capri, Procida, Ischia) has had a huge impact on the harbour activities, contributing to the transit of about 1,068,797 people in 2018 (Prati et al. 2015; Appolloni et al. 2018a).

Fig. 1 Coastal strip of Naples port: 1a, Beverello Pier; 1b, Maritime station; 1c, Angioino Pier; 2, Immacolatella Pier; 3, Pisacane Pier; 4, Ship yards; 5, Freight depot; 6, Eastern Entrance; 7, San Vincenzo Pier

In the same overcrowded area (Appolloni et al. 2018b), two small marine protected areas (Gaiola and Baia) are also present, sensitive to the emissions due to harbours and emissions from ships (Donnarumma et al. 2019; Appolloni et al. 2020). In addition, the harbours are close to a densely populated urban area (about 1,000,000 inhabitants), which is characterized by the presence of many other pollutant emission sources: vehicular traffic, domestic and commercial combustions and air traffic due to the nearby Capodichino Airport. These sources determine the air quality in the urban area, which is characterized by severe PM pollution (Agrillo et al. 2013; Chianese et al. 2019; Dinoi et al. 2017; Riccio et al. 2014; Sirignano et al. 2019).

In September and October 2019, a measurement campaign at the exhaust stack of a high-speed passenger hydrofoil, equipped with two main engines MTU16V-396TE74L, 1960 kW at 1900RPM, with a DF-Diesel fuel consumption of about 1200 kg roundtrip, travelling in the Gulf of Naples, was performed, with the aim of collecting PM_{10} samples representative of shipping emissions. Due to their use over small/medium distances, passenger hydrofoils are very common in the area here considered and, in general, in the ports close to the urban area.

Samples were collected on quartz fibre filters, with a diameter of 45 mm, using a portable pump (Air monitoring System-AMS Analitica) with a flow rate of 35 l/min corresponding to 2 m^3/h and equipped with a PM_{10} selective head, directly inserted into the exhaust stack; on average, a volume of 0.2 m^3 was sampled (a picture of sampling line was reported in Fig. 2).

Filters were immediately stored in petri slides, closed with parafilm and kept at – 20 °C until analysis. A total of 30 filters were collected, destined for different studies; for the measurements presented here, 20 filters were analysed.

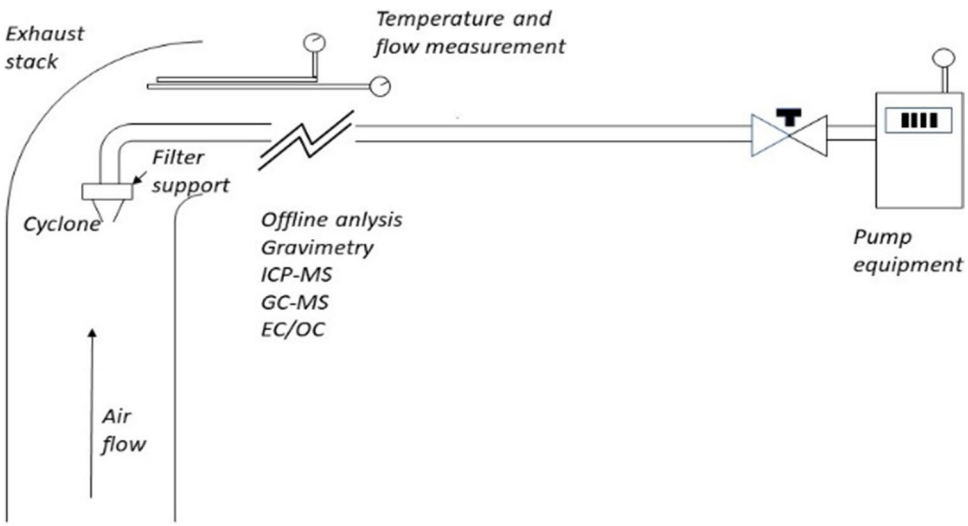

Fig. 2 Schematic diagram for the sampling line

PM_{10} chemical analyses

The quartz fibre filters used during the sampling campaign were heated for 24 h at 700 °C before the sampling, to remove organic residuals. In addition, in order to determine PM mass, before and after sampling, they were properly conditioned for 48 h under controlled environmental conditions (e.g. temperature 22 ± 3 °C and relative humidity 44 ± 7%) and weighed using a Mettler Toledo balance with a precision of ± 1 µg.

The concentration of each chemical species was expressed referring to PM's mass rather than to volume of air sampled; this choice was intended to give information about chemical fingerprint of samples collected, allowing the comparison with samples from other pure sources as well as samples of urban PM.

Analysis of OC and EC

The concentration of carbonaceous fractions, organic (OC) and elemental (EC) carbon, was determined on all samples by the thermo-optical transmittance method (TOT) using a Sunset Laboratory OC/EC analyser (Sunset Laboratory Inc., Tigard, OR, USA). A 1.0 cm^2 punch from each quartz filter was analysed following the EUSAAR2 protocol (Cavalli et al. 2010). Before measurements, a multipoint sucrose (2.198 g/L in water, CPAchem Ltd) calibration of the analyser was performed and used to correct measured OC and EC concentrations. Blank filters were also analysed for correcting the concentrations measured in ambient samples. The detection limit on measured OC and EC mass concentrations estimated by the manufacturer is 0.1 µg/cm^2. The accuracy is generally within 5% for TC and OC and within 10% for EC, as already observed in previous work (Merico et al. 2019).

Metals determination

For the determination of elements, one-fourth of each quartz filter was digested with 8 ml of nitric acid and 2 ml of hydrogen peroxide solutions. Element extraction was performed using a PTFE (polytetrafluoroethylene) digestion vessel in an advanced microwave-digestion system (START E, Milestone S.r.l, ITALY). Three steps of a programmed temperature procedure were used: step 1 (heating), from 35 up to 180 °C in 20 min at 1200 W; step 2 (heating), from 180 up to 220 °C keeping this temperature for 20 min at 1220 W; and step 3 (cooling), from 220 down to 35 °C in 20 min. After the extraction, the vessels were cooled for several hours, and each solution was diluted with ultrapure water at 18 MΩ/cm and stored before analysis. In each extraction sequence, one PTFE vessel containing the mixture of reagents and one-fourth of a blank quartz filter was also used.

The extracted solutions were analysed by ICP-MS iCAP Q System (ThermoFisher Scientific). Before injection, each solution was diluted at a ratio of 1:30 with ultrapure water. The analysis sequences were performed in KED mode with argon nebulizer flow and plasma gas flow at 1 L/min and 18 L/min respectively. Elements were quantified with a six-point calibration curve using multi-element standard solutions in a concentration range between 0.02 and 300 ppb. The correlation coefficients R^2 were > 0.999. Limits of quantification were in the range of 0.2–6.7 ng/ml and the extraction recoveries varied between 88 and 110%. Six multi-element standard solutions were prepared by dilution of the primary standard (a multi-element certified standard mix in 2% nitric acid with a concentration of 20 mg/L, customized by Chemical Research 2000) with 0.6% nitric acid solution obtaining the following concentration levels: 0.02–0.2 ppb, 2 ppb, 20 ppb, 100 ppb and 300 ppb. The internal standard mix contained 8 elements: scandium (Sc), germanium (Ge), rhodium (Rh), indium (In), terbium (Tb), holmium (Ho), lithium (Li) and bismuth (Bi) at 10 mg/L. The standard was purchased from CPA Chem and was used at 10 ppb in nitric acid at 0.6% v/v (Palmisani et al. 2020; Amodio et al. 2014).

Analysis of PAHs

The extraction of PAHs was performed with an acetone/hexane mixture (1:1) through a microwave-assisted solvent extraction (Milestone s.r.l., model Ethos D). The applied procedure was optimized in a previously published paper, and the best operating parameters in terms of temperature, extraction volume, time and microwave source power were set for an effective PAHs extraction (Tutino et al. 2016). The extracted samples were analysed using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Inc., Santa Clara, CA USA) equipped with a programmable temperature vaporization injection system (PTV) and interfaced with a triple quadrupole mass spectrometer (QQQ), operating in electron impact ionization (Agilent MS-7890A). Helium 6.0 (Nippon Gases Italia S.r.l.) was used as carrier gas.

Criteria for the identification of each PAH (anthracene (Ant), pyrene (Pyr), benzo(a)anthracene (B(a)A), chrysene (Chr), benzo(b)fluorene (B(b)F), benzo(k)fluorene (B(k)F), benzo(a)pyrene (B(a)P), benzo(g)perylene (B(g)P) and indeno pyrene (IP)) involved matching the retention times with those of authentic standards (EPA 525 PAH mix A, Supelco: 1 ml vial at 500 µg/ml for each compound in methylene chloride) within ± 1 min of expected values. The quantification was performed based on the ratio of the integrated peak area of the ion to its internal reference standard, acquired in the same time segment (EPA 8270 Semivolatile Internal Standard Mix, Supelco: 1-ml vial at 2000 µg/mL for each compound in methylene chloride). Six-level-based calibration curves were constructed for each PAH within the

dynamic concentration range 0.5–12.5 ng/ml. The analytical performance of the whole procedure (extraction recovery, extraction linearity, analytical repeatability, LOD) was verified in previous studies (Palmisani et al. 2020). Finally, due to co-elution, anthracene and phenanthrene were not quantified separately, and therefore the sums of the anthracene + phenanthrene concentrations were determined.

Data analysis

Data on elemental composition were used to calculate the enrichment factors (EFs) of each element, which report the enrichment of a single element compared to the relative abundance of the element in a crustal sample, in order to assess the contribution of a specific emission source to the element amount. Enrichment factors are calculated considering the chemical composition of the upper continental crust, as indicated in Wedepohl (1995):

$$\mathbf{EF} = \frac{\frac{X_{PM}}{Ref_{PM}}}{\frac{X_{UCC}}{Ref_{UCC}}}$$

where X is the element under consideration (in both PM and upper continental, UCC) and *Ref* is a reference element (usually Al or Fe). For this study, aluminium (Al) was used as reference element (Vaio et al., 2016).

Elements with an EF lower than 10 are assumed to have a crustal origin, while EF values between 10 and 100 suggest moderate enrichment and EF values greater than 100 indicate highly enrichment.

Furthermore, statistical analyses were performed using PERMANOVA (permutational multivariate analysis of variance, Clarke and Gorley 2015) and the psych library (Revelle 2020) of the r-project software (R-Development Core Team 2011) in order to assess differences between shunting operations and offshore sailing emissions (for these analyses, we considered the samples with a complete chemical dataset). This non-parametric approach enables us to investigate and make considerations about correlation among chemical parameters here discussed, despite the number of available samples.

The experimental design includes one factor "emission type" (ET) composed of two levels: samples collected during the shunting operations (SO, $n = 10$) and samples collected during offshore sailing (Off, $n = 5$).

Data were normalized, and, for all the analyses that required a triangular matrix, the Euclidean distances were used. PERMANOVA (Anderson 2001) was performed considering the whole chemical dataset and considering chemical species separately (metals, OC and EC and PAHs) in order to assess significant differences between the ET levels. Multivariate patterns were visualized through principal component analyses (PCA). SIMPER (similar percentage) analyses (Clarke et al. 2014) were used to identify chemical species that mainly affected dissimilarities between ET levels. Species that contributed more than 3.5% were chosen as subset, and PERMANOVA and PCA were performed again. In addition, SIMPER subset permutation tests of multivariate dispersion (PERMDISP; Anderson et al., 2006) were carried out for the factor ET to investigate heterogeneities among samples of the same level. SIMPER variables were finally related to each other by bivariate scatter plots where linear regression models were shown, and Pearson index (ρ) was used as a measure of correlation for each pair of variables.

Result and discussion

PM_{10} concentration and chemical composition

The average PM_{10} mass concentration referred to volume of air sampled was 440.1 ± 747.4 mg/m^3. Collected PM_{10} samples were dominated by carbonaceous species; on average, 61.9% (±20%) of total PM_{10} mass was represented by total carbon (OC, 40.4%, and EC, 21.5%), 0.44% (±1%) by the elemental fraction and the 0.10% (±0.12%) by PAHs.

The most abundant elements were aluminium (2972.5 ± 5090.5 µg/g), iron (858.0 ± 713.7 µg/g), titanium (259.1 ± 226.2 µg/g), zinc (673.8 ± 590.1 µg/g) and vanadium (755.7 ± 179.1 µg/g), usually considered a chemical tracer of ship emissions (Mazzei et al., 2008); also, B(a)P, a known carcinogenic compound, resulted as one of the most abundant PAH with a concentration of 140.4 ± 197.8 µg/g.

Due to the long time spent by ships in ports, it is very important to distinguish between shunting operation (SO) and offshore navigation (Off), when reporting mass concentration and chemical composition of PM.

Considering the differences between samples collected in each phase allows to better evaluate the direct impact of ship emissions on urban PM. In this study, the PM_{10} mass concentration in the ship exhaust was significantly different between the two phases, with average values of 193.4 ± 309.5 mg/m^3 and 714.3 ± 994.2 mg/m^3 during the SO and Off phases, respectively; the maximum value was reached during Off (2370 mg/m^3), while the minimum value was reached during SO (4.78 mg/m^3).

As concerning the dependence of PM emission navigation phase, in Sippula et al. (2014), it was observed that PM emission factor during SO navigation phase (with a load engine of 10%) was two times higher than during Off (load engine of 75–100%). Different observations can be made considering the total amount of emitted PM; in this case, published data reported that the decreasing combustion temperature (occurring during manoeuvring) might determine

increases of the flame lift-off, which may decrease the PM formation inside the spray. In addition, during the offshore navigation, an increased mass of air was sent to the combustion chamber (giving higher speed) also resulting in a turbo charging which in turn increases the total amount of PM emissions (Sarvi et al., 2008).

Also, the relative contribution of EC and OC, PAHs and metals to total PM also differs depending on navigation phases, with a contribution of 19.6%, 39.7%, 0.12% and 0.51 respectively for SO samples and 24.2%, 41.5%, 0.06% and 0.32% for Off samples. These differences will be discussed in more detail in the following sections.

OC/EC

As reported in Table 1, the contributions of EC to the PM mass were 24.2% for the samples collected during Off, and 19.6% for the samples collected during SO, while the contribution of OC was 41.5%, for the samples collected during Off and 39.7% for the samples collected during SO.

Furthermore, contribution of OM (considered an indicator of the contribution to volatile organic species generation) is evaluated with the relation:

$$OM = OC * 1.2$$

as in Petzold et al. (2008) and Moldanova et al. (2009).

OM represented 49.8% (with a concentration of 498.0 ± 244.1 mg/g) of the PM mass collected during Off and 45.8% (with a concentration of 457.6 ± 194.8 mg/g) of PM mass collected during SO, suggesting that half of PM mass consisted of organic species. Moldanova et al. (2009) reported an OM contribution between 20 and 60% of PM_{10} emitted at the exhaust stack of a cargo/passenger ferry, in agreement with our data. In Mueller et al. (2015), the same dependence of OM on engine load was observed, with values decreasing from Off to SO, as for OC and highlighting that a significant contribute to OM (and OC) can be observed also at lower load engine due to the decreasing in combustion temperature and, consequently, in a greater release of unburned fuel. Other published data showed a great variability for OC and EC variation depending on engine load (Sippula et al., 2014).

Table 1 TC, OC and EC average concentrations (± standard deviation) together with the TC/PM, OC/PM and EC/PM average ratios, in PM collected on-board during Off and SO

	TC	OC	EC
	mg/g	mg/g	mg/g
Off	656.7 ± 209.4	415.0 ± 203.4	241.7 ± 248.3
SO	592.0 ± 195.7	396.6 ± 162.3	195.9 ± 151.9

In Hountalas et al. (2014), the effect of load engine on PM emission was also explained with the variation in cylinder conditions and, consequently, in the combustion conditions, so affecting emissions characteristics.

OC and EC were not well correlated, showing a $R^2 = 0.05$ and a $R^2 = 0.34$ for samples collected during SO and Off, respectively; this behaviour reflected the dependence of EC and OC on different operation modes (Petzold et al., 2010; Ristimaki et al., 2010).

A study conducted in Barcelona for the purpose of evaluating the impact of harbour emissions on ambient PM_{10} revealed that OM represented 4.8% of PM_{10} total mass (Pérez et al. 2016). Moldanova et al. (2009) showed that the main components of PM were OC with percentage in between 25 and 60%, followed by EC with percentage in between 10 and 35%, in agreement with the results here found.

Currently available data about EC and OC for the urban area of Naples were reported in studies conducted by Dinoi et al (2017) and by Sirignano et al. (2019). In these studies, it was hypothesized that the sampling site, located in the centre of the urban area of Naples (close to marina, at 53 m a.s.l.), was affected by multiple sources of particulate matter, including road traffic and harbour emissions. In particular, the analysis conducted in Dinoi et al. (2017) found that the mean concentration of PM_{10} (50.8 ± 21.7 μg/m^3) in winter consisted of 31% by total carbon (TC), distributed in 26% by OC and 5% by EC.

In addition, data for the site of Naples were compared with data from an Italian suburban site (Lecce, 35% TC of total PM_{10} mass, divided into 31% OC and 5% EC for PM_{10}), and an Italian costal site (Lamezia Terme, 48% TC of total PM_{10} mass, divided into 42% OC and 6% EC).

Compared to these data on the composition of urban PM, the data obtained from the characterization of PM from ship emissions showed a general enrichment in terms of total carbon content and, in particular, an increase in terms of elemental carbon percentage.

Elemental composition and enrichment factors

Data on metal concentrations in PM_{10} collected during Off and SO phases are reported in Table 2.

The largest contribution of metals to PM_{10} occurs during the SO, with a percentage of 0.51%, while during the Off, it was 0.32%; also, the relative abundance of the elements varied according to the navigation phase as follows:

- Off: Zn > Fe > Al > V > Ti > Ni > Pb > Cu > Cr > Sn > Mn > Ag > Co > As > Cd > Tl > Se > Hg
- SO: Al > Fe > Zn > V > Ti > Cr > Sn > Cu > Ni > Pb > Mn > Hg > Ag > As > Se > Co > Tl > Cd

Table 2 Mean concentration ± standard deviation and EF of the elements collected on-board during Off and the SO phases, divided, for a better understanding, as follows: (a) most abundant metals; (b) moderately abundant metals; and (c) less abundant metals

(μg/g)	Off	SO	Off EF	SO
Most abundant metals				
Al	653.8 ± 867.3	3175 ± 5617	-	-
Ti	152.7 ± 238.2	115.7 ± 193.7	24.0	6.5
Fe	845.3 ± 644.2	865.5 ± 786.2	1.2	0.5
Zn	1084 ± 670.1	427.6 ± 388.8	999.4	344.8
V	201.5 ± 313.2	181.3 ± 382.6	1959	733.2
Moderately abundant metals				
Ni	64.6 ± 62.8	47.2 ± 42.4	79.9	47.6
Cu	45.9 ± 30.4	55.0 ± 76.7	600.8	340.6
Pb	48.5 ± 33.8	31.7 ± 32.6	191.2	71.5
Sn	40.6 ± 49.1	57.9 ± 128.0	212.5	344.8
Cr	42.7 ± 44.3	73.0 ± 104.4	42.6	36.1
Mn	28.8 ± 32.3	25.4 ± 30.5	21.4	5.8
Less abundant metals				
Ag	1.3 ± 2.0	7.6 ± 12.9	1016	1282
Co	0.8 ± 0.5	1.1 ± 1.3	3.0	2.0
As	0.8 ± 0.7	1.3 ± 1.4	16.2	20.5
Se	0.2 ± 0.2	1.2 ± 1.6	573.0	238.9
Cd	0.6 ± 0.1	0.6 ± 0.8	819.7	263.8
Hg	0.1 ± 0.2	11.5 ± 21.1	165.7	1399
Tl	0.4 ± 0.4	0.9 ± 1.1	7.4	9.0

The most abundant elements were Zn for Off (of 1084 ± 670.1 μg/g) and Al for SO (of 3174.8 ± 5617.0 μg/g) followed by Fe, Al and V in the samples collected during offshore navigation and Fe, Zn and V in the samples collected during the shunting operations. The less abundant trace metals were Tl, Se, and Hg and Co, Tl and Cd in PM collected on offshore navigation and shunting operations respectively.

Most of metals here considered showed considerably different concentration depending on navigation phase; among these, Zn, Pb, V and Ni showed higher concentrations in samples collected during Off while Al, Hg, Ag, Cr and Sn during SO.

These results indicate a strong dependence between PM elemental composition and navigation regimes, each metal showing a specific behaviour, in agreement with published data. This behaviour might be partially explained by observing the trend of markers in the exhaust; in fact, a different contribution to particles elemental composition from lubricant oils was reported, probably due to their different metals content depending on duration of use (Sippula et al., 2014).

A detailed analysis was carried out for the detection of chemical tracers of ship emissions, focusing not only on the concentration of chemical species but also on tracer concentration ratios. Mazzei et al. (2008) concluded that heavy oil combustion may be identified by the concentration ratio V/Ni = 3.2 ± 0.8 in all PM fraction; Nigam et al. (2006) measured a ratio V/Ni ranging from 2.3 to 4.5 by directly sampling at the exhausts of different auxiliary ship engines fed by different fuels. Also, Viana et al. (2009) obtained similar results for ambient air concentrations in Spain across the Gibraltar Strait, where valid tracers of commercial shipping emissions in ambient PM_{10} and $PM_{2.5}$ showed ratios of V/Ni = 4 ± 1 and the ratio V/EC < 2. For the samples collected in this study, the V/Ni ratio was in the range 3.1–3.8, and the V/EC ratio showed a constant value of 0.07, in agreement with the published data.

The EFs of 18 elements in PM_{10} samples collected during SO and Off are also shown in Table 2.

Only a few elements showed EF significantly higher during SO (Sn, Hg); the others showed comparable values for EF calculated during Off and during SO (Tl, As, Cr, Ag with differences less 30%) or highest values during Off (Ti, Fe, Zn, V, Ni, Cu, Pb, Cr, Mn, Co, Se, Cd).

The EFs calculated for PM_{10} sampled on board were compared with the EFs for metals in the urban PM_{10} collected by the regional agency for the environment (ARPA Campania) in the same day in the urban area of Naples (Fig. 3). The two stations chosen for the comparison were indicated as "NA01" (Astronomical Observatory) and "Portici" (Parco Reggia). These stations can be both considered background stations: The NA01 station is located in the "Royal Capodimonte Wood", outside the city centre of Naples and about 3 kms from the port area; the "Portici" station is located inside the "Reggia Palace" park, in a green area in the middle of to the urban centre of Portici and the urban centre of Ercolano, about 4 kms from the port area.

As can be seen from Fig. 3, there are some elements (Cr, Mn, Fe, Ni, As) that showed the same EFs in PM_{10} samples collected in both urban area and ship emissions, whereas for the others, the comparison among EFs does not allow to draw specific conclusions. V is the only element whose enrichment factor is univocally attributable to ship emission, showing the EFs for both SO and Off much greater than that of urban PM.

Polycyclic aromatic hydrocarbons

The largest contribution of PAHs to PM_{10} occurred during the SO phase, with a percentage of 0.12%, while during the Off phase, the percentage was 0.06%. The PAH relative abundances also vary according to the navigation procedure:

- Off: B(a)A > Pyr > B(a)P > Chr > B(b)F > B(g)P > B(k)F > I(c)P > Ant
- SO: B(a)A > B(a)P > B(b)F > B(g)P > B(k)F > Chr > Pyr > I(c)P > Ant

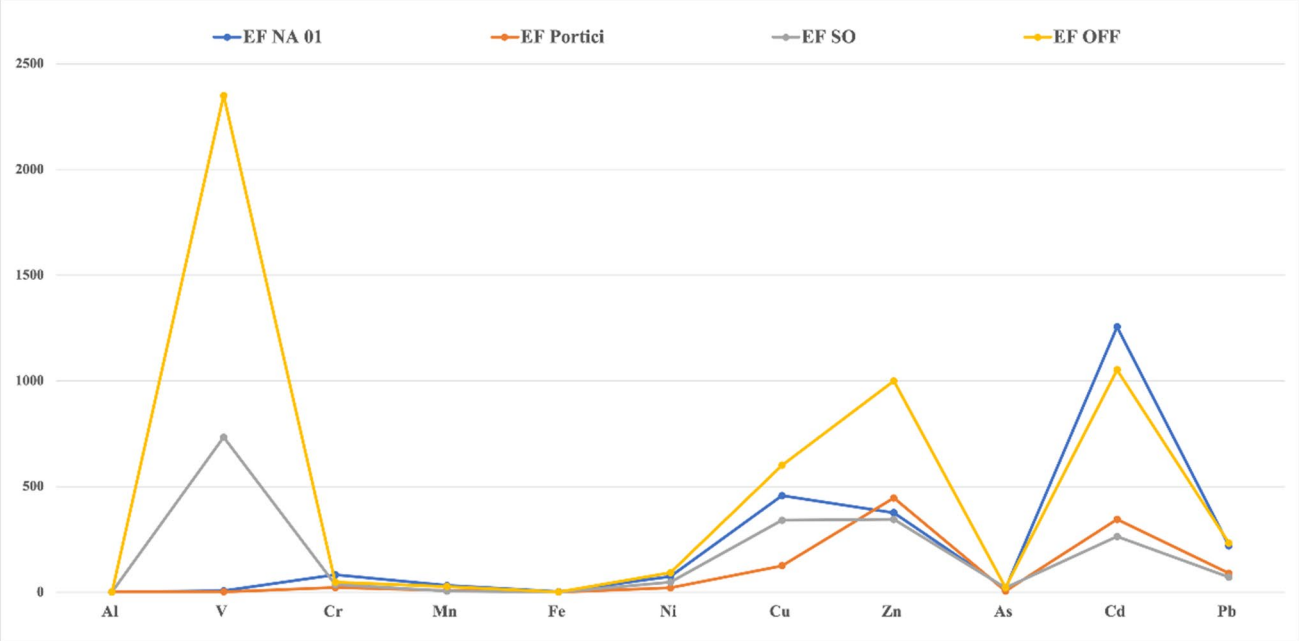

Fig. 3 Comparison between the EFs for urban PM samples (NA01 and Portici) and EFs for PM samples from ship emissions (Off and SO)

The most abundant species was B(a)A for both Off and SO (with concentrations of 128.3 ± 105.3 µg/g and 277.8 ± 159.1 µg/g respectively), followed by Pyr (123.3 ± 132.7 µg/g) and B(a)P (81.7 ± 85.6 µg/g) in the samples collected during Off and followed by B(a)P (187.3 ± 250.3 µg/g) and B(b)F (159.6 ± 208.1 µg/g) in the samples collected during SO.

In addition, the PAHs less abundant were indeno(1,2,3-cd)pyrene (22.3 ± 29.7 µg/g for Off and 69.0 ± 89.1 µg/g for SO) and anthracene + phenanthrene (4.7 ± 4.9 µg/g for Off and 2.6 ± 1.9 µg/g for SO) during both phases of navigation. In general, all the species showed considerable differences in their concentration during the different phases of navigation, with the greatest concentrations during SO, with the exception of anthracene + phenanthrene and pyrene that showed the highest concentrations during Off (Fig. 3).

In Sippula et al. (2014), it was observed a nonlinear dependence of EFs for PAHs (as for OC/EC and metals, as discussed in the previous paragraphs) on engine load, with highest emission factors at low load engine (< 25% corresponding to SO) or at high load engine (50–75% corresponding to Off) depending on considered species and fuel typology. They also discussed the fuel-to-particles emission fractions of polycyclic aromatic compounds for which a general increase during low load engine (SO) was observed.

It is important to note that benzo(a)pyrene, classified as a carcinogen by the IARC (International Agency for Research on Cancer), represented the second most abundant PAH emitted during the shunting operations, that is the phase of greatest exposure for population in the urban area. The other PAHs registered during shunting operations, belonging to Group 2B (possible carcinogens), have concentrations all above 100 ug/g (IARC 2010).

All PAHs showed, as expected, very high concentrations compared with data of PAHs in PM_{10} collected in urban and background stations of Naples (Di Vaio et al. 2016).

The analysis carried out in this study can be considered an evaluation of the pure source "ship emission", given that the sampling was carried out directly inside the ship's exhaust stack, minimizing the interference by other sources of pollution. A similar analysis was carried out in the city of Naples for the pure source "road traffic", through an experiment conducted in an urban tunnel by Riccio et al. (2016). In Fig. 4, the average concentrations (ug/g) of PAHs emitted

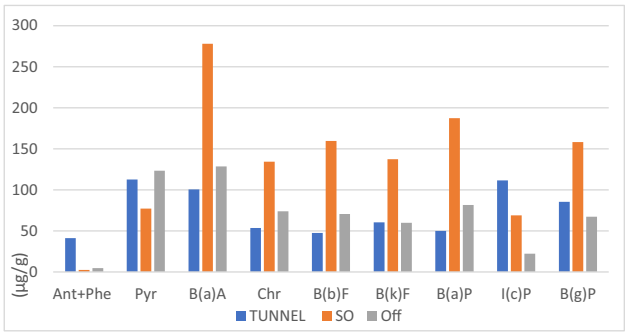

Fig. 4 Comparison between the average concentrations (ug/g) of PAHs emitted in the different navigation phases and the average concentrations (ug/g) of PAHs measured during an urban tunnel experiment in Naples (Riccio et al. 2016)

during the two navigation phases were compared with those determined on the PM_{10} sampled at the exit of the urban tunnel.

It is interesting to observe that the average concentrations of benzo(a)anthracene, B(b)F and B(a)pyrene emitted during the SO were about three times higher than the concentrations emitted by the vehicle fleet in transit through the tunnel, while the concentrations of Chr, B(k)F and B(g)P were about twice.

Finally, only anthracene + phenanthrene and indeno(1,2,3-cd)pyrene were emitted in considerably greater quantities by vehicular traffic compared to the ship emissions (both SO and Off), while pyrene emissions due to vehicular traffic and offshore navigation were comparable.

To compare PAHs profiles, in Fig. 5, the ratios between each PAH and benzo(a)pyrene for ship emission, PM collected at a monitoring station in the urban area of Naples (Urban PM10) and PM collected at a monitoring station outside the urban area (Bkg PM10) were reported (the last two dataset calculated starting from the data published by Di Vaio et al., 2016). Finally, still in Fig. 5, the same data for tunnel emissions are reported (calculated starting from the data published in Riccio et al., 2016).

Benzo(a)pyrene was chosen as reference being a typical combustion product and the principal PAH detected in urban PM.

With the exception of anthracene + phenanthrene, it is important to note that for all the species considered, the highest ratio values were registered for samples collected during tunnel experiment, suggesting that PM_{10} samples of vehicular traffic were "enriched" in terms of PAHs compared to the other samples considered here.

The ratios PAH/B(a)P were generally comparable during SO and Off, indicating that the emission of PAHs may depend on the same process (may be fuel combustion)

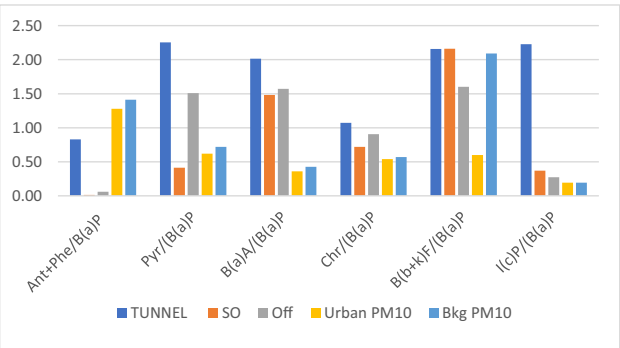

Fig. 5 Comparison among the ratio of measured PAHs and benzo(**a**)pyrene for samples collected in the tunnel experiment, during SO and during Off and in urban and background PM_{10} in the city of Naples (Di Vaio et al. 2016; Riccio et al. 2016)

during both operation modes, with the exception of pyrene and B(b + k)F.

Also, between urban and background PM_{10}, there were no significant differences, with the exception of the ratio B(b + k)F/B(a)P; this ratio for PM_{10} in background station was considerably greater than the ratio for urban PM_{10} and comparable with ratios for Tunnel, SO and Off.

Statistical analysis

As discussed in the previous sections, chemical data were analysed separately for shunting operations and offshore navigation. To evaluate the possible differences between these two emission regimes, a statistical analysis on chemical data was applied.

As a first step, a PERMANOVA analysis was performed; no significant differences were detected between levels of the factor ET (emission type, distinguishing two groups: SO and Off) considering the whole chemical dataset ($p = 0.60$), data on metals concentrations ($p = 0.67$), data on EC and OC ($p = 0.86$) and data on PAHs ($p = 0.40$) separately. In addition, a PCA analyses was performed (Fig. 6), confirming PERMANOVA results and indicating that there were no clusters clearly defined.

Although PERMANOVA and PCA did not identified significant differences in the general chemical composition of samples from SO and Off, SIMPER results indicated that there were seven species (Zn, Pb, Ti, Ni, Mn, Ant + Phe, Pyr) that contributed for the 3.5% to dissimilarities between ET levels.

These species also concurred for about the 40% of total dissimilarities and can be used to assess differences between shunting operations and offshore sailing emissions. This is confirmed by a PERMANOVA analysis on these species ($p = 0.02$).

PCA was applied again to this set of nine chemical parameters (Fig. 7a); also, in this case, there is no clear separation between ET levels (SO and Off), but PERMDISP results revealed differences ($p = 0.01$) in the heterogeneity of samples in the same level. In particular, samples belonging to the Off level were significantly more heterogeneous than those belonging to SO level (Fig. 7b), allowing to affirm that samples from SO are chemically more similar than samples collected during Off.

Finally, as reported in Fig. 8, linear regression models among SIMPER chemical parameters allowed to identify positive correlations among some species (Ti and Mn, Ni and Zn, Ti and Mn with Pyr, Zn and EC). In particular, Ti and Mn were strongly positively correlated, but negatively correlated with EC; on the other hand, Zn, Pb, Anth + Phe and Pyr showed some positive correlations among each other and partially positive correlations with EC, allowing to assume a common origin for them.

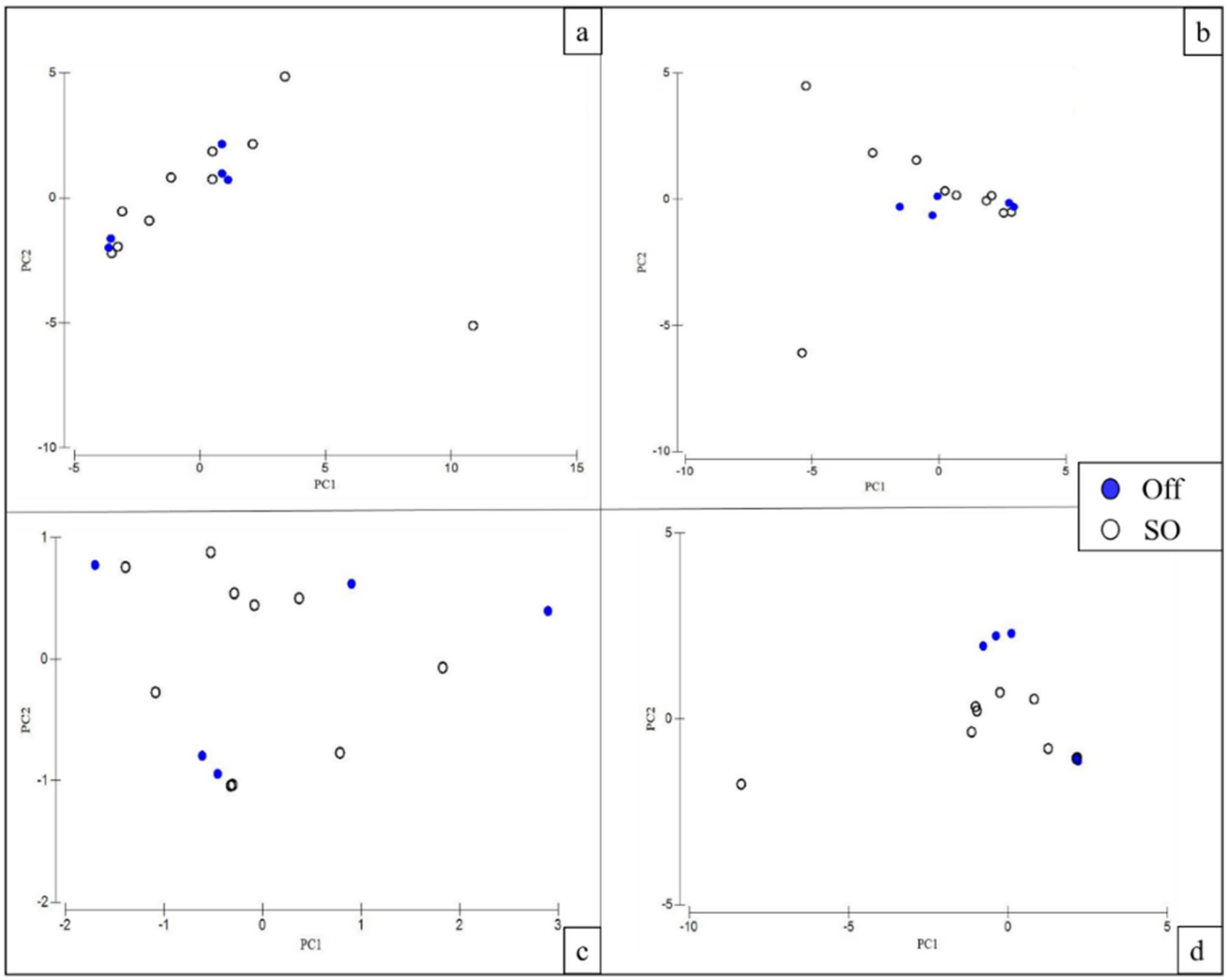

Fig. 6 Principal component analysis on (**a**) whole dataset, (**b**) metals dataset, **c** carbons species dataset and (**d**) PAHs dataset

Conclusions

Samples collected at the exhaust stacks of a hydrofoil travelling in the Gulf of Naples were analysed for their chemical composition, which was summarized as a function of the navigation phase; precisely, PM_{10} samples collected during shunting operations and offshore navigation were characterized in terms of elemental and organic carbon fraction, PAHs and elements.

Results were compared to those obtained by analysing PM_{10} linked to road traffic (collected during a tunnel experiment) and those collected in the urban area (in correspondence of the monitoring stations of the local PM network). More specifically, species concentration and the enrichment factors were evaluated and compared, with the aim of better describing the characteristics of naval emissions, and assess their contribution to PM.

In general, the most important contribution to PM_{10} was due to organic and elemental carbon, with a percentage of about 40% and 21% respectively; emissions during shunting operations and during offshore navigation showed no significant differences in terms of correlation between OC and EC: In both cases, OC and EC were not correlated indicating that they are probably depending on different emission processes. The comparison with the percentage of OC and EC in PM_{10} samples collected in the urban area of Naples and other similar cities with data here presented suggest that shipping emissions could be an important source of EC, due to the greater EC percentage in PM from shipping emissions compared with EC percentage generally observed in the urban PM.

Greater differences between navigation phases were observed for elemental composition, metals concentrations showing great variability in their dependence on navigation mode, with elements characterised by higher concentrations

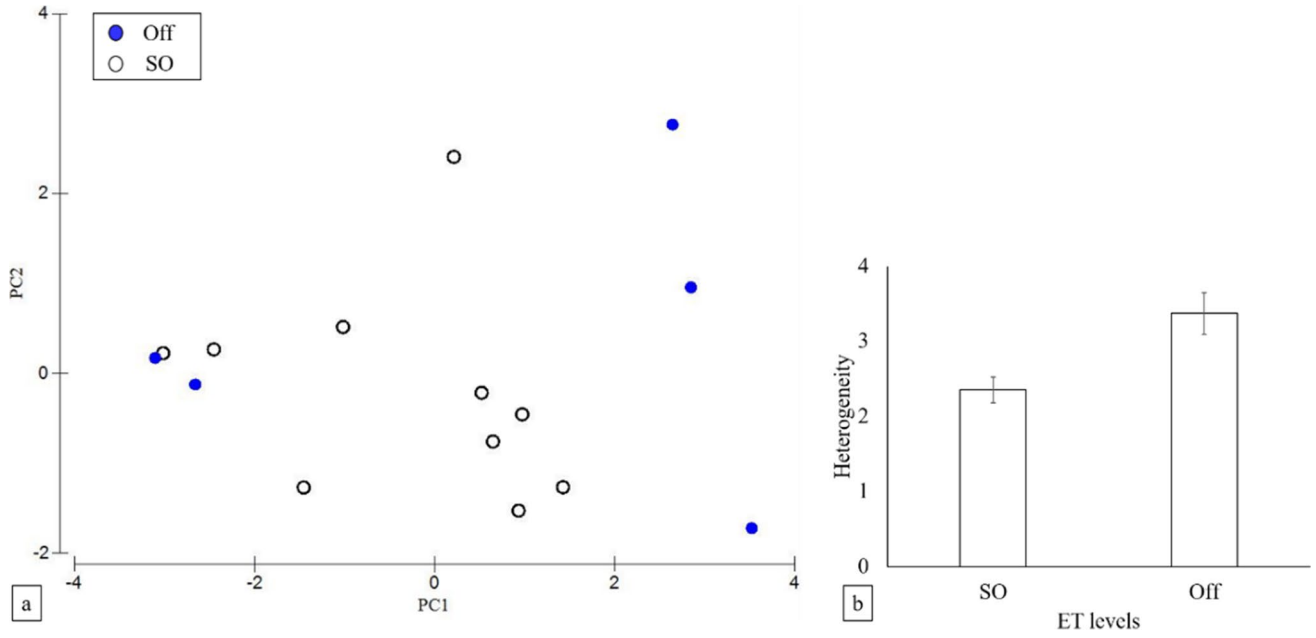

Fig. 7 **a** Principal component analyses on the nine species identified by SIMPER analyses; **b** mean (±SD) multivariate dispersion (PERMDISP) of replicates around ET levels

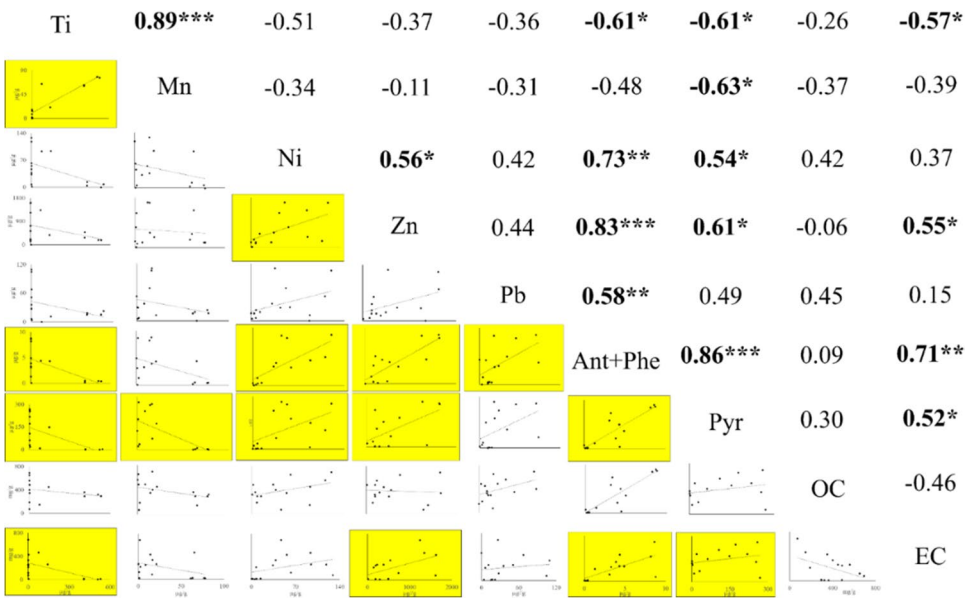

Fig. 8 Linear regression models among chemical species detected by SIMPER analysis (yellow: $p < 0.05$). The variables are on the diagonal. Pearson index is also displayed for each pair of variables, and significant p value is indicated as: *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$

in samples collected during SO (Al, Hg, Ag, Cr, Sn) and elements with higher concentrations in samples collected during Off (Zn, Pb, V and Ni).

The comparison with element profiles determined in PM_{10} background samples confirmed the role of V as a shipping emission tracer (for both phases of navigations).

Differences were observed in terms of PAHs composition: It is possible to distinguish two groups (B(g)P, B(a)P, B(k)F, B(b)F, B(a)A, Chr and Ant + Phen, Pyr) depending on navigation phase. The comparison of PAH profiles from ship and vehicular traffic indicates that the greatest contribution for some PAHs (B(a)A, I(c)P) was due to vehicular traffic; in the other PAHs, the contributions were comparable. Benzo(a)pyrene, classified as a carcinogen by the IARC (International Agency for Research on Cancer), represented the second most abundant PAH emitted during the shunting operations, that is the phase of greatest exposure for population in the urban area.

Finally, the data were statistically analyzed to better evaluate differences between offshore navigation and shunting operation and to highlight correlations among the species considered; in particular, correlations were observed among species as Ti and Mn, Ni and Zn, Zn and EC therefore attributable to the same process.

Results here exposed confirmed the specificity of emission profiles for ship typology (in terms of engine, navigation phase and fuel) and the need to collect more data to improve the emission inventories on that source and to provide a support for control strategies.

Author contribution EC (corresponding author) and AR contributed to the study conception and design. Analyses were performed by EC, GT, AD, JP, ADG, PC and VM. Material preparation and data curation were performed by DC, UD, EC, AR, GC and LA. The first draft of the manuscript was written by GT, EC, AR and LA, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Agrillo G, Chianese E, Riccio A, Zinzi A (2013) Modeling and characterization of air pollution: perspectives and recent developments with a focus on the Campania Region (Southern Italy). Int J of Env Res 7:909–916. https://doi.org/10.22059/IJER.2013.673

Amodio M, de Gennaro G, Di Gilio A, Tutino M (2014) Monitoring of the deposition of PAHs and metals produced by a steel plant in Taranto (Italy). Adv in Met 2014:598301. https://doi.org/10.1155/2014/598301

Anderson MJ (2001) Permutation tests for univariate or multivariate analysis of variance and regression. Can J Fish Aquat Sci 58:626–639. https://doi.org/10.1139/cjfas-58-3-626

Anderson MJ, Ellingsen KE, McArdle BH (2006) Multivariate dispersion as a measure of beta diversity. Ecol Lett 9:683–693. https://doi.org/10.1111/j.1461-0248.2006.00926.x

Appolloni L, Sandulli R, Vetrano G, Russo GF (2018a) a). A new approach to assess marine opportunity costs and monetary values-in-use for spatial planning and conservation; the case study of Gulf of Naples, Mediterranean Sea. Italy Ocean Coast Manag 152:135–144. https://doi.org/10.1016/j.ocecoaman.2017.11.023

Appolloni L, Sandulli R, Bianchi CN, Russo GF (2018b) Spatial analyses of an integrated landscape-seascape territorial system: the case of the overcrowded Gulf of Naples. Southern Italy J Environ Account Manag 6(4):365–380. https://doi.org/10.5890/JEAM.2018.12.009

Appolloni L, Zeppilli D, Donnarumma L, Baldrighi E, Chianese E, Russo GF, Sandulli R (2020) Seawater acidification affects beta-diversity of benthic communities at a shallow hydrothermal vent in a Mediterranean marine protected area (Underwater Archaeological Park of Baia, Naples, Italy). Diversity 12:1–19. https://doi.org/10.3390/d12120464

Cavalli F, Viana M, Yttri KE, Genberg J, Putaud JP (2010) Toward a standardised thermal– optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atm Meas Tech 3:79–89. https://doi.org/10.5194/amt-3-79-2010

Cesari D, Genga A, Ielpo P, Siciliano M, Mascolo G, Grasso MF, Contini D (2014) Source apportionment of PM2.5 in the harbour–industrial area of Brindisi (Italy): identification and estimation of the contribution of in-port ship emissions. Sci Tot Env 497:392–400. https://doi.org/10.1016/j.scitotenv.2014.08.007

Chianese E, Tirimberio G, Riccio A (2019) $PM_{2.5}$ and PM_{10} in the urban area of Naples: chemical composition, chemical properties and influence of air masses origin. J of Atmos Chem 76:151–169. https://doi.org/10.1007/s10874-019-09392-3

Clarke KR, Gorley R, Sommerfield PJ, Warwick RM (2014) Change in marine communities - an approach to statistical analysis and interpretation, 3rd edn. Plymouth, Plymouth, PRIMER-E

Clarke KR, Gorley RN (2015) Primer: User manual/tutorial. Prim. Ltd., Plymouth, UK, p 93

Contini D, Gambaro A, Donateo A, Cescon P, Cesari D, Merico E, Belosi F, Citron M (2015) Inter-annual trend of the primary contribution of ship emissions to PM2.5 concentrations in Venice (Italy): Efficiency of emissions mitigation strategies. Atmos Env 102:183–190. https://doi.org/10.1016/j.atmosenv.2014.11.065

Cooper DA (2001) Exhaust emissions from high-speed passenger ferries. Atmos Env 35:4189–4200. https://doi.org/10.1016/S1352-2310(01)00192-3

Cooper DA (2003) Exhaust emissions from ships at berth. Atmos Env 37:3817–3830. https://doi.org/10.1016/S1352-2310(03)00446-1

Corbett JJ, Winebrake JJ, Green EH, Kasibhatla P, Eyring V, Lauer A (2007) Mortality from ship emissions : a global assessment. Env Sci and Tech 41(24):8512–8518. https://doi.org/10.1021/es071686z

Dinoi A, Cesari D, Marinoni A, Bonasoni P, Riccio A, Chianese E, Tirimberio G, Naccarato A, Sprovieri F, Andreoli V, Moretti S, Gullì D, Calidonna CR, Ammoscato I, Contini D (2017) Intercomparison of carbon content in PM2.5 and PM10 collected at five measurement sites in Southern Italy. Atmos 8(12):243. https://doi.org/10.3390/atmos8120243

Di Vaio P, Cocozziello B, Corvino A, Fiorino F, Frecentese F, Magli E, Onorati G, Saccone I, Santagada V, Settimo G, Severino B, Perissutti E (2016) Level, potential sources of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM10) in Naples. Atmos Env 129:186–196. https://doi.org/10.1016/j.atmosenv.2016.01.020

Donateo A, Gregoris E, Gambaro A, Merico E, Giua R, Nocioni A, Contini D (2014) Contribution of harbour activities and ship traffic to PM2.5, particle number concentrations and PAHs in a port city of the Mediterranean Sea (Italy). Env Sci and Poll Res 21:9415–9426. https://doi.org/10.1007/s11356-014-2849-0

Donnarumma L, Appolloni L, Chianese E, Bruno R, Baldrighi E, Guglielmo R, Russo GF, Zeppilli D, Sandulli R (2019) Environmental and benthic community patterns of the shallow hydrothermal area of Secca delle Fumose (Baia, Naples, Italy). Front Mar Sci 6:685. https://doi.org/10.3389/fmars.2019.00685

Fridell E, Steen E, Peterson K (2008) Primary particles in ship emissions. Atmos Env 42:1160–1168. https://doi.org/10.1016/j.atmosenv.2007.10.042

Gregoris E, Barbaro E, Morabito E, Toscano G, Donateo A, Cesari D, Contini D, Gambaro A (2016) Impact of maritime traffic on polycyclic aromatic hydrocarbons, metals and particulate matter

in Venice air. Env Sci Poll Res 23:6951–6959. https://doi.org/10.1007/s11356-015-5811-x

Hountalas DT, Papagiannakis RG, Zovanos G, Antonopoulos A (2014) Comparative evaluation of various methodologies to account for the effect of load variation during cylinder pressure measurement of large scale two-stroke diesel engines. Appl Energy 113:1027–1042. https://doi.org/10.1016/j.apenergy.2013.08.036

IARC (International Agency for Research on Cancer) (2010) Some non-heterocyclic polycyclic aromatic hydrocarbons andsome related exposure. IARC Monogr Eval Carcinog Risks Hum 92:1

Ledoux F, Roche C, Cazier F, Beaugard C, Courcot D (2018) Influence of ship emissions on NOx, SO_2, O_3 and PM concentrations in a North-Sea harbor in France. J Env Sci 71:56–66. https://doi.org/10.1016/j.jes.2018.03.0301001-0742

Manousakas M, Papaefthymiou H, Diapuoli E, Migliori A, Karydas AG, Bogdanovic-Radovic I, Eleftheriadis K (2017) Assessment of PM2.5 sources and their corresponding level of uncertainty in a coastal urban area using EPA PMF 5.0 enhanced diagnostics. Sci Tot Env 574:155–164. https://doi.org/10.1016/j.scitotenv.2016.09.047

Masiol M, Squizzato S, Rampazzo G, Pavoni B (2014) Source apportionment of PM2.5 at multiple sites in Venice (Italy): Spatial variability and the role of weather. Atmos Poll 98:78–88. https://doi.org/10.1016/j.atmosenv.2014.08.059

Matthias V, Bewersdorff I, Aulinger A, Quante M (2010) The contribution of ship emissions to air pollution in the North Sea regions. Env Poll 158:2241–2250. https://doi.org/10.1016/j.envpol.2010.02.013

Mazzei F, D'Alessandro A, Lucarelli F, Nava S, Prati P, Valli G, Vecchi R (2008) Characterization of particulate matter sources in an urban environment. Sci Tot Env 401:81–89. https://doi.org/10.1016/j.scitotenv.2008.03.008

Merico E, Donateo A, Gambaro A, Cesari D, Gregoris E, Barbaro E, Dinoi A, Giovanelli G, Masieri S, Contini D (2016) Influence of in-port ships emissions to gaseous atmospheric pollutants and to particulate matter of different sizes in a Mediterranean harbour in Italy. Atmos Env 139:1–10. https://doi.org/10.1016/j.atmosenv.2016.05.024

Merico E, Cesari D, Dinoi A, Gambaro A, Barbaro E, Guascito MR, Giannossa LC, Mangone A, Contini D (2019) Inter-comparison of carbon content in PM_{10} and $PM_{2.5}$ measured with two thermo-optical protocols on samples collected in a Mediterranean site. Env Sci Poll Res 26:29334–29350. https://doi.org/10.1007/s11356-019-06117-7

Monaco D, Chianese E, Riccio A, Delgado-Sanchez A, Lacorte S (2017) Spatial distribution of heavy hydrocarbons, PAHs and metals in polluted areas. The case of "Galicia." Spain Mar Poll Bull 121:230–237. https://doi.org/10.1016/j.marpolbul.2017.06.003

Moldanova J, Fridell E, Popovicheva O, Demirdjian B, Tishkova V, Faccinetto A, Focsa C (2009) Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. Atmos Env 43(16):2632–2641. https://doi.org/10.1016/j.atmosenv.2009.02.008

Moldanová J, Fridell E, Winnes H, Holmin-Fridell S, Boman J, Jedynska A, Tishkova V, Demirdjian B, Joulie S, Bladt H, Ivleva NP, Niessner R (2013) Physical and chemical characterization of PM emissions from two ships operating in European emission control areas. Atmos Meas Tech 6:3577–3596. https://doi.org/10.5194/amt-6-3577-2013

Mueller L, Jakobi G, Czech H, Stengel B, Orasche J, Arteaga-Salas JM, Karg E, Elsasser M, Sippula O, Streibel T, Slowik J, Prevot ASH, Jokiniemi J, Rabe R, Harndorf H, Michalke B, Schnelle-Kreis J, Zimmermann R (2015) Characteristics and temporal evolution of particulate emissions from a ship diesel engine. App Energy 155:204–217. https://doi.org/10.1016/j.apenergy.2015.05.115

Murena F, Mocerino L, Quaranta F, Toscano D (2018) Impact on air quality of cruise ship emissions in Naples, Italy. Atmos Env 187:70–83. https://doi.org/10.1016/j.atmosenv.2018.05.056

Nigam A, Welch W, Wayne Miller J, Cocher III DR (2006) Effect of fuel sulphur content and control technology on PM emission from ship's auxiliary engine. In: *Proceedings of the International Aerosol Conference*, St. Paul, USA, 10-15, pp. 1531–1532

Palmisani J, Di Gilio A, Franchini S, Cotugno P, Miniero V, D'Ambruoso P, de Gennaro G (2020) Particle-bound PAHs and elements in a highly industrialized city in Southern Italy: PM2.5 chemical characterization and source apportionment after the implementation of governmental measures for air pollution mitigation and control. Int J Environ Res Public Health 17(13):4843. https://doi.org/10.3390/ijerph17134843

Pérez N, Pey J, Reche C, Cortés J, Alastuey A, Querol X (2016) Impact of harbour emissions on ambient PM_{10} and $PM_{2.5}$ in Barcelona (Spain): evidences of secondary aerosol formation within the urban area. Sci Tot Env 571:237–250. https://doi.org/10.1016/j.scitotenv.2016.07.025

Petzold A, Hasselbach J, Lauer P, Baumann R, Franke K, Gurk C, Schlager H, Weingartner E (2008) Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. Atmos Chem and Phys 8:2387–2403. https://doi.org/10.5194/acp-8-2387-2008

Petzold A, Weingartner E, Hasselbach J, Lauer P, Kurok C, Fleischer F (2010) Physical properties, chemical composition, and cloud forming potential of particulate emissions from marine diesel engines at various load conditions. Env Sci and Tech 44:3800–3805. https://doi.org/10.1021/es903681z

Pey J, Perez N, Cortés J, Alastuey A, Querol X (2013) Chemical fingerprint and impact of shipping emissions over a western Mediterranean metropolis: primary and aged contributions. Sci Tot Env 463:497–507. https://doi.org/10.1016/j.scitotenv.2013.06.061

Popovicheva O, Kireeva E, Persiantseva N, Timofeeva M, Bladt H, Ivleva NP, Niesser R, Moldanova J (2012) Microscopic characterization of individual particles from multicomponent ship exhaust. J of Env Monit 14:3101–3110. https://doi.org/10.1039/C2EM30338H

Prati MV, Costagliola MA, Quaranta F, Murena F (2015) Assessment of ambient air quality in the port of Naples. J Air Waste Manag Assoc 65(8):970–979. https://doi.org/10.1080/10962247.2015.1050129

R Development Core Team R (2011) R: A language and environment for statistical computing. R Found Stat Comput. https://doi.org/10.1007/978-3-540-74686-7

Revelle WR (2020) psych: Procedures for personality and psychological research. R Package Version 2:12

Riccio A, Chianese E, Monaco D, Costagliola MA, Perretta G, Prati MV, Agrillo G, Esposito A, Gasbarra D, Shindler L, Brusasca G, Nanni A, Pozzi C, Magliulo V (2016) Real-world automotive particulate matter and PAH emission factors and profile concentrations: results from an urban tunnel experiment in Naples, Italy. Atmos Env 141:379–387. https://doi.org/10.1016/j.atmosenv.2016.06.070

Riccio A, Chianese E, Agrillo G, Esposito C, Ferrara L, Tirimberio G (2014) Source apportion of atmospheric particulate matter: a joint Eulerian/Lagrangian approach. Env Sci Poll Res 21:13160–13168. https://doi.org/10.1007/s11356-013-2367-5

Ristimaki J, Hellem G, Lappi M (2010) Chemical and physical characterization of exhaust particulate matter from a marine medium speed diesel engine. CIMAC Congress, Bergen, Norway

Romagnoli P, Vichi F, Balducci C, Imperiali A, Perilli M, Paciucci L, Petracchini F, Cecinato A (2017) Air quality study in the coastal city of Crotone (Southern Italy) hosting a small-size harbor.

Env Sci Poll Res 24:25260–25275. https://doi.org/10.1007/s11356-017-0126-8

von Schneidemesser E, Monks PS, Allan JD, Bruhwiler L, Forster P, Fowler D et al (2015) Chemistry and the linkages between air quality and climate change. Chem Rev 115(10):3856–3897. https://doi.org/10.1021/acs.chemrev.5b00089

Sarvi A, Fogelholm CJ, Zevenhoven R (2008) Emissions from large-scale medium-speed diesel engines: 2. Influence of fuel type and operating mode. Fuel Proc Tech 89:520–527. https://doi.org/10.1016/j.fuproc.2007.10.005

Sirignano C, Riccio A, Chianese E, Ni H, Zenker K, D'Onofrio A, Meijer HAJ, Dusek U (2019) High contribution of biomass combustion to $PM_{2.5}$ in the city centre of Naples (Italy). Atmos 10(8):451. https://doi.org/10.3390/atmos10080451

Sippula O, Stengel B, Sklorz M, Streibel T, Rabe R, Orasche J, Lintelmann J, Michalke B, Abbaszade G, Radischt C, Groger T, Schnelle-Kreis J, Harndorf H, Zimmermann R (2014) Particle emissions from a marine engine: chemical composition and aromatic emission profiles under various operating conditions. Environ. Sci. Technol. 48(19):11721–11729. https://doi.org/10.1021/es502484z

Toscano D, Murena F (2019) Atmospheric ship emissions in ports: a review Correlation with data of ship traffic. Atmos Env X 4:100050. https://doi.org/10.1016/j.aeaoa.2019.100050

Tutino M, Di Gilio A, Laricchiuta A, Assennato G, de Gennaro G (2016) An improved method to determine PM-bound nitro PAHs in ambient air. Chemos 161:463–469. https://doi.org/10.1016/j.envpol.2019.112967

Viana M, Amato F, Alastuey A, Querol X, Moreno T, Santos SGD, Herce MD, Fernández-Patier R (2009) Chemical tracers of particulate emissions from commercial shipping. Env Sci Tech 43:7472–7477. https://doi.org/10.1021/es901558t

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232. https://doi.org/10.1016/0016-7037(95)00038-2

Walsh C, Bows A (2012) Size matters: exploring the importance of vessel characteristics to inform estimates of shipping emissions. App Energy 98:128–137. https://doi.org/10.1016/j.apenergy.2012.03.015

Yau PS, Lee SC, Cheng Y, Huang Y, Lai SC, Xu XH (2013) Contribution of ship emissions to the fine particulate in the community near an international port in Hong Kong. Atmos Res 124:61–72. https://doi.org/10.1016/j.atmosres.2012.12.009