



# Influence of number of visitors and weather conditions on airborne particulate matter mass concentrations at the Plitvice Lakes National Park, Croatia during summer and autumn

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We investigated the influence of local meteorological conditions and number of visitors on ambient particulate matter (PM) mass concentrations and particle fraction ratios at the Plitvice Lakes National Park between July and October 2018. Outdoor mass concentrations of particles with aerodynamic diameters of less than 1, 2.5, and 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{10}$ , respectively) and indoor  $\text{PM}_{10}$  were measured with two light-scattering laser photometers set up near the largest and most visited Kozjak Lake. Our findings suggest that the particles mainly originated from background sources, although some came from local anthropogenic activities. More specifically, increases in both indoor and outdoor mass concentrations coincided with the increase in the number of visitors. Indoor  $\text{PM}_{10}$  concentrations also increased with increase in outdoor air temperature, while outdoor PMs exhibited U-shaped dependence (i.e., concentrations increased only at higher outdoor air temperatures). This behaviour and the decrease in the  $\text{PM}_{10}/\text{PM}_{2.5}$  ratio with higher temperatures suggests that the production and growth of particles is influenced by photochemical reactions. The obtained spectra also pointed to a daily but not to weekly periodicity of PM levels.

**KEY WORDS:** anthropogenic PM sources; bivariate polar plot; light-scattering laser photometry; weighted overlapped segment averaging

Ever since Plitvice Lakes National Park (PLNP) with over 294.82 km<sup>2</sup> of karst hills and mountains in central Croatia entered the World Heritage list of the United Nations Educational, Scientific and Cultural Organization (UNESCO) (1), it has been attracting millions of visitors, particularly in the spring, summer, and autumn, when daily weekend numbers would exceed 10,000, mainly around the lakes (2).

A number of studies focused specifically on the PLNP area have investigated anthropogenic influence on lake water, sediment, and soil quality (3, 4), but only a few addressed the atmospheric component, including chemical composition of precipitation and its relationship with weather types (5). A recent study of daily concentrations of the particulate matter (PM) fraction with aerodynamic diameter of  $\leq 2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) and its organic carbon (OC) and inorganic carbon (CC) content in 2015 (6) gave surprising results, as – contrary to the expected –  $\text{PM}_{2.5}$  mass concentrations were the highest in the summer and lowest in the winter. In contrast, a study of three-year measurements of the fraction with aerodynamic diameter  $\leq 10 \mu\text{m}$  ( $\text{PM}_{10}$ ) and  $\text{PM}_{2.5}$  (7) revealed highest concentrations in the winter for both PM fractions. In addition, two studies (8, 9) that analysed data over several years for the entire Croatia, reported the chemical composition of precipitation (8) and PM concentrations

(9) for measuring sites located at the PLNP but did not discuss them specifically.

The aim of this study was to see how outdoor  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and PM with aerodynamic diameter  $\leq 1 \mu\text{m}$  ( $\text{PM}_1$ ) would be influenced by local weather and the number of visitors to the Park, for which reason we focused on summer and autumn (July–October) as the peak visiting season.

We also wanted to see the behaviour of the indoor  $\text{PM}_{10}$  fraction over these months (that is, under the same local outdoor meteorological conditions), as – to the best of our knowledge – only a few studies reported any PM levels in indoor environments in Croatia, mostly urban, including schools and universities (10, 11), or related to simulated or real occupational exposure in hospitals (12) and metal workshops (13), but none in rural background environment.

## MATERIALS AND METHODS

### Sites and measurements

Outdoor mass concentrations (3-minute means) of  $\text{PM}_1$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{10}$  were measured from 7 July to 4 November 2018 using a DustTrak 8533 light-scattering laser photometer (TSI Inc.,

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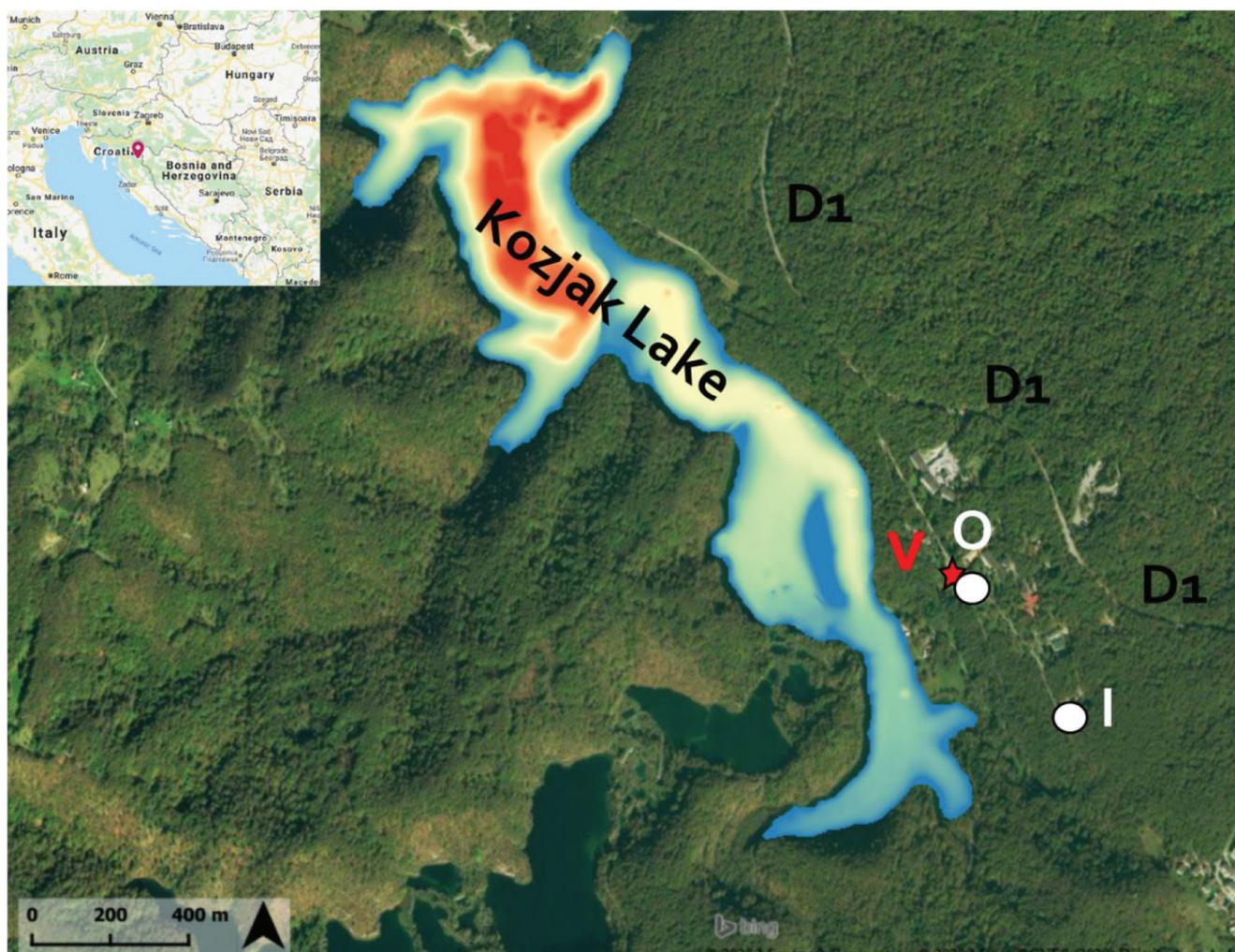
Shoreview, MN, USA), whereas indoor  $PM_{10}$  (6-minute mean) mass concentrations were measured from 7 July to 11 October 2018 (Figure 1) with the 8520 model of the same manufacturer. Both photometers were regularly serviced by the manufacturer.

The outdoor aerosol monitor was placed at the Plitvice Lakes weather station ( $\varphi=44.8811^{\circ}N$ ,  $\lambda=15.6197^{\circ}E$ , 579 m above the sea level (ASL) with inlet at average breathing height of 1.7 m above the ground level (AGL) in line with other studies (11) and the operating procedure of the Institute of Medical Research and Occupational Health (IMROH), Zagreb, Croatia, which calibrated the monitors. The inlet of indoor monitor was positioned about 2 m above the floor in one of the ground floor offices of the Scientific Research Centre “Ivo Pevalek” of PLNP, since its positioning at lower height (that is, at 1.7 m above the floor) would

disturb the office employees (usually one or two) in their routine activities. These employees frequently work outdoors all over the National Park (collecting samples and performing various field measurements) and do not spend all the time in the office but come and go as needed. The office does not have air conditioning and the windows are open from time to time.

The weather station is maintained by the Croatian Meteorological and Hydrological Service (MHS) and provides standard hourly mean data for air temperature, relative humidity, wind speed and direction, precipitation, and atmospheric pressure.

Additionally, hourly mean mass concentrations of  $PM_{2.5}$  and  $PM_{10}$  are routinely monitored and validated by the MHS at the site Čujića Krčevina ( $\varphi=44.8993^{\circ}N$ ,  $\lambda=15.6098^{\circ}E$ , 704 m ASL), about 7 km to the south-southeast of the weather station (not shown).



**Figure 1** Position of Plitvice Lakes National Park (red bubble in a small figure), outdoor  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_{10}$  measurement site indicated with the letter O ( $\varphi=44.8811^{\circ}N$ ,  $\lambda=15.6197^{\circ}E$ , 579 m ASL) near the trackless train station (V) and indoor measuring site (I). D1 denotes the Karlovac-Split state road [Sources: Google Maps (upper left panel) and Bing Maps (big panel)]

This site is part of the National Network for Continuous Air Quality Monitoring (Network) and monitors rural background PM concentrations with optical particle counters (Grimm EDM 180, Grimm Durag Group, Aerosol Technik, Ainring, Germany) (9) at about 4 m AGL and makes data available at <http://iszz.azo.hr/iskzl/postaja.html?id=257>. We used these Network data to check ours and to obtain a wider picture of air quality at PLNP.

The air distance between the outdoor and indoor measuring site was about 400 m. Some 90 m to the northwest of the outdoor site there is a station for trackless trains (V in Figure 1) consisting of a diesel-powered locomotive and two carriages. Their sightseeing tours are usually scheduled every 30 min, but during the peak tourist season they start as soon as they are full. While they wait for tourists to get aboard, their diesel engines keep running. The state road D1, which crosses PLNP from the northwest to the southeast, is approximately 200 m to the northeast of the outdoor site O. The closest settlement Mukinje with several dozen tourist apartments is located 500 and 400 m to the southeast of the outdoor and the indoor site, respectively. At 100–300 m from the outdoor site in a section stretching from the north to the east-south-east of the outdoor measuring site, there are three hotels and a restaurant. They are located some 200–700 m to the north-northwest of the indoor site.

As it is well known that photometers generally overestimate PM concentrations (14, 15), they were calibrated against gravimetric measurements of with samplers at IMROH (according to the EN 12341 and EN 14907 norms), where inlets of all instruments were placed at the same height above the ground (1.7 m). Gravimetric and photometric data collected over 36 days were then compared to obtain correction formulas for each model and PM fraction as follows:

Model 8533

$$[PM]_{1,corrected} = 0.320 \times [PM]_{1,observed} + 2.434;$$

$$[PM]_{2.5,corrected} = 0.383 \times [PM]_{2.5,observed} + 2.556;$$

$$[PM]_{10,corrected} = 0.453 \times [PM]_{10,observed} + 3.941;$$

and

Model 8520

$$[PM]_{1,corrected} = 0.354 \times [PM]_{1,observed} + 4.414,$$

All concentrations are expressed in  $\mu\text{g}/\text{m}^3$ .

Daily numbers of visitors were obtained from the National Park based on information about sold tickets.

### Data analysis

Time series of measurements were analysed with the *openair* package (16, 17), which can be used to identify pollution sources, quantitatively estimate trends and trend variations with a wind sector, and evaluate the performance of an air quality model (9, 16, 18–20). In this study, the *openair* package was used to produce bivariate polar plots of both PM mass concentrations and ratios of different PM fraction concentrations and to establish if these ratios depended on meteorological variables and the number of visitors. For this purpose,

**Table 1** Daily summer and autumn indoor and outdoor PM mass concentrations measured at our outdoor and indoor site and at the Network site

	Indoor PM <sub>1</sub> ( $\mu\text{g}/\text{m}^3$ )	Outdoor PM <sub>1</sub> ( $\mu\text{g}/\text{m}^3$ )	Outdoor PM <sub>2.5</sub> ( $\mu\text{g}/\text{m}^3$ )	Network PM <sub>2.5</sub> ( $\mu\text{g}/\text{m}^3$ )	Outdoor PM <sub>10</sub> ( $\mu\text{g}/\text{m}^3$ )	Network PM <sub>10</sub> ( $\mu\text{g}/\text{m}^3$ )	Visitors (N)
Sampling height (AGL)	2 m	1.7 m	1.7 m	4 m	1.7 m	4 m	
Sampling time	6 min	1 h avg.	3 min	1 h	3 min	1 h avg.	24 h
Mean±SD	9.9±3.7	9.9±3.6	19.3±8.6	22.9±10.1	23.0±10.3	28.6±12.4	9063±3691
Min	4.4	4.4	4.0	4.5	4.5	6.6	1870
Max	52.2	26.3	137.1	172.2	69.1	83.9	18722

AGL – above the ground level; SD – standard deviation

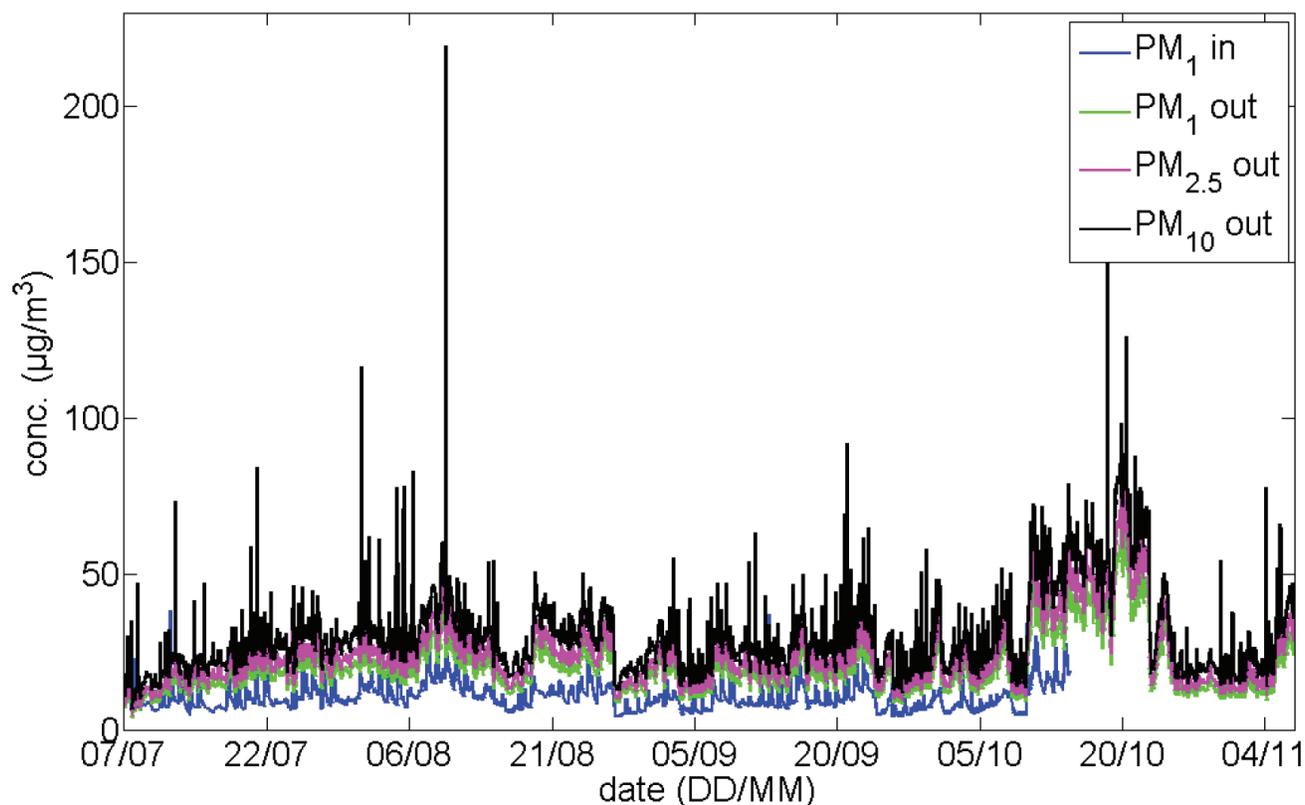


Figure 2 PM mass concentrations measured with aerosol monitors at the outdoor (out) and indoor (in) site (see map in Figure 1)

the hourly and daily mean concentrations were calculated from corrected 6-minute (indoor) and 3-minute (outdoor) time series.

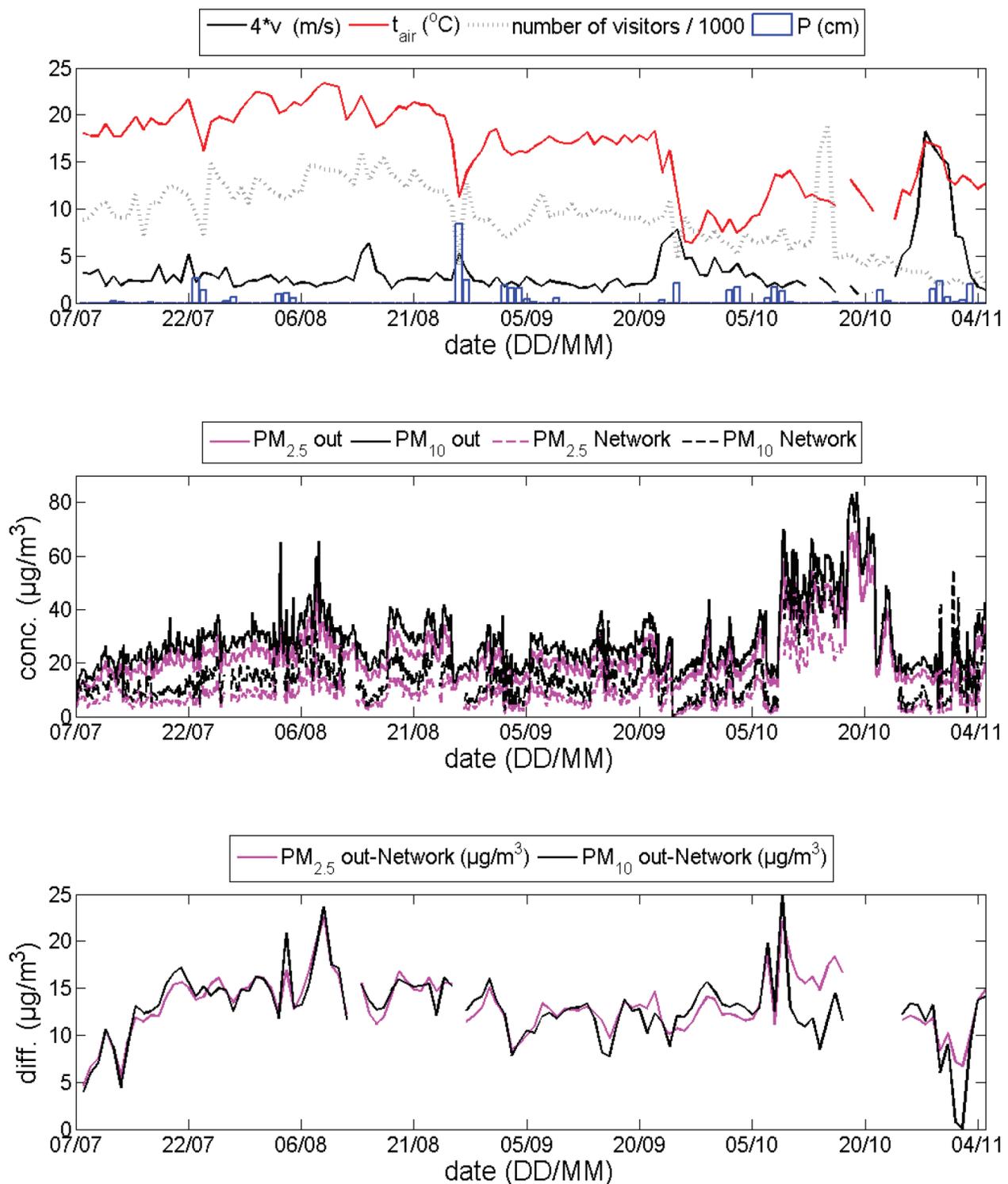
We also used spectral analysis to investigate the periodic behaviour of the time series of measured PM mass concentrations. We calculated power spectral densities (PSDs) using the *pwelch* function, which is based on Welch's method (21, 22) and built in the MATLAB software (version R2010b, MathWorks, Inc., Natick, MA, USA). Each input time series was divided into eight segments of equal length with a 50 % overlap. The trailing (remaining) input values that could not be included in these eight segments were omitted. Each segment was windowed with a Hamming window (23, 24), where the window length (WL) was set to 512 points for hourly and 3-minute outdoor means or to 256 points for the 6-minute indoor means.

## RESULTS AND DISCUSSION

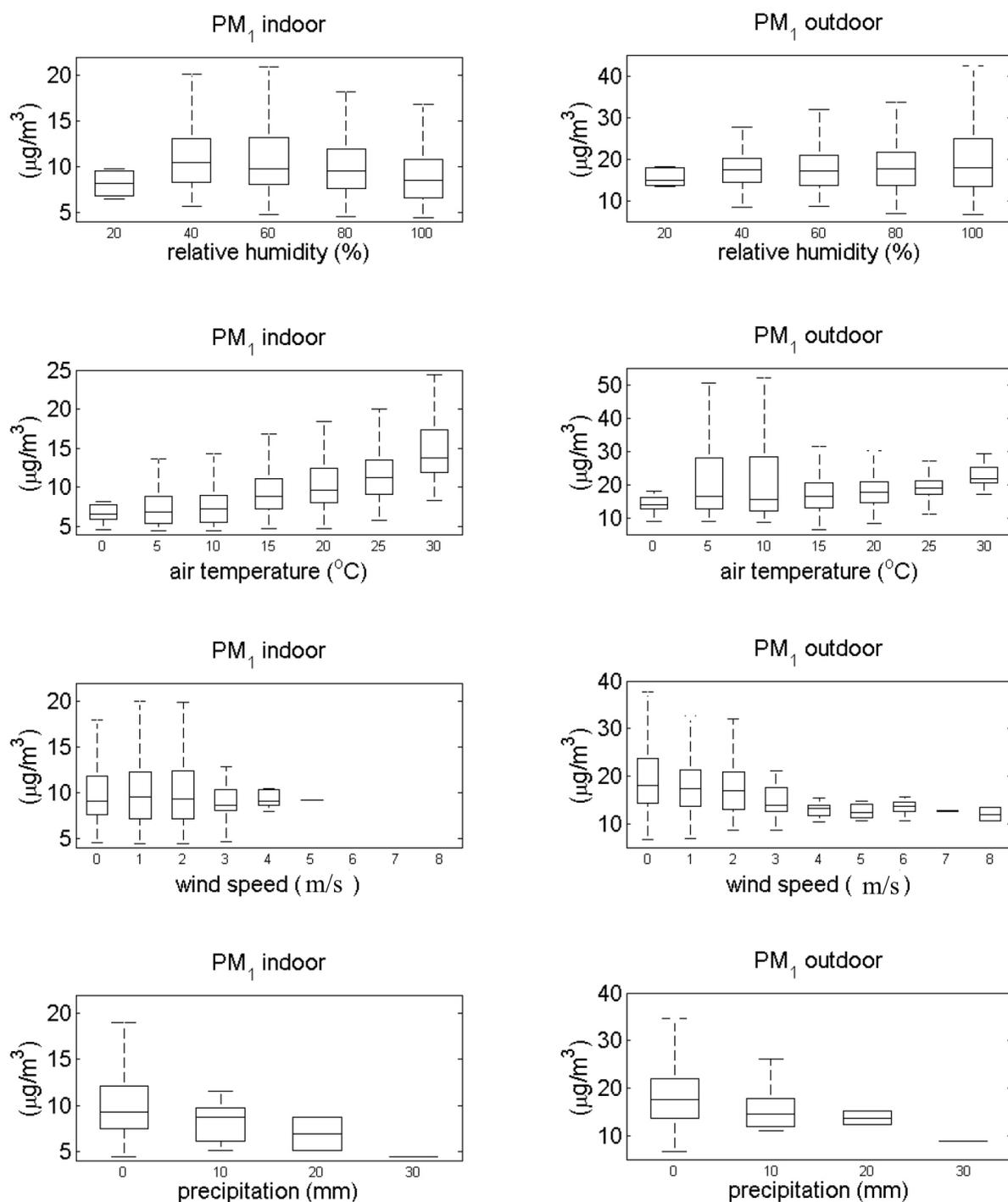
Figure 2 shows that all PM fractions measured at our outdoor (O) and indoor (I) site exhibited similar patterns over the entire study period. Indoor  $PM_{10}$  mass concentrations were generally lower than the outdoor ( $9.9 \mu\text{g}/\text{m}^3$  in average, Table 1). However, the two

measuring sites were approximately 400 m apart and the indoor sampling height was 30 cm higher.

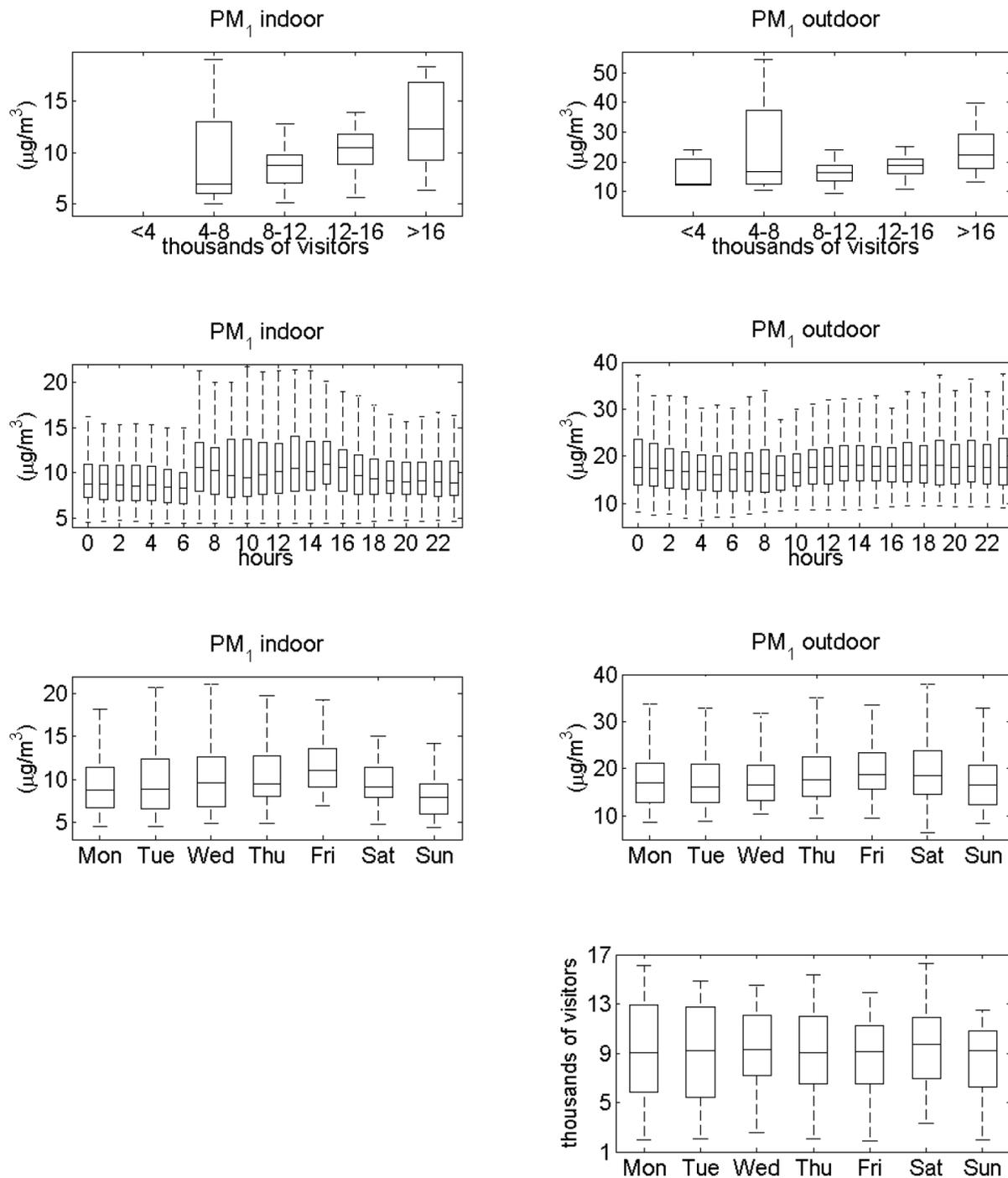
A comparison of hourly outdoor  $PM_{2.5}$  and  $PM_{10}$  concentrations with concurrent outdoor Network values (Figure 3, middle panel) shows very similar patterns at the two locations for both fractions. This suggests that both sites are mainly affected by more distant (background) pollution sources, i.e., there were no major local pollution sources near any of the two sites. The levels of both fractions were generally higher at the outdoor site than at the Network site (Figure 3 and Table 1). Similarly, annual mean  $PM_{10}$  levels at the Network site, which varied between 12 and  $17 \mu\text{g}/\text{m}^3$  between 2011 and 2014 (9), were also lower than the four-month mean of measurements recorded at our outdoor site ( $28.8 \mu\text{g}/\text{m}^3$ , Table 1, hourly data). The average difference for both fractions was  $14 \mu\text{g}/\text{m}^3$  (Table 1), while daily variations ranged from 5 to 25 and from 0 to  $25 \mu\text{g}/\text{m}^3$  for  $PM_{2.5}$  and  $PM_{10}$ , respectively (Figure 3, bottom). The greatest differences occurred on days with low wind speeds (8 August and 9 October), which points to the influence of local sources on these days. These differences are not surprising, as the two measuring sites are 7 km apart and exposed to different local sources of PM (the main local sources being local transport and resuspension), and our outdoor site is at 125 m lower altitude



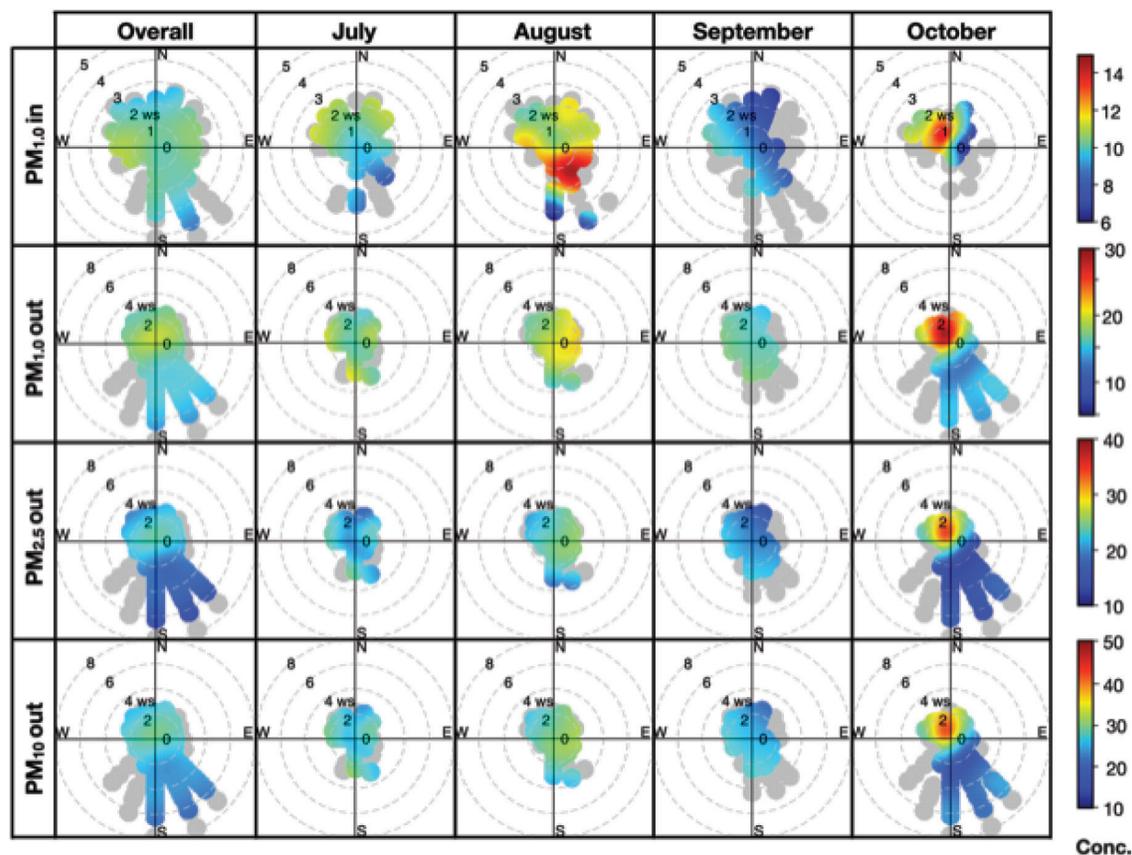
**Figure 3** Daily number of visitors (in thousands), precipitation (P, cm), mean air temperature ( $t_{air}$ ), and wind speed ( $v$ ) multiplied by 4 (top) and comparison of hourly outdoor measurement with Network measurements (centre) and the difference between daily mean outdoor and Network concentrations (bottom)



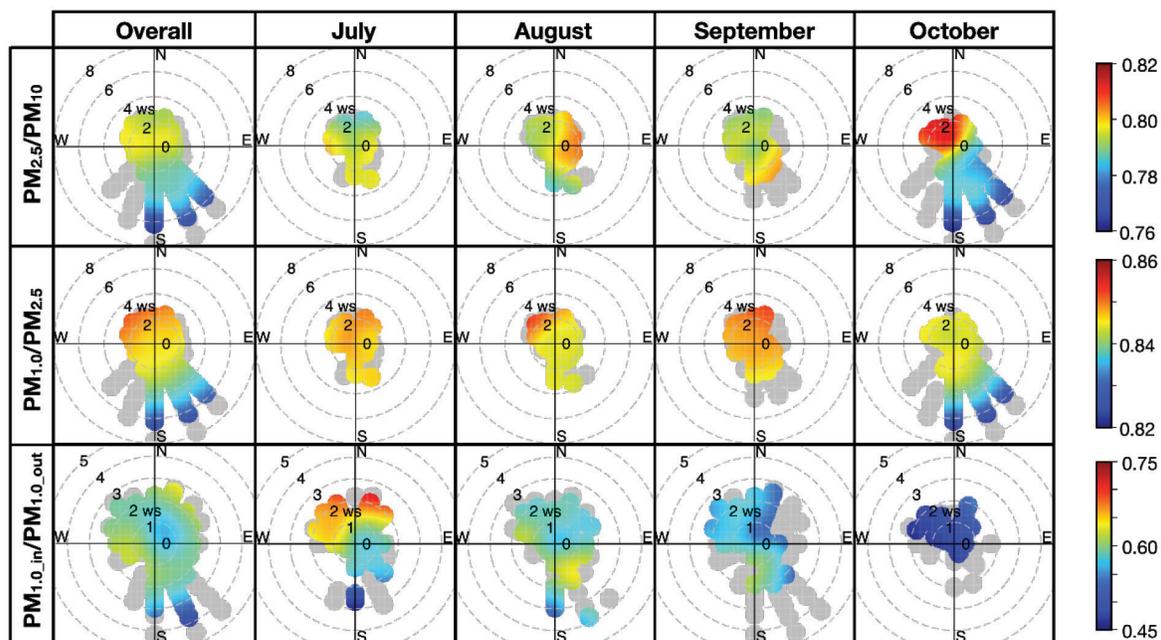
**Figure 4** The relationship between hourly mean PM<sub>1</sub> concentrations and concurrent weather variables. The horizontal line within a box shows the median, and the bottom and the top of the box correspond to the 25<sup>th</sup> and 75<sup>th</sup> percentile, respectively. Horizontal bars (whiskers) show the most extreme data points that are not considered outliers, that is, values that are less than 1.5 times the interquartile range away from the top or bottom of the box.



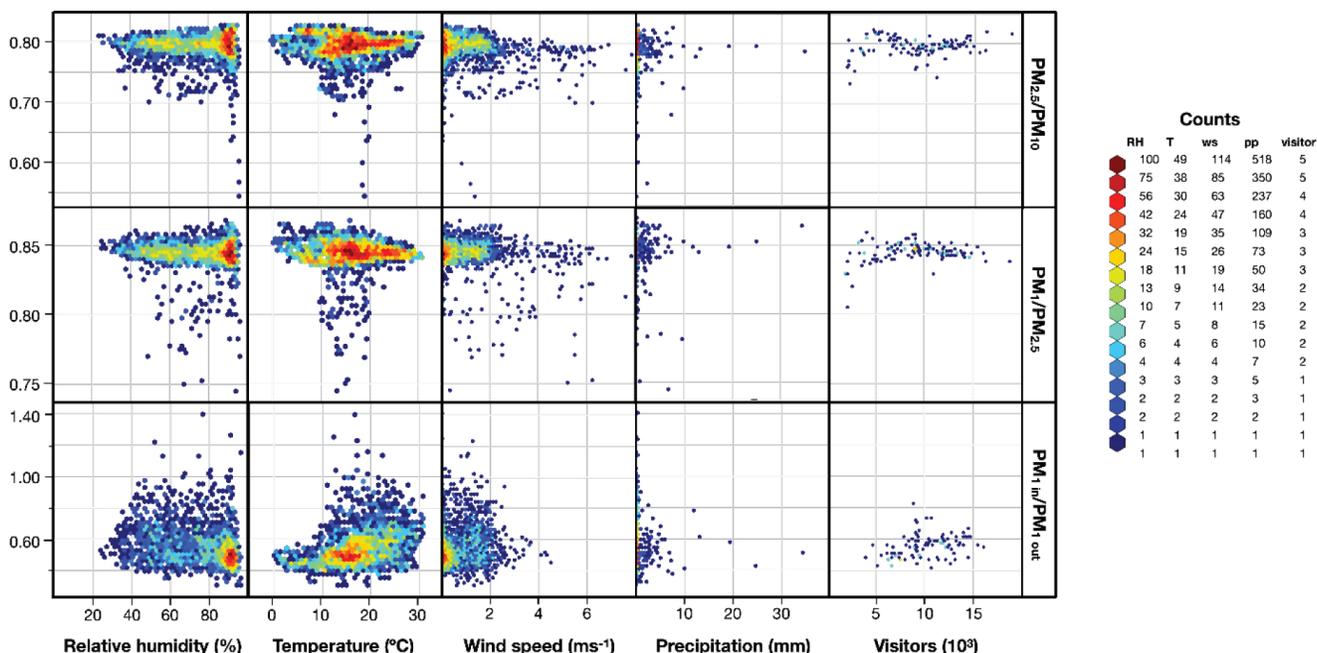
**Figure 5** Dependence of daily mean  $PM_1$  concentrations on number of visitors, diurnal and weekly variations of hourly mean  $PM_1$  concentrations, and weekly variation of number of visitors. Hours correspond to local standard time (LST)



**Figure 6** Bivariate polar plots for hourly mean indoor and outdoor PM levels. Grey circles correspond to single case of particular combination of corresponding wind and concentration data. Conc. – PM concentration in  $\mu\text{g}/\text{m}^3$ ; WS – wind speed (m/s)



**Figure 7** Bivariate polar plots for PM concentration ratios (legend to the right). Grey circles correspond to single case of particular combination of corresponding wind and concentration data. WS – wind speed (m/s)



**Figure 8** Dependence of hourly mean PM fraction ratios on meteorological variables and number of visitors for investigated period (from 7 July to 4 November 2018). Counts – absolute frequencies of  $x, y$  pair values

than the Network site and is located at the sidewall of an almost completely enclosed topographic basin (Figure 1, right panel). Such basins generally favour build-ups of hydrostatically stable pools of cold air at night (25) and inhibit atmospheric mixing, which results in elevated night-time pollutant concentrations (26, 27). In addition, the sampling height at the Network site is 2.3 m higher than at the outdoor site. As higher concentrations are expected closer to the ground, Network concentrations should generally be lower than those observed at the outdoor site, at least over night (27). Finally, mass concentrations at the two sites were measured by different equipment.

Figure 3 shows the effects of ventilation and precipitation on pollution levels. Namely, periods with stronger winds and/or precipitation coincide with the periods of lower PM levels at both sites for both  $PM_{2.5}$  and  $PM_{10}$  fractions (compare top and middle panel).

Figure 4 shows dependence of hourly mean indoor and outdoor concentrations on meteorological variables. As the results for all three outdoor fractions are very similar, here we show only the outdoor  $PM_1$ .

Previous studies of urban residential environment showed a clear increase in  $PM_1$  with relative humidity both indoors (11) and outdoors (28). Here, however, this correlation was less prominent with outdoor  $PM_1$ . Indoor  $PM_1$  showed an inverted U-shape similar to the one found for outdoor  $PM_{2.5}$  in some urban areas (29).

Both indoor and outdoor  $PM_1$  concentrations increased with air temperature (Figure 4). This points to the influence of solar

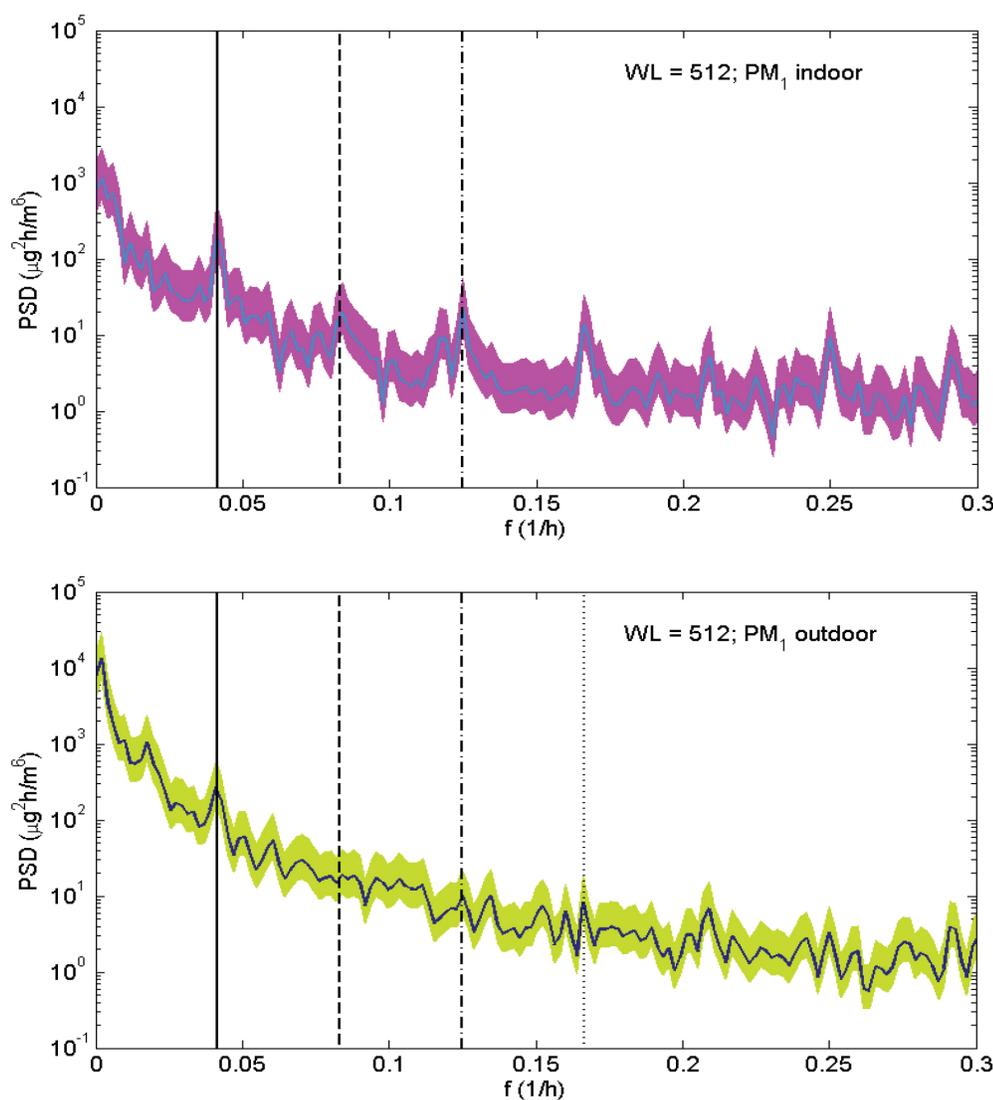
radiation on particle formation (higher air temperatures are the result of higher solar radiation). However, while indoor  $PM_1$  levels increased with temperature over the entire range of measured temperatures, outdoor PM followed this pattern only at temperatures above 10 °C. At lower temperatures (at 5 and 10 °C cut-off points), the range between the median and the 75<sup>th</sup> percentile is quite high, which implies high mean concentrations (higher than median values). Such a U-shaped dependence of outdoor PM levels (as they all had a nearly identical pattern as outdoor  $PM_1$ , data for  $PM_{2.5}$  and  $PM_{10}$  are not shown in Figure 4) on air temperature confirms previous reports of a negative and a positive relationship between  $PM_{2.5}$  and low and high temperature, respectively (30), and explains why ultrafine ( $PM_1$ ) particle levels should be higher in the summer than winter (31). We believe that higher average concentrations at low temperatures observed here are related to local heating sources from nearby ( $\approx 1$  km distant) settlements, hotels, and premises of the National Park. On the other hand, higher PM levels at higher temperatures can be attributed to faster production of secondary aerosols due to higher solar radiation (30), enhanced dust resuspension due to generally drier soil during warm season (32), and elevated summertime biogenic emissions of both primary aerosol and secondary aerosol organic precursors (33). Fair and warm weather also attracts more visitors, which entails higher traffic emissions and higher resuspension from roads and walking trails. In addition, a recent study (34) showed that deposition velocities of  $PM_{2.5}$  and  $PM_{10}$  at air temperatures ranging from 20 to 29 °C decreased with increase in temperature, which means that higher

PM levels are also related to less efficient deposition at higher temperatures.

Average outdoor  $PM_{2.5}$  level at 1.7 m AGL ( $22.9 \mu\text{g}/\text{m}^3$ , Table 1) was below the annual limit of  $25 \mu\text{g}/\text{m}^3$  set by the EU and Croatian legislation (35). However, it is likely that the average concentration over the entire year might be higher than this limit for two reasons: a) contribution of local and regional emissions due to wintertime heating and b) enhanced static stability of the atmospheric boundary layer in the winter, which results in higher near-ground pollutant concentrations (36). On the other hand, average  $PM_{10}$  concentrations ( $28.8 \mu\text{g}/\text{m}^3$ , Table 1, hourly data) were noticeably lower than daily ( $50 \mu\text{g}/\text{m}^3$ ) and annual ( $40 \mu\text{g}/\text{m}^3$ ) limits (35), yet they still exceeded the daily limit of  $50 \mu\text{g}/\text{m}^3$  on 10 days or 231 hours. At the same time, daily mean  $PM_{10}$  levels measured at the Network site kept below this limit for the entire study period.

With respect to the global air quality guidelines published by the World Health Organization (WHO) in 2021 (37), our hourly  $PM_{2.5}$  concentrations at the outdoor site averaged to annual values were below the 2<sup>nd</sup> interim target of  $25 \mu\text{g}/\text{m}^3$ , whereas the Network site concentrations were below the 4<sup>th</sup> interim target of  $10 \mu\text{g}/\text{m}^3$ . Averaged to annual,  $PM_{10}$  concentrations were below the 3<sup>rd</sup> interim target level of  $30 \mu\text{g}/\text{m}^3$  at our outdoor site and the 4<sup>th</sup> target level of  $20 \mu\text{g}/\text{m}^3$  at the Network site.

The effects of wind speed and precipitation on outdoor  $PM_{2.5}$  and  $PM_{10}$  (Figure 3) are also visible for ultrafine particles (Figure 4). Similar to other studies (38, 39), outdoor  $PM_{10}$  levels dropped with higher wind speed, but indoor medians remained similar over the entire span of wind speeds measured at the outdoor site. However, due to smaller instrument memory the indoor PM data series (Figure 2) does not cover October, when the winds were the strongest



**Figure 9** Power spectral densities (PSDs) for hourly indoor (top) and outdoor (bottom)  $PM_{10}$  time series. Frequency ( $f$ ) is shown in  $1/\text{h}$ . Central thin lines show PSDs and coloured areas 95 % confidence intervals. Vertical full lines correspond to 24-hour periods, while corresponding higher harmonics are separated by dashed, dash-dotted, and dotted lines for 12, 8, and 6 h, respectively. WL – window length

(Figure 3, top). On the other hand, both outdoor and indoor  $PM_{10}$  levels decreased with precipitation. A similar wet scavenging effect was reported by a number of other studies (11, 38, 40), although precipitation can also increase  $PM_{2.5}$  concentrations if it is weak or comes with fog (40).

Both indoor and outdoor daily  $PM_{10}$  levels rose with the number of visitors to PLNP (Figure 5) on days when it was above 8,000, most likely owing to denser traffic of trackless trains [involving higher exhaust of diesel engines and non-exhaust emissions (brake, tyre, and road surface wear and tear and particle resuspension from road surfaces (41)] and particle resuspension caused by pedestrians.

Daily indoor and outdoor  $PM_{10}$  variations exhibited different patterns (Figure 5). Indoor levels were the highest during working hours, from 7 to 16 h local standard time (LST), and rather uniform. In the late afternoon and evening they would gradually drop and bottom out between midnight and 6 h LST. As there are no major pollution sources at the National Park premises, this pattern points to particle resuspension due to employee movement (42). In contrast to indoor variation, outdoor levels reached their minimum between 5 and 9 h LST, while they remained uniformly higher between 11 and 24 h LST. Such a long interval of higher  $PM_{10}$  levels is likely owed to tourist activities in the daytime and the forming of a shallow, hydrostatically stable boundary layer that prevents pollutant dispersion and keeps them concentrated in the night time (26).

Weekly variations in  $PM_{10}$  levels (Figure 5) also point to differences between the indoor and outdoor patterns. Indoor levels peaked on Friday (the office is closed on weekend), which points to increased resuspension, probably consistent with the end-of-the-week employee activities. Outdoor concentrations peaked on Friday and Saturday (which also coincided with the number of visitors). Both were the lowest on Sunday.

Figure 6 shows bivariate polar plots for measured PM fractions and Figure 7 for fraction ratios. The lowest outdoor levels over the entire study period (marked as “Overall” in Figure 6) coincided with winds from the south-eastern quadrant with speeds above 1 m/s. However, higher levels show no such association with any specific wind direction as long as their speed was below 1 m/s. This suggests that outdoor concentrations were dominated by background emissions rather than prominent local sources or transport of particles from some specific, more distant emission source. A look at each study month separately reveals the influence of specific wind directions, such as winds from the eastern and north-western quadrants for August and October, respectively.

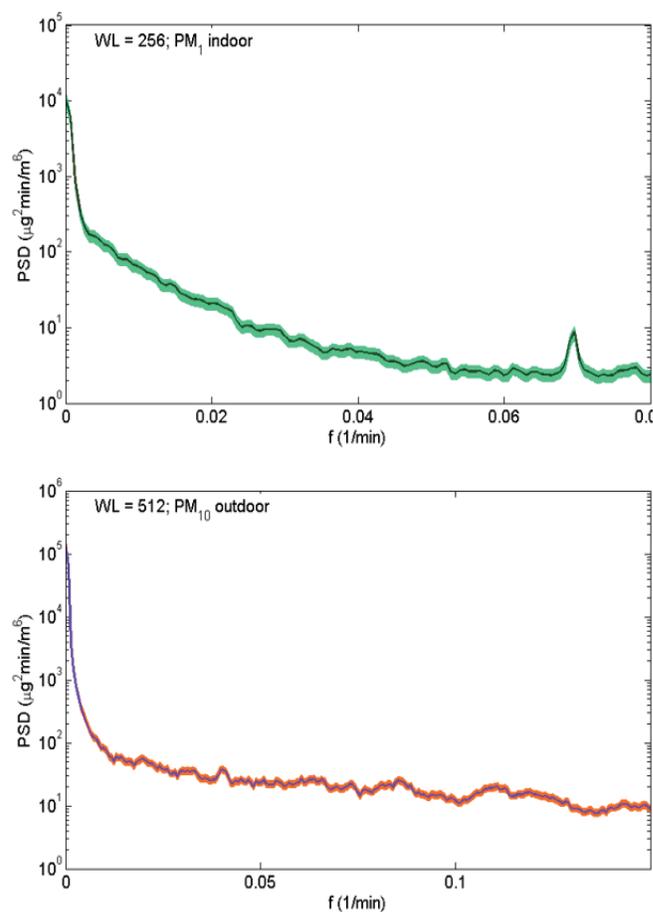
At the indoor site the highest  $PM_{10}$  levels were associated with easterly and westerly winds, and the lowest with northerlies and south-south-easterlies.

Judging by the outdoor  $PM_{2.5}/PM_{10}$  and  $PM_{10}/PM_{2.5}$  ratios for the entire study period (Figure 7), winds from the two northern quadrants showed the highest and winds from the south-eastern quadrant the lowest contribution of  $PM_{2.5}$  to  $PM_{10}$  and  $PM_{10}$  to  $PM_{2.5}$ . Contribution of  $PM_{10}$  to  $PM_{2.5}$  was also somewhat higher with the winds from the north-western than from the north-eastern quadrant,

which may be owed to the trackless train  $PM_{10}$  emissions from the nearby station V (Figure 1) to the north-west of the outdoor site, as  $PM_{10}$  levels are known to decrease more rapidly with distance from the source than the levels of larger particles (43), and it is very unlikely that  $PM_{10}$  originated from more distant sources.

Apart from the wind, PM ratios were also affected by other meteorological parameters and the number of visitors (Figure 8). Higher relative humidity was associated with a drop in  $PM_{2.5}/PM_{10}$  and  $PM_{10}/PM_{2.5}$  ratios and the most prominent drop in the indoor/outdoor  $PM_{10}$  ratio.

While the outdoor  $PM_{10}$  contribution to  $PM_{2.5}$  decreased with increase in temperature for the entire range of measured temperatures, outdoor  $PM_{2.5}$  to  $PM_{10}$  contribution increased with temperature only for temperatures above 15 °C. On the other hand, the indoor/outdoor  $PM_{10}$  ratio exhibited a prominent increase with



**Figure 10** Power spectral densities (PSDs) for 6-min mean  $PM_{10}$  indoor (top) and 3-min mean  $PM_{10}$  outdoor (bottom) time series. Frequency ( $f$ ) is shown in 1/min. Central thin lines show mean PSDs and coloured areas 95 % confidence intervals. WL – window length

temperature for the entire range of measured outdoor temperatures, which might be owed to more intense particle growth (that is,  $PM_1$  loss) outdoors under the influence of direct solar radiation on sunny days. In contrast, indoor particles are mainly exposed to diffuse radiation, even on sunny days, and the growth of indoor particles (that is, a loss of  $PM_1$ ) is less intense. As a result, indoor/outdoor ratio increases.

An increase in wind speed coincided with a decrease in both  $PM_{2.5}/PM_{10}$  and  $PM_1/PM_{2.5}$  outdoor ratios.

Dependences of the  $PM_{2.5}/PM_{10}$  ratio on precipitation are unclear, while the outdoor  $PM_1/PM_{2.5}$  ratio increased with an precipitation intensity above 8 mm/h. The latter supports earlier findings that  $PM_{2.5}$  particles are washed out of the atmosphere more efficiently than  $PM_1$  particles (46).

Finally, all PM ratios increased with the number of visitors. This increase was the most prominent for the indoor/outdoor ratio of  $PM_1$  fraction.

Figures 9 and 10 show power spectral densities of time series. Figure 9 shows only the results for indoor and outdoor  $PM_1$ , as outdoor  $PM_{2.5}$  and  $PM_{10}$  PSDs were very similar to the outdoor  $PM_1$  PSD. Both indoor and outdoor PSDs were computed from hourly means and point to daily periodicity. Namely, each distinct peak corresponds to 0.042 h (frequency) over 24 hours. Daily periodicity was also reported for the same time series for weather variables in a study of Kozjak Lake (22), which suggests that our daily PM periodicity was the result of two periodic forcings: daily weather and human activity. Furthermore, we did not detect weekly periodicity for coarse particles ( $PM_{2.5-10}$ ) (44) (not shown here).

In order to detect possible smaller-scale periodicities we also calculated PSDs from 6-minute (indoor) and 3-minute means (outdoor) (Figure 10). The indoor spectrum exhibited a distinct energy peak at the frequency of 0.0699/min, that is, every 13.35 min (Figure 10 top), the outdoor spectra did not reveal any clear-cut periodicity. This indoor peak at 13.35 min probably coincides with an employee regularly counting bark beetles collected in the National Park in the same office in which  $PM_1$  measurements were taken. This is done by filling a beaker with the beetles, banging it gently on a table surface several times to align them in strata, and filling the next beaker. We believe that banging resuspended the particles resting on the table surface and/or the beakers. The time needed to fill up one beaker roughly corresponds to the frequency observed on the spectrum.

For outdoor  $PM_{10}$  very weak peaks were detected at frequencies of 0.01953, 0.04036, and 0.008529/min, that is, every 51.2, 24.8, and 11.7 min, respectively (Figure 10 bottom). The highest peak obtained for 24.8 min may be associated with bus departure from the bus stop (Figure 1) every 30 min, which becomes more frequent at the height of the season.

## CONCLUSION

Our findings show that PM concentrations mainly originated from background sources, while local anthropogenic sources had a limited effect. This local anthropogenic influence is seen as an increase in PM concentrations with the increase in the number of visitors, diesel-powered trackless train timetable (especially in relation to outdoor  $PM_{10}$ ), and office activity (indoor  $PM_1$ ).

Although PM concentration patterns were very similar between our outdoor measurements (at 1.7 m AGL) and Network measurements (at 4 m AGL), concentrations at our outdoor site were steadily higher. The difference between our outdoor and Network values raises the issue about comparability of air quality measurements at different heights [even though both heights were in accordance with the Croatian air monitoring regulations (45)] and calls for harmonisation of sampling heights at regulatory level. Regardless of the height, the almost identical patterns of our outdoor and Network time series confirm that PM concentrations in the wider PLNP area are mainly under the influence of background sources. Furthermore, the similarity between the indoor and outdoor time series suggests that indoor PM levels are mainly driven by outdoor conditions. This is not surprising, as the indoor site does not have any major pollution sources. Despite differences in daily and weekly periodicity, both indoor and outdoor concentrations generally depended on outdoor relative humidity, wind speed, and precipitation in a sort of inverse relationship. In contrast, they generally rose with temperature, especially above 10 °C, which points to the importance of photochemical reactions in particle formation and growth. This suggests that, if global warming continues, PM concentrations might increase in the future even in unpolluted areas such as PLNP.

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## Utjecaj meteoroloških uvjeta i broja posjetitelja na masene koncentracije atmosferskih lebdećih čestica u Nacionalnom parku Plitvička jezera

Ispitali smo utjecaj lokalnih meteoroloških uvjeta i broja posjetitelja na masene koncentracije atmosferskih lebdećih čestica (PM) i na omjere njihovih frakcija u Nacionalnom parku Plitvička jezera od srpnja do listopada 2018. Masene koncentracije mjerene su laserskim fotometrima. Vani su mjerene koncentracije čestica aerodinamičkih promjera manjih od 1, 2,5 i 10 μm (odnosno PM<sub>1</sub>, PM<sub>2.5</sub> i PM<sub>10</sub>), a u zatvorenom prostoru koncentracije PM<sub>1</sub>. Oba fotometra bila su u blizini najvećega i najposjećenijega jezera (Kozjaka). Rezultati upućuju na to da su atmosferske čestice uglavnom potjecale od pozadinskih izvora, premda je primijećen i utjecaj lokalnih antropogenih aktivnosti. Naime, masene koncentracije povećavale su se s porastom broja posjetitelja i u zatvorenom prostoru i na otvorenome. Koncentracije PM<sub>1</sub> u zatvorenom prostoru povećavale su se s porastom vanjske temperature zraka duž cijelog raspona izmjerenih temperatura, dok su koncentracije na otvorenom pokazivale ovisnost U oblika (rasle su s temperaturom samo pri višim temperaturama). Takvo ponašanje, zajedno s opadanjem omjera PM<sub>1</sub>/PM<sub>2.5</sub> pri porastu temperature, upućuje na važnu ulogu fotokemijskih reakcija u produkciji i rastu čestica. Dobiveni spektri upućuju na dnevnu periodičnost razina PM, a tjedna periodičnost u spektrima nije bila vidljiva.

**KLJUČNE RIJEČI:** antropogeni izvori lebdećih čestica; bivarijantni polarni dijagram; laserska fotometrija raspršene svjetlosti; ponderirano osrednjanje preklapljenih segmenata