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Abstract

Detailed information on in-harbour shipping contribution to size segregated particles in coastal cities are scarce, especially in the busy Mediterranean basin. This poses issues for human exposure and air quality in urban harbour agglomerates, where only criteria pollutants (i.e. PM10 and/or PM2.5) are usually monitored. In this work, particle number and mass size distributions, in a large size range (0.01-31 μm), were obtained in two coastal cities of northern Adriatic Sea: Venice (Italy) and Rijeka (Croatia). Three size ranges were investigated: nanoparticles (diameter $D<0.25$ μm); fine particles ($0.25<D<1$ μm), and coarse particles ($D>1$ μm). Absolute concentrations were larger in Venice for all size ranges showing, using analysis of daily trends, a large influence of local meteorology and boundary-layer dynamics. Contribution of road transport was larger (in relative terms) in Rijeka compared to Venice. The highest contributions of shipping were in Venice, mainly because of the larger ship traffic. Maximum impact was on nanoparticles 7.4% (Venice) and 1.8% (Rijeka), the minimum was on fine range 1.9% (Venice) and <0.2% (Rijeka) and intermediate values were found in the coarse fraction 1.8% (Venice) and 0.5% (Rijeka). Contribution of shipping to mass concentration was not distinguishable from uncertainty in Rijeka (<0.2% for PM1, PM2.5, and PM10) and was about 2% in Venice. Relative contributions as function of particles size show remarkable similitudes: a maximum for nanoparticles, a quick decrease and a successive secondary maximum (2-3 times lower than the first) in the fine range. For larger diameters, the relative contributions reach a minimum at 1-1.5 μm and there is a successive increase in the coarse range.

Keywords particle size distributions; nanoparticles; shipping impacts; ship traffic; harbour pollution

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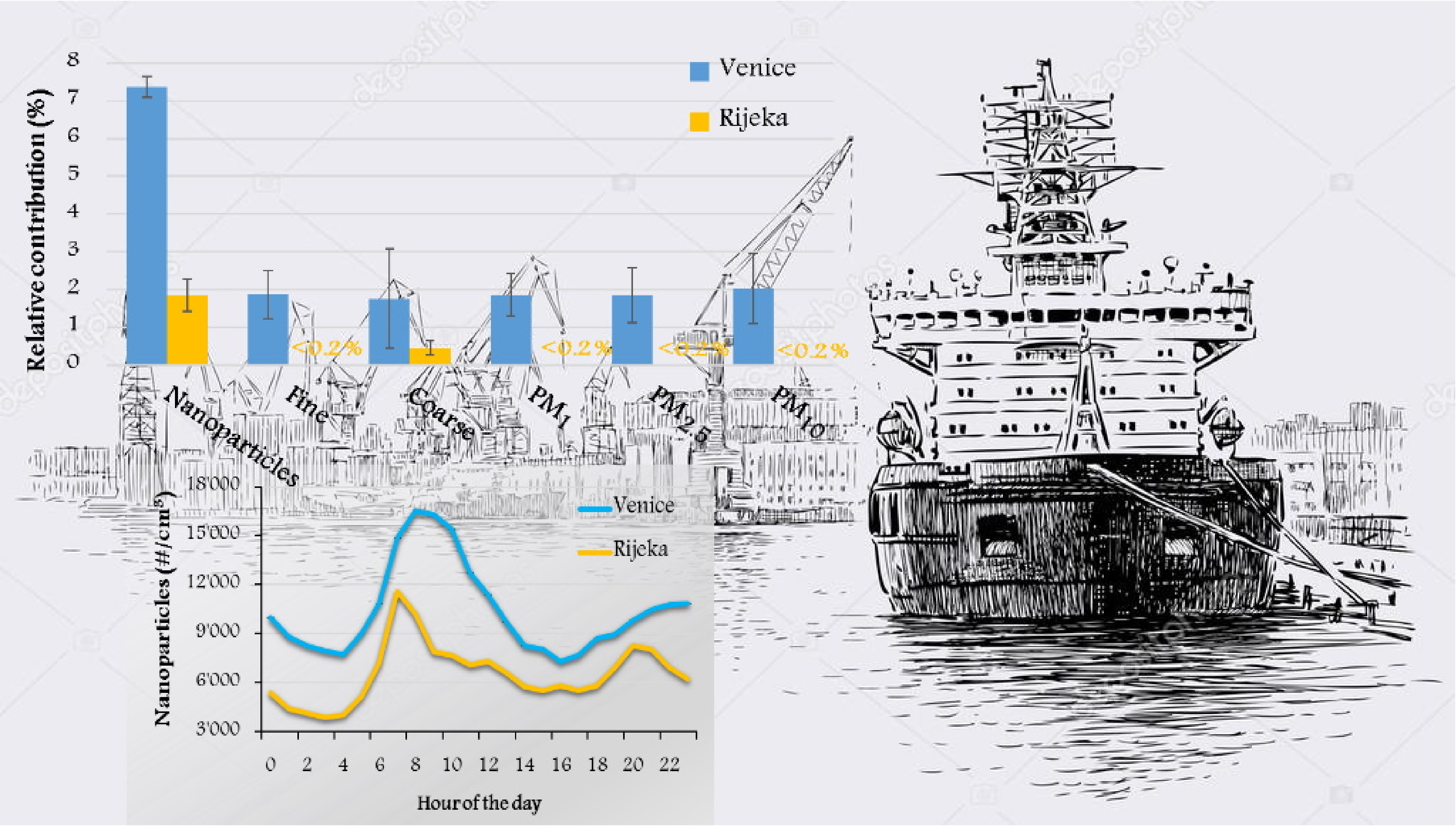
Highlights

- High temporal resolution aerosol data were collected in two Adriatic port cities
- Shipping contribution to particle concentration of different sizes was investigated
- Contributions to nanoparticles were significantly larger compared to other sizes
- Relative contributions to nanoparticles were 7.4% in Venice and 1.8% in Rijeka
- Contributions to PM_1, $PM_{2.5}$ and PM_{10} were about 2% in Venice and <0.2% in Rijeka


Relative contribution (%)
8
7
6
5
4
3
2
1
0
Venice
Rijeka
<0.2%
<0.2%
<0.2%
<0.2%
Nanoparticles
Fine
Coarse
PM_1
$PM_{2.5}$
PM_{10}
Nanoparticles (#/cm^3)
18'000
15'000
12'000
9'000
6'000
3'000
Venice
Rijeka
0
2
4
6
8
10
12
14
16
18
20
22
Hour of the day

Comparison of the impact of ships to size-segregated particle concentrations in two harbour cities of northern Adriatic Sea

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Abstract

Detailed information on in-harbour shipping contribution to size segregated particles in coastal cities are scarce, especially in the busy Mediterranean basin. This poses issues for human exposure and air quality in urban harbour agglomerates, where only criteria pollutants (i.e. PM_{10} and/or $PM_{2.5}$) are usually monitored. In this work, particle number and mass size distributions, in a large size range (0.01-31 μm), were obtained in two coastal cities of northern Adriatic Sea: Venice (Italy) and Rijeka (Croatia). Three size ranges were investigated: nanoparticles (diameter $D<0.25$ μm); fine particles ($0.25<D<1$ μm), and coarse particles ($D>1$ μm). Absolute concentrations were larger in Venice for all size ranges showing, using analysis of daily trends, a large influence of local meteorology and boundary-layer dynamics. Contribution of road transport was larger (in relative terms) in Rijeka compared to Venice. The highest contributions of shipping were in Venice, mainly because of the larger ship traffic. Maximum impact was on nanoparticles 7.4% (Venice) and 1.8% (Rijeka), the minimum was on fine range 1.9% (Venice) and <0.2% (Rijeka) and intermediate values were found in the coarse fraction 1.8% (Venice) and 0.5% (Rijeka). Contribution of shipping to mass concentration was not distinguishable from uncertainty in Rijeka (<0.2% for PM_1, $PM_{2.5}$, and PM_{10}) and was about 2% in Venice. Relative contributions as function of particles size show remarkable similitudes: a maximum for nanoparticles, a quick decrease and a successive secondary maximum (2-3 times lower than the first) in the fine range. For larger diameters, the relative contributions reach a minimum at 1-1.5 μm and there is a successive increase in the coarse range.

Size distributions showed a not negligible contribution of harbour emissions to nanoparticle and fine particle number concentrations, compared to $PM_{2.5}$ or PM_{10}, indicating them as a better metric to monitor shipping impacts compared to mass concentrations ($PM_{2.5}$ or PM_{10}).

Keywords: particle size distributions; nanoparticles; shipping impacts; ship traffic; harbour pollution

Highlights

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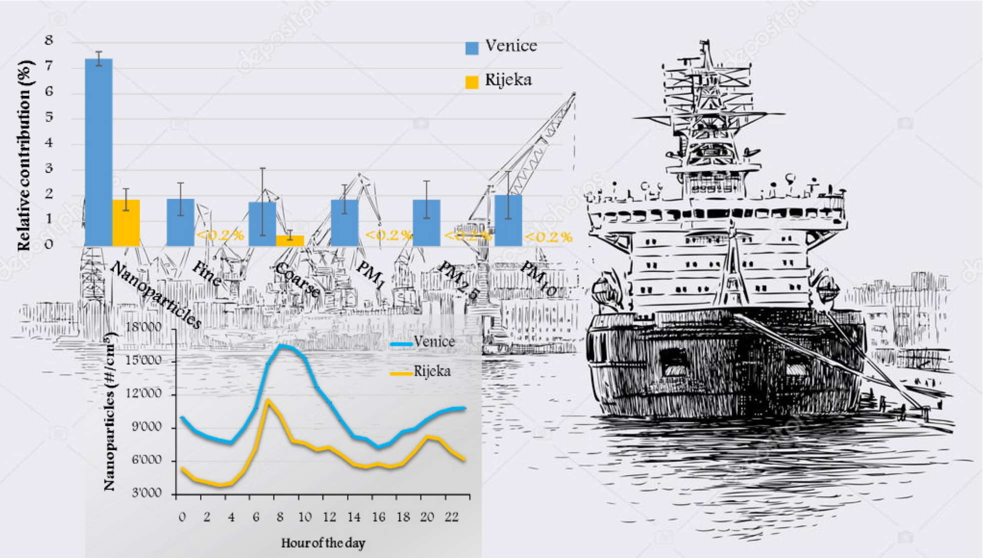
Graphical abstract



1. Introduction

International maritime trade is expected to expand at an average annual growth rate of 3.5% over the 2019–2024 period (driven by containers, dry bulk and gas cargoes), faster than other transportation modes whose emissions are decreasing because of stricter regulations (UNCTAD, 2019). At the same time, the scientific community and policy makers, especially in harbour areas, should address environmental pressures and potential health effects of shipping.

In Europe shipping emissions represent 16%, 11%, and 5% of total anthropogenic NO_X, SO_X, and PM_{10} emissions, respectively, with a certain variability associated to the emission databases used (Russo et al., 2018). Although local (in harbour) emissions represent a small share compared to those at global scale (Sorte et al., 2019), shipping emissions (mainly PM, NO_X and SO_X) can have important effects on air quality and on exposure of coastal communities (Ramacher et al., 2019; Viana et al., 2020). Hotelling phase, when auxiliary engines are used, is usually the largest contributor to local emissions of PM and NO_X, considering that this phase lasts generally more than manoeuvring phase (Jahangiri et al., 2018; Merico et al., 2016; Nunes et al., 2017). Local SO_2 emissions from shipping are generally larger than those due to other transport sectors, because of the different standards of the sulphur content in fuels (Merico et al., 2017).

However, since 01/01/2020 it has been enforced the new IMO regulation that sets the maximum sulphur content of fuels used in ships to 0.5% (IMO, 2019), that will lead to a reduction not only of SOx emission but also of PM (Contini et al., 2015; Liu et al., 2018; Merico et al., 2017; Tao et al., 2013). Environmental and health benefits are expected (Lack et al., 2011; Rouïl et al., 2019; Sofiev et al., 2018; Viana et al., 2020; Winebrake et al., 2009). Globally, projections indicate an expected reduction of ship-related premature mortality and morbidity by 34% and 54%, respectively, compared to 2020 scenario without mitigation actions (Sofiev et al., 2018).

Different approaches have been developed worldwide to assess shipping contributions to atmospheric pollutants. Source-oriented modelling consisting in transport and dispersion simulations on the basis of shipping emissions have been used at both large (global, continental and/or regional) (Chen et al., 2017; Feng et al., 2019; Jeong et al., 2017; Lang et al., 2017; Monteiro et al., 2018; Murena et al., 2018; Tao et al., 2017) and local scale (Merico et al., 2019). Receptor-oriented approaches have been also widely used, based on high temporal resolution measurements correlated with wind conditions and ship traffic (Contini et al., 2011; Ledoux et al., 2018) or on chemical composition of PM looking for oil combustion tracer (Cesari et al., 2014; Gregoris et al., 2016; Saraga et al., 2019; Scerri et al., 2018; Viana et al., 2009). Average contribution of shipping to $PM_{2.5}$ ranges between 0.2% and 14% in Europe, and similar percentages have also been observed for PM_{10} (Sorte et al, 2020; Saraga et al., 2019; Sarigiannis et al., 2017; Viana et al., 2014; 2020). In Europe, a clear gradient was observed, with larger contributions in the Mediterranean Sea sites compared to Northern Europe sites (Viana et al., 2014). This is likely due to several factors including intense shipping traffic and unfavourable dispersion conditions.

Most of the available studies investigate the impact of in-port shipping to criteria pollutants (i.e. $PM_{2.5}$ of PM_{10} for particles). In contrast, other studies regarding non-criteria pollutants like particle number concentration (PNC) or regarding impacts to particles of different sizes (including nanoparticles) are relatively scarce (Contini et al., 2015; Donateo et al., 2014; Gobbi et al., 2020; Ledoux et al., 2018; Merico et al., 2017). This is a gap on current knowledge because size and chemical characterisation of ship-emitted particles should be considered for their health and environmental implications (Gwinn and Vallyathan, 2006; Viana et al., 2020). In particular, UFP (ultrafine particles) can act as carriers for transition metals (i.e., vanadium) in the human body with possible adverse influence on respiratory diseases. The implementation of the new IMO regulation for use of low-sulphur content fuel, since 2020, is expected to reduce mortality and morbidity related to $PM_{2.5}$ shipping emissions (Sofiev et al., 2018). Available results (Merico et al., 2016) show that relative contribution on ultrafine particles (diameter <0.3 μm) could be up to 3-4 times larger than those to mass concentration (either $PM_{2.5}$ or PM_{10}). Few studies investigate size-segregated contribution of shipping to particles considering number size distributions (PNSD) or mass size distributions (PMSD). High temporal resolution measurements of ship plumes at the stack or inside harbour area, show a reduction of mass, but not number, of emitted particles in cleaner fuels (from HFO to distillate fuels), with the size distribution moving towards smaller particles (Anderson et al., 2015; Zetterdahl et al., 2017). Typically, ship emissions are characterised by a bimodal size distribution in number (PNSD) and in mass (PMSD). PNSD shows two modes at around 0.04-0.06 μm and 0.1-0.2 μm (Kivekäs et al., 2014; Pirjola et al., 2014), but also other modes in nucleation range (at about 0.01 μm) were also observed (Diesch et al., 2013). In terms of PMSD, the bimodal shape of distribution has a first mode in accumulation range (0.4-0.5 μm) and a second one in coarse range (> 1 μm), thus influencing differently the different PM fractions (Merico et al., 2016; 2017; Moldanová et al., 2013).

This work aims to contribute to fill the gap in knowledge on the impact of shipping traffic and related-harbour activities on particulate matter of different sizes (ranging from nanoparticles to PM_{10}), both in number and in mass concentrations. The sampling campaigns were performed in two Adriatic port-cities (Rijeka in Croatia and Venice in Italy) by using the same instrumental set-up, integrating high temporal resolution data of size distributions of particles with meteorological measurements and ship traffic information. Shipping contributions to particle concentrations as function of particle size were compared at the two sites and with the only results previously available in the Mediterranean basin (for the harbour town of Brindisi in Italy).

2. Methodological approach

2.1 Sampling sites

Sampling campaigns were carried out in two port cities of the Northern Adriatic Sea (Fig. S1): Venice (Italy), and Rijeka (Croatia). The sites are diametrically opposed, separated by the Istrian peninsula, in the northernmost region of the Mediterranean Sea, bounded by the Italian territory westward and the Balkans eastward. Here, intense surface (wind stress, heat and water fluxes) and lateral (river runoffs and open southern boundary transports) fluxes occur. The dominant winds are the Bora, a north-easterly cold, dry and gusty wind, mostly prevailing in winter, and the sirocco, a warm and humid wind blowing from the Southeast along the axis of the Adriatic basin. The Bora winds are strongly sheared due to the orography along the Croatian coasts while events of sirocco, together with other processes like low atmospheric pressure and high astronomical tides, cause flooding in the shallow lagoons (including the Venice Lagoon).

The two measurement sites are important logistic hubs for commercial (Rijeka) and tourist (Venice) sea traffic, being both core seaports included in the Mediterranean corridor of TEN-T network (https://ec.europa.eu/transport/themes/infrastructure/ten-t_en). The inclusion in the Baltic-Adriatic corridor is completed for Venice but underway for Rijeka. Both port authorities are strongly enhancing their efforts to upgrade and modernise their infrastructures and capabilities for intermodal connectivity of the ports within wider areas.

Rijeka is the third largest city in Croatia (128,624 inhabitants) and its seaport, located on the shore of the Kvarner Gulf at the bottom of the Rijeka bay, is the largest Croatian port. In numbers, a cargo throughput of 17.8 million tonnes in 2018 (liquid+dry+bulk+general cargo) and 260,375 containers (in TEUs) were recorded for year 2018; also, a cruisers' flow of 151,983 passengers (15.2% of the total passengers) and Ro/Ro and ferries of 128,882 were accounted (https://www.portauthority.hr/).

The city of Venice (Veneto Region) is located in the Venetian Lagoon, an extremely fragile ecosystem because of its environmental and cultural heritage capital. The area includes a highly populated urban territory (260,520 inhabitants, including Mestre and islands), the largest European coastal industrial settlement of Porto Marghera as well as agricultural and artisan activities. The port is organised in two operative areas with their own separated access, with commercial terminals and passenger piers at Porto Marghera zone and Marittima basin, respectively. The Venice Terminal Passenger (VTP) includes the Marittima station, located near the 4-km causeway that links the historic city with the mainland that hosts the largest cruise ships, and the San Basilio pier, just around the corner in the Giudecca Canal, which is devoted to local ferries and catamarans (https://www.port.venice.it/). Venice is designated as one of the best Mediterranean homeports with about 1.6 million of cruise passengers in 2018 (https://www.port.venice.it/). The tourist harbour at Marittima can hosts several cruise ships at 5 km of quayside of 10 multifunctional passenger terminals and recently it was re-newed for berthing mega yachts too.

2.2 Measurement campaigns and instruments used

Two different measurement campaigns were performed in Venice and Rijeka, with the same instrumental set-up (described thereinafter) and close to each harbour area (Fig 1a-c). The measurement periods were 06/09/2018-27/11/2018 and 28/03/2019-13/05/2019 for Venice and Rijeka, respectively.

The site chosen in Rijeka was on the roof of the Public Health building (45°19'56'' N, 14°25'33" E, 34 m a.s.l.) in front of the harbour entrance (approximately 500 m from the main sailing routes and at about 200 m from the closest quay, in a straight line, handling bulk cargo, approximately 1 km from the passenger area, and at 2.5-3.0 km from the new container area). It was a background urban site, separated from the port commercial area with an intense cranes activity, by a busy seaside street (named Kresimirova).

In Venice, the site was located on the Sacca Fisola island (45°25'42'' N, 12°18'46'' E, 3 m a.s.l.), in front of the Stazione Marittima tourist harbour and beside a fixed environmental monitoring station of the Protection and Prevention Agency of Veneto region (ARPAV). It faces the Giudecca channel that includes the main ship routes, being at about 500 m from the location of ships at berths.

The equipment was set inside an outdoor two-modular air-conditioned cabinet, as shown in Fig. S1. High-temporal resolution data were taken to collect real-time measurements of main meteorological parameters and concentration of particles of different sizes ranging from 0.01 to 31 μm using instruments remotely-controlled via PC. Specifically the setup included:

- an ultrasonic anemometer (Gill R3 at 100 Hz) coupled with a thermo-hygrometer (Rotronic MP100A, Campbell Scientific) placed on the roof of the cabinet (about 3m above the ground), measuring wind velocity, wind direction, temperature, and relative humidity at 1-min resolution;

- A CPC (Grimm 5.403) able to measure the total number of sub-micrometric particles, with 1-min resolution. Aerosol was sampled through a 70 cm-long sampling inlet and a portion of the main flow was injected into the CPC through a 50 cm-long conductive silicon tube and a diffusion dryer (silica gel cartridges) to reduce water vapour concentration before the CPC (Merico et al., 2016). The total counting efficiency was evaluated as the product of the penetration factor and the counting efficiency of the CPC obtained from Heim et al. (2004). The cut-off diameter (50% efficiency) was 9 nm, thereby the system was measuring particles in the size range 0.009-1 µm (the latter is the upper limit of the CPC).
- An OPC (Grimm 11-A) able to measure particle number size distributions in the size range 0.25-31 µm in 31 size channels, operating at controlled flow of 1.2 L/min. It used the same inlet as the CPC and it operated with 1-min time resolution. The internal software was also able to reconstruct mass size distributions as well as PM_1, $PM_{2.5}$, and PM_{10} mass concentration.
- A video camera operating at two frames per minute, used to synchronise data of ship movements provided by the port authorities with concentrations and meteorological measurements.

The OPC and the CPC measured at the same height above the ground (approximately 3 m) and underwent periodic zero tests, on average once per week, during the campaigns.

2.3 Statistical approach for evaluation of the impact of shipping

Data of particle concentration, ship traffic (manoeuvring/hotelling) and wind direction were statistically processed on 30-min averages. The methodological approach used in this study for estimating primary ship contribution was originally introduced by Contini et al. (2011) for the Venice harbour, successively applied to the Brindisi harbour (Donateo et al., 2014; Merico et al., 2016) and to other sites (Gregoris et al., 2016; Ledoux et al., 2018; Wang et al., 2019). The contribution was estimated using the differences between measured concentrations in cases influenced and not influenced by emissions of ships, selecting wind direction favourable to measure ship plumes (measurement site downwind of the emissions).

In Venice, the site was downwind in the range 315° - 360° during hotelling and between 315° - 45° during manoeuvring of ships (Fig. S1b). Similarly, the wind direction intervals defined for Rijeka were 122.5° - 180° (for hotelling) and 122.5° - 247.5° (for manoeuvring) (Fig. S1c).

The relative contribution of in-port ship activities to average atmospheric concentration was estimated, for each size range, by the Eq. (1):

$$\varepsilon_C = \frac{(C_{DP} - C_{DSP})F_P}{C_D} = \frac{\Delta_C F_P}{C_D} \quad . \qquad \text{(Eq. 1)}$$

Where (C_{DP}-C_{DSP}) = Δ_C is the difference between average concentration in periods potentially influenced (C_{DP}) and not influenced (C_{DSP}) by ship when the site is downwind; C_D is the average concentration in the downwind sector; F_P is the fraction of cases (i.e. 30-min averages) influenced by ship.

Uncertainties have been evaluated looking at the variability of ε_C calculated in elaborations done with and without wind calm (velocities <0.2 m/s) and with small changes by ±10° in wind direction intervals definition. It should be said that this method could have other uncertainties due to some specific factors (Ausmeel et al., 2019; Wang et al., 2019): choices of wind directions; distance from the docks; choice of cases influenced and not by ship from traffic database; temporal resolution of measurements; non stationary meteorological conditions; collinearity with other surrounding sources present upwind of the measurement site in the same sector where ships are located.

3. Results and discussion

3.1 Meteorological conditions and ship traffic data

Local meteorology of each site should be carefully investigated due to its influence on measurements. As briefly described in Section 2.1, the climate in Northern Adriatic (and therefore at the site) is extremely influenced by the orography of Gorski Kotar and the Dinarides. In summer, there are north-western winds (etesians) in the open sea, and, at the same time, local daily periodic circulation is developed between the larger islands and the coast, generating a sea breeze regime. In winter (and at night), local conditions are dominant. Dominant wind (especially in the coastal area of Istria) is Bora, reaching up to several tens of kilometers per hour, thus creating problems to road and maritime traffic (Poje, 1992). In Venice, the daily cycle of the wind direction is recognized within the general air circulation pattern of the Venice lagoon (Contini et al., 2011; Prodi et al., 2009). It can be described as having two prevalent wind directions: a nocturnal prevailing wind direction from N-NE and a diurnal one from S-SE.

The wind roses for the two measurements campaigns are shown in Fig. S2. During the sampling campaign in Rijeka, there was a dominant wind direction from ESE and a second wind direction sector from S to NE with slightly stronger winds from E-ENE. This indicated that the site was influenced mainly by Sirocco. Instead, for the Venice site, the wind rose showed a dominant direction from NE (mainly during night, coming from Alps mountains) and, a second direction from SE (from the Adriatic Sea) during daytime. This is the typical circulation of Venice lagoon, also observed in other measurement campaigns in the same area, especially in spring and summer seasons (Contini et al., 2015).

Furthermore, starting from high-temporal resolution hourly averaged data, daily patterns of temperature and relative humidity were obtained for both sites (Fig. S2). Both variables were lower, on average, in Rijeka compared to Venice, as a consequence of the different measurement periods as well as of local circulation conditions. Average temperatures of about 15° and 17°C were measured in Rijeka and Venice, respectively. Relative humidity was between 50% and 66% in Rijeka, instead, a higher value, about 80%, was observed in Venice with 70% reached only in diurnal hours between 10:00 and 17:00).

In the period between 24 and 26 April 2019 (during Rijeka campaign), an intense event of Saharan dust occurred on a large scale interesting also the measurement site. Back-trajectories of air masses calculated by Hysplit model (Fig. S3a) and the simulations of the Dust REgional Atmospheric Model (BSC-DREAM8b) (Fig. S3b) confirmed the phenomenon. The event lead to a significant increase in the number of coarse (D> 1 μm) particles, while a limited contribution on the concentration of sub-micrometric particles was observed (Fig. S3c). For this reason, corresponding data were excluded by the analysis of the ship contribution in order to avoid their influence on average concentrations.

As described in Section 2.3, measurements when the site was downwind (and during manoeuvring and/or hoteling phases) need to be selected. Ship traffic (arrivals/departures) in both harbours (using data provided by Rijeka and Venice Port Authority synchronised with concentration measurements) were used to evaluate the daily pattern. These are compared with the daily patterns of the percentage of time in which the site is downwind of the harbour areas at the two sites (Fig. 1). In total, 92 and 240 ships in Rijeka and Venice, respectively, were recorded during the entire sampling campaigns, with vessel traffic in Rijeka harbour of about 8.6% in gross tonnage (about 820,000 tons) of that in Venice (around 9,500,000 tons). Both at arrival and departure, gross tonnage and number of vessels showed a gradual decrease (25-30%) of the total number going from September to October in Venice, however, a rapid reduction was present in November (about 70%) both in gross tonnage and number, due to the end of the cruise period in the area. Contrarily, in Rijeka, many smaller ships (i.e. ferries) were recorded since mid-April compared to the first days of the same month and in May (46% less than April but with larger ships such as cargoes and bulk carrier).

A clear daily trend is present for Venice with arrival of ships mainly concentrated in the first hours of the morning (6:00-8:00) and ship departure in the afternoon (16:00-18:00). In this case, considering that the percentage of downwind cases was significantly larger (>70%) during the night and the morning (time interval 2:00-10:00) and decreased by half (down to <30%) during afternoon, it is reasonable that ship arrival will give the most relevant contribution at the site studied (Fig. 1a). This is also found in previous works (Contini et al., 2015) 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 Stazione Marittima of Venice). For Rijeka, a clear daily trend of ship traffic was not observed (Fig. 1b), even if there is a greater traffic volume in the central hours of the day compared to the night. The site in Rijeka was potentially influenced (>60% of cases) by ships during the whole day (time interval 8:00-18:00) and this means by the majority of ship traffic (both in arrival and departure).

3.2 Particle mass and number concentrations

Combining the CPC data with measurements of the OPC allowed to obtain the average size distribution in number (Fig. 2a) and in mass (Fig. 2b) for both sites. Particles associated with high mass are those in the coarse fraction, usually associated to dust from breaks or road surfaces, bio-aerosol, sea spray; while high number concentration could be due to combustion emissions of ultrafine particles of soot, sulphates, primary organic aerosol (POA), and secondary organic aerosol (SOA). Looking at size distributions, three size ranges, likely influenced by different sources and processes, were identified and used for further post-processing: nanoparticles (or ultrafine particles D<0.25 μm); fine particles (0.25<D<1 μm); coarse particles (D>1 μm).

Average number concentrations in the different size ranges are reported in Table S1, showing lower concentrations in Rijeka compared to Venice: ranging from 47.5% of the concentration observed in Venice for fine particles up to about 77.6% for coarse particles. Nanoparticles in Rijeka are 64.4% of those observed in Venice. The number size distributions have very similar shape for Venice and Rijeka, with the highest value of about 10,000 #/cm^3 in the nanoparticles range, decreasing up to a few particles per cm^3 at diameters of 0.6 μm. Size distributions in mass are similar at the two sites showing a bimodal shape, even if concentrations in Venice are larger than those in Rijeka. The first mode is centred at diameters around 0.3-0.4 μm (at both sites) and it is likely influenced by combustion sources including shipping; instead the second mode is broad (size range 2-5 μm) in Venice and slightly narrow in Rijeka (2-3 μm), being influenced also by mechanical processes and natural sources like soil dust and sea spray (Fridell et al., 2008; Merico et al., 2016; Moldanová et al., 2013). It should be noted that local road vehicles could influence particle concentrations mainly in Rijeka, taking into account the location site near a traffic-loaded road and logistic activities in the harbour area (i.e. loading/unloading of ships). Instead, this influence is likely more limited in Venice, being the site located on an island directly facing the passenger terminal.

Average mass concentrations of PM_{10}, $PM_{2.5}$ and PM_1 measured at both sites were significantly different, more than 50% higher values were observed in Venice compared to Rijeka (Tab. 1). The same trend was found for accumulation particles that differ significantly at both sites with number particle concentration in Rijeka accounting for 48% compared to that in Venice. Instead, nanoparticles and coarse particles had a relative lower difference with 22% and 35% between the two locations (with larger values in Venice).

Daily patterns of number concentration of nanoparticles and larger particles (i.e. sum of fine and coarse fractions) at both sites were compared in Fig. 3. The daily trends at the two sites are quite different. Looking at nanoparticles, in Rijeka two evident peaks are visible associated to typical rush hours in the morning (up to about 12,000 #/cm^3) and in the evening (up to about 8000 #/cm^3), followed by a low decrease in the night. In Venice a much broader morning peak is observed between 7:00 and 10:00 up to about 17,000 #/cm^3, instead, in the evening it is not visible a peak, rather there is a slow increase likely related to the development of the shallow stable nocturnal boundary-layer. This slow increase, related to the boundary-layer dynamics, starting in late afternoon and continuing up to late night, was also observed for $PM_{2.5}$ concentrations in other sites of the Venice lagoon (Donateo et al., 2012). The decrease after 10:00 is related to the change of wind direction, that typically happens at that time (Fig. 1a), in which sea breeze starts to bring air masses from the SSE-SE direction cleaner compared to the nocturnal and early morning air masses coming from the NNW sector that travel above the urban area and the harbour of Venice.

Looking at particles with D>0.25 μm, larger concentrations are observed in Venice with a complete different daily trend compared to Rijeka. Concentrations in Rijeka exhibited a small peak in the morning between 7:00 and 9:00, likely influenced by emissions of specific urban sources (i.e. road traffic) being correlated with the analogous peak in nanoparticles. Furthermore, there is a second peak in the evening rush hours at around 20:00-21:00. In Venice, the trend is completely different, having a shape typical of urban background and rural sites (Dinoi et al., 2017) with a modulation due to the atmospheric stability and boundary-layer height. Specifically, it shows a decrease starting early in the morning (at about 5:00) reaching a minimum (about -28% lower than nocturnal values) in the early afternoon and a slow increase starting late in the afternoon and during the night.

Looking at mass concentrations, daily trends of PM_1 concentration have the same behaviour (almost superimposable) of particles with D > 0.25 µm at both sites. A completely different pattern was observed for PM_{10-1} (coarse mode). At both sites, larger concentrations are observed during the day. In Venice, two maxima are individuated: in the morning and the late afternoon, with concentration peaks of about 9 µg/m^3 and 7.5 µg/m^3, respectively. Instead, in Rijeka a broad increase in diurnal hours was evident, with a maximum value in the morning peaks of approximately 4 µg/m^3.

This analysis suggests that, at both sites, local meteorology has played a role in determining concentrations and its influence was more evident in the Venice site. Even if the observed concentrations are lower compared to Venice, it appears that road traffic has a large relative impact on the Rijeka site.

3.3 Primary contribution of shipping emissions to particles of different sizes

For Venice, in order to limit the influence of the boundary layer dynamics maintaining almost all ship traffic (as reported in Fig. 1a), the Eq. (1) was applied on a subset of data selecting only hours between 5:00 and 23:00. Instead, from Rijeka dataset, the period 24-26 April 2019 was removed, corresponding to the intense African dust advection event, as previously described (§3.1).

The absolute contributions of ship traffic, at the two sites, are reported in Table S2 for particles in the different size ranges, the relative contributions are reported in Fig. 4. In Venice, the contribution to nanoparticles was about 1000 #/cm^3, about eight times that observed for Rijeka (around 130 #/cm^3). Contributions to fine and coarse particles are obviously much smaller than that to nanoparticles and they are larger in Venice compared to Rijeka.

The relative contribution of shipping to nanoparticles was 7.4±0.3% in Venice and 1.8±0.4% in Rijeka and smaller contributions were found for number particle concentrations in the other two size ranges, between 1.7% and 2.0% in Venice and between 0.2% and 0.5% in Rijeka. The contribution of shipping to measured concentrations is larger in Venice for all size ranges, as consequence of the larger traffic of ships (section 3.1) and of the smaller distance of the site from the emissions (i.e. the harbour area). It is known that contribution of shipping emissions to air quality peaks near the harbour area and it quickly decreases with distance from the harbour (Merico et al., 2019). The general trend, in relative terms, is the same at both sites: larger contribution to nanoparticles, lower contribution to fine particles and a slight increase in the coarse range. Usual metrics for mass concentrations have comparable or only slightly variable contributions in both absolute and relative terms. This is because primary emissions from ships are due to exhaust plumes and are characterised by ultrafine particles as observed in several studies (Diesch et al. 2013; Kivekäs et al., 2014; Pirjola et al., 2014; Merico et al., 2016; Ledoux et al., 2018; Ausmeel et al., 2019). In some studies, relatively fresh ship exhaust particle size distributions revealed either unimodal or bimodal structures, however, a typical bimodal size distribution was observed with the two modes centred at around 40-60 nm and 100-200 nm (Kivekäs et al., 2014; Pirjola et al., 2014). In the harbour area of Calais it has been observed that when wind was blowing from the harbour the number of particles was ten times higher compared to background level, with the highest differences in the 30-67 nm and the 109-167 nm size ranges (Ledoux et al., 2018). A contribution of shipping in the nucleation range (at about 10 nm) was found at the banks of the Elbe in Northern Germany in Diesch et al. (2013).

In terms of mass concentrations, the absolute contributions to PM_1, $PM_{2.5}$, and PM_{10} were comparable and in the range 0.4-0.5 μg/m^3 in Venice. In Rijeka, these were not clearly distinguishable above the uncertainties. The relative contributions were about 2% in Venice, similar for the different size ranges, and <0.2% in Rijeka. Looking at Venice, it is interesting to observe that absolute contribution to PM_1 was essentially comparable with that to $PM_{2.5}$ and was about 80% of the contribution to PM_{10}. This is very similar to the results obtained in another port city (Brindisi) of the Adriatic Sea in which the contribution to PM_1 was about 80% of that to PM_{10} and the contribution of $PM_{2.5}$ was about 84% of that to PM_{10} (Merico et al., 2016). This happens because the vast majority of the exhaust emissions from ships are in the ultrafine range (Kasper et al., 2007). The results obtained here support the idea that particle number concentrations, in the nanoparticle or ultrafine size ranges could be a better metric, compared to PM_1, $PM_{2.5}$, or PM_{10}, to investigate the impact of shipping to local air quality as suggested also in other studies (Merico et al., 2016; Muntean et al., 2019; Gobbi et al., 2020).

3.4 Comparison with other studies

Relatively few works are focused on impact of shipping to nanoparticles and fine particles number concentrations, however, several studies were performed on the impacts to mass concentrations, mainly PM_1, $PM_{2.5}$, and PM_{10} (Viana et al., 2014; 2020; Merico et al., 2017; Sorte et al., 2020). In Europe, the contributions to $PM_{2.5}$ or PM_{10} ranges between 0.2% and 14% and there is a clear gradient with larger contribution in Mediterranean area compare to northern Europe. The contribution to total particle number concentrations (PNC) are expected to be 3-4 times larger than that to $PM_{2.5}$ (Merico et al., 2016). The values found here are essentially comparable with the previous observations in other Mediterranean cities.

Previous estimates for Venice (Contini et al., 2015, Gregoris et al., 2016) and Rijeka (Merico et al., 2017), done with similar methodological approaches but in different sites, could be compared with the results found here. In Rijeka (Merico et al., 2017), the contributions of shipping in the period 2013-2014 estimated for a site located at the harbour entrance were 0.5% (±0.2%) for $PM_{2.5}$ and 0.3% (±0.1%) for PM_{10}, with a decreasing trend moving from 2013 to 2014. These values are comparable with those observed in this work, however, information on contributions of shipping to nanoparticles or fine particles in number were not previously available. In Venice, the relative contributions of shipping to PM_{10} were found in the range between 1.9% and 2.5% at three different sites (Gregoris et al., 2016). Contributions of ships to total particle number concentrations (PNC) in the size range 0.005-3 μm and to $PM_{2.5}$ in Venice were estimated for the summer 2012 at the Sacca San Biagio site, located near that studied here (less than 200 m), in Contini et al. (2015). The comparison of absolute and relative contributions found in 2012 and 2018 is reported in Fig. 4. Looking at absolute contributions, that to $PM_{2.5}$ was very similar in the two years (approximately 0.4 $\mu g/m^3$), however, there was an increase of the contribution to PNC from 800 $\#/cm^3$ in 2012 to over 1000 $\#/cm^3$ in 2018. The relative contributions depends on the average concentrations observed that were larger in 2018 for both PNC and $PM_{2.5}$. This leads, when relative contributions are considered (Fig. 5), to comparable impacts to PNC, taking into account uncertainty, and lower relative contribution to $PM_{2.5}$.

Several measurements of the contributions of ships to atmospheric particle concentrations are available for the port city of Brindisi, located in South Italy facing the Adriatic Sea (Cesari et al., 2014; Donateo et al., 2014; Merico et al., 2016). These refer to two sites: one located inside the harbour area near the docks of ferries, and the other one located in the urban area at about 1.4 km from the harbour. Contributions to $PM_{2.5}$ ranged from 2.8% (urban area) to 7.8% (inside harbour area). Contributions to PNC, measured only inside the harbour area ranged between 23% and 26% in different years. In the year 2014, a characterisation of the size distributions of shipping impact was done for the Brindisi harbour area (Merico et al., 2016) using the same instruments and the same methodological approach used in this work. The size distributions of relative shipping contributions in Venice and Rijeka are compared with the results obtained in Brindisi in Fig. 6. Results obtained in the three harbour cities show different details but also remarkable similarities in the general shape. Relative contributions show a maximum for nanoparticles a quick decrease and a successive secondary maximum in the fine range. The secondary maximum is not distinguishable in Rijeka above the uncertainty, but it is present in Brindisi (in the range 0.3-0.45 μm) and in Venice (in the range 0.4-0.7 μm) being 2-3 times lower than the absolute maximum. For larger diameters, the relative contributions reach a minimum in the size range between 1 μm and 1.5 μm and successively, in the coarse size range, there is growth of the relative contribution for all sites.

4. Conclusions

This study represents an attempt to estimate the local impact of harbour activities on particulate matter concentration of different sizes, and, therefore, with different environmental and health issues. High temporal resolution measurements of size distribution and local meteorology were collected in two Adriatic coastal cities with the same instruments and processed with the same methodology. This allowed a direct comparison of results between sites and, in addition, with previous studies conducted with the same approach in other harbours of the Adriatic region.

Analysis of size distributions in number and mass allowed focus the results in three size ranges: nanoparticles (diameter D <0.25 μm); fine particles (0.25 μm <D <1 μm), and coarse particles (D >1 μm). Results show that absolute concentrations in number were larger in Venice (from 28% to 100% larger according to the size range) and the same happens for mass concentrations (PM_1, $PM_{2.5}$, and PM_{10}) that were approximately twice compared to Rijeka.

Daily trends of particles in the different size ranges showed significant differences when the two sites were compared. In Venice there was a larger influence of local meteorology and boundary-layer dynamics, and a clear influence of anthropogenic sources was observed mainly in the nanoparticle range. In Rijeka, the contribution of road transport was instead evident and larger (in relative terms) compared to Venice.

The contributions of shipping to measured particle concentrations were significantly larger in Venice compared to Rijeka as consequence mainly of the larger ship traffic and partly because of the largest distance of the measurement site from the docks. However, a similar trend for the different particle sizes was observed. The maximum impact was found on nanoparticles 7.4±0.3% in Venice and 1.8±0.4% in Rijeka, the minimum was observed in the fine range 1.9±0.6% (Venice) and <0.2% (Rijeka) and intermediate values were found for the coarse fraction 1.8±1.3% (Venice) and 0.5±0.2% (Rijeka). Contribution of shipping to mass concentration was not distinguishable from uncertainty in Rijeka (<0.2% for PM_1, $PM_{2.5}$, and PM_{10}) and was approximately 2% (±0.7%) in Venice. These values correspond to absolute contributions ranging from 0.4 $\mu g/m^3$ for PM_1 and $PM_{2.5}$ to 0.5 $\mu g/m^3$ for PM_{10}. It is interesting to observe that the absolute contribution to $PM_{2.5}$ is about 80% of that to PM_{10}. This suggests that primary shipping emissions are mainly composed by ultrafine particles and number concentrations, especially in the nanoparticles size range, that could be a better metric to investigate this source compared to air quality standards ($PM_{2.5}$ or PM_{10}).

Detailed analysis of the relative contribution as function of particle size was extended comparing results with those previously obtained in another harbour of the Adriatic Sea (Brindisi). Results obtained in the three harbour cities show different details but also remarkable similarities in the general shape. Relative contributions show a maximum for nanoparticles a quick decrease and a successive secondary maximum in the fine range. The secondary maximum is not distinguishable in Rijeka above the uncertainty but it is present in Brindisi (in the range 0.3-0.45 μm) and in Venice (in the range 0.4-0.7 μm) being 2-3 times lower than the absolute maximum. For larger diameters, the relative contributions reach a minimum in the size range between 1 μm and 1.5 μm and successively, in the coarse size range, there is growth of the relative contribution for all sites. In conclusion, this study points out the significant relevance of harbour activities for human exposure and local air quality mainly for nanoparticles that are more harmful for human health. This is of particulate interest for harbours of the Mediterranean basin where such studies are scarce and and increase of maritime traffic is expected in near future. Future efforts in sustainable harbour management should be focused on monitoring and reducing nanoparticles, not currently included in legislation, in order to achieve both climate and health benefits.

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Figure 1

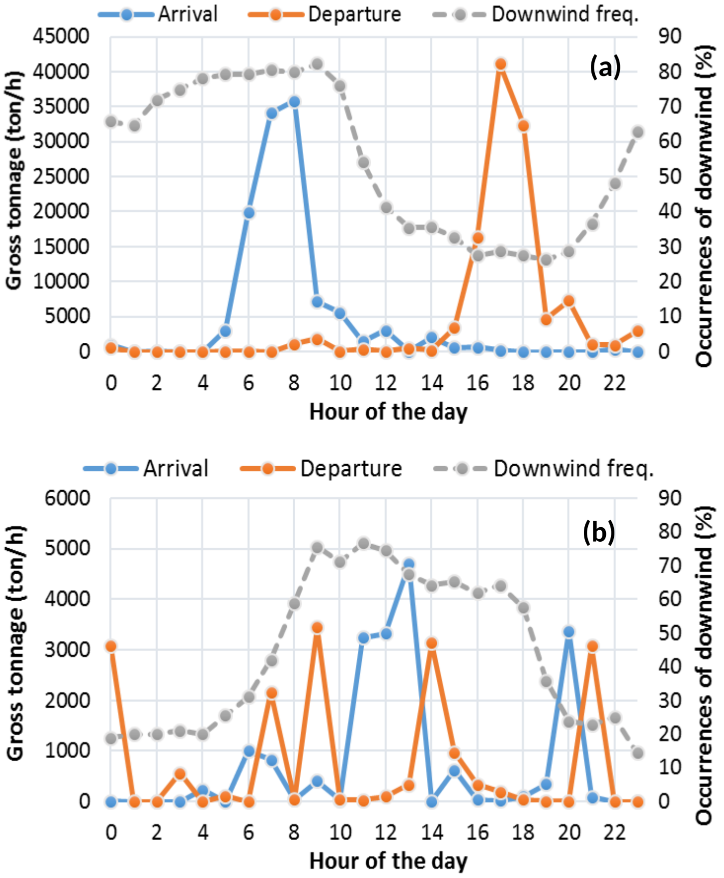

Figure 1) Daily trend of ship traffic (in terms of gross tonnage per hour) and of the percentage of time when the sites of Venice (a) and Rijeka (b) were downwind of ship emissions.

Figure 2

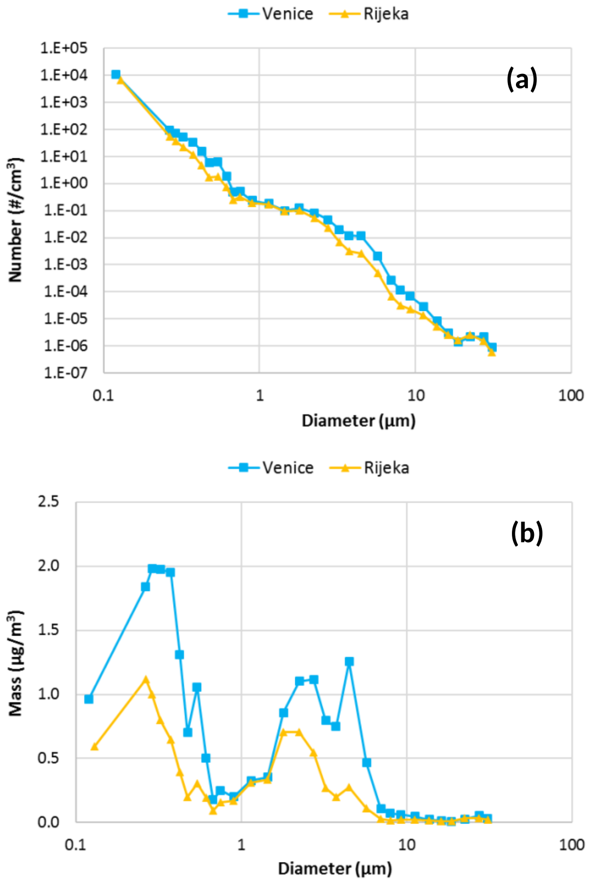

Figure 2) Average particle size distribution in number (a) and in mass (b) in the two sites.

Figure 3

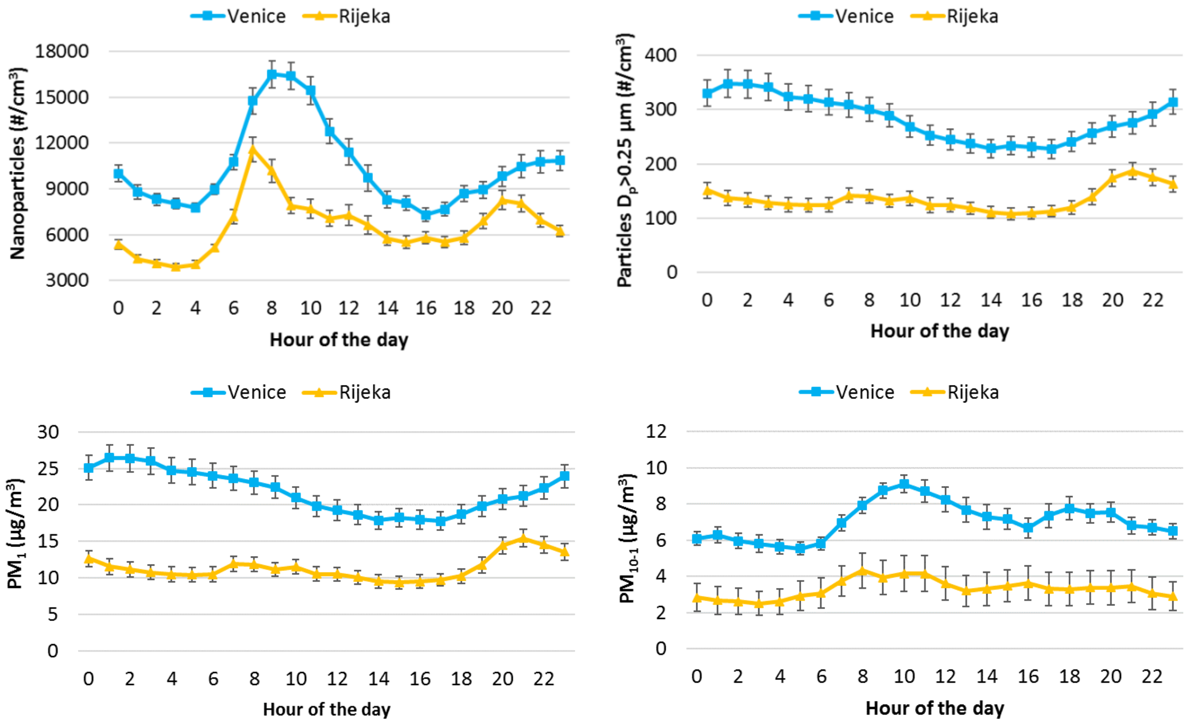

Figure 3) Average daily patterns of concentration in number (upper) and mass (lower) in Rijeka and Venice (with error standard indicated by the error bars).

Figure 4

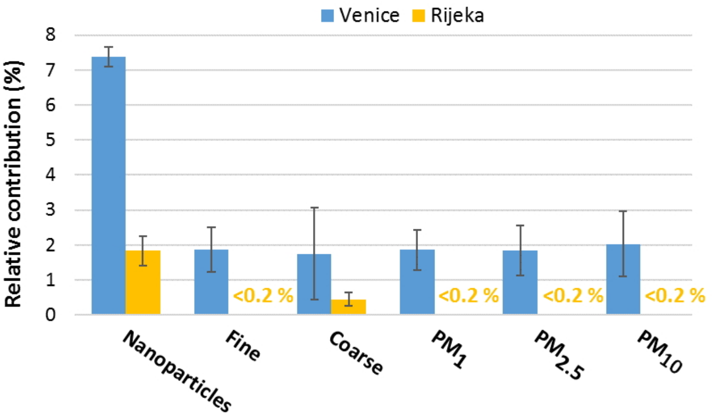

Figure 4) Relative contribution to particles concentration (in mass and number) in Rijeka and Venice for the different size ranges.

Figure 5

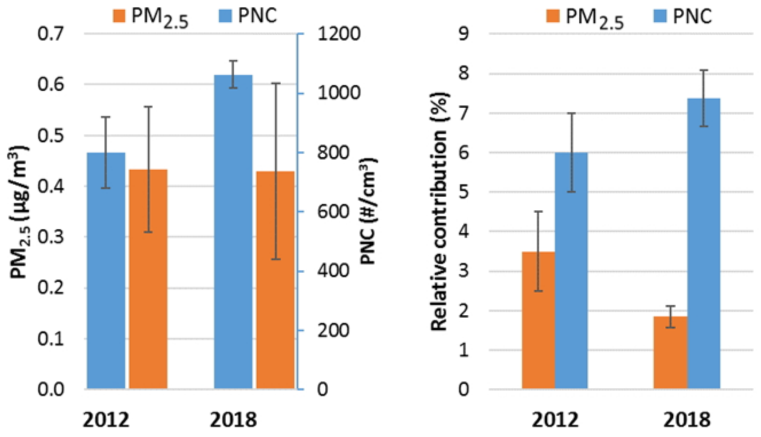

Figure 5) Comparison in terms of absolute (left) and relative (right) contributions of ships to PNC and PM$_{2.5}$ observed in Venice in 2012 and in 2018.

Figure 6

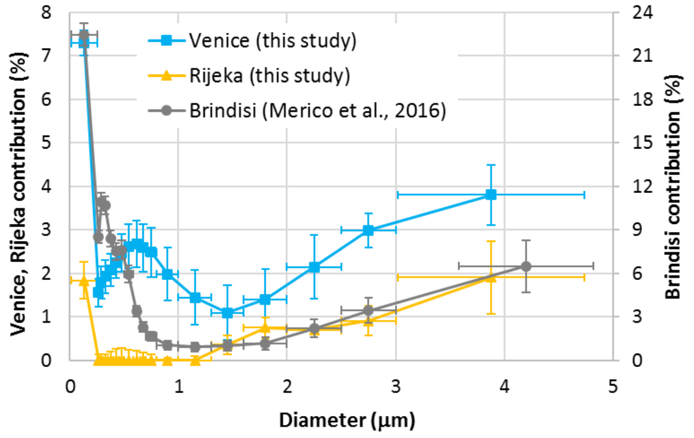

Figure 6) Comparison of relative contributions of shipping to atmospheric particle concentrations as function of size for three harbour towns of the Adriatic Sea. Vertical bars represent the errors and horizontal bars the size of the channel used in the evaluations.

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:

CRediT authorship contribution statement

E. Merico: conceptualization, formal analysis, investigation, data curation, writing – original draft, visualisation, writing – review & editing. **M. Conte**: investigation, data curation. **F.M. Grasso:** investigation, data curation. **D. Cesari**: investigation, data curation. **A. Gambaro**: conceptualization, funding acquisition, project administration, resources. **E. Morabito**: investigation, validation, visualization. **E. Gregoris:** investigation, validation, visualization. **S. Orlando**: Funding Acquisition, resources. **A. Alebić-Juretić**: conceptualization, funding acquisition, data curation, formal analysis, investigation, methodology, resources, supervision, validation, visualization, writing – original draft, writing – review & editing. **V. Zubak**: investigation, data curation. **B. Mifka**: investigation, data curation, validation. **D. Contini**: conceptualization, funding acquisition, data curation, formal analysis, investigation, methodology, resources, supervision, validation, visualization, writing – original draft, writing – review & editing

Comparison of the impact of ships to size-segregated particle concentrations in two harbour cities of northern Adriatic Sea

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Supporting information

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Figure S1

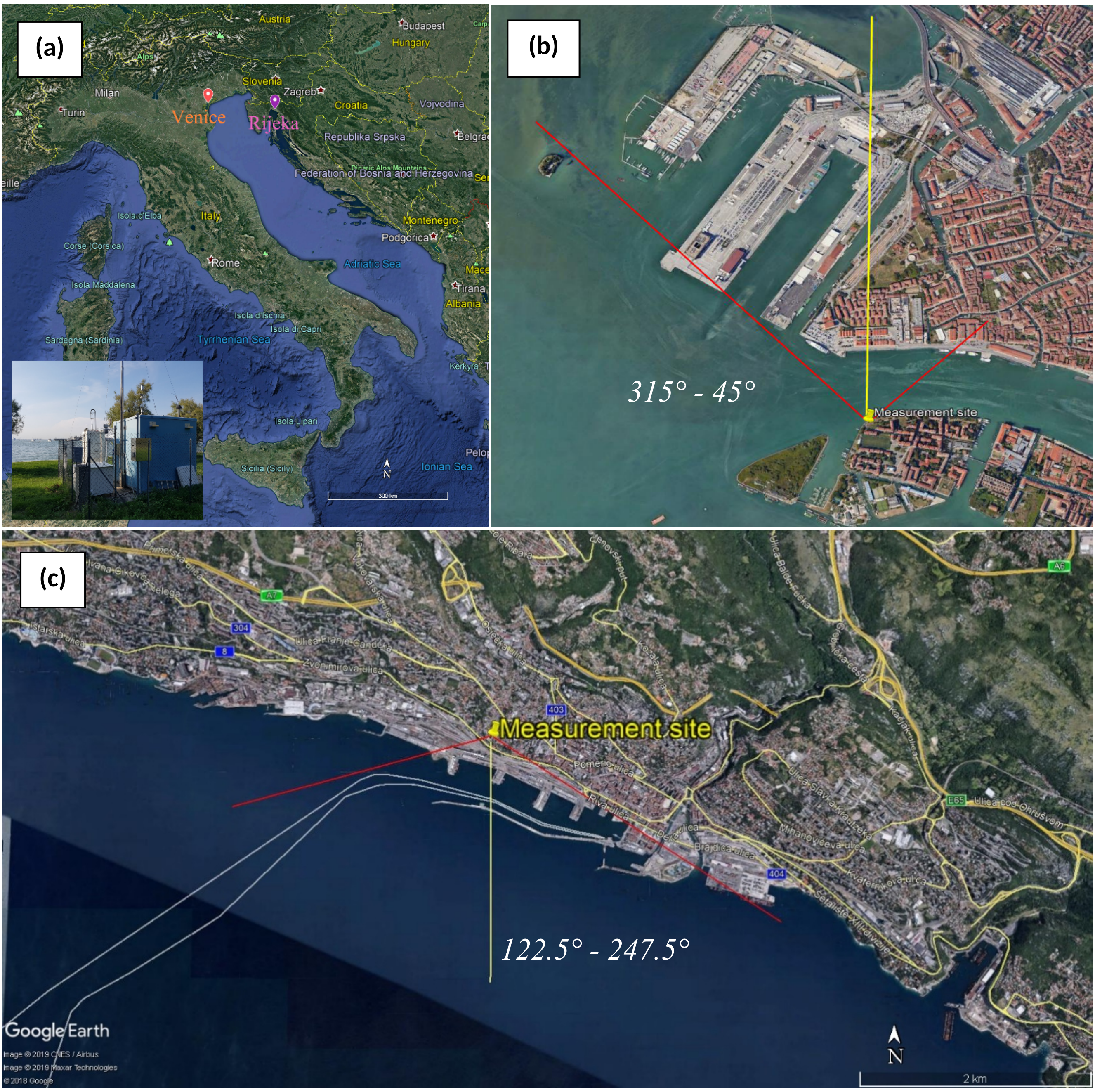

Figure S1) Measurement sites and setup used (a) with indication of the angles used to select data in post-processing in Venice (b) and Rijeka (c).

Figure S2

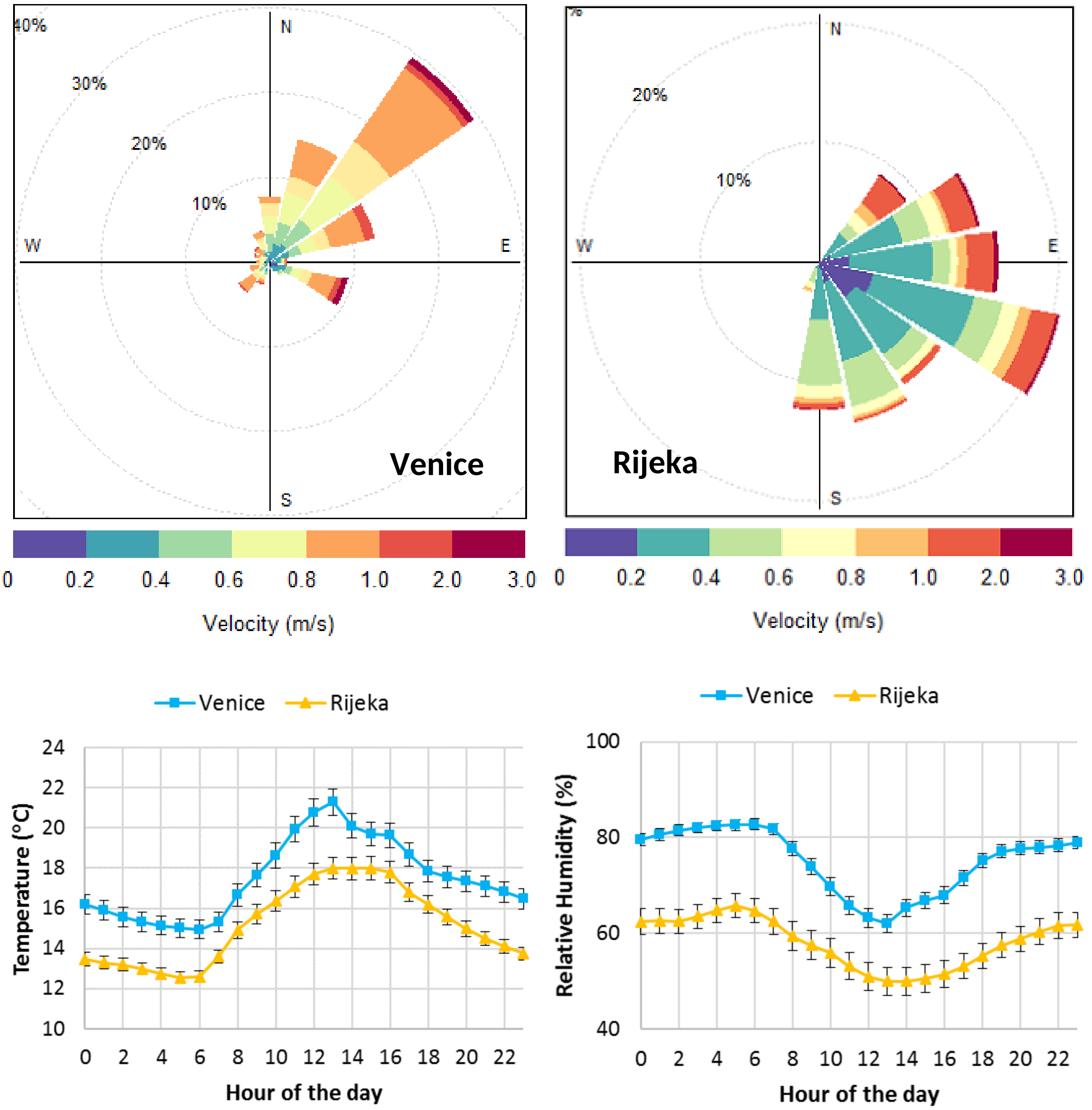

Figure S2) Wind roses for the two measurement campaigns (top) and average daily trends of the temperature and relative humidity (bottom) in Rijeka and Venice (with standard errors indicated by the error bars).

Figure S3

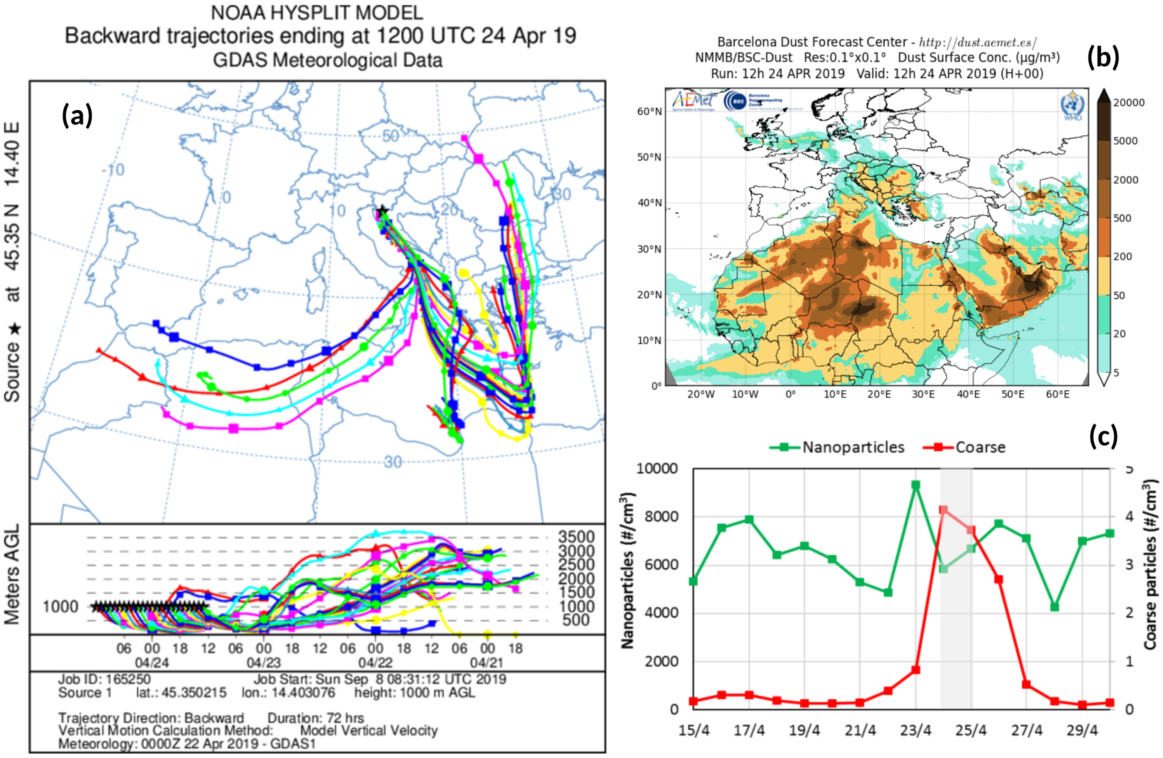

Figure S3) (a) Back-trajectories (http://arl.noaa.gov/ready/), (b) NMMB/BSC images (https://ess.bsc.es/bsc-dust-daily-forecast) and (c) daily number concentration of coarse particles and nanoparticles for the Saharan dust event recorded in Rijeka starting on 24/04/2019.

Table S1

Table S1. Average and standard deviation of particle concentration in mass and number at both sites (Rijeka – RJ, Venice – VE) and for the different size fractions. The last line is the average ratio between measurements in Rijeka and in Venice.

	Site	PM_1 (µg/m^3)	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)	Nanoparticles (#/cm^3)	Fine (#/cm^3)	Coarse (#/cm^3)
Average	RJ	11.4	13.4	14.8	6552	134.1	0.45
STD	RJ	6.9	8.8	10.4	3738	90.4	0.89
Average	VE	21.8	24.8	28.9	10166	282.0	0.58
STD	VE	13.6	14.1	15.2	6326	188.2	0.42
Ratio (%)	-	52.3	54.0	51.2	64.4	47.5	77.6

Table S2

Table S2. Average absolute contributions of shipping to particle concentrations in mass and number at both sites for the different size ranges. In parenthesis the uncertainties.

	PM_1 (µg/m^3)	$PM_{2.5}$ (µg/m^3)	PM_{10} (µg/m^3)	Nanoparticles (#/cm^3)	Fine (#/cm^3)	Coarse (10^{-3} #/cm^3)
Rijeka	< 0.03	< 0.03	< 0.03	130 (±30)	< 0.3	1.2 (0.5)
Venice	0.41 (0.18)	0.43 (0.17)	0.53 (0.35)	1063 (±50)	4.8 (1.8)	10 (7)