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 ± 0.12%), total carbon (61.9% ± 20.0%, with 40.4% of organic carbon, OC, and 21.5% of elemental carbon, EC) and elemental fraction (0.44% ± 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)
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 Tanjijn ports, respectively). The Italian ports show significant 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://adspitrrenocentrale.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, 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).
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 MTU16V396TE74L, 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.
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., 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)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k) F), benzo(a)pyrene (B(a)P), benzo(g)perylenne (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 detection range between 0.02 and 300 ppb.

Analysis of PAHs

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).
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 \( (\rho) \) 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:

\[
\text{OM} = \text{OC} \times 1.2
\]

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 mass 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).

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; Ristimäki et al., 2010).

A study conducted in Barcelona for the purpose of evaluating the impact of harbour emissions on ambient PM revealed that OM represented 4.8% of PM 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 PM\(_{10}\) mass, divided into 31% OC and 5% EC for PM\(_{10}\), and an Italian coastal 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 > M
  n > Ag > Co > As > Cd > Tl > Se > Hg
- SO: Al > Fe > Zn > V > Ti > Cr > Sn > Cu > Ni > Pb > M
  n > Hg > Ag > As > Se > Co > Tl > Cd

|     | 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 |

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.
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 PM10 and PM2.5 showed ratios of V/Ni = 4 ± 1 and the 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 PM10 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 (Tl, Fe, Zn, V, Ni, Cu, Pb, Cr, Mn, Co, Se, Cd).

The EFs calculated for PM10 sampled on board were compared with the EFs for metals in the urban PM10 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 PM10 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 proportion of PAHs to PM10 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

| 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 |
|-----------------|-----------------|-----------------|-----------------|
|                | Off             | SO              | Off             | SO              |
|                | (μg/g)          | (μg/g)          | EF              | (μg/g)          |
| **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 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 μg/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 (μg/g) of PAHs emitted...
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, Br(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/Br(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) 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/Br(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.
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. 6 Principal component analysis on (a) whole dataset, (b) metals dataset, c carbons species dataset and (d) PAHs dataset
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 shiping 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.

**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: *$p<0.05$, **$p<0.01$, ***$p<0.001$
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.

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