RESEARCH ARTICLE

Chemical characterization of fine aerosols in respect to water-soluble ions at the eastern Middle Adriatic coast

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Abstract

Fine particulate matter ($PM_{2.5}$) concentrations at the Middle Adriatic coastal site of Croatia were affected by different air-mass inflows and/or local sources and meteorological conditions, and peaked in summer. More polluted continental air-mass inflows mostly affected the area in the winter period, while southern marine pathways had higher impact in spring and summer. Chemical characterization of the water-soluble inorganic and organic ionic constituents is discussed with respect to seasonal trends, possible sources, and air-mass inputs. The largest contributors to the $PM_{2.5}$ mass were sea salts modified by the presence of secondary sulfate-rich aerosols indicated also by principal component analysis. SO_4^{2-} was the prevailing anion, while the anthropogenic SO_4^{2-} (anth-$nssSO_4^{2-}$) dominantly constituted the major non-sea-salt SO_4^{2-} ($nssSO_4^{2-}$) fraction. Being influenced by the marine origin, its biogenic fraction (bio-$nssSO_4^{2-}$) increased particularly in the spring. During the investigated period, aerosols were generally acidic. High Cl^- deficit was observed at Middle Adriatic location for which the acid displacement is primarily responsible. With $nssSO_4^{2-}$ being dominant in Cl^- depletion, sulfur-containing species from anthropogenic pollution emissions may have profound impact on atmospheric composition through altering chlorine chemistry in this region. However, when accounting for the neutralization of H_2SO_4 by NH_3, the potential of HNO_3 and organic acids to considerably influence Cl^- depletion is shown to increase. Intensive open-fire events substantially increased the $PM_{2.5}$ concentrations and changed the water-soluble ion composition and aerosol acidity in summer of 2015. To our knowledge, this work presents the first time-resolved data evaluating the seasonal composition of water-soluble ions and their possible sources in $PM_{2.5}$ at the Middle Adriatic area. This study contributes towards a better understanding of atmospheric composition in the coastal Adriatic area and serves as a basis for the comparison with future studies related to the air quality at the coastal Adriatic and/or Mediterranean regions.

Keywords $PM_{2.5}$ · Water-soluble ions · Sea salt · Secondary sulfate · Aerosol acidity · Cl^- depletion · Adriatic Sea

Introduction

Marine aerosols play an important role in the direct and indirect effects on the global climate (O'Dowd and de Leeuw 2007). Chemical composition and size distribution of marine

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aerosols are important properties which affect their transport, transformation, removal, and the extent of global aerosol radiative forcing (Seinfeld and Pandis 2006). Water-soluble ionic constituents, particularly those within the fine-mode particles, could be important sources of cloud condensation nuclei (CCN), affecting cloud microphysics and consequently the climate (Ayers and Gras 1991; Liss and Lovelock 2007). In general, water-soluble ions account for about 60–70% of particulate mass (Wang and Shooter 2001). However, the water-soluble ion concentrations and distribution in atmospheric particles are characteristics of particular regions, because they considerably depend on local sources, weather conditions, and long-range transport (Abdalmogith and Harrison 2006). Thus, the ionic properties of atmospheric particles have been extensively studied in recent years.

In coastal areas, aerosols originate from natural and anthropogenic sources. Sodium chloride (NaCl) and other common

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seawater ions (such as SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+}) resulting from the primary emission by the action of the wind on sea surface are major constituents of sea-spray aerosols (e.g., Monahan et al. 1986), which significantly contribute to particulate mass in the coastal atmosphere (Adachi and Buseck 2015; Lewis and Schwartz 2004; Piazzola et al. 2009; Yoon et al. 2007). In addition, generation of smaller particles in the marine environment results from the secondary production from volatile biogenic precursors, such as dimethyl sulfide (DMS) of phytoplankton origin and isoprene from vegetative transpiration (e.g., Charlson et al. 1987; Meskhidze and Nenes 2006; Warneck 2003; Unger 2013). Moreover, coastal areas are significantly affected by continental and other anthropogenic sources (i.e., local transport and domestic heating), contrary to remote marine sites (Abbasse et al. 2003; Takami et al. 2005; Topping et al. 2004). In the Adriatic-Ionian port areas, the study of atmospheric impacts using inventories, experimental data, and modeling showed that ship traffic contributed 0.5–7.4% to particulate matter ($PM_{2.5}$) mass (Merico et al. 2016). Although it is well-recognized that marine aerosols have a significant effect on the local air quality (Knipping and Dabdub 2003), their complex mixing with anthropogenic pollutants in coastal areas is still poorly understood.

The Mediterranean is recognized as a biodiversity hotspot, and one of the most susceptible areas to climate change, yet with large uncertainties regarding the fine-scale climate processes associated with the complex physiography of the region (Mermex Group 2011). The area continuously receives anthropogenic aerosols from industrial and domestic activities from the European region (Kanakidou et al. 2011). It is assumed that the impacts of human activities, including biomass burning (BB), are proportionally stronger in the Mediterranean than in any other sea-area of the world. Besides, the 85 million hectares of forests around the basin are also an occasional intense source of aerosols due to wildfire emissions (Turquety et al. 2014). Therefore, conducted field campaigns substantially contribute to the better process-level understanding of atmospheric physics and chemistry in the region. However, compared with the intensive research on the chemical characterization of airborne particles in other Mediterranean countries (e.g., Koçak et al. 2004, 2007; Luria et al. 1996; Mihalopoulos et al. 1997), in the Adriatic Sea sub-basin, such investigations are scarce. With the exception of the northern part and the area in the vicinity of the Venice lagoon (e.g., Gambaro et al. 2009; Ivošević et al. 2016; Morabito et al. 2014; Piazzola et al. 2016; Rossini et al. 2005; Stortini et al. 2009; Turšič et al. 2006), no extensive investigations on chemical composition of aerosols and their potential sources have been conducted at the Adriatic region thus far. As typical for coastal areas, the Adriatic is under the combined influence of local, regional, and long-range natural and anthropogenic pollution sources (Richon et al. 2017). Additionally, during summer, the risk

of fire is assessed as high to very high, especially in the Middle Adriatic.

Our current study includes an intensive sampling program, which was conducted seasonally from April 2015 to July 2016 at the eastern coast of Middle Adriatic, Croatia. The primary objective was to get an insight into the variability of the chemical composition of fine aerosol particles in respect to water-soluble inorganic and organic ions in relation to different seasons, air-mass impacts, and special events at the local level, such as open-fire emissions typical for the Middle Adriatic area. Relative contributions of local and long-range transported particles as well as relative contributions of natural and anthropogenic sources to fine atmospheric aerosol loadings are important issues for the coastal Adriatic due to the limited data available in this region thus far. To our knowledge, our study presents the first data evaluating the composition of water-soluble ions and their possible sources in $PM_{2.5}$ at the Middle Adriatic area. Every new quantitative data set on aerosol components and its sources in still poorly explored or completely unexplored regions will help in future improvements of atmospheric models, which are necessary to resolve and clarify the aerosol impact on the global climate.

Materials and methods

Sampling

Aerosol sampling was conducted at the peninsula Gradina in the vicinity of the small touristic settlement Rogoznica (43°31′52"N 15°57′34"E) at the Middle Adriatic coast, Croatia (Fig. 1). The topography of this suburban region is characterized by a wide belt of hinterland with fields in the karst landscape and Mediterranean vegetation as well as mountainous area in the north and northeast. The sampling site is located 2 km away from the most eastern part of the eastern Adriatic coast (Cape Planka) where the north and south winds collide strongly. The eastern Middle Adriatic is generally characterized by the extensive tourism and mariculture, and the low impact of local industrial activities. The region is affected by the arid summer conditions of the Mediterranean and thus under high to very high fire risks.

The $PM_{2.5}$ samples were collected using the low volume sequential sampler SEQ 47/50 (SEQ47/50) (Sven Leckel, Ingenieuburo GmbH, Germany) on a pre-combusted (450 °C for 4 h) glass fiber filters (Whatman, Grade GF/F, d = 47 mm) at a flow rate of 2.3 m³/h for 48 h from April 2015 to July 2016, capturing 6 consecutive seasons: spring 2015 (8 April–6 May 2015), summer 2015 (15 July–15 September 2015), autumn 2015 (23 September–29 October 2015), winter 2016 (20 January–24 March 2016), spring 2016 (29 March–22 June 2016), summer 2016 (22 June–13 July 2016). Three subsequent winter samples as well as two

Fig. 1 The location of the sampling site at the eastern Middle Adriatic coast, Croatia (blue circle). The area related to the intensive open-fire episode during summer 2015 is denoted with the red dotted circle
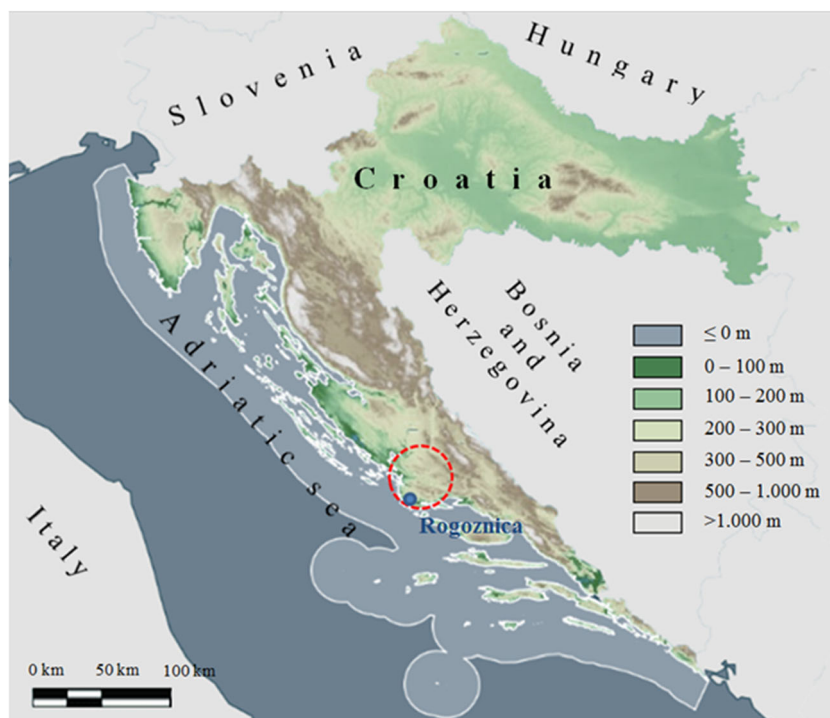
subsequent spring samples from 2016 were removed from the data set because of a suspected direct contamination. The concentrations of sea salt in those samples were more than ten times higher than in the sample with the next highest concentration. A total of 143 samples were stored in Petri Slides (Millipore Inc.) in a freezer (− 50 °C) until the analysis.

Aerosol chemical analyses

The $PM_{2.5}$ mass was obtained using Mettler Toledo XP205DR microbalance (reading precision of 10 μg) by weighing the filters before and after the sampling under constant conditions of 20 ± 1 °C and the relative humidity (RH) of $50 \pm 5\%$. For ion analysis, approximately 25% of exposed filter was extracted with 10 mL Milli-Q water (18.2 MΩ; 20 min ultrasonic bath; stored at 4 °C overnight). The solutions were filtrated through 0.22 μm PTFE disk filters and analyzed through ion chromatography. The anions were measured on a Dionex ICS 3000 with a conductivity detector. Anion separation was achieved on an analytical column (Dionex IonPac AS11-HC, 4 × 250 mm) with a precolumn (Dionex IonPac AG11-HC, 4 × 50 mm) at 1 mL min^{-1} flow rate applying the following elution program: 0–15 min isocratic elution with 1 mM KOH, 15–29 min gradient to 15 mM KOH, 29–42 min gradient to 30 mM KOH, 42–50 min gradient to 60 mM KOH, and 50–55 min isocratic elution to 60 mM KOH. Injection volume was 50 μL. Under these conditions, 12 anions were quantified: fluoride (F$^-$), lactate (C$_3$H$_5$O$_3^-$), acetate (C$_2$H$_3$O$_2^-$), formate

(CHO$_2^-$), methanesulfonate (CH$_3$SO$_3^-$, MS$^-$), chloride (Cl$^-$), nitrate (NO$_3^-$), malate (C$_4$H$_4$O$_5^{2-}$), maleate (C$_4$H$_2$O$_4^{2-}$), sulfate (SO$_4^{2-}$), oxalate (C$_2$O$_4^{2-}$), and phosphate (PO$_4^{3-}$). The cations, sodium (Na$^+$), ammonium (NH$_4^+$), and potassium (K$^+$), were measured on a Thermo Separation Products ion chromatograph equipped with a Shodex CD-5 conductivity detector, using a Dionex IonPac CG/CS12A precolumn (4 × 50 mm) and column (4 × 250 mm). The isocratic elution with 20 mM methanesulfonic acid (MSA) at the flow rate of 1.5 mL min^{-1} was set up for 23 min and the injection volume was 50 μL. The limits of quantification (LOQ) for cations and anions in $PM_{2.5}$ samples were < 0.006 μg m^{-3} and < 0.002 μg m^{-3}, respectively.

Chloride depletion calculations

Chloride depletion refers to the percentage loss in Cl$^-$ from sea salt leading to higher Na$^+$ to Cl$^-$ ratios due to the Cl$^-$ reaction with inorganic and organic acids and is estimated as mass percentage:

$$\%_{Cl}-\text{depletion} = (1.8 \times (\text{Na}^+)-(\text{Cl}^-))/(1.81 \times (\text{Na}^+)) \times 100\% \quad (1)$$

where (Na$^+$) and (Cl$^-$) are mass concentrations (μg m^{-3}) and 1.81 is the typical mass ratio of Cl$^-$ to Na$^+$ in seawater.

The theoretical maximum amount (%) of observed Cl$^-$ depletion that could be attributed to a specific acidic species was estimated by the following equation:

Cl^- depletion attributabe to A

$$= (A) x y x (MW_{chloride}/MW_A)/(1.81 x (Na^+)-(Cl^-)) x 100\% \quad (2)$$

where A is the mass concentration ($\mu g\ m^{-3}$) of the acidic species in ambient air, y is the charge of the fully deprotonated conjugate base of A, and $MW_{chloride}$ and MW_A represent molecular weights of chloride and acid species, respectively.

Accounting that $nssSO_4^{2-}$ reacts with available NH_4^+, concentration (in $\mu g\ m^{-3}$) of the $nssSO_4^{2-}$ not associated with ammonium, ($ex-nssSO_4^{2-}$) was obtained following the equation by Brown et al. (2017):

$$ex-nssSO_4^{2-} = (nssSO_4^{2-})-MW_{sulfate}/MW_{ammonium}$$
$$\times (NH_4^+)/2. \quad (3)$$

Meteorological data

Meteorological parameters recorded at the ground meteorological station located 400 m away from the sampling site are presented in Fig. 2 which include 2-day average atmospheric temperature, wind speed, RH, and precipitation level measured during the campaign. Local ambient temperature affected by solar radiation varied throughout the year from 6 to 30 °C (average 19 ± 6 °C). Air temperature started to increase in March and reached its maximum in July–August (approximately 27 °C) after which it decreased below 10 °C in January. From October to March, the wind circulation was northerly (from NNE to ENE), while from April to September, the wind direction changed southerly with a domination of SW wind during the summer (coming from the sea). The sampling site was relatively wet during the autumn, winter, and early spring and was mostly dry during the summer
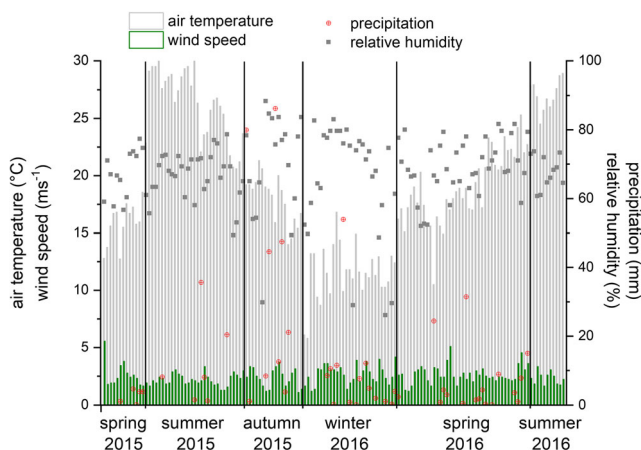
months. In summer, the whole Mediterranean region is typically dry; therefore, the removal of aerosol particles by wet deposition is minimized.

Air-mass backward trajectories

The air-mass backward trajectory analysis was performed by using the NOAA HYSPLIT model (https://www.ready.noaa.gov/HYSPLIT.php) and GDAS 1 (Global Data Assimilation System) meteorological datasets at 10 m a. g. l. to differentiate major air-mass origins in order to assist in the data interpretation. The plots represent a trajectory ensemble of 3 single backward trajectories, ending at the sampling site. All trajectories were calculated for 72 h time intervals and are, within an ensemble, shifted for 24 h, which corresponds to the three representative time points during the 48 h sampling (at the beginning, middle, and end of the sampling time for each sample).

In order to identify the potential importance of different source regions on the aerosol composition, the 143 samples collected were generally classified into airflow sectors according to the dominant air-mass trajectory direction: (a) marine (MAR)—the air mass spent most of the time over the open Adriatic Sea, Mediterranean, and/or coastal region (Fig. 3a) and (b) continental (CONT)-the air mass spent most of the time over the continental Europe (Fig. 3b). On average, only 35% of the air masses arriving at the Middle Adriatic site originated from the continental north sector (online supplementary information, SI Tables 1–5). MAR inflow significantly impacted the area with a lower contribution during the autumn and winter (on average 50 and 55%, respectively) in comparison to the spring (spring 2015, 72%; spring 2016, 64%) and summer (summer 2015, 67%; summer 2016, 64%) periods. This is in line with the mean wind vectors over the sampling site ("Meteorological data" section).

Open-fire events

A fire-influenced sample set was identified in summer 2015 (6 samples; from 04 August–16 August 2015) according to the air-mass backward trajectory analysis and the Šibenik county fire department archive data (http://www.vatrogastvo-sibenik-knin.hr/), where compiled information on the intervention type (e.g., air-force intervention), fire duration, attacked surface area, and type of vegetation affected are registered. During the selected period, intensive simultaneous and/or continuous open fires (overall 42 registered events) of grass, low plants, and pine and olive tree forests were reported in the N/NW Šibenik county area in the radius of around 30 km from the sampling location (Fig. 1). The overall affected area was over 2 km². On 15 August 2015, an open-fire event happened in Rogoznica, 50 m away from the sampling site.
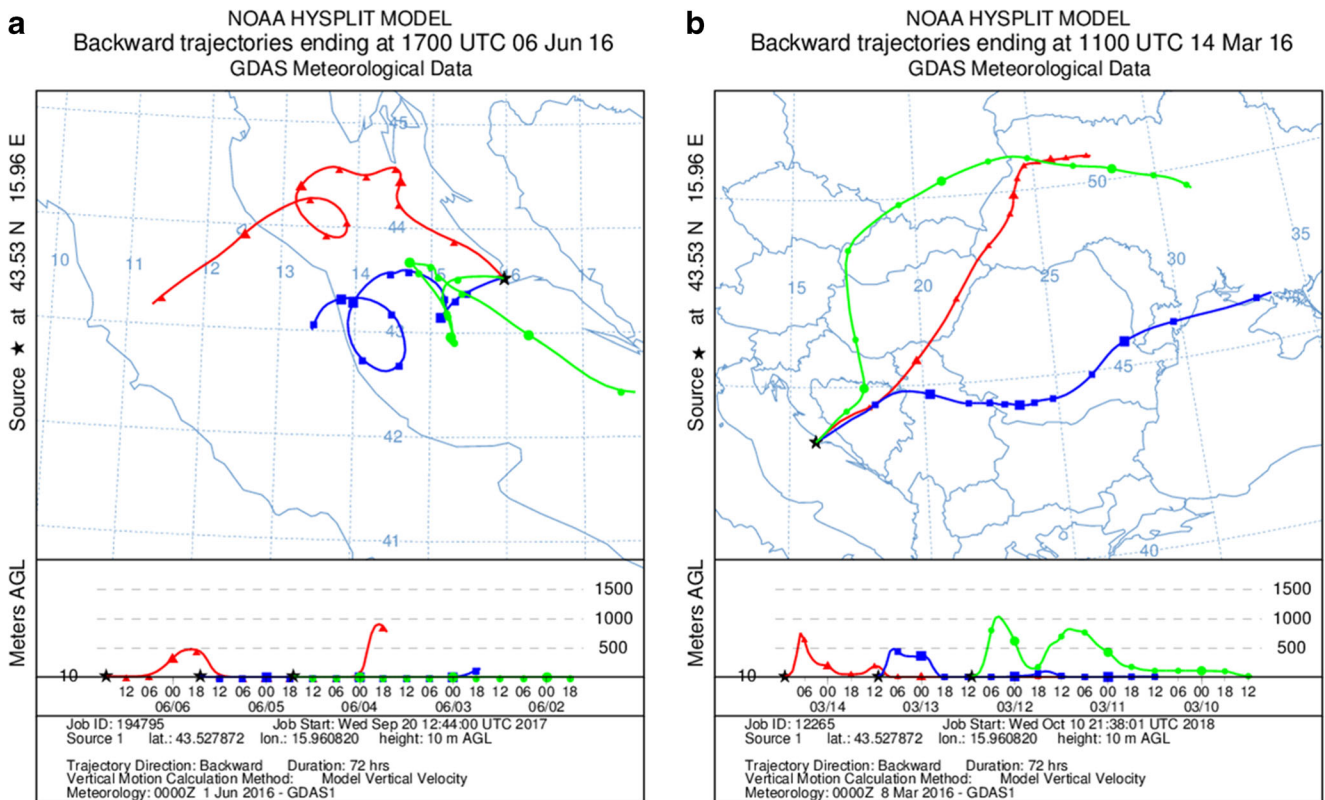

Fig. 2 Temporal variability of meteorological parameters covering the sampling period at the costal Middle Adriatic site

Fig. 3 Typical NOAA HYSPLIT air-mass backward trajectories of two types of air masses ending up at the sampling site at the eastern Middle Adriatic coastal site at 10 m a. g. l.: (**a**); marine (MAR) and (**b**); continental (CONT)

Statistical data treatment

To evaluate the sources of major ions, a multivariate statistical method principal component analysis (PCA) by Statistica Release 7.0 was performed. PCA was performed after data set homogenization (half-range and central value transformation), cross-validation, and normalization (varimax rotation).

Results and discussion

Temporal variability of PM$_{2.5}$ concentration and ion composition

Figure 4 presents the PM$_{2.5}$ mass concentrations for the Middle Adriatic site, including the period with intensive regional open fires marked with yellow. Results of average individual water-soluble ion concentrations along with the average contributions of the main ion constituents to PM$_{2.5}$ at the coastal Middle Adriatic site during the investigated period are presented in Table 1. Note that only samples without the identified influence of open-fire emissions were further considered while fire-event samples will be discussed separately in the "Impact of open fires on water-soluble ion composition" section. In addition, data from 18 autumn samples corresponding to 12% of all data are not included in the further discussion

related to ion composition because of high analytical uncertainties due to the low PM$_{2.5}$ mass concentrations (caused by intensive rainfalls in autumn 2015). Complete data set presenting concentrations of PM$_{2.5}$ mass and ion species in different seasons are shown in SI Tables 1–5. In the following, the temporal and seasonal variations of the PM$_{2.5}$ constituents are discussed with respect to the meteorological conditions, air-mass origin, and interrelationship between ionic species.

PM$_{2.5}$ mass concentration

Excluding the fire period, the average PM$_{2.5}$ mass showed seasonal variability and decreased in the order: summer 2016 (13.4 ± 5.4 μg m^{-3}) > summer 2015 (12.7 ± 4.8 μg m^{-3}) > spring 2015 (10.8 ± 3.2 μg m^{-3}) > winter 2016 (9.0 ± 4.9 μg m^{-3}) > spring 2016 (7.4 ± 2.5 μg m^{-3}) > autumn 2015 (5.0 ± 2.5 μg m^{-3}). High summer PM concentrations are also typical for the whole Mediterranean (e.g., Erduran and Tuncel 2001; Koçak et al. 2004, 2007; Luria et al. 1996). The average PM$_{2.5}$ mass concentration (9.2 ± 4.7 μg m^{-3}) obtained for the investigated period at the Middle Adriatic site is enclosed with the ranges reported for several rural sites in Portugal (between 5.6 and 17.8 μg m^{-3}) (Freitas et al. 2005) and suburban Lisbon area (2.4–30.0 μg m^{-3}) (Almeida et al. 2006). The comparable average PM$_{2.5}$ mass of 12.6 μg m^{-3} was also observed at the regional
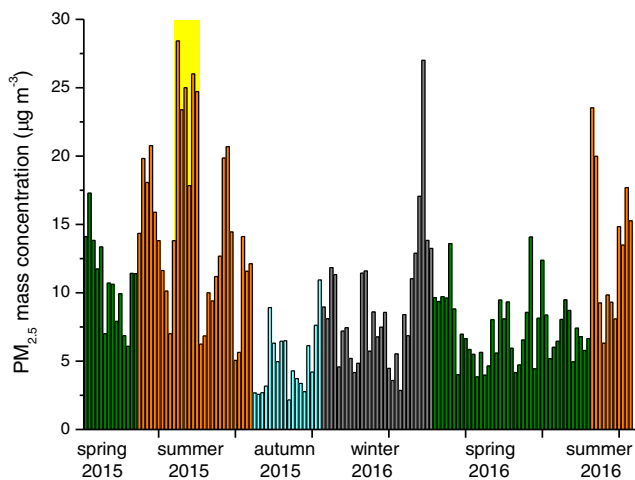
Fig. 4 Temporal variability of $PM_{2.5}$ mass concentrations at the coastal Middle Adriatic site during the sampling periods (period with intensive regional open fires is marked with yellow)

background site in the western Mediterranean in the period from 2002 to 2010 (Cusack et al. 2012). In contrast, higher $PM_{2.5}$ concentrations were reported for several European regions, such as suburban (19 ± 9 μg m^{-3}) (Perrone et al. 2011) and urban sites (34.5 ± 19.4 μg m^{-3}) of Italy (Daher et al. 2012) and rural sites of Crete (23.5 ± 5.8 μg m^{-3}) (Kopanakis et al. 2012). Higher annual mean value of 25 ± 8 μg m^{-3} was reported also at a coastal site in the south of Italy, located away from large sources of local pollution, but exposed to periodic dust events (Perrone et al. 2013).

Meteorological conditions largely affected temporal $PM_{2.5}$ variabilities in the area. A positive correlation between $PM_{2.5}$ mass and air temperature ($r = 0.478$, $p < 0.01$, $N = 143$; SI Fig. 1a) points to the possible influence of photochemical processing and the related secondary aerosol formation during summer contributing to the highest measured PM concentrations in this period. High $PM_{2.5}$ concentrations in summer can be also attributed to the prolonged lifetime of aerosol particles in the atmosphere due to the absence of rain shower, since weak but still significant negative correlation between the $PM_{2.5}$ mass and precipitation level was observed ($r = 0.324$, $p < 0.05$, $N = 51$; SI Fig. 1b). Accordingly, during abundant rain events in autumn 2015 (Fig. 2), $PM_{2.5}$ concentrations drastically decreased, possibly because rain droplets efficiently scavenged particles from the atmosphere. More frequent and intensive rainfalls during spring 2016 (Fig. 2) most probably caused also lower average PM concentrations in comparison to spring 2015, despite higher temperatures measured. A negative correlation between wind speed and PM mass concentrations ($r = 0.291$, $p < 0.01$, $N = 143$; SI Fig. 1c) additionally suggests some PM dispersal with the increasing wind speed at the coastal Middle Adriatic site, as typically observed over urban locations in comparison to the open ocean (Vardoulakis and Kassomenos 2008; O'Dowd and Hoffmann 2005).

As far as the long-range transport of atmospheric PM is concerned, PM samples mostly affected by the continental

north sector were generally characterized by higher average concentrations (except in autumn with comparable average masses of CONT and MAR samples; see Fig. 5). This indicates more polluted continental impact in comparison to the air masses arriving from the southern marine regions. Considering also the frequency of samples influenced by the different air-mass origins in particular season ("Air-mass backward trajectories" section), more polluted continental air-mass inflows mostly affected the area in the winter period. The highest $PM_{2.5}$ concentrations measured in summer could be also expected due to the pronounced photochemistry as well as higher impact of southern marine pathways during the stagnant summer meteorological conditions.

Total ion composition

The average total water-soluble ion concentrations (Table 1) showed a similar pattern to the $PM_{2.5}$ mass concentrations (Fig. 4) with the minimum in winter and the maximum in summer. The sum of ions contributed an average of 76% to $PM_{2.5}$. No significant difference in the total ion concentrations with regard to the air mass origin was observed. (SI Table 7). The most abundant ion was SO_4^{2-} followed by Na^+, NO_3^-, Cl^-, NH_4^+, and the anions of carboxylic acids (hereafter organic acids) indicating that secondary inorganic aerosol (SIA) and sea salts presented the major portion of $PM_{2.5}$ at the Middle Adriatic site. The percentages of SIA (i.e., the summation of SO_4^{2-}, NO_3^-, and NH_4^+) ranged from 20 to 85% (average $49 \pm 13\%$) and from 11 to 64% (average $36 \pm 9\%$) in total measured ions and $PM_{2.5}$ mass, respectively, having the minimum in winter and the maximum in summer.

Sea salt

Sea salt concentration estimated as $[ss] = [Cl^-] + [Na^+] \times 1.47$ (Quinn et al. 2002), contributed on average 52 and 40% to the total measured ions and $PM_{2.5}$ mass, respectively (Fig. 6, Table 1). Despite no significant correlation between sea salt concentrations and average wind speeds, the highest contribution of sea salts was observed during winter and spring 2016, when the highest average wind speeds were detected as well (Fig. 2). In marine environment, more turbulent weather conditions during transitional winter and spring periods are expected to enhance the primary emission of sea salt aerosols in contrast to summer, characterized by weaker winds and a calmer sea surface. Thus, since higher sea salt contributions to total ions were observed when both MAR (spring 2015) and CONT (winter 2016) inflows preferentially influenced the area (SI Table 7), we may assume that the regional/local meteorological conditions become more important factor for the sea salt enhancement in PM than the southern marine air inflows.

Table 1 The average concentrations of individual water-soluble ions, total ions, sea salts (ss), non-sea-salt SO_4^{2-} (nssSO_4^{2-}), and biogenic non-sea-salt SO_4^{2-} (bio-nssSO_4^{2-}) as well as the contributions (%) of main ions to $PM_{2.5}$ mass (in brackets) obtained for different seasons and intensive open-fire period at the Middle Adriatic site. The confidence interval was obtained with the Student t statistics and is given with 95% confidence

Species	Overall period	Spring 2015	Summer 2015	Fire period 2015	Winter 2016	Spring 2016	Summer 2016
F⁻	0.07±0.03	0.06±0.01	0.05±0.01	0.05±0.01	0.08±0.02	0.08±0.02	0.08±0.05
lactate	0.01±0.01	0.02±0.01	0.010±0.004	0.01±0.004	0.01±0.01	0.01±0.01	0.002±0.001
acetate	0.03±0.02	0.04±0.01	0.02±0.01	0.02±0.007	0.05±0.01	0.03±0.02	0.010±0.003
formate	0.02±0.02	0.05±0.01	0.04±0.01	0.05±0.01	0.03±0.01	0.01±0.01	0.001±0.002
MS⁻	0.06±0.04	0.08±0.04	0.07±0.03	0.07±0.01	0.01±0.01	0.07±0.04	0.09±0.02
Cl⁻	0.80±0.33 (11±7)	0.38±0.06 (4±1)	0.61±0.18 (6±4)	0.50±0.21 (2±1)	0.83±0.35 (12±7)	0.95±0.27 (14±6)	1.04±0.34 (9±5)
NO₂⁻	0.04±0.04	0.05±0.02	0.03±0.01	0.03±0.01	0.10±0.05	0.02±0.02	0.01±0.01
Br⁻	0.006±0.005	0.020±0.001	0.010±0.001	0.010±0.001	0.002±0.002	0.003±0.002	0.005±0.002
NO₃⁻	0.48±0.54 (5±3)	0.70±0.25 (7±2)	0.41±0.12 (4±1)	0.41±0.03 (2±0)	0.75±1.00 (8±4)	0.32±0.12 (5±2)	0.28±0.09 (2±1)
malate	0.04±0.02	0.04±0.02	0.08±0.03	0.09±0.02	0.03±0.01	0.03±0.02	0.05±0.020
maleate	0.01±0.01	0.02±0.01	0.01±0.01	0.02±0.001	0.010±0.004	0.01±0.01	0.01±0.002
SO_4^{2-}	2.79±1.66 (28±8)	2.79±1.16 (26±8)	4.09±2.52 (32±6)	8.62±1.73 (36±4)	1.89±1.36 (20±7)	2.26±0.97 (31±6)	4.28±2.20 (31±6)
oxalate	0.29±0.17	0.28±0.10	0.62±0.18	0.64±0.15	0.18±0.07	0.23±0.09	0.44±0.14
PO_4^{3-}	0.03±0.03	0.020±0.003	0.020±0.004	0.02±0.004	0.020±0.003	0.03±0.03	0.08±0.04
Na⁺	1.72±0.44 (20±7)	1.99±0.22 (18±5)	2.10±0.36 (18±5)	2.44±0.17 (10±2)	1.39±0.28 (19±8)	1.60±0.34 (24±7)	2.11±0.68 (17±6)
NH₄⁺	0.50±0.49 (4±3)	0.63±0.38 (5±3)	0.83±0.54 (6±3)	2.23±0.17 (9±2)	0.35±0.58 (3±3)	0.27±0.22 (3±2)	0.64±0.44 (4±2)
K⁺	0.30±0.14 (3±1)	0.45±0.07 (4±1)	0.47±0.16 (3±1)	0.68±0.07 (3±0)	0.23±0.10 (3±1)	0.22±0.10 (3±1)	0.34±0.12 (3±1)
[a]total ions	7.0±2.7 (76±16)	7.4±2.1 (70±15)	8.8±2.8 (71±7)	15.5±2.7 (65±9)	5.8±2.5 (70±16)	6.1±1.5 (87±16)	9.4±3.4 (72±11)
[b]ss	3.3±0.8 (40±16)	3.1±0.4 (31±8)	3.6±0.5 (32±11)	4.1±0.2 (17±3)	3.0±0.6 (40±18)	3.3±0.7 (49±16)	4.2±1.3 (35±13)
[c]nssSO_4^{2-}	2.4±1.6 (23±8)	2.3±1.1 (21±8)	3.6±1.7 (27±7)	8.0±1.7 (33±4)	1.5±1.3 (15±8)	1.9±0.9 (25±6)	3.8±2.1 (26±6)
[d]bio nssSO_4^{2-}	0.61±0.41 (7±6)	0.75±0.43 (8±5)	0.75±0.34 (5±2)	0.70±0.19 (3±1)	0.13±0.06 (2±1)	0.71±0.38 (11±6)	0.90±0.20 (8±4)
[e]bio-nssSO_4^{2-}	0.06±0.04	0.08±0.04	0.07±0.03	0.07±0.01	0.01±0.01	0.07±0.04	0.09±0.02

[a] Calculated as the sum of individual concentrations of all cations and anions measured

[b] Calculated following Quinn et al. (2002), $[ss] = [Cl^-] + [Na^+] \times 1.47$

[c] Calculated as $[nssSO_4^{2-}] = [SO_4^{2-}] - [Na^+] \times 0.252$, 0.252 is the mass ratio of (SO_4^{2-}/Na^+) in bulk seawater

[d] Bio-nssSO_4^{2-} calculated following Park et al. (2017), $[bio-nssSO_4^{2-}] = [MS^-] \times 10$, considering asymptotically determined specific nssSO_4^{2-}/MS⁻ ratio of 10

[e] Bio-nssSO_4^{2-} calculated following Hoffmann et al. (2016), $[bio-nssSO_4^{2-}] = [MS^-]$

Sulfate and methanesulfonate

SO_4^{2-} as the prevailing anion constitutes on average 28% of the $PM_{2.5}$ mass (Table 1) and 37% of the total measured ion fraction (Fig. 6) with the minimum in winter and the maximum in the summer time. The average SO_4^{2-} concentration of 2.79 ± 1.66 μg m^{-3} obtained for this study agrees with high SO_4^{2-} concentrations observed over the Mediterranean (Bougiatioti et al. 2013; Koçak et al. 2004).

By using Na⁺ as a sea-spray marker to determine the concentration of SO_4^{2-} associated with sea salt as $[ssSO_42-] = [Na^+] \times 0.252$, where 0.252 is the (SO_4^{2-}/Na^+) mass ratio of bulk seawater (Millero 2006), it was found that on average ssSO_4^{2-} contributed only up to 19% of the total SO_4^{2-} measured. Thus, the variations observed in the SO_4^{2-} time series are attributed to the variations in the prevailing non-sea-salt fraction (nssSO_4^{2-}). Besides gas-phase oxidation and gas-to-particle conversion of anthropogenic SO_2, as well as in-cloud oxidation of dissolved SO_2 (Harris et al. 2013), a substantial amount of secondary nssSO_4^{2-} (as well as MS⁻) could originate from biogenic phytoplankton emissions of DMS and its subsequent oxidation in the marine troposphere (Andreae et al. 1985; Charlson et al. 1987; Stefels et al. 2007).

Methane sulfonic acid is a well-known oxidation product of DMS and, hence, an important constituent of marine aerosols, especially in spring and summer (Sciare et al. 2009). Seasonal trend was indeed observed for MS⁻ concentrations in fine aerosols at the coastal Adriatic site, with much higher concentrations measured in spring–summer than in winter (Table 1). Significantly, higher MS⁻ contribution to MAR aerosols was observed in spring, being attributed to the increased phytoplankton activity (SI Table 7).

The observed average nssSO_4^{2-} concentration (2.4 ± 1.6 μg m^{-3}) is in a good agreement with the annual nssSO_4
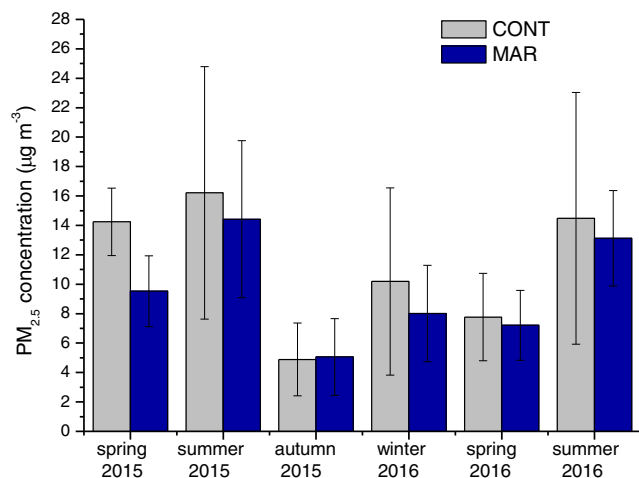
Fig. 5 Seasonal average $PM_{2.5}$ mass concentrations influenced by northern continental (CONT) and southern marine (MAR) air masses

$^{2-}$ average of several Mediterranean cities (2.2–3.9 μg m^{-3}) (Salameh et al. 2015) but considerably higher than those for remote marine regions (Savoie and Prospero 1989), implying that the studied aerosols comprised both anthropogenically (anth-nssSO$_4^{2-}$) and biogenically (bio-nssSO$_4^{2-}$) derived nssSO$_4^{2-}$.

The bio-nssSO$_4^{2-}$ content is often estimated as the product of MS$^-$ concentration and the asymptotic value of nssSO$_4^{2-}$/MS$^-$ ratio during enhanced MS$^-$ levels which is assumed to be a characteristic of investigated region and exclusively related to DMS (Park et al. 2017; Udisti et al. 2012; Udisti et al. 2016). Seasonal variabilities of average bio-nssSO$_4^{2-}$ and anth-nssSO$_4^{2-}$ following the asymptotic approach by Park et al. (2017) are shown in SI Fig. 2a. On average, the bio-nssSO$_4^{2-}$ contribution to total water-soluble ions and PM$_{2.5}$ was 9 and 7%, respectively. Since anth-nssSO$_4^{2-}$ background levels at the sampling site presumably affected the asymptotic value assumed to relate exclusively to DMS oxidation, the obtained bio-nssSO$_4^{2-}$ concentrations (average
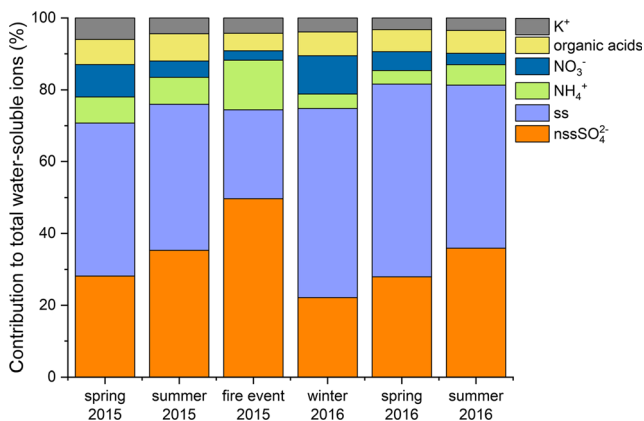
0.61 ± 0.41 μg m^{-3}) are considered to be overestimated. Up to 50% overestimation of bio-nssSO$_4^{2-}$ by the asymptotic approach was also indicated by its correlation with that using the stable S-isotope ratio (Park et al. 2017). If accounting for the recent modeling simulation findings implying that the multiphase DMS oxidation produces equal amounts of MS$^-$ and SO$_4^{2-}$ (Hoffmann et al. 2016), bio-nssSO$_4^{2-}$ concentrations (average 0.06 ± 0.04 μg m^{-3}) are an order of magnitude lower than those obtained by the asymptotic approach (Table 1). We may assume that the realistic bio-nssSO$_4^{2-}$ content is between the both calculated limit values.

Independent of the applied approach, bio-nssSO$_4^{2-}$ contributions to the total nssSO$_4^{2-}$ were particularly high in spring, followed by the summer periods (SI Fig. 2a and b) when air-mass inputs from the southern marine pathways were enhanced ("Air-mass backward trajectories" section). This is in agreement with the well-known increased phytoplankton primary production in the Adriatic Sea in spring due to favorable conditions, i.e., the availability of sunlight and nutrients within the sea surface layers (Marić et al. 2012). Significant correlation between the air temperature and the nssSO$_4^{2-}$ concentrations was detected ($r = 0.512$, $p < 0.01$, $N = 119$; SI Fig. 3). Thus, in addition to the lower rate of wet removal during summer, photochemical processing could also enhance the formation of secondary nssSO$_4^{2-}$ via oxidation by OH radicals. Note however, anth-nssSO$_4^{2-}$ dominantly constituted the nssSO$_4^{2-}$ fraction (SI Fig. 2a and b) being generally enhanced in the samples affected by the CONT inflow (SI Table 7) and having the highest impact on the Middle Adriatic area in winter.

Nitrogen-containing species

The determined NO$_3^-$ concentrations were approximately 5–10 times lower than those of SO$_4^{2-}$, indicating that secondary inorganic aerosols at the Middle Adriatic originated dominantly from the sulfur-containing sources rather than being nitrogen-controlled. Opposite to nssSO$_4^{2-}$, the lowest NO$_3^-$ contribution to the total measured ions was determined in summer, while the maximum was detected in winter (Fig. 6). A good correlation between the NO$_3^-$ and nssSO$_4^{2-}$ observed only in winter (Table 2) implies that nssSO$_4^{2-}$ and NO$_3^-$ had a common anthropogenic origin during that period. During spring and summer, an additional source of nssSO$_4^{2-}$, such as the production through photochemical processes from both anthropogenic and biogenic precursors occurred.

In winter, higher NO$_3^-$ levels are expected due to the larger availability of NO$_x$ precursors resulting from additional emissions not operating in summer (e.g., domestic heating). Moreover, since the equilibrium dissociation constant for NH$_4$NO$_3$ is sensitive to temperature and humidity, more NH$_4$NO$_3$ (from the same quantity of ammonia and nitric acid vapor) is expected to form at low temperature and at high

Fig. 6 The average contributions of the main ions to the total water-soluble ions in PM$_{2.5}$ collected at the Middle Adriatic coastal site during 2015 and 2016

relative humidity as observed in winter 2016. NO_3^- contribution did not differ significantly within MAR and CONT inflows (SI Table 7), implying comparable impacts of both CONT and MAR air-mass inflows in the area. In addition, local emission sources (e.g., domestic heating, land and ship traffic, and agricultural activities) could be important factors for the NO_3^- levels at the Middle Adriatic coastal site.

The average NH_4^+ concentrations at the Middle Adriatic site (Table 1) were lower than the average values determined at the eastern Mediterranean coastal sites (Bougiatioti et al. 2013; Koçak et al. 2007). Being the principal neutralizing agent for atmospheric acids, ammonia plays an important role in the secondary aerosol formation, while its conversion depends on the content of acidic species, temperature, and humidity in the atmosphere. Significant correlation with $nssSO_4^{2-}$ (Table 2) points to their related secondary origin. No seasonal trends or significant difference between CONT and MAR samples were observed at the Adriatic site, the same as for NO_3^-, indicating that both long-range transport and/or local sources could influence NH_4^+ levels in fine aerosols (SI Table 7). Local/regional sources of NH_3 in the coastal and suburban Adriatic region are likely to come from agricultural practices, such as fertilizers use and agricultural waste burning.

Oxalate and potassium

Among the organic acid ions, oxalate was the most abundant species (Table 1). The oxalate levels, especially those measured during summer, are in very good agreement with the values reported by Bardouki et al. (2003) for Finokalia, Crete, in summer. These levels are among the highest reported in the literature for rural and even urban areas (Kawamura and Ikushima 1993). High insolation and the high levels of O_3 prevailing in summer in the Mediterranean (Kouvarakis et al. 2002) could account for the extreme concentrations of oxalate in this region, indicating the influence of photochemistry on the ambient aerosol composition. It is believed that marine emissions of DMS, ethane, isoprene, and other biogenic precursors in combination with subsequent photochemical aqueous-phase reactions lead to the formation of oxalate in the marine atmosphere (Kawamura and Bikkina 2016; Kawamura and Sakaguchi 1999). On the other hand, a significant correlation of airborne oxalate with SO_4^{2-} and NO_3^- has been reported, suggesting also the pollution source (Norton et al. 1983). Significant correlation observed in this work between oxalate and $nssSO_4^{2-}$ (Table 2) suggests its common secondary origin, likely related to in-cloud formation in the atmosphere.

High correlation between the oxalate and K^+ was also obtained during the investigated period (Table 2). K^+ emitted from sea salt (determined as $[ssK^+] = [Na^+] \times 0.038$, where 0.038 is the ($K^+/Na^+$) mass ratio in bulk seawater (Millero

2006)) was a minor contributor to the total K^+ (on average 2%). The anthropogenic origin of K^+ indicates the relation to the combustion of vegetation and wood and waste incineration (Pachon et al. 2013 and reference herein). The oxalate/K^+ mass ratio in this work averaged at 1.1, which is apparently larger than the reported values for the oxalate directly measured in BB plumes (0.03–0.1) (Yamasoe et al. 2000). Hence, the secondary formation of oxalate from vegetation and wood burning emitted VOCs could not be excluded.

Correlation of acidic species with NH_4^+ and implications for aerosol acidity

The most acidic constituents of atmospheric aerosol particles are H_2SO_4 and HNO_3, both of secondary origin and predominantly related to anthropogenic pollution sources. Gas-to-particle partitioning of oxidized nitrogen species to form particulate NO_3^- is largely affected by acidic sulfate and neutralizing ammonium content (Seinfeld and Pandis 2006). The sum of measured $nssSO_4^{2-}$ and NO_3^- concentrations during the campaign at the coastal Middle Adriatic was strongly correlated with NH_4^+ (Table 2), with a slope of linear regression larger than 1, indicating an incompletely neutralized system. Such a strong correlation was due to the dominance of $nssSO_4^{2-}$ over NO_3^- governing the acidity of the atmosphere. There were several samples from April to May 2015 (spring 2015) and July 2015 (summer 2015) as well as from March 2016 (winter 2016) that were characterized by significantly higher NH_4^+ content, possibly due to the increased emissions of NH_4^+ from local agricultural activities and more intensive BB in the region. Specifically, those samples were characterized with $NH_4^+/nssSO_4^{2-}$ molar ratios > 1.2 as well as NO_3^- concentrations being on average up to 30% higher in comparison to seasonal averages. The excess in NH_4^+ during April, May, and August was also observed in the coastal Aveiro area, Portugal (Alves et al. 2007). In general, the average molar $NH_4^+/nssSO_4^{2-}$ ratio of 0.8 obtained for the overall period suggests that aerosols were acidic and predominantly in the form of NH_4HSO_4. Due to NH_4^+-limited conditions, HNO_3 could not be fully neutralized by NH_4^+ to NH_4NO_3. Therefore, a statistically significant correlation between NH_4^+ and NO_3^- could only be observed in winter 2016 (Table 2). This is in line with higher NO_3^- content observed in winter as discussed previously.

A positive correlation was found between $NH_4^+ + nssK^+$ and $nssSO_4^{2-} + NO_3^- +$ organic acids in equivalent concentrations (on average $r = 0.812$, $p < 0.01$, slope = 0.70, $N = 96$) and the ratio of the main cations to anions decreased in the order: summer 2015 > spring 2015 > summer 2016 > spring 2016 > winter 2016 (Table 2). Thus, except for several samples in spring and summer 2015, acidic components generally dominated over alkaline ones, rendering an acidic nature of aerosols throughout the sampling period. According to these

Table 2 The correlation coefficients (r, significant $p < 0.01$) between mass concentrations of major ions and molar ratios of NH_4^+ and $nssSO_4^{2-}$ as well as cations (as sum of NH_4^+ and $nssK^+$) and anions (as sum of $nssSO_4^{2-}$, NO_3^-, and organic acid anions) in different seasons. Only statistically relevant correlations are presented with the number of r

	Spring 2015	Summer 2015	Winter 2016	Spring 2016	Summer 2016
$nssSO_4^{2-}$ vs. NO_3^-	-	-	0.507	-	-
$nssSO_4^{2-}$ vs. NH_4^+	0.972	0.879	0.926	0.878	0.905
$nssSO_4^{2-}$ vs. oxalate	0.797	0.830	0.552	0.735	0.877
$nssSO_4^{2-}$ vs. K^+	0.894	0.678	0.702	0.804	0.876
NO_3^- vs. NH_4^+	-	-	0.669	-	-
oxalate vs. K^+	0.952	0.998	0.449	0.751	0.716
$nssSO_4^{2-} + NO_3^-$ vs. NH_4^+	0.968	0.885	0.941	0.839	0.901
NH_4^+ vs. $nssSO_4^{2-}$	1.289	1.087	0.712	0.661	0.778
$NH_4^+ + nssK^+$ vs. $nssSO_4^{2-} + NO_3^- +$ organic acid ions	0.915	0.962	0.439	0.529	0.662

calculations, winter samples were the most acidic, which is related to enhanced anthropogenic emissions and less pronounced Cl^- depletion due to shorter residence time of aerosol particle in the atmosphere in this season (refer here to the following section). This in fact also agrees with the higher contribution of polluted CONT air masses in comparison to spring and summer aerosols.

Processes controlling Cl^- depletion

In the atmospheric aerosols along the coastline, Cl^- can be partially depleted due to chemical reactions of sea salts with acidic aerosol components, forming volatile HCl. Cl^- deficit in marine aerosols has been observed at many coastal sites in the Mediterranean (e.g., Athanasopoulou et al. 2015; Malaguti et al. 2015; Mihalopoulos et al. 1997). In the polluted areas, where precursors of strong acids (H_2SO_4 and HNO_3) constituting aerosols are abundant, simple acid-displacement reactions are likely responsible for the majority of Cl^- depletion, leading to large Cl^- deficits (and concomitantly pH increase) in respect to sea salt composition if only enough time is available.

The relationship between Na^+ and Cl^- was examined in the Middle Adriatic samples for the first time. Cl^-/Na^+ mass ratios (on average 0.50) were lower than that of bulk seawater (0.81), revealing a substantial Cl^- depletion in the investigated fine aerosols. Moreover, no significant correlation could be found between Na^+ and Cl^- in the Middle Adriatic samples ($r = 0.138$, $N = 143$), pointing to complex processes leading to Cl^- depletion in the investigated samples.

The calculated Cl^- depletion (Eq. 1) at the Middle Adriatic ranged from 27 to 93% (on average $72 \pm 12\%$) (Fig. 7a). Cl^- deficits were higher in summer than in winter, which could be explained by the highest content of main acidic components, such as $nssSO_4^{2-}$, NO_3^-, and organic acids in summer aerosols. Note, however, that despite the lower content of acidic species, winter aerosols were the most acidic. The lowest

calculated Cl^- depletion (and the highest aerosol acidity) of winter samples are attributable to shorter aerosol lifetimes in the atmosphere during winter, not giving enough time for efficient Cl^- depletion. In addition, other mechanisms than acid-displacement reactions, such as photochemical reactions with O_3 or NO_x (Behnke and Zetzsch 1990) could be responsible for the observed enhanced Cl^- depletion during hot summer period. Due to limited data set regarding the role of meteorological conditions or irradiation, our data suggest, but do not prove that photochemical reactions could play a role in the observed Cl^- deficit.

Theoretically, $nssSO_4^{2-}$ contributed the most to the observed Cl^- depletion (Eq. 2) in the fine aerosols of all seasons (on average $72 \pm 36\%$), with the maximum of 96% in summer and the minimum of 54% in winter (Fig. 7b). Assuming the upper limit of bio-$nssSO_4^{2-}$ concentrations obtained by the asymptotic approach following Park et al. (2017) (Table 1), bio-$nssSO_4^{2-}$ alone could account for up to 17% of Cl^- displacement, with the maximum of 27% during the spring period. However, after accounting for the neutralization of H_2SO_4 by NH_3 (Eq. 3), the average contribution of the obtained ex-$nssSO_4^{2-}$ drops to 37% (Fig. 7c), which should also be considered in the case of bio-$nssSO_4^{2-}$ contribution. In general, in the atmosphere over the Middle Adriatic, the reaction of sea salt with H_2SO_4 is the important pathway for the reduction of aerosol acidity in the atmosphere.

The chemical reaction between sea salt particles and HNO_3 leading to Cl^- depletion has been also well-documented (Hsu et al. 2007; Quinn and Bates 2005; Wu and Okada 1994). However, owing to lower NO_3^- concentrations in aerosols over the Middle Adriatic, the other acid-displacement reaction between H_2SO_4 and NaCl to Na_2SO_4 and HCl was favored. The calculated average (($Cl^- + NO_3^-)/Na^+$) ratio was around 0.4, confirming that the contribution of HNO_3 in the chemical displacement in the sea salt aerosols was minor. However, considering the

theoretical scenario of lower $nssSO_4^{2-}$ availability after accounting for the neutralization by NH_4^+, the role of HNO_3 becomes more significant for the Cl^- depletion, especially in winter and spring (Fig. 7c).

Considerable theoretical contribution of total organic acids to the observed Cl^- depletion was detected, clearly exceeding that of NO_3^- in summer (Fig. 7b). Among the organic acid anions, oxalate, MS^-, and malate exhibited the highest theoretical contributions to the observed Cl^- depletion (Fig. 7d). The maximal contribution of MS^- to Cl^- depletion (in respect to the contribution of the total fraction of organic acids) was up to 19% in spring, which is in relation to the enhanced phytoplankton productivity and DMS emissions. On the other hand, oxalate potentially contributed the most to the observed Cl^- loss among all organic acids (on average $65 \pm 10\%$), with the maximum in summer (Fig. 7d). Note that the formation and precipitation of organic salts in fine marine aerosols can modify the internal composition of atmospheric particles and, in turn, inhibit acid-catalyzed reactions to secondary organic aerosol (SOA) aging (Laskin et al. 2012). Moreover, the ability of particles to serve as CCN can be modified. Due to the

high abundance of sea salt and SOA, acid-displacement reactions may have a considerable impact on the climate in coastal areas, where marine aerosols are mixed with anthropogenic and/or biogenic emissions.

Overall, assuming that all available NO_3^-, $nssSO_4^{2-}$, and organic acids were involved in Cl^- depletion (even without considering their neutralization with other nss-cations), acid contribution could explain the total Cl^- loss only in summer, and up to 80% in spring and winter times. At this point, the unexplained Cl^- loss can be attributed to the replacement by organic acids not considered within this study. In addition, this could also imply that at the coastal Middle Adriatic, being influenced by combined air-mass inputs and variable meteorology throughout the year, alternative pathways may also play a partial role in triggering the Cl^- liberation from sea salt. The additional particulate Cl^- loss can be thus partially attributed to heterogeneous and interface chemistry with a variety of atmospheric trace species, including OH, HO_2, O_3, NO_2, N_2O_5, and $ClONO_2$ (Finlayson-Pitts 2003 and references therein).
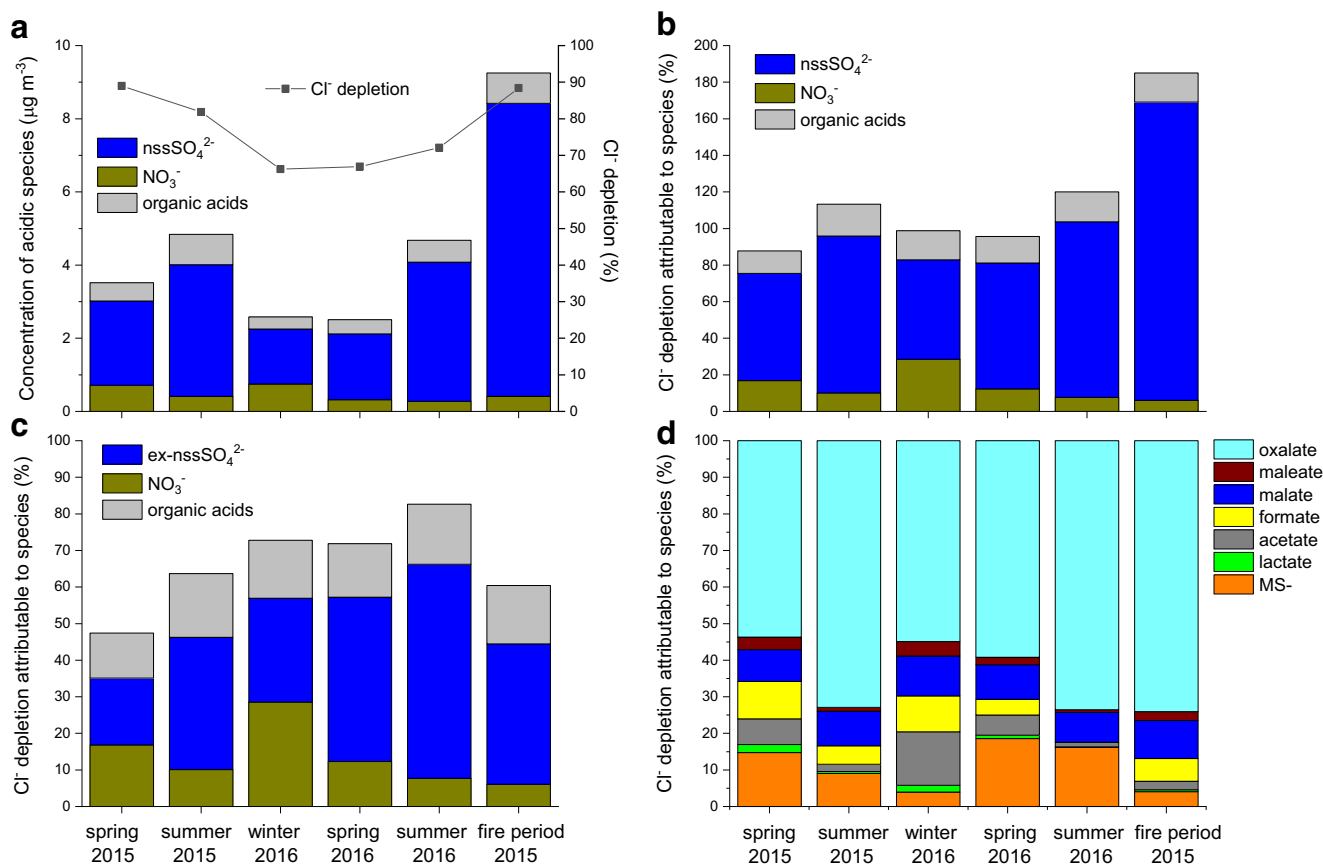

Fig. 7 Total Cl^- depletion and average concentrations of acidic compounds: non-sea-salt sulfate ($nssSO_4^{2-}$), NO_3^-, and the sum of organic acid anions, (a); theoretical Cl^- depletion for acidic species: $nssSO_4^{2-}$, NO_3^-, and the sum of organic acid anions, (b); theoretical Cl^- depletion for acidic species: ex-$nssSO_4^{2-}$ (obtained after $nssSO_4^{2-}$ neutralization by NH_4^+), NO_3^-, and the sum of organic acid anions, (c); and theoretical Cl^- depletion for organic acid species capped at 100%, (d); obtained for different seasons, and intensive open-fire period in the summer 2015 at the Middle Adriatic site

Sources of major ions of PM$_{2.5}$

A principal component analysis (PCA) was applied to identify the factors influencing the variance of the major ionic constituents in different seasons to get more insight into the possible sources of aerosol components at the Middle Adriatic site. Thus, the MS$^-$, Cl$^-$, NO$_3^-$, oxalate, Na$^+$, NH$_4^+$, K$^+$, and nssSO$_4^{2-}$ concentrations obtained in different seasons were the discriminating variables used in the analysis. No restrictions to principal components (PCs) were made prior to the analysis and the decision of how many were selected relied on the Kaiser criterion (factors having an eigenvalue greater than 1.0) (Kaiser 1960). The rotated factors loading matrix from PCA is shown in Table 3. Results show that 74.9, 84.1, and 72.1% of the total variance in spring 2015, summer 2015, and winter 2016, respectively, can be explained by two PCs. Three PCs were able to explain the main variances in spring and summer 2016 (they accounted for 80.9 and 93.1% of the variabilities, respectively) (Table 3).

For all seasons, the main principal component (PC1) was loaded with Na$^+$, nssSO$_4^{2-}$, NH$_4^+$, oxalates, and K$^+$ and occasionally NO$_3^-$, Cl$^-$, and MS$^-$. This suggests that marine aerosols (sea salts and biogenic emissions) modified by the presence of secondary components (sulfur and nitrogen compounds and oxalates) were the largest contributors to the analyzed PM$_{2.5}$ samples. nssSO$_4^{2-}$, oxalates, and K$^+$ were always included only in PC1, indicating their constant inflow. Moreover, Na$^+$ and NH$_4^+$ were underrepresented in 2016 in comparison to 2015 samples if only accounting for PC1. Therefore, their enrichment in 2016 was corrected by the addition of PC2. The observed correlation between Na$^+$ and NH$_4^+$ could also point to the connection between NH$_4^+$ and natural marine sources in the Middle Adriatic, as has previously been observed in other marine regions (Clarke and Porter 1993; Fomba et al. 2014; Jickells et al. 2003; Quinn et al. 1988). Cl$^-$ tends to be a more variable contributor to the PM mass as Na$^+$ (less significant correlation in PC1 or minor PC2 was observed), which indicates that acid catalyzed Cl$^-$ depletion is dependent on the weather conditions. In general, the second and third source factors (PC2 and PC3) can be considered as correction factors of PC1. PC2 is mainly related to natural marine sources and describes the enrichment of sea-spray aerosols in 2016 and Cl$^-$ depletion, as well as the seasonal biogenic marine sources of secondary MSA aerosols (i.e., MS$^-$ together with PC3). In addition, PC2 also accounts for the variations in NO$_3^-$ concentrations, again together with PC3.

Impact of open fires on water-soluble ion composition

Numerous studies have investigated BB impacts on ambient aerosol mass and composition (e.g., Chuang et al. 2013;

Engling et al. 2009; Jaffe et al. 2008). Distinct regional characteristics of BB smoke have been observed, suggesting that local BB emissions dominate aerosol chemistry. However, the transport and mixing of BB aerosols from upwind sources are also common (e.g., Zhang et al. 2012). Our results showed that fire events in summer 2015 substantially increased PM$_{2.5}$ mass concentrations (Fig. 4) and changed the abundance of the main ions in comparison to the no-fire samples in the same season (Table 1, Fig. 6). PM$_{2.5}$ mass concentrations reached on average 24.2 μg m^{-3} (summer average was 12.7 μg m^{-3}), and the significant increase of average of SO$_4^{2-}$, NH$_4^+$, and K$^+$ concentrations was also observed (Table 1, SI Table 6). While no significant changes were observed for ssSO$_4^{2-}$, the average concentration of nssSO$_4^{2-}$ increased by more than twice (from 3.6 to 8.0 μg m^{-3}). On the other hand, there was also no significant change in the concentrations of NO$_3^-$. BB particles were thus more likely exposed to high ambient levels of H$_2$SO$_4$ than HNO$_3$. The fresh BB particles which are thought to be initially composed of KCl, have most likely chemically evolved by H$_2$SO$_4$ + KCl reactions, due to the abundance of H$_2$SO$_4$ (Yamasoe et al. 2000; Li et al. 2003).

According to the NH$_4^+$/nssSO$_4^{2-}$ molar ratio being on average 1.5, all NH$_4^+$ was consumed in the neutralization with nssSO$_4^{2-}$ and (NH$_4$)HSO$_4$ was predominantly formed in the aerosol phase. Overall, Cl$^-$ depletion increased slightly from 82 to 88% in relation to the no-fire period (Fig. 7a). Other studies have also shown that Cl$^-$ is more efficiently depleted in wildfire plumes (Brown et al. 2017; Maudlin et al. 2015; Zauscher et al. 2013). The theoretical maximum percentages of observed Cl$^-$ loss attributable to the specific acidic species during the fire period are shown in Fig. 7b. Assuming that all available nssSO$_4^{2-}$ was involved in Cl$^-$ depletion, its contribution could explain the total Cl$^-$ loss during the open-fire events in summer 2015. However, after accounting for the neutralization of nssSO$_4^{2-}$ by NH$_4^+$, the average contribution from ex-nssSO$_4^{2-}$ again dropped to 38% (Fig. 7c).

Conclusions

Seasonal PM$_{2.5}$ concentrations, water-soluble ion composition, and possible sources were investigated for the first time at the Middle Adriatic coast, Croatia, in the period from April 2015 to July 2016. PM$_{2.5}$ is shown to be generally more affected by the southern marine inflow, especially in spring and summer, while more polluted continental air masses had more pronounced influence in winter. In addition, meteorological conditions largely affected temporal PM$_{2.5}$ levels in the area. Hot arid stagnant conditions typical of the region in summer are pertinent for prolonged lifetime of airborne particles and their photochemical aging in the atmosphere. As a result, more long-range transport and secondary aerosols were observed in

Table 3. Varimax rotated principal component analysis (PCA) loadings and statistical parameters of extracted components for the main water-soluble ions of PM$_{2.5}$ at the Middle Adriatic site obtained in different seasons. Values in italic are treated as statistically significant

Season	Spring 2015		Summer 2015		Winter 2016		Spring 2016			Summer 2016		
Variable	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3
MS$^-$	-0.29	*0.82*	-0.73	*0.59*	-0.93	0.23	-0.44	*0.59*	0.26	0.18	-0.02	*0.96*
Cl$^-$	*-0.58*	*0.57*	*0.49*	0.39	-0.05	*0.87*	0.04	*0.91*	-0.26	-0.17	*0.97*	-0.02
NO$_3^-$	*-0.75*	-0.21	*-0.58*	*0.80*	*-0.80*	0.13	-0.32	0.14	*0.90*	*-0.62*	0.47	0.25
oxalate	*-0.62*	-0.22	*-0.98*	0.03	*-0.78*	-0.06	*-0.89*	-0.01	0.15	*-0.85*	-0.44	0.25
Na$^+$	*-0.91*	0.11	*-0.93*	0.10	*-0.70*	*0.67*	*-0.70*	*0.61*	-0.04	*-0.74*	*0.64*	-0.04
NH$_4^+$	*-0.92*	-0.12	*-0.80*	-0.34	*-0.50*	*-0.64*	*-0.69*	*-0.51*	-0.35	*-0.81*	*-0.57*	-0.05
K$^+$	*-0.96*	-0.26	*-0.96*	-0.20	*-0.59*	*-0.42*	*-0.73*	0.05	-0.13	*-0.97*	0.18	-0.04
NssSO$_4^{2-}$	*-0.95*	-0.01	*-0.89*	-0.41	*-0.81*	-0.26	*-0.90*	*-0.31*	-0.21	*-0.93*	-0.29	-0.08
% variance	60.1	14.8	65.8	18.3	48.1	24.0	42.4	24.2	14.3	52.2	27.6	13.3
Eigen value	4.86	1.18	5.27	1.46	3.84	1.92	3.39	1.93	1.14	4.17	2.21	1.06

summer, in comparison to rainy autumn and windy winter and spring times.

The most abundant ion was SO$_4^{2-}$ followed by Na$^+$, NO$_3^-$, Cl$^-$, NH$_4^+$, and anions of carboxylic acids. Chemical analysis of PM$_{2.5}$ supported by PCA indicated that both secondary sulfate aerosols and sea salts from primary sea-spray emissions were the major contributors to fine aerosols at the coastal Adriatic area. Anthropogenic sulfates (anth-nssSO$_4^{2-}$) dominantly constituted the nssSO$_4^{2-}$ fraction throughout the year and are shown to be enhanced by the continental air transport to the Middle Adriatic site. In spring and summer periods, when air-mass inputs from the southern marine pathways prevailed, the estimated contribution of biogenic sulfates (bio-nssSO$_4^{2-}$) to the total nssSO$_4^{2-}$ presumably increased due to the enhancement of primary DMS production by phytoplankton and subsequent photochemical processing.

The investigated aerosols were mostly acidic. A substantial Cl$^-$ depletion was observed, greatly corresponding to the gas-phase loss in a form of HCl. The calculated average Cl$^-$ depletion was $72 \pm 12\%$, with the highest contribution of nssSO$_4^{2-}$ in all seasons. When accounting for the neutralization of H$_2$SO$_4$ by NH$_3$, the potential of HNO$_3$ and organic acids to considerably influence Cl$^-$ depletion is shown to increase. Due to the fraction of unexplained Cl$^-$ loss by nssSO$_4^{2-}$, NO$_3^-$, and organic acid ions, additional atmospheric chemistry processes potentially play a role in Cl$^-$ loss at the coastal Middle Adriatic area, but it merits further investigation.

We show that in addition to long-range transport, regional/local emission sources, such as domestic heating, land and ship traffic, and agricultural activities could influence air quality of the area. In particular, intensive open-fire events in summer 2015 substantially increased PM$_{2.5}$ mass concentrations, changed water-soluble ion composition in favor of nssSO$_4^{2-}$,

NH$_4^+$, and K$^+$, and slightly increased aerosol acidity, being also in line with the observed slight increase in Cl$^-$ depletion.

As there is no available data on the chemical composition of ambient aerosols at the Middle Adriatic coast, the present study serves as a basis for the comparison with future studies related to their various sources as well as the air quality conditions in the Adriatic and/or Mediterranean regions. Moreover, the presented data provides valuable background knowledge to better understand the type and variabilities of atmospheric deposition to this highly oligotrophic area of the Adriatic Sea and the other air–sea exchange processes.

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