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PHOTOCHEMICAL OXIDANTS IN THE TROPOSPHERE ABOVE ZAGREB

Fotokemijski oksidansi u troposferi iznad Zagreba

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Abstract — The behaviour of photo oxidants in the troposphere above the city of Zagreb was investigated on the basis of ozone measurements over many years and periodical measurements of nitrogen oxides, ^7Be and meteorological parameters. At the Ruđer Bošković Institute (RBI) site a pronounced influence of the town was found. Photochemically polluted air comes to this measuring site mostly from the southern sector. Nevertheless, ozone levels are most of the time within the limits of most national air quality standards. The Puntijarka site is only weakly influenced by the town and other sources of primary pollutants. Consequently, this site is suitable for determining the background concentration, for comparison with model results, as well as for a trend analysis of ozone and an investigation of long range transport phenomena.

Keywords: ozone, nitrogen oxides, photo-oxidants, atmospheric pollution, photochemical pollution, ^7Be

Sažetak — Na temelju višegodišnjih mjerenja ozona i povremenih mjerenja dušikovih oksida, ^7Be te meteoroloških parametara, dan je prikaz ponašanja fotooksidansa u troposferi iznad Zagreba. Izražen utjecaj urbane sredine primijećen je na postaji na Institutu Ruđer Bošković pri čemu fotokemijski onečišćen zrak pristiže iz južnog sektora. Razine ozona većinu se vremena nalaze unutar okvira većine zemaljskih standarda kvalitete zraka. Na postaji Puntijarka primijećen je vrlo slab utjecaj Zagreba i drugih izvora primarnih onečišćujućih tvari. Zbog toga ta postaja može poslužiti za procjenjivanje pozadinskih koncentracija, kao izvor podataka za usporedbu s rezultatima modela, praćenje višegodišnjih trendova i istraživanja daljinskog transporta onečišćujućih tvari.

Ključne riječi: ozon, dušikovi oksidi, fotooksidansi, onečišćenje atmosfere, fotokemijsko onečišćenje, ^7Be

INTRODUCTION

The atmosphere is the main recipient of waste gases from the industrialised society. Ozone (O_3) is a natural trace constituent of the atmosphere which can be considered as an air pollutant in the troposphere acting as a strong oxidant and greenhouse gas. Although only about 10 % of all the atmospheric ozone is located in the troposphere, this small amount of ozone is nevertheless of fundamental importance for the troposphere. Ozone is involved in a series of chemical reactions whithin the troposphere which are initiated by solar radiation. These reactions are strongly influenced by the concentrations of some trace gases such as nitrogen oxides and volatile organic compounds which always accompany fossil fuel burning. For this reason, anthropogenic activities connected with solar radiation can lead to photochemical air pollution episodes in urban areas.

The hydroxyl radical ($OH^\bullet$) plays a very important role in tropospheric air chemistry. Despite the fact that its average volume mixing ratio in the troposphere is only about 3×10^{-14} it starts a series of reactions leading to ozone formation when solar radiation is present. Hydroxyl, which is produced by the action of short wave solar ultraviolet radiation on ozone and water vapour, is responsible for the first step in the removal of most gases of natural and antropogenic origin from the atmosphere.

For example, such two series of reactions initialised by $OH^\bullet$ radical are:

$$
\begin{array}{l}
CO + OH^\bullet + O_2 \longrightarrow CO_2 + HO_2^\bullet \\
HO_2^\bullet + NO \longrightarrow OH^\bullet + NO_2 \\
NO_2 + h\nu \longrightarrow NO + O \quad (\lambda \leq 400\ \text{nm}) \\
O + O_2 + M \longrightarrow O_3 + M \\
\hline
\Sigma\text{:}\ CO + 2O_2 \longrightarrow CO_2 + O_3
\end{array}
$$

$$
\begin{array}{l}
RH + OH^\bullet \longrightarrow R^\bullet + H_2O \\
R^\bullet + O_2 + M \longrightarrow RO_2^\bullet + M \\
RO_2^\bullet + NO \longrightarrow RO^\bullet + NO_2 \\
RO^\bullet + O_2 \longrightarrow \text{Carb} + HO_2^\bullet \\
HO_2^\bullet + NO \longrightarrow OH^\bullet + NO_2 \\
NO_2 + h\nu \longrightarrow NO + O\ (2\times) \quad (\lambda \leq 400\ \text{nm}) \\
O + O_2 + M \longrightarrow O_3 + M\ (2\times) \\
\hline
RH + 4O_2 \longrightarrow \text{Carb} + H_2O + 2O_3
\end{array}
$$

The series involving volatile hydrocarbons RH is very important. It produces two molecules of ozone and one molecule of carbonyl compound (Carb) which can react further to give another molecule of ozone.

The last two steps in such a series of reactions (i.e. photolysis of NO_2 and formation of O_3) are the only known important chemical source of ozone in the troposphere.

$$NO_2 \xrightarrow[\lambda < 400\ \text{nm}]{h\nu} NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

O_3 formation is a trimolecular process in which M is a third body, usually N_2 or O_2, carrying away the excess energy.

The ozone content of the troposphere is generally determined by three processes: 1) the transfer of ozone-rich air from the stratosphere, 2) photochemical formation and destruction of ozone within the troposphere and 3) ozone removal by dry and wet deposition and reactions on various surfaces.

In the atmosphere, pollutants are diluted during transport from the sources to remote, cleaner areas and most of the regional transport and deposition takes place within the atmospheric boundary layer. During a temperature inversion, transport phenomena can be blocked resulting in the trapping of air pollutants below the inversion height. This meteorological condition often leads to air pollution episodes in urban areas. In addition, strong winds above the inversion layer facilitate long-range transport phenomena.

Stratospheric air intrusion is also a meteorological event with great influence on the spatial and temporal distribution of ozone volume fractions in the troposphere. The stratosphere contains cca. 90% of all ozone in the atmosphere which means that such an event should be accompanied by significant changes in ozone concentrations. Peak values are not necessarily connected with the most intense solar radiation as in the case of photochemical formation of ozone. Although such intrusion events are a significant source of ozone in the troposphere, they can only very rarely be observed below 3 km - in less than 1% cases of ozone intrusions. A convenient tracer for stratospheric air is ^7Be which is more abundant in the stratosphere due to its formation via cosmic ray induced spallation in the upper atmosphere.

Surface ozone measurements in Zagreb, the capital of Croatia, were performed already at the end of the 19th century, but have been analyzed and described only recently (Lisac, Grubišić, 1991). The analytical method used at that time was the Schoenbein method based on potassium iodide paper and a colorimetric scale of 11 degrees (Lodge, 1989). Measurements were performed twice a day in the period from 1889 to 1900. The first ozone measurements using automatic monitoring equipment took place in the centre of Zagreb in the spring and summer of 1975 (Cvitaš et al., 1976, Božičević et al., 1979).

The aim of this work is to investigate the level of photochemical air pollution in the atmospheric boundary layer above Zagreb and the nearby elevated Puntijarka site.

METHODS AND INSTRUMENTS

Modern ozone measurements are based on spectroscopic measurements which use intense ozone absorption at 255 nm. UV light passes through an air sample with a given path length and if the sample contains ozone the light intensity is lower than in ozone-free air. The degree to which the light is attenuated is given by the Lambert Beer equation:

$$I = I_0 e^{-alc}, \qquad or, \qquad c = (al)^{-1} \ln \frac{I_0}{I}$$

I_0 and I are the light intensity with no ozone and with ozone in the gas sample, respectively, a is the absorption coefficient of ozone, l is the path length and c is concentration.

Ozone has been continuously monitored by commercial Dasibi and Environment monitors. The monitoring period described here spans from 1989 to 1995.

Nitrogen oxides data have been measured using the Cranox $NO/NO_x/O_3$ system (Eco Physics, Switzerland). Chemiluminescent measurements of the gas reaction between nitric oxide and ozone have been recognised as the most convenient method for NO determination in the air, especially in the ppt range. By that method, NO is measured directly and NO_2 indirectly after a quantitative reduction to NO. The basis for measurement is provided by the following reactions:

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

$$NO_2^* + M \longrightarrow NO_2 + M^*$$

Part of the excited NO_2 molecules can relax either by collision or by radiation. In order to produce more radiation it is necessary to carry out a chemiluminescence reaction under low pressure conditions.

All monitors were regularly checked and calibrated. The ozone monitors were calibrated by a Dasibi model 1008 PC which was checked against an ozone standard within the EUROTRAC / TOR project. The Cranox system is specially equipped for very precise measurement and is calibrated with commercial NO calibration gas. Meteorological data were obtained using standard equipment.

The radioactivity of beryllium-7 was measured in the dust deposit obtained on filter paper by a high volume sampler. For counting the radioactivity of ^7Be (nuclide ^7Be has a gamma-ray energy of 477.56 keV and a 10.3% intensity (Erdtman, Soyka, 1979)) a high-purity intrinsic germanium detector (HPGe), constantly cooled with liquid nitrogen, with a 1.86 keV resolution, a 25% equivalent efficency and a peak to compton ratio of 46:1 for the 1332 keV line of ^{60}Co was used. The detector was shielded by 10 cm of pre-World War II iron and 5 cm lead on all sides. Amplified and shaped pulses from the detector were analysed by GENIE PC Canberra software. The detector was calibrated using Amersham single-nuclide gamma-ray standards. The efficiency of the detector was determined using a standard ^{152}Eu on bentonit (IZ-INTA) for filter paper thickness.

LOCATIONS

This work is part of the investigations carried out under the EUROTRAC/TOR (Tropospheric Ozone Research) project . One of the aims of the EUROTRAC / TOR project was to assess the levels of ozone in the lower troposphere over Europe by collecting data from some 20 stations (Cvitaš, Kley, 1994) into a databank for subsequent detailed analysis by intercomparison (Scheel, 1994; Scheel et al, 1997) and modelling (Hass et al, 1994; Simpson, 1991). The data obtained at the stations in Zagreb and Puntijarka (Božičević et al, 1993; Kezele et al, 1995; Butković et al, 1995.) are included in the data bank.

The Puntijarka site is a rural continental site on the ridge of the northern side of Mount Medvednica, located at 45° 54' N; 15° 58' E and 980 m a.s.l. The other site is a nearby urban site located at the Ruđer Bošković Institute in Zagreb. Detailed information on both sites is given in Cvitaš and Kley, 1994.

RESULTS

Measurements at both stations resulted in 10 minute ozone averages for the period 1989 - 1995. Nitrogen oxides were measured at both stations for shorter periods of time, resulted in 10 minutes average volume fractions of NO and NO_2. These periods are October '91 - April '92 for the RBI site and June - September '95 for the Puntijarka site.

The results are given in figures 1 - 6. The results of the ^{7}Be measurements are given in Table 1.

Tablica 1. Specifične aktivnosti (S_A) ^{7}Be na postaji Puntijarka.

Table 1. Specific activity (S_A) of ^{7}Be at the Puntijarka site.

date of collecting	volume measured m^3	day of counting	S_A ^{7}Be mBq/m^3
14. 11. 1994	200	16.11.1994	-
18. - 21. 11. 1994	5000	22. 11. 1994	3.39
23. - 25. 11. 1994	5000	29.11. 1994	2.92
25. - 28. 11. 1994	5000	02. 12. 1994	2.15
28. 11.- 2. 12. 1994	3138	05. 12. 1994	4.27
02. - 05. 12. 1994	5000	19. 12. 1994	6.59
05. - 09. 12. 1994	5000	21. 12. 1994	1.61
09. - 12. 12. 1994	5600	20. 01. 1995	3.92
12. - 15. 12. 1994	3120	24. 01. 1995	11.3
19. - 22. 12. 1994	5000	25. 01. 1995	4.97

DISCUSSION

Raw data are converted into hourly averages and evaluated statistically in relation to the meteorological data.

The monthly variation of the ozone volume fraction at the RBI site is typical for photochemical ozone formation (summer maxima). Smaller variations at the Puntijarka site are due to contribution of ozone photochemical formation and transport (to the background concentration) (Figures 1a and b).

This is why the average diurnal variation is pronounced at the RBI and negligible at the Puntijarka site (Figures 2a and b). The levels of nitrogen oxides and reactive volatile hydrocarbons have a key role in ozone formation. This influence is very pronounced in urban areas where two types of processes take place. First, the degradation of ozone through chemical reactions, resulting in a decrease of ozone concentration, especially during winter and at night, due to fast reactions of ozone to emitted NO and other substances in the air. Second, ozone formation resulting in high concentrations of more than 80 ppb during the summer months and sunny hours can be observed under favourable meteorological conditions i.e. stagnant air or circulating wind systems. Reaction cycles (see above) are initiated and lead to high ozone values. For such reasons, an analysis of environmental monitoring data in many cases cannot involve the assumption of a Gaussian distribution because their distribution can be strongly skewed. The quantile concept can be useful in such a case. For a normal probability density function, 2.28 % of data lie below (μ - 2σ), meaning that (μ - 2σ) is the quantile of rank 0.0228. Similarly, the median is the quantile of rank 0.5 (Gilbert, 1987).

Low values of the boundary layer ozone do not necessarily mean that the place is a rural site. The sums of O_3 and NO_2 concentrations representing total oxidants and denoted as Ox, do not exhibit such a deviation toward low values during the night and the cold season of the year and they give us a better indication of whether a place can be classified as rural or not (Kley et al, 1994). This is best described by the histogram plot in Figure 3. The distribution of oxidants resembles the normal distribution much better than the ozone values alone.

By carefully looking at ozone data at night, an ozone maximum can be observed. This can be described by local meteorological phenomena which lead to the formation of a nocturnal inversion layer. Such a layer which prevents the mixing of air aloft with air from below, normally becomes depleted in ozone due to deposition and reactions with pollutants. The air above the inversion stays relatively rich in ozone and strong winds, which can exist above inversion layers, can suddenly bring ozone down to the ground.

The mean ozone volume fraction at Puntijarka is 45 ppb which is 9 ppb higher than the estimated average background concentration in the boundary layer over Europe (Scheel at al, 1997). This discrepancy should be compared with higher ozone values measured in the southeast part of Europe (Krvavec, Slovenia; K-puszta, Hungary; Exelberg

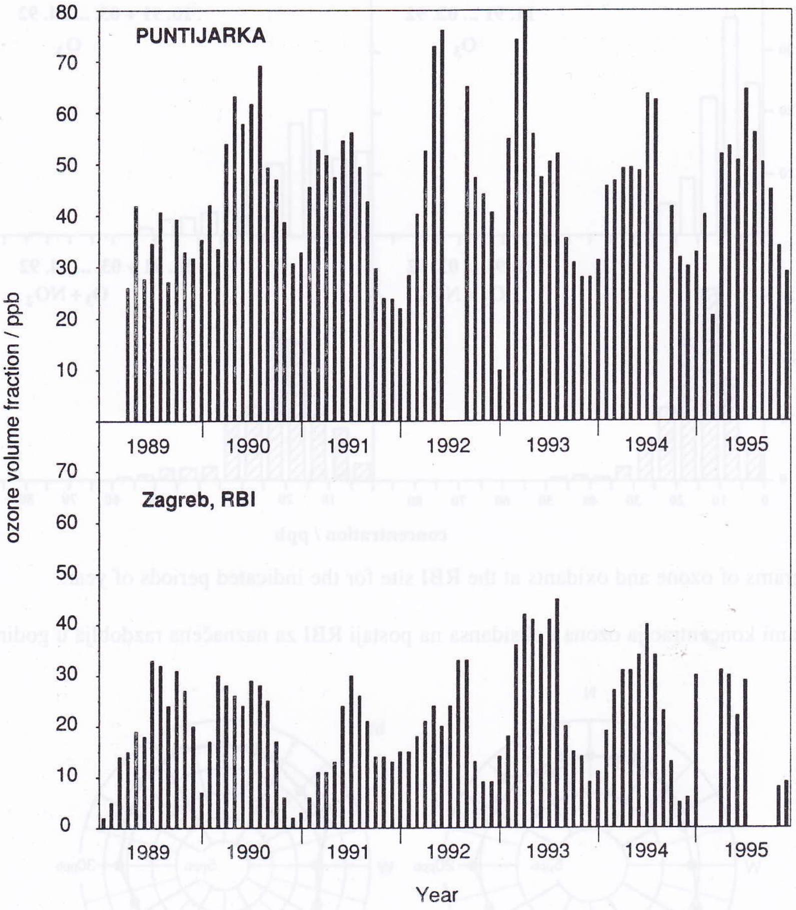

Figure 1. Histograms of the monthly average ozone volume fraction at Puntijarka and the Ruđer Bošković Institute from 1989 to 1995.

Slika 1. Histogrami prosječnih mjesečnih volumnih udjela ozona na Puntijarki i Institutu Ruđer Bošković od 1989. do 1995.

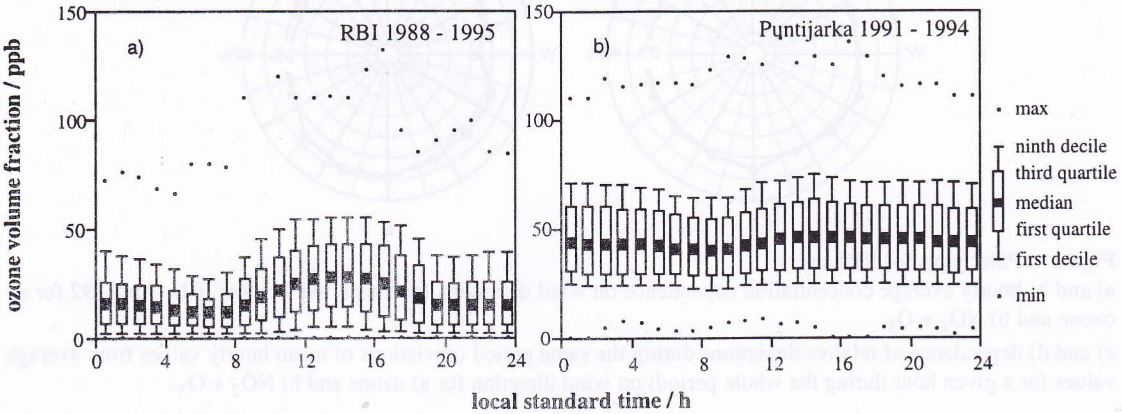

Figure 2. Average diurnal variation during the indicated periods.

Slika 2. Prosječni dnevni hod tijekom razdoblja označenih na slici.

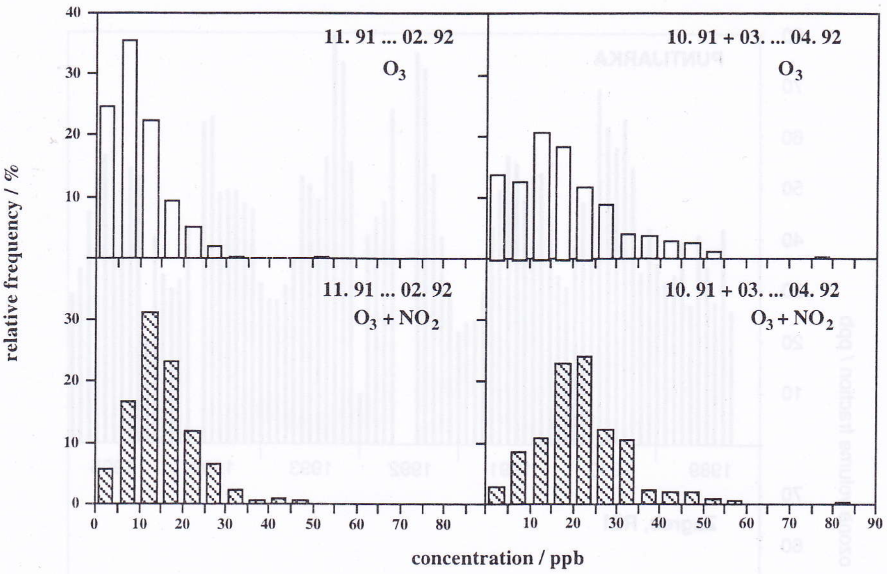

Figure 3. Histograms of ozone and oxidants at the RBI site for the indicated periods of year.

Slika 3. Histogrami koncentracija ozona i oksidansa na postaji RBI za naznačena razdoblja u godini.

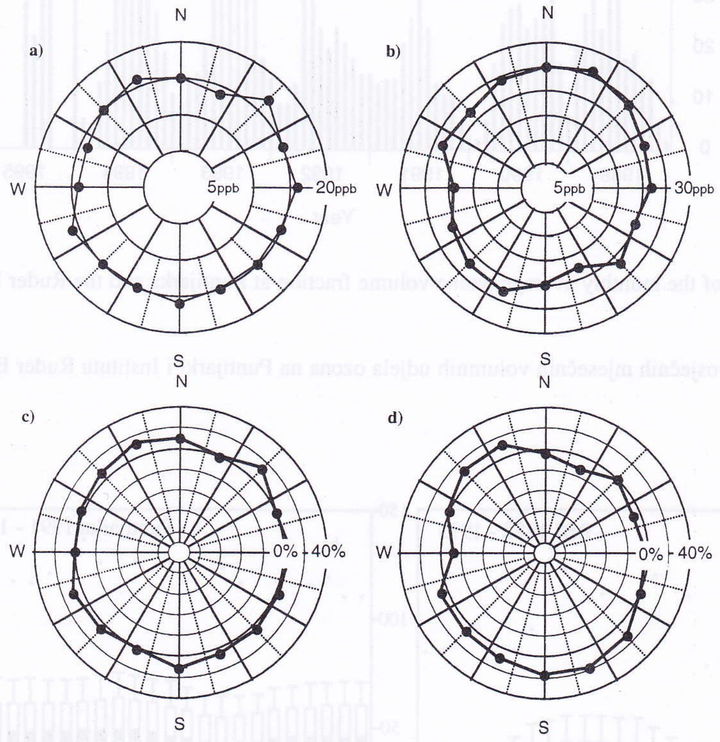

Figure 4. Polar plots for RBI site:

a) and b) hourly average concentration dependence on wind directions for the period October ‘91 - April ‘92 for a) ozone and b) $NO_2 + O_3$;

c) and d) dependence of relative deviations during the same period (deviations of mean hourly values from average values for a given hour during the whole period) on wind direction for a) ozone and b) $NO_2 + O_3$.

Slika 4. Polarni dijagrami za postaju RBI:

a) i b) ovisnost prosječne satne koncentracije u ppb o smjeru vjetra za razdoblje listopad ’91. - travanj ’92. za a) ozon i b) za $NO_2 + O_3$;

c) i d) ovisnost relativnih odstupanja tijekom istog razdoblja (odstupanja srednjih satnih vrijednosti od prosječne vrijednosti za dani sat tijekom cijelog razdoblja) o smjeru vjetra c) ozon i d) za $NO_2 + O_3$.

and Illmitz, Austria; Wank and Schauinsland, Germany). Additionally, possible causes for this higher average ozone value could be transport phenomena from urban areas and, as will be shown later, a certain quantity of freshly emitted primary pollutant.

The polar plots (wind direction versus concentration) for the RBI site are shown for ozone and oxidants in Figures 4a and b, respectively.

One cannot underline any distinct direction connected with predominantly polluted or unpolluted air. The wind, as well as ozone concentrations, can have diurnal variations. In order not to draw wrong conclusions, it is better to plot the relative deviations from average behaviour as shown in Figures 4c and d. In this case, there are positive deviations of 20% connected with southerly winds which bring air masses from the centre of town and the industrial zone. Although ozone concentrations at the RBI site are generally not alarming yet, it must be emphasised that the main NO_x and VOC sources in the town should be identified and their emission should be reduced, in order to prevent future photochemical smog episodes. There are a number of computer simulation models developed for describing the relation between emissions, ozone concentrations and removal processes like deposition, e. g. the EUMAC zooming model (Moussiopoulos, 1994).

At the Puntijarka site, seasonal effects on ozone distribution are analysed by a quantile comparison in Figures 5a, b and c, where the straight line represents two identical distributions. The highest values for ozone are observed in the summer period, while the lowest are in winter. The same is valid for a standard deviation of the distribution.

Reactions of photochemical ozone formation in the troposphere always include nitrogen oxides,

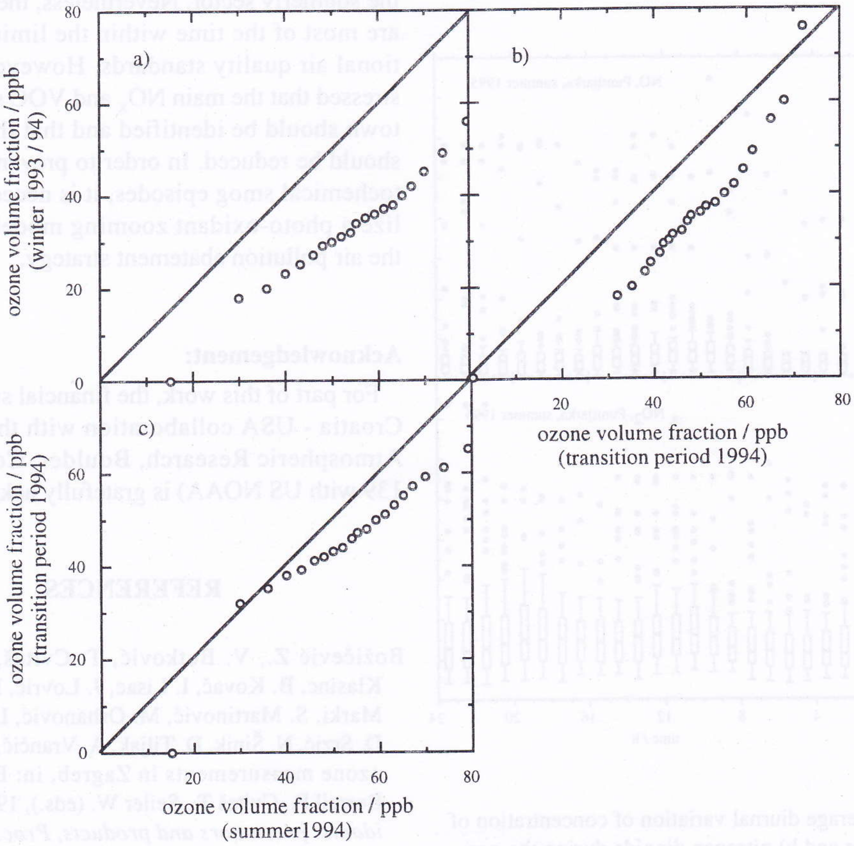

Figure 5. Quantile - quantile distribution comparison of ozone volume fraction during the three seasons in 1993 / 94 at Puntijarka site. a) winter - transition period; b) winter - summer; and c) transition period - summer.

Slika 5. Usporedba kvantila razdioba ozonskih koncentracija svih triju razdoblja tijekom 1993/94. na Puntijarki. a) usporedba zima-prijelazni period; b) usporedba zima-ljeto; i c) usporedba prijelazni period-ljeto.

and for that reason it is very important to measure them together with ozone. The mean value for the measurement period (May - August '95) is 115 ppt and 1.55 ppb for NO and NO_2, respectively. These values can be considered low and they indicate relatively clean air. Hourly distributions for NO and NO_2 are shown in Figure 6. In this Figure the median, first and third quartiles, lower and upper limits and severe and mild outlayers for every hour during the day are presented. The frequent occurrence of high value outlayers due to local site characteristics is obvious.

^{7}Be concentrations have been measured for only a short period of time (see Table 1), but for the period of 12 - 15 December 1994, in comparison with other measurements, a much higher radioactivity is observed.

In a detailed analysis of this period no unusual ozone behaviour was found, except for 14 December 1994 with very low ozone values connected with a cold frontal passage over Puntijarka. There was no precipitation during those days so that a beryllium transport can be excluded. A very deep anticyclonic activity can possibly be connected with this high ^{7}Be result.

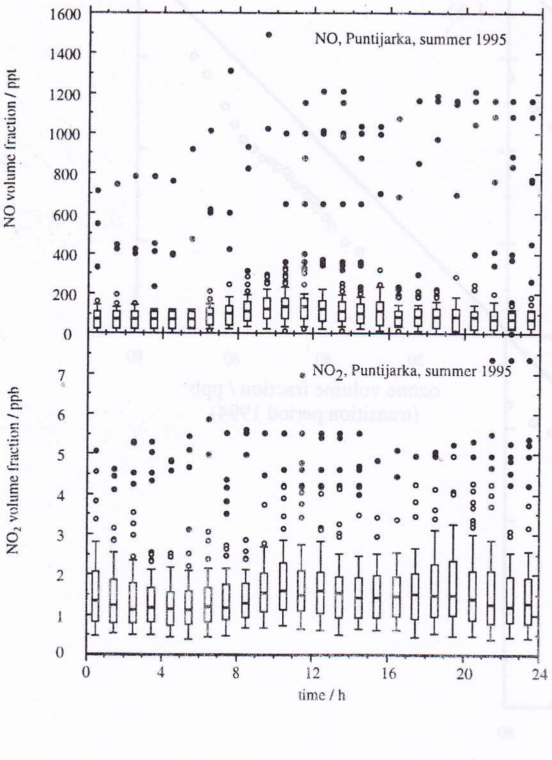

Figure 6. Average diurnal variation of concentration of a) nitric oxide and b) nitrogen dioxide during the period from June to August 1995.

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Slika 6. Prosječni dnevni hod koncentracija a) dušikova monoksida i b) dušikova dioksida u razdoblju od lipnja do kolovoza 1995.

CONCLUSIONS

A comparison of ozone levels between the Puntijarka and RBI sites shows higher ozone levels at the latter site. The monthly and daily variations are weaker at Puntijarka. This behaviour is due to the higher elevation of the Puntijarka site and the absence of sources of primary photochemical pollutants. The Puntijarka site is thus suitable for measuring background concentration in this geographical area. At the RBI site, a very pronounced influence of the town was found. Photochemically polluted air comes to the measuring site mostly from the southerly sector. Nevertheless, the ozone levels are most of the time within the limits of international air quality standards. However, it must be stressed that the main NO_x and VOC sources in the town should be identified and that their emission should be reduced. In order to prevent future photochemical smog episodes, it is neccessary to utilize a photo-oxidant zooming model to optimise the air pollution abatement strategy.

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