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Analysis of Ozone Data from the Puntijarka Station for the Period between 1989 and 2009

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Abstract

Monitoring data on ambient ozone collected at the Puntijarka station located on the mountain Medvednica 980 m a.s.l. and 10 km to the north of the Croatian capital Zagreb during a 21-year period (1989-2009) have been analysed in order to check whether any regularities such as periodicities or trends in the data could be detected. Only two types of cycles could be observed: an annual cycle with higher ozone fractions during spring and summer and a diurnal cycle with the highest values at noon and in the early afternoon. Both can be related to insolation with the same periodicity confirming the photochemical nature of ozone formation. Conclusions about trends are less pronounced; for the first decade of the observational period no significant trend was found and for the second decade there was a significantly negative trend of -1.38 ppb yr^{-1}.

Keywords:

tropospheric ozone, ozone trend, background ozone, frequency analysis, photochemical pollution, long-term data analysis

1. Introduction

Continuous ambient ozone measurements at the Puntijarka station, located on the mountain Medvednica in the vicinity of Zagreb, started in 1989 (Cvitaš *et al.* 1997). This station once operated within the EUROTRAC/TOR and TOR-2 projects (Cvitaš and Kley 2001)(Scheel *et al.* 1997)(Midgley and Reuther 2002), together with the now abandoned RBI (Rudjer Boskovic Institute) station (Cvitaš *et al.* 1997). Position of both stations are shown on fig. 1. RBI station was located few kilometres on the South and was situated in the city. It has been operating for over two decades prompting this long-term data analysis. Additionally, these two stations for ozone monitoring, which are now conducted by automated ozone monitors based on UV absorption, may be seen as distant continuation of the ozone monitoring from the Zagreb area at the end of 19th century (Božičević *et al.* 1993) with the Schönbein's method and in 1975 by chemiluminescence monitor (Božičević *et al*. 1976)(Cvitaš *et al.* 1979). As a part of a European wide monitoring network, the importance of this station is far beyond local.

Ozone is a known greenhouse gas (Paoletti and Cudlin 2012) and, in addition to being very important for sustaining life near the Earth's surface by absorbing harmful UV radiation within the stratosphere (Matsumi and Kawasaki 2003), it is also an air pollutant in the troposphere affecting, as a strong oxidant, many life forms and materials (Paoletti *et al.* 2007). Normal background concentrations are usually measured at relatively remote sites unaffected by local pollution sources. The Puntijarka station was chosen as such a site and the presence of ozone there can be connected with either a long-distance transport or a rare but intense vertical transport from the stratosphere. Such an unusual event was observed at Puntijarka only once in the monitoring period 1989 – 2009 (Cvitaš *et al.* 1997)(Lisac *et al.* 1993) which was then confirmed by the similar observation on the other stations in the few kilometres radius.

Grennfelt *et. al.* (1987; 1988) and Feister and Pedersen (1989), as part of OXIDATE network, were the first to show the spatial increase in ozone levels at background stations in Europe from the north-west to the south-east but not considering southern Europe. In their work, Simpson *et al.* (1997) estimated the summer ozone levels at background stations for Zagreb area to be greater than 46 ppb which can be experimentally confirmed by our measurements. Vingarzan (2004) reviewed global background ozone levels in the lower troposphere, based on the data from the Northern hemisphere, and concluded that the levels had doubled over the past century. Over the past few decades this rise was found to be between 0.5 and 2 % per

year. The increase was, however, somewhat slower during the 1990s in comparison with the 1970s and 1980s. The rise of the background ozone levels in the future was also predicted by Stevenson *et al.* (2006) by as much as 5 to 16 %. The expected rise of the ozone levels in the region was one of the arguments for starting the TOR-subproject of EUROTRAC in 1988. These predicted ozone increases at least for the South-European region (stations Puntijarka and Krvavec (Scheel *et al.* 1997)) seem not to have occurred. For Southern parts of Europe, this was also confirmed in a thorough analysis by Wilson *et al.* (2012). They concluded that, on a European scale, can be confirmed only slight increase in ozone levels (less than 0.2 ppb yr^{-1}) with the difference between Mediterranean region and Northern parts of the continent. Mediterranean region has negative ozone trend which further confirms our results since Puntijarka is located only about 100 km east from the Croatian (Mediterranean) seaside.
Monitoring trends of the ozone levels are also very important and studies were conducted to prove it (Jonson *et al.* 2006)(Guicherit and Roemer 2000)(Oltmans *et. al.* 2006)(Lelieveld and Dentener 2000). For a reliable trend analysis, a long-term data acquisition is required (Wilson *et al.* 2012). It is believed that the recent two-decade period of the ozone data acquisition in this geographic region would represent a valuable set for drawing conclusions on a possible trend.
Long-term (trend) analyses are fairly common way for investigating of ozone levels and its changings (Jonson *et. al.* 2006)(Fiore *et al.* 2005)(Wilson *et al.* 2012).

2. Methods

All data used in this article were gathered at the Puntijarka station (coordinates 45.91° N, 15.97° E, 980 m a.s.l.) in the period between 1989 and 2009. This station was part of both EUROTRAC/TOR and TOR-2 projects (fig 1). The Puntijarka station is located on the mountain Medvednica approximately 10 km to the north of Zagreb. Data acquisition was performed by automatic ozonometers (Dasibi monitors of type 1008 AH and 1008 PC and Environnement model O341M) calibrated regularly against primary ozone standards using known ozone volume fractions in the range from 0 to 200 ppb. The original data were collected every minute and from these data the hourly average volume fractions have been calculated and have been used for the analysis. All hourly ozone volume fractions are shown in ppb. Levels of nitrogen oxides have been measured with CRANOX $NO/NO_X/O_3$ system (manufacturer: Eco Physics). For the wind speed and direction anemometer VMZ11 (manufacturer: Jožef Štefan, Ljubljana) was used. All other meteorological data on that station was measured by Meteorological and Hydrological Service of Croatia. Several calculation methods have been used for data analysis: hourly averages by months and years, monthly averages, box & whiskers plots for the average diurnal distribution of ozone fractions, Fourier transformation of data for a possible cycles detection and, for the calculation of the ozone trend, we have used linear regression and the Mann-Kendall test.

3. Results and discussion

The Puntijarka station, located to the north of Zagreb, has been chosen as a convenient background station since it had been a meteorological station for very long period (Cvitaš *et al.* 1995). It must be noted that for Puntijarka station it is assumed status of a background monitoring station derived from the meteorological data showing wind direction (Fig. 1) in periods prior to and at the beginning of these measurements. This is later been further supported by the absence of extremely low ozone concentrations in the morning which are characteristic for polluted sites. Although, these data imply a possibility of a westward and southward horizontal transfer, in comparison with the data from the Rudjer Boskovic Institute (RBI) station, an influence on this station is very low (Butković *et al.* 2000). It was even concluded that the station might be above the mixing layer for the area because of its altitude.

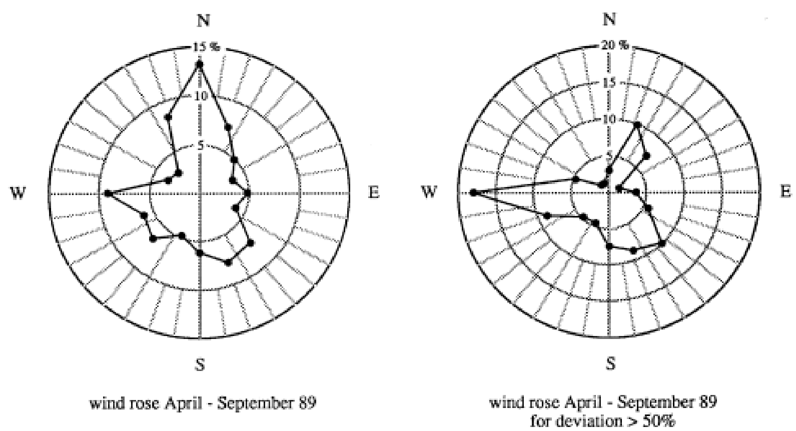

Figure 1a: Wind rose at Puntijarka station for the whole period between April and September 1989 on the left and for the selected 10 % observations when the ozone volume fraction exceeded the average by more than 50 %.

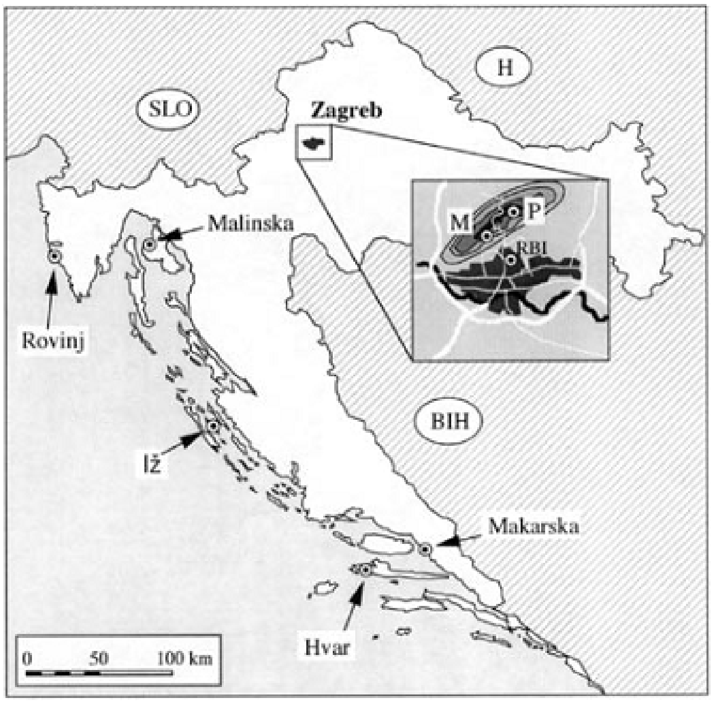

Figure 1b: Location of ozone monitoring stations in Croatia. Puntijarka station is marked with letter P in the enlarged part of the figure.

Figure 1c: Location of Croatia (orange) in Europe (blue).

Monthly averages of ozone volume fractions together with 12-months moving averages are shown in figure 2. Regular annual cycles can be observed in all the years with elevated values during summer which is a consequence of a horizontal transport. The Puntijarka station is located some 800 m above the surrounding plain and there is no local pollution source near the site. The presence of slightly elevated levels of NO_x is causing the rise of the ozone levels during the summer, which can only be attributed to an air mass transport. Still, it must be said that even then this elevated levels of NO_x would still be comparatively small and not much higher from the usual values for rural sites. However, these results, in comparison with a negative ozone trend (see below), which is at odds with the global positive trend in the background ozone (Vingarzan 2004), cannot be explained otherwise than by also presuming at least some horizontal transport of ozone. The proof of the horizontal transfer may be found in a fact that daily maxima, although only slightly different from the other values, are observed later in the day than usual for a polluted site as can be seen on the figures in supplement. The most prominent source of ozone is a westward wind from Slovenia and most probably from Italy. Furthermore, this can be indicative for lowering the level of ozone precursor concentrations at least locally and regionally which would then influence the background concentration of ozone as well. Since this results are very indicative, it is also obvious that the air transferred to the site is not very polluted. This can be further argued by a comparison with contemporary data for the coastal region of the Rijeka bay (Alebić-Juretić 2012). According to these data, on all sites in the Rijeka bay region, ozone concentrations declined. The lowest decline was on the site in a resort area, while the highest was observed at a suburban site.

It must also be said that Puntijarka, Krvavec and Rijeka bay stations are not globally exceptional with their negative trends (Logan *et. al.* 1999)(Low and Kelly 1992) but it is always important to show that in some regions lower background levels of ozone can be expected even in the areas which normally tend to be more prone to photochemical pollution. There are still some global problems with attributing these effects. The problem may be in the some kind of variability in the troposphere, in the high reactivity of ozone or, for example, simply in the absence of the good global dataset (Staehlin *et al.* 2001). Still, this analysis can contribute to the better understanding of what is really going on.

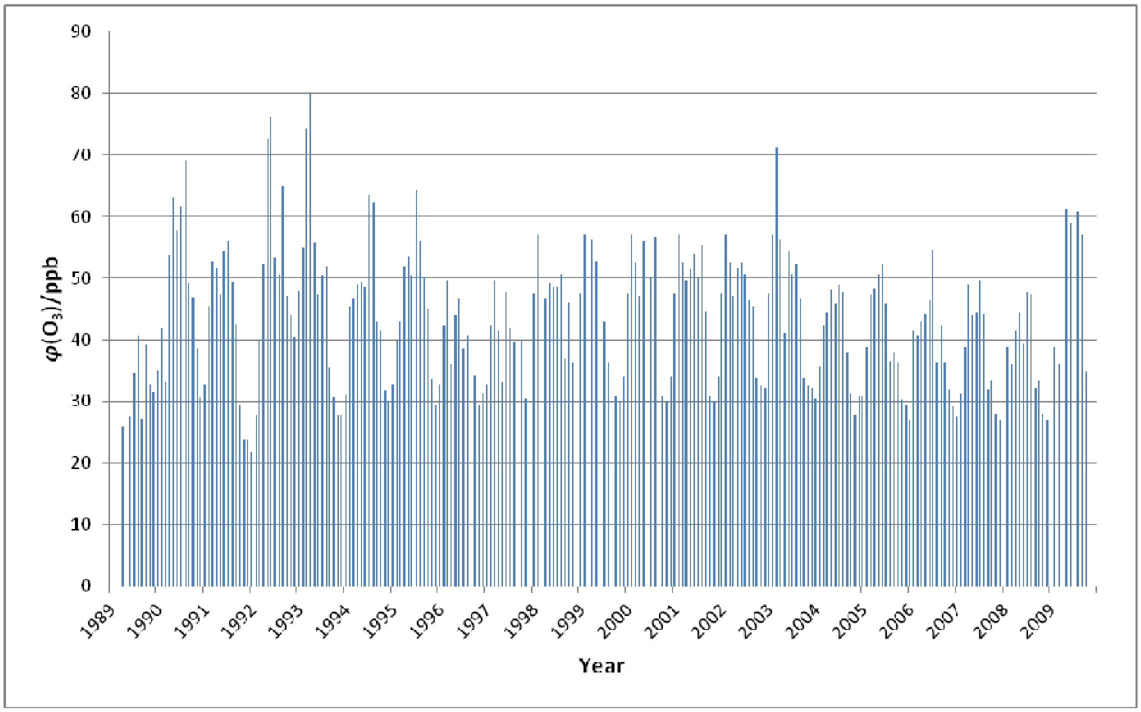

Figure 2a

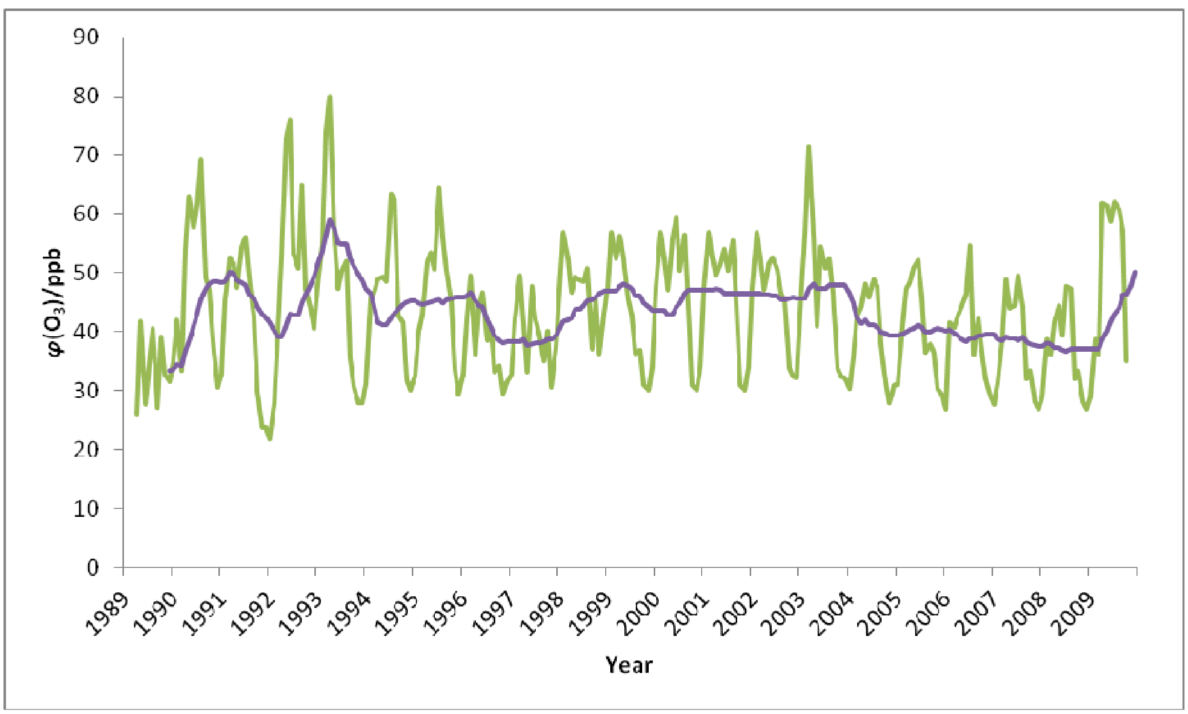

Figure 2a

Figure 2: Monthly averages of ozone volume fractions (a), 12-months moving averages of ozone volume fractions (green line) and monthly mean (blue line) (b) for the whole period of observation. Missing data are extrapolated from the data for the same month of the previous and/or the following year.

It can also be observed (Fig 3.) that the daily variations of average ozone volume fractions are almost constant – the difference between an average maximum and a minimum being around 15 ppb – during the whole period of the observation with no major differences in total range and with all values less than 80 ppb. Hardly any variation of the ozone volume fraction can be observed during the day indicating that no significant local photochemical production takes place. This implies furthermore that no changes in photochemical pollution are expected for the whole period of the observation.

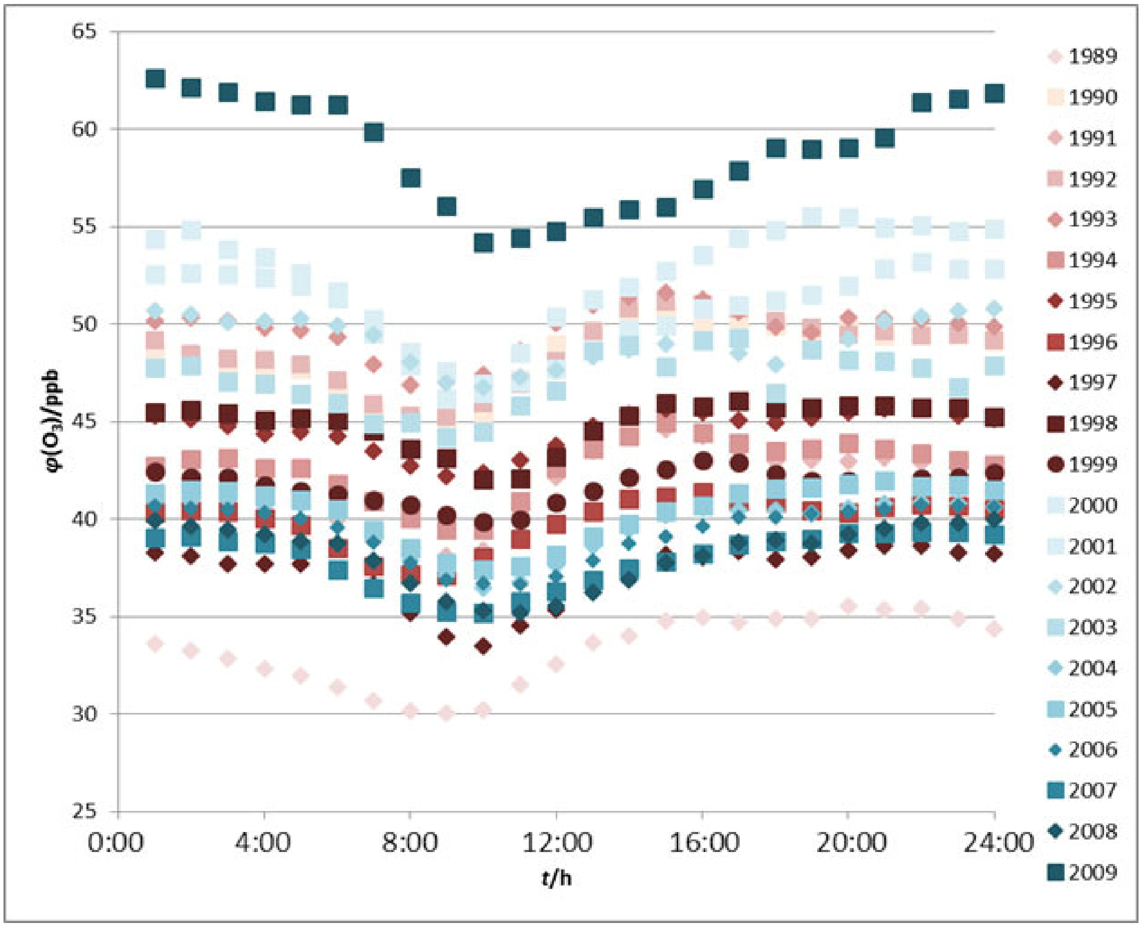

Figure 3: Diurnal ozone volume fractions for each year. At this figure, an average of all data for the respective hour during one year are shown as the single point.

If further consideration is taken into account, the diurnal cycles for each months (example shown in Fig. 4; please refer to the supplement for all data) were somewhat higher values during summer months which can be attributed to the higher insolation connected with the longer period of daylight in the vicinity of the site following the transport of ozone to the site.

This can also be shown considering the distribution of the hourly values (Fig. 5) which is typical for unpolluted sites with the most common values being those around the mean value.

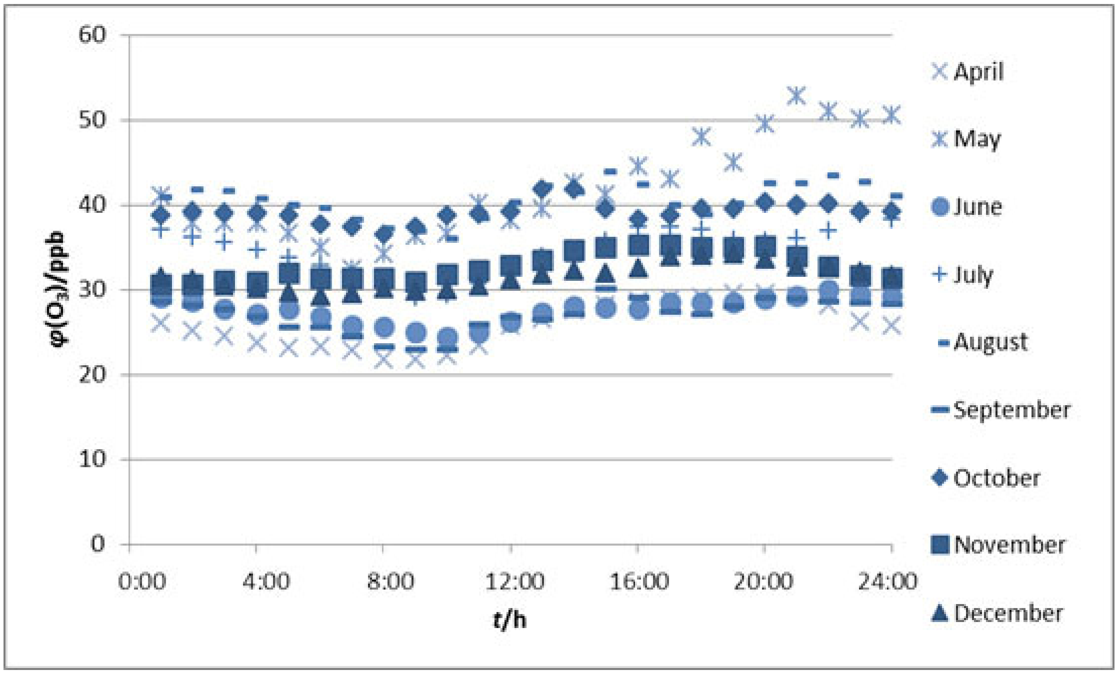

Figure 4: Variations of average ozone volume fractions during the day based on the monthly average values of ozone volume fractions for the year 1989 (for other years please refer to the supplement data). At this figure, an average of all data for the respective hour during one month are shown as the single point. Only available data are shown on this figure.

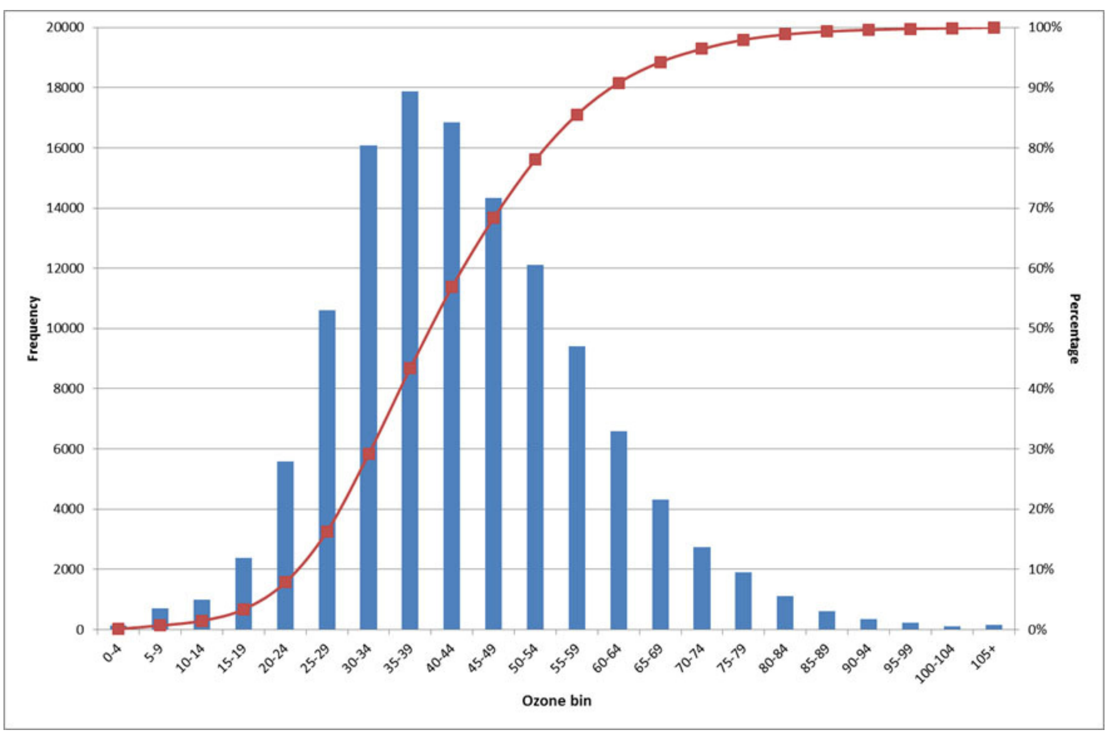

Figure 5: Distribution of the hourly average ozone volume fractions for the whole period of observation. Hourly averages of ozone volume fraction are distributed in the sets (bins) with the range of 5 ppb and shown with vertical columns. Red line shows the percentage of hourly averages of ozone volume fractions which are taken into account until the given set.

Box & whiskers plots (example shown in Fig. 6; please refer to the supplement for all data) can be used for a better explanation of the actual range in which the majority of hourly average ozone volume fractions are observed. The majority of higher values are obtained during summer periods (compare with Fig. 4) while the majority of lower values are observed during the winter. It can easily be seen that the average values in June are around 50 ppb while the average values in December are around 30 ppb. Usual background stations without any (or at least with low) anthropogenic influence should be no more than 10 ppb (Anfossi *et al.*, 1991)(Marenco *et al.* 1994) as it was in Europe in the 19th century. However, present day measurements in the USA shows summer background levels between 20 and 45 ppb (Fiore *et al.*, 2002). Situation in Europe is similar (Marenco *et al.*, 1994) with that in the USA and our analysis further confirms this findings. The difference is also almost the same as in the case of the diurnal cycle which was already mentioned.

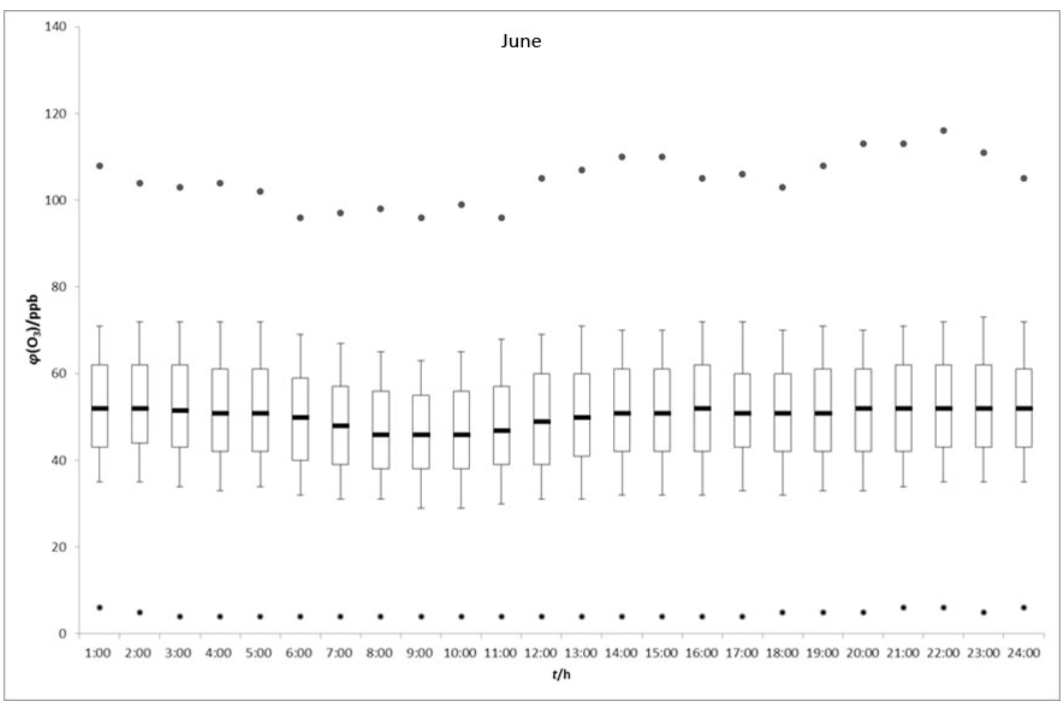

Figure 6a

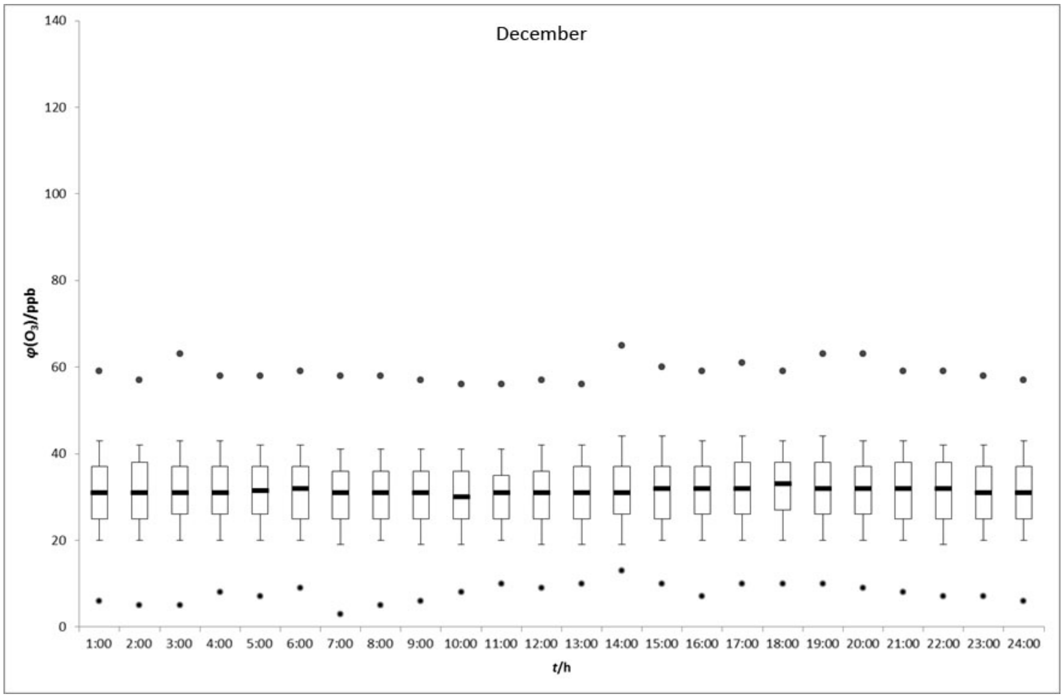

Figure 6b

Figure 6: Box & whiskers plot of the hourly ozone volume fractions during one month over all years. Data for the (a) June and (b) December are shown here and for the other months please refer to supplement data. Maxima and minima (upper and lower extremes) are shown with a dot, upper whisker shows 90-percentile, upper box line shows 75-percentile, inner box line shows median, lower box line shows 25-percentile and lower whisker line shows 10-percentile.

Generally, various diurnal, seasonal and annual cycles can be observed from the long-term data. While expected ozone cycles such as diurnal or annual can be easily observed using other methods, Fourier transformation of data can point to some other unusual or otherwise less evident cycles (Fernández-Macho, 2011), *e.g.* contribution of traffic during workdays and weekends (Marr and Harley, 2002). Peaks in spectra show the most important cycles. Since Fourier transformation requests data continuity, missing data for this analysis has been extrapolated. Observed frequencies are shown at fig. 7. The most important frequencies are those of annual and diurnal cycles which are always connected with annual and diurnal changes in the insolation. Other peaks can be attributed to regional air circulation (Sebald *et al.*, 2000). However, continuous measurements which can confirm that are not available. Other peaks are also of less intensity.

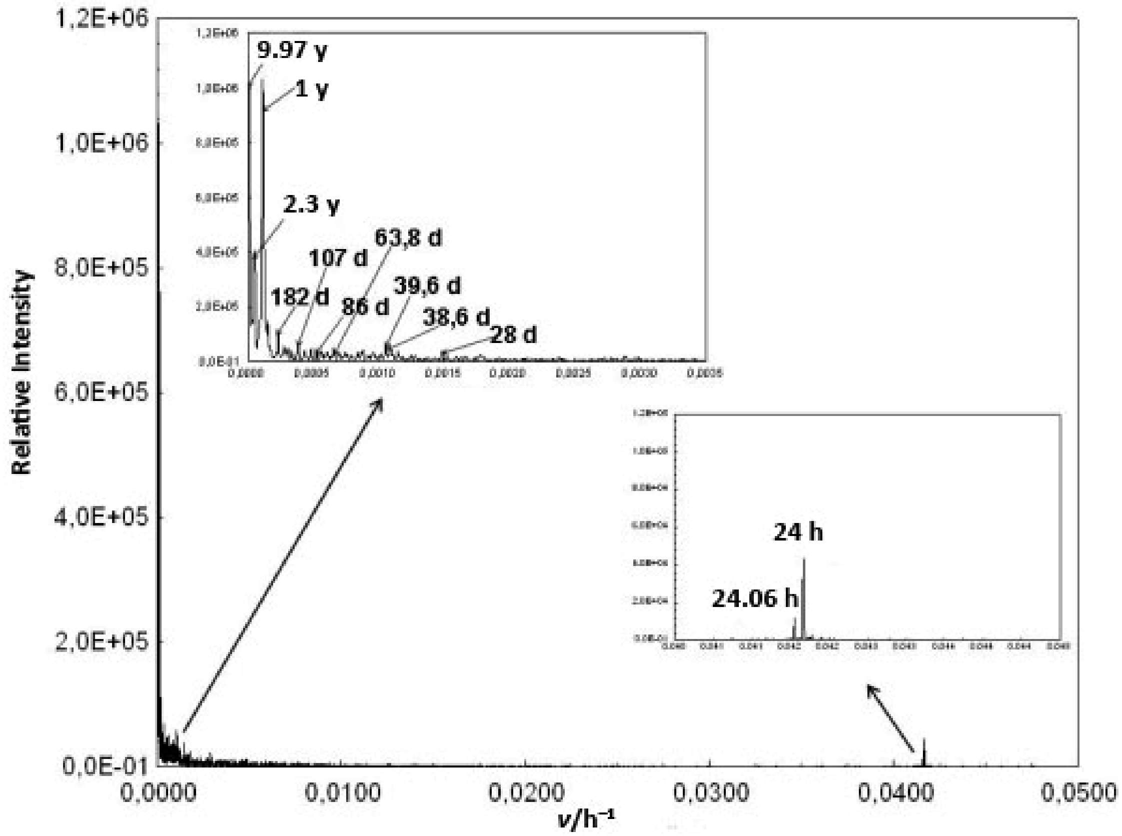

Figure 7: Fourier transformation of all the hourly ozone volume avarages acquired on Puntijarka station during the period from 1989 to 2009.

Concerning the trend of the mean hourly ozone averages, previously analysed data (Butković *et al.* 2000.) show a possibility of a negative trend for the ozone levels at the Puntijarka station. This was attributed to reduction in industrial emission, road and air traffic over Zagreb due to the war conditions (1991 – 1995). Effects of the war in this area were predominantly indirect (*e.g.* reduction in traffic and industry) since there was only sporadic direct war activity in Zagreb area. Since Croatia still continues to slowly advance toward a post-industrial era, this argument still remains, however, the traffic was more intense in the last decade than previously. Nevertheless, a linear regression, trend in the last decade (2000s) was more significant than it was in the 1990s when there was no decisive conclusion of its existence (Fig. 8). If only data for the summer period (April to September) are considered, it can be seen that the negative trend existed during the whole period of the observation and that it was even more pronounced during the first decade. That can also be seen in Fig. 2 by the lower ozone volume fractions measured during the summer months. By using the Mann-

Kendall test, it was further shown that the trend certainly exists during the second 10-year period with the level of significance of 0.001 for both the summer and the whole year period, while there is no trend during the first decade (Tab. 1). However, if we consider the level of significance of 0.05, which indicates a lesser degree of certainty, then even in the first decade during the summer period, the negative trend can be observed. If the whole two-decade period is taken into account, then the negative trend, predominantly driven by the situation during the second decade, can also be confirmed with the level of significance at 0.01.

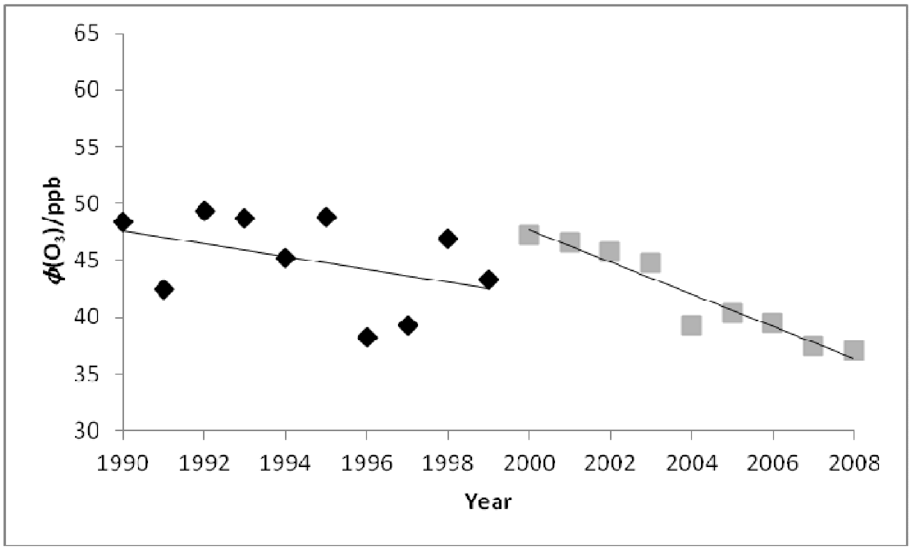

Figure 8a

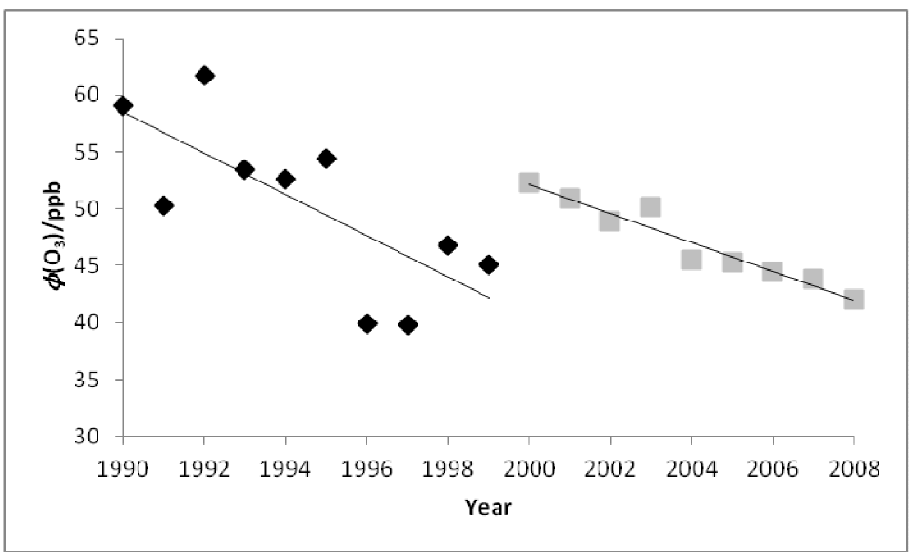

Figure 8b

Figure 8: Linear regression of the mean hourly ozone fractions in two decade period for the whole year periods (a) and for the season April-to-September only (b). Observed trend lines are also shown with the following slopes: fig. 8a → –0.56 ppb yr^{-1} (until 1999) and –1.41 ppb yr^{-1} (from 2000); fig. 8b → –1.81 ppb yr^{-1} (until 1999) and –1.27 ppb yr^{-1} (from 2000).

Table 1: Results of the Mann-Kendall analysis of the trend of the mean hourly ozone volume fractions at the Puntijarka station for the whole period of observations and for the first and the second decade separately.

Time series	From year	Until year	n	Test S	Test Z	Significance	Slope/ ppb yr^{-1}	Intercept/ppb
Whole year $\varphi(O_3)$/ppb	1990	1999	10		–0.89	–	–0.53	48.7
Summer $\varphi(O_3)$/ppb	1990	1999	10		–1.97	0.05	–1.62	60.7
Whole year $\varphi(O_3)$/ppb	2000	2008	9	–32		0.001	–1.38	62.9
Summer $\varphi(O_3)$/ppb	2000	2008	9	–34		0.001	–1.25	65.8
Whole year $\varphi(O_3)$/ppb	1990	2008	19		–2.87	0.01	–0.54	49.0
Summer $\varphi(O_3)$/ppb	1990	2008	19		–3.01	0.01	–0.71	56.5

We can further analyse the trend of the 95-percentile of the hourly ozone averages. 95-percentile is considered to be a better measure for the analysis of the high values of the hourly ozone averages (Monteiro *et al.* 2012). These high values are of higher importance for assessing the photochemical pollution. With the same explanations as above, based on the linear regression, it can be concluded here that the 95-percentile values decrease during the observed period of time, with the same negative slope during the first and the second decade considering the whole year period (Fig. 9). However, the summer values show slightly different result, where a negative slope is obvious as well, though much slower during the second than during the first decade. The Mann-Kendall test is also used to confirm the existence of the negative trends during both the observed periods and the whole two-decade period (Tab. 2). With the level of significance at 0.05 we can estimate that the negative trend exists in all observed periods. The whole year period for the first decade is also included here. Level of significance increases from 0.05 to 0.01 in only one case – when all data (both periods, whole year) are taken into account. Finally, it can be concluded that the negative trend of the 95-pecentile of the hourly ozone averages exists at least with the level of significance as high as 0.05.

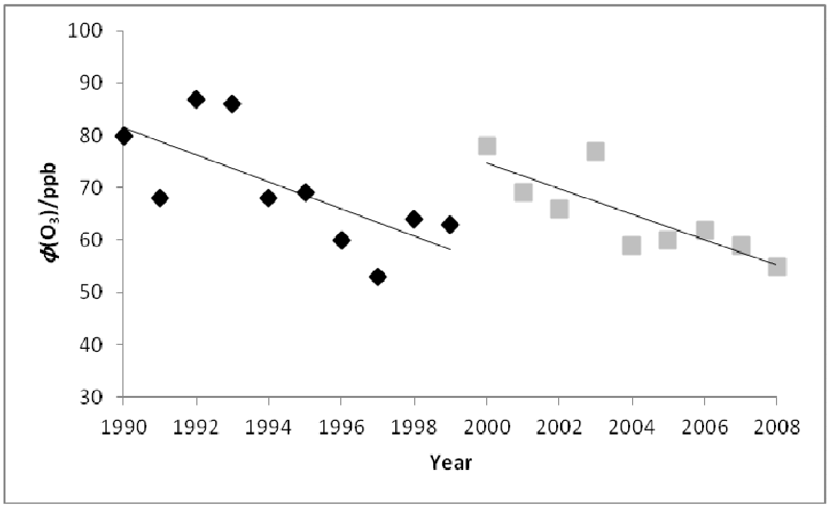

Figure 9a

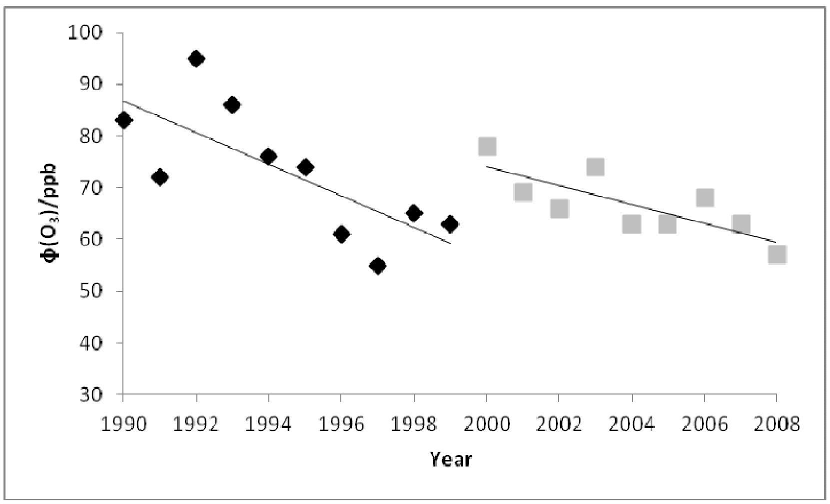

Figure 9b

Figure 9: Linear regression of the 95-percentile of hourly ozone fractions in two decade period for the whole year periods (a) and for the season April-to-September only (b). Observed trend lines are also shown with the following slopes: fig. 9a → –2.59 ppb yr^{-1} (until 1999) and –2.45 ppb yr^{-1} (from 2000) fig. 9b → –3.07 ppb yr^{-1} (until 1999) and –1.82 ppb yr^{-1} (from 2000).

Table 2: Results of the Mann-Kendall analysis of the trend of the 95-percentile hourly ozone volume fractions at the Puntijarka station for the whole period of observations and for the first and the second decade separately.

Time series	From year	Until year	n	Test S	Test Z	Significance	Slope/ ppb yr^{-1}	Intercept/ppb
Whole year $\varphi(O_3)$/ppb	1990	1999	10		–2.07	0.05	–2.20	82.2
Summer $\varphi(O_3)$/ppb	1990	1999	10		–2.15	0.05	–2.83	90.3
Whole year $\varphi(O_3)$/ppb	2000	2008	9	–25		0.05	–2.46	101.7
Summer $\varphi(O_3)$/ppb	2000	2008	9	–23		0.05	–1.69	90.1
Whole year $\varphi(O_3)$/ppb	1990	2008	19		–2.67	0.01	–0.93	74.9
Summer $\varphi(O_3)$/ppb	1990	2008	19		–2.50	0.05	–1.18	81.8

Based on this information, one can conclude that during the first period (1990s) the maximum values of the ozone concentrations are observed and after that definite proof exists that the trend is negative. This concurs with the results for the nearby stations on Krvavec and in the Rijeka bay making this a proof for the negative trend at least at a regional scale.

The sole exceptions from the regular background values during which very high values of the hourly averages of ozone volume fractions had been observed were attributed to the ozone intrusions from the stratosphere. Although there is a suspicion on the possibility that such a high vertical transfer may occur, the proof for the intrusion lays in favourable meteorological conditions on that day and in a fact that some other stations in the vicinity of this one also measured elevated concentrations of ozone. It is also known that such intrusions really occur in Europe and may last for several consecutive days (Borrell *et. al.*, 1995). They are easily observed in the cities since the morning levels of ozone are very low (especially in much photochemically polluted cities (Bouscaren, 1991) of southern Europe (Millán, 1993), however if the levels are several times higher than normal and additionally confirmed with some other data, intrusions may be observed even from the background measurements.

4. Conclusion

After more than two decades of continuous monitoring of ozone at the Puntijarka station, it has been concluded that this site can be regarded as a representative for the background station in spite of the vicinity of the major urban area of the Croatian capital Zagreb. A horizontal transport from the nearby city, although meteorologically favoured (as shown by the wind rose), is negligible because of the difference in altitude. The most important reason for being so important as a background station is its location near the urban area (which shows that urban area needs not to affect its neighbourhood and to be helpful in comparison between city stations and this one). It is located at the boundary between the Central and Southern Europe (the most photochemically polluted area in Europe) so it can be included in the research connected to both areas. This station must not be omitted in any analysis connected with the air flows from Italy eastwards and since Italy is the predictably area with the highest background levels of ozone this station has even greater importance. All data analyses consistently show a very low local photochemical pollution production with a small diurnal cycle of ozone volume fractions and only an annual cycle being more pronounced. Both cycles are connected directly to the insolation *i.e.* higher values are observed diurnally at noon and in the early afternoon whereas on an annual basis during spring and summer. The only exceptions from these background levels could be observed during the periods of the rare stratospheric ozone intrusions. During the intrusions, extreme rises in ozone levels were observed at the two sites in the vicinity of Puntijarka station almost simultaneously and for similar short time periods.

Another very important conclusion lays in the fact that a negative ozone level trend is observed in the second decade. During the first 10 years the trend in the ozone concentration is either slightly negative or non-existent. This, accompanied by the data for Krvavec and Rijeka bay stations, is a valuable finding at least on the regional scale especially compared with the predictions of global rise in the tropospheric ozone concentration.

5. Acknowledgments

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