ECOlogical supporting for traffic
Management in cOastal areas By using
an InteLligenT sYstem
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Report assessing and comparing the impact of ship traffic to particulate matter of difference sizes in the two cities

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WP3: Assessment of the effect of ship traffic to particulate matter

ACT 3.3: Assessment of the impact of shipping to particulate matter in Venice and Rijeka

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1 Introduction

Seaborne trade is growing faster than other transportation modes whose emissions are decreasing because of national and international stricter regulations (UNCTAD, 2017). Over 80% of World trade is carried by sea. Overall, 25% of world delivered energy consumption is employed for transport. About 75% of this energy is employed for road transport, 12% for shipping and 12% for air transport (EIA 2016). Compared to other anthropogenic sources, shipping has different features: global shipping trade is a worldwide source of air pollutants, current International Maritime Organization (IMO) legislation is effective mainly on nitrogen oxides (modulated by Tier I, II, III) and sulphur oxides. Harbours can boost economic and social development of port-cities and coastal areas (Caramuta et al., 2018), however, they have an environmental cost (McArthur and Osland, 2013; Maragkogianni and Papaefthimiou, 2015). Therefore, atmospheric impacts of shipping at regional scale, especially on coastal cities, need an increasing knowledge because of direct and indirect effects of harbour traffic and related logistic activities. This is particularly true in the Adriatic-Ionian area were an intense traffic of commercial, tourist and cruise ships affecting air quality in coastal is present (Muntean et al., 2019).

Most of the study available characterise the impacts of shipping to air quality (gaseous and particulate pollutants) by means of large spatial scale chemical transport models, of local spatial scale dispersion modelling, of receptor models based on chemical composition (mainly for particulate matter), of statistical analysis approaches based on high temporal resolution concentration measurements (Viana et al., 2014; Marelle et al., 2016; Cesari et al., 2014; Merico et al., 2016; Gregoris et al., 2016). The variety of the approaches used makes sometimes difficult a direct comparison of the results (Viana et al., 2014; Merico et al., 2017). Furthermore, specific studies in port-cities of the Adriatic-Ionian area investigating the impact of shipping to particles of different sizes are extremely scarce (Merico et al., 2016).

This report tries to fill some of these gaps applying the methodologies (Merico et al., 2017) based on both chemical characterization of particulate matter and high-temporal resolution online measurements, used in the POSEIDON project (Pollution Monitoring of ship emissions: an Integrated approach for harbours in the Adriatic basin, Interreg MED program 2007-2013) that is capitalized in ECOMOBILITY, to characterize the impact of ship traffic to particulate matter of different size starting from nanoparticles and up to PM_{10}. The same approach and the same measurement instruments have been used in the two areas (Venice and Rijeka) to ensure comparability of results.

The report is organised in the following chapters: description of the methodology used to estimate impact of ships using high temporal resolution measurements; description of the methodology used to post-process chemical analysis; a summary of data previously available in the two areas regarding impact of ships to air quality; discussion of results separating Venice and Rijeka areas; comparison of the impacts found in the two cities; conclusions summarizing the main findings.

This report is organized in the following sections:

- Chapter 2 describes the methodology used for post-processing high-temporal resolution data.
- Chapter 3 describes the methodology used for post-processing of size-segregated chemical composition.
- Chapter 4 summarises data previously available in Venice and Rijeka regarding the impact of shipping to atmospheric particulate matter.
- Chapter 5 discusses the results obtained in ECOMOBILITY regarding the impact of shipping to atmospheric particles of different size obtained
- Chapter 6 includes a comparison of the impacts of shipping to atmospheric particulate matter in Venice and Rijeka

Conclusions and bibliographic references follow.

2 Methodology used for post-processing of high temporal resolution data

High temporal resolution data have been collected at 1 minute resolution using a Condensation Particle Counter (CPC Grimm 5.403), to measure the total number concentration of particles in the size range between 0.01 – 0.25 µm, and an Optical Particle Counter (Grimm 11-A) able to measure particle number size distributions in the size range 0.25-31 µm in 31 size channels. Additional meteorological measurements are also taken at the same temporal-resolution. A full description of the instruments used is reported in the deliverable "Analysis report in Venice". The same instrumental setup was used in both areas (Venice and Rijeka). The dataset collected in each site allows to identify concentration peaks associated to the plumes of the ships (Fig. 2.1). This makes possible to statistically investigate the influence of these peaks to measured concentrations.

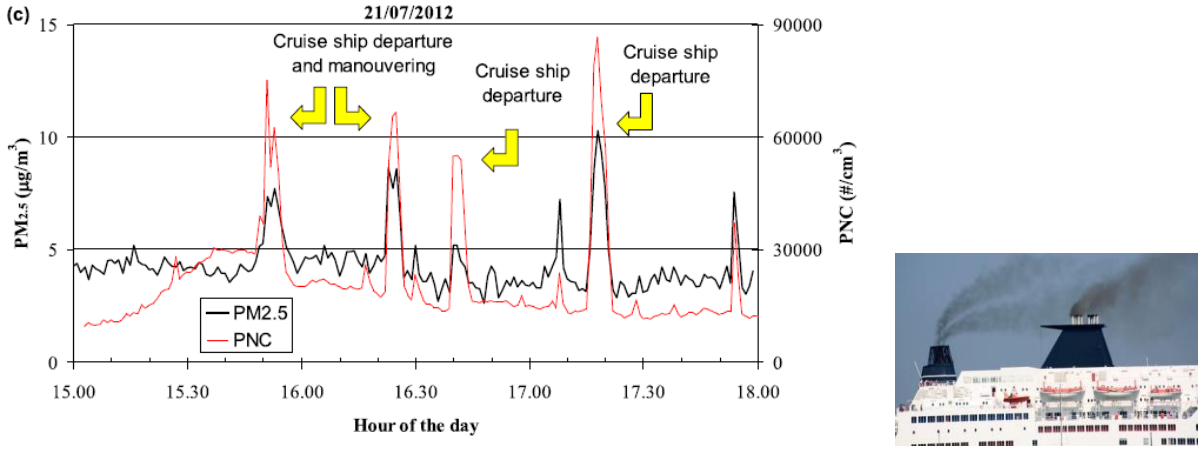

Figure 2.1. $PM_{2.5}$ and total particle number concentration (PNC) at 1-min resolution with indication of ship arrival and departure. Obtained from Contini et al. (2015).

Data is post-processed on 30-minutes average and combined with the information relative to ship traffic to evaluate the relative contribution (ε) to particle concentrations in each size range. The evaluation of ε could be due using the formula initially developed in Contini et al. (2011):

$$\varepsilon = \frac{(C_{DP} - C_{DSP})F_P}{C_D} = \frac{\Delta_P F_P}{C_D}$$

where:

- C_{DP} is the average concentrations in the selected wind direction sector (in which the site is downwind of the emissions) considering periods potentially influenced by ship emissions;
- C_{DSP} is the average concentrations not significantly influenced by ship emissions;
- C_D is the average concentration in the specific wind direction sector;
- F_P is the fraction of cases influenced by ship emissions.

3 Methodology used for post-processing of size-segregated chemical composition

Weekly samples have been collected in both areas (Venice and Rijeka) using a model 110 MOUDI cascade impactor that allowed to collect particulate matter in 12 different size ranges on quartz

fiber filters. The filters have been chemically analysed as described in the deliverables “Analysis report in Venice” and “Analysis report in Rijeka” to determine the content of carbon, major water soluble ions and metals. Chemical composition was analysed with the Positive Matrix Factorization (PMF) receptor model (EPA PMF5 code) for the individuation and characterisation of the main sources of particulate matter in the different size ranges.

Due to the large variability of the sources contributing to such a great number of different size ranges, the original dataset was divided into two different datasets, based on the size of particles: one dataset included only coarse particles (particles > 1 µm, corresponding to the first six stages of the MOUDI impactor); the second datasets included only fine and ultrafine particles (particles < 1 µm, corresponding to the last six stages of the MOUDI impactor). On this basis, data were refined in order to obtain more robust datasets. Variables with more than 50% of missing values or 50% of values under the detection limit (DL) were rejected. Values under DL were substituted by half of DL. As uncertainty, the standard deviations of the method, normalized for the average sampling volumes of each campaign, were used for metals and ions; the uncertainty of values under DL was 5/6 DL. Uncertainties on carbon were determined accordingly to Merico et al. (2019). Outliers have been excluded from the input of the model. Before running the PMF model a discrimination between "strong", "weak" and "bad" variables has been made, according to the signal to noise (S/N) ratio criterion, the residual analysis and evaluating the observed/predicted scatter plots. PM_{10} was always labels as "total variable" and therefore categorised as "weak", following the approach reported in Gregoris et al. (2016).

After running the model the stability of the solution and the uncertainty associated to the results were estimated using the Bootstrap (BS) error estimation. Within this estimation new datasets are randomly constructed from blocks of the original dataset. A number of BS datasets are then processed with PMF and the BS factors are compared to the base run factors. The solution was considered robust if each BS factor was correlated to a single base run factor, thus all factors were "mapped". Rotational ambiguity was explored using the displacement error estimation: the solution was considered valid only if no swaps were observed for the lowest displacement (dQmax=4), thus it means that the solution has no rotational ambiguity.

In order to individuate the right number of factors different solutions were explored. If various solutions were considered robust according to the BS and the DISP error estimations, the parameters IM (maximum of the average of the scaled residual) and IS (maximum of the standard deviation of the scaled residuals), together with the Q value (goodness of the fit) were examined, following the approach reported in Contini et al. (2012).

Among the different factor/sources, that characterised by V and Ni is a typical indicator of emissions associated with heavy oil combustion, including shipping (Viana et al., 2009). However, shipping is not the only source of V and Ni being possible other contribution of industrial origin and related to heavy-duty diesel vehicles, and the V/Ni ratio is generally variable in the different port-cities suggesting that this factor/source could effectively represent a mixed contribution with industrial emissions that are present in the different study areas. Therefore, the contribution of ship emissions to primary PM was extracted considering the V as a marker for the combustion in ships' engines as it was done in Zhao et al. (2013). The primary contribution PM_{ship} of ship emissions to the atmospheric PM was calculated using the formula:

$$PM_{ship} = R * \frac{V}{F_{V,HFO}} \quad \text{(Eq. 3.1)}$$

where R equals 8205.8 (Agrawal et al., 2009), a value internationally applied for locations with HFO-burning ship emissions; V is the in-situ ambient concentration of Vanadium (ng/m^3); $F_{V,HFO}$ is the typical V content (ppm) in HFOs used by vessels; in the absence of chemical analyses of fuel, the value of 65 ± 25 ppm was used to cover the typical range of $F_{V,HFO}$ (Cesari et al., 2014). The obtained primary contribution was converted in percentage dividing for the corresponding PM concentration.

4 Data previously available in Venice and Rijeka

The available information on the impact of ship traffic in the two areas (Venice and Rijeka) were collected during POSEIDON project and other publications available in the scientific literature. The weight of shipping emissions compared to road traffic for year 2010 is reported in Fig. 4.1 (taken from Merico et al., 2017). It shows that shipping has a non-negligible contribution comparable to that of road traffic and even larger for SO_2.

Other publications focused on impact of shipping to air quality in coastal towns of the Adriatic-Ionian macro-area and the results of the POSEIDON project, that is capitalized in ECOMOBILITY, are summarized in Fig. 4.2. These results indicate that impact to total particle number concentration (PNC) is significantly larger than that to mass concentrations ($PM_{2.5}$, and PM_{10}) and that there are not detailed information of the impact of shipping on size-segregated particles for this area.

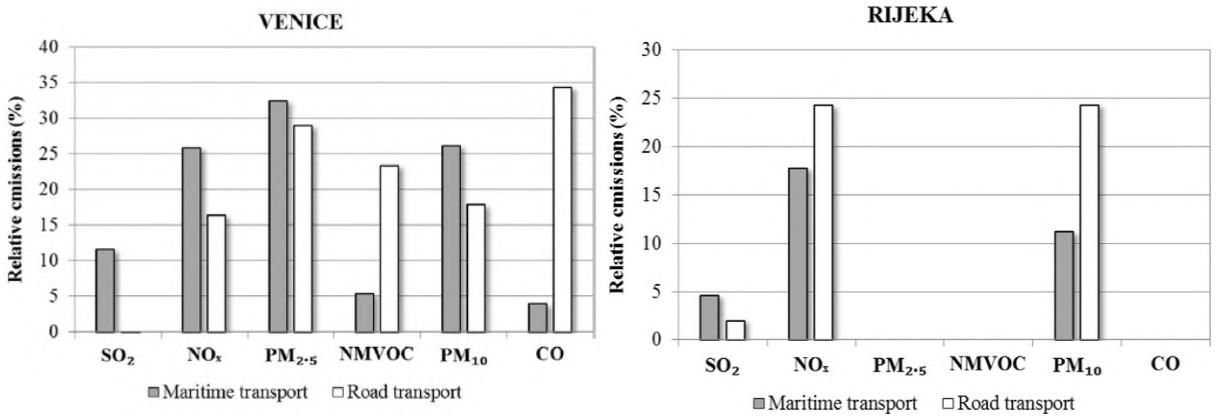

Figure 4.1. Comparison for the year 2010 of maritime and road transport emissions for specific pollutants in Venice and Rijeka. Taken from Merico et al. (2017). Data are presented as percentage of total emission in the Municipality.

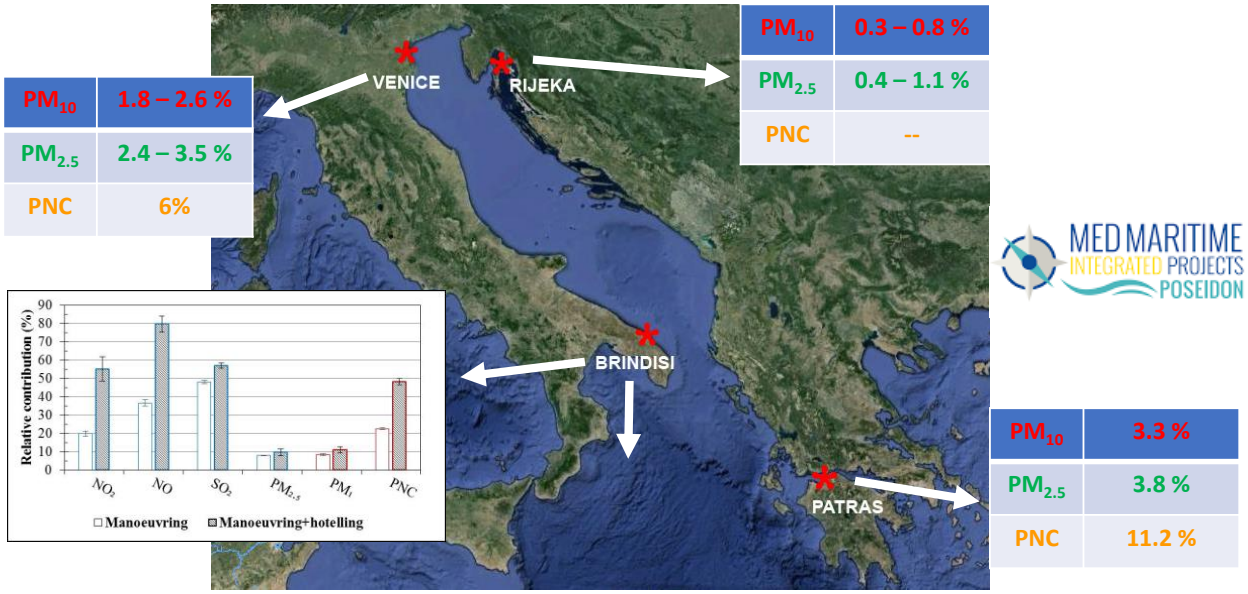

Figure 4.2. Average relative impact of shipping to atmospheric particle concentrations in different sites of the Adriatic-Ionian macroarea.

5 Discussion of results

This chapter will be divided in different paragraphs for Venice and Rijeka sites and a comparison of results will be done in the Conclusion chapter.

5.1. Impact of maritime activities in Venice

High temporal resolution measurements.

The approach discussed in Chapter 3 has been applied to the data collected at high temporal resolution at the measurement site of Sacca Fisola in Venice between 06/09/2018 and 27/11/2018. The average size distributions in number and in mass obtained combining the measurements of the CPC and OPC are shown in Fig. 5.1. It is possible to identify three size ranges for further analysis of number concentrations: Nanoparticles (D< 0.25 µm); Fine particles (0.25<D<1 µm); Coarse particles (D>1 µm). The concentration in mass will be analysed in the standard size ranges PM_1, $PM_{2.5}$, and PM_{10}.

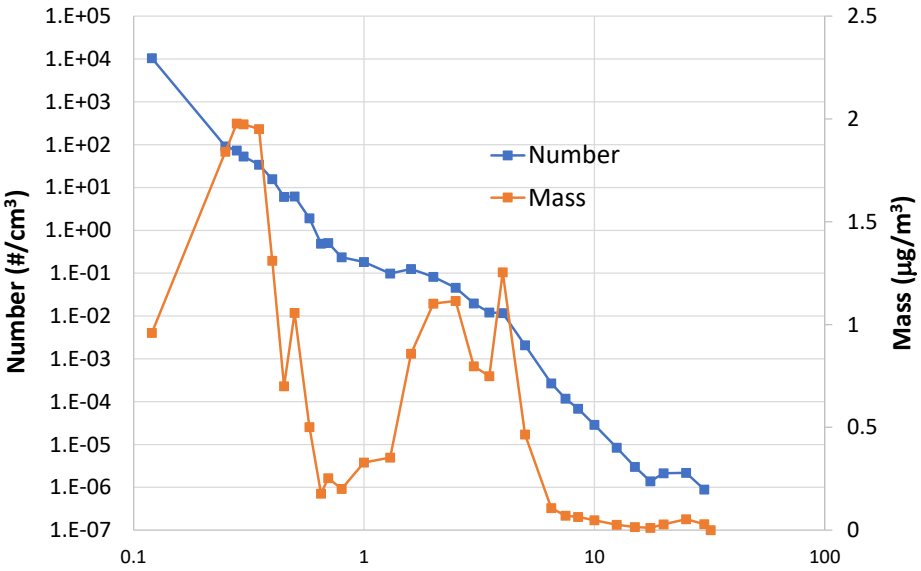

Figure 5.1. Average particle size distribution in number and in mass.

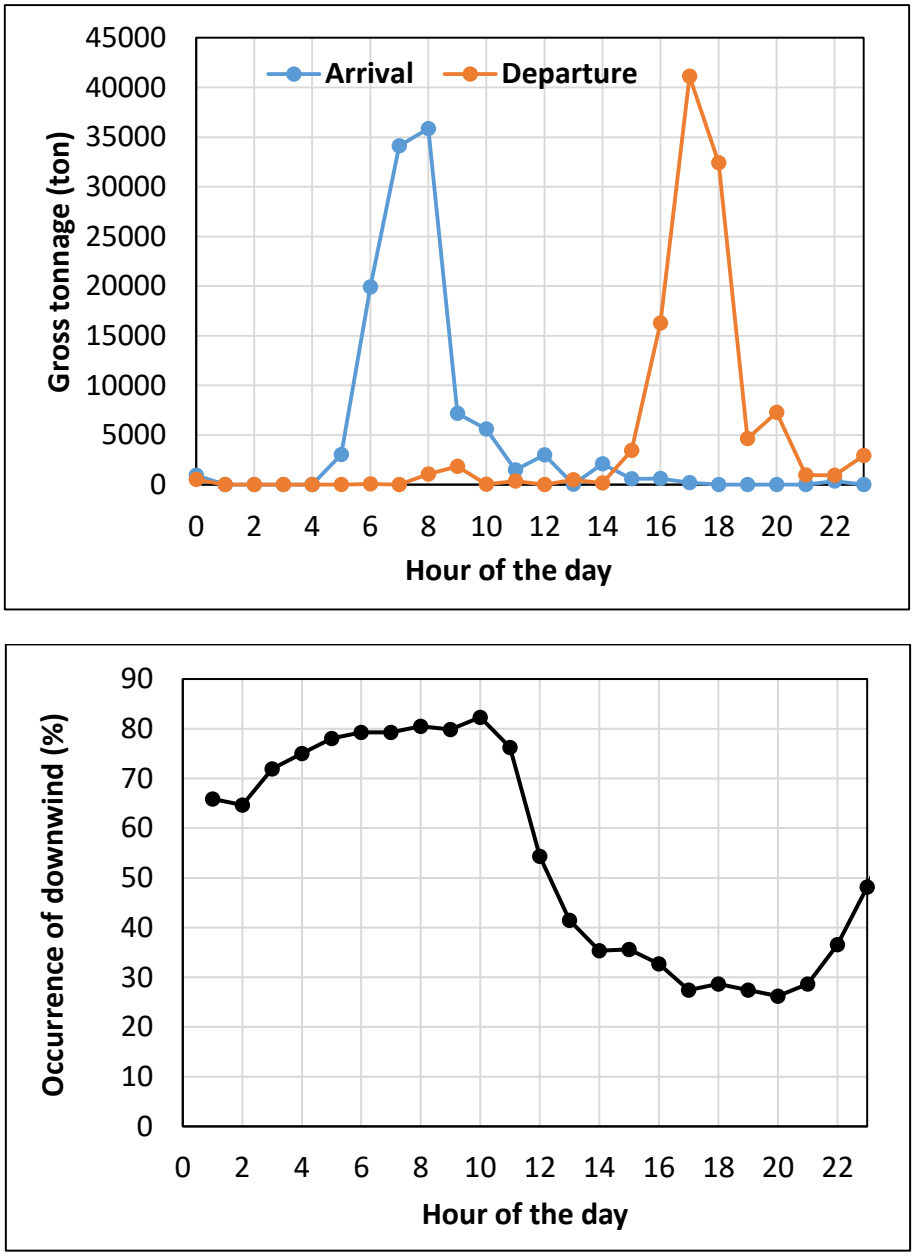

Figure 5.2) Daily trend of ship traffic (top) and daily trend of the percentage of time in which the site is downwind of the emissions located in the tourist harbour area.

The data of ship traffic furnished by Venice Port Authority for the period of the campaign included 240 ships. The arrival and departure times were synchronised with concentration measurements

using information obtained from the videocamera. Ship traffic shows a characteristic daily pattern reported in Fig. 5.2. Arrival of ships is mainly concentrated in the first hour of the morning and ship departure in late afternoon. Wind direction has also a characteristic pattern in the area of Venice with two prevalent wind directions with winds coming from NNE-NE directions, following a circulation from the Alps mountains, mainly during the night and winds coming from SSE-SE during the day (from the Adriatic Sea). This circulation could be considered typical of the Venice lagoon and it has been observed also in other measurement sites in the area, especially in spring and summer seasons (Contini et al., 2015). The measurement site (Fig. 5.3) is downwind of emissions for wind directions in the range 315°-360° (hotelling of ships) and 315°-45° during manoeuvring of ships. The daily pattern of the percentage of time in which the site is downwind of ship emissions is reported in Fig. 5.2. The percentage is significantly larger during the night and the morning and decrease during afternoon. The comparison of the top and bottom graphs in Fig. 5.2 suggests that the measurement site is influenced by ship traffic mainly during the first hours of the day meaning that ship arrival will give the most relevant contribution.

Figure 5.3) Measurement site in Venice with indication of the angles used in post-processing.

This is in agreement with previous measurements taken for evaluation of the impact of ship traffic to air quality in a nearby site (in Sacca San Biagio, 45° 25' 38.50'' N – 12° 18' 33.86'' E at 1 km south of the passenger terminal (Stazione Marittima) of Venice, Contini et al., 2015). The weekly tonnages and number of ships during the is reported in Fig. 5.4 showing a decrease of the total number of ships going from September to November, however, the gross tonnage shows little change until the end of October.

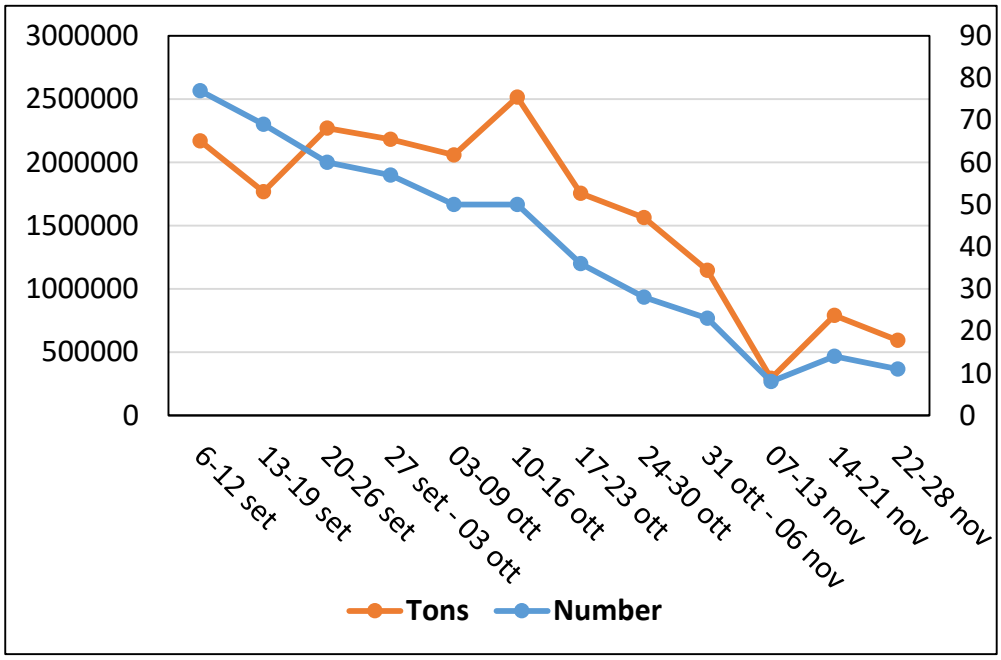

Figure 5.4) Weekly trend of number and gross tonnage of ships calling (sum of arrival and departures) at the tourist harbour of Venice.

The average and standard deviation of particle concentrations measured for the different size ranges analysed in mass and in number are reported in Table 5.1 with their standard deviations.

	PM_1 ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	Nanoparticles ($\#/cm^3$)	Fine ($\#/cm^3$)	Coarse ($\#/cm^3$)
Average	21.8	24.8	28.9	10166	282.0	0.58
STD	13.6	14.1	15.2	6326	188.2	0.42

Table 5.1) Averages and standard deviations of mass and number concentrations of particles for the different size ranges analysed in Venice

In the "Analysis report in Venice" it was observed that diurnal trend of accumulation mode particles could be influenced by the daily trend of the boundary-layer height with larger nocturnal

concentrations when there is essentially not traffic of ships. For this reason, the application of the formulae previously described to estimate ship traffic impact was done on a subset of data selecting only hours between 05:00 and 23:00. This will limit the influence of the boundary-layer dynamics maintaining almost all ship traffic.

The absolute impact of shipping to particles in the different size ranges is shown in Fig. 5.5 and the relative impact is shown in Fig. 5.6. Uncertainties (error bars) have been evaluated using the variability observed in calculations done with and without wind calm (wind velocities < 0.2 m/s) and with small (+/- 10°) changes in the definition of the sectors of wind direction influenced by ships.

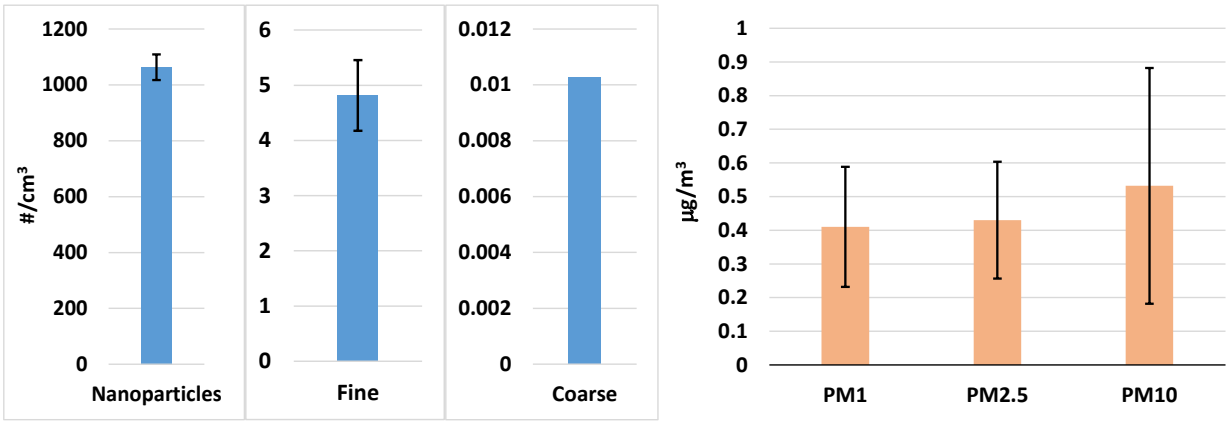

Figure 5.5) Absolute contributions of ships to particle concentrations in number and in mass for the different size ranges in Venice.

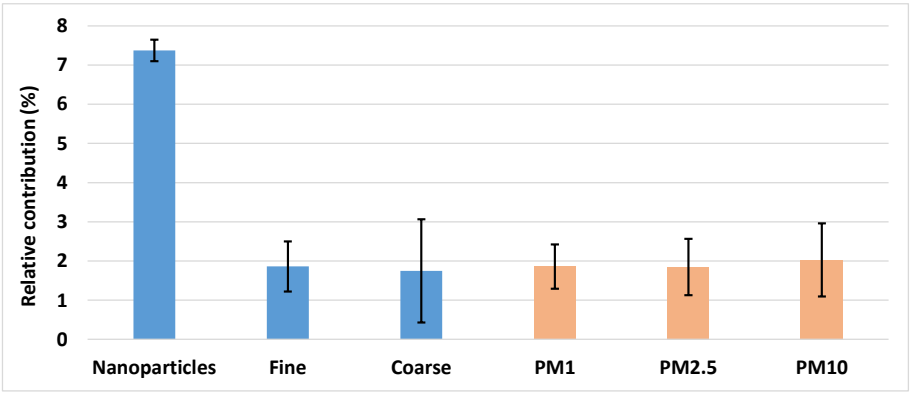

Figure 5.6) Relative contributions of ships to particle concentrations in number and in mass for the different size ranges in Venice.

Looking at Fig. 5.5 it appears that the impact on nanoparticles is significantly larger compared to that on ultrafine and coarse particles as expected from previous studies (Merico et al., 2016). The contributions to mass concentrations PM_1, $PM_{2.5}$ and PM_{10} are comparable considering the uncertainties. The relative contributions to nanoparticles in number is about 7% and it is around 2% for the other size fractions and to mass concentrations.

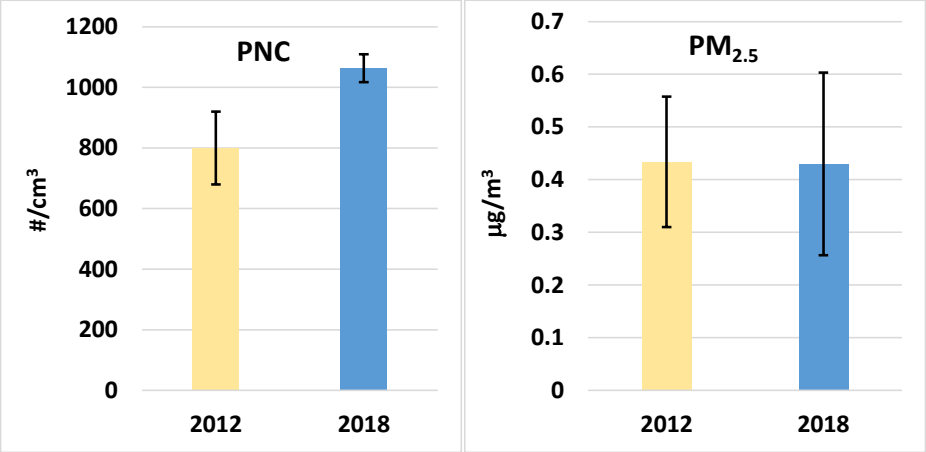

Figure 5.7) Comparison of the absolute contributions of ships to PNC (in number) and $PM_{2.5}$ (in mass) obtained in 2012 and 2018 in Venice.

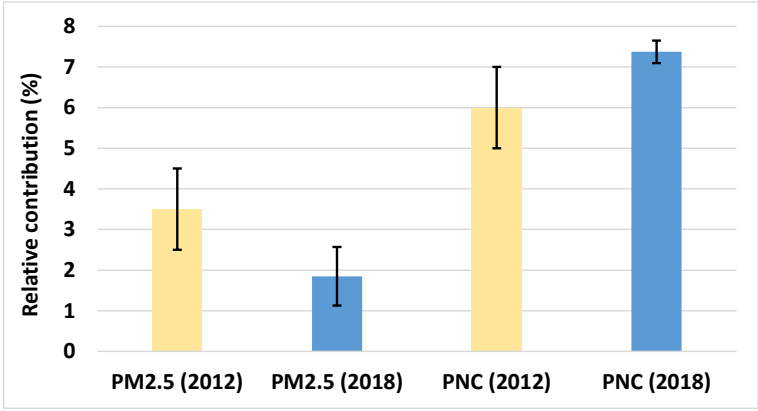

Figure 5.8) Comparison of the relative contributions of ships to PNC (in number) and $PM_{2.5}$ (in mass) obtained in 2012 and 2018 in Venice.

The contributions to PNC (total particle number concentration) and to $PM_{2.5}$ estimated in 2018 could be compared to that estimated in summer 2012, using the same methodological approach (Contini et al., 2015) in the measurement site of Sacca Fisola located at about 200 m from the site in which ECOMOBILITY measurements have been taken. The comparison of the absolute contributions are reported in Fig. 5.7 and the comparison of relative contributions in Fig. 5.8.

Looking at absolute contributions it appears that the impact of ships is essentially very similar for $PM_{2.5}$ in the two years and only slightly larger for PNC. For relative contributions the opposite trend is observed with similar impact to PNC and a lower impact to $PM_{2.5}$. This is a consequence of the different average concentrations observed during the two campaigns. PNC concentrations in 2012 and 2018 are comparable, instead, $PM_{2.5}$ concentrations are significantly larger for the 2018 campaign. This could be due to the different sites and also to the different measurement period that include also a part of autumn in 2018.

Analysis of sources from chemical composition data in Venice

After the preliminary dataset refining, seventeen variables were chosen as input for the model using the dataset of coarse particles and eighteen variables for the dataset of fine-ultrafine particles. The number of samples was 84 in the dataset of the coarse fraction and 83 in the dataset of the fine-ultrafine fraction, leading to datasets of 1428 and 1494 values for the coarse and the fine-ultrafine fractions, respectively. The two datasets respected the suggestions of Henry et al. (1984), requiring that the minimum number of samples should be the one that yields a ratio between degrees of freedom and number of variables higher than 60. Moreover, they also respected the requirement of Thurston and Spengler (1985), since the number of samples exceeded the number of variables by a factor higher than three.

The conditions of the PMF runs are reported in Tab 5.2. The robustness of solutions was evaluated based on DISP and BS (number of bootstraps: 100; minimum correlation R values: 0.6). Starting from the coarse particles dataset, various solutions with different number of factors were considered valid; the trends of the Q-value, IM and IS were examined in order to select the most reasonable solution. From the fine-ultrafine particle run, only the solution with 5 factors was robust based on the BS and DISP error estimation. The analysis of G-space plot performed for the factor contributions obtained from the base solutions revealed no evident edges, so the factors were assumed to be linearly independent among them, in both solutions. The comparison of reconstructed concentration by the PMF and the measured values showed that PMF reconstructed the observed concentrations of the coarse fraction with slope 0.9387 and R^2 0.8131 and of the fine-ultrafine fraction with slope 0.8561 and R^2 0.6768.

	Coarse particles dataset		Fine-ultrafine particles dataset	
Categorisation of variables	Species	Category	Species	Category
	Nitrate	Strong	Chloride	Strong
	SO_4	Strong	Nitrate	Weak
	MSA	Strong	SO_4	Strong
	Br	Strong	MSA	Strong
	Oxalate	Strong	Br	Strong
	Malonate	Strong	Oxalate	Strong
	Succinic	Weak	Malonate	Strong
	Malic	Strong	Malic	Strong
	NH_4	Strong	K	Weak
	V	Strong	Mg	Strong
	Mn	Strong	Ti	Weak
	Fe	Weak	V	Weak
	Ni	Strong	Mn	Strong
	Cu	Strong	Fe	Strong
	Zn	Weak	Cu	Strong
	Rb	Strong	Zn	Strong
	PM	Total	Ge	Strong
			PM	Total
Additional uncertainty	10%		10%	
Number of factors	5		5	

Table 5.2) PMF run conditions for coarse and fine-ultrafine particles datasets.

In Fig. 5.9, the profiles of each factor obtained from the coarse particles dataset is reported in terms of absolute concentrations (bars) and in terms of relative concentrations (points).

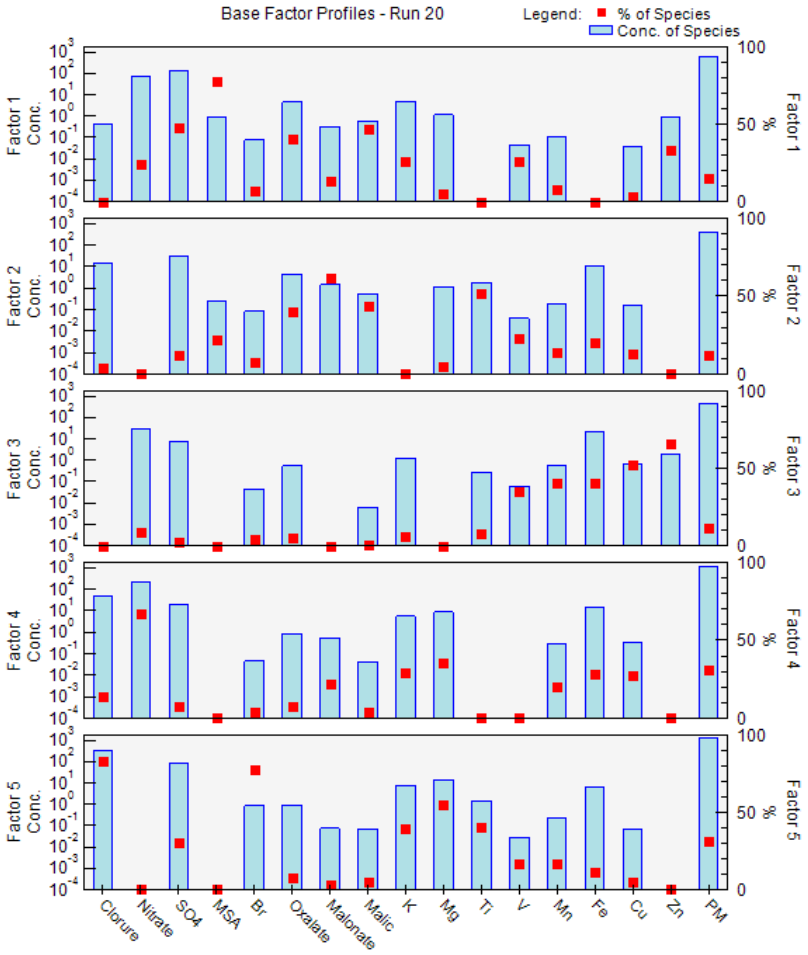

Figure 5.9) Source profile for coarse particles by PMF model.

The first factor showed high contribution of MSA, typical tracer of marine biogenic emissions. The factor showed also a contribution of sulfate, often associated to biogenic emission together with MSA, since they are both products of the algal bloom (with dimethyl sulfide and sulfur dioxide as intermediates). Various variables contributed to the second factor, mainly oxalate, malonate, malic and titanium, that makes difficult the association of this factor to a specific source. The third factor was mainly characterised by the presence of various metals of different origin, such as vanadium, manganese, iron, copper and zinc. Vanadium could be associated to heavy oil combustion, iron and manganese have generally a crustal origin, copper and zinc are mainly associated to vehicular traffic. The fourth factor is secondary nitrate and the fifth factor is related to particles of marine origin. The fourth factor was characterised by a high contribution of nitrate

that could originate also from aged sea salt. High sea salt concentrations, typical of coastal areas, could lead to the production of secondary nitrate in the coarse mode (Barbaro et al., 2019). The fifth factor was characterised by chloride and bromide, typical component of the primary sea spray, which produce aerosol in the coarse mode. In this sampling site, almost entirely surrounding by water, the factors associated to marine origin contributed by most of the total mass of coarse particles (primary sea salt and aged sea salt both contributed for 31%; marine biogenic emissions for 15% to coarse particles mass). A factor associated to heavy oil combustion, including shipping, was not individuated using the dataset composed of only coarse particles.

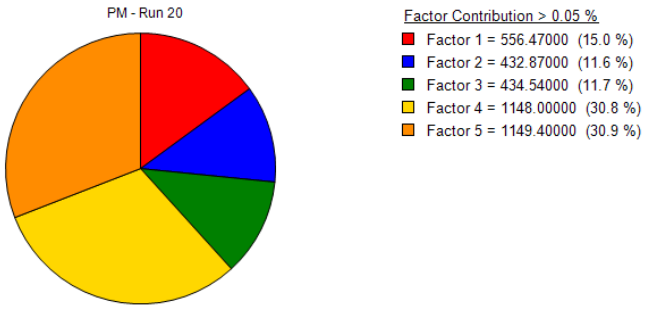

Figure 5.10) Sources contribution estimated by PMF model for coarse particles.

The source profile obtained for fine and ultrafine particles is reported in Fig. 5.11 and the relative contributions of the factors in Fig. 5.12. The first factor cannot be associated to a specific source, since many variables, related to various origin, contribute to this factor. The second factor was characterised by bromide and carboxylic acids (oxalate, malonate, succinate and malic). Atmospheric bromide could be related to various sources, such as sea, agriculture, urban traffic and biomass burning; carboxylic acids are mostly produced by photochemical oxidation of organic precursors by ozone, OH radical, NO_x and other oxidants, but can be also produced by biomass burning, fossil fuel combustion and urban traffic. Given so many possible sources and without a specific tracer, also the second factor cannot be associated to a specific source.

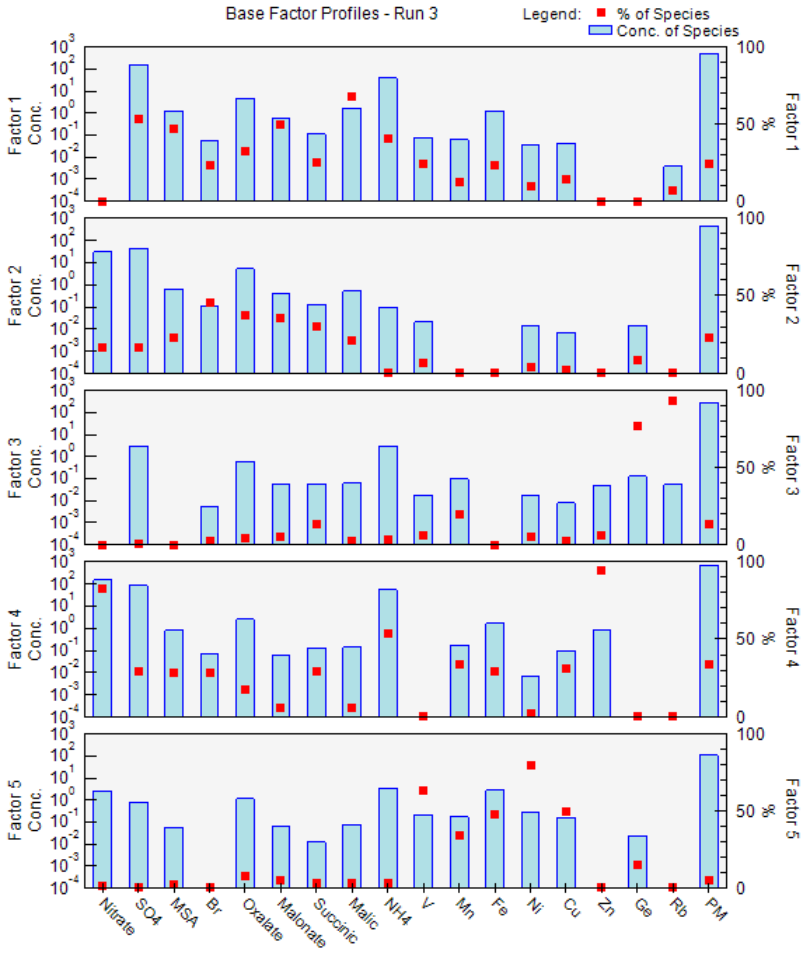

Figure 5.11) Source profile for fine particles by PMF model.

The third source was characterised by a high contribution of germanium and rubidium, that are crustal elements, and it contributed to 13% of total mass of fine and ultrafine particles. The fourth factor was characterised by nitrate, ammonium and zinc. The presence of ammonium could be related to use of nitrogen-fertilizers, while zinc is mainly related to traffic emissions; nitrate could be associated to both sources, given that could be produced by the oxidation of ammonium from agriculture and of nitrogen oxides generated by traffic.

The last factor was characterised by vanadium and nickel, thus it could be associated to heavy oil combustion, including shipping. The high concentration of nickel in the factor suggested an additional contribution of other sources to the factor, also confirmed by the significant contribution

of manganese, iron and copper: manganese and iron are crustal elements, while copper is often associated to vehicular traffic. The relative contribution of this factor is comparable to that expected for shipping emission.

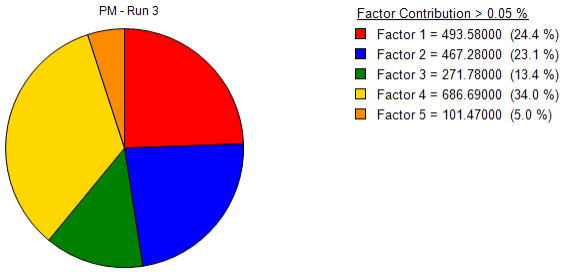

Figure 5.12) Sources contribution estimated by PMF model for coarse particles.

Despite ship traffic contributed only partially to factor 5, the size distribution of its contribution was investigated (Fig. 5.13).

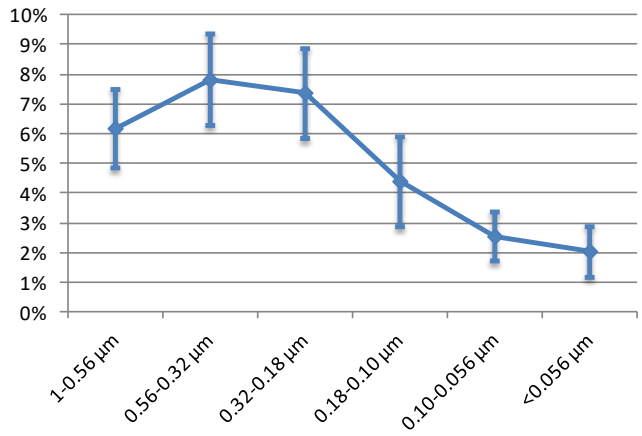

Figure 5.13) Size distribution of the contribution of Factor 5 (mixed shipping traffic emissions) to fine and ultrafine particulate mass.

The factor had an increase in the contribution passing from particles of diameter 1-0.56 µm (6%) to 0.56-0.32 µm particles (8%); moving towards smaller particles the contribution decreased from 8% at 0.56-0.32 µm to 2% in the smallest fraction. This distribution does not match with the relative contributions of ships calculated from high-temporal measurements, where the contribution of nanoparticles was higher than the contribution of fine and coarse particles (Fig. 5.6). As mentioned before, other sources, such as industrial activities or urban traffic, could give a contribution to the factor, probably more in the fine fraction with respect to the ultrafine fraction.

Since mixed sources cannot be efficiently distinguished using PMF, an alternative methodology to assess the primary contribution of ship traffic, considering only vanadium as a marker for the combustion in ships' engines, was adopted. The results are discussed in the following paragraph.

Primary contribution of shipping, based on vanadium concentration

The primary contribution of ship traffic based on atmospheric vanadium as tracer of ship emission, calculated with the methodology as reported in Chapter 3 (Eq. 3.1), ranged from 0.1% to 39%, with an average of 2.5%. The average size distribution of the primary contribution of ship traffic to particulate matter is shown in Fig. 5.14a, with the interquartile range in whiskers. The average contribution was below 2% for particles > 1 µm and rapidly increased for smaller particles, reaching an average of 15% for particles between 0.10 µm and 0.056 µm.

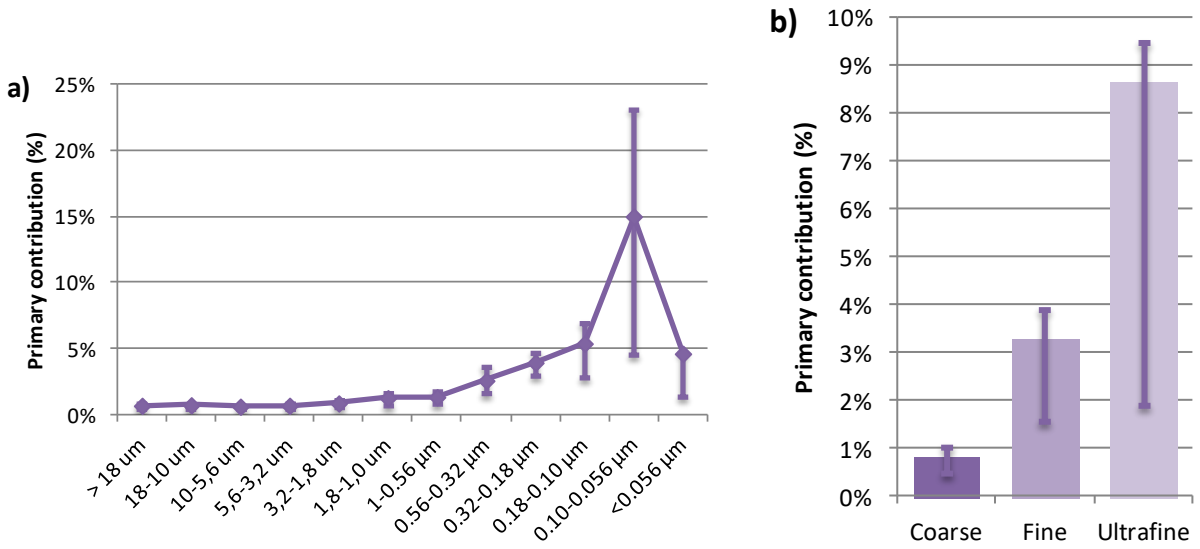

Figure 5.14) Primary contribution of maritime traffic in different particle size.

In Fig. 5.14b the average values of the primary contribution to coarse, fine and ultrafine particles is shown, with the interquartile range in whiskers. On average the contribution of ship traffic to the coarse particles (> 1 µm) mass was around 1%, to the fine particles (between 1 µm and 0.1 µm) mass was around 3% and to ultrafine particles mass was around 9%, with a great variability in the obtained measures. The increase observed passing from fine particles to ultrafine particles is in accordance with the contribution obtained from high-temporal measurements (Fig. 5.6), while

a difference was observed in the comparison between coarse and fine particles, among the two methodologies.

The contribution estimated in 2018 was compared to that estimated during the period 2007-2013, within the POSEIDON project, using the same methodological approach (Gregoris et al., 2016) and in a measurement site (Sacca Fisola) very closed to the site in which ECOMOBILITY measurements have been taken (Fig. 5.15). In order to conduct this comparison the primary contribution of shipping was calculated also to PM_{10} (particles with diameter < 10 μm, corresponding to stages from 2 to backup) and to PM_1 (particles with diameter < 1 μm, corresponding to stages from 6 to backup), while $PM_{0.1}$ (particles with diameter < 0.1 μm) corresponds to nanoparticles of Fig. 5.14b. The interquartile range is represented by the whiskers. The contribution to PM_{10} calculated from 2018 was comparable to that previously observed. The calculation of the contribution to PM_1 and $PM_{0.1}$ have been conducted from the first time in this area.

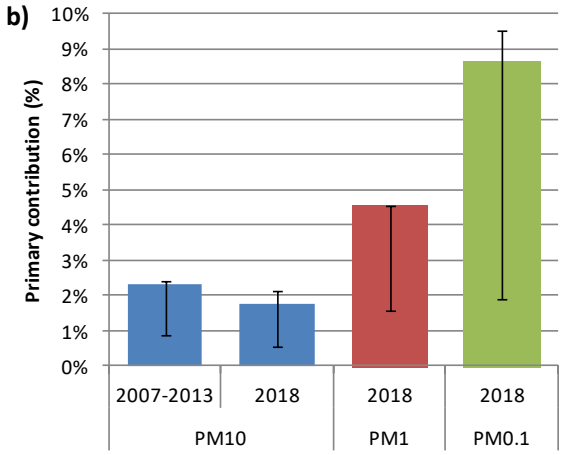

Figure 5.15) Comparison between the primary contribution of ship traffic to particulate matter, calculated using vanadium as tracer of shipping emissions, obtained within POSEIDON (indicated with 2007-2013) and ECOMOBILITY (indicated with 2018) projects.

The incremental trend of the contribution with decreasing particle size was in accordance to what previously observed in various sites in Europe (Viana et al., 2014). Specifically in Europe the comparison have been conducted among PM_{10}, $PM_{2.5}$ and PM_1, so far. In this work the contribution to PM_1 was about 2.5 times higher with respect to the contribution to PM_{10}, comparable to what observed in Spain (Viana et al., 2009) and Lampedusa (Becagli et al., 2012). As to our knowledge the contribution of shipping traffic to nanoparticles/$PM_{0.1}$ is not available in other sites in Europe with the exclusion of the Brindisi harbour in which measurements were done limited to optical measurements (Merico et al., 2016).

5.2. Impact of maritime activities in Rijeka

High temporal resolution measurements.

The approach discussed in Chapter 3 has been applied to the data collected at high temporal resolution at the measurement site (located on the roof of the Health Teaching Institute of the University of Rijeka, 45°19'55.58''N – 14°25'32.84''E) in Rijeka between 28/03/2019 and 13/05/2019. The average size distributions in number and in mass obtained combining the measurements of the CPC and OPC are shown in Fig. 5.16. It is possible to identify the same three size ranges already identified in Venice for further analysis of number concentrations: nanoparticles (D< 0.25 µm); fine particles (0.25<D<1 µm); coarse particles (D>1 µm). The concentration in mass will be analysed in the standard size ranges PM_1, $PM_{2.5}$, and PM_{10}.

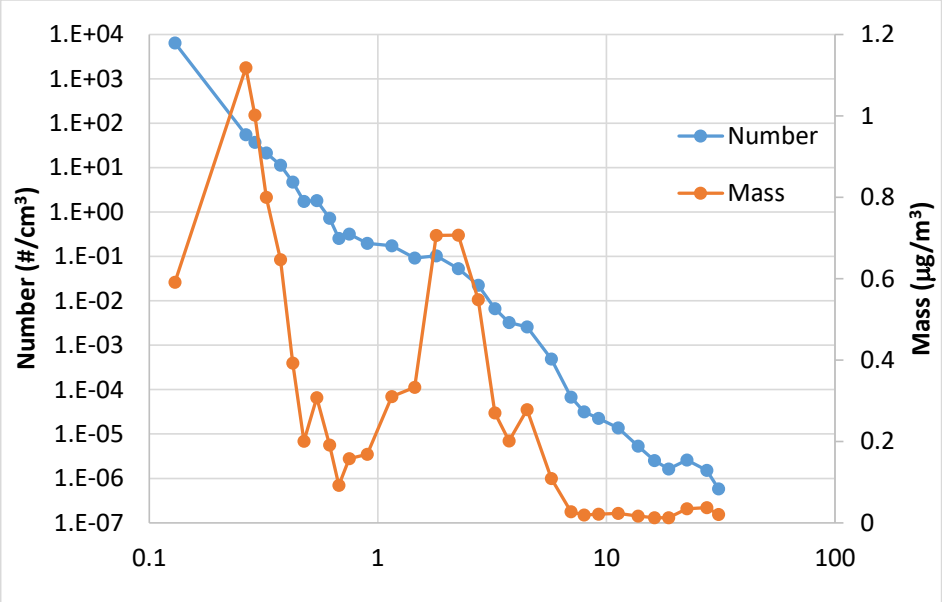

Figure 5.16. Average particle size distribution in number and in mass in Rijeka.

The data of ship traffic furnished by Rijeka Port Authority for the period of the campaign included 92 ships. The arrival and departure times were synchronised with concentration measurements using information obtained from the videocamera. Ship traffic does not have a clear daily pattern (Fig. 5.17). The measurement site (Fig. 5.18) is downwind of emissions for wind directions in the range 122.5°-180° (hotelling of ships) and 122.5°- 247.5° during manoeuvring of ships. The daily pattern of the percentage of time in which the site is downwind of ship emissions is reported in

Fig. 5.19. It indicates that the site is potentially influenced by ships during diurnal hours and this means by the majority of ship traffic.

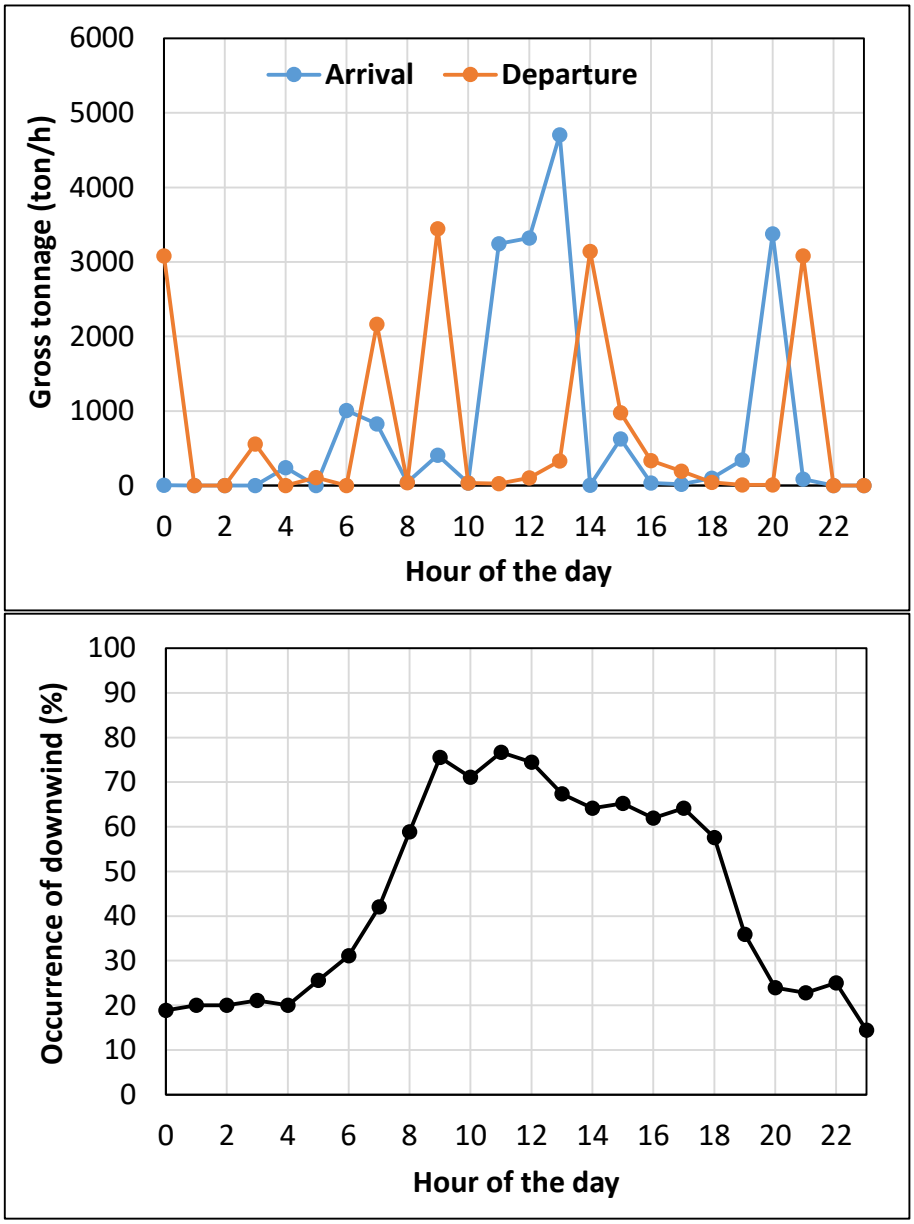

Figure 5.17) Daily trend of ship traffic (top) and daily trend of the percentage of time in which the site is downwind of the emissions located in the harbour area in Rijeka.

Figure 5.18) Measurement site in Rijeka with indication of the angles used in post-processing.

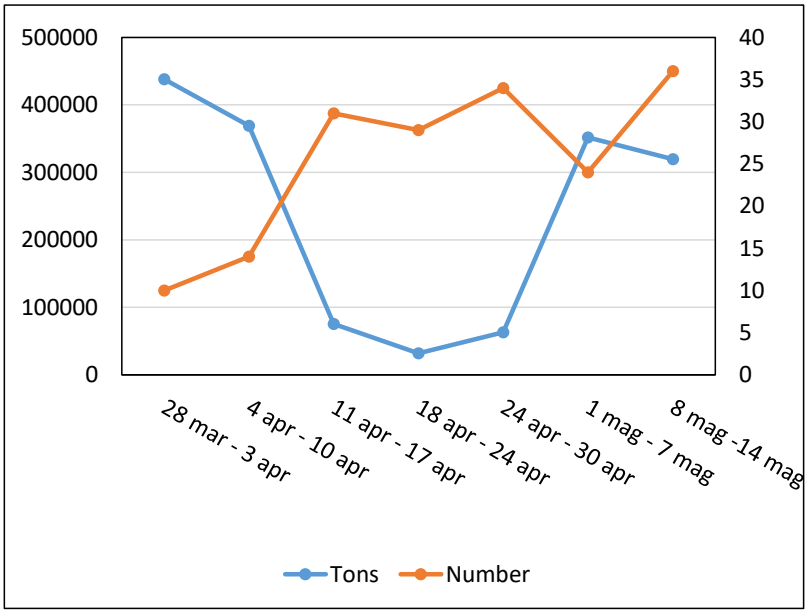

Figure 5.19) Weekly trend of number and gross tonnage of ships calling (sum of arrival and departures) at the harbour of Rijeka.

The average and standard deviation of particle concentrations measured for the different size ranges analysed in mass and in number are reported in Table 5.3 with their standard deviations. The concentration values are smaller than those found in Venice (Table 5.1) for all size ranges.

	PM_1 ($\mu g/m^3$)	$PM_{2.5}$ ($\mu g/m^3$)	PM_{10} ($\mu g/m^3$)	Nanoparticles ($\#/cm^3$)	Fine ($\#/cm^3$)	Coarse ($\#/cm^3$)
Average	11.4	13.4	14.8	6552	134.1	0.45
STD	6.9	8.8	10.4	3738	90.4	0.89

Table 5.3) Averages and standard deviations of mass and number concentrations of particles for the different size ranges analysed in Rijeka.

The formulae discussed in Chapter 3 have been used to investigate the impact of shipping to measured concentrations. These have been applied on a subset of data in which it has been removed the period between 24 and 26 April 2019 because in which an intense event of African dust advection was observed. This event will change the balance between fine and coarse particles introducing a confounding effect on the determination of the impact of shipping.

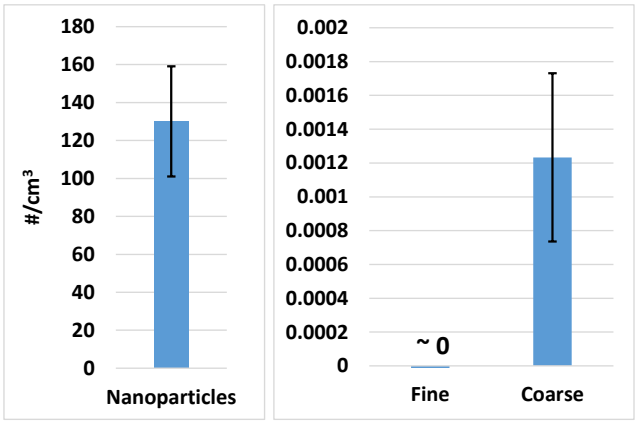

Figure 5.20) Absolute contributions of ships to measured concentrations (in number) in Rijeka. Contributions to PM_1, $PM_{2.5}$, and PM_{10} are negligible and not shown.

Absolute contribution of ships to measured concentrations in the different size ranges is reported in Fig. 5.20. It is observed that contributions to mass concentrations are essentially negligible and not discernible among the different sources acting on the site studied. The same apply for ultrafine particles, instead, a non-negligible contribution is observed for coarse particles in number. Relative contribution to nanoparticles is about 1.8% (Fig. 5.21) and a measurable (about 0.5%) contribution to coarse particles was observed. In all the other cases, the relative contributions were negligible (< 0.2%).

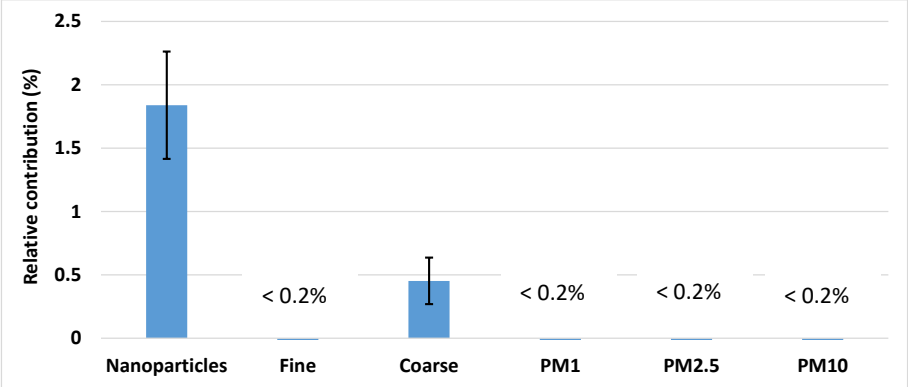

Figure 5.21) Relative contributions of ships to measured concentrations in Rijeka for the different size ranges.

Analysis of sources from chemical composition data in Rijeka

Airborne particulate samples were collected with 10 stages (plus inlet and back-up filter) cascade impactor during two campaigns: autumn, October 16th-December 10th 2018, and spring, March 26th- May 21st 2019. The obtained results were further analysed by Principle Matrix Factorization (PMF) receptor model to identify the principle sources of particulate pollutants, including maritime traffic. As some parameters appear mostly in coarse (d >1 µm) and other in fine and ultrafine fractions (d <1 µm), three sets od data were analysed:

- the whole set with all 11 fractions. We did not take into account the 12th fraction, since these data were missing for the autumn campaign.
- the coarse fraction, including stages 1-6.
- the fine fraction, including stages 7-11.

The factors identified this way were 4 for fine, 5 for coarse and 6 factors for the whole set.

ALL FRACTIONS

The input data were 16 samples from 11 stages cascade impactor collected in autumn 2018 and spring 2019. The 12th stage was not included in the analysis since we missed the whole autumn period. The information on data statistics is described in Table 5.4. Uncertainties are calculated from analytics and sampler flow measurements. Below detection limit (BDL) data is replaced with half of detection limit and corresponding uncertainty with 5/6 of detection limit (DL) values. The 15% of extra modeling uncertainty is added to all data. PM_{10} is set as total variable.

Around 6% of PM concentrations were less than zero, and were excluded form analysis. The other parameters excluded were:

- NH_4 (due to 69% data BDL), OC and TC to avoid doubling of parameters and PO_4 and Cd because of difficulties with interpretation.
- Signal to noise ratio (S/N) for Al, and Sb was less than 2 and is also set as 'weak' (uncertainty is tripled); K with 53% of data BDL and Mg with 50% data BDL were also set as "weak", while Ca and Zn were "weak " due to interpretation of factors.
- Several outliers were excluded as well as data from 1st and 13th week were excluded due to Saharan dust episodes.

species	samples	fractions	weeks	PM <0	BDL	excluded
24	176	11	16	6 %	19 %	20 %

Table 5.4: Input data for PMF with all size fractions included

The number of factors is determined by calculating the maximum of the average (IM) and maximum of the standard deviation of the scaled residuals (IS):

$$IM = \max_{1\ldots m}\left(\frac{1}{n}\sum_{i=1}^{n} r_{ij}\right); \qquad IS = \max_{1\ldots m}\left(\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(r_{ij}-\bar{r}_{ij}\right)^2}\right).$$

The number of factors according to IMIS is 5 or 6, and the chosen number is 6. The bootstrapping factors were mapped to proper PMF factors in more than 86% of cases, therefore the obtained factors can be explained (Figure 5.22). The interpretation of factors is difficult because some of analyzed species appear mostly in coarse or fine fractions.

- **Factor 1** was attributed to crustal source due to abundance of Ca, Al, Fe and Mn present within.
- **Factor 2** with higher percentage of EC**,** organics (WSOC, OC-WSOC), K ad Mg indicates combustion sources with a contribution from biomass burning.
- **Factor 3** with high percentage of Na, Cl, Mg and nitrate is associated with sea-spray.
- **Factor 4** is associated with traffic due to higher contribution of copper, zinc, antimony and nitrate. The same parameters might indicate metal industry, i.e. ship building and ship repair facilities within the city (2). It has to be mentioned that a contribution of exhaust emissions could also be present in Factor 2.
- **Factor 5** with high contribution of V (90%) and Ni (70%) and much lower EC, WSOC could indicate the heavy fuel oil (HFO) burning used in ships.

- **Factor 6** characterized with sulphate, organics, EC, and surprisingly Pb. These parameters indicate a certain combustion or Secondary Inorganic Aerosols (SIA). As NH_4 was excluded from the analysis due to >50% of data BDL, we are lacking a confirmation for SIA.

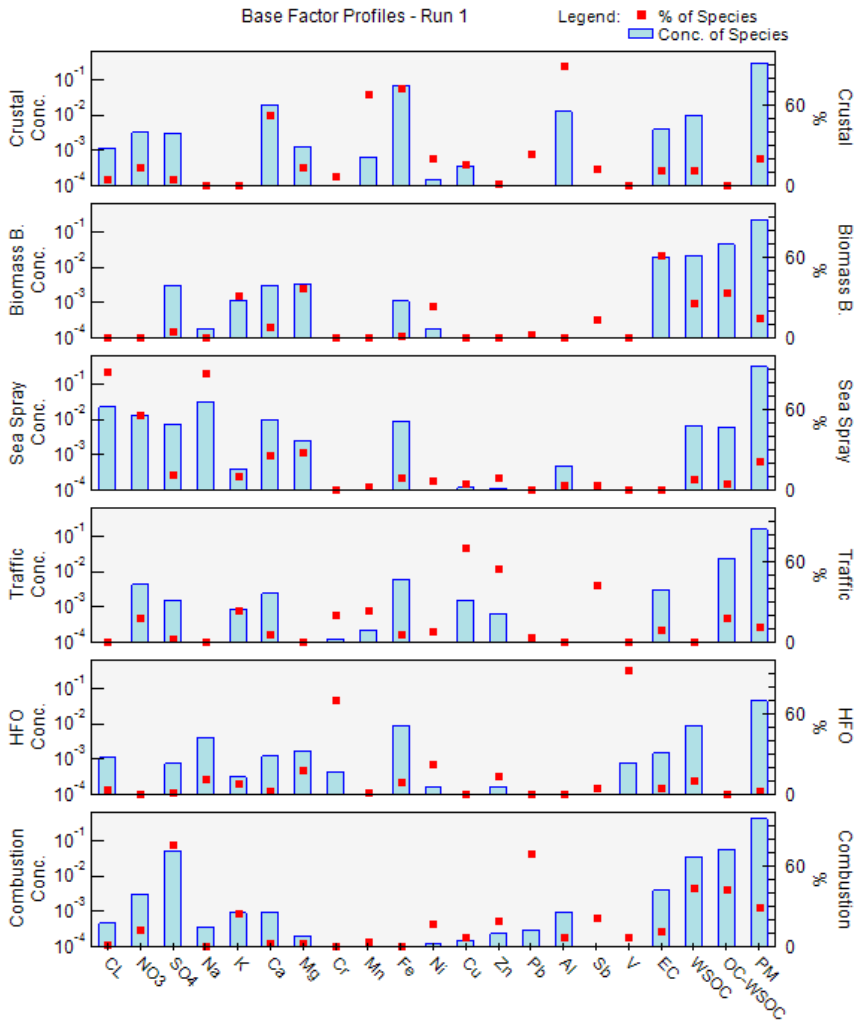

Figure 5.22. Factor profiles for complete data set.

The highest contribution (29.3%) is attributed to combustion sources or SIA (Figure 5.23). Similar percentage for SIA is found in the period 2008 -2010 (20.8-35%) as reported in the POSEIDON project (Deliverable 2.5, 2015), but with contribution of Pb not exceeding 20%. The second highest contribution (21.3%), originates from sea spray. This contribution is also within the previous

results (9.0-20.4%). Contribution of biomass burning (15%) is also in the range of earlier results: 12.5-27.5%. These three factors are confirmed with the previous study.

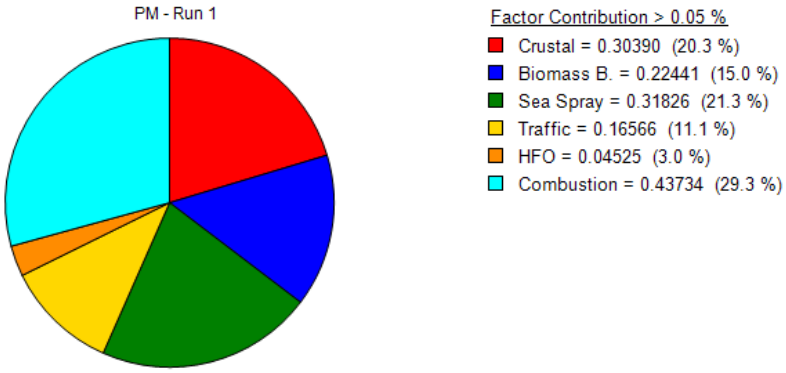

Figure 5.23. Factor contributions for the complete data set.

The fourth factor is attributed to traffic (11.1%). Since the same trace parameters (Fe, Zn, Cu, Pb, Cd) are emitted from the metal industry, in this case ship repair facility (Alebić-Juretić and Matković, 2000), in the previous study this factor was attributed to metal industry, in the same range values (8.1-19%). The fifth factor, HFO burning has a contribution of only 3%. This is a new identified factor, and further study is needed to confirm it.

COARSE FRACTIONS

The input was 16 samples including first 6 of 11 fractions measured. Data excluded due to high percentage of below detection limit data were NH_4 (95%) and K (64%). Due to difficulties in explaining the factors were also excluded, as well as OC, TC and WSOC. Ca, Mg, Cd, Ni, Zn, Sb were set as weak because they tend to form factors with no PM concentrations. The PM was set as total variable (weak). Additionally, 10% data were excluded due to outliers and Saharan dust episode during 1st and 13th week of sampling. The 10% of extra modeling uncertainty is added to all data (Table 2).

samples	fractions	weeks	BDL	excluded
96	6	16	16.5%	11%

Table 5.5: Input data for PMF

Correlation between model and observations is well except for species set as 'weak'. The bootstrapping error showed that more than 86% of bootstrapping factors were correctly mapped

to PMF factors. Therefore the factors were explained accordingly (Figure 5.24). Coarse particulates are assumed to originate from natural sources or abrasion/mechanical processes. Airborne fine particulates originate from chemical reactions in the atmosphere, but once formed could aggregate to bigger particulates. Such a situation we met during this project, when a sample with high content of Saharan dust contained also high contribution of fine and ultrafine particulates (aerodynamic diameter <1 µm), contrary to the results from Turkish colleagues who found no particulates of this size in samples with Saharan dust (Uzunpinar et al., 2019). According to IMIS method results, we identify 5 factors that can be explained in following manner:

- **Factor 1** can be attributed to sea spray with high contribution of Na, Cl, NO_3, but also Ca and SO_4, though both being also of marine origin, might also be shared with other subsequent Factor 2. We could not separate these parameters using 6 factors.
- **Factor 2** with high contribution of EC and insoluble OC, and less sulphate (possibly mixed with sea spray) might indicate combustion.
- **Factor 3** resembles Factor 5 in the whole set, with high percentage of V (80%) but lower Ni (30%) as well as Cr, Mn and Ca, but being in the coarse fraction is more likely to originate from ship building facility, i.e. cutting of the steel containing this trace metals. Other possibility is the aggregated combustion products of HFO deposited on the soil, since soil contains more V due to petroleum refinery located in and close to the city (Prohić, 1994).
- **Factor 4** could be attributed to crustal sources, with high content of Al, Cd, Fe, Mn, Ca and unexpectidly Pb. The waste metal reload in the harbour could contribute to this factor.
- **Factor 5** is attributed to road traffic, due to high content of Cr, Mn, Fe, Cd, Cu, Zn, Sb.

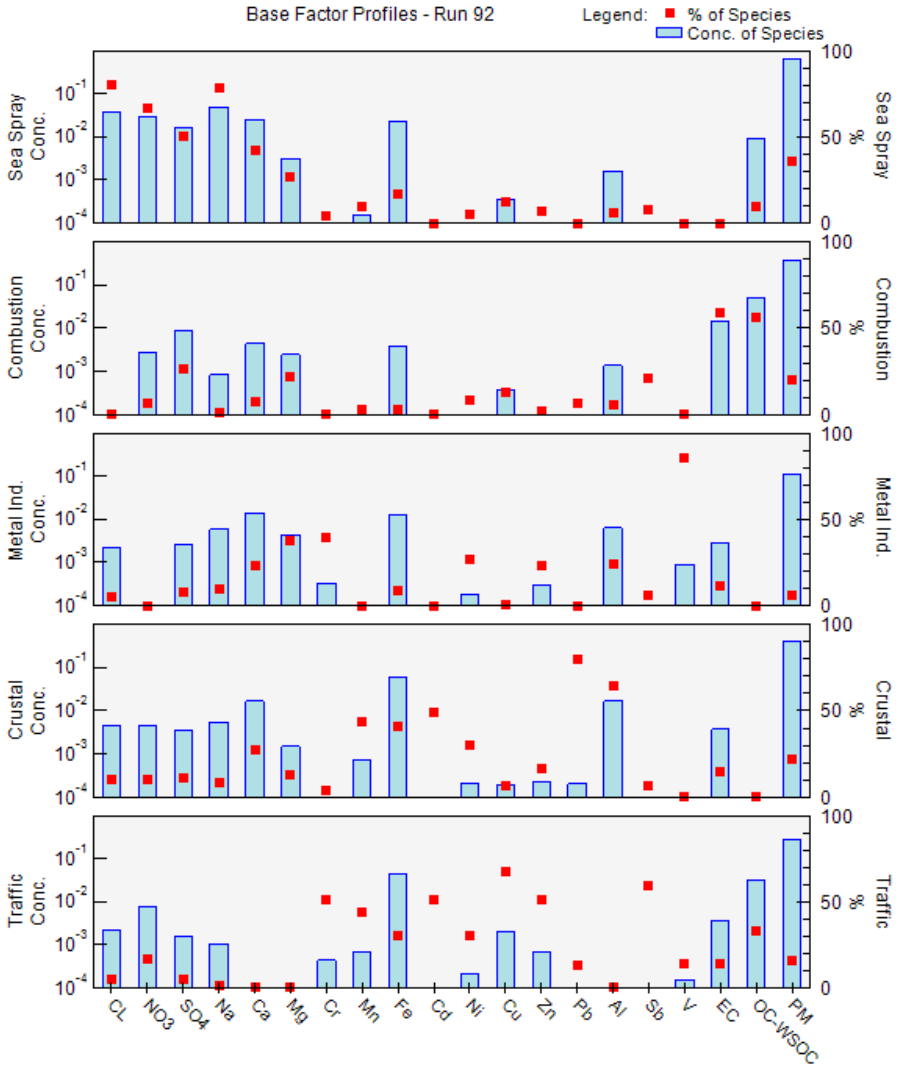

Figure 5.24: PMF factor profiles for coarse fractions.

As expected, the highest contribution in the coarse fraction (Figure 5.25) comes from natural sources: sea spray (36.1%) and crustal soil (22.1%). While crustal contribution is similar as obtained in the set with all fractions, the contribution of sea spray is higher relative to the result of the whole fraction set (21.3%). The contribution of traffic and biomass burning are similar to the values obtained in the whole set (11.1 and 15%, respectively).

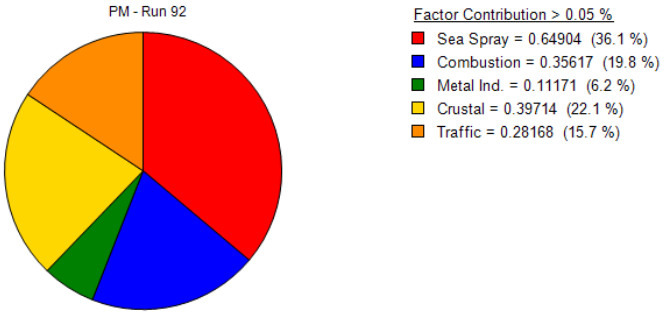

Figure 5.25: Factor contributions estimated by PMF model for coarse particles.

These four factors seems to be constant in the PMF analyses of airborne particulates in Rijeka. Factor 3 (6%) with high content of V and Ni that is very similar to HFO burning but found in the coarse fraction, with higher content of other metals might be attributed to metal industry (construction shipyards). Other source of this factor is aggregation and deposition of fine particulates derived from HFO combustion (Prohić, 1994).

FINE FRACTION

The fine fraction comprises stages from 7 to 11. Parameters characteristic for the coarse fraction as Na, Cl, Mg (63% data is BDL), Ca and Sb were excluded from the analysis. OC, TC, PO_4, were also eliminated. Due to poor S/N ratios, NH_4 and Al were set as weak, as well as Cd due to formation of strange factors. The PM was set as total variable ('weak'). The 10% of extra modeling uncertainty is added to all data (Table 5.6).

samples	fractions	weeks	BDL	excluded
80	5	16	21%	11%

Table 5.6: Input data for PMF for fine fractions

Bootstrapping was the best for 4 factors, with more than 85% successful mappings provided best solution, also significant drop in IM is present after 3rd factor. The obtained factors are explained accordingly to the factor profiles (Figure 5.26).

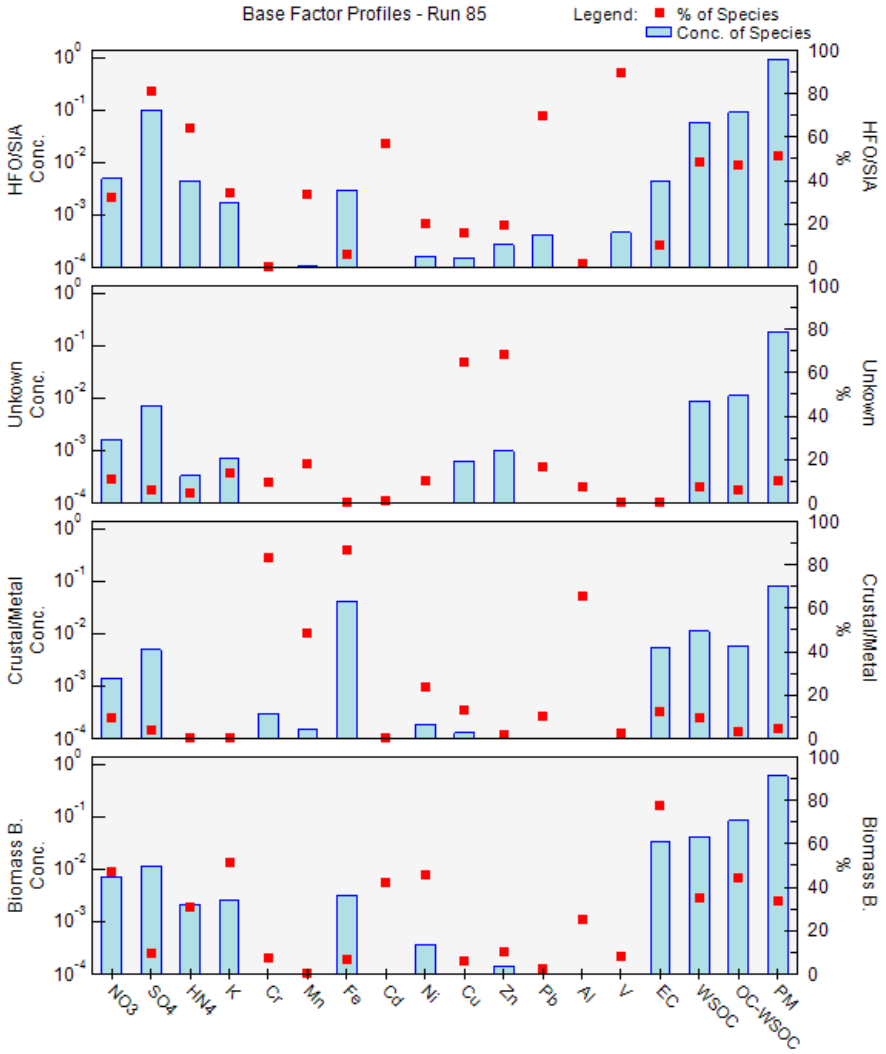

Figure 5.26. PMF factor profiles for fine fractions.

- **Factor 1** with high carbonaceus species, V and Ni might indicate HFO combustion in ships. Combustion sources are confirmed with high SIA: SO_4, NO_3, NH_4, but also Pb, and Cd. It looks like this is a combination of HFO and SIA that could not be separated introducing more factors. The combination of these two factors gives also the largest contribution of 51% (Figure 5.27)
- **Factor 2** with high contribution of Zn and Cu is unknown. The higher content of these metals is found in soil in the Northern Adriatic area (Prohić, 1994), but soil particulates emitted by erosion would deposit in the coarse fraction. Factor contribution time series

indicates that this factor had maximum in the second week of monitoring, following the extremely high concentrations of Mn, Pb and Sb that were excluded from the PMF analysis having this in mind, this factor likely originate from repair shipyard.

- **Factor 3** with high content of Fe, Al, Mn, Cr in fine fraction might derive from anthropogenic sources, i.e. metal industry with crustal contribution.
- **Factor 4** with high carbonaceous species and potassium is attributed to combustion sources including traffic and biomass burning. This contribution is doubled relative to all fraction set.

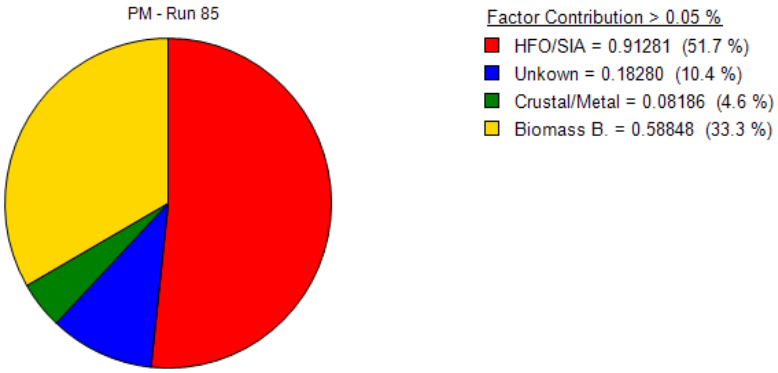

Figure 5.27. Factor contributions estimated by PMF model for fine particles.

Primary contribution of shipping in Rijeka, based on Vanadium concentration

Vanadium is a well indicator of ship emission, even if not univocal. The presence of vanadium in fine and ultrafine fractions (nanoparticles) indicate combustion as its source. The overall average of Vanadium per size fraction obtained during both campaign was 1.50±1.45 ng/m^3. The high standard deviation indicates high variability of the results. Thus, the minimum obtained was 0.1 ng/m^3, while the maximum 4.8 ng/m^3. No vanadium was detected in 22 out of 178 fraction samples. The Vanadium profile by fraction is given in Fig. 5.22. As seen from the figure, the obtained average vanadium in $PM_{2.5}$ and PM_{10} were 13.9 and 16.7 ng/m^3, respectively, and are approximately three times higher than the concentrations previously obtained during the project POSEIDON (Deliverable 2.5, 2015). Higher concentrations in vanadium could indicate an higher contribution of primary particulate emissions from the ships but also form diesel vehicles and/or from specific industrial emissions. One must have in mind that there are other sources of vanadium in the Rijeka area, as shipbuilding facilities as well as diesel traffic within the city area that could

contribute to vanadium in higher particulate fractions. This might be the reason that the highest concentration of vanadium was found in the coarse fraction (Fig. 5.28)

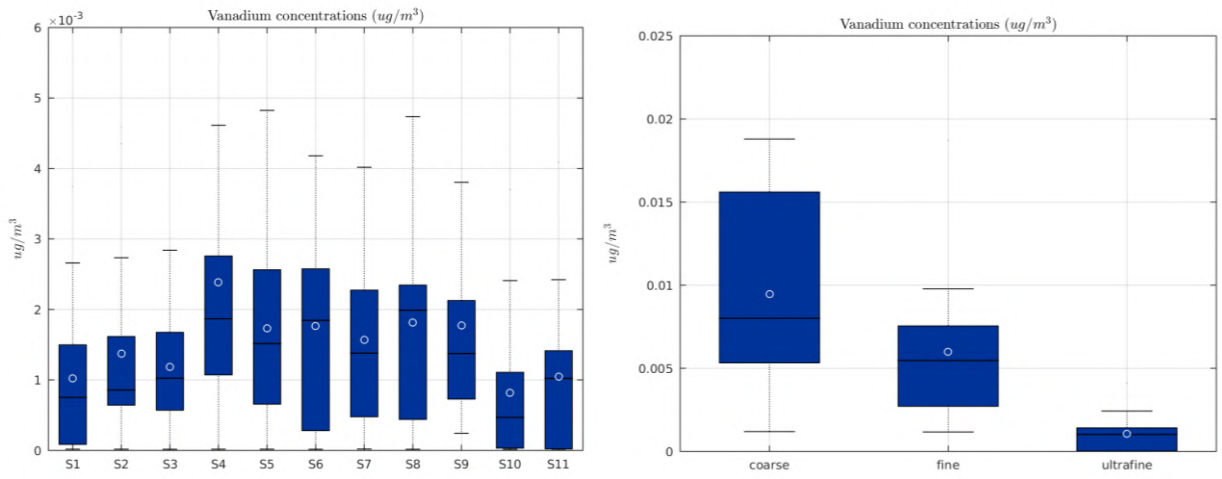

Figure 5.28. (left) Vanadium profile in different size fractions; (right) distribution of Vanadium in coarse, fine and ultrafine fractions. Data in µg/m³.

The primary contribution of ship traffic based on atmospheric vanadium as tracer of ship emission, calculated with the methodology as reported in Chapter 3 (Eq. 3.1), ranged from 5.8% to 17.4%. These values are in the range of the same parameter obtained in Venice, but unlike Venice, the coarse fraction gives the largest contribution. The average size distribution of the primary contribution of ship traffic to particulate matter is shown in Fig. 5.29 (with corresponding error). The average contribution is in the range of 5% to 17%, with maxima in the coarse fractions. This suggests that other sources are actually contributing to V because ship traffic mainly contribute to small particles (Merico et al., 2016). This profile could be the result of either mechanical ground particulates or aggregated primarily fine particulates from the combustion sources (also diesel traffic) or to other industrial contributions as was also inferred by the PMF analysis.

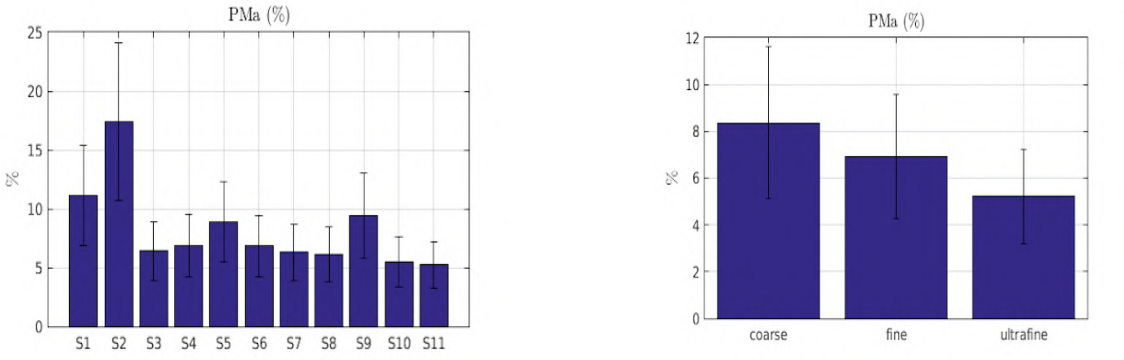

Figure 5.29. Primary contribution of maritime traffic in: different particle sizes (left); different fractions (right). Average - white circle, median - horizontal line in a box, box- 1st and 3rd quartile, whiskers - minimum and maximum).

The absolute contributions estimated in 2019 was compared to that estimates done during the period 2012-2014, within the POSEIDON project. The monitoring site in POSEIDON was located approximately 1200 m East from the Institute building and with elevation of 4 m asl (Deliverable 2.5, 2015). In order to conduct this comparison, the primary contribution of shipping was calculated also for PM_{10} (particles with diameter < 10 µm, corresponding to stages from 2 to backup) and for PM_1 (particles with diameter < 1 µm, corresponding to stages from 6 to backup), while $PM_{0.1}$ (particles with diameter < 0.1 µm) corresponds to nanoparticles of Fig. 5.29. There has been an increase in commercial and passenger ship traffic in the nearby harbour in last years, thus recuperating and exceeding the traffic from 2008 (Fig. 5.30). Thus the container traffic is doubled, while general cargo reload and number of passengers increased by approximately 50%, (Port authority, 2019) relative to the period 2012-2014 elaborated in the project POSEIDON (Deliverable 2.5, 2015). Container ships and cruisers are known to be the biggest polluters in maritime fleet.

The contribution to $PM_{2.5}$ and PM_{10} calculated from 2019 data was considerably higher than the previously observed in 2013-14 (Fig.5.31). The estimation of contribution to PM_1 and $PM_{0.1}$ have been conducted for the first time in this area. It is interesting to note that the calculated contributions have a different trend moving from nanoparticles to coarse fraction compared to what is expected and that contributions are significantly higher than those observed previously. This confirm that there are other sources of V in the area and that this approach does not identify the contributions due to ships in this area.

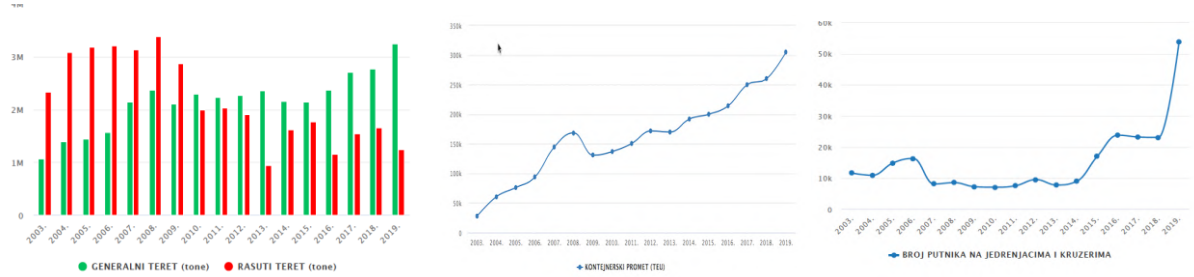

Figure 5.30. Harbour activity regarding (left) general cargo (green), (centre) container reload, and (right) passenger traffic in the port of Rijeka (Port Authority, 2019).

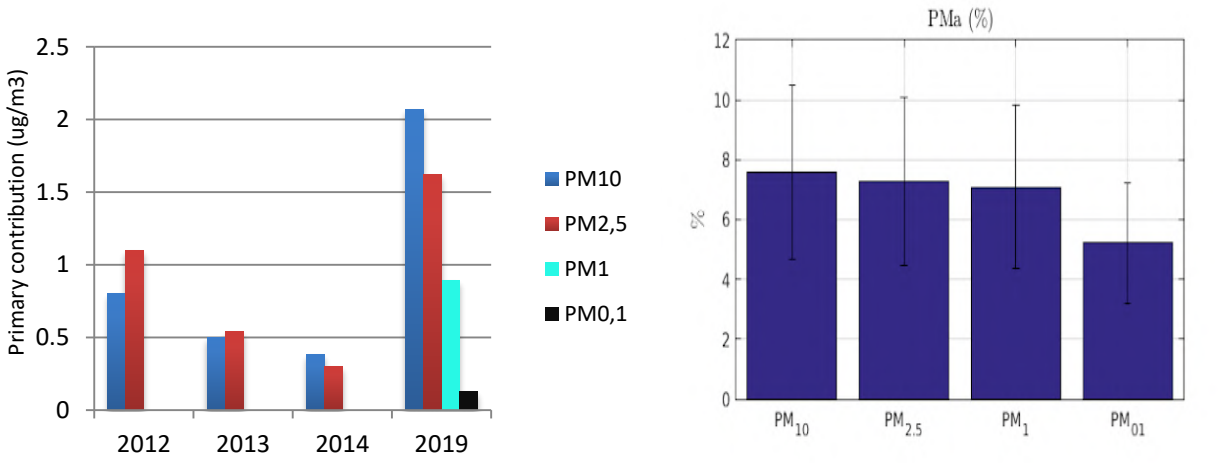

Figure 5.31. (left) Comparison between the primary contribution of ship traffic to particulate matter, calculated using vanadium as tracer of shipping emissions, obtained within POSEIDON (2012-14) and ECOMOBILITY (2019) projects. (left) relative primary contribution (%) to different particle size in 2019.

6 Comparison of the impacts of shipping in Venice and Rijeka

Comparison of measured concentrations and size distributions in Rijeka and Venice showed larger values, both in terms of number and mass concentrations in the Venice site compared to Rijeka site. However, the general shape of the size distributions is similar at the two sites and this allowed to individuate three size ranges (ultrafine, fine, and coarse particles) that were analysed separately. Regarding PM_{10}, $PM_{2.5}$ and PM_1, the concentration measured in Rijeka were approximately 50% of those obtained in Venice (though the monitoring time was different). The same is valid for fine particulate, while coarse are lower by approximately 30% and ultrafine by approximately 40%.

At both sites, ship traffic contributions to measured concentrations was determined using two independent approaches: statistical analysis of high temporal resolution data; source apportionment using PMF receptor model and evaluation of primary contributions from ships based on V concentrations.

In Venice, the statistical analysis of high temporal resolution data allowed to evaluate the primary ship traffic contributions to number and mass concentrations of particles. The impact of ship traffic was about 2% for number concentrations of fine and coarse fraction but it reached about 7.2% for ultrafine particles corresponding to about 1000 #/cm^3. The impact to PM_1, $PM_{2.5}$, and PM_{10} was about 2% corresponding to 0.4-0.5 µg/m^3. The results of the approach based on chemical composition showed that the use of PMF, separately on coarse and fine fractions, did not allow to separate ship contribution from other sources. However, the approach based on measured V concentrations allowed having an independent estimate of primary ship contributions to particles of different sizes. Results shows an average contribution of ship traffic to the coarse particles (> 1 µm) mass around 1%, to the fine particles (between 1 µm and 0.1 µm) mass around 3% and to ultrafine particles mass around 9%. If calculation is done for PM_{10}, a contribution around 2% was observed comparable to that found using high temporal resolution approaches. The comparison is good also for ultrafine particle concentration in number and in mass confirming that the contribution to ultrafine particles is about 4 times larger compared to the contribution to PM_{10} (or $PM_{2.5}$). The results found in this work compare well with the previous analysis of ship traffic impact to PM_{10} in different sites of the lagoon that was about 2% (Gregoris et al., 2016) and to the impact to total particle number concentration found in a previous work in Sacca Fisola about 6% (Contini et al., 2015).

In Rijeka, the statistical analysis of high temporal resolution data allowed to evaluate the primary ship traffic contributions to number concentrations that was about 2% for ultrafine particles (corresponding to roughly 130 #/cm^3) and to coarse fraction (about 0.5%). The impact to

fine particles resulted < 0.2% and comparable with experimental uncertainty. The same happens for the estimated contribution to PM_1, $PM_{2.5}$, and PM_{10}. Therefore, primary contribution to particle concentration of shipping is significantly lower than that observed in Venice. This is explainable considering that the distance of the site from the harbour was much larger than that of the Venice site and it is known that the impact of harbour emissions to local air quality is quickly decreasing when the distance from the harbour increase (Merico et al., 2019). Further, it has to be considered that average ship traffic in Rijeka is approximately 40% lower (in number) and 85% lower in gross tonnage compared to the traffic in Venice during the measurement campaigns. This results are in a reasonable agreement with previous results in another site in Rijeka in which a contribution to $PM_{2.5}$ and PM_{10} variable between 0.2% and 0.4% was observed and have the same trend observed in Venice with a significantly larger (about 4 times) contribution to ultrafine particles compared to fine and coarse fractions. The application of PMF to chemical composition did not allow the separation of shipping contribution from the other sources even if a certain impact of heavy fuel oil burning was clearly present. The use of V concentration to determine primary contributions from ships also was not clearly applicable in Rijeka because of the presence of other V sources. As matter of fact, maximum contribution based on V content is found in the coarse fractions, that obviously cannot be attributed to maritime traffic. The other sources of vanadium in the Rijeka area higher V content is soil dust, (Prohić, 1994) due to long term combustion of HFO in petroleum refinery, as well as ship building and ship repair in two still active shipyards.

7 Conclusions

Measurement campaigns have been done in Venice and Rijeka, in sites located near the harbour areas, using the same instruments. Specifically, atmospheric particulate matter samples in different size ranges were taken using a multi-stage impactor (12 size ranges) and collected samples were chemically analysed (carbon content, major water soluble ions, and major metals). In parallel, measurements of particle number concentrations and size distributions were performed at high temporal resolution using optical counters (CPC and OPC) coupled with local meteorological information. Further, detailed data of ship traffic were collected from Port Authority in both areas.

Measurements were post-processed at the two sites using comparable approaches already applied in POSEIDON project (Med Programme 2007-2013). Specifically, two independent approaches were used: statistical analysis of high temporal resolution data, and receptor model (PMF) application on measured chemical composition. The application of PMF at both sites did not allow to separate shipping contribution from the other sources acting on the area. Therefore, an approach based on measurement of V size-segregated concentrations was also applied. This

was successfully in Venice site but in Rijeka the presence of other V sources did not allow to evaluate contributions of ships with this approach. At both sites the statistical analysis of high temporal resolution measurements allowed to estimate impacts to particle number and mass concentrations in different size ranges.

In Venice the contribution of shipping to $PM_{2.5}$ and PM_{10} was around 2% and a similar percentage was found also for fine and coarse particle number concentrations. A contribution four times large was found for ultrafine particles in both number and mass (about 7-9% according to the different approaches used). In Rijeka, contributions of ships to ultrafine particle number was around 2% and it was reduced to about 0.5% in coarse fraction. The contributions to mass concentrations were found lower than 0.2%. Also for this site is it evident the largest impact of shipping to ultrafine particle concentrations. The lower impact observed in Rijeka is due to the larger distance of the site from the harbour compared to Venice and to the lower intensity of ship traffic (about 85% lower on gross tonnage) compared to Venice.

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