Atmospheric Pollution Research xxx (xxxx) xxx–xxx

HOSTED BY

ELSEVIER

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: www.elsevier.com/locate/apr

Original Article

Seasonal variation of carbonaceous $PM_{2.5}$ in an Istanbul traffic site

Rosa M. Flores[a,*], Hüseyin Özdemir[b], Bülent O. Akkoyunlu[c], Alper Ünal[d], Mete Tayanç[a]

[a] Marmara University, Department of Environmental Engineering, 34722, Istanbul, Turkey
[b] Bahcesehir University, Department of Civil Engineering, 34353, Istanbul, Turkey
[c] Marmara University, Department of Physics, 34722, Istanbul, Turkey
[d] Istanbul Technical University, Eurasia Institute of Earth Sciences, 34469, Istanbul, Turkey

ARTICLE INFO

Keywords:
Organic carbon
Elemental carbon
Air pollution
Fine particulate matter
Megacity
OC/EC
Turkey

ABSTRACT

The seasonal variation of fine carbonaceous aerosol was evaluated in an urban traffic site in Istanbul. $PM_{2.5}$ samples were collected on selected days during four seasons between Jan 2017–Jan 2018. Daily $PM_{2.5}$ concentrations were obtained experimentally by the gravimetric method in Beşiktaş, while hourly concentrations were obtained from the Air Quality Monitoring Network of Istanbul in Çatladıkapı, Silivri, Kağıthane, and Ümraniye. Organic carbon (OC) and elemental carbon (EC) concentrations were determined by a thermo-optical carbon analyzer for samples collected in Beşiktaş. The 24-h US-EPA air quality standard of 35 μg m^{-3} was exceeded 13, 25, 41, 42, and 57% of the time in Çatladıkapı, Silivri, Kağıthane, Ümraniye, and Beşiktaş, respectively. These exceedances occurred mainly during the fall and winter owing to a combination of emissions from fuel combustion for residential heating, traffic and industry, and poor air dispersion due to weak atmospheric motion and low mixing heights. Average OC concentrations ranged as 6.62–7.32 μg m^{-3} during spring and summer, and 13.76–14.1 μg m^{-3} during fall and winter. The OC concentrations observed in this work during the summer and winter were 2–4 and 3–6 times higher than concentrations observed in the USA and Europe, respectively. The EC concentrations did not show considerable seasonal variation, with values between 2.16 and 3.26 μg m^{-3}. EC concentrations in Beşiktaş were 7 and 9 times higher than concentrations observed in the USA and Europe, in order. Results obtained in this study could be helpful for future implementation of policies and strategies to reduce emissions from combustion sources in order to comply with the air quality standards.

1. Introduction

According to the World Health Organization, outdoor air pollution is the world's largest environmental health risk, causing 4.2 million premature deaths worldwide in 2016 (WHO, 2016). Organic aerosol (OA) is of special interest because it comprises a large fraction of fine PM and it has adverse effects on human health and climate change. In addition, OA may be of both primary and secondary origin, therefore, it may be composed of thousands of individual organic species (Flores and Doskey, 2015). Recently, it has been found that particles emitted by combustion sources are more relevant to human health than the bulk mass concentration of PM_{10} and $PM_{2.5}$. For this reason, it has been recommended to decrease the exposure to $PM_{2.5}$ and combustion-related chemical components (Janssen et al., 2011).

Carbonaceous aerosol is composed of organic carbon (OC) and elemental carbon (EC). Organic carbon is composed of primary organic carbon (POC), which is emitted directly by natural and anthropogenic sources. POC may undergo atmospheric aging and form secondary organic carbon (SOC). Elemental carbon, also known as black carbon, is a tracer for carbon fuel-based combustion processes, particularly from diesel emissions. Primary organic carbon can be a good parameter for the development of air pollution control strategies (Bahner et al., 2007), and EC has been suggested as an additional indicator for the evaluation of local control strategies and exposure to PM emitted from combustion sources (Janssen et al., 2011).

In Istanbul, air pollutant concentrations have decreased since the mid-1990s due to the establishment of a natural gas line for heating and industry (Tayanç, 2000). However, high concentrations of particulate matter are frequently observed (Çapraz et al., 2017). The main sources of air pollutants in Istanbul are traffic, industry, construction activities, residential heating, and ship emissions (Markakis et al., 2012). In addition, regional and long-range transport, especially from desert dust,

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.
* Corresponding author.
E-mail address: rflores@marmara.edu.tr (R.M. Flores).

https://doi.org/10.1016/j.apr.2020.06.022
Received 12 February 2020; Received in revised form 26 May 2020; Accepted 22 June 2020

contribute to high particulate matter concentrations (Flores et al., 2017). $PM_{2.5}$ concentrations have been recently reported by various studies. Gokce et al. (2020) evaluated the effect of the Eurasia Tunnel, that spans across the European and Asian parts of the city, on air pollutant levels between February 2016 and February 2019. It was found that $PM_{2.5}$ concentrations slightly decreased (12–24%) within two years after the tunnel started operations. This decrease was particularly observed on the Asian side of the tunnel, possibly due to slightly higher traffic observed on the European side of the Tunnel. $PM_{2.5}$ concentrations were reported between 2013 and 2015 in 3 stations that are part of the Air Quality Monitoring Network in Istanbul. The concentrations were used to test a model that used aerosol optical depth to estimate ground-level concentrations over Turkey (Zeydan and Wang, 2019). The effect of Mediterranean Cypress trees on $PM_{2.5}$ concentrations in short periods of approximately one month in 2015 was evaluated at a traffic site. A slight decrease in $PM_{2.5}$ concentrations of 17% was observed when there were no gaps between the trees (Ozdemir, 2019). Kahya et al. (2017) studied the spatial and temporal variations of $PM_{2.5}$ over the Marmara region and reported daily $PM_{2.5}$ in 3 stations between March 2013 and February 2014. It was found that the sampling stations in Istanbul exhibited the second highest concentrations in the Marmara Region. Flores et al. (2019) reported the diurnal and seasonal variations of $PM_{2.5}$ in a traffic site between January 2017 and January 2018. Hourly concentrations indicated that 43% of the days were classified as polluted.

In Turkey, OC/EC measurements in ambient air have been scarcely performed. Theodosi et al. (2010) collected daily PM_{10} samples on selected days between July 2008 and June 2009 in Istanbul. Average OC and EC concentrations were comparable to other megacities in developed countries with maximum daily concentrations of approximately 35 and 10 μg m^{-3}, respectively. Recently, OC and EC concentrations were determined in high-time resolved $PM_{2.5}$ samples in Istanbul (Flores et al., 2019). Strong diurnal variations were observed with high concentrations in the morning and evening rush hours, particularly for EC. In Bolu, the maximum daily OC and EC concentrations in $PM_{2.5}$ were approximately 150 and 15 μg m^{-3} during the winter of 2014 (Öztürk and Keleş, 2016). Additionally, OC and EC concentrations were determined in a tunnel study in order to estimate emission factors in total suspended particulate matter (Demir et al., 2019; Gaga et al., 2018). It was concluded that emission factors of OC and EC were nearly 2–3 times higher than others studies in the USA, Austria, and Mexico, but two times lower than other studies in China (Demir et al., 2019).

In this work, we evaluate seasonal variations of $PM_{2.5}$ concentrations in Çatladıkapı, Kağıthane, Silivri, and Ümraniye stations that belong to the continuous Air Quality Monitoring Network in Istanbul. Additionally, $PM_{2.5}$ samples were collected on selected days between January 2017 and January 2018 with a low volume sampler at an urban traffic station in Istanbul (Beşiktaş), and $PM_{2.5}$ concentrations were determined with the gravimetric method. In order to understand the seasonal variation of carbonaceous aerosol, OC and EC concentrations were determined in daily $PM_{2.5}$ samples collected in Beşiktaş. OC and EC concentrations obtained in this work were compared with the findings of the other studies done in the USA and Europe.

2. Materials and methods

2.1. $PM_{2.5}$ sampling

The sampling site is located in the touristic/residential area of Beşiktaş, Istanbul, at approximately 44 m above sea level and 10–15 m from the road (Fig. 1). $PM_{2.5}$ samples were collected over 24 h periods on 47 mm quartz microfiber discs using a Zambelli low volume sampler at a flow rate of 1 m^3 h^{-1}. $PM_{2.5}$ concentrations were determined with the gravimetric method by subtracting the initial mass of the filter sample from the final mass and next divided by the volume of the air passed through it. Before sampling, filters were pre-conditioned by placing them into a desiccator at room temperature for 24 h to obtain constant humidity. After the conditioning process, filters were weighted using an analytical balance with 10^{-4} g precision. A careful analysis of meteorological forecast models (e.g. GFS from https://www.wetterzentrale.de/en/topkarten.php?model=gfs) was done to identify the possible future episodes occurring during strong high pressure systems associated with low wind speeds and weak vertical motion. Therefore, the sampling dates were determined as follows: spring: May 3–9, 2017, summer: July 6–12, 2017, fall: October 20–26, 2017, and winter: January 4–10, 2018.

Hourly $PM_{2.5}$ concentrations were obtained from the Air Quality Monitoring Network in Istanbul for four sampling sites: Çatladıkapı, Kağıthane, Silivri, and Ümraniye (Fig. 1). Averaged daily concentrations were calculated based on hourly measurements. Continuous $PM_{2.5}$ monitoring was performed by the Turkish Ministry of Environment and Urbanization as part of the national air pollution monitoring network. $PM_{2.5}$ concentrations were determined with an automatic MP101M Beta Gauge instrument (Environment SA, France) according to the EU standard method EN14907:2005 (IBB, 2020). Beta Gauge instruments provide accurate and precise measurements with minimum sample manipulation. Data is widely available and has been used in various research studies (Agacayak et al., 2015; Kabatas et al., 2014; Karaca et al., 2009; Karaca and Camci, 2010). Data quality in the selected stations was high with small amounts of missing data. Data availability throughout the stations was as follows: Spring 96–100%, Summer 95–100%, Fall 86–100%, and Winter 90–100%. Data was not available at Çatladıkapı in Fall and Winter. With the exception of Ümraniye (86 and 90% in the Fall and Winter, respectively), data availability exceeded 95% at all other stations and seasons.

The $PM_{2.5}$ concentrations observed on the sampling campaigns determined in our study and their comparison with the rest of the season can be observed in Fig. S1 (supplementary material). Since the periods were selected by considering meteorology and carefully studying the numerical weather forecasts, the samples collected in our study can be considered representative of the seasons of choice. Hourly and daily $PM_{2.5}$ concentrations were compared with the threshold values to understand their impact on the human health and overall air quality.

2.2. Determination of organic carbon and elemental carbon

Organic carbon (OC) and elemental carbon (EC) concentrations were determined by a Sunset Laboratory thermo-optical transmission OC/EC analyzer according to the NIOSH 870 protocol. For OC/EC analysis, a 1.5 cm^2 filter punch was inserted into the analyzer and heated in two steps: (1) for determination of organic carbon, at temperature ramps of 310, 475, 615, and 870 °C in a 100% helium atmosphere and (2) for determination of elemental carbon, at temperature ramps of 550, 625, 700, 775, 850, and 870 °C in a 2% oxygen atmosphere (Flores et al., 2019). Organic carbon and soot carbon are oxidized to CO_2 during combustion, converted to CH_4 in a manganese dioxide (MnO_2) oxidizing oven, and quantified by a flame ionization detector (FID). A small fraction of the OC may be transformed into pyrolytic carbon and quantified as EC in a process called charring. To correct for charring, a laser is used to measure the transmission of light through the sample. A split point between OC and EC is determined when the transmittance is the same as the initial value before the filter is first heated (Karanasiou et al., 2011). The total area under the OC and EC curves is calculated and converted to concentration using an external calibration of sucrose analytical standard. For calibration, a known amount (10 μL) of sucrose from Supelco (product #47289) was spiked on a pre-combusted quartz fiber filter and analyzed daily. The standard deviation of these analyses in triplicate ranged between 1.1 and 7.5% with an average of 4.0% (Flores et al., 2019).

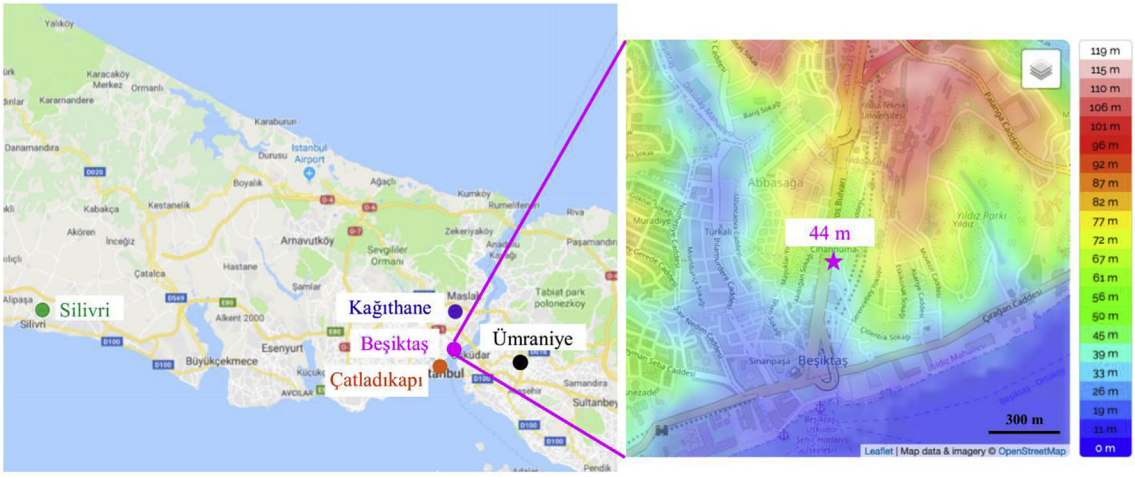

Fig. 1. $PM_{2.5}$ sampling sites in Istanbul (left), and the altitude of Beşiktaş station (right).

2.3. Meteorological data

Meteorological data were obtained from Weather Underground at Balmumcu station (41.0580 N, 29.0169 E) located approximately 1.5 km in the northeast direction of the Beşiktaş sampling station. Meteorological data include temperature (°C), pressure (hPa), wind speed (m s^{-1}), solar radiation (W m^{-2}), and total daily precipitation (mm). Boundary layer height (BLH) forecasts were obtained every 3 h from the global data assimilation system (GDAS, 1° × 1°) operated by National Oceanic and Atmospheric Administration (NOAA)'s air resource laboratory (ARL, http://ready.arl.noaa.gov/READYamet.php). Ventilation coefficients (VC, m^2 s^{-1}), calculated as the product of the BLH and the average wind speed, give an estimation of the regional atmospheric dispersion. Low and fair air pollution dispersion are observed when VC is < 2000 m^2 s^{-1} and 2001–4000 m^2 s^{-1}, respectively. Good and excellent air pollutant dispersion occur when the VC is 4001–6000 m^2 s^{-1}, and > 6000 m^2 s^{-1}, respectively (Tayanç, 2000; Zakey et al., 2006).

3. Results

3.1. $PM_{2.5}$ concentrations

Table 1 shows daily $PM_{2.5}$ concentrations in Beşiktaş, Çatladıkapı, Kağıthane, Silivri, and Ümraniye stations of Istanbul obtained during the seasonal sampling campaigns of spring, summer, and fall 2017, and winter 2018. Data for Çatladıkapı was only available for spring and summer 2017. High correlation coefficients (i.e., R = 0.77–0.90) were obtained among Çatladıkapı, Kağıthane, Silivri, and Ümraniye automatic stations. Since emission sources vary among these sampling sites (i.e., rural, urban, and industrial), the small changes in $PM_{2.5}$ concentrations are likely owing to the variations in the emission sources and meteorology. Data at the Ümraniye station was unavailable on 25–26 October 2017. Ümraniye station had similar concentrations and behavior as Kağıthane (R = 0.84). Kağıthane and Ümraniye have populations of approximately 450,000 and 700,000, respectively. Lower population of 165,000 live in Silivri, thus lower concentrations of $PM_{2.5}$ can be expected during the winter. The 24-h air quality standards established by the World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA) for $PM_{2.5}$ are 25 and 35 μg m^{-3}, in order. $PM_{2.5}$ daily averages have not been established in the European Union and Turkey. On the other hand, standards for yearly averages have been established as 10, 12, and 25 μg m^{-3} according to WHO, EPA, and EU, respectively. During the study period, the 24-h WHO air quality standard of 25 μg m^{-3} was exceeded 33.3,

Table 1
Daily average $PM_{2.5}$ concentrations in Istanbul (μg m^{-3}).

Date	Beşiktaş	Çatladıkapı	Kağıthane	Silivri	Ümraniye
Spring 2017					
May 03, 2017	40.3	30.6	27.6	18.0	20.9
May 04, 2017	30.9	38.3	29.3	22.0	23.9
May 05, 2017	50.0	33.6	28.8	23.2	22.3
May 06, 2017	72.00	30.3	31.6	28.3	24.9
May 07, 2017	36.6	20.6	30.5	18.9	17.0
May 08, 2017	40.4	23.1	22.8	12.9	15.2
May 09, 2017	31.4	20.5	32.6	16.9	16.9
% Exceedance WHO	**85.7**	**57.1**	**85.7**	**14.3**	**0.0**
% Exceedance US-EPA	**71.4**	**14.3**	**0.0**	**0.0**	**0.0**
Summer 2017					
July 6, 2017	116.6	9.4	12.8	11.3	10.2
July 7, 2017	22.7	15.3	18.8	14.6	12.1
July 8, 2017	21.3	8.1	20.1	12.8	9.2
July 9, 2017	28.3	22.0	27.0	18.7	11.8
July 10, 2017	27.2[a]	16.1	25.0	14.6	15.2
July 11, 2017	20.5	12.9	19.9	10.1	11.2
July 12, 2017	25.1	18.6	18.4	17.7	10.8
% Exceedance WHO	**57.1**	**0.0**	**28.6**	**0.0**	**0.0**
% Exceedance US-EPA	**14.3**	**0.0**	**0.0**	**0.0**	**0.0**
Fall 2017					
October 20, 2017	55.2	42.9	62.5	45.2	51.4
October 21, 2017	215.9	–	94.9	82.3	75.8
October 22, 2017	[a]	–	72.6	62.1	54.1
October 23, 2017	63.5[a]	–	42.6	32.9	36.8
October 24, 2017	37.9	–	59.4	25.9	52.1
October 25, 2017	13.2	–	30.0	30.0	–
October 26, 2017	22.3	–	–	18.3	–
% Exceedance WHO	**66.7**	**–**	**100**	**85.7**	**100**
% Exceedance US-EPA	**66.7**	**–**	**83.3**	**42.9**	**100**
Winter 2018					
January 5, 2018	76.6	–	29.5	27.1	30.5
January 6, 2018	50.0	–	97.4	47.6	53.8
January 7, 2018	35.7	–	71.3	49.8	44.1
January 8, 2018	42.0	–	60.7	60.9	45.6
January 9, 2018	23.0	–	79.8	47.6	59.5
January 10, 2018	29.0	–	35.8	24.4	36.1
January 11, 2018	43.5	–	56.0	34.0	62.0
% Exceedance WHO	**85.7**	**–**	**100**	**85.7**	**100**
% Exceedance US-EPA	**71.4**	**–**	**85.7**	**57.1**	**85.7**
Overall study period					
% Exceedance WHO	**74.0**	**33.3**	**77.8**	**46.4**	**46.2**
% Exceedance US-EPA	**55.6**	**13.3**	**40.7**	**25.0**	**42.3**

Note 1. WHO 24-h air quality guideline is 25 μg m^{-3}
Note 2. USA-EPA daily air quality standard is 35 μg m^{-3}
[a] Due to technical issues, samples were collected for 19, 2, and 14 h.

Table 2
Meteorological conditions and OC contribution to $PM_{2.5}$ during the sampling campaigns.

Date	T (°C)	P (hPa)	WS (m s^{-1})	BLH (m)	Solar (W m^{-2})	VC (m s^{-2})	Precip (mm)	OC/$PM_{2.5}$ (%)
Spring 2017								
May 3, 2017	15.50	1015.85	3.45	242.08	275.20	974.98	0.00	18.52
May 4, 2017	15.91	1014.96	3.73	252.92	284.25	983.85	0.00	NA
May 5, 2017	15.17	1012.84	2.33	193.75	281.46	507.04	0.00	20.42
May 6, 2017	13.11	1011.60	1.53	284.58	119.66	460.74	15.49	10.17
May 7, 2017	16.31	1007.18	1.87	371.25	258.97	694.88	5.84	26.10
May 8, 2017	16.97	1006.21	1.31	NA	248.05	NA	0.51	23.05
May 9, 2017	16.49	1004.07	3.44	255.42	235.37	933.35	0.76	25.96
Average	**15.64**	**1010.39**	**2.52**	**266.67**	**243.28**	**759.14**	**22.60**	**20.70**
Std. Dev	**1.27**	**4.58**	**1.01**	**59.15**	**57.40**	**238.39**	**5.80**	**5.97**
Summer 2017								
July 6, 2017	21.58	1016.73	5.18	899.58	281.08	4701.53	0.00	18.91
July 7, 2017	21.36	1016.91	3.11	710.67	219.39	2254.82	0.00	35.53
July 8, 2017	21.47	1015.33	3.29	NA	323.53	NA	0.00	45.59
July 9, 2017	24.74	1013.87	1.15	133.63	310.34	162.66	0.00	31.16
July 10, 2017	24.00	1016.17	4.79	852.50	321.30	4148.79	0.00	NA
July 11, 2017	22.94	1016.49	4.27	792.50	317.53	3439.96	0.00	35.21
July 12, 2017	23.08	1012.90	3.06	515.17	323.36	1614.94	0.00	32.93
Average	**22.74**	**1015.49**	**3.55**	**650.67**	**299.50**	**2720.45**	**0.00**	**33.22**
Std. Dev	**1.33**	**1.55**	**1.35**	**287.09**	**38.34**	**1700.81**	**0.00**	**8.62**
Fall 2017								
October 20, 2017	17.29	1017.87	0.57	142.58	154.68	108.90	0.00	39.80
October 21, 2017	16.87	1016.75	0.87	111.83	149.62	120.28	0.25	9.01
October 22, 2017	16.66	1015.09	2.34	NA	137.49	NA	0.51	NA
October 23, 2017	17.93	1009.17	1.91	176.25	137.88	274.51	0.00	NA
October 24, 2017	17.19	1005.88	1.26	413.83	29.96	485.80	5.08	37.11
October 25, 2017	15.35	1014.18	3.57	457.25	44.95	1737.21	7.11	58.07
October 26, 2017	12.12	1023.59	3.62	548.75	43.96	2013.99	1.02	40.19
Average	**16.20**	**1014.65**	**2.02**	**308.42**	**99.79**	**790.12**	**13.97**	**36.84**
Std. Dev	**1.96**	**5.80**	**1.23**	**186.89**	**56.82**	**856.28**	**2.88**	**17.64**
Winter 2018								
January 5, 2018	7.72	1012.42	2.22	430.83	43.23	924.49	0.25	18.53
January 6, 2018	8.14	1020.90	0.63	132.25	95.20	131.35	0.51	52.33
January 7, 2018	10.58	1025.90	0.81	171.08	97.91	199.56	0.25	42.94
January 8, 2018	11.51	1030.41	0.47	NA	119.75	NA	0.00	50.62
January 9, 2018	9.66	1030.97	2.36	360.83	15.39	856.16	0.00	42.89
January 10, 2018	8.93	1017.50	0.74	245.83	2.00	284.70	0.00	47.91
January 11, 2018	9.34	1012.69	1.32	91.17	38.43	118.78	0.00	38.49
Average	**9.41**	**1021.54**	**1.22**	**238.67**	**58.84**	**419.17**	**1.01**	**41.96**
Std. Dev	**1.33**	**7.80**	**0.78**	**133.83**	**45.35**	**370.32**	**0.20**	**11.41**
Overall average	**16.00**	**1015.52**	**2.33**	**366.11**	**175.36**	**1172.22**	**37.58**	**33.18**

WS: wind speed. BLH: boundary layer height. Solar: solar radiation. VC: ventilation coefficient. Precip: total precipitation.

46.4, and 46.2% of the time in Çatladıkapı, Silivri, and Ümraniye, in order. Concentrations in Beşiktaş and Kağıthane station exceeded the WHO air quality standard 74.0% and 77.8% of the time. The threshold limit values were mostly exceeded during the fall and winter at all sampling stations, except for Beşiktaş and Kağıthane, which also showed 85.7% exceedance during the spring (Table 1). Both stations are near busy roads, thus one can expect these stations to be highly affected by the continuous emissions of the heavy traffic and high $PM_{2.5}$ concentrations. In addition, contributions from desert dust transport events were important, especially, during spring (Flores et al., 2017).

The 24-h US-EPA air quality standard of 35 μg m^{-3} was exceeded 13.3, 25.0, 40.7, and 42.3% of the time during the study period in Çatladıkapı, Silivri, Kağıthane, and Ümraniye, respectively. The number of exceedances in Çatladıkapı was underestimated owing to the missing data of the fall and winter. As expected, results obtained for the WHO limit values were higher. Beşiktaş station had the highest exceedance (55.6%) of the US-EPA standard compared to the other stations. This high exceedance with respect to the EPA air quality standard mainly occurred during the fall and winter and was due to the increased residential heating emissions and poor dilution conditions with low surface wind speeds and mixing heights (Table 2). Higher daily $PM_{2.5}$ concentrations were also observed in Beşiktaş during the spring and summer seasons (Table 1). During the spring, concentrations in Beşiktaş were up to two times greater than those recorded in Kağıthane. During the winter however, concentrations in Kağıthane were up to 3.5 times higher than those recorded in Beşiktaş. High concentrations in Kağıthane during the winter may be due to increased emissions from residential heating as the population density in Kağıthane (30,129 km^{-2}) is 3 times higher than that in Beşiktaş (10,142 km^{-2}). During the summer, concentrations in Beşiktaş and Kağıthane were comparable. In Beşiktaş, the WHO and EPA air quality standards were exceeded 74.0 and 55.6% of the time during the complete sampling campaign, respectively (Table 1). Although lower concentrations were observed during spring and summer, the WHO and EPA air quality standards were exceeded 57.1–85.7% and 14.3–71.4% of the time, respectively. Decreasing $PM_{2.5}$ concentrations to comply with the regulations, particularly in Beşiktaş and Kağıthane, requires strict traffic control. In addition, other important stations such as Çatladıkapı require continuous monitoring and continuous data availability.

Fig. 2 shows the distribution of hourly concentrations in Çatladıkapı, Kağıthane, Silivri, and Ümraniye during (a) spring 2017, (b) summer 2017, (c) fall 2017, and (d) winter 2018 for dates specified in Table 1. During the studied period, there was a clear difference in hourly $PM_{2.5}$ concentrations observed in fall/winter compared to spring/summer at all sampling stations. Maximum hourly concentrations of ~100–200 μg m^{-3} were observed during the fall and winter (Fig. 2c and d). On the contrary, all hourly concentrations recorded during the spring and summer were below 60 μg m^{-3} (Fig. 2a and b), except in Kağıthane during the spring (91 μg m^{-3}). This is consistent with observed low temperatures during the winter and the use of low

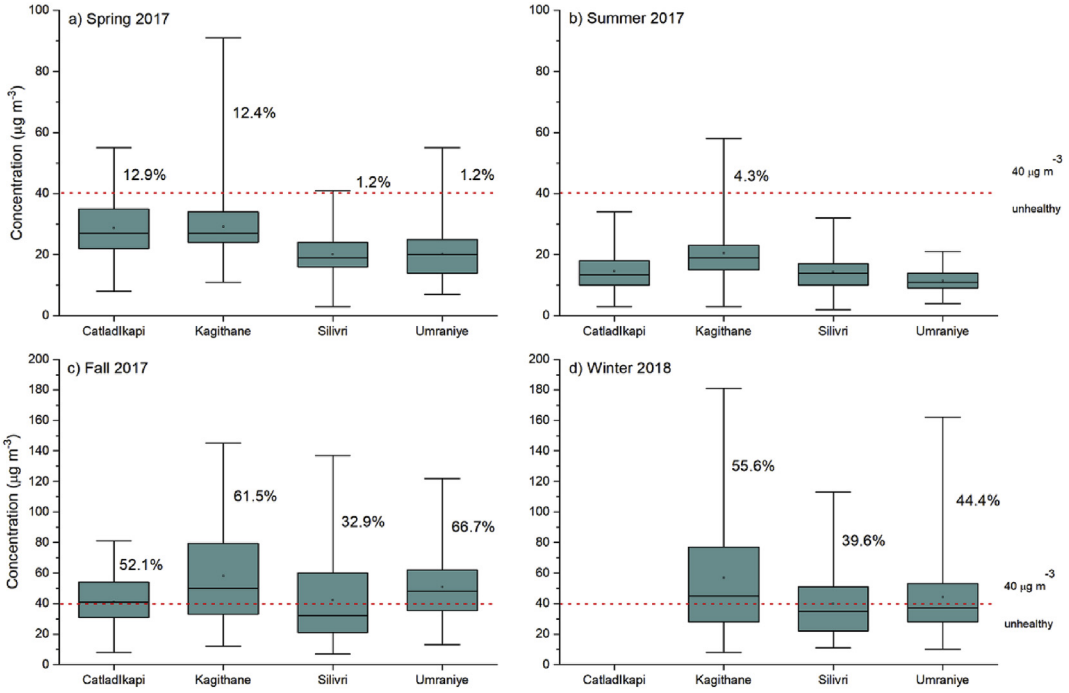

Fig. 2. Distribution of hourly $PM_{2.5}$ concentrations in Istanbul in (a) spring 2017, (b) summer 2017, (c) fall 2017, and (d) winter 2018. The dates correspond to Table 1. The boxes indicate 25 and 75 percentiles, and the bars indicate the minimum and maximum values. Mean (dot) and median (line) of the data are shown inside the boxes. 40 μg m^{-3} is used as an indicator of unhealthy air quality.

quality of fuels for residential heating combined with poor dispersion of air pollutants due to low mixing heights, lack of vertical dispersion of contaminants, and low wind speeds during the winter. Although low correlations between $PM_{2.5}$ measured in this work and other criteria pollutants were obtained (R^2 = 0.38–0.55), concentrations followed similar trends during the sampling campaign as can be observed in Table 1. The analysis of trends and magnitudes of hourly concentration is useful for source apportionment and evaluation of air quality control strategies. In addition, epidemiological studies may be combined with hourly $PM_{2.5}$ concentrations for the establishment of new air quality standards. For these reasons, monitoring of fine particulate matter at a high time resolution of 1 h or less should be continuously and routinely performed.

Similarly to the European Commission, the National Environment Protection Council (NEPC) of Australia has established the air quality standard of 25 μg m^{-3} as 24 h average (NEPC, 2015). Although no standard has been established for hourly $PM_{2.5}$ concentrations, NEPC has recommended a value of 40 μg m^{-3} as an indicator of poor and unhealthy air quality (EPA, 2018). In this work, less than 5% of the hourly $PM_{2.5}$ concentrations exceeded the recommended value of 40 μg m^{-3} during the spring and summer, except for Çatladıkapı and Kağıthane. On the other hand, poor and very poor air quality were observed during the fall and winter at all stations, except Silivri, with over 50% of the hourly $PM_{2.5}$ concentrations exceeding 40 μg m^{-3}. Although lower $PM_{2.5}$ concentrations were observed in Silivri, 32.9 and 39.5% of the data exceeded the threshold value during the fall and winter, respectively. Although Silivri has the lowest population density (215 km^{-2}) of the studied sampling sites (15,338–25,679 km^{-2}), average concentrations and their distributions were comparable with the other sampling sites (e.g., Ümraniye) and high concentrations were particularly observed during the fall and winter (Fig. 2c and d). This shows the importance of implementing and supporting high quality fuel use for residential heating, especially during the cold season.

3.2. Temporal variation of OC and EC

Fig. 3 shows the seasonal variability of OC, EC, $PM_{2.5}$, OC/TC, and OC/EC ratios in Beşiktaş station. Table 2 shows meteorological variables and the contribution of OC to $PM_{2.5}$ (%). The annual averages of OC and EC concentrations were 10.45 and 2.83 μg m^{-3}, respectively. Average OC concentrations ranged between 6.62 and 7.32 μg m^{-3} during spring and summer, and over twice as much (13.76–14.1 μg m^{-3}) during the fall and winter (Fig. 4). OC concentrations had a significant correlation with wind speed (R = −0.48) and wind direction (R = 0.53) indicating that OC concentrations increased with stable atmospheric condition (i.e., low advection and convection) and were also transported from nearby areas. During the summer, high OC and EC concentrations of 17.42 and 4.64 μg m^{-3} observed on July 6 coincided with a high daily-averaged wind speed of 5.18 m s^{-1} (Table 2) and a maximum hourly wind speed of nearly 9.0 m s^{-1}. On this day, high $PM_{2.5}$ concentrations of 116.59 μg m^{-3} were observed in Beşiktaş station, while low concentrations of 9.44–12.85 μg m^{-3} were observed in other stations (Table 1). It is possible that high concentrations of organic aerosol were transported from the north direction with high wind speed owing to a combustion activity near the sampling site.

EC concentrations did not show considerable seasonal variation, with average values between 2.16 and 3.26 μg m^{-3} during all four seasons (Fig. 4). Contrary to OC, EC had lower correlation coefficients with wind speed (R = 0.22) and wind direction (R = 0.19). Since the sampling site is located near a road with heavy traffic, continuous emissions from vehicle exhaust can be expected. The contributions of OC to TC were on average 76.46%. The highest contribution was during the winter (83.46%), showing that, although OC was the predominant carbon contributor, EC also had a significant contribution to organic aerosol at this particular traffic sampling site. The contribution of OC to $PM_{2.5}$ was on average 33.18% (Table 2) and was more significant during the winter (41.96%), indicating that emissions from fossil fuel combustion for residential heating are an important source of fine particulate matter during the winter. On the other hand, the lowest OC

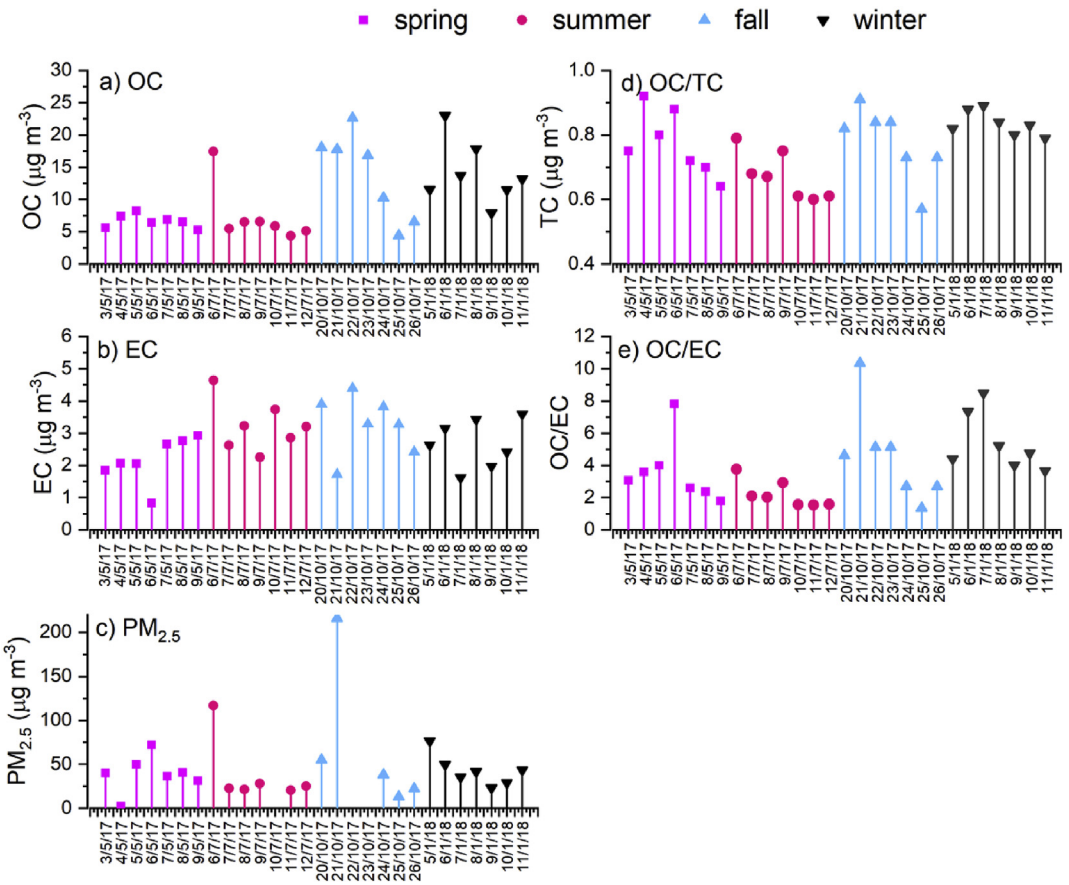

Fig. 3. Average daily concentrations (μg/m^3) of (a) OC, (b) EC, (c) TC, and (d) $PM_{2.5}$ and (e) OC/EC ratios in spring-fall 2017 and winter 2018.

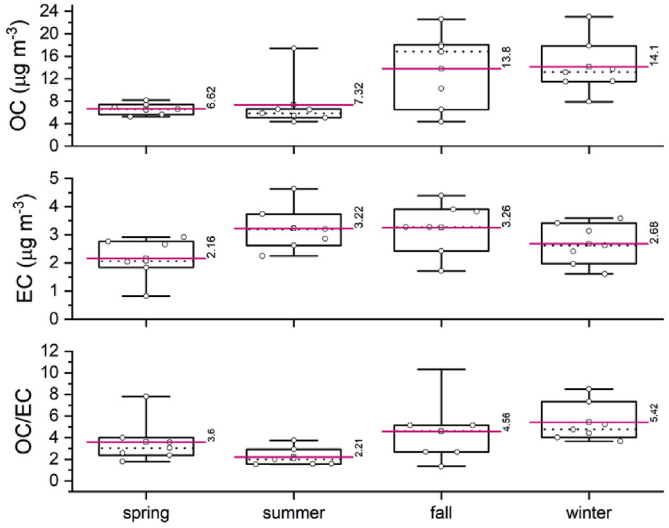

Fig. 4. Seasonal variation of (a) OC, (b) EC, and (c) OC/EC ratios in spring-fall 2017 and winter 2018. The limits of the boxes indicate 25 and 75 percentiles, respectively. The bars indicate the minimum and maximum values, respectively. The red horizontal line indicates the mean value.

contribution of 20.7% was observed during the spring, indicating that other sources of $PM_{2.5}$, such as mineral dust transport and inorganic aerosol, were predominant during the spring season (Figs. S2 and S3) (Flores et al., 2017).

3.3. Comparison with other regions

The OC concentrations observed in this work during the summer and winter were nearly 2–4 times and 3–6 times higher than concentrations observed in the USA and Europe, respectively (Fig. 5). A much higher ratio was observed for EC concentrations in Beşiktaş, which was 7–9 times higher than concentrations observed in the USA and Europe. Higher EC concentrations observed in Europe than in the USA could reflect the higher use of diesel vehicles. In Beşiktaş, the traffic is mainly light-duty vehicles that could use both gasoline or diesel, and diesel-operated public transportation. The elevation of the road is another important factor, as the slope is considerably steep in Beşiktaş (Fig. 1), accelerating vehicles going upward emit more pollutants. High average EC concentrations have been also reported in Korea and Beijing with values of 7.3 and 8.7 μg m^{-3}, in order (He et al., 2001; Park et al., 2002).

In Turkey, OC and EC concentrations have been investigated by Theodosi et al. (2010) and Öztürk and Keleş (2016) in the cities of Istanbul and Bolu, respectively. Average annual and wintertime OC concentrations were 6.6 and 59.9 μg m^{-3} in Istanbul and Bolu, respectively. OC concentrations in our work were 58% higher than those found by Theodosi et al. (2010) but 4 times lower than the results of Öztürk and Keleş (2016). The great variation in the reported concentrations is owing to the contribution of different sources at the sampling sites. The lowest OC concentrations obtained by Theodosi et al. (2010) were obtained at the top of a building away from direct sources, our sampling site receives direct emissions from vehicle exhaust, and the very high concentrations obtained by Öztürk and Keleş (2016) were due to biomass burning for residential heating. The annual average EC concentration obtained in this work (2.83 μg m^{-3}) is more or less similar to the value obtained by Theodosi et al. (2.92 μg m^{-3}),

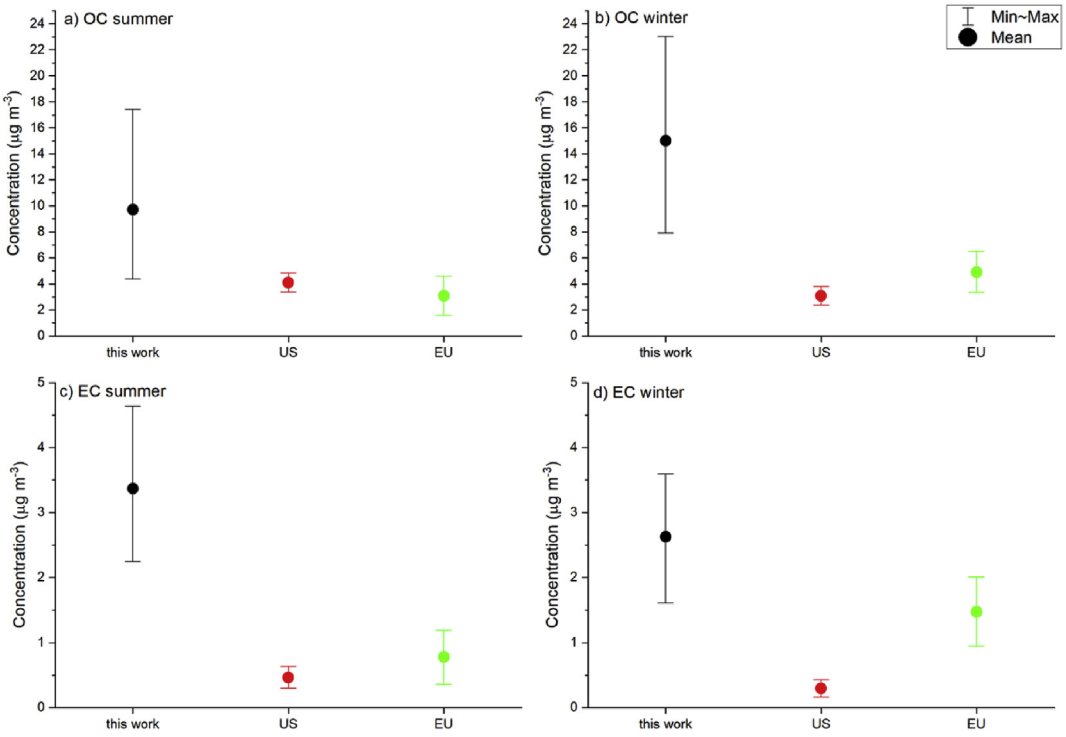

Fig. 5. Comparison of OC and EC concentrations (μg/m^3) obtained in this work with other studies in the US and EU. Adapted from Weijers et al. (2013).

but 2 times lower than Öztürk and Keleş (5.62 μg m^{-3}). This shows the importance of continuous monitoring of organic aerosol at various sampling sites to evaluate contributions from different sources.

3.4. Source analysis

OC/EC ratios are helpful to distinguish emission sources of organic aerosol. OC/EC ratios lower than 1 are owing to high EC concentrations and indicate emissions from diesel vehicles. High OC/EC ratios are indicators of increasing emissions of OC. OC/EC ratios of 2.2, 2–3, and 4.15 indicate emissions from light-duty gasoline vehicles, ship emissions, and residential wood combustion. OC/EC ratios ranging between 12.7 and 14.5 are indicators of emissions from natural gas home appliances, paved road dust, and forest fires. A very high OC/EC ratio such as 67.6 indicates emissions from meat charbroiling (Na et al., 2004). In this work, the average OC/EC ratio during the four seasons period was 3.95 (Fig. 3e). The lowest average ratios of 3.6 and 2.21 were observed during the spring and summer, respectively. The highest average ratios of 4.56 and 5.42 were observed during the fall and winter. Three episodes had the highest OC/EC ratios of 7.81, 8.49, and 10.34 (Fig. 3e). These high ratios were owing to low EC concentrations rather than high OC concentrations (Fig. 3a and b). Low EC concentrations were due to a combination of lack of northeasterly winds (Fig. 6) and precipitation (Table 2). The lowest daily OC/EC ratios of 1.34–1.56 were mostly owing to a decrease in OC concentrations, however, EC concentrations were also slightly increased. The lowest OC/EC ratios also coincide with precipitation events. The OC/EC ratios observed in Beşiktaş were due to a combination of light-duty gasoline and diesel vehicles and shipping emissions during the spring and summer, and residential heating emissions during the fall and winter.

These findings were supported by OC/TC ratios, which can be also used to differentiate emission sources of organic aerosol. OC/TC ratios of 0.48–0.67 are indicators of road aerosols. Ratios of 0.73, 0.81, and 0.94 indicate emissions from residential coal combustion, residential wood combustion, and forest fires (Klejnowski et al., 2017). In this work, OC/TC ratios during the heating season suggested emissions from residential coal and wood combustion (Fig. 3d). Conditional bivariate probability function (CBPF) plots were also used for source analysis (Uria-Tellaetxe and Carslaw, 2014). CBPF plots (Fig. 7) showed that the dominant wind direction during the sampling campaigns was from the NE. Sources of $PM_{2.5}$ and OC were near the sampling site and high concentrations were obtained during low wind speeds, generally lower than 1.5 m s^{-1}. On the other hand, in addition to continuous emissions

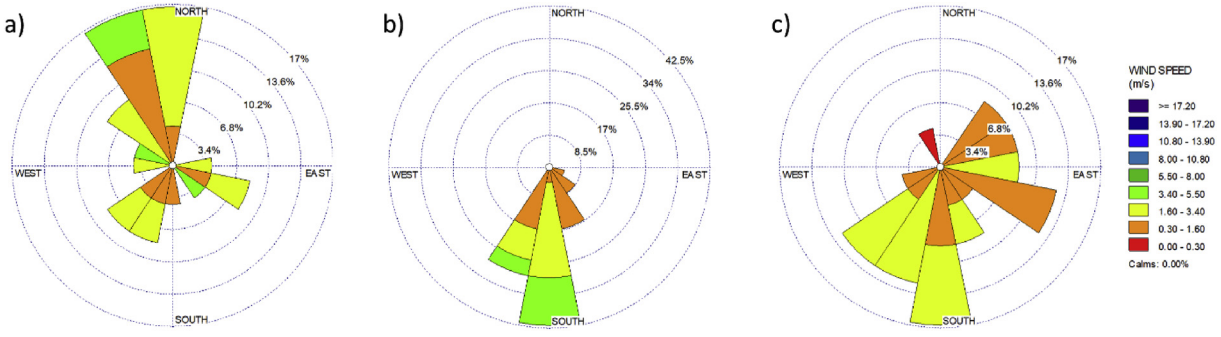

Fig. 6. Wind roses on (a) May 6, 2017, (b) Oct 21, 2017, and (c) Jan 6, 2018

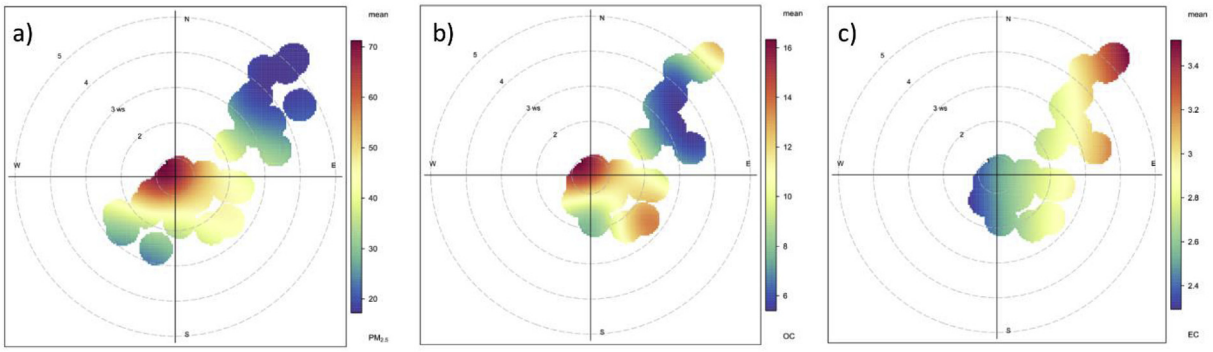

Fig. 7. Polar plots of (a) $PM_{2.5}$, (b) OC, and (c) EC. The colored bars indicate concentration in μg m^{-3}.

Table 3
Pearson correlation coefficients (R) between meteorological variables, OC, and EC.

	Spring		Summer		Fall		Winter	
	OC	EC	OC	EC	OC	EC	OC	EC
$PM_{2.5}$	−0.07	−0.54	0.99	0.87	0.71	−0.68	0.26	0.34
Temperature	−0.13	0.96	−0.36	−0.35	0.64	0.38	0.00	−0.05
Wind direction	−0.04	0.02	−0.10	−0.59	0.73	−0.14	0.67	−0.03
Pressure	0.36	−0.66	0.31	0.35	−0.09	−0.41	0.04	−0.33
Precipitation rate	−0.08	−0.76	NA	NA	−0.70	0.16	NA	NA
Solar radiation	0.28	0.61	−0.20	0.09	0.89	0.03	0.75	0.24
Wind speed	−0.24	0.13	0.45	0.83	−0.64	−0.08	−0.71	−0.30
Boundary layer height	−0.18	0.17	0.34	0.71	−0.95	0.07	−0.60	−0.43
Ventilation coefficient	−0.48	0.50	0.50	0.83	−0.92	−0.16	−0.62	−0.35

NA-not applicable due to lack of precipitation.

from traffic near the sampling site, EC was transported from shipping emissions from NE of the sampling site on the existence of wind speeds higher than 6 m s^{-1} (Fig. 7c).

3.5. Effect of meteorology on OC and EC concentrations

Table 3 shows the Pearson correlation coefficients between meteorological variables and OC and EC concentrations. OC and EC concentrations were affected differently by meteorology. Low correlations obtained for OC during the spring and summer may be owing to a combination of low emissions and mixed meteorological conditions such as precipitation and high wind speed. On the other hand, higher correlation coefficients obtained during the fall and winter resulted from a stable atmosphere associated with stagnant conditions. Meteorological conditions that are indicators for atmospheric mixing such as wind speed, boundary layer height, and ventilation coefficient had a significant negative effect on OC concentration, except during the summer. During the summer, high positive Pearson correlation coefficients were obtained between EC, wind speed, boundary layer height, and ventilation coefficient, which are indicators of possible transport from nearby areas as shown in Fig. 7. Although low atmospheric dilution conditions were observed during the fall, decreased OC concentrations were owing to precipitation events as shown by a high negative Pearson correlation coefficient of −0.70. These results show that seasonal variations of OC and EC concentrations are owing to variations in emission sources and meteorological conditions. Although precipitation events were observed in the fall and winter sampling campaigns, high concentrations were due to increased emissions from residential fuel combustion and favorable meteorological conditions. Therefore, significant efforts are necessary to improve the quality of fuel used for residential heating.

4. Conclusions

Seasonal variations of OC and EC in the daily $PM_{2.5}$ samples were studied at a traffic site of the Beşiktaş district in Istanbul. Hourly and daily $PM_{2.5}$ concentrations were also evaluated in terms of air quality standards and recommended thresholds in order to understand the impacts on human health and air quality, respectively. Over the whole study period, the WHO and US-EPA standards of 25 and 35 μg m^{-3} were exceeded at all stations, particularly during the fall and winter. Among all stations, Beşiktaş had the highest number of exceedances with 74.0 and 55.6% of the concentrations exceeding the threshold limits. Average OC concentrations were over twice as high during the fall (13.8 μg m^{-3}) and winter (14.1 μg m^{-3}) compared to spring (6.62 μg m^{-3}) and summer (7.32 μg m^{-3}), indicating the necessity of supporting the use of high-quality fossil fuels for residential heating and implementing strategies for traffic control. The highest contribution of OC to $PM_{2.5}$ was observed during the winter (41.96%) owing to residential fuel combustion. The lowest contribution was observed during the spring (20.70%), indicating that natural and anthropogenic sources of inorganic fine aerosol can be more important during this season. The OC concentrations observed in this work are nearly 2–6 times higher than concentrations observed in other studies in the USA and Europe. A much higher ratio was observed in the EC concentrations of Beşiktaş, which were 7–9 times higher than concentrations observed in the USA and Europe. Problems in the measurements and missing data gaps can generate quality issues in the overall data set, bringing uncertainties to the analysis. Continuous and long-term observations of organic aerosol and improved data availability at urban stations like Beşiktaş, Kağıthane, and Çatladıkapı, are necessary for a more reliable analysis of aerosol variability and trends. The results in this work may be further used for the evaluation and establishment of air quality control strategies and policies, particularly during the heating season.

CRediT authorship contribution statement

Rosa M. Flores: Conceptualization, Funding acquisition, Methodology, Writing - original draft, Writing - review & editing, Formal analysis, Visualization. **Hüseyin Özdemir:** Project administration. **Bülent O. Akkoyunlu:** Project administration. **Alper Ünal:** Resources. **Mete Tayanç:** Conceptualization, Writing - review & editing.

Declaration of competing interest

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

Acknowledgements

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBITAK) through project No. 115Y625. The authors thank Elif Mertoğlu and Ayşegul Pursa for their assistance, IETT-Beşiktaş for use of their facilities, and the Ministry of Environment and Urbanization and Department of Transportation for the data provided. The authors gratefully acknowledge the Air Resources Laboratory (ARL) at NOAA for the provision of HYSPLIT air mass trajectories and the Earth's Science Department at BSC for the provision of DREAM8b v2.0 dust loading forecasts.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2020.06.022.

References

Agacayak, T., Kindap, T., Unal, A., Pozzoli, L., Mallet, M., Solmon, F., 2015. A case study for Saharan dust transport over Turkey via RegCM4. 1 model. Atmos. Res. 153, 392–403.

Bahner, M.A., Weitz, K.A., Zapata, A., DeAngelo, B., 2007. Use of black carbon and organic carbon inventories for projections and mitigation analysis. Proceedings of the 16th annual international emission inventory conference emission inventories: integration analysis and communications, Raleigh.

Çapraz, Ö., Deniz, A., Doğan, N., 2017. Effects of air pollution on respiratory hospital admissions in İstanbul, Turkey, 2013 to 2015. Chemosphere 181, 544–550.

Demir, T., Yenisoy-Karakaş, S., Karakaş, D., 2019. PAHs, elemental and organic carbons in a highway tunnel atmosphere and road dust: Discrimination of diesel and gasoline emissions. Build. Environ. 160, 106166.

Epa, V., 2018. PM2.5 particles in air. Accessed on. https://www.epa.vic.gov.au/for-community/environmental-information/air-quality/pm25-particles-in-the-air, Accessed date: 27 February 2019.

Flores, R.M., Doskey, P.V., 2015. Evaluation of multistep derivatization methods for identification and quantification of oxygenated species in organic aerosol. J. Chromatogr. A 1418, 1–11.

Flores, R.M., Kaya, N., Eşer, Ö., Saltan, Ş., 2017. The effect of mineral dust transport on PM10 concentrations and physical properties in Istanbul during 2007–2014. Atmos. Res. 197, 342–355.

Flores, R.M., Mertoğlu, E., Özdemir, H., Akkoyunlu, B.O., Demir, G., Ünal, A., Tayanç, M., 2019. A High-Time Resolution Study of PM2.5, Organic Carbon, and Elemental Carbon at an Urban Traffic Site in Istanbul. Atmospheric Environment, pp. 117241.

Gaga, E.O., Arı, A., Akyol, N., Üzmez, Ö.Ö., Kara, M., Chow, J.C., Watson, J.G., Özel, E., Döğeroğlu, T., Odabasi, M., 2018. Determination of real-world emission factors of trace metals, EC, OC, BTEX, and semivolatile organic compounds (PAHs, PCBs and PCNs) in a rural tunnel in Bilecik. Turkey. Sci. Total Environ. 643, 1285–1296.

Gokce, H.B., Arıoğlu, E., Copty, N.K., Onay, T.T., Gun, B., 2020. Exterior air quality monitoring for the Eurasia tunnel in Istanbul, Turkey. Sci. Total Environ. 699, 134312.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of PM2.5 in Beijing, China. Atmos. Environ. Times 35, 4959–4970.

IBB, 2020. Air Quality Network. (in Turkish). Accesed on May 1, 2020. Available at: https://havakalitesi.ibb.gov.tr/Icerik/hakkimizda/olcum-cihazlari.

Janssen, N.A.H., Hoek, G., Simic-Lawson, M., Fischer, P., van Bree, L., ten Brink, H., Keuken, M., Atkinson Richard, W., Anderson, H.R., Brunekreef, B., Cassee Flemming, R., 2011. Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5. Environ. Health Perspect. 119, 1691–1699.

Kabatas, B., Unal, A., Pierce, R.B., Kindap, T., Pozzoli, L., 2014. The contribution of Saharan dust in PM10 concentration levels in Anatolian Peninsula of Turkey. Sci. Total Environ. 488–489, 413–421.

Kahya, C., Balcik, F.B., Oztaner, Y.B., Ozcomak, D., Seker, D.Z., 2017. Spatio temporal analysis of PM 2.5 over Marmara region, Turkey. Fresenius Environ. Bull. 26, 1.

Karaca, F., Anil, I., Alagha, O., 2009. Long-range potential source contributions of episodic aerosol events to PM10 profile of a megacity. Atmos. Environ. 43, 5713–5722.

Karaca, F., Camci, F., 2010. Distant source contributions to PM10 profile evaluated by SOM based cluster analysis of air mass trajectory sets. Atmos. Environ. 44, 892–899.

Karanasiou, A., Diapouli, E., Cavalli, F., Eleftheriadis, K., Viana, M., Alastuey, A., Querol, X., Reche, C., 2011. On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols. Atmos. Meas. Tech. 4, 2409–2419.

Klejnowski, K., Janoszka, K., Czaplicka, M., 2017. Characterization and seasonal variations of organic and elemental carbon and levoglucosan in PM10 in krynica zdroj, Poland. Atmosphere 8, 190.

Markakis, K., Im, U., Unal, A., Melas, D., Yenigün, O., İncecik, S., 2012. Compilation of a GIS based high spatially and temporally resolved emission inventory for the greater Istanbul area. Atmos. Pollut. Res 3, 112–125.

Na, K., Sawant, A.A., Song, C., Cocker, D.R., 2004. Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California. Atmos. Environ. 38, 1345–1355.

NEPC, 2015. National environment protection (ambient air quality) measure. available at: https://www.legislation.gov.au/Series/F2007B01142.

Ozdemir, H., 2019. Mitigation impact of roadside trees on fine particle pollution. Sci. Total Environ. 659, 1176–1185.

Öztürk, F., Keleş, M., 2016. Wintertime chemical compositions of coarse and fine fractions of particulate matter in Bolu, Turkey. Environ. Sci. Pollut. Control Ser. 23, 14157–14172.

Park, S.S., Kim, Y.J., Fung, K., 2002. PM2.5 carbon measurements in two urban areas: seoul and Kwangju, Korea. Atmos. Environ. 36, 1287–1297.

Tayanç, M., 2000. An assessment of spatial and temporal variation of sulfur dioxide levels over Istanbul, Turkey. Environ. Pollut. 107, 61–69.

Theodosi, C., Im, U., Bougiatioti, A., Zarmpas, P., Yenigun, O., Mihalopoulos, N., 2010. Aerosol chemical composition over Istanbul. Sci. Total Environ. 408, 2482–2491.

Uria-Tellaetxe, I., Carslaw, D.C., 2014. Conditional bivariate probability function for source identification. Environ. Model. Software 59, 1–9.

Weijers, E.P., Rocca, S., Verheggen, B., 2013. Carbonaceous aerosol: where is it coming from? Eur. Chem. News 45 News, ECN Report No. ECN-E–13-001, Petten.

WHO, 2016. Ambient (Outdoor) Air Quality and Health Fact Sheet. World Health Organization (WHO), Geneva.

Zakey, A.S., Solmon, F., Giorgi, F., 2006. Implementation and testing of a desert dust module in a regional climate model. Atmos. Chem. Phys. 6, 4687–4704.

Zeydan, Ö., Wang, Y., 2019. Using MODIS derived aerosol optical depth to estimate ground-level PM2.5 concentrations over Turkey. Atmospheric Pollution Research 10, 1565–1576.