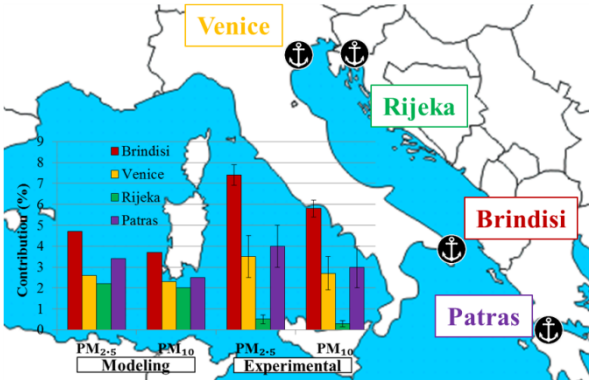
Graphical abstract



Atmospheric impact of ship traffic in four Adriatic-Ionian port-cities: comparison and harmonization of different approaches

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Abstract

Shipping is a growing transport sector representing a relevant share of atmospheric pollutant emissions at global scale. In the Mediterranean Sea, shipping affects air quality of coastal urban areas with potential hazardous effects on both human health and climate. The high number of different approaches for investigating this aspect limits the comparability of results. Furthermore, limited information regarding the inter-annual trends shipping impacts is available. In this work, an approach integrating emission inventory, numerical modelling (WRF-CAMx modelling system), and experimental measurements at high and low temporal resolution is used to investigate air quality shipping impact in the Adriatic/Ionian area focusing on four port-cities: Brindisi and Venice (Italy), Patras (Greece), and Rijeka (Croatia). Results showed shipping emissions of particulate matter (PM) and NOx comparable to road traffic emissions at all port-cities, with larger contributions to local SO_2 emissions. Contributions to $PM_{2.5}$ ranged between 0.5% (Rijeka) and 7.4% (Brindisi), those to PM_{10} were between 0.3% (Rijeka) and 5.8% (Brindisi). Contributions to particle number concentration (PNC) showed an impact 2-4 times larger with respect to that on mass concentrations. Shipping impact on gaseous pollutants are larger than those to PM. The contribution to total polycyclic aromatic hydrocarbon (PAHs) concentrations was 82% in Venice and 56% in Brindisi, with a different partition gas-particle because of different meteorological conditions. The inter-annual trends analysis showed the primary contribution to PM concentrations decreasing, due to the implementation of the European legislation on the use of low-sulphur content fuels. This effect was not present on other pollutants like PAHs.

Keyword: shipping, particulate matter, receptor models, emission inventory, WRF-CAMx

1. INTRODUCTION

Maritime transport handles over 80% of the volume of global trade (UNCTAD, 2015). Although shipping represents a growing asset within the transport sector, it was difficult, prior to 2008, to quantify its global emissions because these were one of the least regulated anthropogenic sources of atmospheric pollution (IMO, 2008). Due to methodological difficulties in allocating emissions to countries, international shipping was also not regulated by the Kyoto Protocol. Great efforts have been made in Europe to reduce other types of land-based emission sources (industrial, power generation, road traffic), and this resulted, for some pollutants, in an increase of the relative weight of shipping emissions with respect to total anthropogenic emissions (Viana et al., 2014). Recent analysis of global GHG emissions (expressed on a CO_2 basis) of international shipping showed a decrease in relative terms from 2.8% in 2007 to 2.2% in 2012 (Smith et al., 2014). In the Marine Strategy Framework Directive 2008/56/EC of the European Parliament, emissions from ships are mentioned explicitly in the list of pressures and impacts that should be reduced or minimized in order to maintain or to obtain a good ecological status (Blasco et al., 2014). Consequently, several research were dedicated to the analysis of green harbours (Davarzani et al., 2015).

Oceangoing ships were estimated to emit (prior to 2009) annually 1.2–1.6 Tg of particulate matter (PM), 4.7–6.5 Tg of sulphur oxides (SO_X as S), and 5–6.9 Tg of nitrogen oxides (NO_X as N) (Healy et al., 2009). More recent estimates (Smith et al., 2014) are 5.6 Tg of NO_X (as N) and 5.3 Tg of SO_X (as S). In the Mediterranean Sea shipping is responsible for 40 and 49% of the total European shipping emissions of CO_2 and SO_X, respectively (Jalkanen et al., 2016). Given its importance in both health effects and radiative forcing, research efforts have also been devoted to investigate black carbon (BC) emissions from shipping that represent about 2% of global BC emissions (Corbett et al., 2010; Lack and Corbett, 2012). Shipping typically contributes with 1-7% to the annual mean PM_{10} levels, with 1-20% to $PM_{2.5}$, and with 8-11% to PM_1, especially in coastal areas (Viana et al., 2014). Emissions within harbours are a relatively small fraction of global shipping emissions but they can have important effects on human health and climate in coastal areas and nearby towns. The estimate of their impact is also challenging because of the dependence of emissions from engine types and loads, fuels, and the different operating profiles of ships at berth, during manoeuvring and normal cruising. Size distribution of PM emissions is an important parameter, to investigate impacts of shipping, that has been thoroughly studied in several research works showing that shipping emissions in number are dominated by small particles (Kasper et al., 2007; Petzold et al., 2008; Kivekäs et al., 2014; Merico et al., 2016).

The assessment of impacts from shipping is a difficult task because these include environmental effects that occur on very different temporal and spatial scales. The climate effect of ship emissions is complex with opposite contributions: a short-term cooling and a long-term warming (Fuglestvedt et al., 2009). CO_2 and black carbon (BC) emissions from the shipping sector have a warming effect while NO_X increase the levels of greenhouse gases (GHG) and ozone (O_3), reducing methane (CH_4) levels. In summary, nowadays the net radiative forcing (RF) caused by the shipping sector is negative, about -0.4 W/m^2 in 2005 (Eyring et al., 2009). The reduction of SO_2 emissions tends to amplify the warming effect (Fuglestedt et al., 2009), however, it has

to be considered that this reduction could be accompanied with changes of emissions of other pollutants so that the global effect on climate is still unclear.

The environmental regulations expected to have the greatest impact on the future bunker fuel mix are the SO_X and NO_X limits set by the IMO (International Maritime Organization) with the MARPOL Annex VI, which will become more stringent in the future. According the current legislation (Fig. 1), ships trading in designated zones (Emission Control Areas-ECAs) from 1 January 2015 have to use on board fuel oil with sulphur content up to 0.1%, against the limit of 1% in effect until 31 December 2014. Outside the ECA, the current limit for sulphur content of fuel oil is 3.5%, reduced to 0.5% w/w after 1 January 2020. These requirements were adopted in October 2008 by consensus and entered into force in July 2010. The EU Directive 2005/33/EC on sulphur emissions from ships incorporates the IMO sulphur regulation, but requires in addition that from January 2010 onwards all ships at berth in harbours use fuels with sulphur content of less than 0.1% by weight. There are also effective national regulations or initiatives that aim to reduce SO_2 emissions from ships, such as voluntary agreements (Contini et al., 2015) at local scale in the Mediterranean Sea and in harbours along the California coastline (Tao et al., 2013). These measures are typically voluntary speed reduction programmes, cold ironing, and fuel policies (enforced before international legislation) that could produce a reduction of emissions (Zis et al., 2014). Negative biological effects of shipping emission on human lungs were observed for both HFO and cleaner diesel fuel (Oeder et al., 2015). However, recent studies showed that low-sulphur fuel could on the long run significantly reduce premature deaths associated to shipping (Winebrake et al., 2009; Viana et al., 2015; Broome et al., 2016).

Existing studies evaluating the impacts of shipping emissions on air quality in the studied region are based on different approaches including experimental observations, numerical modelling and emission inventory analysis (Gregoris et al., 2015; Dragovic et al., 2015; Maragkogianni & Papaefthimiou, 2015). It could be difficult to compare the results obtained with different approaches, furthermore, there is a lack of comparable data in the Adriatic/Ionian area as shown in a recent review (Viana et al., 2014). This work aims to inter-compare the impact of shipping on atmospheric pollution in four port-cities in the Adriatic/Ionian Sea (non-ECA) evaluated using homogeneous and comparable state-of-the-art methodologies that integrates analysis of the emission inventories, statistical treatment of experimental data, and numerical modelling using the WRF-CAMx modelling system. The port-cities studied are: Brindisi (Italy), Venice (Italy), Rijeka (Croatia) and Patras (Greece). A discussion of the inter-annual trends of primary impacts on PM concentrations is reported.

2. METHODOLOGY

2.1 Study areas and measurement sites

The four measurement areas, shown in Fig. 2, were located in Adriatic-Ionian port-cities: Brindisi (Italy), Venice (Italy), Rijeka (Croatia), and Patras (Greece). The four port-cities were chosen because they represent important maritime hubs of the Adriatic-Ionian region having both passenger (including cruises) and

commercial traffic. In addition, their locations cover the four corners of the region and they are subjected to different local meteorological conditions. The four harbours have a different vocation and consequently different volumes of ship traffic and different sources of pollution in their surroundings. In addition, local meteorology is significantly different in each port area. The Brindisi area is included in the list of SIN (National Sites of Interest) for relevant and dangerous pollution, according to the Italian legislation (D. M. 471/99), and it presents a complex mixture of anthropogenic emissions. The area includes the town of Brindisi (88,500 inhabitants), an international airport (located at 3 km NNE of the town), a large industrial area, and a harbour. The harbour, located east of the urban area, is divided in three zones: internal (2 km of docks dedicated to tourist activities); the intermediate and outer parts (dedicated to commercial ships). In total, the harbour has an annual traffic of more than 9.5 Mt of goods, over 520,000 passengers and over 175,000 vehicles (source: Brindisi Port Authority). Data from two measurement sites were available for this area. The first site (40° 38′ 05.78″ N, 17° 57′ 10.00″ E) is located in an urban background at about 1.3 km from the harbour and about 1.4 km from the city centre. In this site daily $PM_{2.5}$ samples were collected during summer 2012 (from June to October) and analysed chemically in order to determine the main water soluble ions and carbonaceous species and metals. Details are provided in Cesari et al. (2014). The site was also equipped with two high-volume samplers, one of them with a wind selective capability, to determine the impact of harbour/industrial activities on gaseous and particulate phase concentrations of polycyclic aromatic hydrocarbons (PAHs). The second measurement site was a mobile laboratory installed inside the harbour area (40° 38′ 43.32″ N, 17° 57′ 36.39″ E) facing the sea and the docks. The mobile laboratory performed high temporal (1 minute) resolution measurements of $PM_{2.5}$, using a real-time optical detector (pDR-1200, Personal Data logging Real time Aerosol Monitor by Thermo Electron Corp), particle number concentrations (PNC, size range 0.009-1 μm) using a condensation particle counter (Grimm CPC5.403), and local micrometeorology using a Gill R3 ultrasonic anemometer. Measurements were available for the summers of 2012 and 2014; details are provided in Donateo et al. (2014).

Patras is a medium sized city-port surrounded by rural areas, i.e. agricultural and mountainous (mostly to the west and southwest). Road traffic, shipping, central heating and industrial activities emit significant amounts of gaseous and particulate matter pollutants in the urban atmosphere resulting in air quality issues (Karagiannidis et al., 2015; Markakis et al. 2010a; 2010b). The Patras harbour covers almost all the coastal zone of the city and it has three main areas: Area #1 (a marina for yachts and boats under 15 m length); Area #2 is the north (old) port (where some cargo vessels moor and also used for long term mooring of cargo ships); Area #3 is the south (new) port used by the ferries. In Patras, the measuring platform was the mobile laboratory "Mobilab" (Zarvalis et al., 2008) in the new port area (38° 13' 33" N, 21° 43' 14.5" E). This was equipped with a real-time dust monitor, based on light-scattering measurement principle, able to measure simultaneously PM_1, $PM_{2.5}$, and PM_{10} (TSI, DustTrak DRX 8533) and a Condensation Particle Counter (TSI, model 3776). Measurements were performed in the new port of Patras in the framework of two 8-day measuring campaigns in Patras performed during the periods from 25/8/2013 to 1/9/2013 and from 19/1/2014 to 26/1/2014 (4-day measurements in the new port of Patras in the summer 2013 and winter 2014 campaigns).

Rijeka has the biggest, mostly trade oriented Croatian port, located at the bottom of the Rijeka bay and it is the third populated city in the Republic of Croatia (130,000 inhabitants, with neighbouring agglomeration of more than 200,000 inhabitants). During the sixties and the seventies of the past century, the area was heavily industrialised (new petroleum refinery, oil fuelled power plant and a coke plant), which resulted to increased anthropogenic air pollution in the eighties. The current cargo traffic in the port of Rijeka is of moderate intensity with approximately 8.6-9.0 Mt/year of cargo traffic for the years 2012-2014. In the same period, the harbour throughput is approximately 170-190,000 containers and 170,000 passengers per year in 2012-2013, with a reduction to 155,000 in 2014, due to the elimination of some passenger lines (Source: Rijeka Port Authority). Data from two traffic stations in the port proximity were included in the study. For the 2012 measurements, samples were taken at the first floor of the Education and Teacher Training Agency Department Rijeka (45° 19' 57'' N, 14° 26' 01" E, 6 m a.s.l.). This site is opposite to the harbour area and divided from the harbour by a busy street (Trpimirova Str.). Since 2013 the sampling site was based at the port entrance (45° 19' 39" N, 14° 26' 12" E, 3 m a.s.l.). Daily $PM_{2.5}$ samples were collected and chemically analysed by Particle Induced X- ray Emission (PIXE) and Laser Integrated Plate Method (LIPM). Details are provided by Ivošević et al. (2014; 2015).

The Venice harbour is in a lagoon located in a highly populated area and subjected to pollution deriving from agricultural drainage, from industrial inputs (Porto Marghera district), from urban activities (traffic and domestic heating) of the cities of Mestre and Venice (Contini et al., 2012), and from the airport. The harbour of Venice can simultaneously host numerous ships of different types and sizes with 30 km of quayside, 163 active berths, 7 commercial terminals and 19 privately-owned terminals, 8 passenger terminals (source: Venice Port Authority). Like in other Mediterranean cities, the tourist harbour (passenger ships dock at the Stazione Marittima) is located near the urban area; instead the commercial harbour is located in the industrial area of Porto Marghera at 6 km WNW from the town. The measurement site was located in the Sacca San Biagio island (45° 25' 38.50" N, 12° 18' 33.86" E), at about 1 km S of the harbour passenger terminal, at the end of the Giudecca channel, the deep water passage for passenger ships moving to and from the Venice cruise ship terminal. Measurements were taken in summer 2007, 2009 and 2012. $PM_{2.5}$ concentrations at high temporal resolution were measured using an optical detector pDR-1200 and a Gill R3 ultrasonic anemometer. During the 2012 campaign a Condensation Particle Counter (TSI, 3775 model) was used to measure (1 min resolution) the total particle number concentrations (size range 0.005-3 μm). The site was also equipped with a $PM_{2.5}$ SkyPost PMHV low-volume automatic sequential sampler (TCR Tecora) for collection of daily samples and with two high-volume samplers, one of them with a wind selective capability, to determine the impact of harbour/industrial activities on gaseous and particulate phase concentrations of PAHs.

2.2 Experimental and modelling approaches

This section describes the approaches used for evaluation of ship emissions and for evaluating shipping contributions to atmospheric pollution based on numerical dispersion modelling and measured concentrations.

2.2.1 Emission inventories

Emission inventories for the four areas under study were compared for the year 2010, emphasizing on shipping activities emissions (included in SNAP08 in the CORINAIR classification). Maritime emissions were calculated using the bottom-up approach of the European methodologies of EMEP/EEA (2013). Shipping activity data were obtained starting from the database of ship movements provided by the local Port Authority and this allowed evaluating hotelling and manoeuvring times as function of ship type. Fuel consumption factors were given as a function of gross tonnage for each ship category according to EEA (2006). Fuel consumption was given as a function of gross tonnage for each ship category according to EEA (2006) and manoeuvring phase was differentiated by hotelling on the base of fuel consumption (factor 40% for manoeuvring) and 20% for hotelling (32% for passenger ships). Following the EMEP/EEA methodology, ship emissions were estimated for different combinations of engine type (gas/steam turbines, high/medium/low speed diesel engines) and fuel type (Bunker Fuel Oil-BFO, Marine Diesel/Gas Oil-MDO/MGO). If no data about fuel and engine type were available, the statistical distribution of the World Fleet in 2010 was used (EMEP/EEA, 2013). If data for individual ships were not available, the proportion of slow speed to medium speed engines by gross tonnage for each ship category was used.

In all port-cities, estimated emissions of NO_X, NMVOC, SO_2, PM and CO were computed taking into account the hotelling and manoeuvring phases separately. Emissions of PM_{10} and $PM_{2.5}$ were assumed equal since ship emissions are essentially composed by fine particles.

Emission factors were taken from different publications (Entec 2007; Cooper and Gustafsson, 2004; Lloyd's Register, 1995; Cooper et al., 1996). Emission factors for SO_2 were calculated as EF = 20*S, where S was the percentage of sulphur by mass in the fuel, applying 0.1% value for hotelling phase and a different value in manoeuvring phase for passenger ships (1.5%) and all other ship typologies (3.5%). However, for Patras, in both hotelling and manoeuvring phases, a sulphur content of 0.1% by mass was used because, according to Greek legislation, all ships have to use a fuel sulphur content not exceeding 0.1% by mass before entering into the ports of Greece.

Uncertainties on emission factors are generally between 20% and 50% for the different pollutants (Cooper and Gustafsson, 2004). Other uncertainties are related to ship traffic details, engines typologies, and details of the fuels used. Considering that errors are random, some underestimations could be balanced by other overestimations so that a reasonable value of 30% could be assumed as uncertainty on estimated emissions (Broome et al., 2016; Merico et al., 2016).

2.2.2 Statistical treatment of experimental data

Chemical composition of $PM_{2.5}$, available for Brindisi, Venice and Rijeka, was analysed with the Positive Matrix Factorization (PMF) receptor model (EPA PMF3.0 code) for the individuation and characterisation of the main sources of $PM_{2.5}$. In all sites, a factor/source characterised by V and Ni was identified and this is a typical factor associated with heavy oil combustion, including shipping (Viana et al., 2009; Bove et al., 2014). However, the V/Ni ratio was variable in the different port-cities suggesting that this

factor/source could effectively represent a mixed contribution with industrial emissions that are present in the different study areas. Therefore, the contribution of ship emissions to primary $PM_{2.5}$ was extracted considering the V as a marker for the combustion in ships' engines as it was done in Zhao et al. (2013). The primary contribution PM_{ship} of ship emissions to the atmospheric $PM_{2.5}$ was calculated using the formula:

$$PM_{ship} = R * \frac{V_a}{F_{V,\ HFO}} \quad (1)$$

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

Statistical analysis of high temporal resolution data from Venice, Brindisi, and Patras, allowed detecting ship plumes like short and intense peaks in concentrations of atmospheric pollutants, because of the intermittent nature of ship emissions. Given the typical manoeuvring time and the possibility to have multiple peaks associated to a single ship (Contini et al., 2015), 30-minutes average concentrations (10 mins per Patras) of $PM_{2.5}$ and PNC were used for the evaluation of the impacts of shipping. The approach used, developed by Contini et al. (2011) for the harbour of Venice, is based on the integration and synchronization of data of wind direction, pollutant concentrations, and ship traffic (departures/arrivals and manoeuvring). The impact ε_C on the concentration C was estimated comparing the average concentration in cases influenced by ships to that in cases not influenced, when the measurement station was downwind of potential emissions, using the formula:

$$\varepsilon_C = \frac{(C_{DP} - C_{DSP})F_P}{C_D} = \frac{\Delta_P F_P}{C_D} \quad (2)$$

with C_{DP} average concentration in the sector of wind directions associated to the harbour in periods potentially influenced by ships; C_{DSP} average concentration not significantly influenced by ships; C_D average concentration in the wind direction sector associated with the harbour; and F_P fraction of cases influenced by ships. The uncertainties of the estimated contributions were calculated by examining the variability (maximum-minimum contributions) of the results obtained with slight changes (± 10°) in the wind direction sector definitions and also by eliminating data of wind calm (velocity < 0.5 m/s) or low winds (velocity < 1 m/s).

The impact of harbour on Polycyclic Aromatic Hydrocarbons (PAHs) concentration was obtained using a methodology based on the simultaneous use of two high-volume samplers, providing gas/particle phase partitioning of PAHs in Venice and Brindisi. One sampler was wind-selective and it was programmed to turn on when the wind was blowing from the sector of the harbour while the second one collected air samples continuously (all wind directions). In this way, it was possible to discriminate PAHs concentrations from the harbour sector with respect to the average concentration. The coefficient χ expressed the contribution of the

harbour sector to PAHs, independently of the wind strength and direction and normalized for the effective sampling time (Gregoris et al., 2015):

$$\chi(\%) = \frac{Q_{P,h}}{Q_{P,h} + Q_{A,h}} = \frac{Q_P h_P}{Q_P h_P + \frac{Q_{360} - Q_P}{h_{360} - h_P}} * 100 \quad (3)$$

with $Q_{A,\,h}$ hourly ΣPAHs amount, in aerosol coming from all directions, with the exception of the harbour sector; Q_P ΣPAHs quantity during sampling (48 h or 72 h), in aerosol coming from the harbour area; Q_{360} ΣPAHs quantity during sampling (48 h or 72 h), in aerosol coming from all direction; h_P sampling time (hours) of the wind-select sampler; h_{360} sampling time (hours) of the other sampler.

2.2.3 Numerical modelling

Numerical simulations were performed using the modelling system composed by the Weather Research and Forecast - Advanced Research Weather model (WRF) and the Comprehensive Air Quality Model with Extensions (CAM_X). The numerical model WRF (version 3.5.1) is a next-generation Numerical Weather Prediction modelling system. It develops initial and boundary conditions based on the re-analysis forecast of ECMWF with a 0.125° spatial resolution; model runs were performed with a 6 km spatial resolution. Parameterizations follow specific schemes as reported in Tab. 1. A detailed description of the model can be found in Skamarock et al. (2008). The Eulerian photochemical dispersion model CAM_X (version 5.3) simulates the emission, dispersion, chemical reactions and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of three-dimensional grid(s) (ENVIRON, 2010). CAMx was applied over a domain covering the Central and Eastern Mediterranean area with 367 x 227 grid cells of 6 km spatial resolution with 17 vertical layers in total extending up to about 10 km above ground level. The CAMx gaseous and PM chemical boundary conditions were derived from results of the IFS-MOZART global modeling system (Morcrette et al., 2009). Tab. 1 presents the CAMx parameterizations used for the simulation of the chemical processes in the atmosphere.

The anthropogenic emissions (CO, NO_X, SO_2, NH_3, NMVOCs, PM_{10} and $PM_{2.5}$) were extracted from the European scale anthropogenic emissions database prepared by The Netherlands Organization (TNO) for the reference year 2009 in the framework of the EU FP7 project Monitoring Atmospheric Composition and Climate Interim Implementation (MACC II) (Kuenen et al., 2014). Using the MOSESS anthropogenic emission model these data were spatially allocated (in 6 km resolution), temporally analysed (hourly values) and chemically speciated (Markakis et al., 2013). The Natural Emission MOdel (NEMO), developed by the Laboratory of Atmospheric Physics of the Department of Physics of the Aristotle University of Thessaloniki, was used in order to calculate spatially (6 km) and temporally (hourly) resolved, biogenic NMVOCs, sea salt and wind-blown dust emissions driven by the WRF meteorology (Liora et al., 2015; 2016; Poupkou et al., 2010). Anthropogenic source sectorial contribution to pollutant emissions over the simulation domain indicated that maritime sector represented the second source of NO_X and $PM_{2.5}$ in the area in the summer

period. Emissions of maritime traffic are maximum in the summertime and their contributions to the total of yearly anthropogenic emissions are about 2.6% for CO, 28% for NO_X, 16.5% for SO_X, 9.75% for PM_{10} and about 13% for finer particles ($PM_{2.5}$).

In order to estimate shipping contribution over the Central and Eastern Mediterranean pollutant concentrations (surface concentrations) were estimated using the WRF-CAM_X modelling system for a winter (January 2012) and a summer (July 2012) month. Model runs were performed for two different emission scenarios for each of these months. In the first scenario, all natural and anthropogenic emission sources were included, while in the second scenario the shipping pollutant emissions were excluded. This approach called "zero-out method" aimed to compute the concentration differences between the two scenarios, which were attributed to the impact of maritime activities on the air quality, expressed as relative contribution by δ:

$$\delta\ (\%) = \frac{Conc_{with} - Conc_{no}}{Conc_{with}} * 100 \qquad (4)$$

with $Conc_{with}$ and $Conc_{no}$ the averaged surface concentrations with and without shipping emissions respectively.

3. RESULTS AND DISCUSSION

3.1 Emission inventories results

In order to obtain a quantitative picture of shipping emissions at local scale, the analysis was conducted at Municipality level comparing relative emissions of maritime sector to total emissions. Clearly, this evaluation was site-dependent, i.e. it was dependent not only on shipping emissions but also on all sources of pollution present in the areas studied. Absolute values for the main pollutants NO_X, SO_2, and $PM_{2.5}$, with the indication of annual ship traffic associated to each harbour, are reported in Fig. 3. Maritime emissions in Venice were generally the highest ones, followed by Brindisi and Patras, which had comparable values. On the other hand, Rijeka had higher SO_2 emissions and lower $PM_{2.5}$ emissions with respect to the others sites. In order to analyse shipping estimates, the different profile of each harbour should be considered. In fact, Venice and Patras are two important cruise ports; Brindisi and Rijeka are essentially commercial harbours, characterised by traffic of cargo ships, containers, tankers, bulk carriers etc. This was confirmed by the fact that general cargo and container carriers were the greater emitters in Brindisi and Rijeka respectively, unlike passenger ships in Venice and Patras. The port-cities most affected by maritime sector activities were Venice and Patras for NO_X, SO_2 and CO. Venice had higher contribution percentages in especially regarding PM (PM_{10}, $PM_{2.5}$).

The comparison between annual shipping emissions and those of road traffic (over the same municipality domain) for NO_X, $PM_{2.5}$, PM_{10}, SO_2, CO, and NMVOC (Fig. 4) for each port-city highlights that the weight of shipping is a significant additional emission source in port-cities compared to road transport (in the area of Venice, road traffic includes also water traffic from public transport). Road traffic and maritime sector had comparable emissions especially for NO_X and $PM_{2.5}$ in all port-cities (Fig. 4), except a slight

countertrend for Rijeka (probably related to the context of local emissions). Obviously, shipping was the transport sector mainly responsible for SO_2 emissions.

3.2 Statistical analysis of experimental data

In Tab. 2 measured impacts on the four harbour areas for PM and particle number concentration (PNC) were summarized, indicating the specific methods used. PNC included sub-micrometric particles down to about 10 nm in diameter (i.e. including nanoparticles). Some relative contributions in Table 2 were calculated indirectly considering the same absolute contribution of shipping to $PM_{2.5}$ and PM_{10}. This assumption is often done in analysis of shipping impacts to PM concentrations (Viana et al., 2015) and it is justified because emissions of particles from shipping are mainly in the submicron size range and a recent study show that the uncertainty on contributions evaluated with this approach are between 10% and 15% (Merico et al., 2016). Typical ratios $PM_{2.5}/PM_{10}$ were equal to 0.78 (Venice and Brindisi) and 0.75 (Rijeka). Results showed that the contributions to $PM_{2.5}$ ranged from 0.5% to 7.4% and from 0.3% to 5.8% to PM_{10}. These values are in good agreement with the typical values reported in European harbours (Viana et al., 2014). The contribution to PNC is significantly larger (range 6%-26%) than those to mass concentrations (either $PM_{2.5}$ or PM_{10}). This is in agreement with measurements performed close to other harbours (Healy et al., 2009; Diesch et al., 2013) and confirms that ultrafine particles dominate the emissions of ships; therefore it is the concentration of ultrafine particles that would be a more suitable metric to investigate this type of pollution source.

The contributions to PAHs, evaluated using Eq. (3) in summer 2012 for Brindisi and Venice, are reported in Fig. 5. The contributions were evaluated separately for gas and particulate phase as well as for total (gas plus particulate) PAHs. In Venice harbour contribution to PAHs is larger with respect to Brindisi and it has a different partitioning between gas and particulate phase. In Venice the contribution to gaseous PAHs is larger than that to particulate PAHs; instead in Brindisi the two contributions are comparable taking also into account their uncertainties. This is likely a consequence of the different meteorological conditions in the two areas, which influence the gas-particulate equilibrium of PAHs.

3.3 Numerical modelling results

Numerical simulation results of the shipping contribution to the various atmospheric pollutants are shown in Fig. 6 (July 2012) and in Fig. 7 (January 2012) for the Central and Eastern Mediterranean domain. In summer period, NO_X and SO_2 were substantially affected by shipping emissions that gave a contribution up to 90% along the main international shipping routes (southern part of the simulation domain); a contribution over 70% (NO_X) and 60% (SO_2) was observed in the Adriatic and Ionian Seas decreasing along the coasts of the Adriatic/Ionian area to about 30% (NO_X) and 40% (SO_2). $PM_{2.5}$ and PM_{10} surface concentrations were impacted by more than 15% and 13% respectively over the main shipping routes and more than 5% and 3% respectively in the Adriatic-Ionian area. The contributions to $PM_{2.5}$ and PM_{10} decreased to less than 3% along the coasts of the Adriatic/Ionia area. In all the Adriatic-Ionian area it was observed, on average, a seasonality of shipping contributions to surface concentrations, with lower values in wintertime. SO_2 contribution had the

highest variability between the two seasonal periods. The contributions estimated in the cells of the simulation domain that better represent the measurement sites in the four port-cities were extracted and reported in Tab. 3 for the summer and winter periods. Numerical modelled contributions for $PM_{2.5}$ and PM_{10} were in reasonable agreement with the calculations obtained from measured data. Further, results show that the contributions to gaseous pollutants (NO, NO_2, and SO_2) exceeded those to $PM_{2.5}$ and PM_{10}. Brindisi presented the largest contributions for all pollutants, whereas Rijeka was the less impacted from shipping. In Venice the difference between gaseous and particulate pollutants was weaker with respect to the other sites and the shipping contribution to SO_2 was lower than those observed for Patras and Brindisi in both winter and summer periods. The contributions to $PM_{2.5}$ and PM_{10} were comparable in Brindisi between winter and summer but the seasonality was more accentuated for the other pollutants and for the other harbours.

3.4 Analysis of shipping impact trends

Experimental data from Venice, Brindisi and Rijeka were available for different years allowing the investigation of the trends of shipping contributions to $PM_{2.5}$, PM_{10}, and PNC under similar measurement conditions. Fig. 8a reports the trends in Venice; a decrease of the primary impact of shipping is observed despite that the gross tonnage of ship traffic increased by 47%. This effect is clear in the the 2007-2009 period, with a first decrease and also between 2009 and 2012, even if the reduction of contributions is smaller with respect to the previous step and comparable with experimental uncertainties. The decrease in contributions was due to the implementation (starting from 01/01/2010) of the 2005/33/EC Directive in the area and to mitigation strategies (Venice Blue Flag voluntary agreement). The two voluntary agreements (Venice Blue Flag, one in 2007 and the second in 2008) for the reduction of SO_2 emissions of passenger ships have been enforced to progressively reduce the sulphur content in fuel used by large cruise ships between 2007 and 2009 in Venice. The agreements foresaw the use of fuels with maximum S content of 2.5% (±0.5% in mass) for 2007 during manoeuvring and at berth; this limits were changed at 2% (±0.5%) for manoeuvring and 1.5% (±0.25%) at berth during 2008 and to 2% (manoeuvring) and 1.5% at berth during 2009 (Contini et al., 2015).

Experimental data in Brindisi were available for summer 2012 and summer 2014 at the same measurement site and taken with the same instruments in comparable meteorological conditions. The estimated contributions, reported in Fig. 8b, showed almost constant contributions to $PM_{2.5}$ and PM_{10} and a slightly decreased contribution to PNC, while the total ship traffic increased by 8% in the same period. It must be said that both measurement periods followed the implementation of the 2005/33/EC Directive.

The data available in Rijeka cover periods from 2012 to 2014. The trends of the shipping contribution to $PM_{2.5}$ and PM_{10} are reported in Fig. 8c. The ship traffic (2083, 2055 and 2133 ships, respectively) are practically constant during the studied period. However, a marked decrease was observed between 2012 and 2013. This could be in agreement with the implementation of the MARPOL International Convention for use of low-sulphur fuels in Croatia since July 2013, but also due to the fact that February 2012, when most of the sampling was performed, was colder than usual; higher metal content might also be result of accumulated

pollution under exceptionally unfavourable weather conditions. The comparison of 2013 and 2014 results showed a much more limited decrease, not significant when taking into account the experimental uncertainties.

Regarding contributions to PAHs, data in Venice were available for 2009 and 2012 and the estimated contributions are compared in Fig. 9 for gaseous, particulate phases and for total PAHs (gas plus particulate). Results show an almost constant contribution with no differences within the experimental uncertainty, indicating that the use of low-sulphur content likely does not have a relevant effect on PAHs emissions from shipping. The analysis in Gregoris et al. (2015) showed that this behaviour was also observed for shipping contribution to metals concentrations. These results suggest that the use of low-sulphur fuels produces a reduction of SO_2 and primary particulate emissions, but have limited or negligible effects on other pollutants like PAHs and metals.

4 CONCLUSIONS

The Adriatic-Ionian Sea hosts a dense network of shipping routes and harbours that provide freight and passenger maritime services of international, national and regional significance. Therefore, shipping emissions could impact on air quality in coastal populated areas.

This study was carried out to quantify and to characterise the impact of maritime transport sector on air quality in this region focusing on the impacts on four port-cities. The inter-comparison analysis of impacts on gaseous and particulate pollutants was conducted using an integrated approach based on emission inventory, numerical modelling and analysis of experimental data. The main results could be summarised as follows.

- Emissions inventories at local scale pointed out that in the four port-cities, maritime sector should be considered a significant source of pollutants, at same level of road traffic for PM and NO_X and more important than road traffic for SO_2.
- The two approaches used to statistically post-process available measured data, Eq. (1) and Eq. (2), gave consistent results, within the experimental uncertainty, when it was possible to compare them directly (Venice site). The relative impacts to particles concentrations, estimated with the numerical models (Table 3) are in good agreement with those obtained from experimental data in the four port-cities (Table 2).
- Impact on gaseous and particulate pollutants was variable, also depending on the specific vocation of harbours. In particular, impacts on $PM_{2.5}$ ranged between 0.5% (Rijeka) and 7.4% (Brindisi), those on PM_{10} were between 0.3% (Rijeka) and 5.8% (Brindisi). PNC contributed from 6% (Venice) to 23% (Brindisi), thereby an impact 2-4 times larger with respect to that on mass concentrations. This indicates that PNC, even if not included in the European air quality standards, could be a more suitable metric to investigate the impact of this specific source. Shipping impacted on gaseous pollutants (NO_X and SO_2) much more with respect to $PM_{2.5}$ or PM_{10}.
- The contribution to total PAHs concentrations (gas plus particulate) was 82% in Venice and 56% in Brindisi, with a different partition between gas and particles, likely consequence of the different meteorological conditions in the two areas.

- The available data allowed to analyse the inter-annual trends of the impacts on particulate matter concentrations and on PAHs in some of the sites. Impacts on PM concentration showed a decreasing trend in Venice and Rijeka even when ship traffic increased. This is likely due to the decrease of the primary contribution to particle mass concentrations due to the implementation of the European legislation on the use of low-sulphur content fuels. However, the effect was not present on other pollutants like PAHs concentrations. In Brindisi, measurements were taken after enforcement of European legislation and this decrease was not observed.

Further research should take into account that evaluation of the impact of maritime activities on local air quality should be addressed at transnational level using comparable approaches integrating modelling and experimental results to identify mitigation strategies that could be applied at large scale (i.e. Mediterranean scale or European Macro-region scale) without hindering economic competitiveness of the harbours involved. Further research is needed for broad investigations of shipping impacts on ultrafine particles, and, to investigate the effects of different fuels on the emissions of this particles. Additional studies are also needed to ascertain the role of mitigation strategies on shipping impact to specific pollutions like NOx, metals and PAHs and future actions could involve improvement of the international legislation or guidelines to curb emissions of these pollutants.

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TABLE 1

Tab. 1. Parametrization schemes applied in the WRF-CAM$_X$ modelling system.

Model	Data/process	Parametrization/source	Reference
WRF	Microphysics processes	New Thompson et al. scheme	Thompson et al., 2008
	Convention	Grell-Devenyi ensemble scheme	Grell and Devenyi, 2002
	Shortwave/longwave radiation	RRTMG shortwave/longwave scheme	Iacono et al., 2008
	Surface layer	Eta similarity scheme	Janjic, 2002
	Planetary boundary layer	Mellor-Yamada-Janjic scheme	Janjic, 1994
	Land surface processes	Noah Land Surface Model	Tewari et al., 2004
CAM$_X$	Gaseous and PM chemical boundary conditions	Results of the IFS-MOZART global modeling	Morcrette et al., 2009
	Gas-phase chemical mechanism	Carbon Bond 2015 version (CB05)	Yarwood et al., 2005
	Aerosol size distribution	Static two-mode coarse/fine scheme	-
	Aerosol aqueous inorganic chemistry	RADM-AQ aqueous chemistry algorithm	Chang et al., 1987
	Gas/aerosol phase partitioning of the inorganic aerosol constituents	ISORROPIA thermodynamic module	Nenes et al., 1998
	Secondary organic aerosol formation	SOAP scheme	Strader et al., 1999

TABLE 2

Tab. 2. Different approaches used in each site in order to estimate the harbour impact. (*) Indirect calculation obtained considering the same absolute contribution of shipping to $PM_{2.5}$ and PM_{10} and a ratio $PM_{2.5}/PM_{10}$ concentrations equal to 0.78 (Venice and Brindisi) and 0.75 (Rijeka).

Area	Site	Typology	Period	Method	$PM_{2.5}$ (%)	PM_{10} (%)	PNC (%)
Brindisi	ASI	Urban	Summer 2012	Eq. (1)	2.8 (±1.1)	2.1 (*) (±0.8)	-
	Terminal Passeggeri	Harbour	Summer 2012	Eq. (2)	7.4 (±0.5)	5.8 (*) (±0.4)	26 (±1)
Venice	Sacca San Biagio	Urban	Summer 2012	Eq. (1)	3.0 (*) (±1.0)	2.3 (±0.9)	-
				Eq. (2)	3.5 (±1.0)	2.7 (*) (±0.8)	6 (±1)
Patras	New port	Urban	Summer 2013 and winter 2014 campaigns	Eq. (2)	3.8 (±1.4)	3.3 (±1.3)	11.2 (±3.8)
Rijeka	Regional Educational Centre	Urban	18 daily samples 2012	Eq. (1)	1.1 (±0.4)	0.8 (*) (±0.3)	-
	Harbour entrance	Harbour	237 daily samples 2013-2014	Eq. (1)	0.5 (±0.2)	0.3 (*) (±0.1)	-

TABLE 3

Tab. 3. Model results of the impact of maritime activities on air quality in all port-cities during summer (July) and during winter (January) in 2012.

Area	Period	NO (%)	NO_2 (%)	NO_X (%)	SO_2 (%)	$PM_{2.5}$ (%)	PM_{10} (%)
Brindisi	Winter	17.9	16.7	16.5	23.5	5.0	3.9
	Summer	23.1	32.5	31.7	46.3	4.7	3.7
Venice	Winter	5.7	2.8	3.6	5.2	1.2	1.2
	Summer	5.0	9.1	8.9	16.5	2.6	2.3
Patras	Winter	15.4	14.6	14.3	8.8	2.6	2.1
	Summer	18.2	22.5	21.6	24.7	3.4	2.5
Rijeka	Winter	12.9	9.7	10.2	2.4	1.1	1.0
	Summer	14.3	21.9	21.7	4.1	2.2	2.0

FIGURE 1

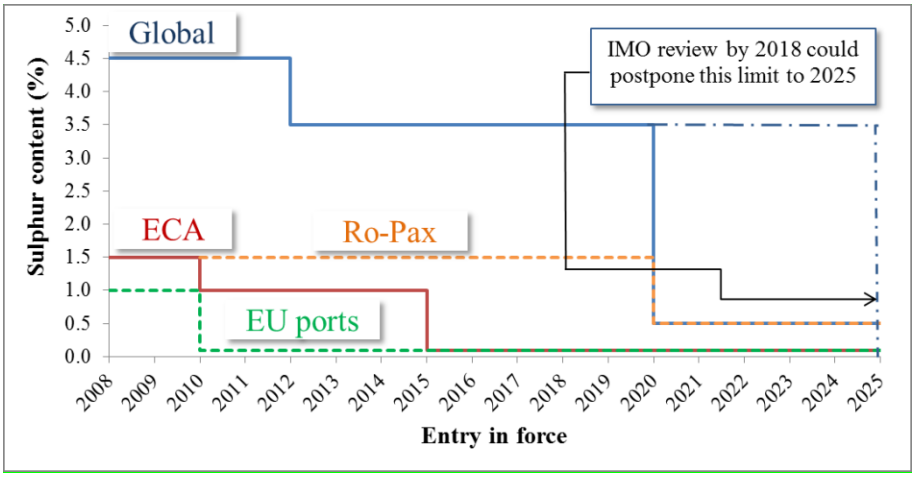

Fig. 1. Maximum sulphur content in fuels according to IMO and EU legislation.

FIGURE 2

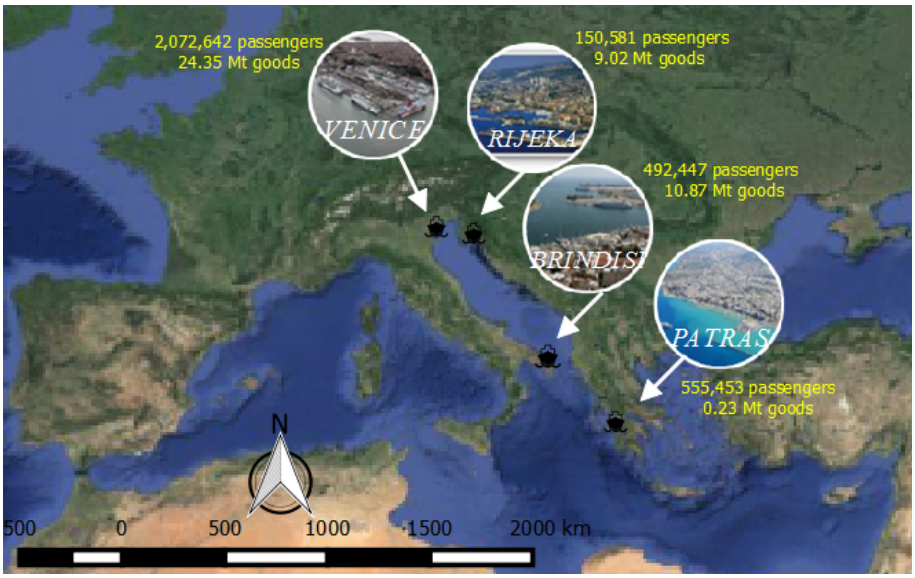

Fig. 2. Study areas included in the POSEIDON project and related ship traffic for the year 2014.

FIGURE 3

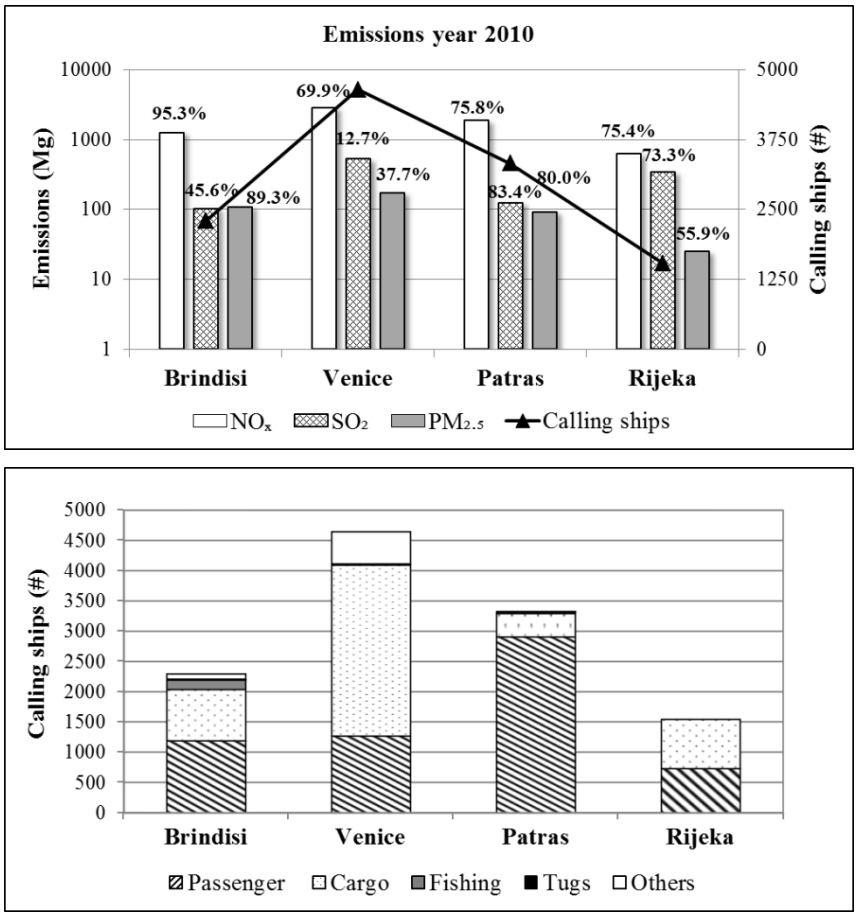

Fig. 3. (a) Absolute shipping (manoeuvring+hotelling) emissions of NO_X, SO_2 and $PM_{2.5}$ at Municipality level for all sites with (in percentage) hotelling contribution; (b) total calling ships by type in each harbour.

FIGURE 4

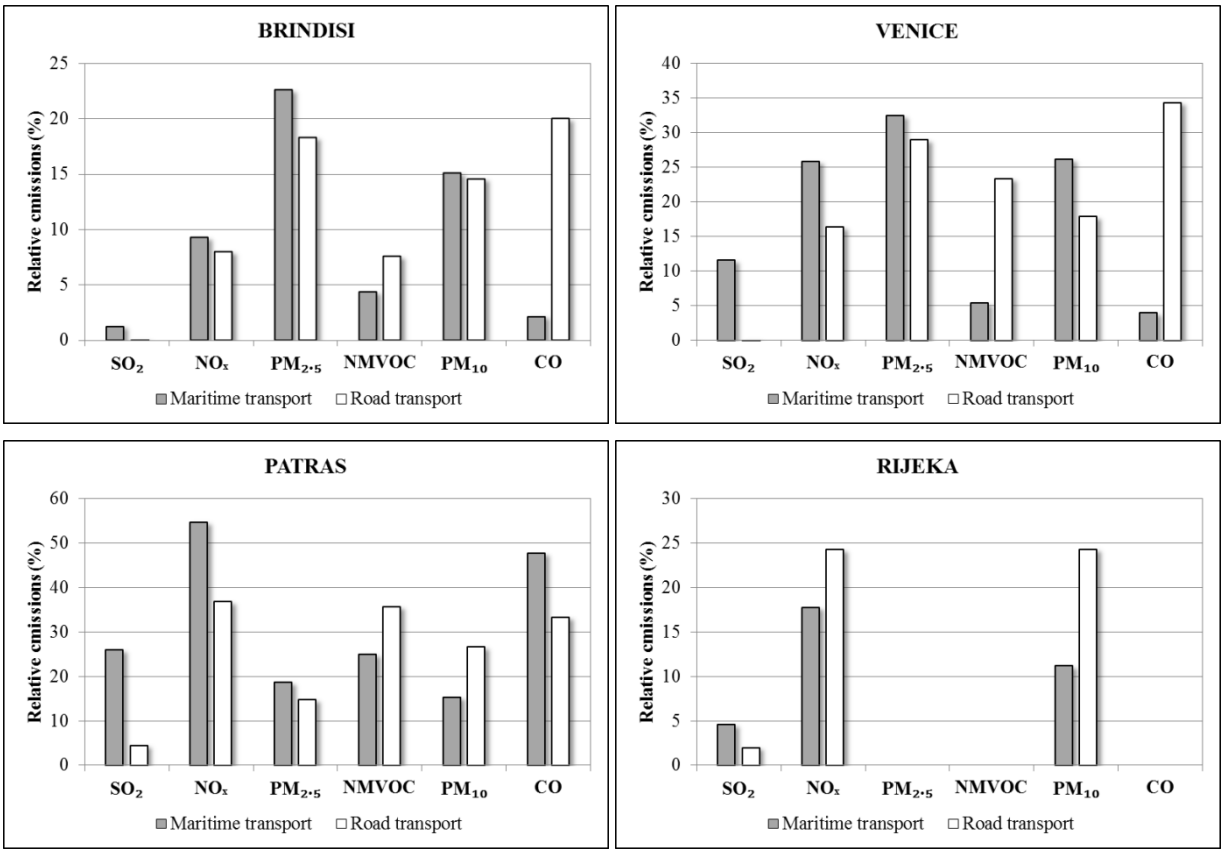

Fig. 4. Comparison of relative emissions associated to maritime and road transport in the four port cities.

FIGURE 5

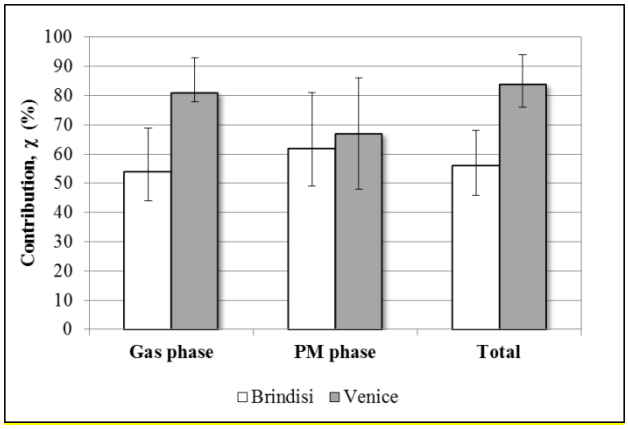

Fig. 5. Contribution to PAHs in total, gaseous and particulate phase in Brindisi and Venice for 2012.

FIGURE 6

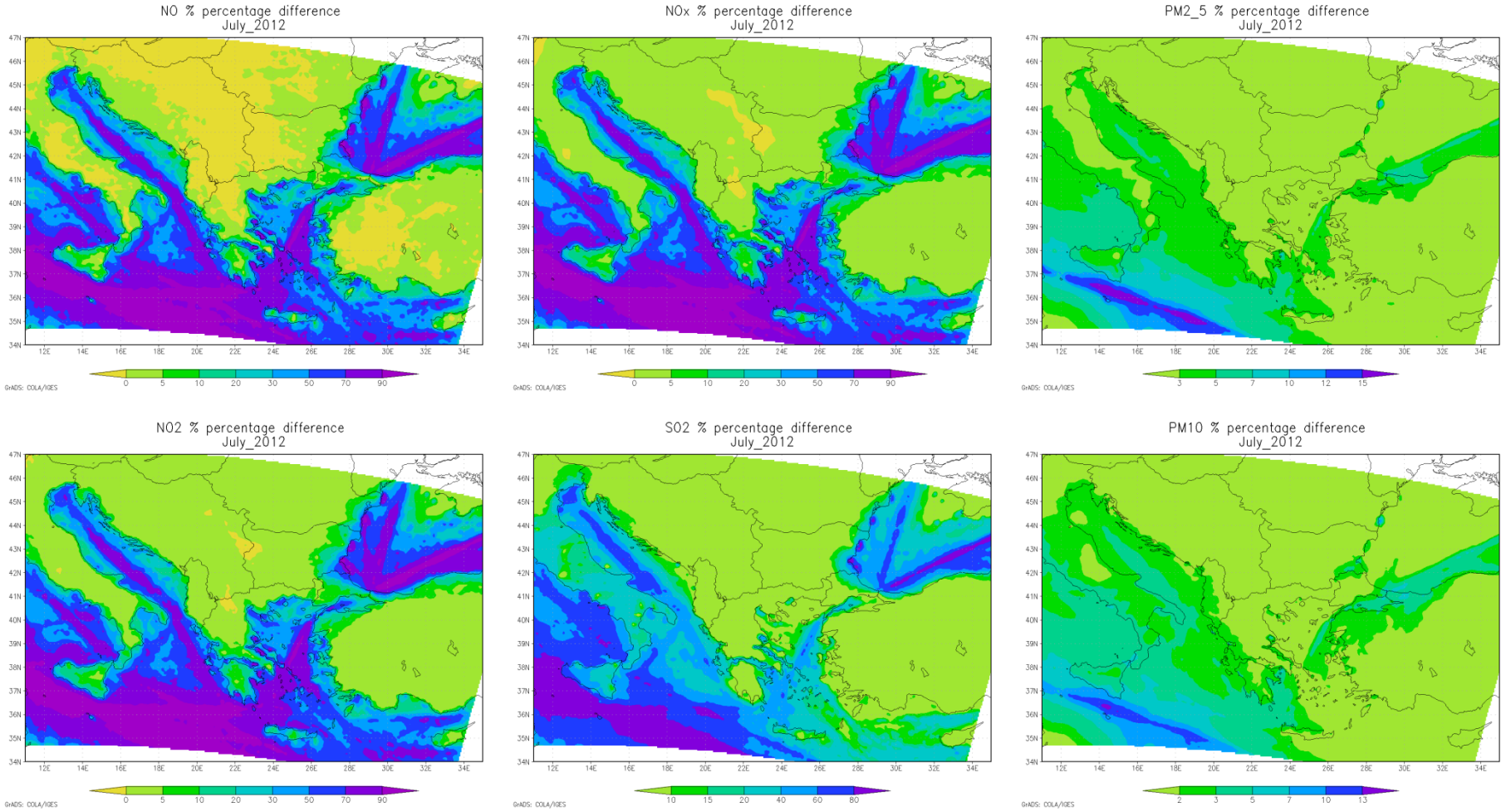

Fig. 6. Modelled relative impact on atmospheric pollutants on a regional scale for July 2012.

FIGURE 7

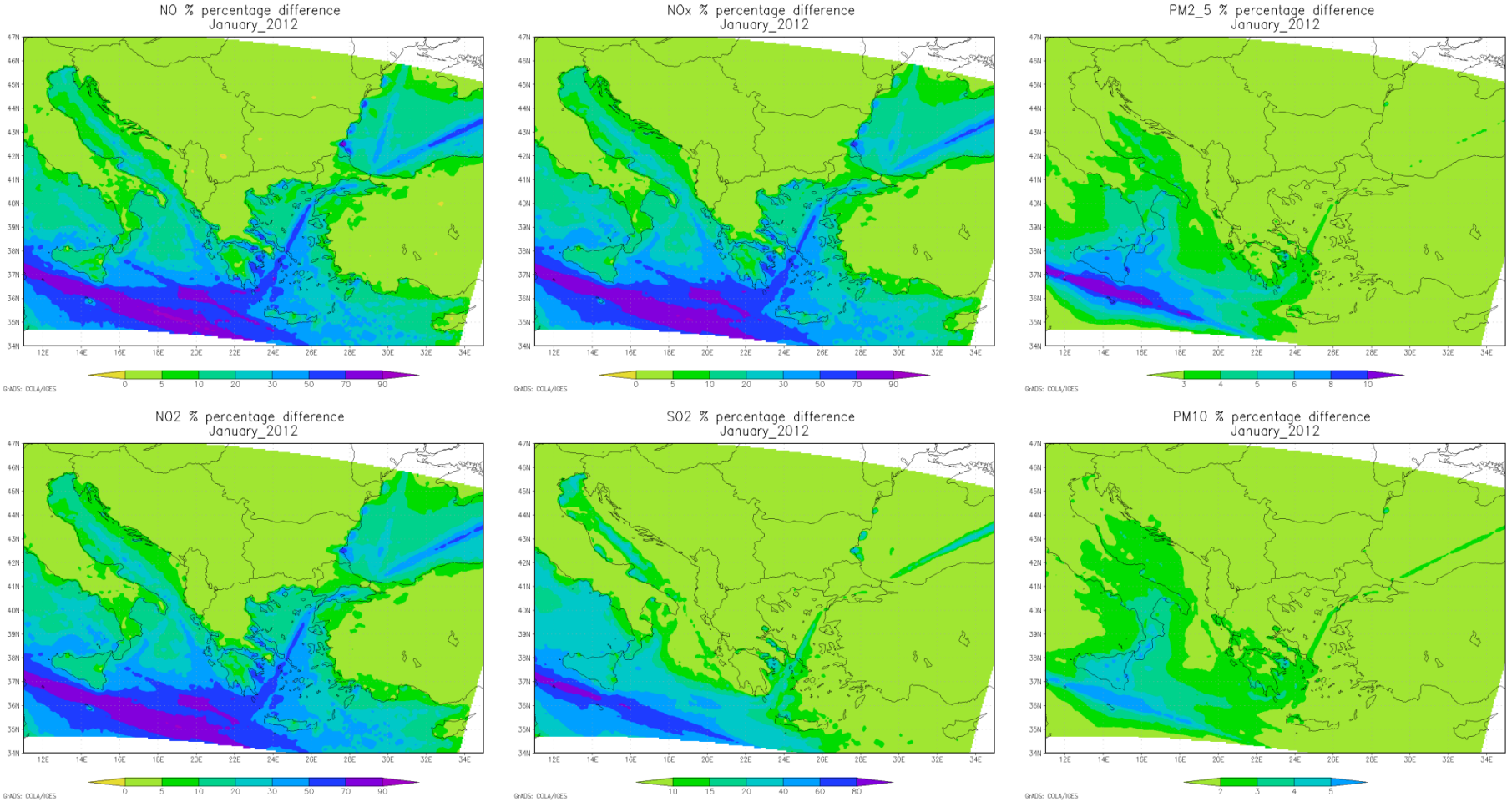

Fig. 7. Modelled relative impact on atmospheric pollutants on a regional scale for January 2012.

FIGURE 8

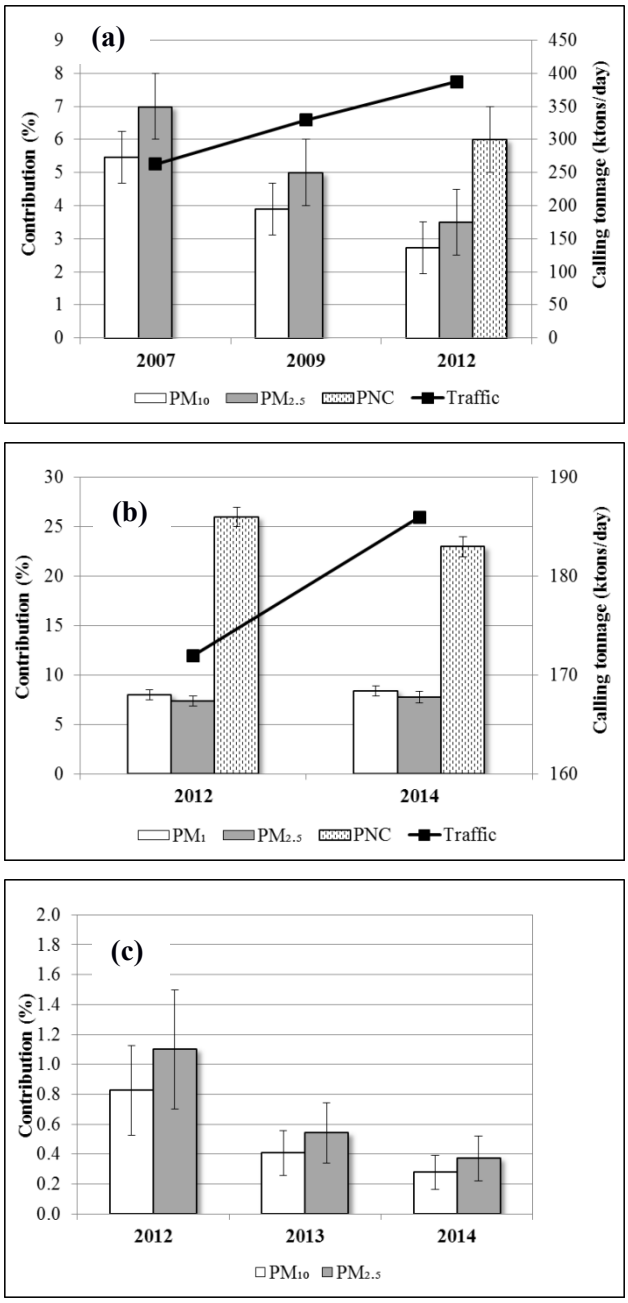

Fig. 8. Trends of shipping contributions to $PM_{2.5}$, PM_{10}, and PNC concentrations, with indication of ship traffic (in ktons/day gross tonnage of ships) in Venice (a), Brindisi (b), and Rijeka (c).

FIGURE 9

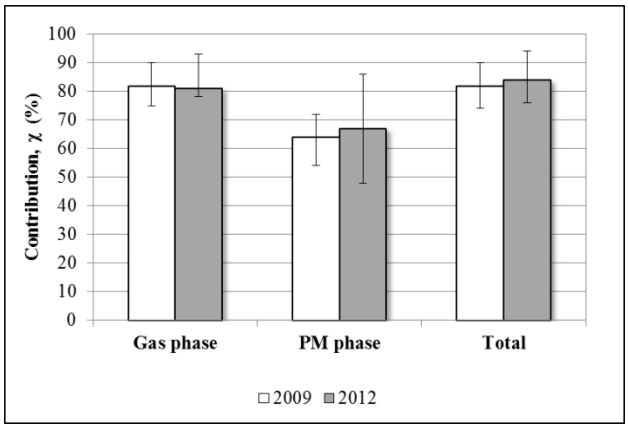

Fig. 9. Comparison of harbour contributions to PAHs in gaseous, particulate, and total (gas+particulate) phases in Venice during summer 2009 and summer 2012.

Highlights

- Impact of shipping on air quality in the Adriatic/Ionian area is studied.
- An approach based on emission inventory, modelling and data was used.
- Emissions from maritime and road sector are comparable for PM and NO_X.
- Relative impacts on NO_X and SO_2 concentrations are significantly larger than those on PM.
- Relative impacts on PNC are 2-4 times larger than those on $PM_{2.5}$ and PM_{10}.
- Analysis of trends shows a decreasing impact on PM concentrations but not on PAHs.