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An inter-comparison of size segregated carbonaceous aerosol collected by low-volume impactor in the port-cities of Venice (Italy) and Rijeka (Croatia)

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Abstract:	The knowledge of the size-resolved chemical composition of carbonaceous aerosols is essential, when studying their sources and environmental impacts. Size-segregated analysis of organic and elemental carbon in aerosol are scarce, especially in coastal areas stressed by emissions from human activities and with complex interactions between anthropogenic and natural emissions. Aiming to fill this lack of information, a study of aerosol size segregated samples was undertaken between 2018 and 2019, using a MOUDI impactor. Measurements were performed in two port-cities of Northern Adriatic Sea, Venice (Italy) and Rijeka (Croatia). A thermal-optical analysis (EUSAAR2) allowed elemental and organic carbon determination (EC, OC) in different size ranges. For Rijeka site, the water soluble organic carbon content (WSOC) has been analysed. OC and EC average concentrations in Venice were 3.16 (± 0.97) and 0.40 (±0.13) μg/m3, while in Rijeka were 2.48 (± 0.65) and 0.37 (±0.08) μg/m3. The OC size distributions were bimodal at both sites, with an accumulation and a coarse mode. EC showed a bimodal distribution in Rijeka, a single fine mode in Venice. The EC/TC ratio was large in the fine mode at both sites, however, in Rijeka non-negligible values were found in coarse fraction suggesting possible contributions from resuspension of carbon-loaded dust and mixing of anthropogenic particles with sea spray. The analysis of the ratio WSOC/OC as function of particle size showed a total value of 0.51 (± 0.12) with an increase in the coarse fraction likely due to contributions of water soluble carbon from sea spray and biogenic emissions.

Highlights

- PM and EC/OC size distributions were analysed for Venice and Rijeka port-cities.
- PM size distributions were bimodal in Venice and three-modal in Rijeka.
- OC size distributions were bimodal in both sites, EC was limited to fine fraction in Venice.
- EC/TC ratio was larger in the fine mode but in Rijeka coarse EC (15% of TC) was found.
- WSOC/OC ratio in Rijeka increased in coarse fraction due to biogenic and marine aerosol.

An inter-comparison of size segregated carbonaceous aerosol collected by low-volume impactor in the port-cities of Venice (Italy) and Rijeka (Croatia)

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Abstract

The knowledge of the size-resolved chemical composition of carbonaceous aerosols is essential, when studying their sources and environmental impacts. However, size-segregated analysis of organic and elemental carbon in aerosol are scarce, especially in coastal areas stressed by emissions due to human activities and with complex interactions between anthropogenic and natural (sea spray) emissions. Aiming to partially fill this lack of information, a study of aerosol size segregated samples was undertaken between August 2018 and May 2019, using the 10-stages MOUDI impactor. Measurements were performed in two port-cities of Northern Adriatic Sea, Venice (Italy) and Rijeka (Croatia), different in type and volume of vessel traffic. Following, a thermal-optical analysis (EUSAAR2) allowed elemental and organic carbon determination (EC, OC) in different size ranges.

Further, for Rijeka site, the water soluble organic carbon content (WSOC) has been analysed. Similar carbonaceous concentrations at both sites were observed: OC and EC average concentrations in Venice were, respectively, 3.16 (± 0.97) and 0.40 (±0.13) μg/m^3, while in Rijeka were 2.48 (± 0.65) and 0.37 (±0.08) μg/m^3. The OC size distributions were bimodal at both sites, with an accumulation mode in the size range 0.56 - 0.32 μm and a coarse mode in the range 5.6 - 3.2 μm. EC showed a bimodal distribution in Rijeka, a single fine mode in Venice. The EC/TC ratio was large in the fine mode at both sites, however, in Rijeka non-negligible values (up to 0.15) were found in the coarse fraction suggesting possible contributions from resuspension of carbon-loaded dust and mixing of anthropogenic particles with sea spray. The analysis of the ratio WSOC/OC as function of particle size in Rijeka showed a total value of 0.51 (± 0.12) with an increase in the coarse fraction likely due to a contribution of water soluble carbon from sea spray and biogenic emissions.

Keywords: carbonaceous aerosol, carbon size distributions, OC/EC, WSOC, port-cities.

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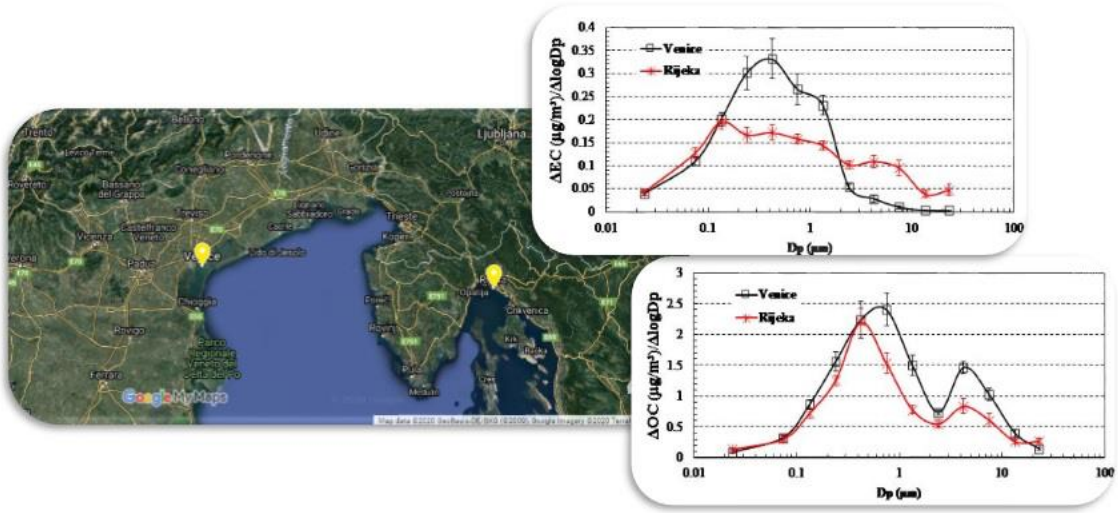
Graphical abstract



1. Introduction

Carbonaceous aerosols, including both organic carbon (OC) and elemental carbon (EC), are a key part of atmospheric aerosols, representing generally between 20% and 50% of the total aerosol mass (Kanakidou et al., 2005; Putaud et al., 2010), and play a crucial role in understanding regional air pollution, climate change, and atmospheric chemistry. Further, as the particles become smaller, carbonaceous fraction could contribute even more to the PM mass and be the dominant contributor to ultrafine PM mass (Kleeman et al., 2008; Kam et al., 2012). Knowledge of the size-resolved content of carbon in aerosol is useful when studying the environmental impact of specific sources, because size distributions can provide important information about anthropogenic sources, new particle formation and growth mechanisms (Hinds, 1999).

In the atmosphere, a multi-stage impactor can typically be used to collect particles in the size range 30 nm-10 μm (aerodynamic diameter). Impactor stages operating in the range of 0.5-10 μm are also quite common (for example high volume impactors). However, in order to extend the size range below approximately 0.5 μm, two basic approaches have been used: in the design of Hering et al. (1978), there is a critical non-collecting orifice reducing the pressure of the lowest stages enabling collection of sub-0.5 μm particles. In the design of the Berner low-pressure impactor (BLPI; Berner and Lurzer, 1980), the pressure is reduced gradually using different combinations of the number of the nozzles and their diameters for each stage. In this way, a low pressure and high jet velocities allow the collection of particles down to about 30 nm. In the micro-orifice uniform deposit impactor (MOUDI), designed by Marple et al. (1991), the extension of the particle size range is made using micro-orifices and in a more recent design called nano-MOUDI, the size range is extended down to 10 nm using a combination of micro-orifices and low pressure (Marple and Olson 1999; Marple, 2014; MSP, 2012).

The size distribution of carbonaceous aerosol can be studied by sampling size-segregated aerosol using multi-stage (cascade) impactors (Mercer et al., 1970), followed by a thermo-optical analysis (TOA; Chow et al. 1993; Birch and Cary, 1996) of the samples collected for the estimation

of OC and EC fractions present in the dimensional stages. According to the TOA, the sampling media have to resist to temperatures of up to 700–900°C and then quartz fiber filters are commonly used. It could be difficult to use such kind of filters in some impactors (Saarikoski et al., 2005) compared to dense films or foils as a collection medium, (i.e. aluminium foils, polycarbonate filters, cellulose ester filters or Teflon membranes). For this reason, size-segregated studies on carbonaceous aerosol, using the approach before described based on multi-stage impactors followed by a TOA technique, are in general quite scarce. Alongside the heavy work load required in the field as well as in the laboratory that the multi-stage impactors need, another important limiting factor in European areas is that the presently in-force European Directive 2008/50/EC on air quality requires the control of PM_{10} and $PM_{2.5}$ and then many studies have been focused on the size integrated particulate matter (Mirante et al., 2013 and references therein). For example, in the last two decades, for the European area, about 30 studies reporting size segregated aerosol collected using low-volume impactor are reported (from ISI WEB OF KNOWLEDGE database), and studies focused on size segregated carbon composition are even less (12).

Among these, some studies were focused for determining new methodological approaches or specific set-up adopted for measurements of organic compounds in size segregated aerosol particles (Neussus et a., 2000; Viidanoja et a., 2002; Gietl & Klemm, 2009; Cuccia et al., 2013). Another part of these studies is, instead, focused on specific organic compounds. In this framework, attention has been given to polycyclic aromatic hydrocarbons (PAHs) and their nitro- and methyl- derivatives, particularly in urban areas, because of their carcinogenicity (Duan et al., 2005; Wang et al., 2009; van Pinxteren et al., 2016; Rougla-Kozlowska et al., 2016; Di Filippo et al., 2010). Other works analysed the size distribution of HUmic-Like Substances (HULIS) (Frka et al., 2018), of photo-oxidation products of α-pinene (Feltracco et al., 2018), or in general of the water soluble organic carbon (Barbaro et al., 2019; Contini et al., 2014a; Timonen et a., 2008) while in other, specific compounds such as quinones were investigated for their redox activity, in aerosol size segregated samples, in order to determine the Oxidative Potential (OP) of the different aerosol size classes (Lyu et al., 2018).

Finally, some field monitoring campaigns performed with low-pressure impactors followed by EC/OC determinations have been done to characterise the size distribution of the elemental and organic carbon in different environments, such as rural, urban, urban background and hot-spot areas, and to infer potential sources of carbonaceous aerosol (Gnauk et al., 2005; Saarikoski et al., 2005; Almeida et al., 2006; Hitzenberger et al., 2006; Gietl et al., 2008; Bougiatioti et al., 2013). In some cases, data were used as input data for receptor models in source apportionment studies (Contini et al., 2014a; Pokornà et al., 2015).

While is evident how in-depth studies of the size distribution of carbon content in PM are needed, and how these could help in the framework of emission containment strategies. Up to now, OC and EC size segregated studies remained scarce, especially for areas very stressed by human activities, where it is possible to have numerous and heavy atmospheric pollution episodes over the year by different sources. With the aim to address this lack of information, a study of aerosol size segregated samples was undertaken in the framework of ECOMOBILITY project, using low-volume multistage impactors. Samples were subjected to thermo-optical analysis in transmittance (TOT) to determine size distribution of OC and EC in two different port-cities of Mediterranean basin, located in the northern Adriatic sea: Venice (Italy) and Rijeka (Croatia), which differs in type and volume of ship traffic (Merico et al. 2017). Size distributions of PM, OC, and EC in the two port-cities are studied to investigate the role of different sources acting in the two coastal areas and the mixing of anthropogenic emissions and sea spray.

2. Experimental methods

2.1 Measurement sites and sampling strategy

In Figure 1 the two sampling sites in Venice and Rijeka cities chosen for data collection are shown. The Italian site is located in front of the tourist harbour of Venice and faces the Giudecca Channel that includes the main ship routes. Size-segregated weekly samples were collected at the monitoring station of the Protection and Prevention Agency of Veneto region (ARPAV) in Sacca Fisola, Venice

(45°25’42’’ N, 12°18’46’’ E, 3 m a.s.l.), from August to November 2018 (Table 1). The Croatian site was on the roof of the Public Health building in Rijeka, in front of the entrance of the harbour (45°19’56’’ N, 14°25’33” E, 34 m a.s.l.). Size-segregated aerosol samples were collected using the same approach at the two sites. In Rijeka, weekly size-segregated samples were collected in the periods October – December 2018 and March – May 2019 (Table 1).

In both sampling sites, weekly size-segregated samples were collected on 47 mm quartz filters (Whatman) using a ten-stage (plus inlet and backup filter stages) micro-orifice uniform deposit impactor (MOUDI, MSP Corp., USA; Model 110NR) operating at a flow rate of 30 L/min. The equivalent aerodynamic cut-off diameters (D_p) of each stage of MOUDI impactor were, starting from the inlet: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and 0.056 µm, respectively. The backup filter was used to collect particles with D_p <0.056 µm. The quartz fiber filters were pre-fired at 400°C for 4 h in a muffle furnace to remove original organic traces. Field blank and sampled filters were weighed before and after the sampling, with a microbalance (Sartorius CP225D, reading precision 10 µg for Venice samples; Mettler Toledo MT XPE 206, reading precision 10 µg, for Rijeka samples), three times over 24 h, after a conditioning period of 48 h at temperature of 20 (±5)°C and a relative humidity of 50 (±5)%.

Figure 1. Location of the measurement sites in Venice (Italy) and Rijeka (Croatia). Maps from D-maps.com and Google Earth.

Table 1. Sampling periods for Venice and Rijeka sites.

Sample	Sampling period in Venice	Sampling period in Rijeka
1	02 - 09 August 2018	16 - 23 October 2018
2	09 - 16 August 2018	23 - 29 October 2018
3	16 - 23 August 2018	29 October - 05 November 2018
4	23 - 30 August 2018	05 - 12 November 2018
5	30 August - 05 September 2018	12 - 19 November 2018
6	10 - 17 September 2018	19 - 26 November 2018
7	17 - 24 September 2018	26 November - 03 December 2018
8	24 September - 02 October 2018	03 - 10 December 2018
9	02 - 09 October 2018	26 March - 02 April 2019
10	09 - 16 October 2018	02 - 09 April 2019
11	16 – 23 October 2018	09 - 16 April 2019
12	23 – 30 October 2018	16 - 23 April 2019
13	30 October – 07 November 2018	23 - 30 April 2019
14	7 - 14 November 2018	30 April - 07 May 2019
15	14 – 22 November 2018	07 - 13 May 2019
16	22 – 27 November 2018	13 - 21 May 2019

Relative standard deviation of the weights was always below 0.5%. Concentration values below the detection limit, calculated as the blank average plus three times the standard deviation of the blanks, were rejected. In total, 16 weekly samples were successfully collected in each site, every sample counted 12 filters, for a total of 192 filters in Venice, and 178 in Rijeka, as backup filters were not analysed in the autumn campaign. Since the aerosol particle size exhibits an approximately normal distribution towards the particle diameter on a logarithmic scale (Marple et al., 1991), $\Delta C/\Delta \log_{10} D_p$ (where C is mass concentration and D_p is aerodynamic diameter) has been used to represent the size resolved concentrations in this study.

2.2 Analysis of carbon and of water soluble organic carbon (WSOC)

Samples collected in Venice and Rijeka were analysed for OC and EC content applying the thermo-optical transmittance (TOT) method, for charring carbon correction, using a Sunset laboratory carbon analyser (Sunset Laboratory Inc., OR, USA) with temperature offset correction. The procedure used is the same applied in previous studies (Merico et al., 2019). Punches of 1.0 cm^2 were cut from the fibre quartz filters and analysed according to the EUSAAR2 protocol (Cavalli et al. 2010). To ensure the accuracy of the OC and EC analysis, the analyser was calibrated (multipoint) using, as external standard, a sucrose solution (2.198 g/L in water, CPAchem Ltd). Linear calibration had a slope of 0.94 (±0.003), a negligible intercept (0.05±0.08), and a determination coefficient $R^2 \sim 1$ for Venice dataset. For Rijeka dataset the linear calibration had a slope of 0.96 (±0.01), a negligible intercept (0.06±0.22), and a determination coefficient $R^2 \sim 1$. Measured OC and EC concentrations were corrected using these calibrations. Blank filters were also analysed for correcting the concentrations measured in ambient samples. Specifically, 16 blanks were analysed with the EUSAAR2 protocol. For OC average contamination levels were found equal to 2.65 $\mu g/cm^2$ (standard error: ±0.05 $\mu g/cm^2$). Negligible contamination for EC (< 0.1 $\mu g/cm^2$) was found. The uncertainty on measured OC and EC concentrations has a systematic part (0.1 $\mu g/ cm^2$) and a random part, 5%, for both OC and EC. WSOC was determined from the water extracts obtained by sonication (30min) of the punched half of the

filters in 30 ml of demineralized water. The extracts were filtered through a PTFE filter (0.45 µm pore size), and WSOC was determined using a TOC analyzer (Shimatzu TOC-VCPH with NDIR detector). The uncertainty on measured WSOC is 5,4%. A total of 16 blanks were analysed (one per each sample set) and subtracted their values from collected samples

3. Results and discussion

3.1 Aerosol size distributions

Figure 2 reports the average PM size distributions for Venice and Rijeka sites. Regarding Venice, a bimodal distribution was found, with peaks of concentration at diameters around 0.75 µm and 4.23 µm.

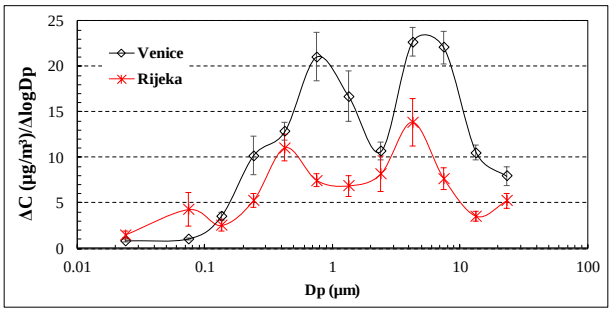


Figure 2. Average PM size distribution for Venice and Rijeka sites. Error bars represent the standard errors.

In a previous study focused on the size distribution of particulate matter collected with a similar sampler in another area of Venice (Barbaro et al., 2019) it was present also a third mode at diameter below 0.056 µm, that is not clearly visible in this work. Coherently, the previous study reported a higher percentage of ultrafine particles (D_p <0.1 µm) to total suspended particulate (18%) compared to this work (1%). In Rijeka site, the average PM size distribution showed a three-mode behaviour, with maxima at diameters around 0.07 µm, 0.42 µm and 4.23 µm. Particularly, the size distribution of PM in Rijeka is shifted to the respective profile from Venice, indicating similar, but different sources and fate of pollutants. According to these findings, collected data has been analysed

separating three size ranges: coarse (D_p >1 µm) particles represented by stages inlet to 6; fine particles (0.1 µm< D_p <1 µm) represented by stages from 7 to 10; ultrafine particles (D_p <0.1 µm) represented by stage 11 plus backup filter. Figure 4 shows the trend of PM concentrations, in Venice (Fig. 3a) and Rijeka (Fig. 3b), separately for the three size ranges: coarse, fine, and ultrafine particles.

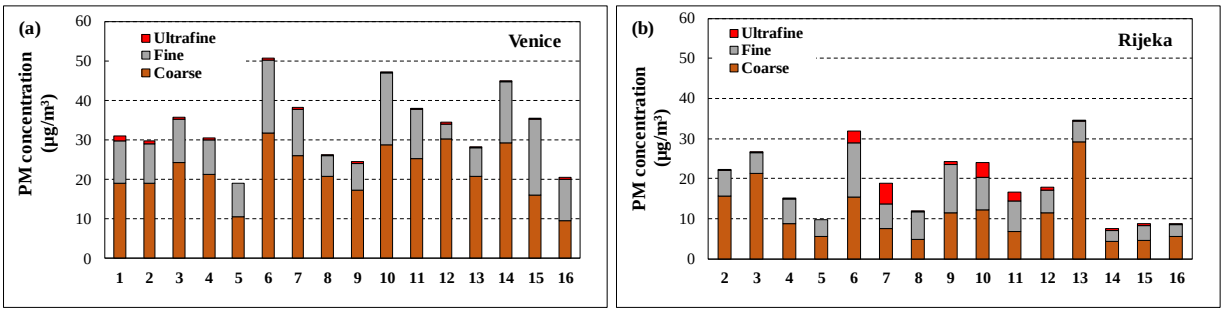


Figure 3. PM concentrations of the weekly samples, collected in Venice (a) and Rijeka (b), separated in coarse, fine, and ultrafine size ranges.

In Venice, weekly values of total particulate matter, calculated as the sum of all stages, ranged from 19.0 µg/m^3 to 51.5 µg/m^3 during the measurement period, with an average of 33.8 µg/m^3. No specific trend during the sampling period was observed comparing samples taken during the warm (samples from n. 1 to n. 8) and cold periods (samples from n. 9 to n. 16). In average terms, the total PM during the sampling period distribution of coarse, fine, and ultrafine particles in the samples shows that 65% of particulate matter (in mass) is constituted of coarse particles, 33% of fine particles, and 2% of ultrafine particles.

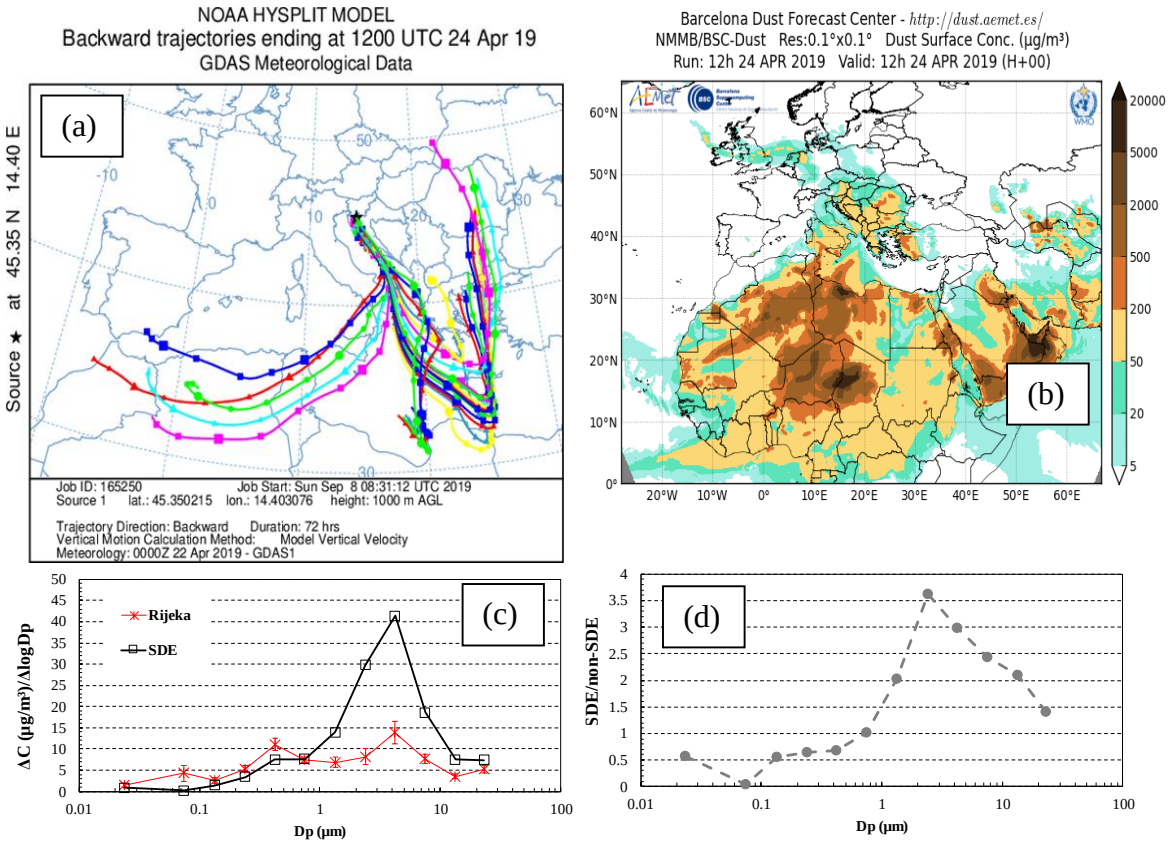


Figure 4. (a) Back-trajectories (http://arl.noaa.gov/ready/); (b) NMMB/BSC images (https://ess.bsc.es/bsc-dust-daily-forecast); (c) PM size distribution of sample n. 13. (d) ratio of PM concentration during SDE and the average value for non-SDE cases as function of particle size.

In Rijeka, sample n. 1 has been excluded from the statistical analysis because some filters were damaged and it did not insure sufficient quality. Weekly values of total particulate matter ranged from 7.6 µg/m^3 to 34.9 µg/m^3 with an average value of 18.6 µg/m^3, significantly lower than the average observed in Venice. The collected weekly samples showed an average distribution with coarse fraction representing 59%, fine fraction 34%, and ultrafine fraction representing 7%.

Sample n. 13 showed the maximum total PM concentration and it was influenced between 24/04/2019 and 26/04/2019 by an intense Saharan Dust Event (SDE) occurring on a large spatial scale interesting also the studied area. This transport was confirmed by the back-trajectories of air masses calculated by Hysplit model (Fig. 4a) and the simulations of the Dust REgional Atmospheric Model (BSC-DREAM8b) (Fig. 4b). The event lead to a significant increase in the concentration of

coarse fraction, whith a limited contribution on the concentration of fine and ultrafine particles. The analysis of the sample collected during the SDE showed a high content of coarse particles (84%) with very low fine and ultrafine concentrations, respectively 14% and 2%, compared to the average distribution. The PM size distribution associated to the sample n.13 (Fig. 4c) showed a single coarse mode at around 4.23 μm and, in general, the major contributions associated to the range 2.40-7.48 μm, confirming that during a Saharan Dust Event the coarse fraction is mainly involved in the process of long range transport. Figure 4(d) shows the ratio of concentrations measured during SDE and the average found for non-SDE periods. It shows the SDE contributes to concentrations of particles larger than about 1 μm with a maximum at about 3 μm. This finding is in agreement with results reported literature: for example, in Conte et al. (2020), where the comparison of size distributions measured during SD and non-SD days shows that Saharan dust advection significantly increases the particle number concentrations for diameters (D_p) larger than about 0.9-1 μm, with the maximum contribution observed for particles with D_p around 2.5-3 μm. Other previous studies, in Southern Italy, found contributions to particles in the size range 2-5 μm during Saharan dust outbreaks (Blanco et al., 2003; Contini et al., 2014b).

The samples collected in Venice did not show a clear trend moving from summer to autumn period, instead, differences in the weight of the different size classes were observed in Rijeka comparing the warm and the cold period with the last three samples having concentrations significantly lower than the previous ones. This could be attributed to differences in the strength of the aerosol sources affecting the studied area and/or differences in meteorological conditions in the last three weeks of monitoring, in which, in particular, some regional air quality stations revealed bora winds (with prevalent direction from NE), that blowed with an intensity also of 9 m/s.

3.2 OC and EC size distributions

Size distributions of organic and elemental carbon obtained in Venice and in Rijeka are compared in Fig. 5. OC concentration measured in Venice shows a bimodal behaviour with the first mode at around

4.23 µm (corresponding to the range 5.6-3.2 µm) and the second mode close to 0.75 µm (corresponding to the range 1.0-0.56 µm). Also for Rijeka there is a bimodal trend in the concentrations of OC in the various samples, with the first mode at around 4.23 µm (corresponding to the range 5.6-3.2 µm) and the second mode is shifted toward lower diameters compared to Venice, at about 0.42 µm (corresponding to the range 0.56-0.32 µm).

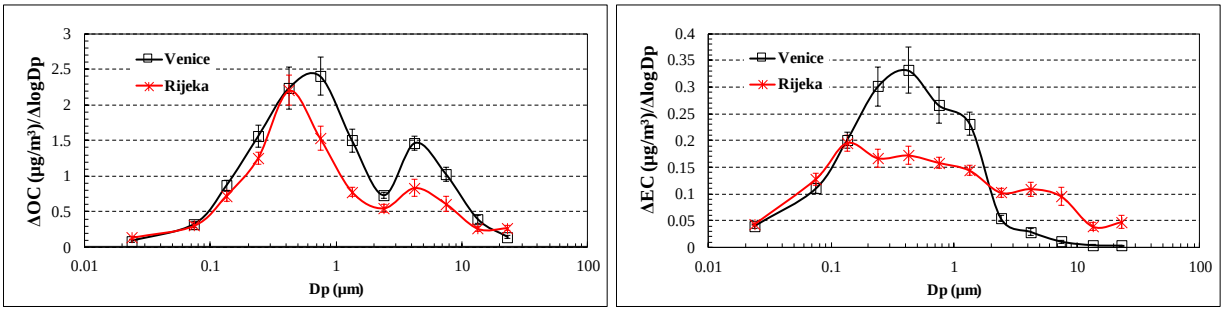


Figure 5. Average OC and EC size distributions for Venice and Rijeka sampling sites. Error bars represent the standard error.

The EC size distribution of Venice shows a unimodal trend with increasing concentrations in the finer particles, with the highest concentration corresponding to the ranges 0.56-0.32 µm and covering all the sizes between 0.1 µm and 1 µm. In a previous study performed by Huang et al., 2008, it has been reported that the EC fine mode was observed in two possible size bins, respectively of 0.32-0.56 µm and 0.56-1.0 µm, associating EC mode of size range 0.56-1.0 µm to aged aerosols, while size range 0.32-0.56 µm was typical of freshly emitted EC. Then, the EC size distribution of Venice could be interpreted with the presence, in the collected samples, of both fresh and aged aerosol, with the prevalence, in terms of concentrations, of the former. Finally, given the purely primary nature of the EC (considered a good tracer of combustion processes), in the port area it is probable to have a contribution also from the ship emissions that could influence this site (Contini et al., 2015; Merico et al., 2017).

For Rijeka, the size distribution of EC presents different behaviour compared to Venice. There is a broad mode in the fine particles with a contribution in the size range 0.1-1 µm, probably due to

283 the emissions of fresh EC particles and aged EC as seen for Venice. However, non-negligible
284 concentrations are also observed for coarse particles, in the size range 3.2-5.6 μm. The presence of
285 EC in the coarse mode is not clear, however it has been already documented in literature; for example
286 Huang et al. (2008) found a peak mode in the range 5.6-3.2 μm, while Hitzenberger and Tohno (2001)
287 reported an EC mode in the super-micrometric size range peaking at 4.65 μm, finally Berner et al.
288 (1996) showed an EC coarse mode in the range 1.6-2.4 μm. Particularly, in Berner et al. (1996), the
289 hypothesis of the sea spray, generated from polluted water, as possible responsible of the presence
290 of carbonaceous particles in coarse mode was assumed.

291 In Figure 6 the average OC and EC trends in the three size ranges (coarse, fine, and ultrafine)
292 are reported for Venice and Rijeka. In the Venice samples the concentration of OC, calculated as the
293 sum of all stages, ranged from 2.02 $\mu g/m^3$ to 5.67 $\mu g/m^3$ with an average value of 3.16 $\mu g/m^3$
294 (corresponding to 9.3% of the total PM). Coarse fraction OC account for 41% of total carbon, while
295 the fine and ultrafine fractions account for 55% and 5% respectively. The concentration of EC,
296 calculated as the sum of all stages, ranged from 0.20 $\mu g/m^3$ to 0.67 $\mu g/m^3$, with an average value of
297 0.40 $\mu g/m^3$ (corresponding to 1.2% of the total PM). In the coarse fraction EC is 20% of the total EC,
298 while the fine and the ultrafine fraction represents, respectively, 66% and 14%. Considering the
299 temporal trend of OC and EC collected in Venice site, two evident peaks are noticed, associated with
300 the samples 6 and 10, related to the sampling period of 10 - 17 September and 9 - 16 October,
301 respectively, associated with the stage 7 (corresponding to the range, 1-0.56 μm). These peaks are
302 evident also in temporal trend of PM concentrations, particularly for sample n. 6. However, a clear
303 trend comparing summer and autumn samples was not observed, similarly to what happens for PM
304 concentrations.

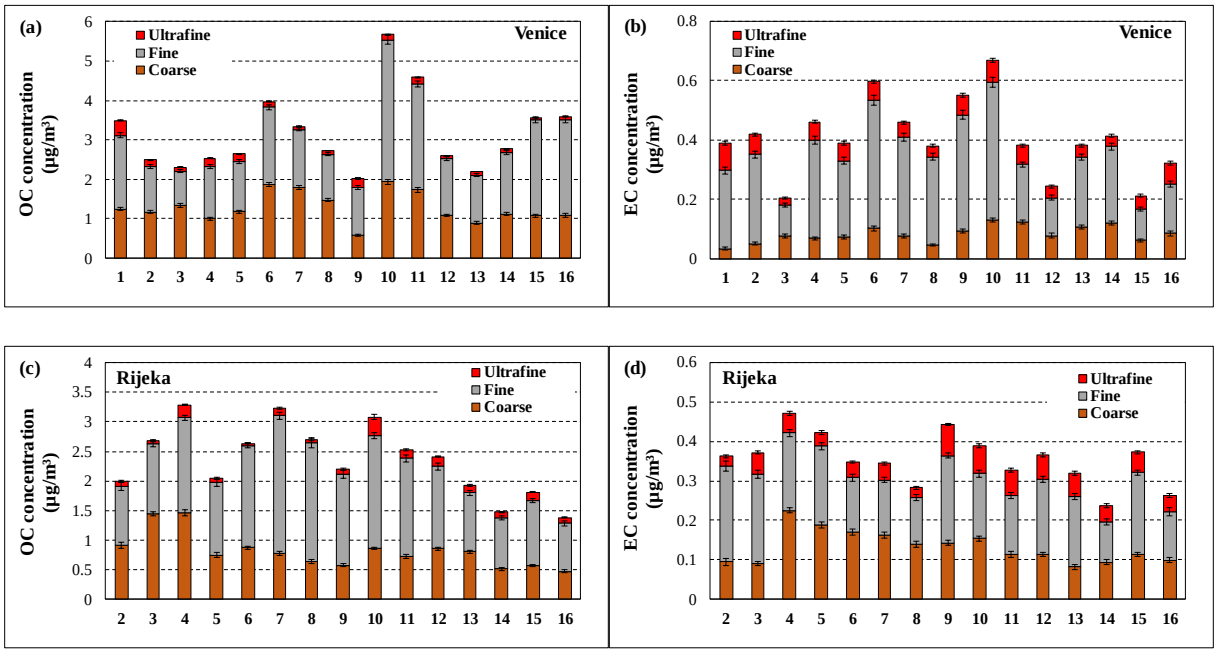


Figure 6. OC and EC concentrations of the weekly samples, collected in Venice (a, b) and Rijeka (c, d), segregated in coarse, fine and ultrafine fractions.

In Rijeka, the concentration of OC, calculated as the sum of all stages ranged from 1.39 µg/m^3 to 3.29 µg/m^3, with an average value of 2.36 µg/m^3 (corresponding to 12.7% of the total PM). In the coarse fraction, OC concentration represented 35% of total OC, while in fine and ultrafine fraction is 60% and 5%, respectively. The concentration of EC, calculated as the sum of all stages, ranged from 0.24 µg/m^3 to 0.47 µg/m^3, with an average value of 0.35 µg/m^3 (corresponding to 1.9% of the total PM). In the coarse fraction, EC concentration represented 37% of total EC, while in fine and ultrafine fraction is respectively 49% and 14%. In figure 7, a comparison of the average OC and EC size distributions observed during SD events (indicated as SDE) with those observed in the other period (indicated with no-SDE) is shown for Rijeka site. Particularly, OC size distribution associated to the SD event showed lower concentrations for fine and ultrafine particles, while for coarse particles, similar concentrations were observed with a slightly larger concentrations observed during SD event. This result is in agreement with previous studies reported in literature, that are based on specific Saharan dust outbreaks in which a slight increase of OC on PM_{10} fraction during SD days has been

observed (Oduber et al., 2019; Vasilatou et al., 2017; Aymoz et al., 2004; Putaud et al., 2000). Further, as reported in literature (Salvador et al., 2016) Saharan dust transported to the Mediterranean regions could be enriched of PM due to anthropogenic combustion emissions located in north African coast. In a recent study (Conte et al., 2020) the comparison of carbon content between SD and non-SD days, performed on fine and coarse ($PM_{2.5}$ and PM_{10}) samples, showed, similarly to our results, that only coarse fraction could be slightly enriched in organic carbon of secondary origin, suggesting that SD events could contribute to secondary organic aerosol in the coarse fraction, likely due to the aging of dust travelling above the Mediterranean Sea, favoured by the reactivity of dust particles surface. Comparison of EC in SD days and non-SD days showed a different behaviour. No significant differences were observed for particles up to about 2 µm that are generally less influenced by dust advection, but a decrease of EC was observed for particles larger than about 2 µm. Only one SD case is present in this dataset and further studies are likely needed to better understand how dust advection influences distribution of OC and EC. In literature, only Chuang et al. (2003) observed the presence of significant coarse mode EC in different SD-related aerosol samples, indicating in the coagulation of EC during long range transport of mineral dust mixed with air mass impacted by anthropogenic emissions the reason of the presence of EC coarse mode. No other studies reporting EC concentrations size distributions during the dust episodes are available. A seasonal trend is observable for OC with the last three samples having significantly lower concentrations compared to the samples of the cold period similarly to what happens for PM concentrations, however, this is not clearly visible on EC concentrations.

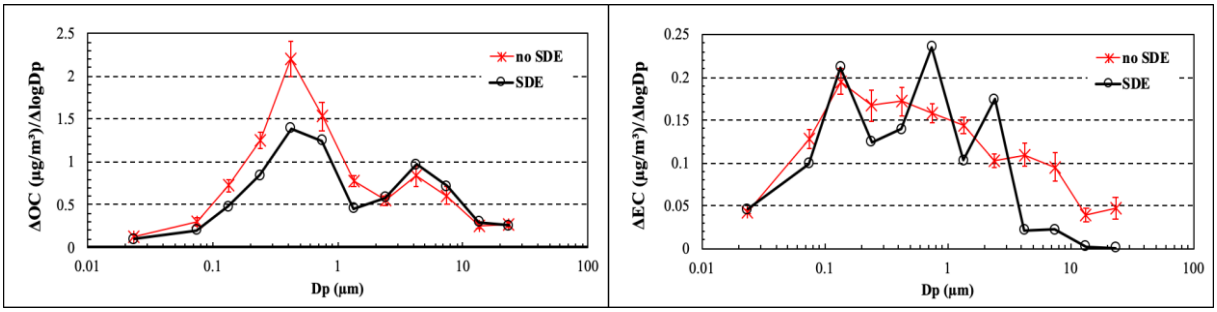


Figure 7. Comparison of average OC and EC size distribution associated to "no SDE" and to "SDE" event for Rijeka sampling site. Error bars represent the standard errors.

3.3 EC/TC ratio and WSOC distribution

The EC and OC values determined for each sample were also used for the EC/TC ratio analysis. In figure 8 the average ratios of EC/TC in size segregated particles for Venice and Rijeka samples are compared. Considering all stages, the average EC/TC values were 0.12 (±0.02) and 0.16 (±0.03) for Venice and Rijeka respectively. These numbers are comparable with typical EC/TC ratios, ranging from 0.10 to 0.22, and not depending much on PM concentration levels (especially in winter) in regional background sites of Europe (Cavalli et al., 2016) and in Italy (Sandrini et al., 2014; Dinoi et al., 2017; Cesari et al. 2018).

Considering the coarse, fine, and ultrafine fractions in Venice samples, the ratios were, respectively: 0.04 (±0.01), 0.14 (±0.03) and 0.28 (±0.06), showing a clear increment moving towards the finer particles according with the primary origin of EC from combustion processes emitting in the finer fractions of aerosols. In Rijeka the average ratios were 0.14 (±0.03) for coarse fraction, 0.12 (±0.02) for fine fraction and 0.27 (±0.05) for ultrafine fraction. Therefore, a similar trend has been observed, compared to Venice, for finer particles (D_p < 1μm), while a higher ratio was measured for coarse fraction. The higher concentration of EC in coarse fraction in Rijeka could probably be associated to the presence of resuspended dust containing carbonaceous particles previously deposited and/or to a contribution of industrial emission or to a mixing between anthropogenic matter and sea spray that is composed mainly of coarse particles. The analysis of the EC/TC ratios could be

useful in order to identify the possible source types of ECs. Previous studies have pointed out that EC/TC ratios range from 0.6 to 0.7 in fuel combustion emissions and from 0.1 to 0.2 in biomass combustion emissions (Salam et al., 2003; Zhang et al., 2014). Primary emissions from ships are characterised by EC/TC ratios very variable (on average between 0.1 and 0.5) depending on the typology of ships, on the fuel used, and on the particle size. Furthermore, in typical ship emissions TC is mainly found in fine fraction even if percentages up to 15% are observed in particles larger than 5.8 µm (Zhang et al., 2020). Then, the EC/TC ratios observed in the fine fractions of Venice and Rijeka suggest a certain contributions of biomass burning that adds to that of shipping and road traffic. Further, the linear regression between EC and OC in both sampling sites (not shown), showed R^2 values of 0.58 for Venice and 0.51 for Rijeka which indicated weak correlations, suggesting the presence of different local sources having different EC/OC ratios that eventually sum to medium and long-range transport.

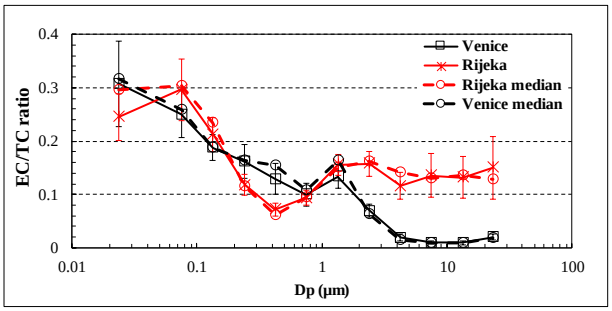


Figure 8. Average (solid line) and median (dashed line) ratios of: EC/TC in size segregated particles for Venice and Rijeka samples. Error bars represent the standard errors.

In Fig. 9 the average ratios of WSOC/OC in size segregated particles for Rijeka samples are reported. Particularly, WSOC is an important component of OC and consists of oxygenated organic compounds (e.g., monocarboxylic acids, dicarboxylic acids, and aldehydes). Secondary oxidation of organic precursors has been identified as the main source of WSOC in aerosols, and thus WSOC is considered an approximate measure of SOA (Weber et al., 2007). In the present study, the average WSOC concentration, considering all stages, is 1.00 (±0.28) µg/m^3, while considering the fractions

coarse, fine and ultrafine, the following values has been observed respectively: 0.40 (±0.05) μg/m^3, 0.52 (±0.05) μg/m^3, 0.030 (±0.005) μg/m^3. The average fraction of WSOC in OC (WSOC/OC ratio), considering all stages, is 0.51 (±0.12). This value is in agreement with the very board range (from 0.1 to 0.8) found in previous studies due to the high variability related to season, location, time-of-day, and particle size (Agarwal et al., 2010; Duarte and Duarte, 2007; Merico et al., 2020). Looking at the different cumulative size ranges, the ratios were 0.64 (±0.17) for the coarse fraction; 0.38 (±0.06) for the fine fraction; 0.36 (±0.08) for the ultrafine fraction. The large fraction of water soluble carbon in the coarse fraction could be due to a relevant contribution of marine aerosol that, in other sites, was observed to contribute significantly to WSOC in this size range (Timonen et al., 2008). Another explanation could be the contribution of primary biogenic OC sources that could contribute to coarse particles (Yttri et al., 2011; Barbaro et al., 2019).

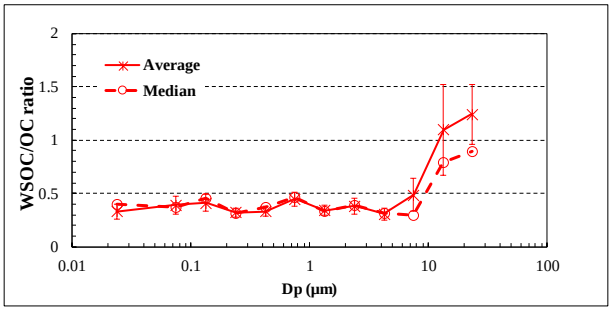


Figure 9. Average (solid line) and median (dashed line) ratios of WSOC/OC in size segregated particles for Rijeka samples. Error bars represent the standard errors.

Conclusions

A study of aerosol size-segregated samples in terms of PM and carbon content has been performed in two different port-cities of the Adriatic Sea: Venice (Italy), from August to November 2018, and in Rijeka (Croatia), in the periods October – December 2018 and March – May 2019, using similar set-up and following the same methodological approach.

411 The study evidenced some differences in Italian and Croatian PM size distributions, resulting
412 from different aerosol sources and/or atmospheric processes. In Venice, a PM bimodal distribution
413 has been observed, with peaks of concentration at diameters around 0.75 μm and 4.23 μm. No specific
414 temporal trends were observed in the sampling period. In average terms, the total PM during the
415 sampling period was distributed in 65% of particulate matter (in mass) for coarse mode, 33% for fine
416 mode, and 2% for ultrafine mode. In Rijeka, a PM three-mode size distribution was observed with
417 maxima at about 0.07 μm, 0.42 μm, and 4.23 μm. The total PM during the sampling period was
418 distributed in 59% of particulate matter (in mass) for coarse mode, a contribution of 34% for fine
419 fraction, and of 7% for ultrafine particles, with differences in the weight of the different size classes
420 observed between warm and cold periods.
421 An intense case of Saharan Dust outbreak (SDE) has been detected during the sampling
422 measurement in Rijeka; the relative PM size distribution was characterised by high content of coarse
423 particles (84%) compared to the average value. Maximum increases in concentrations were observed
424 for diameters around 2-3 μm. During SD the size distribution of OC detected in Rijeka showed the
425 same general shape with lower concentration in the fine fraction and a slightly higher concentration
426 in the coarse fraction (i.e. range 5.6-10 μm). This suggests that SD events could contribute to
427 secondary organic aerosol in the coarse fraction, likely due to the aging of dust travelling above the
428 Mediterranean Sea, favoured by the reactivity of dust particles surface. The EC size distribution was
429 not influenced in the fine mode but lower concentrations were associated to SD event for the coarse
430 mode suggesting that dust advection was not enriched in primary EC.

431 Size distribution of OC showed a bimodal trend at both sites, with the same coarse mode
432 peaking at around 4.23 μm and a submicron mode close to 0.75 μm, for Venice, and to 0.42 μm for
433 Rijeka. The EC size distribution of Venice shows a unimodal trend with increasing concentrations in
434 the finer particles indicating the presence of both fresh and aged aerosol. For Rijeka, the size
435 distribution of EC presents a different behaviour with a mode in the fine particles due to the emissions

of fresh EC particles, and a second mode observed for coarse particles, in the range 5.6-3.2 μm, likely due to resuspension of dust and a mixing of anthropogenic and marine aerosol.

The average ratios of EC/TC and the correlation between OC and EC for Venice and Rijeka samples suggested that different sources with different OC/EC ratio are acting on the area (road traffic, shipping, and biomass burning). The larger value of the EC/TC ratio in the coarse fraction observed in Rijeka compared to Venice could be a consequence of resuspension of dust and of mixing of anthropogenic particles with sea spray. The analysis of the ratio WSOC/OC as function of particle size in Rijeka showed a total values of 0.51 (±0.12) with an increase in the coarse fraction likely due to a contribution of water soluble carbon from sea spray and from biogenic emissions.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: