

# Seasonal Variability of Large-Sized Particulate Matter Concentrations

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Abstract Human exposure to particulate matter (PM) is of great scientific interest due to its impact on both human health and the environment (climate change, reduced visibility, deterioration of archaeological sites, etc.). The aim of the current paper was to study the concentration of large-sized particulate matter (PM10) in relation to the season of the year. Measurements were performed with the help of a personal Button Sampler in three repeated cycles, namely summer, autumn, and winter, in order to obtain comparable results from three different seasons of the year. A total of 45 samples were collected, 27 of which were obtained from a peri-urban Pinus brutia forest and 18 from an adjacent urban area (9 and 6 samples in each repeated sampling cycle, respectively). Results obtained from both sampling areas show a significant increase in PM10 levels during the summer (8.86 mg m<sup>-3</sup>/24 h) in comparison with the

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Department of Agricultural Economics and Rural Development, Agricultural University of Athens, 75 118 55 Athens, PC, Greece e-mail: malesios@aua.gr autumn and winter concentrations (3.71 mg m<sup>-3</sup>/24 h and 4.12 mg m<sup>-3</sup>/24 h, respectively).

## **1** Introduction

Air pollution is undoubtedly one of the most serious environmental concerns in most major urban centers globally (Nowak & Crane, 2006). For this reason, in recent years, through internationally agreed Global Environmental Goals (GEGs) derived from United Nations summits and conferences as well as multilateral environmental agreements, countries have pledged to address the issue of air pollution with a view to improving air quality (GEGs, 2010). The atmosphere in urban centers receives massive inputs of anthropogenic pollutants originating from both stationary sources, such as power stations, industries, domestic heating systems, etc., and mobile sources (e.g., activities related to vehicles and road transportation) (Bradl, 2005). Particles emitted into the atmosphere may also be due to natural causes including windblown dust, sea spray, combustion generated soot and fly ash, biogenic emissions, volcanic eruptions etc. (Boubel et al., 1994; Nakajima & Aryal, 2018).

For these suspended atmospheric particles, the term *particulate matter* (PM) is used referring to small-sized solid or liquid matter suspended in the

air. The majority of atmospheric PM consists of inorganic ions, metal compounds, elemental carbon, organic compounds and crustal compounds (EPA, 2004). Also, the term *aerosols* is used to encompass matter both in its particulate and its gaseous phase (Hinds, 1999). Particulate matter can be classified into primary (particles emitted by specific sources) and secondary (particles formed in the atmosphere from precursor air pollutants [SO<sub>2</sub>, NOx, NH<sub>3</sub>, VOC and NMVOC]) (Chrysikou et al., 2008).

Depending on its size, which is measured in microns (µm), PM is deposited either in the nasal cavity and the mouth ( $< 100 \mu m$ ), or in the respiratory tract below the larynx (<10  $\mu$ m), or in the alveolar region of the lungs ( $<4 \mu m$ ). Based on its penetration into the human body, PM is distinguished into inhalable, thoracic, and respirable, the former referring to PM entering the upper respiratory tract (nasopharynx). This fraction includes total airborne particles of less than 10 µm in diameter (PM10). The thoracic fraction refers to particles less than 7 µm in diameter (PM2.5-10) which manage to penetrate beyond the larynx and enter the airways of the lung. Respirable particles, the fraction with a diameter of less than  $2.5 \,\mu\text{m}$  (PM2.5), are considered to have the most serious effects on human health, as they manage to penetrate into ever-narrowing bronchi and reach the alveoli, through which oxygen enters the blood (Londahl et al., 2006; Blisidis, 2015; Pope et al., 2006; Dockery & Pope, 1994; Schwartz et al., 1996). Generally speaking, exposure to PM10 is commonly accompanied by effects on the respiratory system, whereas exposure to respirable PM2.5 is associated with cardiovascular issues (Pope et al., 2006; Dockery & Pope, 1994; Schwartz et al., 1996).

According to the PHE (Department of Public Health, Environmental and Social Determinants of Health), the exposure limit of urban populations to inhalable dust (PM10 and PM2.5–10) on a 24-h basis is 50 mg m<sup>-3</sup> and it is not allowed to be exceeded for more than 35 days per year (PHE, 2012; Chrysikou et al., 2008; SCOEL, 2003).

Data from the European Environment Agency (EEA) for the period 1997–2004 reveal that the percentage of the urban population exposed to PM10 concentrations in excess of the 50 mg m<sup>-3</sup>/24 h exposure limit ranged between 23 and 45%. Despite the significant reductions in PM precursor and primary PM emissions over the period 1990–2004 (about 45%), these are not reflected in observed PM10 concentrations, which remained stable from 1997, when they began to be systematically monitored, till 2004 (EEA).

Particulate matter levels have been measured in a number of research papers. Eeftens et al. (2012) correlated PM10 concentrations with an array of important air quality predictors, such as population density, traffic intensity, and altitude, and concluded that concentrations were higher in Southern Europe than in Western and Northern Europe.

In the paper by Salameh et al. (2015) reporting measurements of PM concentrations in five European cities (Barcelona, Marseilles, Genoa, Venice, and Thessaloniki), mean annual PM10 levels were found to range between 23 and 46 mg m<sup>-3</sup>, with the highest concentrations being recorded in Thessaloniki and Venice.

These findings are in line with other studies focusing on the European South. In the Western Mediterranean Basin, and more specifically, in the suburban site of Castillo de Bellver, measurements carried out by Soriano et al. (2012) found PM10 concentrations ranging between 15 and 37 mg m<sup>-3</sup>. Pey et al. (2009), working in the same study area, found PM10 levels equal to 29 mg m<sup>-3</sup> and attributed the seasonal variability of PM10 levels at this particular suburban site to meteorological phenomena rather than local anthropogenic activities.

Enamorado-Báez et al. (2015), from measurements of total suspended particles (PM10 and PM2.5) performed in Seville, SW Spain, found that particulate matter levels exhibited temporal variability; more specifically, they recorded particularly high concentrations in the summer months, reaching 79.7 mg m<sup>-3</sup>. These high levels were considered to be related to dust coming from the Sahara (Saharan Dust Intrusions—SDI). The same study included comparisons between Seville and Huelva, a highly industrialized city nearby Seville, and showed higher levels of anthropogenic elements in Huelva than in Seville.

In PM10 measurements carried out in Berlin by Lenschow et al. (2001), it was found that at kerbside sites on main streets, levels were up to 40% higher than in the urban background. The study concluded that half of this particulate matter was due to motor vehicle exhaust emissions and tyre abrasion and the other half to re-suspended soil particles.

From all the research papers quoted above, it is more than obvious that PM levels are a serious cause of concern in most European countries, despite the differences observed between the European South and North. It is crucial that governments embark on a number of reduction measures. Ways of reducing PM concentrations in urban environments include the planting of trees or the creation of peri-urban forests, which have the ability to retain and absorb in their foliage significant amounts of PM (Uni et al., 2017). Research so far has focused on measurements of particulate matter carried out in urban centers; however, references to methods to be adopted for the protection of cities from undesirable PM levels or measures to be taken for the reduction of particulate matter in urban centers are rather scant in the literature.

The aim of the paper is to explore seasonal variability in PM10 concentrations. In order to achieve this, (a) we measured PM10 concentrations both in the urban environment and in the peri-urban forest, and b) we made comparisons between the concentrations in the urban area and the peri-urban forest in three different seasons of the year.

The two areas chosen for the measurement of PM10 concentrations were, on one hand, the city of Alexandroupolis, a medium-sized urban fabric in the north of Greece with a population of approximately 60.000 and, on the other, an adjoining peri-urban *Pinus brutia* public forest located to the north—northeast of the city, about 3.5 km away from the city center.

Measurements were performed in three repeated time cycles (Table 1) so that PM10 data could be collected from three different seasons of the year. Data were obtained from a total of 15 sites, 9 of which were located in the peri-urban forest and 6 in the urban fabric. Overall, data collection was carried out from July to early March and included 45 sampling days. More specifically, the 1<sup>st</sup> measurements cycle took place during the summer, from mid-June to late-July (12–06-2019 to

Table 1 Sampling periods per site

Sampling Season Cycles		Sampling Si	te	Number of samples
		peri-urban forest	city	
1 <sup>st</sup> Cycle	Summer	9	6	15
2 <sup>nd</sup> Cycle	Autumn	9	6	15
3 <sup>rd</sup> Cycle	Winter	9	6	15
Total		27	18	45

27–07-2019); the  $2^{nd}$  cycle was performed in autumn, from early October to late November (01–10-2019 to 30–11-2019) and the  $3^{rd}$  cycle was held in winter and early spring (13–01-2020 to 11–03-2020).

## 2 Materials and Methods

## 2.1 Sampling Positions in the Peri-urban Forest

With regard to the 9 sampling sites (Fig. 1) in the forest, these were chosen to be close to the forest boundaries. In particular, 6 of them (positions 1, 2, 3, 4, 5, and 7) were located along a front line spanning 270 m and at a distance of 150 m from the city and the other 3 (positions 8, 9, and 11) were extended along a zone 130 m long and at a distance of 50 m from the urban fabric of Alexandroupolis. Figure 1 shows all the sampling sites in the peri-urban forest and Fig. 2 shows two of them, namely positions 1 (Fig. 2a) and 2 (Fig. 2b). The individual characteristics of the sampling sites are illustrated in Table 2.

# 2.2 Sampling Positions in the Urban Fabric

Sampling positions in the urban fabric included a total of five representative sites scattered around the city center and one location in a suburb. The distribution of the sampling positions was done in such a manner as to help obtain representative PM10 concentration data from the entire city and not only its center. To this end, we chose not only urban spots that are crowded and receive great traffic loads, but also spots that attract fewer people and receive a moderate traffic load (Fig. 3). The individual characteristics of each sampling position are displayed in Table 3.

To collect the data, a portable air sampling kit was used, namely the Air Sampling SKC (Model 224-51MTX), which allows for special 25 mm diameter filters to be installed on an IOM-type sampling head for inhalable particles (Institute of Occupational Medicine) (Kalatoor et al., 1995). The instrument operated with a Button Sampler pump (SKC Sidekick Pump) that had a flow rate of 5–3000 ml-min (www.hse.gov.uk; Dimou et al., 2020). The IOM Sampler was connected to the SKC Sidekick Pump by means of a flexible tube (Tygon Tube). The pump was calibrated at the beginning of each measurement to operate at a flow rate of 2 l/min (www.hse.gov.uk). At the end of the sampling procedure



Fig. 1 Sampling positions in the peri-urban forest



**Fig. 2** Positions 1 (**a**) and 2 (**b**) in the peri-urban forest

another measurement of the flow rate was carried out as pump performance was likely to be affected after prolonged operation; as a result, the average of the two flow rate measurements was taken into consideration.

For each new measurement, a new filter was placed in the IOM Sampler cassette (Dimou et al., 2020; Marchi et al., 2017). In order to collect the inhalable fraction data in the peri-urban forest, the instrument was properly secured on the trunk of each selected tree at a height of about 1.70 m, while in the urban area, the instrument was mounted at fixed points at a similar height.

<b>Table 2</b> Features ofsampling positions in the	No	Position	X (m)	Ύ (m)	Z (m)	Slope (%)	Aspect
peri-urban forest	1	1	657,065	4,528,404	176.00	25	Ν
	2	2	656,944	4,528,430	171.50	30	Ν
	3	3	656,964	4,528,424	173.00	40	$N-N\Delta$
	4	4	657,101	4,528,369	172.50	15	Ν
	5	5	657,180	4,528,371	173.50	25	Ν
	6	7	657,222	4,528,371	172.50	10	N-NA
	7	8	657,130	4,528,270	140.00	20	Ν
	8	9	657,206	4,528,268	138.50	35	Ν
	9	11	657,256	4,528,277	138.00	35	Ν



Fig. 3 Sampling positions in the urban fabric

Table 3 Features of sampling positions in the city center

No	Position	X (m)	Ύ (m)	Z (m)	Location in city
1	6	658,124	4,523,163	07.50	center
2	10	657,072	4,524,222	26.00	suburb
3	12	657,913	4,522,983	08.50	center
4	13	657,979	4,523,064	09.50	center
5	14	657,950	4,523,103	10.00	center
6	15	657,895	4,523,135	10.50	center

PM mass in the inhalable fraction was determined by weighing the filters before and after each sampling session by means of a precision scale accurate to  $\pm 0.0001$  g. Prior to the sampling tests, filters were conditioned in a climatic cabinet at a temperature of  $20 \pm 1$  °C and moisture of  $48 \pm 2\%$  for 24 h (Chrysikou et al., 2008; Dimou et al., 2020).

The duration of each sampling day was 8 h. In the end, sampling data was expressed as a time-weighted average (TWA) over 24 h.

On each sampling day, ambient temperature and humidity measurements were also performed and recorded with the use of a digital thermometer-hygrometer (HUM DC-103) both at the beginning and at the end of data collection, and the average temperature and humidity were also calculated. Wind speed data for each sampling day was provided by the Alexandroupolis Airport Meteorological Station (www.wunderground.com).

## 2.3 Statistical Methodology

In order to effectively model the concentration of PM10 based on carefully chosen explanatory variables, we utilized a statistical regression model (Draper & Smith, 1998). In particular, we examined the associations between the variable of "concentration of PM10 (mg m<sup>-3</sup>)," and other variables (i.e., sampling cycle, sampling location, meteorological variables), assuming an influence on the former variable. Sample size for the fit of the regression model consisted of 45 observations collected via the personal SKC Button Sampler.

With this in mind, linear regression estimation and inference were performed assuming the following model Eq. (1):

$$\begin{aligned} \left( Dust(\mu g \cdot m^{-3}) \right)_i &= \beta_0 + \beta_1 \times (cycle = 1st)_i + \beta_2 \times (cycle = 2nd)_i \\ &+ \beta_3 \times (1st \ location = urban \ forest)_i + \beta_4 \times (humidity)_i + \\ &+ \beta_5 \times (temperature)_i + \beta_6 \times (wind)_i + e_i (i = 1, 2, \dots, 45) \end{aligned}$$

$$\end{aligned}$$

where  $\beta_0$  is the intercept,  $\beta_j (j = 1, ..., 6)$  the regression coefficients of the categorical explanatory variables of "cycle (reference category: 3.<sup>rd</sup> cycle)" ( $\beta_1, \beta_2$ ) and "location (ref. category: urban)" ( $\beta_3$ ), whereas with ( $\beta_4$ ,  $\beta_5, \beta_6$ ) we denote the estimated coefficients of the meteorological variables of "humidity," "temperature," and "wind speed," respectively. With  $e_i$  we denote the error term, assumed to follow a Gaussian distribution with zero mean and constant variance $\sigma^2$ , i.e. $e_i$  N(0, $\sigma^2$ )

In addition, we have included in the regression Eq. (1) all two-way interaction terms for the association between the explanatory variables.

In order to estimate the regression model parameters, the maximum likelihood method was utilized, whereas the selection of the best fitted model that includes only statistically significant explanatory variables was performed by utilizing a backward stepwise selection technique. The latter was chosen in order to account for potential correlation among the initially included covariates, starting with all initially selected explanatory variables and stepwise deleting at each step the less statistically significant covariate. Goodness-of-fit for both models was assessed by the coefficient of determination,  $R^2$ . Further, to check the robustness of the fitted model and evaluate prediction ability we calculate the mean square prediction error (*MSPE*) of the final best selected model from our multiple linear regression modeling and compare its value with the *MSPE* of a simple linear regression model that associates concentration of PM10 with location. The *MSPE* is calculated by the following formula:

$$MSPE = E\left[\left(y_i - \hat{y}_o\right)^2\right]$$
(2)

where  $y_i$  corresponds to the empirical values of the response variable of concentration of PM10 and  $\hat{y}_i$  are the predictions obtained by the fitted regression model(s). Lower values for the *MSPE* indicate the best fit to the *data*.

Data were fitted to the multiple linear regression model via the use of SPSS 21.0 statistical software (IBM Corporation, 2012).

#### **3** Results and Discussion

## 3.1 Descriptive Analysis Results

Figure 4 illustrates the results of PM10 concentration measurements of all the three sampling cycles corresponding to different seasons of the year. As mentioned above, the 1<sup>st</sup> cycle took place in the summer, the 2<sup>nd</sup> in the autumn and the 3<sup>rd</sup> cycle was held in the winter. PM10 concentration means were 2.95 mg m<sup>-3</sup>, 1.24 mg m<sup>-3</sup> and 1.37 mg m<sup>-3</sup>/8 h for the three sampling cycles, respectively.

Table 4 presents the distribution of PM10 concentrations in the peri-urban and urban environment per sampling season as well as the maximum and minimum concentration values recorded on an 8-h sampling basis. In addition, in the last column, depicting rainfall height per sampling cycle, it can be seen that the maximum rainfall height (81RR) was recorded in the  $2^{nd}$  sampling cycle, i.e., in autumn, while in the other two cycles (summer and winter), rainfall height was more or less the same (Hellenic National Meteorologigal Service, n.d.). Mean PM10 concentrations in the city amounted to 2.27 mg·m<sup>-3</sup>, 0.91 mg·m<sup>-3</sup>, and 0.70 mg·m<sup>-3</sup> /8 h in summer, autumn, and winter, respectively. The corresponding PM10 concentration means in the





peri-urban forest were 0.68 mg·m<sup>-3</sup>, 0.32 mg·m<sup>-3</sup>, and 0.67 mg m<sup>-3</sup>/8 h, respectively. In the 5<sup>th</sup> column, Table 4, the results are expressed on a 24-h basis.

Figures 5 and 6 depict temperature, ambient humidity, and wind speed means. As can be seen, mean temperature in the peri-urban forest was 29 °C, 23.1 °C, and 10.5 °C for each sampling cycle, respectively, humidity means were 53%, 54.83%, and 54.77%, and wind speed values were 4.9 m/s, 4.5 m/s, and 5.9 m/s, respectively. In the urban environment, temperature means were 28.9 °C, 17.3 °C, and 12.7 °C, respectively, humidity amounted to 44%, 61.58%, and 56.25% and wind speeds were 4.8 m/s, 3.2 m/s, and 4.8 m/s for each cycle, respectively.

Table 5 shows the classification of PM10 concentrations into five classes for the peri-urban forest and another five for the urban environment (Classes A, B, C, D, and E). The classes were created on the basis of the increasing PM10 levels as determined by the filter weights. More specifically: Class A consists of MP10 concentrations  $\leq 0.5 \text{ mg} \cdot \text{m}^{-3}$ , Class B of concentrations between 0.5 and 1 mg $\cdot \text{m}^{-3}$ , Class C between 1 and 2 mg $\cdot \text{m}^{-3}$ , Class D between 2 and 5 mg $\cdot \text{m}^{-3}$ , and Class E over 5 mg $\cdot \text{m}^{-3}$ . The corresponding rows of Table 5 (1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> cycle) show for each class and each sampling cycle, the number of samples as well as the percentage in relation to the total of samples for the peri-urban forest and the urban environment respectively. In addition, the table includes the percentages of the samples in brackets, mean temperatures, moisture, and wind speed for the corresponding days and concentration classes.

Figure 7 illustrates the total percentage distribution of the samples per sampling season (summer, autumn, winter) per class.

Table 4 Mean PM10 concentrations (mg m<sup>-3</sup>) per day; maximum and minimum concentrations per cycle and location; *SD* standard deviation

Sampling location per cycle	Mean PM10/8 h $(mg \cdot m^{-3})$ , SD	$\begin{array}{c} \text{Min PM10} \\ (\text{mg} \cdot \text{m}^{-3}) \end{array}$	$Max PM10 (mg \cdot m^{-3})$	Mean PM10 /24 h $(mg m^{-3})$ , SD	Rainfall height RR
	1	2	3	4	5
1 <sup>st</sup> Cycle peri-urban forest	0.68 (±0.70)	0.10	2.49	2.04 (±2.11)	45
2 <sup>nd</sup> Cycle peri-urban forest	0.32 (±0.26)	0.10	0.96	0.96 (±0.79)	81
3 <sup>rd</sup> Cycle peri-urban forest	0.67 (±0.20)	0.30	1.02	2.01 (±0.60)	32.33
1 <sup>st</sup> Cycle city	2.27 (±2.26)	0.10	5.33	6.81 (±6.79)	45
2 <sup>nd</sup> Cycle city	0.91 (±0.26)	0.60	1.35	2.73 (±0.79)	81
3 <sup>rd</sup> Cycle city	0.70 (±0.34)	0.18	1.17	2.10 (±1.03)	32.33









# 3.2 Results of Statistical Regression Modeling

As previously described, a regression model, including as explanatory variables both categorical and continuous variables, was fitted to the collected data, where the dependent variable was the concentration of PM10 and the explanatory variables used were the meteorological variables of humidity, temperature and wind speed (continuous variables) accompanied by the categorical variables of seasonality (cycles) and location.

All the two-way interaction terms between the factors of "cycle" and "location" as well as with the meteorological variables were tested for their importance, since it is anticipated that the effects of location on the response variable of PM10 concentration may vary according to the specific period of year.

Hence, the parameter estimation results of the final best selected regression model with the utilization of backward elimination technique are summarized in Table 6. These include the estimated regression coefficients (b's) of the statistically significant predictors, the standard error of the estimates, the corresponding level of significance (p-value) and the 95% confidence intervals of these estimates.

Most of the initially chosen explanatory variables, apart from the categorical variable of "cycle," were found to be non-statistically significant for the estimation of the response variable of "PM10". Specifically, it was found that the 1<sup>st</sup> cycle (summer period) has a strong positive effect on PM10 concentration (b=1.417; *p*-value <0.05) in comparison to the other two cycles (i.e., autumn and winter). On the contrary, location had no significant effect on the response

Table 5 PM10	0 concentration fr	equency values (r	ng/m <sup>2</sup> ), temperatur	re (°C), humidity (	%), and wind	l speed (m/s) p	er PM10 concentr	ation class; N: Nu	mber of samples	
	Peri-urban for	est				Urban environ	ment			
	< 0.5 mg/m3	$0.5 < x \le 1 mg/m^3$	$1 < x \le 2 \text{ mg/m}^3$	$2 < x \le 5 \text{ mg/m}^3$	>5 mg/m <sup>3</sup>	<0.5 mg/m3	$0.5 < x \le 1 \text{ mg/}$	$1 < x \le 2 \text{ mg/m}^3$	$2 < x \le 5 \text{ mg/m}^3$	>5 mg/m <sup>3</sup>
	I (class A)	2 (class B)	3 (class C)	4 (class D)	5 (class E)	I (class A)	2 (class B)	3 (class C)	4 (class D)	5 (class E)
	(Udass A) N (%)	(Uldass D) N (%)	(Ulass U) N (%)	(UI335 L) N (%)	(UI455 L) N (%)	(V1455 A) N (%)	(U (22) N (%)	(Ulass U) N (%)	(Ulass D) N (%)	(LIASS L) N (%)
Summer 1 <sup>st</sup> Cycle	4 (44.44)	4 (44.4)	ı	1(11.11)	·	2(33.33)	1(16.67)		1 (16.77)	2 (33.33)
Autumn 2 <sup>nd</sup> Cycle	7 (77.78)	2 (22.2)	ı	I	·		4(66.67)	2 (33.33)		
Winter 3 <sup>rd</sup> Cycle	2 (22.2)	6 (66.67)	1 (11.11)		ı	2(33.33)	2(33.33)	2 (33.33)		ı
Temp(°C)	22.9	19.47	11.7	23.85		20.96	18.52	12.76	30.15	29.67
Hum. %	53.07	52.95	62	76		50.5	57.28	63.25	34.00	40.50
Wind speed (m/s)	4.85	5.34	5.01	3.21		5.19	4.51	3.08	5.44	3.91

variable. The same holds for the three examined meteorological covariates.

Regarding the potential importance of interaction effects between the explanatory variables on the response variable of PM10 concentration, the results of the statistical modeling showed that the only statistically significant effect is the one associated with interaction effects between cycle and location. Specifically, it was found that the combination of the 1<sup>st</sup> cycle (summer period) with the urban environment (b=-1.459; p-value < 0.05) affects positively the concentration of PM10, when compared to the rest of the combinations between the levels of the two categorical variables.

Finally, in terms of model fit, the final selected model's  $R^2$  value was 33%, indicating a moderate fit to the data, which is anticipated since the majority of initially selected explanatory variables were found to be non-significant for the explanation of variability in the response variable of "concentration of PM10 (mg m<sup>-3</sup>)."

Predictability of the final selected multiple linear regression model is assessed through calculation of *MSPE*. For The latter model the obtained value is 0.786, significantly lower when compared to the calculated *MSPE* for the simple regression model with the single predictor of location (MSPE = 1.045).

To further examine the quality of the fit of the best fitted model in terms of meeting the assumptions of linear regression, such as the normality of residuals derived from the fitted model, we look at the normal probability plot (QQ-plot) of the residuals (Fig. 8) along with the histogram plot of standardized residuals (Fig. 9). Inspection of both Figures indicates that there are very few moderate deviations from normality.

## 4 Discussion

The present study revealed significant differences in PM10 concentrations recorded in the urban area during the summer (2.27 mg·m<sup>-3</sup>/8 h) in comparison to those measured in autumn and winter (0.91 mg·m<sup>-3</sup>/8 and 0.70 mg·m<sup>-3</sup>/8, respectively), which, incidentally, presented no statistically significant difference between them (Fig. 4, Table 6). The equivalent measurements carried out in the peri-urban forest showed no statistical difference in PM10 levels among the three sampling seasons, in other words, no seasonal variability was detected in PM10 concentrations in the forest.

The 2<sup>nd</sup> sampling cycle (autumn) coincided with high rainfall levels observed at this time of the year amounting

**Fig. 7** Percentage of PM10 concentration per concentration class



to 81 RR (the average monthly rainfall height for autumn being approx. 67.1 RR); this fact considerably reduced autumn PM10 concentrations in the peri-urban forest, whereas the same factor does not appear to have had a similar impact on particle levels in the city (Table 4).

These data are expressed on a 24-h basis according to the European Environment Agency (EEA) in Table 4, 5<sup>th</sup> column; this means that the corresponding highest 24-h TWA PM10 concentration is 6.81 mg m<sup>-3</sup>, recorded in the urban area. In the 2<sup>nd</sup> cycle (autumn), PM10 concentrations in the urban (0.91 mg m<sup>-3</sup>/8 h) and peri-urban environment (0.32 mg m<sup>-3</sup>/8 h) are reduced in comparison with the 1<sup>st</sup> cycle, with the lowest values recorded in the forest again.

In a similar study by Chrysikou et al. (2008), in which PM10 concentration measurements were carried out only in an urban area, the corresponding mean concentration values both for the cold and warm seasons were significantly higher ( $45.1 \pm 20.6 \text{ mg m}^{-3}/24 \text{ h}$ ) compared to the average concentration values of the present study for all sampling cycles carried out in the city ( $3.9 \pm 4.5 \text{ mg m}^{-3}/24 \text{ h}$ ).

The difference in concentration values between the study by Chrysikou et al., (2008) and the present study is probably due to the sampling method followed in each. In the former, PM10 samples were taken solely from a central point of the urban center (located at the junction of two busy roads) receiving heavy traffic loads, whereas in the current project sampling positions (Fig. 3) were scattered so that PM10 samples could be collected from the outskirts of the city as well for the best representation of the entire urban fabric. Moreover, the two urban centers studied in the two research projects are considerably different, a fact that may have contributed significantly to the differences in PM10 levels: in this paper measurements were conducted in a non-industrialized city with a population size of app. 60.000, while the measurements by Chrysikou et al. (2008) were carried out in the center of a heavily industrialized city (Thessaloniki).

From similar measurements performed with the same sampling method in the center of Athens, average PM10 concentrations were found to amount to 75.5 mg·m<sup>-3</sup>/24 h (Chaloulakou, 2003). Four years later, Chaloulakou et al. (2008) repeated the experiment, but this time

<b>Table 6</b> Parameter	Parameter	β	S.E	<i>p</i> -value	95% Confidence	Interval
corresponding significance					Lower Bound	Upper Bound
( <i>p</i> -value) and 95% confidence intervals for the best selected model	Intercept ( $\beta_0$ ) Cycle (reference) 2 <sup>rd</sup> evelo)	2.236	1.612	n.s	-1.030	5.501
best selected model	$1^{\text{st}}$ cycle ( $\beta_1$ )	) 1.417	0.621	0.028*	0.160	2.674
	$2^{nd}$ cycle ( $\beta_2$ )	0.011	0.588	n.s	-1.180	1.202
n.s.: not statistically significant: $\frac{1}{2}$ n < 0.05	Cycle*location (reference:	: 1 <sup>st</sup> cycle*ur	ban)			
	(1 <sup>st</sup> cycle) * (location = peri-urban forest)	-1.459	0.551	0.012*	-2.575	-0.342

**Fig. 8** Normal probability plot of the residuals of the best fitted regression model



**Fig. 9** Histogram of the residuals of the best fitted regression model

samples were taken from an Athens area away from the centre, where PM10 concentrations amounted to  $57.5\pm27.8 \text{ mg m}^{-3}/24 \text{ h}$ . The corresponding mean urban concentrations in mainland Europe have been estimated at  $7.0\pm4.1 \text{ mg m}^{-3}$  (Chrysikou et al., 2008), a value that is closer to the present study results ( $3.9\pm4.5 \text{ mg m}^{-3}$ ) pertaining to the urban environment.

Table 5 and Fig. 7 present the classification of the samples into the 5 PM10 classes. As regards seasonal variability, it can be noted that the greatest percentage of samples (N) from all three sampling periods belong to low concentration classes, namely Class A and B (0.5 mg·m<sup>-3</sup> and  $0.5 < x \le 1$  mg·m<sup>-3</sup>). It is worth mentioning that only in the summer cycle (1<sup>st</sup> cycle), 13.3% of the samples belong to higher concentration classes, namely Class D and E ( $2 < x \le 5$  mg·m<sup>-3</sup> and  $3^{rd}$  cycles) none of the samples falls in these high concentration classes (D and E class).

As regards temperature, ambient humidity and wind speed measurements, these do not differ considerably from class to class, a finding that shows that these variables did not decidedly determine the average PM10 concentration values nor has it been found from the statistical data analysis that these variables (temperature, humidity, wind speed) positively affect PM10 concentrations. In none of the sampling cycles was there any presence of strong wind. More specifically, in all sampling cycles in the forest, as is evident from the wind speed mean values, the wind can be characterized as mild (soft breeze) to moderate (moderate breeze), whereas according to the corresponding mean values of the wind speed in the urban environment, the most appropriate term would be weak (light breeze) to moderate (moderate breeze) (weatheronline.gr).

As far as the even-aged *Pinus brutia* peri-urban forest is concerned, it can safely be concluded that its relatively young age (the forest was replanted 30 years ago) in combination with its relatively small sized foliage type as a coniferous species did not decisively affect its retention capacity.

## 5 Conclusion

With regard to seasonal variability, there were higher concentrations in the summer months both in the urban and peri-urban environment, while during the autumn and winter months there were reduced values in both environments.

The values recorded in the present study were significantly lower  $(3.9\pm4.5 \text{ mg m}^{-3}/24 \text{ h})$  than the average PM10 concentrations in the two most densely populated cities in Greece, namely Athens and Thessaloniki  $(45.1\pm20.6 \text{ mg m}^{-3}/24 \text{ h})$  and 75.5 mg m $^{-3}/24 \text{ h})$ ; however, measurements in the latter were only in single sampling points located in their centres. In any case, the average PM10 values are below the 50 mg m $^{-3}/24$  h threshold set by the European Environment Agency (EEA, 2007).

Seasonal variability of MP10 concentrations was more marked in the urban area during the summer months (2.27 mg·m<sup>-3</sup>/8 h) in comparison to autumn and winter. In the latter periods, PM levels were almost the same (0.91 mg·m<sup>-3</sup>/8 h) και 0.70 mg·m<sup>-3</sup>/8 h). In the forest, there was no statistical difference among PM10 concentrations, so there was no seasonal variability. It should be noted that in the forest the high rainfall contributed to the retention of particulate matter.

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**Data Availability** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

#### Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

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