Environmental Science and Pollution Research (2021) 28:36640–36650
https://doi.org/10.1007/s11356-021-13295-w

RESEARCH ARTICLE

Assessment of ozone concentration data from the northern Zagreb area, Croatia, for the period from 2003 to 2016

Brunislav Matasović[1] · **Gordana Pehnec**[2] · **Ivan Bešlić**[2] · **Silvije Davila**[2] · **Dinko Babić**[2]

Received: 19 September 2020 / Accepted: 1 March 2021 / Published online: 11 March 2021

Abstract

A measurement station located in an urban area on the southern slope of the Medvednica Mountain (120 m a.s.l.), close to the Croatian capital Zagreb, provided data for an analysis of the photosmog in the city of Zagreb. Data for the period 2003–2016 obtained from this station and analysed in this work can also be compared with the nearby Puntijarka station (980 m a.s.l.) for which a similar analysis has already been carried out. In Puntijarka station analysis, it has been shown that there is most probably no significant change in ozone concentrations during the observed period. In this study the mean value of the annual ozone volume fractions showed a linear trend of 0.23 ppb yr^{-1}, a growth that is in the worst case scenario among the lowest global prediction, while the seasonal (April-to-September) mean values had a trend of 0.32 ppb yr^{-1}, which is a certain clearly observable growth. The 95-percentile values had trends of 0.009 ppb yr^{-1} (annual data) and −0.072 ppb yr^{-1} (seasonal data), respectively. Both of these values show very small changes if any at all. By using FT analysis, with the calculation of uncertainties, we have observed three prominent cycles of 169 ± 4 h (weekly cycle), 24 ± 1 h and 12 ± 1 h (diurnal cycles). Uncertainties were low which strongly indicate that the cycles are present. However, since high concentrations of ozone were observed only sporadically, ozone pollution in the northern part of Zagreb is at the present rather low. A Fourier transformation was used to analyse the data for periodic behaviour, which revealed the existence of diurnal and weekly modulations. Nevertheless, constant monitoring is important and will continue in the future as part of continuous monitoring of the ozone levels in the area.

Keywords Ozone · Pollution · Photosmog · Long-term analysis · Trend analysis · Periodicity

Introduction

Ozone is a substance that is commonly used in industry, for instance in water treatment facilities (Mundy et al. 2018). Moreover, its presence in the stratosphere is necessary for protecting terrestrial lifeforms—including humans—from harmful effects due to excessive irradiation by ultraviolet (UV) radiation from the Sun (Andersen 2015). However, the presence of ozone in the tropospheric layer is the sign of a pollution known as photosmog. Photosmog, or photochemical smog, is a term used to describe atmospheric reactions that need sunlight. In these reactions, various volatile organic compounds and/or nitrogen oxides (NO_x) react directly or indirectly with the oxygen molecule (O_2), giving ground-level ozone as one of the products. Since one of the major sources of NO_x is the emission from diesel engines, photosmog is strongly correlated with traffic intensity. Tropospheric ozone thus acts completely oppositely from its stratospheric counterpart—it is harmful for terrestrial lifeforms. There are several major negative influences of ozone in the troposphere. Ozone is a strong oxidant and it therefore damages plant tissue and material (Paoletti et al. 2007), which holds for animal tissue as well. Since it is a gas at standard conditions, the main danger is related to the development of pulmonary diseases, especially when other atmospheric conditions are involved, too (de Souza et al. 2016; Pintarić et al. 2016; Faridi et al. 2018).

Responsible Editor: Gerhard Lammel

✉ Brunislav Matasović
bmatasov@kemija.unios.hr

[1] Josip Juraj Strossmayer University of Osijek, Ulica cara Hadrijana 8a, HR-31000 Osijek, Croatia

[2] Institute for Medical Research and Occupational Health, Ksaverska cesta 2, HR-10000 Zagreb, Croatia

Finally, ozone is a greenhouse gas (Paoletti and Cudlin 2012), which makes it interesting from that point of view as well (Mohan 2018).

During the last few decades, it has been proposed that the global levels of background tropospheric ozone are continuously rising (Vingarzan 2004). Based on the northern hemisphere data, ozone levels have doubled during the past century. A future rise of background tropospheric ozone levels by as much as 16% has already been predicted by Stevenson et al. (2006). Interestingly, the situation in Europe seems to be less dramatic. Wilson et al. (2012) pointed out that measurement in Europe indicated only a slight increase in the background ozone levels and even a decrease in the south. This decrease was already confirmed experimentally by a previous analysis of the long-term data from the Puntijarka background station in the period between 1989 and 2009 (Matasović et al. 2014). A similar decrease in Iran was observed by Faridi et al. (2018). Recently, tropospheric ozone assessment report (TOAR) group addressed global trends of ozone (Schultz et al. 2017) and its influence on human health (Fleming et al. 2018) and vegetation (Mills et al. 2018). All this reports also suggest that the ozone levels are low to moderate in the western Balkan region, although with some possible influence from Italy and southern zones (for example Greece).

Long-term (trend) analyses are a fairly common way for investigating both ozone levels and its shifts (Jonson et al. 2006) as well as other pollutants (Yang et al. 2018; Faridi et al. 2018). New forecasting methods are also being developed (Freeman et al. 2018). Calculations of various pollution indicators from long-term ozone datasets (Paoletti et al. 2007) that should indicate overall atmospheric pollution (Kovač-Andrić et al. 2010; Matasović et al. 2012; Matasović et al. 2013) are also pretty common.

In this paper, an analysis of long-term data was conducted for an urban background station with medium traffic density. The aim of the study was to determine the long-term trends of ozone concentrations and compare the results with ozone trends observed at similar locations. A Fourier transformation (FT) of the data was used to reveal a periodic behaviour with periodicities much shorter than one year, these not being of a seasonal character.

Methods

The ozone measurements were carried out in the northern, residential part of Zagreb with modest population and traffic density. The measurement station was located at the Institute for Medical Research and Occupational Health, IMROH (45° 50′ 04″ N; 15° 58′ 41″ E, 120 m a.s.l.), approximately 50 m from the nearest road. The station is part of the Zagreb local network for air quality monitoring, funded by the City of Zagreb.

Zagreb has been the capital of Croatia almost continuously since medieval times. Presently, it has a population of around 800,000. It has a humid continental climate (Köppen classification: Dfb) with four clearly distinguishable seasons.

This paper presents the results for the period from 2003 to 2016. The determination of the ozone mass concentration was carried out by an automatic analyser Horiba APOA 360 until the end of 2012. Since 2013, measurements were performed using a type-approved Horiba APOA 370 analyser. Measurements were carried out in accordance with the EN 14265: 2012 standard using a non-dispersive ultraviolet absorption (NDUV) method (the laboratory is accredited in accordance with the requirements of the ISO/IEC 17025 standard for the reference method of ozone measurements). The analyser measures the ozone mass concentration in ambient air every 1 s. Hourly averages of the concentration were used in data analysis. Data are not adjusted in any way after they are validated (validated data are chosen in the start) and hourly ozone volume fraction has been calculated.

The uncertainty (expressed at a 95% confidence level) for each individual measurement was less than 15% of target value (120 $\mu g/m^3$) for ozone according to EU Directives (EU 2008/50/EC and EU 2015/1480/EC).

Meteorological data (wind direction and wind velocity, in the form of vector average) for the nearest station of the Croatian Meteorological and Hydrological Service (Maksimir; 45° 49′ 25″ N; 16° 2′ 9″ E) were used for the interpretation of ozone concentration results.

All calculations were carried out using Statistica software (Fourier transformation) and MS Excel (all other calculations).

Results and discussion

The station located at the Institute for Medical Research and Occupational Health (IMROH-station) was one of the first stations used for monitoring air quality both in Zagreb and in Croatia. It is located in an urban area with a rather low population (for a big city), no industry, and moderate traffic. It is protected from the northern wind by the Medvednica Mountain, and from the more polluted air from the south by the wind direction that is predominantly northeast and north (Fig. 1). Therefore, the dominant anthropogenic pollution is due to the traffic. Also, the presence of vegetation, which is undoubtedly denser than in the city centre, may have some influence, albeit natural, on the ozone concentration as well. A previous study carried out in the summer of 2006 at different locations in and around Zagreb showed that ozone concentrations were the highest south from Zagreb. The measurement site Velika Gorica (about 15 km south from the IMROH-station) indicated a strong local photochemical pollution, partly due to the transport of ozone precursors from Zagreb to

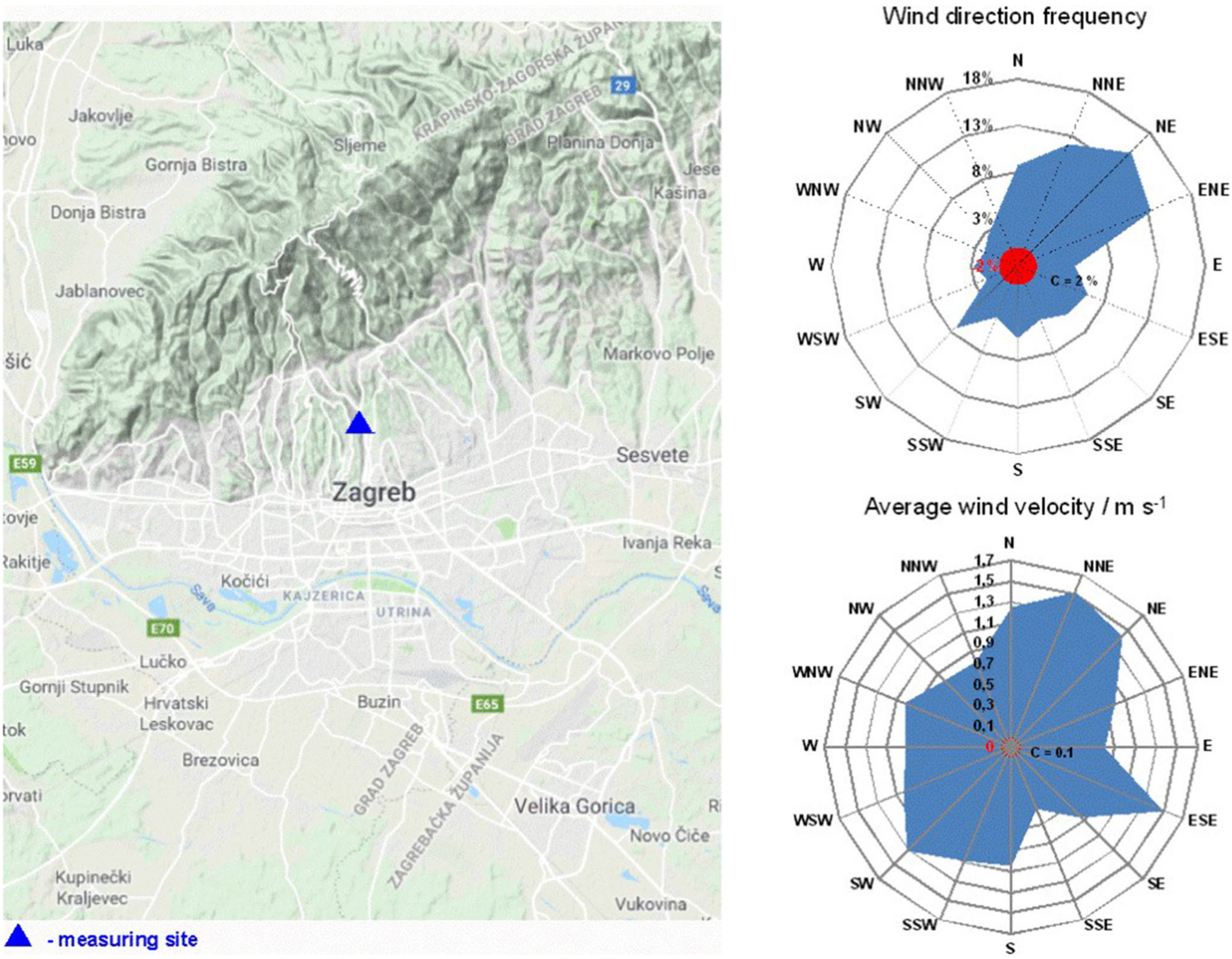


Fig. 1 Location of the IMROH measuring site and wind roses (wind direction frequency and average wind velocity, C-calm)

Velika Gorica. However, the wind rose suggests a low probability that the ozone from Velika Gorica could reach Zagreb (Pehnec et al. 2009a). If we consider a cross-correlation of ozone data with the wind speed and the wind direction, calculated values are well below 0.7 which is also a good indication for on site pollution rather than a transfer.

As can be seen from Fig. 2, the majority of hourly data in this study fell below 19 ppb, which is rather low considering that the vast majority—over 80%—were below 34 ppb. Average value for the whole period was about 20 ppb. Similar ozone concentrations were measured at urban and urban background locations with continental climate and similar altitude and pollution sources in North Macedonia (Anttila et al. 2016) and Poland (Warmiński and Bęś 2018), but also in mainland Portugal (Fernández-Guisuraga et al. 2016) and some urban locations in Ireland, United Kongdom, London and New Jersey, USA (Tripathi et al. 2012; Diaz et al. 2020; Williams et al. 2014; Roberts-Semple et al. 2012). Much higher levels were observed in the Mediterranean region: in Spain (Adame and Sole 2013; Adame Carnero et al. 2010; Castell-Balaguer et al. 2012), Greece (Kopanakis et al. 2016) and Italy (Gagliardi and Andenna 2020), especially in less urbanized areas. The analysis of ozone data in Bavaria, Germany, showed that urban background stations have more than 33.3% and 14.4% days with 8-h ozone concentrations higher than 50 and 60 ppb, respectively (Hertig 2020), which is higher than in this study. The reason could be higher concentrations of ozone precursors in the area. Detailed comparison of ozone data from this and other studies is presented in Table S1 of the Supplementary Information.

Monthly averages of ozone volume fractions are shown in Fig. 3. Clear annual cycles with higher values during summer and lower during winter can easily be observed which was expected due to ozone photochemical origin and seasonality in sunlight intensity. However, no other periodicity can be clearly seen in this figure, which implies a necessity for applying an FT to the data in order to search for more subtle periodic phenomena. From the position of the station, the periodicity shorter than one year can be attributed to NO_x variations due to the traffic. Since the traffic is moderate,

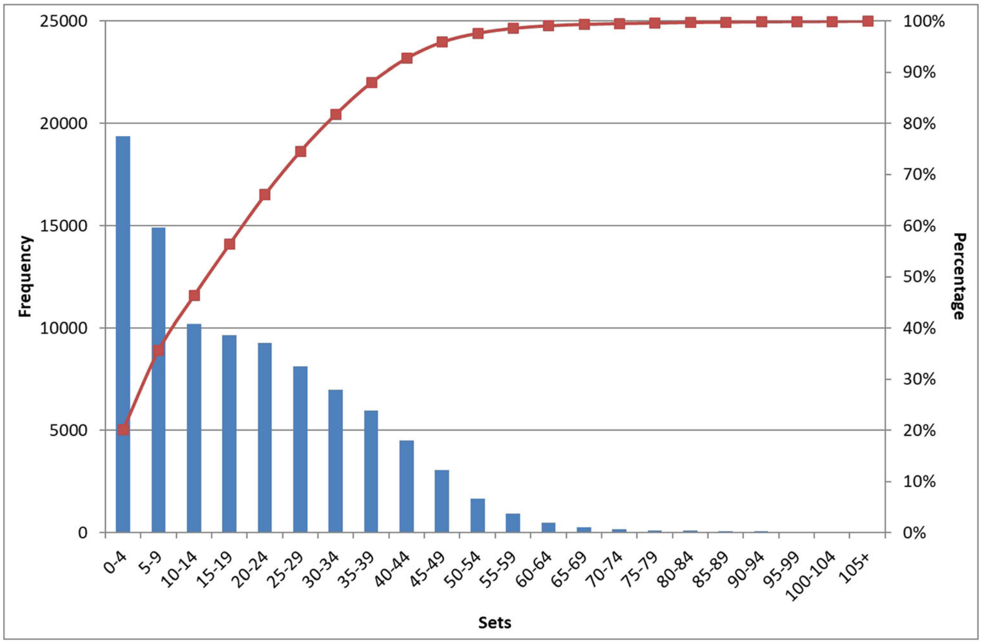


Fig. 2 Distribution of the hourly average ozone volume fractions for the whole period of observation. Hourly averages of the ozone volume fraction are distributed in sets with the range of 5 ppb and shown with vertical columns. The red line shows the percentage of hourly averages of ozone volume fractions taken into account until the given set

average values for the ozone volume fractions are fairly low, the local atmosphere being more prone to ozone destruction than formation. Of course, there is a certain influence of air transfer from other locations to this one that is unavoidable as in all urban areas. Fig. 4 shows usual diurnal variations in ozone volume fractions, and it can be seen that these variations are very weak—the median values varied from the early morning minimum of *circa* 15 ppb to the early afternoon maximum of *circa* 30 ppb—which indicated a very low level of ozone pollution in this area.

It is obvious from Figs. 3 and 4 that the ozone concentrations show characteristic and well known variations with the highest values during the summer months, and also at noon and early afternoon, when the sunlight is the most intense. Besides the usual maxima at around 14:00 h there are also some unusual ones at around 2:00 h (Fig. 4) which could be due to the overnight thinning of the atmospheric boundary layer as well as the night-time chemistry of $NO_3\cdot$ radical (Jeričević et al. 2004; Acker et al. 2008). However, computational methods such as FT may reveal a finer periodic structure (Fernandez-Macho 2011). For example, if there is a difference between workdays and weekends (Marr and Harley 2002), this can be seen in an FT. An FT of our data reveals three strong peaks (Fig. 5a and b) centred at 0.042 h^{-1}, 0.0833 h^{-1} (Fig. 5a), and 0.0059 h^{-1} (Fig 5b). By following an approach of Babić and Senčar (2018), we determined the mean values and uncertainties of the corresponding periods. The longest period was 169 ± 4 h (7.1 ± 0.2 days), and the mentioned method of the calculation of the uncertainty was fully applicable to this case. For the two shorter periods, however, the FT algorithm produced densely spaced calculation points, separated by much less than 1 h, which led to calculated uncertainties being considerably smaller than 1 h. Since this was clearly an underestimation due to numerical artefacts, we

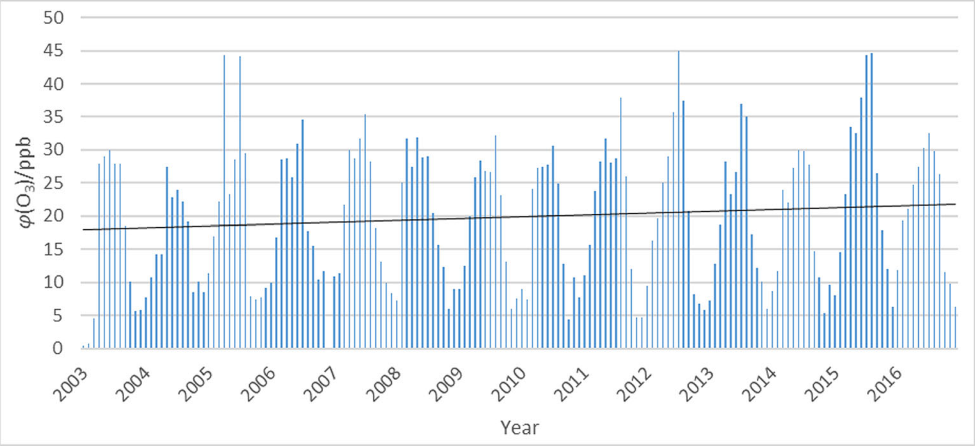


Fig. 3 Monthly averages of ozone volume fractions for the whole period of observation. $\varphi(O_3)$ stands for hourly ozone volume fractions. Black line represents the trend in ozone volume fractions

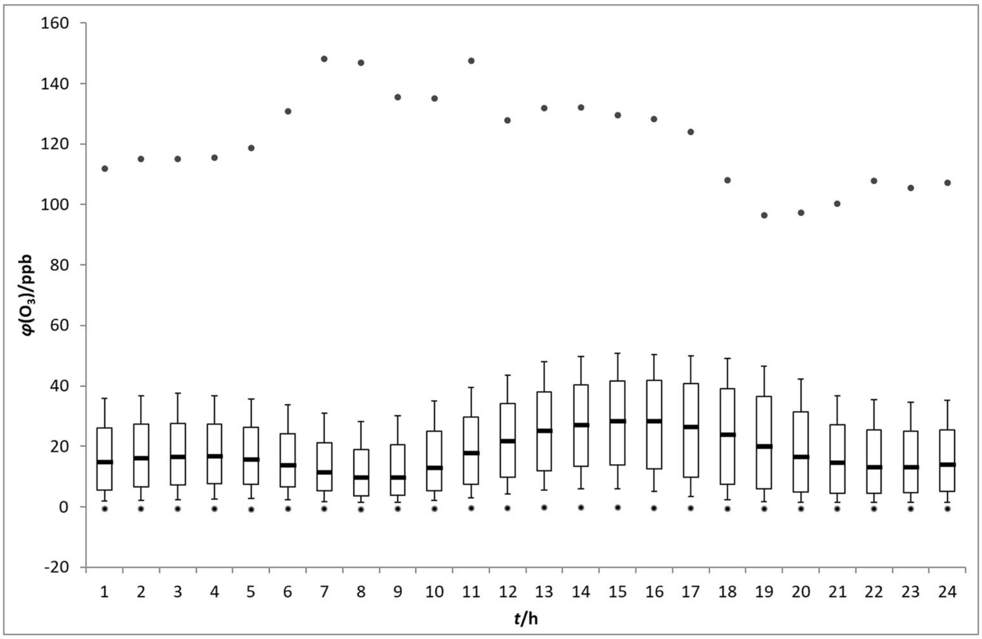


Fig. 4 Box & whiskers plot of the hourly ozone volume fractions with statistical values from the whole dataset. Maxima and minima (upper and lower extremes) are shown with a dot, the upper whisker shows the 90-percentile, the upper box line shows the 75-percentile, the inner box line shows median, the lower box line shows the 25-percentile and the lower whisker line shows the 10-percentile. $\varphi(O_3)$ stands for hourly ozone volume fractions

estimated that the uncertainties were 1 h for these two periods. Hence, these peaks corresponded to 24 ± 1 h and 12 ± 1 h, representing ozone variations over the day. The longest period, on the other hand, indicates weekly cycle and workday/weekend differences.

In previous study carried out in Zagreb and its surroundings during the summer of 2005 ozone and NO_2 concentrations have been measured at differently polluted sites, including IMROH station (Pehnec et al. 2009b). It was found that NO_2 concentrations were the lowest on Saturdays and Sundays and differed significantly from all weekdays. In the same time ozone concentrations were higher during weekends compared to working days, but the difference was not statistically significant. On weekends, traffic intensity is usually lower, and so is NO_2 emission from vehicle exhausts (as well as the emission of some other ozone precursors). Similar diurnal patterns and working day-weekend differences were found by Han et al. (2011). Although negative correlation between ozone and nitrogen dioxide should be expected (Han et al. 2011), previous summer measurements at urban background location in Zagreb did not find significant correlation between O_3 and NO_2 during night-time and only a weak negative correlation during daytime (Acker et al. 2008). Ozone working day/weekend variations could be explained by: O_3/NO_x chemistry: a reduction in NOx emissions on weekends that reduces the titration of ozone with NO, a weekend shift in the timing of NO_x peak that allows more efficient production of ozone, increased sunlight due to a reduction in the amount of soot present in the air; increase in weekend emissions from off-road sources such as domestic heating, etc. (Atkinson-Palombo et al. 2006; Pehnec et al. 2009b).

As the traffic at the IMROH station is moderate, the weekend/working day differences are not clearly pronounced. Simple statistical tests could probably find them not statistically significant over the shorter measuring periods. However, FT applied in this long-term study clearly revealed weekly cycles of ozone concentrations.

Some extremely high values, which by far exceeded target value of 60 ppb as well as information (90 ppb) and alert (120 ppb) thresholds set by EU Directive 2008/50/EC, can be attributed to either stratospheric intrusions that are not completely uncommon for this area (Lisac et al. 1993; Matasović et al. 2014), or, which is more likely, occasional unfavourable air mass transfer from more polluted areas. Most of such episodes of high ozone volume fractions occurred during summer—in July and August. They were indeed more common in recent years (2012 and 2015) but had also occurred earlier (in 2005 and 2007). One such episode was especially problematic, with constant high values, often higher than 60 ppb, measured throughout an entire week (from 29 June to 5 July 2015). Since this occurred during not very hot but sunny days (hotter days were yet to follow) and during the period of a very low wind speed (far less than 2 m s^{-1}), the reason for such a result could have been, again, a stratospheric intrusion. What is unusual here is the rather prolonged period of a supposed intrusion, which should last shortly (1–3 days) and not for the whole week (although it is not impossible for an intrusion to be prolonged (Greenslade et al. 2017)). On the other hand, in the middle of the episode, the strongest wind was from the ESE and ENE directions which could bring ozone precursors from the local smaller industrial area located about 10–12 km in this sector, or even from industrial towns

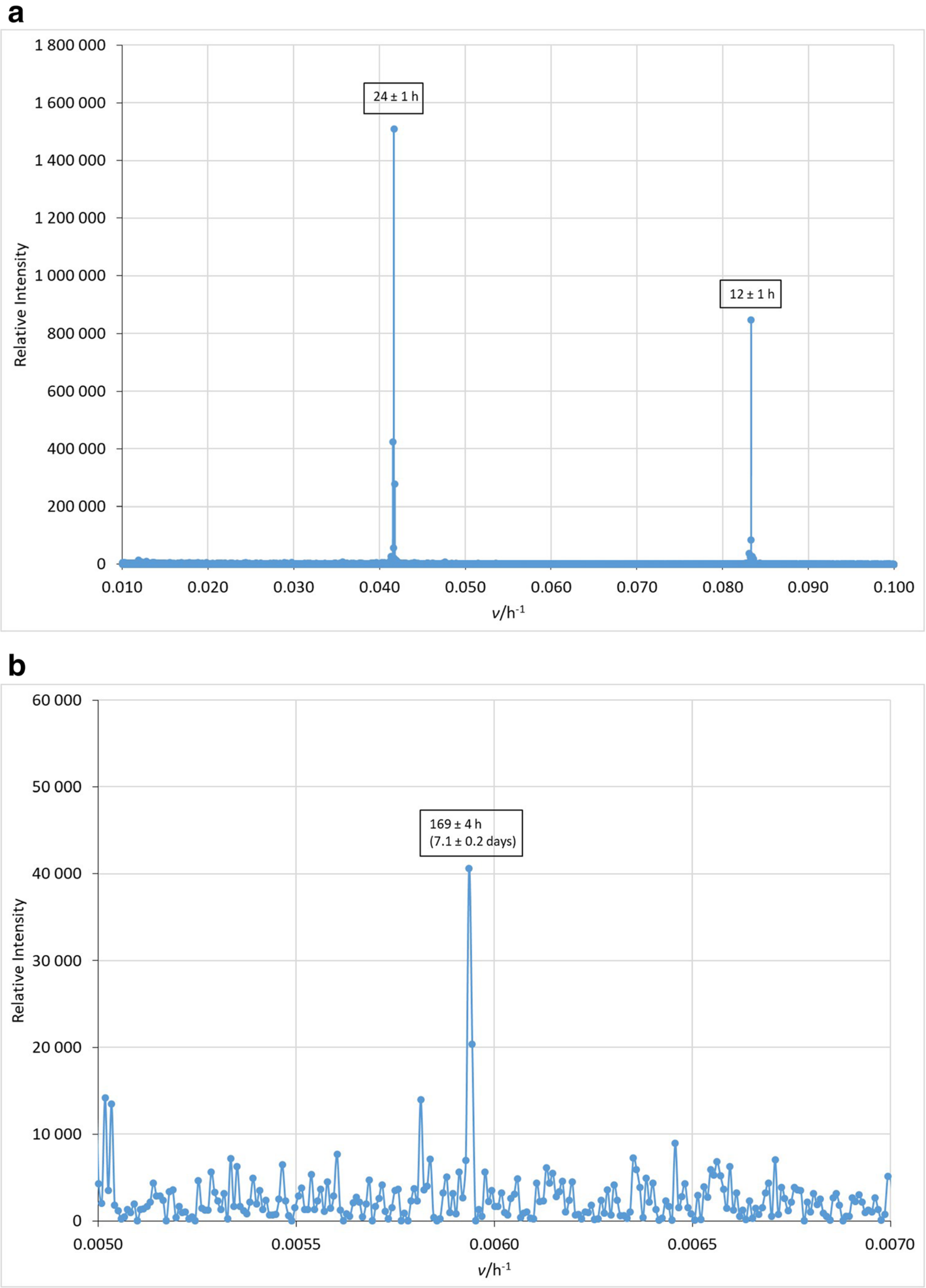


Fig. 5 **a** Fourier transformation of the hourly ozone volume fractions versus frequency (ν) in h^{-1}. The peak at 0.042 h^{-1} corresponds to the period of 24 ± 1 h and that at 0.083 h^{-1} to 12 ± 1 h **b** Fourier transformation of the hourly ozone volume fractions versus frequency (ν) in h^{-1}. The 0.0059 h^{-1} peak corresponds to the period of 169 ± 4 h (7.1 ± 0.2 days)

Sisak and Kutina (50–60 km in SE and ESE direction), causing photosmog pollution in this part of the town. Although it is not clear if those high values are caused by stratospheric intrusions or by precursors carried downwind, such episodes are relatively rare and in general the station shows very low ozone pollution with usual variations for such stations.

One of the most important statistical techniques for the assessment of air pollution is trend analysis. Linear regression is a basic trend analysis method which we supplemented by the commonly used Mann-Kendall test (Chattopadhyay et al. 2012). If the whole set of data— which are hourly ozone volume fractions—for all the years, is taken into account, the linear regression of the yearly means gives a slightly positive trend. The slope of the linear regression is still beyond the lowest predicted global growth of 2% annually, as the obtained value is 0.34 ppb yr^{-1} (Fig. 6, Table 1). To obtain a better insight into the higher measured values, the same analysis was calculated on the 95-percentile values (Fig. 7, Table 1). The 95-percentile is a better suited measure for high values as extremes (maxima) are cut off. However, a very similar result, with a slope value of 0.21 ppb yr^{-1} was obtained.

Table 1 Comparison of trend values by simple linear regression and Mann-Kendall's test analysis of the mean hourly ozone volume fractions for the whole year (WY $\varphi(O_3)$), 95-percentile of the mean hourly ozone volume fractions for the whole year (WY 95-per $\varphi(O_3)$), mean hourly ozone volume fractions for the April-to-September part of the year (S $\varphi(O_3)$/ppb) and 95-percentile of the mean hourly ozone volume fractions for the April-to-September part of the year (S 95-per $\varphi(O_3)$)

Time series	Linear regression	Mann-Kendall test
WY $\varphi(O_3)$/ppb	0.34 ppb yr^{-1}	0.23 ppb yr^{-1}
WY 95-per $\varphi(O_3)$/ppb	0.21 ppb yr^{-1}	0.009 ppb yr^{-1}
S $\varphi(O_3)$/ppb	0.42 ppb yr^{-1}	0.322 ppb yr^{-1}
S 95-per $\varphi(O_3)$/ppb	0.28 ppb yr^{-1}	−0.072 ppb yr^{-1}

Furthermore, if we take into account only seasonal (April-to-September) values which are, as expected and proven (Fig. 3), higher than those in winter, the results are also very optimistic. Mean values (Fig. 8, Table 1) are somewhat higher here but still exhibit a modest growth of 0.42 ppb yr^{-1}, which is somewhere around 2% annually. The same season-to-whole year slope ratio is present if, again, 95-percentiles are calculated instead of means. As shown in Fig. 9 and Table 1, the slope value for this set of data is 0.28 ppb yr^{-1}. Such results show very little positive changes in ozone volume fractions during the observed period of time. This is in contrast with both predictions—the global one which presumes elevation of ozone concentrations with time and with generally higher pace, and regional, which presumes a decrease in its concentrations. However, since the present values itself are within safe limits, this result is indeed very good comparing to global prediction of ozone concentration growth.

The Mann-Kendall test, which is more accurate than simple linear regression, confirmed our results showing a low growth of ozone concentrations. Mean values for whole year data (Fig. 6, Table 1) exhibited a slope value of 0.23 ppb yr^{-1} with a 99%-confidence interval between −0.306 and 0.838 ppb yr^{-1} and a 95%-confidence interval between −0.203 and 0.702 ppb yr^{-1}. None of these values indicate significant growth in ozone concentrations. In the worst-case scenario, if upper boundaries (i.e. the highest values) were taken into account, it would take several decades for the ozone volume concentration to double. This corresponds to the lowest global prediction for ozone concentration growth. On the other hand, the best-case scenario which would include lower boundaries shows a lowering of ozone concentration values although at an even slower pace. The 95-percentile values (Fig. 7, Table 1) showed no changes at all during the observed period of time. The calculated slope value was barely distinguishable from zero, being 0.009 ppb yr^{-1}. However, the confidence interval here was somewhat wider. The 99%-confidence interval values were between −1.145 and 1.371 ppb yr^{-1}. The 95%-confidence interval values were, on the other hand, between −0.925 and 0.888 ppb yr^{-1}. The 99%-confidence interval boundaries here must be discussed and taken into account. Depending on chosen boundary of slope coefficient, or any values inside the interval, they can indicate either growth or a reduction in ozone volume fractions depending on the boundary chosen. However, it should be noted that the confidence interval shows us the possibility that the true value was within the interval boundaries. It was still more probable that the true value was somewhere in the middle of the interval and not really near its limits.

Seasonal data showed somewhat different results in Mann-Kendall test than in linear regression. Mean values (Fig. 8, Table 1) had a slope of 0.322 ppb yr^{-1}. The 99%-confidence interval was between −0.328 and 1.385 ppb yr^{-1}. The 95%-confidence interval was between −0.146 and 1.030 ppb yr^{-1}. Provided that the slope was indeed correct, one could conclude that a low increase in ozone concentrations was

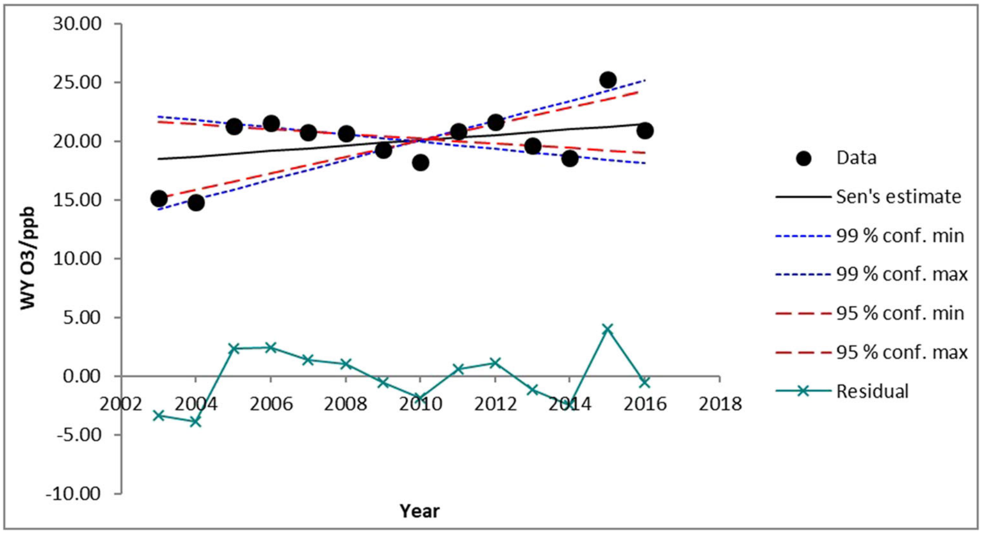
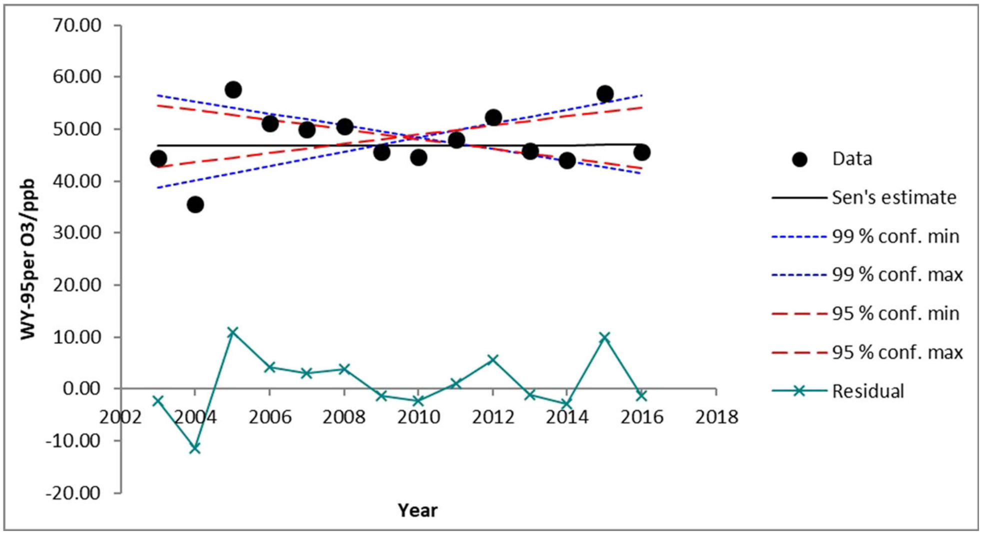


Fig. 6 Mann-Kendall's test analysis of the mean hourly ozone volume fractions for the whole year. Sen's estimate is equal to the trend slope. Blue and red lines show confidence intervals for the analysis. Designation WY (ordinate axis) stands for whole year data

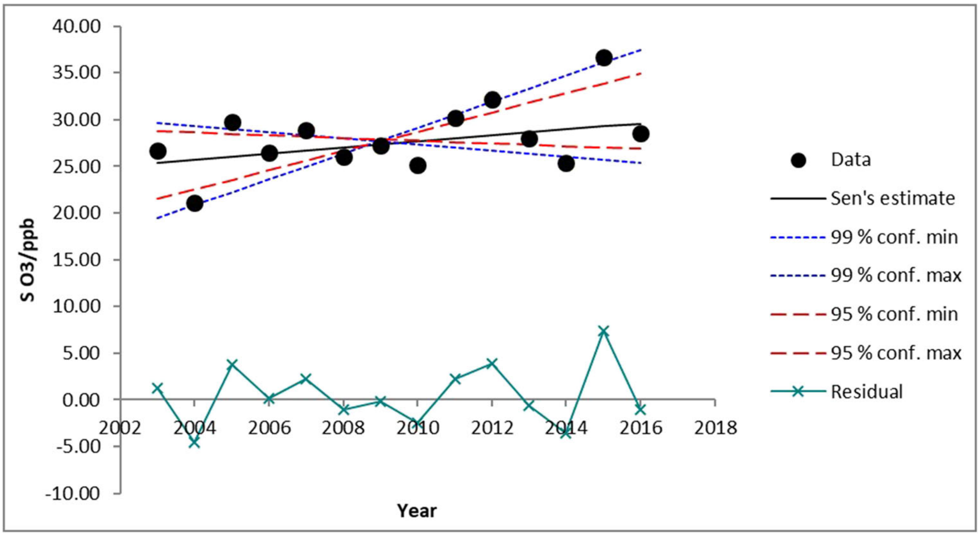
Fig. 7 Mann-Kendall's test analysis of the 95-percentile of the mean hourly ozone volume fractions for the whole year. Sen's estimate is equal to the trend slope. Blue and red lines show the confidence intervals for the analysis. Designation WY-95per (ordinate axis) stands for 95-percentile of the whole year data



observed, although somewhat lower than calculated from the linear regression. Confidence intervals are wider than in the case of the whole year data but it can still be concluded, with rather high certainty that part of the increase occurred during the observed period. On the other hand, 95-percentiles (Fig. 9, Table 1) showed possibly a different picture. The slope here was negative −0.072 ppb yr^{-1}. This value alone can show a different trend in ozone concentrations but it should be noted that this was still a low negative value. If confidence intervals are taken into account, then it is obvious that, in this case, we cannot reach any conclusion about the positivity or negativity of the trend. Both intervals were very wide. The 99%-confidence interval was between −2.028 and 2.090 ppb yr^{-1}. 95%-confidence interval was between −1.185 and 1.374 ppb yr^{-1}. Trend is calculated over the whole period from 2003 till 2016 but even if subperiods of, for example, seven years are considered, because of high residual values (Figs. 6 to 9), only trend direction can be confirmed.

Although the observed trends are generally modest, it must not be omitted that background stations in the vicinity (Matasović et al. 2014) and in the region (Wilson et al. 2012) for the period covered by this analysis show a negative trend in hourly ozone volume fractions. An increase in the ozone levels as the result of human activity would most probably be higher if the regional natural background trend was not negative. Perhaps it would be at the level of 2% or more, as generally expected (Vingarzan 2004). However, this may only be speculated based on the results of this and abovementioned previous studies. Total trend values are always a combination of natural causes and human influence. In this case, anthropogenic influence is still somewhat amplified in the vicinity of the station. Air transfer may have influence on our urban

Fig. 8 Mann-Kendall's test analysis of the mean hourly ozone volume fractions for the April-to-September part of the year. Sen's estimate is equal to the trend slope. Blue and red lines show the confidence intervals for the analysis. Designation S (ordinate axis) stands for seasonal data



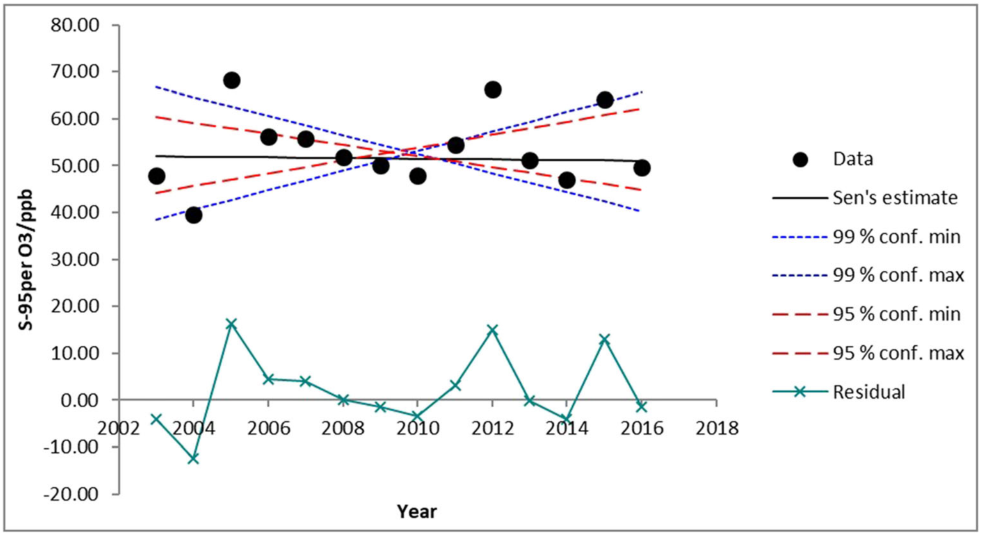


Fig. 9 Mann-Kendall's test analysis of the 95-percentile of the mean hourly ozone volume fractions for the April-to-September part of the year. Sen's estimate is equal to the trend slope. Blue and red lines show the confidence intervals for the analysis. Designation S-95per (ordinate axis) stands for 95-percentile of the seasonal data

background station giving sometimes unusual results. Very similar increasing trends were observed at urban locations in the United Kingdom while at rural stations they were almost twice lower (Diaz et al. 2020). Ozone levels more rapidly increased in Portugal (Fernández-Guisuraga et al. 2016) and in Spain for summer season (Adame and Sole 2013). Yan et al. (2018) carried out an extensive study for more than a hundred EMEP and Airbase stations over Europe for the period 1995–2014. Increasing trend of yearly means was observed at suburban and urban locations, while 95th percentile annual mean showed the decreasing trend which was more pronounced for the daytime period (Table S1 of the Supplementary Information).

Conclusion

After assessing all of the ozone data in the observed period of time (2003–2016), it can be concluded that pollution levels in northern Zagreb are rather low, with the exception of a few episodes. Both linear regression and, more importantly, Mann-Kendall's test essentially did not show a high increasing trend which is good comparing to global prediction of ozone concentration growth. Although thorough analyses may be inconclusive in some cases, it can be safely said that ozone levels will remain within the similar range for the foreseeable future. A Fourier transform of the data indicates diurnal and weekly ozone cycles. An annual cycle is also present but it was not tested via FT, since such an analysis is more appropriate for a larger number of periods within a dataset and is also well seen in the data. Occasional episodes with high ozone volume fractions were also observed but, except for one in 2015, were not long lasting.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-13295-w.

Author contribution Matasović: Conceptualization, Formal analysis, Writing - Original Draft, Visualization
Pehnec: Conceptualization, Writing - Review & Editing, Supervision
Bešlić: Formal analysis, Investigation, Writing - Review & Editing
Davila: Formal analysis,Investigation, Writing - Review & Editing
Babić: Methodology, Writing - Review & Editing, Visualization

Funding Ozone measurements were funded by the City of Zagreb, City Office for Economy, Energetics and Environment Protection, as a part of the local air quality monitoring programme.

Data availability Supporting data may be obtained from the website: http://iszz.azo.hr/iskzl/, either through the query on the website or by the written request

Declarations

Ethics approval and consent to participate Not applicable. Manuscript does not report studies involving human participants, human data nor human tissue.

Consent for publication Not applicable. Manuscript does not contain individual person's data in any form (except affiliations of authors and e-mail, telephone and fax number of corresponding author).

Competing interests The authors declare no competing interests.

References

Acker K, Kezele N, Klasinc L, Möller D, Pehnec G, Šorgo G, Wieprecht W, Žužul S (2008) Atmospheric H_2O_2 measurement and modeling campaign during summer 2004 in Zagreb, Croatia. Atmos Environ 42:2530–2542

Adame JA, Sole JG (2013) Surface ozone variations at a rural area in the northeast of the Iberian Peninsula. Atmos Pollut Res 4:130–141. https://doi.org/10.5094/APR.2013.013

Adame Carnero JA, Bolívar JP, de la Morena BA (2010) Surface ozone measurements in the southwest of the Iberian Peninsula (Huelva, Spain). Environ Sci Pollut Res 17:355–368. https://doi.org/10.1007/s11356-008-0098-9

Andersen SO (2015) Lessons from the stratospheric ozone layer protection for climate. J Environ Stud Sci 5:143–162

Anttila P, Stefanovska A, Nestorovska-Krsteska A, Grozdanovski L, Atanasov I, Golubov N, Ristevski P, Toceva M, Lappi S, Walden J (2016) Characterisation of extreme air pollution episodes in an urban valley in the Balkan Peninsula. Air Qual Atmos Health 9: 129–141. https://doi.org/10.1007/s11869-015-0326-7

Atkinson-Palombo CM, Miller JA, Balling RC Jr (2006) Quantifying the ozone “weekend effect” at various locations in Phoenix, Arizona. Atmos Environ 40:7644–7658

Babić D, Senčar J (2018) Periodic behaviour in ground-level environmental radioactivity: fingerprints of solar activity? Proc R Soc A 474:20180109. https://doi.org/10.1098/rspa.2018.0109

Chattopadhyay G, Chakraborthy P, Chattopadhyay S (2012) Mann-Kendall trend analysis of tropospheric ozone and its modeling using ARIMA. Theor Appl Climatol 110:321–328. https://doi.org/10.1007/s00704-012-0617-y

Castell-Balaguer N, Téllez L, Mantilla E (2012) Daily, seasonal and monthly variations in ozone levels recorded at the Turia river basin in Valencia (Eastern Spain). Environ Sci Pollut Res 19:3461–3480. https://doi.org/10.1007/s11356-012-0881-5

de Souza A, Kovač-Andrić E, Matasović B, Marković B (2016) Assessment of ozone variations and meteorological influences in west center of Brazil, from 2004 to 2010. Water Air Soil Pollut 227:313–323. https://doi.org/10.1007/s11270-016-3002-0

Diaz FMR, Khan MAH, Shallcross BMA, Shallcross EDG, Vogt U, Shallcross DE (2020) Ozone trends in the United Kingdom over the last 30 years. Atmosphere 11:534. https://doi.org/10.3390/atmos11050534

Faridi S, Shamsipour M, Krzyzanowski M, Kunzli N, Amini H, Azimi F, Malkawi M, Momeniha F, Gholampour A, Hassanvand MS, Naddafi K (2018) Long-term trends and health impact of PM2.5 and O-3 in Tehran, Iran, 2006-2015. Environ Int 114:37–49. https://doi.org/10.1016/j.envint.2018.02.026

Fernández-Guisuraga JM, Castro A, Alves C, Calvo A, Alonso-Blanco E, Blanco-Alegre C, Rocha A, Fraile R (2016) Nitrogen oxides and ozone in Portugal: trends and ozone estimation in an urban and a rural site. Environ Sci Pollut Res 23:17171–17182. https://doi.org/10.1007/s11356-016-6888-6

Fernandez-Macho J (2011) Spectral estimation of global levels of atmospheric pollutants. Environ Pollut 159:2947–2953. https://doi.org/10.1016/j.envpol.2011.04.026

Fleming ZL, Doherty RM, von Schneidemesser E, Malley CS, Cooper OR, Pinto JP, Colette A, Xu X, Simpson D, Schultz MG, Lefohn AS, Hamad S, Moolla R, Solberg S, Feng Z (2018) Tropospheric ozone assessment report: present-day ozone distribution and trends relevant to human health. Elementa-Sci Anthrop 6:12. https://doi.org/10.1525/elementa.273

Freeman BS, Taylor G, Gharabaghi B (2018) Forecasting air quality time series using deep learning. J Air Waste Ma 68:866–886. https://doi.org/10.1080/10962247.2018.1459956

Gagliardi RV, Andenna C (2020) A machine learning approach to investigate the surface ozone behavior. Atmosphere 11:1173. https://doi.org/10.3390/atmos11111173

Greenslade JW, Alexander SP, Schofield R, Fisher JA, Klekociuk AK (2017) Stratospheric ozone intrusion events and their impacts on tropospheric ozone in the Southern Hemisphere. Atmos Chem Phys 17:10269–10290. https://doi.org/10.5194/acp-17-10269-2017

Han S, Bian H, Feng Y, Liu A, Li X, Zeng F, Zhang X (2011) Analysis of the relationship between O_3, NO and NO_2 in Tianjin, China. Aerosol Air Qual Res 11:128–139. https://doi.org/10.4209/aaqr.2010.07.0055

Hertig E (2020) Health-relevant ground-level ozone and temperature events under future climate change using the example of Bavaria, Southern Germany. Air Qual Atmos Health 13:435–446. https://doi.org/10.1007/s11869-020-00811-z

Jeričević A, Špoler Čanić K, Vidič S (2004) The prediction of mixing height and stability in complex orography. Hrvatski meteorološki časopis 39:3–14

Jonson JE, Simpson D, Fagerli H, Solberg S (2006) Can we explain the trends in European ozone levels? Atmos Chem Phys 6:51–66. https://doi.org/10.5194/acp-6-51-2006

Kopanakis I, Glytsos T, Kouvarakis G, Gerasopoulos E, Mihalopoulos N, Lazaridis M (2016) Variability of ozone in the Eastern Mediterranean during a 7-year study. Air Qual Atmos Health 9: 461–470. https://doi.org/10.1007/s11869-015-0362-3

Kovač-Andrić E, Šorgo G, Kezele N, Cvitaš T, Klasinc L (2010) Photochemical pollution indicators-an analysis of 12 European monitoring stations. Environ Monit Assess 165:577–583. https://doi.org/10.1007/s10661-009-0969-7

Lisac I, Marki A, Tiljak D, Klasinc L, Cvitaš T (1993) Stratospheric ozone itrusion over Zagreb, Croatia, on February 6, 1990. Meteorol Z 2:224–231

Marr LC, Harley RA (2002) Spectral analysis of weekday-weekend differences in ambient ozone, nitrogen oxide, and non-methane hydrocarbon time series in California. Atmos Environ 36:2327–2335. https://doi.org/10.1016/S1352-2310(02)00188-7

Matasović B, Cvitaš T, Klasinc L (2012) On photochemical air pollution potential in southern California derived from ozone data from 16 monitoring stations. Croat Chem Acta 85:71–76. https://doi.org/10.5562/cca2008

Matasović B, Herjavić G, Klasinc L, Cvitaš T (2014) Analysis of ozone data from the Puntijarka station for the period between 1989 and 2009. J Atmos Chem 71:269–282. https://doi.org/10.1007/s10874-014-9294-9

Matasović B, Klasinc L, Cvitaš T (2013) Growth season photochemical pollution over the UK Based on 1990-2006 ozone data. Croat Chem Acta 86:57–64. https://doi.org/10.5562/cca2177

Mills G, Pleijel H, Malley CS, Sinha B, Cooper OR, Schultz MG, Neufeld HS, Simpson D, Sharps K, Feng Z, Gerosa G, Harmens H, Kobayashi K, Saxena P, Paoletti E, Sinha V, Xu X (2018) Tropospheric ozone assessment report: present-day tropospheric ozone distribution and trends relevant to vegetation. Elementa-Sci Anthrop 6:47. https://doi.org/10.1525/elementa.302

Mohan RR (2018) Time series GHG emission estimates for residential, commercial, agriculture and fisheries sectors in India. Atmos Environ 178:73–79. https://doi.org/10.1016/j.atmosenv.2018.01.029

Mundy B, Kuhnel B, Hunter G, Jarnis R, Funk D, Walker S, Burns N, Drago J, Nezgod W, Huang J, Rakness K, Jasim S, Joost R, Kim R, Muri J, Nattress J, Oneby M, Sosebee A, Thompson C, Walsh M, Schulz C (2018) A review of ozone systems costs for municipal applications. Report by the Municipal Committee - IOA Pan American Group. Ozone-Sci Eng 40:266–274. https://doi.org/10.1080/01919512.2018.1467187

Paoletti E, Cudlin P (2012) Ozone, climate change and forests Introduction. Environ Pollut 169:249. https://doi.org/10.1016/j.envpol.2012.05.024

Paoletti E, De Marco A, Racalbuto S (2007) Why should we calculate complex indices of ozone exposure? Results from Mediterranean background sites. Environ Monit Assess 128:19–30. https://doi.org/10.1007/s10661-006-9412-5

Pehnec G, Vađić V, Bešlić I, Žužul S (2009b) Summer ozone concentrations in Zagreb area. Arh Hig Rada Toksikol 60:35–42

Pehnec G, Klasinc L, Šorgo G, Vađić V (2009a) Analysis of summer 2006 ozone pollution in Zagreb. Croat Chem Acta 82:329–335

Pintarić S, Zeljković I, Pehnec G, Nesek V, Vrsalović M, Pintarić H (2016) Impact of meteorological parameters and air pollution on emergency department visits for cardiovascular diseases in the city of Zagreb, Croatia. Arh Hig Rada Toksikol 67:240–246. https://doi.org/10.1515/aiht-2016-67-2770

Roberts-Semple D, Song F, Gao Y (2012) Seasonal characteristics of ambient nitrogen oxides and ground–level ozone in metropolitan northeastern New Jersey. Atmos Pollut Res 3:247–257. https://doi.org/10.5094/APR.2012.027

Schultz MG, Schröder S, Lyapina O, Cooper OR, Galbally I, Petropavlovskikh I, von Schneidemesser E, Tanimoto H, Elshorbany Y, Naja M, Seguel RJ, Dauert U, Eckhardt P, Feigenspan S, Fiebig M, Hjellbrekke A-G, Hong Y-D, Kjeld PC, Koide H, Lear G, Tarasick D, Ueno M, Wallasch M, Baumgardner D, Chuang M-T, Gillett R, Lee M, Molloy S, Moolla R, Wang T, Sharps K, Adame JA, Ancellet G, Apadula F, Artaxo P, Barlasina ME, Bogucka M, Bonasoni P, Chang L, Colomb A, Cuevas-Agulló E, Cupeiro M, Degorska A, Ding A, Fröhlich M, Frolova M, Gadhavi H, Gheusi F, Gilge S, Gonzalez MY, Gros V, Hamad SH, Helmig D, Henriques D, Hermansen O, Holla R, Hueber J, Im U, Jaffe DA, Komala N, Kubistin D, Lam K-S, Laurila T, Lee H, Levy I, Mazzoleni C, Mazzoleni LR, McClure-Begley A, Mohamad M, Murovec M, Navarro-Comas M, Nicodim F, Parrish D, Read KA, Reid N, Ries L, Saxena P, Schwab JJ, Scorgie Y, Senik I, Simmonds P, Sinha V, Skorokhod AI, Spain G, Spangl W, Spoor R, Springston SR, Steer K, Steinbacher M, Suharguniyawan E, Torre P, Trickl T, Weili L, Weller R, Xiaobin X, Xue L, Zhiqiang M (2017) Tropospheric ozone assessment report: database and metrics data of global surface ozone observations. Elementa-Sci Anthrop 5:58. https://doi.org/10.1525/elementa.244

Stevenson DS, Dentener FJ, Schultz MG, Ellingsen K, van Noije TPC, Wild O, Zeng G, Amann M, Atherton CS, Bell N, Bergmann DJ, Bey I, Butler T, Cofala J, Collins WJ, Derwent RG, Doherty RM, Drevet J, Eskes HJ, Fiore AM, Gauss M, Hauglustaine DA, Horowitz LW, Isaksen ISA, Krol MC, Lamarque JF, Lawrence MG, Montanaro V, Muller JF, Pitari G, Prather MJ, Pyle JA, Rast S, Rodriguez JM, Sanderson MG, Savage NH, Shindell DT, Strahan SE, Sudo K, Szopa S (2006) Multimodel ensemble simulations of present-day and near-future tropospheric ozone. J Geophys Res-Atmos 111:D08301. https://doi.org/10.1029/2005JD006338

Tripathi OP, Jennings SG, O'Dowd C, O'Leary B, Lambkin K, Moran F, O'Doherty SJ, Spain TG (2012) An assessment of the surface ozone trend in Ireland relevant to air pollution and environmental protection. Atmos Pollut Res 3(3):341–351. https://doi.org/10.5094/APR.2012.038

Vingarzan R (2004) A review of surface ozone background levels and trends. Atmos Environ 38:3431–3442. https://doi.org/10.1016/j.atmosenv.2004.03.030

Warmiński K, Bęś A (2018) Atmospheric factors affecting a decrease in the night-time concentrations of tropospheric ozone in a low-polluted urban area. Water Air Soil Pollut 229:350. https://doi.org/10.1007/s11270-018-4012-x

Williams ML, Atkinson RW, Anderson HR, Kelly FJ (2014) Associations between daily mortality in London and combined oxidant capacity, ozone and nitrogen dioxide. Air Qual Atmos Health 7:407–414. https://doi.org/10.1007/s11869-014-0249-8

Wilson RC, Fleming ZL, Monks PS, Clain G, Henne S, Konovalov IB, Szopa S, Menut L (2012) Have primary emission reduction measures reduced ozone across Europe? An analysis of European rural background ozone trends 1996-2005. Atmos Chem Phys 12:437–454. https://doi.org/10.5194/acp-12-437-2012

Yan Y, Pozzer A, Ojha N, Lin J, Lelieveld J (2018) Analysis of European ozone trends in the period 1995–2014. Atmos Chem Phys 18:5589–5605. https://doi.org/10.5194/acp-18-5589-2018

Yang B-Y, Qian ZM, Li S, Fan S, Chen G, Syberg KM, Xian H, Wang S-Q, Ma H, Chen D-H, Yang M, Liu K-K, Zeng X-W, Hu L-W, Guo Y, Dong G-H (2018) Long-term exposure to ambient air pollution (including PM1) and metabolic syndrome: the 33 Communities Chinese Health Study (33CCHS). Environ Res 164:204–211. https://doi.org/10.1016/j.envres.2018.02.029