RESEARCH ARTICLE



PM_{10} and $PM_{2.5}$ composition over the Central Black Sea: origin and seasonal variability

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Abstract Daily PM₁₀ and PM_{2.5} samples were collected between April 2009 and July 2010 at a rural site (Sinop) situated on the coast of the Central Black Sea. The concentrations of PM_{10} and PM_{25} were 23.2±16.7 and 9.8±6.9 µg m⁻³, respectively. Coarse and fine filters were analyzed for Cl⁻, NO₃⁻, SO₄²⁻, C₂O₄²⁻, PO₄³⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ by using ion chromatography. Elemental and organic carbon content in bulk quartz filters were also analyzed. The highest PM2.5 contribution to PM10 was found in summer with a value of 0.54 due to enhanced secondary aerosols in relation to photochemistry. Cl⁻, Na⁺, and Mg²⁺ illustrated their higher concentrations and variability during winter. Chlorine depletion was chiefly attributed to nitrate. Higher nssCa²⁺ concentrations were ascribed to episodic mineral dust intrusions from North Africa into the region. Crustal material (31 %) and sea salt (13 %) were found to be accounted for the majority of the PM₁₀. The ionic mass (IM), particulate organic matter (POM), and elemental carbon (EC) explained 13, 20, and 3 % of the PM₁₀ mass, correspondingly. The IM, POM, and EC dominated the PM2.5 (~74 %) mass. Regarding EU legislation, the

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exceeded $PM_{2.5}$ values were found to be associated with secondary aerosols, with a particular dominance of POM. For the exceeded PM_{10} values, six of the events were dominated by dust while two and four of these exceedances were caused by sea salt and mix events, respectively.

Keywords $PM_{10} \cdot PM_{2.5} \cdot Mass closure \cdot Natural and anthropogenic exceedances \cdot The Black Sea$

Introduction

Aerosol (particulate matter) is a term for defining the particles suspended in the atmosphere. During the last three decades, the research focusing on the aerosols has tremendously increased and these studies have revealed their key functions in the earth system sciences and public health. They may play an essential role in geophysical and geochemical global processes such as climate change, hydrological cycle, and biogeochemical cycles. Aerosols can modify the Earth's radiation budget and can affect climate directly by scattering and absorbing both solar and Earth's radiation (Arimoto 2001; Harrison et al. 2001; Satheesh and Moorthy 2005). Aerosols serve as ice nuclei (IN) or cloud condensation nuclei (CCN), and they can influence the concentration and size distribution of cloud droplets, alter the distribution of rainfall and their radiative properties (Levin et al. 2005; Huang et al. 2006; Chen et al. 2007). Atmospheric deposition (wet and dry modes) may have negative and positive impacts on marine environments. They supply macronutrients and micronutrients, such as P and Fe, respectively, or trace elements such as copper, which might play a significant role in low nutrient low chlorophyll (LNLC) and high nutrient low chlorophyll (HNLC) regions of the world oceans (Herut et al. 2005; Paytan et al. 2009). Their adverse effect on public health

has been shown by a great deal of studies, by means of deposition in the lungs and potential toxicity to human (Singh et al. 2002; Englert 2004 and references therein). The European Community has introduced legislative values for PM₁₀ and PM_{2.5} concentrations for monitoring particulate matter monitoring. The annual mean PM₁₀ and PM_{2.5} values have been bounded to 40 and 25 μ g m⁻³, respectively. However, the daily PM₁₀ value has been limited to 50 μ g m⁻³, which is only to be 35 events/year (EU legislation; Directive 2008/50/EC).

Many studies have been carried out in the Western and Eastern Mediterranean, with a focus on temporal and spatial variability of PM_{10} and $PM_{2.5}$, origin of PM_{10} and PM_{2.5}, aerosol trace metal and ionic composition, impact of atmospheric deposition on marine productivity, groundbased lidar/sun photometer, and remote sensing observations for monitoring aerosol vertical structure and their optical properties (Koçak et al. 2012 and references therein). On one hand, in the Black Sea region, research about atmospheric sciences is limited, and the reported works were performed either during short oceanographic cruises or addressed one class of elements (ionic composition or trace metals, Hacisalihoğlu et al. 1991; Kubilay et al. 1995; Karakaş et al. 2004). No work reported organic carbon (OC) and elemental carbon (EC) levels for the area. On the other hand, studies have been carried out to assess the atmospheric deposition of trace elements, nitrogen, phosphorus, and sulfur over the Black Sea (Bartnicki and Fagerli 2008; Medinets and Medinets 2012; Theodosi et al. 2013; Im et al. 2013).

The Black Sea is bordered by industrialized and semiindustrialized countries which act as a continuous source of man-made aerosols (Kubilay et al. 1995; Karakaş et al. 2004). In contrast, the arid desert regions such as North Africa may provide mineral dust particles which are transported in the form of episodic dust pulses (Kubilay et al. 1995). The present long-term study aims at determining PM₁₀ and PM_{2.5} levels, the origin, and aerosol chemical composition of their exceedances in the Central Black Sea. Furthermore, the temporal variability and the probable sources of water-soluble ions have been explored. The final aim is to provide for the first time to our knowledge an organic and elemental carbon levels and variability in the Black Sea and a comprehensive picture on aerosol chemical composition and sources at this under-sampled area of the world based on a daily sampling performed during a year long period.

Materials and methods

Site description and sample collection

Aerosol sampling campaign was carried out at a rural site located on the coastline of the Central Black Sea, Sinop

(42.04° N. 35.04° E). Turkey (Fig. 1). Low-volume dichotomous stacked filter unit (SFU) was located at Sinop University, Fisheries Faculty (at an altitude of ~13 m, \sim 200 m away from the sea). From north-southeast, sampling site looks directly out over the Black Sea. The immediate vicinity of the sampling site is surrounded by forest trees and small villages. Sinop is a small city with a population of 100,000. A total of 404 daily aerosol filter samples were collected by using dichotomous stacked filter unit low-volume sampler flow rates of around 16 L min⁻¹ on nuclepore polycarbonate filters (47 mm). Gent type SFU sampler was utilized in order to collect atmospheric aerosol particles in two size classes namely coarse (n=404) and fine (n=404). Overall, Gent type SFU consists of two-stage filter holder, cylindrical cassette holder with a 10-um cut of point, protective shield. gas meter, and diaphragm pump. SFU acts as a two-stage sampler when sampler operates at a flow rate of 16 L min⁻ (Koçak et al. 2007b). In addition to polycarbonate filters, a total of 289 bulk quartz filters (diameter 47 mm) were simultaneously obtained by using low-volume vacuum pump throughout the sampling period. The quartz filter were prebaked for 6 h at 450 °C and wrapped in pre-baked aluminum foil.

Aerosol sampling for nuclepore filters was commenced in April 2009 and ended in July 2010, with a temporal resolution of 24 h. The percentage of sampling coverage per month at Sinop over the whole sampling period was found to range from 60 to 97 %, with a mean annual coverage of 84 %. The sampling was generally interrupted due to official holidays. Aerosol sampling for quartz filters was started in April 2009 and terminated in February 2010. Considering the sampling



Fig. 1 Location of sampling site at the Central Black Sea region, Sinop

period (April 2009–July 2010), the percentage of coverage for quartz filters was about 60 %.

Aerosol measurements

Particulate mass concentrations in polycarbonate filters (coarse and fine modes) were determined gravimetrically with a microbalance ($\sim 0.5 \ \mu g \ m^{-3}$). After sampling, filters were equilibrated and weighted under well-stabilized temperature and relative humidity (~25 °C and ~50 % RH; Koçak et al. 2007a). Water-soluble ions in polycarbonate filters were measured by ion chromatography instrument. For this purpose, one quarter of the filter was extracted for 45 min in 10 mL of ultra-pure water (18.2 Ω) by sonic shaker, and about 100 µL chloroform was added as preservative to prevent biological activity after removing the filter substrate. The concentrations of water-soluble anions (Cl⁻, NO₃⁻, SO₄²⁻, C₂O₄²⁻, PO_4^{3-}) were determined with a Dionex AS4A-SC separation column, sodium hydroxide eluent, and ASRS-I suppressor. Nevertheless, water-soluble cation (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca^{2+}) concentrations were measured with a Dionex CS12-SC separation column, methane sulfonic acid eluent, and CSRS-I suppressor (for more details, see Bardouki et al. 2003). The detection limits for water-soluble ions were better than 1 ppb while the blank contributions were less than 10 %. The thermal-optical transmission (TOT) technique (Birch and Cary 1996; Sunset Laboratory OC/EC Analyzer) was applied to determine the concentrations of OC and EC in the quartz filters (for more details on sampling and measurements, see Bardouki et al. 2003; Koulouri et al. 2008 and Theodosi et al. 2010).

Briefly, 1-cm² punch from a quartz filter was placed in a boat and placed in the path of a red light diode laser, monitoring transmittance of the filter throughout analysis (in order to establish OC/EC split time). The carbon species presented in the filter were converted to carbon dioxide in an oxidation oven immediately downstream from the primary oven, and then, the carbon dioxide is reduced to methane before passing into a flame ionization detector. The first consisted of He mode, keeping the sample in helium atmosphere while heating the sample in four steps: 310, 480, 610, and 850 °C. The second step comprised of He/O₂ mode, keeping the sample in He/O₂ mixture and heating the filter by applying consecutive temperature steps: 600, 675, 750, 825, and 890 °C. Blanks for EC were close to the detection limit (0.1 ugC/cm²) whereas for OC never exceeded 20 % of the measured value.

Calculation of mass closure and air mass back trajectories

Following Sciare et al. (2005), Gerasopoulos et al. (2006), and Guinot et al. (2007), the total amount of crustal material can be derived by multiplying $nssCa^{2+}$ mean concentration by a factor of 8–12.5.

About 70 samples were used for assessing our calculation by comparing the amount of crustal material using both Fe and nssCa²⁺. The amounts of crustal material for these samples were calculated by the mean Fe concentration assuming a relative ratio to the upper crust of 3.1 % (Koçak et al. 2007a) and by multiplying nssCa²⁺ mean concentration by a factor varying between 8.5 and 12 (Guinot et al. 2007). The best fit between the two "dust" estimations was achieved using a conversion factor of 9 as under these circumstances, a slope of 3.2 (r=0.9) was obtained. Based on Cesari et al. (2012), the choice of the reference crustal element and the soil type affects the uncertainties of such dust estimation, reaching up to 100 %, and thus, our estimation of crustal material may have notable uncertainty.

The sea salt contribution was calculated from Na⁺ concentration assuming that it had pure marine origin (Turekian 1976; Koçak et al. 2007a). Ionic mass (IM) was the sum of $nssSO_4^{2-}$, NO_3^- , $C_2O_4^{2-}$, NH_4^+ , $nssK^+$, and $nssMg^{2+}$. Elemental carbon mass was equivalent to the arithmetic mean concentration of EC. Conversion factors of 1.4 and 1.7–2.1 have been suggested for urban (Putaud et al. 2004; Lonati et al. 2007) and rural (Bardouki et al. 2003; Bougiatioti et al. 2013) atmospheres to estimate particulate organic matter (POM) contributions to PM mass, respectively. Subsequently, POM mass was calculated by using mean value of OC and a factor of 1.8. Furthermore, POM and EC mass distributions between PM_{2.5} and PM₁₀ were assumed to be the ratios of 7/10 and 9/10, respectively (Bardouki et al. 2003).

Five-day backward trajectories reaching at 1, 2, 3, and 4 km level between April 2009 and February 2010 were computed by the HYSPLIT Dispersion Model for Sinop sites (HybridSingle Particle Langrangian Integrated Trajectory; Draxler and Rolph 2003) and presented by 1-h endpoint locations with regard to latitude and longitude. Cluster analysis was applied in order to classify air mass back trajectories (Kocak et al. 2009 and references therein). The results from cluster analysis is given in Fig. 2, along with the means of clusters and calculated frequencies for each cluster. Starting from northwest, there are two clusters (1: northwest-long and 2: northwest-short). The first cluster (NWL) demonstrates trajectories with long fetch (high wind speeds) from the Atlantic then sweeping Europe and explaining 8.8 % of the airflow. The second cluster (NWS) also indicates air flows from northwest; however, there are relatively shorter (or slower) than those the first cluster and accounting 24.7 % of the trajectories. The third cluster (3, NES) shows trajectories with slow wind speed (short fetch) from Azov Sea then passing through the south of the former Soviet Union, representing 24.7 % of the air flow. The fourth cluster (4) illustrates short trajectories originating from south Turkey (ST, particularly Anatolia), elucidating 20.9 % of the air flow. The fifth and sixth clusters (5: SAH and 6: SWL) reveal trajectories originating from



Fig. 2 Average air mass back trajectory clusters for 1 km level. The percentages of each air flow presented in parenthesis

southwest, clarifying 5.9 and 15.1 % of the air flow, respectively. The fifth cluster originates from North Africa then sweeping west of the Turkey. The sixth cluster emerges from Atlantic; then, air flows pass through Spain, Italy, Greece, and the Marmara region of the Turkey before arriving sampling site.

Results and discussion

General characteristics of data set

Tables 1 and 2 shows statistical summary for the aerosol data set attained from Central Black Sea between 1 April 2009 and 23 July 2010, including arithmetic mean concentrations as well as their standard deviations and minimum and maximum values. The mass concentrations of PM₁₀ and PM_{2.5} in Sinop site were in the range of 1.4–160 and 0.3–50.2 μ g m⁻³, with arithmetic mean mass concentrations of 23.2 ± 16.7 and $9.8\pm$ 6.9 μ g m⁻³, respectively. The mean PM₁₀ concentration at Sinop was substantially lower than those levels reported for Mediterranean and Black Sea, with an exception of Montseny. The PM_{2.5} value was comparable to that observed for Erdemli, whereas as in the case of PM10, PM2.5 values were considerably lower than those detected for the sampling sites in the Mediterranean and the Black Sea. For instance, PM₁₀ and PM_{2.5} values at Sinop were found to be 2.3 and 3 times lower than those observed for Zonguldak, respectively. This difference can be mainly ascribed to steel production, power generation, coal-related economy, and coal production in the vicinity of Zonguldak (Tecer et al. 2008).

Relative size distribution of PM and water-soluble ions in coarse and fine fractions are demonstrated in Fig. 3. About 58 % of the atmospheric particulate mass was associated with coarse mode while the remaining mass (42 %) was accounted for fine fraction. As stated before (Putaud et al. 2004; Koçak et al. 2007a; Querol et al. 2009), the $PM_{2.5}/PM_{10}$ ratios denoted large variability from sampling site to sampling site due mainly to aerosol chemical composition which is influenced by myriad of sources (natural and anthropogenic). The ratio of approximately 0.4 at Sinop implied that the site was mainly affected by primary aerosols such as sea salt and/or crustal material.

The PM_{2.5} mass concentrations demonstrated strong seasonal variability in comparison to PM₁₀ with not clear seasonal trend (Table 1). The highest PM_{2.5} was detected in summer/ winter with a value of 11.4/10.3 μ g m⁻³ and the lowest mass concentration in spring/autumn (~8.5 μ g m⁻³). The PM₁₀ concentration in autumn was found to be 13 % lower than those observed in remaining seasons. This slight difference might be attributed to relatively lower concentrations of sea saltoriginated ions (such as Na⁺ and Cl⁻, see Fig. 5a). In fact, the PM_{2.5} mass concentrations of the former were found to be 1.2 times higher than the latter. PM_{2.5}/PM₁₀ ratio was lowest in spring (0.36) and highest in summer (0.54) while this ratio in autumn was comparable to that of calculated for winter (around 0.42).

Considering water-soluble ions (Table 2, TS1), the highest average mean concentration was calculated for sulfate with a

Fig. 3 Relative contributions of PM and aerosol species in the fine and coarse modes



value of $1.69\pm1.23 \ \mu g \ m^{-3}$ while nitrate, calcium, and ammonium concentrations were 0.44 ± 0.34 , 0.81 ± 0.85 , and $0.41\pm0.32 \ \mu g \ m^{-3}$, respectively. Potassium, oxalate, and phosphate had mean concentrations of 0.23 ± 0.11 , 0.08 ± 0.05 , and $0.06\pm0.03 \ \mu g \ m^{-3}$, in turn. Concentrations of sea salt-derived watersoluble ions Cl⁻, Na⁺, and Mg²⁺ were in order of 1.45 ± 1.60 , 0.94 ± 0.94 , and $0.13\pm0.13 \ \mu g \ m^{-3}$. OC and EC concentrations were 3.1 ± 2.1 and $0.55\pm0.33 \ \mu g \ m^{-3}$, respectively.

Table 3 shows the water-soluble ion and organic and elemental carbon concentrations measured at Mediterranean and Black Sea. Concentrations of sea salt-originated aerosols (such as Cl^- , Na^+ , and Mg^{2+}) in Sinop were found to be almost 3.5 times lower than those observed for Erdemli while their concentrations were comparable to those detected at Finokalia and İstanbul. On the other hand, chloride concentration was approximately five times higher than that of Amasra since the latter site was 3.5 km away from the coast of the Black Sea. The lowest concentrations of secondary aerosols (such as sulfate, nitrate, oxalate, and ammonium) were observed at Sinop. Water-soluble calcium at Sinop was 30 to 50 % less than those observed for İstanbul, Finokalia, and Erdemli. However, its concentration was found to be 2.5 times higher comparing to value reported for Amasra. OC and EC concentrations at Sinop and Finokalia were substantially (at least two times) lower than values reported for İstanbul since the later is megacity and considerably influenced by various combustionrelated sources such as traffic, fossil fuel, solid fuel, and municipal incineration (Theodosi et al. 2010; Koçak et al. 2011). On the other hand, OC/EC ratios for Sinop (7.7) and Finokalia (5.1) were found to be 2.5 times higher than value observed for İstanbul (1.98), denoting that the OC concentrations at Sinop and Finokalia sites were mostly aged/oxidized and their

Table 1Mean PM_{10} and $PM_{2.5}$
concentrations ($\mu g m^{-3}$) and
corresponding PM _{2.5} /PM ₁₀ ratios
for different types of Black Sea
and Mediterranean sites

Region	Sampling Site	Category	PM_{10}	PM _{2.5}	PM _{2.5} /PM ₁₀	Reference
Central Black Sea	Sinop	Rural	23.2	9.8	0.42	Present study
Winter			24.7	10.3	0.42	
Spring			23.5	8.4	0.36	
Summer			23.1	11.4	0.54	
Autumn			20.0	8.5	0.43	
Western Black Sea	Zonguldak	Industrial	53.2	29.4	0.57	Tecer et al. (2008)
Eastern Mediterranea	n					
	Finokalia	Natural	31	18	0.58	Querol et al. (2009)
	Erdemli	Rural	36.4	9.7	0.25	Koçak et al. (2007a)
Western Mediterranea	an					
	Montseny	Rural	17	13	0.77	Querol et al. (2009)
	Tarragona	Urban	37.4	21.8	0.58	Querol et al. (2004)
	Madrid	Kerbside	47.7	34.1	0.72	Querol et al. (2004)

Table 2 Statistical summary of ionic composition, OC, and EC($\mu g m^{-3}$) measured in PM10 collected at Sinop over the period of April2009 and July 2010

Species	Mean (±std. dev.)	Min-max
Cl	1.45 (±1.60)	0.01-12.88
NO_3^-	0.44 (±0.34)	0.02-2.79
SO_4^{2-}	1.69 (±1.23)	0.02-23.52
$C_2 O_4^{2-}$	0.08 (±0.05)	0.00-0.29
PO4 ³⁻	0.06 (±0.03)	0.01-0.22
Na ⁺	0.94 (±0.94)	0.03-7.15
$\mathrm{NH_4}^+$	0.41 (±0.32)	0.01-6.95
K^+	0.23 (±0.11)	0.01-0.92
Mg^{2+}	0.13 (±0.13)	0.01-0.93
Ca ²⁺	0.81 (±0.85)	0.08-11.77
OC	3.59 (±1.80)	0.80-17.50
EC	0.47 (±0.30)	0.09–2.22

404 and 289 samples were analyzed for ions and OC/EC, respectively

substantial amount were impacted by secondary organic aerosols. The estimation of the secondary organic carbon is difficult mainly due to the absence of unique OC/EC ratio representing primary carbonaceous source. Aforementioned ratio might be affected by meteorology, diurnal and seasonal variations in emissions, and local and distant sources (Na et al. 2004). Thus, the relationship between OC and EC during February was used in order to calculate OC/EC ratio since the meteorological conditions in this month was relatively limited photochemistry. There was a strong correlation coefficient between OC and EC (r=0.88) with an OC/EC ratio around 5.

Based on simple formula $[OC_{secondary}=OC_{tot}-(OC_{primary}/EC_{primary})\times EC_{primary}]$, OC/EC=5, (Bougiatioti et al. 2013 and

references therein) 35 % of the organic carbon might be attributed to secondary organic aerosols. On the other hand, Kupiainen and Klimont (2004) estimated a ratio of 0.7 for fossil fuel sources in the "old" 15 EU countries, but a ratio of 1.2 for the new member states. Therefore, if OCprimary/ EC_{primary} ratio of 1 applied (Bougiatioti et al. 2013 and references therein), the secondary organic aerosol contribution to OC could reach 85 %. As is well documented in the literature (Koçak et al. 2007b; Koulouri et al. 2008) sea salt-originated species (Cl⁻, Na⁺, and Mg²⁺), and calcium were mainly found to be associated with the coarse fraction and more than 75 % of their observed mass concentrations were found in this mode. On the other hand, water-soluble ions such as nitrate, oxalate, and phosphate were moderately monopolized by coarse mode. Approximately, 55 % of their mass concentrations were accounted for aforementioned aerosol fraction. Contributions of coarse fraction for nitrate and phosphate were lower than those observed for Eastern Mediterranean sites (Markaki et al. 2003; Koçak et al. 2007b). In sharp contrast, the water-soluble ions ammonium and sulfate were primarily dominated by fine aerosol particle, comprising of 90 and 75 %, respectively, which are in agreement with the previous studies (Bardouki et al. 2003; Koulouri et al. 2008). Taking into account potassium, only 60 % of its detected mass concentration was attributed to fine mode.

Ion balance in coarse and fine fractions

An ion balance has been applied as a tool to determine any missing parameters for the ionic composition. For this purpose, the relationship between sums of anion and sums of the cations as equivalents will be used for assessing any missing parameters. The relationship between sums of ions and sums of cations for coarse and fine fractions are illustrated

Table 3 Statistical summary of ionic and OC and EC ($\mu g m^{-3}$) composition measured in PM₁₀ collected at different sides over Black Sea and Mediterranean

PM ₁₀ (μg m ⁻³)	Erdemli, TR Koçak et al. 2007b	Finokalia, GRE Koulouri et al. 2008	İstanbul, TR Theodosi et al. 2010	Amasra, TR Karakaş et al. 2002	Sinop, TR This study
Cl	5.49	1.51	1.66	0.31 ^a	1.45
NO_3^-	1.85	1.73	1.74	0.92	0.44
SO_4^{2-}	4.95	5.48	4.73	4.9	1.69
$C_2 O_4^{2-}$	0.39	0.19	0.21	-	0.08
Na^+	3.43	1.38	2.69	-	0.94
$\mathrm{NH_4}^+$	0.85	1.62	0.92	1.4	0.41
K^+	0.20	0.19	0.71	-	0.23
Mg^{2+}	0.49	0.19	0.23	-	0.13
Ca ²⁺	1.56	1.30	1.49	-	0.81
OC	_	2.53	6.65	-	3.10
EC	-	0.31	2.92	_	

^a Chloride was obtained by Neutron activation instrument

as scatter plot with corresponding slopes of regressions and correlation coefficients in Fig. 4a, b, respectively. The slope of the regression line for coarse mode demonstrated value of 1.14 accompanying with a strong correlation coefficient (r=0.94, intercept=17.6). The observed slope was found to be considerably higher than unity, and it might be attributed to the presence of carbonate and/or bicarbonate in the coarse fraction. If this is the case, one should expect to find an association of calcium with anion deficiencies. Indeed, a statistically significant correlation was observed when nssCa²⁺ and nssMg²⁺ calcium concentrations were plotted against the anions deficiency (y=-0.8x - 1.9; r=0.95 and y=-0.09x - 0.7; r=0.58, respectively), described as an excessive amount of positively charged ions, suggesting that about 80 and 9 % of the anion deficit was explained by nssCa²⁺ and nssMg²⁺, respectively, and implying carbonate (11 %) as a probable missing anion in coarse mode. Similar findings have been reported for Western Mediterranean (Contini et al. 2014a). On the other hand, as can be noticed from Fig. 4b, the slope of the



Fig. 4 Relationship between sum of cations and anions (neq m^{-3}). Coarse fraction (a) and fine fraction (b). *S.C* and *S.A* refer to sum of cations and sum of anions, respectively

regression line for the fine mode was found to be slightly lower than unity with a value of 0.94 (r=0.96, intercept= 8.8). This slight difference might be attributed to association of H⁺ with sulfate. In fact, there was a statistically significant relationship between sulfate and cation deficiency, with correlation coefficient of 0.67.

Temporal variability of the Black Sea aerosols

The temporal variability in the concentrations of the watersoluble ions in PM₁₀ over the study period from April 2009 to July 2010 is demonstrated in Fig. 5. As can be clearly noticed from the figures, the concentrations for all species demonstrated prominent variability. The daily change in concentrations was order of magnitude, leading to elevated standard deviations (see Table 1). It should be noted that the lowest values of PM₁₀ and water-soluble ion were observed in May 2010. In order to identify contrast between May 2009 and 2010, aerosol optical thickness, air mass back trajectories, and regional rain amount were used (see SF1). The noticeable difference might be particularly ascribed to (a) increase in the amount of rain from 2009 to 2010 and (b) increase in the air flow originating from NWS and NES (see section "Calculation of mass closure and air mass back trajectories" and SF1). This is also supported by aerosol optical thickness (AOT) derived for May 2009 and 2010 over the whole region including Black Sea coast, former Soviet Union, Balkans, and Eastern Europe. For example, AOT over the Sinop in May 2010(0.13) was almost two times lower that of observed for 2009 (0.28).

Scrutinizing the temporal variability of the water-soluble ions illustrated in Fig. 5, the following general summary may be made:

1. The sea salt-originated water-soluble atmospheric particles such as Cl-, Na+, and Mg2+ essentially illustrated (Fig. 5a) their higher concentrations and variability during winter months (December, January, and February). These species did not reveal obvious changes in their concentrations between April and September months. In contrast, sea salt species presented substantial increase in their concentrations from autumn to winter, reaching the highest values (for example $Cl^{-} \sim 13 \ \mu g \ m^{-3}$) particularly in February. This remarkable increase in the concentrations of sea salt species from spring to winter might be attributed to local meteorological conditions such as wind speed. As it is well established, the sea salt species are produced at the sea surface by the bursting of air bubbles as a result of entrainment of air induced by wind stress (Blanchard and Cipriano 1983; O'Dowd et al. 1997). These bubbles are most potent in whitecaps associated with the breaking of waves which commences at about $3-4 \text{ m s}^{-1}$ (O'Dowd et al. 1997). The unsettled weather



Fig. 5 Daily variability in the concentrations of aerosol species in PM₁₀ at Sinop site between April 2009 and July 2010. Na⁺ and Cl[−] (a), nssSO₄^{2−} and NH₄⁺ (b), NO₃[−] and nssCa⁺ (c), OC and EC (d)

conditions during winter season (wind speed $\sim 3.2 \text{ m s}^{-1}$) may lead to enhanced sea salt generation and hence sea salt-originated species in the atmosphere. Similar findings at Amasra (Western Black Sea) have been reported for marine elements such as Na (Karakaş et al. 2004). The slope of the regression lines between Na⁺ and Mg²⁺ (r=0.99) and Na⁺ and Cl⁻ (r=0.98) were 0.13 and 1.64, respectively. Furthermore, the Mg²⁺/Na⁺ ratio was identical to that observed for seawater (0.12). On the other hand, the Cl^{-}/Na^{+} ratio (1.68) was lower than that reported for seawater (1.79), suggesting Cl⁻ depletion. On average, Cl⁻ depletion was found to be around 6 %. This might be attributed to reaction between alkaline sea salt particles and acidic species (Bardouki et al. 2003). For example, this ratio demonstrated dramatic decrease from spring (1.79) to summer (1.42) period. Similar observations have been reported in Eastern and Western Mediterranean (Bardouki et al. 2003; Kocak et al. 2004; Contini et al. 2014a). For instance, Cl⁻/Na⁺ ratios at Finokalia for winter and summer were 1.76 and 1.16, respectively. However, Cl⁻ depletion (35 %) at Finokalia during summer was higher than that calculated for Sinop (21 %). In fact, a significant relationship (r=0.79) was found when the excess Na^+ (µeq m⁻³, relative to Cl⁻) was plotted against NO₃⁻ (μ eq m⁻³) during summer with a slope of 0.68 and intercept of 0.003. Therefore, chlorine deficiency can mainly be ascribed to reaction between sea salt particles and gaseous nitric acid. Since the excess Na⁺ was only sufficient to neutralize 68 % of the nitrate (NaNO₃), other forms of nitrate might be present such as Ca(NO₃)₂ and Mg(NO₃)₂ (Contini et al. 2014a).

Unlike sea salt aerosols, water-soluble aerosols $nssSO_4^{2-}$, 2. NO_3^- , and NH_4^+ ($C_2O_4^{2-}$ as well) denoted (Fig. 5b, c) relatively more complex temporal variability. Watersoluble species nssSO₄²⁻, NO₃⁻, and NH₄⁺ values although they did not present a clear seasonality, generally higher values were found during summer and spring months. Indeed from April to September, a steep increase in $nssSO_4^{2-}$, NO_3^{-} , and NH_4^+ concentrations was clearly recognized with values frequently exceeding their calculated arithmetic means. As it is well documented in the literature (Luria et al. 1996; Mihalopoulos et al. 1997; Erduran and Tuncel 2001; Bardouki et al. 2003), the prevailing summer conditions (high solar radiation and hence photochemistry) result in enhanced levels of aforementioned water-soluble species. From September to mid-November, their concentrations were found to be diminishing gradually, with values substantially smaller than their arithmetic means. This decline might be attributed to decrease in photochemistry and efficient wet scavenging relative to summer period (temperature \sim 23 °C). In spite of low photochemistry and efficient precipitation scavenging, higher concentrations of these species were also obvious in winter months. Elevated values during winter might be as a result of local activities, i.e., the residential heating and vehicular traffic (Tecer et al. 2008).

- 3. As it is well documented in the literature, in addition to Al, Fe, Si, and Ti, Ca is also considered as an indicator of crustal material (Kubilay et al. 1995; Kubilay and Saydam 1995; Güllü et al. 1998; Karakas et al. 2004). Daily concentrations of water-soluble nssCa²⁺ (Fig. 5c) indicated strong variability. The nssCa²⁺ concentrations varied in order of magnitude from day to day. For instance, $nssCa^{2+}$ concentration was around of 0.6 µg m⁻³ on 7 November 2009 whereas reached concentration of $9 \,\mu g \,m^{-3}$ on 8 November nssCa²⁺, with a 15-fold increase when the air masses trajectories originating from the Saharan Desert (see Fig. 7a-c). Indeed, Kubilay et al. (1995) has been shown that aerosol chemical composition over the Black Sea atmosphere was significantly influenced by air masses originating from North Africa, which is a prime source of the atmospheric mineral dust particles. On the other hand, previous studies (Karakaş et al. 2002, 2004) in the region showed that crustal elements such as Al, Fe, and Ca had higher concentrations in the summer, and this seasonality was attributed to easier resuspension of the soil particles throughout dry summer period. In the present study, nssCa²⁺ generally demonstrated lower values in summer 2009 while nssCa²⁺ showed higher concentrations in summer 2010. The Central Black Sea region is considerably influenced by precipitation during the summer (Moulin et al. 1998). Furthermore, the vicinity of the sampling site is covered by forests and soilage. In order to clarify difference between summer 2009 and 2010, aerosol optical thickness, air mass back trajectories, and regional rain amount were used (see SF2). The distinct difference might be attributed to (a) increase in southerly air flow (43 %) in summer 2010 compared to 2009 (15 %) and (b) decrease in the amount of rain from summer 2009 to summer 2010. The AOT also supports the difference between summer 2009 and 2010, the later was (0.28) at least 1.7 times higher compared to 2009 (0.16).
- 4. As can be deduced from the Fig. 5d, organic carbon demonstrated higher concentrations and variability during May. The lower values were observed in summer particularly in June and July; then, apparent increase was detected in August. Afterward, OC concentrations denoted substantial enhancement throughout autumn and winter seasons. It should be highlighted that the observed seasonality for OC at Sinop site (Central Black Sea), with a

summer minimum, is contrasting to that of Eastern Mediterranean (Bougiatioti et al. 2013). These authors have suggested that the elevated OC concentrations in summer were resulted from increased photochemistry while the lowest values during the winter (January and February) were associated with reduced photochemistry and enhanced precipitation scavenging. On the other hand, elevated OC concentrations over Lombardy region, Italy (Western Mediterranean), in winter period were attributed to increased secondary OC formation (condensation) and lower boundary layer height compare to summer (Lonati et al. 2007). Consequently, the relatively high OC values in winter might be attributed to enhanced condensation of semi-volatile gaseous precursors and temperature inversions limiting dilution and allowing super saturation conditions. High OC concentrations in winter may be also associated with the adsorption of semi-volatile organic compounds onto existing aerosols and the dissolution of soluble gases that may go through reactions on particle surfaces (Lonati et al. 2007). In general, EC concentrations showed steady decrease from spring to autumn, with a minimum in September. Thereafter, EC concentrations gradually enhanced from autumn to winter. Higher EC values in spring might be a result of the biomass burning in the region owing to farming facilities (Sciare et al. 2008) while elevated concentrations in winter might be associated with residential heating, coal burning, and lower boundary height.

Chemical composition of PM₁₀ and PM_{2.5}: exceeded levels of the European daily limit value

Unfortunately, the complete characterization for aerosol composition at Sinop was not possible since the trace metal measurements were not available for the whole data set. Nonetheless, the chemical characterization of the exceeded PM₁₀ and PM₂₅ levels would be useful for identifying origin of the aforementioned events. Figure 6a, b illustrates constructed chemical composition for PM₁₀ and PM_{2.5}. As can be deduced from the diagrams, the chemical composition of the aerosol population denoted substantial variability between PM₁₀ and PM_{2.5}. As expected, primary aerosols, namely dust and sea salt, were found to be accounted for the majority of the PM₁₀, with contributions of 31 and 13 %, respectively. The IM, POM, and EC contributions explained 13, 21, and 2 % of the PM₁₀ mass, correspondingly. The contributions for dust and sea salt decreased about three and two times in PM_{25} , being 11 and 8 % of the fine mode, respectively. The mass closure for fine mode demonstrated that IM, POM, and EC dominated the PM_{2.5} (~75 %) mass, explaining 22, 48, and 5 % of the observed mass. Considering mass closure,



Fig. 6 Mass closure for $PM_{10}(a)$ and $PM_{2.5}(b)$

approximately 20 and 6 % of the PM_{10} and $PM_{2.5}$ were attributed as unknown. The residual fractions might be attributed to the sources that are not accounted due to the absence of trace metals such as V, Ni, Pb, Cd Zn (residual oil, incineration, emissions from vehicular traffic from City of Sinop etc.), and residual water.

Figure 7a, b demonstrates the histogram for PM_{10} and $PM_{2.5}$, respectively, along with the corresponding legislative PM_{10} and $PM_{2.5}$ limit values established by European Commission for the PM monitoring. Throughout the study period, the majority (~94 %) of the PM_{10} values were found to be less than 50 µg m⁻³, but only 3 % (12 events) of the measured PM_{10} were exceeded the legislative value for PM_{10} . Likewise, the most (~98 %) of the $PM_{2.5}$ concentrations were less than 25 µg m⁻³ while 2 % of the concentrations were



Fig. 7 Histogram for PM_{10} (**a**) and $PM_{2.5}$ (**b**) along with corresponding exceeded days and EU limit values

higher than that of legislative $PM_{2.5}$ value. PM_{10} concentrations for exceeded values were found to be ranging from 52 to 160 µg m⁻³ with an arithmetic mean of 70 µ m⁻³. On the other hand, exceeded values of $PM_{2.5}$ were found to be between 25.5 and 50.20µg m m⁻³ with a mean concentration of 33.4 µ m⁻³. As expected, exceeded $PM_{2.5}$ values were found be associated with secondary aerosols, with a particular dominance of POM.

Unlike PM_{2.5}, the origin of the PM₁₀ exceedances denoted great variability. For the exceeded PM₁₀ values, half of the events were dominated by dust (n=6) whereas two of them exceedances were caused by sea salt (n=2; 17 %). The remained values (mix events=4; 33 %) were not monopolized by any particular aerosol source. Similar studies were carried out in the Eastern (Kocak et al. 2007a), Western Mediterranean (Contini et al. 2014b), and over the Europe along with Eastern and Western Mediterranean (Viana et al. 2014). For instance, 90 % of the PM_{10} exceedances in the Eastern Mediterranean were attributed to natural aerosols namely mineral dust and sea salt. On the other hand, Viana et al. (2014) demonstrated that the PM_{10} exceedances in the Eastern Mediterranean were substantially influenced by natural aerosols up to 88 % (mineral dust, sea salt, and wild fires) compared to Western Mediterranean, relatively later being effected by man-made sources. The highest PM₁₀ concentration was observed on 8 November 2009 with a value of 160 $\mu g \ m^{-3}$ while the second highest value was found on 20 February 2010 with a concentration of 103 μ g m⁻³. Figure 8a, c presents air mass back trajectories and ozone mapping spectrometer aerosol index (OMI-AI) 8 November and 12 February, respectively, while Fig. 8b illustrates back trajectories and aerosol optical depth for 20 February 2010 due to the absence of OMI-AI. Air mass back trajectories for these events demonstrated at all levels airflow originating from south. All trajectories suggested that air masses arriving at Sinop were substantially influenced by North Africa. Furthermore, the satellite images for these events indicated the existence of the mineral dust over the whole Eastern Mediterranean and Black Sea. For example (as can be noticed from OMI-AI image, Fig. 8a), aerosol index over the Central Black Sea exceeded the value of 2.0 during 8 November. The dust origin of this event was also confirmed by the chemical composition (see Fig. 9). The source apportionment demonstrated that about 56 % of the observed PM10 mass originated from dust. Sea salt, IM, and POM accounted for 4.6, 2.4, and 4.4 % of the PM_{10} while EC contribution was negligible with a value of 0.4 %. On the other hand, the aerosol optical depth over the Central Black Sea was found to be high during 20 February, ranging from 0.6 to 1.0, while the source apportionment denoted that dust contribution accounted for about 54 % of the PM₁₀. Sea salt and POM explained 21.7 and 10.9 % of PM₁₀ mass, whereas IM and EC contributed only 3.4 and 1.6 %, respectively. Exceeded events on 8 November and 20 February were ascribed to dust episodes since their PM₁₀ masses were mainly dominated by aforementioned source. Even though, the event on 12 February was found to be considerably impacted by dust (27.5 %), it was attributed to sea salt since sea salt explained 42.9 % of the PM₁₀ mass. IM, POM, and EC accounted for 5.5, 17.4, and 1.8 % of the observed PM_{10} , respectively.

Fig. 8 Three-day back trajectories demonstrating the transport of air masses to the sampling site and OMI absorbing aerosol index (or aerosol optical depth). 8 November 2009 (a), 20 February 2010 (b), and 12 of February 2010 (c)



Interspecies correlation as a function of season

Correlations between aerosol species denote the degree to which they vary together. As pointed out in literature

(Bardouki et al. 2003; Koçak et al. 2004), strong correlation coefficients between two aerosol species point out (a) similar sources, (b) similar generation and/or removal mechanisms, and/or (c) similar transport patterns. Correlation coefficients



Fig. 9 Source apportionment analysis for PM_{10} during exceeded events. 8 November 2009, dust event (a), 20 February 2010, dust event (b), and 12 February 2010, sea salt event (c). *D* dust, *SS* sea salt, *IM* ionic mass, *POM* particulate organic carbon, *EC* elemental carbon

between aerosol species as a function of season revealed that how relationship between each one another varies with the origin of the source (Table 4).

Sea salt ions (Na⁺, Cl⁻, Mg²⁺) As expected, sea salt-derived ions denoted strong correlation coefficients between one another for all air flow categories, indicating that they are mainly arise from sea salt generation. These species demonstrated moderate correlation coefficients with acidic species sulfate, nitrate, and oxalate in spring and summer, denoting reaction between alkaline sea salt particles and acidic species (Mamane and Gottlieb 1992; Aymoz et al. 2004; Bardouki et al. 2003; Putaud et al. 2004).

nssSO₄²⁻ **and NH**₄⁺ Considering all seasons, nssSO₄²⁻ and NH₄⁺ showed strong correlation coefficients (p>0.80), representing neutralization of acidic sulfate by basic ammonium. Application of the regression analysis for each season revealed that around 80 % of the sulfate was neutralized by ammonium, with values ranging from 77 to 82 %. However, the complete neutralization was not achieved, implying the presence of NH₄HSO₄ (Bardouki et al. 2003). In general, these species showed moderate correlation coefficients with nitrate and oxalate, this relationship might be attributed to secondary aerosols.

 NO_3^{-} and $C_2O_4^{2-}$ Nitrate and oxalate indicated moderate correlation coefficients with OC and EC in winter. This might be ascribed to influence of combustion processes on the observed values of these species during winter, particularly due to residential heating (Tecer et al. 2008).

nssCa²⁺, nssK⁺, and PO₄³⁻ These water-soluble species has mixed origin. Phosphate may originate from both natural and anthropogenic sources such as mineral dust, sea salt, primary biogenic particles, and combustion (Mahowald et al. 2009 and references there in). Potassium may arise from crustal material, sea salt, biomass burning, and coal combustion (Mihalopoulos et al. 1997; Sciare et al. 2008; Bougiatioti et al. 2013). In spring and summer, there were moderate correlation coefficients between nssCa²⁺ and nssK⁺, revealing the possible influence of crustal source on potassium. In summer, the strong and moderate correlation coefficients were found between nssCa²⁺ and nssSO₄²⁻, nssCa²⁺ and NO₃⁻/C₂O₄²⁻, respectively. This might be attributed to either oxidation of gaseous precursors on the crustal particles or coagulation between fine particles of these acidic crustal aerosols (Aymoz et al. 2004; Kocak et al. 2007b). The moderate correlation coefficients between $nssK^+$ and $nssSO_4^{2-}$, NH_4^+ and $NO_3^$ might be attributed to secondary aerosols. There was a strong correlation coefficient between $nssK^+$ and PO_4^{3-} in autumn, dictating their common origin. There was a moderate correlation between phosphate and EC in winter, showing primary carbonaceous aerosols as potential sources for phosphate.

OC and EC Relatively lower correlation coefficients between OC and EC was found in summer and spring (r=0.62 and 0.67, respectively) while the correlation coefficients between these species were 0.83 and 0.73 in autumn and winter, respectively. This kind of relationships was attributed to various sources rather than a single dominant source (Na et al. 2004). Relatively weaker correlation coefficients in summer and spring might be associated with secondary organic aerosol formation. For instance, the moderate correlation coefficients between OC and NO₃^{-/}C₂O₄²⁻ might show the secondary nature (such as biomass burning) of OC in summer. In winter, these species denoted moderate correlation coefficients with nssCa²⁺, suggesting possible influence of man-made combustion processes on the calcium.

Influence of air flow on aerosol species

Table 5 demonstrates statistical summary for aerosol species as a function of air flow. The lowest PM_{10} concentration was found when air flow originated from NES. The observed value was at least 20 % lower than those calculated for other air flows. The higher PM_{10} mean values were associated with air flows from SAH and NWL probably due to enhancement in the

Table 4 Interspecies relationship as a function of season: winter (a), spring (b), summer (c), and autumn (d)

(a) Winter	Cl	NO ₃ -	SO4 ²⁻	$C_2O_4^{2-}$	PO ₄ ³⁻	Na ⁺	NH_4^+	K ⁺	Mg ²⁺	Ca ²⁺	OC	EC
Cl ⁻	1.00											
NO ₃ -	0.37	1.00										
SO4 ²⁻	-0.03	0.28	1.00									
$C_2O_4^{2-}$	0.42	0.51	0.31	1.00								
PO4 ³⁻	0.23	0.32	0.04	0.08	1.00							
Na ⁺	0.99	0.37	0.00	0.43	0.21	1.00						
NH_4^+	-0.25	0.26	0.93	0.24	0.04	-0.22	1.00					
K ⁺	-0.13	0.29	0.43	0.15	0.28	-0.09	0.45	1.00				
Mg ²⁺	0.98	0.39	0.00	0.45	0.26	0.99	-0.23	-0.08	1.00			
Ca ²⁺	0.58	0.46	0.00	0.49	0.48	0.53	-0.16	0.02	0.59	1.00		
OC	0.41	0.48	0.06	0.47	0.29	0.39	0.04	0.16	0.43	0.55	1.00	
EC	0.40	0.51	0.14	0.31	0.40	0.35	0.09	0.03	0.41	0.67	0.73	1.00
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(b) Spring	Cl	NO ₃ -	SO4 ²⁻	$C_2O_4^{2-}$	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²⁺	Ca ²⁺	OC	EC
Cl	1.00											
NO ₃	0.68	1.00										
SO4 ²⁻	0.48	0.62	1.00									
$C_2O_4^2$	0.27	0.27	0.42	1.00	1.00							
PO ₄ ³⁻	0.01	0.02	-0.03	0.00	1.00	1.00						
Na ⁺	0.92	0.63	0.50	0.27	-0.03	1.00	1.00					
NH ₄	0.38	0.61	0.86	0.32	-0.10	0.40	1.00	1.00				
K'	0.50	0.72	0.64	0.10	0.66	0.38	0.73	1.00	1.00	-		
Mg ²⁺	0.94	0.65	0.55	0.18	-0.13	0.97	0.46	0.44	1.00	1.00		
Car	0.48	0.37	0.26	0.26	0.33	0.23	0.15	0.57	0.28	1.00	1.00	
OC EC	-0.10	-0.21	-0.12	0.25	0.06	-0.10	-0.14		-0.13	0.38	1.00	1.00
EC	-0.22	-0.22	0.04	0.30	-0.10	-0.21	-0.11		-0.25	0.39	0.07	1.00
(c) Summer	Cl	NO ₂ ⁻	SO ₄ ²⁻	$C_2 O_4^{2-}$	PO ₄ ³⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²	+ Ca ²	+ OC	EC
(c) Summer Cl ⁻	Cl ⁻	NO ₃	SO42-	C ₂ O ₄ ²⁻	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	+ OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻	Cl ⁻ 1.00 0.59	NO ₃	SO ₄ ²⁻	C ₂ O ₄ ²⁻	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	EC
(c) Summer Cl ⁻ NO_3^- SO_4^{2-}	Cl ⁻ 1.00 0.59 0.55	NO ₃	SO ₄ ²⁻	C ₂ O ₄ ²⁻	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	+ OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻	Cl ⁻ 1.00 0.59 0.55 0.41	NO ₃ 0 1.00 0.40 0.43	SO ₄ ²⁻ 1.00 0.33	C ₂ O ₄ ²⁻	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	EC
(c) Summer Cl ⁻ NO_3^- SO_4^{2-} $C_2O_4^{2-}$ PO_4^{3-}	Cl ⁺ 1.00 0.59 0.55 0.41 0.20	NO ₃ 1.00 0.40 0.43 0.30	SO4 ²⁻ 1.00 0.33 0.35	$C_2 O_4^{2-}$	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺	Cl ⁻ 1.00 0.59 0.55 0.41 0.20 0.95	NO ₃ 0 1.00 0.40 0.43 0.30 0.64	SO ₄ ²⁻ 1.00 0.33 0.35 0.46	$ \begin{array}{c} C_2O_4^{2-} \\ \hline 1.00 \\ 0.35 \\ 0.49 \end{array} $	PO4 ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	EC
(c) Summer Cl [*] SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺	Cl ⁻ 1.00 0.59 0.55 0.41 0.20 0.95 0.54	NO ₃ 1.00 0.40 0.43 0.30 0.64 0.35	SO4 ²⁻ 1.00 0.33 0.35 0.46 0.98	C ₂ O ₄ ²⁻ 1.00 0.35 0.49 0.14	PO4 ³⁻	Na ⁺	NH4 ⁺	K ⁺		+ Ca ²	* OC	
(c) Summer Cl [*] NO ₃ [*] SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺	Cl ⁻ 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40	NO ₃ 1.00 0.40 0.43 0.30 0.64 0.35 0.44	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64	C ₂ O ₄ ²⁻ 1.00 0.35 0.49 0.14 0.22	PO4 ³⁻	Na ⁺	NH4 ⁺	K ⁺		+ Ca ²	* OC	
(c) Summer Cl [*] NO ₃ [*] SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺	Cl ⁻ 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.40 0.97	NO ₃ 1.00 0.40 0.43 0.30 0.64 0.35 0.44 0.64	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59	C ₂ O ₄ ²⁻ 1.00 0.35 0.49 0.14 0.22 0.41	PO4 ³⁻ 1.00 0.28 0.25 0.44 0.21	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺	Cl ⁻ 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57	NO ₃ 1.00 0.40 0.43 0.30 0.64 0.35 0.44 0.64 0.42	SO4 ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86	C ₂ O ₄ ²⁻ 1.00 0.35 0.49 0.14 0.22 0.41 0.45	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29	Na ⁺ 1.00 0.40 0.41 0.97 0.43	NH4 ⁺	K ⁺	Mg ²	$\begin{array}{c} + & \mathbf{Ca}^2 \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $	+ OC	
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03	NO3 1.00 0.40 0.43 0.30 0.64 0.35 0.44 0.64 0.42 0.42	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \end{array}$	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29 0.23	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	+ OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08	NO3 0 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.64 0.43 0.40 0.43 0.43 0.43 0.43 0.43 0.43 0.44 0.44 0.44 0.44 0.44 0.44	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \end{array}$	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08	NO3 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.44 0.45 0.44 0.44 0.44 0.44 0.44 0.44 0.44 0.44 0.44 0.44 0.44	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05	$\begin{array}{c c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \end{array}$	PO ₄ ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11	Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca^{2}	+ OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00	NO3 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.40 0.43 0.40 0.43 0.43 0.44 0.64 0.44 <	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \end{array}$	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO ₄ ³⁻	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca^{2}	* OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ⁻	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24	NO3 0	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \end{array}$	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺ 1.00 0.46 0.59 0.06 -0.09 K ⁺	Mg ²	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	* OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ²⁻	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24	NO3 0 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.44 0.44 0.42 0.24 0.09 NO3 0.09	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \end{array}$	PO ₄ ³⁻	Na ⁺	NH4 ⁺	K ⁺	Mg ²	$ \begin{array}{c} ^{+} Ca^{2} \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	* OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ CO ²⁻	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24 0.24 0.20	NO3 0 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.64 0.43 0.43 0.44 0.64 0.42 0.24 0.09 NO3 0.043 0.043	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \\ \end{array}$	PO ₄ ³⁻	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺	NH4 ⁺	K ⁺ 1.00 0.46 0.59 0.06 -0.09 K ⁺	Mg ²	$\begin{array}{c} + & \mathbf{Ca}^2 \\ & &$	* OC	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24 0.08 0.24 0.08	NO3 0 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.64 0.43 0.43 0.44 0.44 0.42 0.24 0.24 0.09 NO3 0.43 0.43 0.43 0.43 0.43	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \\ \hline \\ \hline \\ 1.00 \\ 0.47 \end{array}$	PO ₄ ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO ₄ ³⁻	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC 	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24 0.08 0.16 -0.03 0.03 0.24 0.08	NO3 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.43 0.30 0.64 0.43 0.43 0.44 0.42 0.24 0.24 0.09 NO3 0.43 0.43 0.43 0.43 0.43 0.15	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.47 \\ 0.14 \end{array}$	PO4 ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO4 ³ 1.00 0.00	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC 	EC
(c) Summer Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ NA ⁺ NH ₄ ⁺	Cl 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 Cl 1.00 0.24 0.08 0.16 -0.03 0.98 0.55	NO3 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.43 0.30 0.64 0.43 0.43 0.44 0.42 0.24 0.24 0.09 NO3 0.43 0.43 0.43 0.15 0.30	SO42- 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO42- 1.00 0.35 0.05 0.37 0.26 0.14 0.94	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.47 \\ 0.14 \\ 0.34 \end{array}$	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO ₄ ³⁻ 1.00 0.000 0.34	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC 	EC
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ NH ₄ ⁺ K ⁺	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 CI 1.00 0.24 0.08 0.16 -0.03 0.98 0.55	NO3 0 1.00 0.40 0.43 0.30 0.64 0.35 0.40 0.43 0.30 0.64 0.43 0.43 0.44 0.64 0.42 0.24 0.24 0.09 NO3 0.43 0.43 0.43 0.15 0.30 0.29	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ 1.00 \\ 0.35 \\ 0.49 \\ 0.14 \\ 0.22 \\ 0.41 \\ 0.45 \\ 0.31 \\ 0.13 \\ \hline \\ C_2 O_4^{2-} \\ \hline \\ \hline \\ \hline \\ 0.13 \\ 0.13 \\ \hline \\ 0.35 \\ \hline \end{array}$	PO ₄ ³⁻ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO ₄ ³⁻ 1.00 0.00 0.00 0.034 0.74	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04 0.04 0.01 0.01 0.12 0.04	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC	EC
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ MH ₄ ⁺ K ⁺ MH ₄ ⁺ M	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 CI 1.00 0.24 0.08 0.16 -0.03 0.98 -0.01 -0.15 0.97 0.97 0.03	NO3 0	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻ SO ₄ ²⁻ 0.10 0.37 0.26 0.14 0.96 0.52 0.12 0.52 0.12 0.52	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $	PO4 ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO4 ³ 1.00 0.00 0.00 0.34 0.75 0.05	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04 -0.09 0.97 0.97 -0.09 0.97 -0.97 -0.97 -0.97 -0.97 -0.97 -0.97 -0.97 -0.97 -0.12 -0.04 -	NH4 ⁺	K ⁺	Mg ²	+ Ca ²	* OC 	EC
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 CI 1.00 0.24 0.08 0.16 -0.03 0.98 -0.01 -0.15 0.97 0.25	NO3 0	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻ 0.10 0.37 0.26 0.14 0.96 0.52 0.15 0.15 0.15 0.15 0.10 0.10 0.15 0.10 0.15 0.07 0.05 0.1	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $	PO4 ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO4 ³ 1.00 0.00 0.34 0.77 0.05 0.18	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04 -0.09 0.97 0.97 0.25 0.97 0.00 0.97 0.01 0.97	NH4 ⁺	K ⁺ 1.00 0.46 0.59 0.06 -0.09 K ⁺ 1.00 0.06 0.09	Mg ²	+ Ca ²	* OC 	EC
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Ca ²⁺ Ca ²⁺ CC EC (d) Autumn Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ NA ⁺ NH ₄ ⁺ K ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ Ca ²⁺ OC	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 CI 1.00 0.24 0.08 0.16 -0.03 0.98 -0.01 -0.15 0.97 0.25 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.03 -0.08 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.97 0.03 0.98 0.98 0.97 0.03 0.98 0.98 0.98 0.98 0.97 0.03	NO3 0	SO ₄ ²⁻ 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO ₄ ²⁻ SO ₄ ²⁻ 0.10 0.37 0.26 0.14 0.96 0.52 0.17 0.13	$\begin{array}{c} C_2 O_4^{2-} \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $	PO4 ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO4 ³ 1.00 0.00 0.34 0.77 0.05 0.18 0.38 0.39	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04 -0.09 0.97 0.26 -0.12	NH4 ⁺	K ⁺ 1.00 0.46 0.59 0.06 -0.09 K ⁺ 1.00 -0.08 0.04 0.04	Mg ²	* Ca ² • Ca ² • 1.00 • 1.00 • 0.20 • Ca ² • 0.21 • 0.22	* OC	EC
(c) Summer Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ Na ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ OC EC (d) Autumn Cl NO ₃ ⁻ SO ₄ ²⁻ C ₂ O ₄ ²⁻ PO ₄ ³⁻ NA ⁺ NH ₄ ⁺ K ⁺ Mg ²⁺ Ca ²⁺ Ca ²⁺ Ca ²⁻ C ₂ O ₄ ²⁻	CI 1.00 0.59 0.55 0.41 0.20 0.95 0.54 0.40 0.97 0.57 0.03 -0.08 CI 1.00 0.24 0.08 0.16 -0.03 0.98 -0.01 -0.15 0.97 0.25 0.97 0.24 0.03 -0.08 0.03 -0.08 0.09 -0.08 0.09 -0.09 0.09 -0.00	NO3 1.00 1.00 0.40 0.43 0.30 0.44 0.44 0.42 0.24 0.24 0.24 0.24 0.24 0.42 0.42 0.42 0.24 0.24 0.33 0.03 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.30 0.29 0.07 0.37 0.31 0.29 0.29 0.34	SO42- 1.00 0.33 0.35 0.46 0.98 0.64 0.59 0.86 0.07 0.05 SO42- 1.00 0.37 0.26 0.14 0.96 0.52 0.17 0.15 0.13	$\begin{array}{c} \mathbf{C_2 O_4}^2 \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $	PO4 ³ 1.00 0.28 0.25 0.44 0.21 0.29 0.23 0.11 PO4 ³ 1.00 0.00 0.34 0.77 0.05 0.18 0.39 0.31	Na ⁺ 1.00 0.40 0.41 0.97 0.43 0.01 -0.12 Na ⁺ 1.00 0.04 -0.12 0.01 -0.12 -0.11 -0.12 -0.11 -0.12 -0.11 -0.12 -0.11 -0.11 -0.12 -0.11 -0.11 -0.11 -0.11 -0.12 -0.11 -	NH4 ⁺	K ⁺ 1.00 0.46 0.59 0.06 -0.09 K ⁺ 1.00 -0.08 0.04 0.26 0.12	Mg ² 1.00 0.55 0.00 -0.07 Mg ² 1.00 0.37 -0.02 0.00	+ Ca ²	* OC 	EC

SO₄²⁻, K⁺, Ca²⁺ in the tables are non-sea salt fractions. Gray-shaded fonts and italic fonts show strong and moderate correlation coefficients, respectively SO₄²⁻, K⁺, Ca²⁺ in the tables are non-sea salt fractions

concentrations of crust-originated $\ensuremath{nssCa^{2+}}\xsca^{2+}$ and manmade aerosols such as OC, EC, and nitrate, respectively. The highest $PM_{2.5}/PM_{10}$ ratio was associated with air

flow from NWL with a value of 0.51, showing influence of anthropogenic dominated nature of the aerosol population. Nonetheless, the lowest ratio (0.40) was

	Cluster 1 NWL $(n=42)$	Cluster 2 NWS $(n=118)$	Cluster 3 NES $(n=118)$	Cluster 4 ST $(n=100)$	Cluster 5 SAH $(n=72)$	Cluster 6 SWL $(n=28)$
	Mean±Std	Mean±Std	Mean±Std	Mean±Std	Mean±Std	Mean±Std
PM10	24.73±12.85	19.61±17.28	18.42±11.93	20.24±12.84	30.06±28.39	19.81±10.62
PM10/PM2.5	0.51	0.44	0.48	0.43	0.40	0.47
Cl	1.28 ± 1.12	$1.49{\pm}1.97$	$1.00{\pm}0.83$	1.38 ± 1.32	2.11±2.25	2.31 ± 2.44
NO_3^-	$0.53 {\pm} 0.45$	$0.38 {\pm} 0.40$	$0.40 {\pm} 0.36$	$0.45 {\pm} 0.44$	$0.54{\pm}0.42$	$0.42 {\pm} 0.33$
SO_4^{2-}	$1.38 {\pm} 0.91$	1.57 ± 1.50	1.72 ± 1.55	1.57 ± 1.50	2.03 ± 2.39	2.04 ± 1.57
Ox	$0.07 {\pm} 0.04$	$0.07 {\pm} 0.04$	$0.08 {\pm} 0.04$	$0.09 {\pm} 0.06$	$0.08 {\pm} 0.04$	$0.08 {\pm} 0.06$
PO4 ³⁻	$0.05 {\pm} 0.04$	$0.05 {\pm} 0.03$	$0.05 {\pm} 0.04$	$0.06 {\pm} 0.04$	$0.06 {\pm} 0.04$	$0.06{\pm}0.02$
Na ⁺	$0.69 {\pm} 0.52$	$0.84{\pm}0.98$	$0.59 {\pm} 0.48$	$0.85{\pm}0.80$	1.27 ± 1.29	$1.48 {\pm} 1.38$
$\mathrm{NH_4}^+$	$0.42 {\pm} 0.35$	$0.49 {\pm} 0.49$	0.52 ± 0.43	$0.46 {\pm} 0.42$	$0.52 {\pm} 0.47$	$0.54 {\pm} 0.49$
K^+	$0.12 {\pm} 0.10$	$0.14{\pm}0.10$	$0.16 {\pm} 0.13$	$0.15 {\pm} 0.12$	$0.17 {\pm} 0.10$	$0.18{\pm}0.09$
Mg^{2+}	$0.10{\pm}0.08$	0.12 ± 0.14	$0.09 {\pm} 0.07$	$0.13 {\pm} 0.11$	$0.18 {\pm} 0.17$	0.21 ± 0.17
Ca ²⁺	$0.72 {\pm} 0.65$	$0.75 {\pm} 0.85$	$0.60 {\pm} 0.66$	$0.84 {\pm} 0.63$	1.28 ± 1.83	$0.65 {\pm} 0.41$
OC	4.14 ± 3.10	$3.40{\pm}1.86$	$3.30{\pm}1.11$	$3.38 {\pm} 2.34$	3.53 ± 1.52	$3.38 {\pm} 1.45$
EC	$0.51 {\pm} 0.42$	0.39 ± 0.22	$0.41 {\pm} 0.17$	$0.57 {\pm} 0.33$	$0.58 {\pm} 0.34$	$0.47 {\pm} 0.40$

Table 5 Arithmetic means and standard deviations for PM₁₀, ions, OC, and EC along with PM₁₀/PM_{2.5} ratio as a function of air flow

Std standard deviation

found when air flow originated from North Africa (SAH), supporting the contribution of crust-dominated particles.

OC and EC concentrations in NWS and NES were found to be lower than those of remaining air flow. The higher mean values of these species in NWL, ST, and SWL might probably be attributed to air flows sweeping continental Europe, central Anatolia (power generation by coal), Spain, Italy, Greece, and industrialized Marmara region (Kocak et al. 2009, 2012). For example, the highest EC (2.2 μ g m⁻³) concentration was found on 23 February 2010 when air mass back trajectory with a long fetch originated from Atlantic Ocean and then passed through Europe. The observed concentrations of OC and NO₃⁻ for same event were around 8.6 and 1.9 μ g m⁻³, respectively. Similarly, nitrate showed higher values in NWL, ST, and SWL.

The lowest mean $nssSO_4^{2-}$ was associated with air flow from NWL, and this might be attributed to the decrease of sulfur emissions over Europe (Lelieveld et al. 2002). As expected, ammonium denoted similar variability as a function of air flow category. The highest $nssCa^{2+}$ mean concentration (~1.3 µg m⁻³) was observed when air mass back trajectories originated from North Africa continent.

Conclusions

In this study, the PM_{10} and $PM_{2.5}$ concentrations, the temporal variability of water-soluble ions, the chemical composition of

 PM_{10} and $PM_{2.5}$, origin of the exceeded events in the Black Sea have been investigated.

Approximately 60 % of the PM10 was associated with coarse mode, suggesting the predominance of the primary aerosol such sea salt and crustal material. The highest $PM_{2.5}$ contribution to PM_{10} was found in summer with a value of 0.5 due mainly to enhanced secondary aerosols in relation to photochemistry. As expected, sea salt-originated ions and calcium were primarily associated with coarse fraction (>75 %) while sulfate and ammonium were mostly originated from fine particles (>75 %).

The sea salt-originated Cl⁻, Na⁺, and Mg²⁺ illustrated their higher concentrations and variability during winter months (December, January, and February) because of unsettled weather conditions in winter season. The Cl⁻/Na⁺ ratio was lower than that reported for seawater (1.79), suggesting Cl⁻ depletion particularly in summer due to reaction between alkaline sea salt particles and nitrate. Water-soluble aerosols nssSO₄²⁻, NO₃⁻, C₂O₄²⁻, and NH₄⁺ denoted bimodal temporal variability over the study period. The nssCa²⁺ concentrations were found to be varied order of magnitude from day to day. Higher concentrations were ascribed to episodic mineral dust intrusions from North Africa into the region.

Crustal material and sea salt were found to be accounted for majority of the PM_{10} , with contributions of 31 and 13 %, respectively. The IM, POM, and EC contributions explained 13, 21, and 2 % of the PM_{10} mass, correspondingly. The mass closure for fine mode demonstrated that IM, POM, and EC dominated the $PM_{2.5}$ (~75 %) mass, explaining 22, 48, and

5 % of the observed mass. The crustal material and sea salt elucidated 11 and 8 % of the fine mode, respectively. The majority of the PM₁₀ and PM_{2.5} concentrations (\geq 95 %) were found to be less than 50 and 25 µg m⁻³ limit values established by European Commission. The exceeded PM_{2.5} values were found be associated with secondary aerosols, with a particular dominance of POM. For the exceeded PM₁₀ values, six of the events were dominated by dust (*n*=6) while two and four of these exceedances were caused by sea salt and mix events.

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Conflict of interest The authors declare that they have no conflict of interest.

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