

*Originalan naučni rad
UDC: 546.214+541.183:551.5*

AIR POLLUTION BY OZONE IN THE URBAN AREA OF BELGRADE (SERBIA): SURFACE OZONE PHENOMENOLOGY AND THE RELATION BETWEEN OZONE AND SOME METEOROLOGICAL PARAMETERS

Dragan A. Marković¹, Dragan M. Marković¹, Mladjen Ćurić²

¹*Faculty of Applied Ecology, Singidunum University, Danijelova 32, Belgrade 11000, Serbia*

²*Institute of Meteorology, Dobračina 16, Belgrade 11000, Serbia*

ABSTRACT

Meteorological conditions favorable for the build up of ozone (O₃) are frequent in Belgrade and the surrounding area. Measurements, for the seasons 1993 to 2004 performed at three different sites inside the city, revealed two main patterns of photochemical smog events in the Belgrade area: a progressive increase and accumulation of photochemical oxidants during period of warm and stable weather with frequent high daytime ozone concentrations, and transport of local oxidants with sporadically occurring high ozone concentrations during the night. In most cases diurnal ozone concentrations generally showed the typical pattern of photo-smog formation; a steep rise of ozone in the morning, a maximum in the early afternoon (sometimes with 1-h ozone levels greater than 110 ppb) and a rapid decrease in the evening. During such events nocturnal ozone concentrations were usually as low as 10 to 20 ppb (below the background level), but in some cases they were as high as 80 ppb. These variations of ozone concentrations were ascribed to transport of pollutant, ozone depletion chemistry (mainly with nitric oxide NO during the night) and enhanced deposition of ozone on wet surfaces at high humidity. A strong anticorrelation was found between elevation of nocturnal ozone concentration and relative humidity probably affected by small, local rise of temperature.

Keywords: daytime high ozone; water vapor; nocturnal ozone events.

OZONSKO ONEČIŠĆENJE VAZDUHA U URBANIM PODRUČJIMA BEOGRADA (SRBIJA): FENOMENI OZONSKIH PODRUČJA I ODNOSI IZMEĐU OZONA I NEKIH METEOROLOŠKIH PARAMETARA

REZIME

Meteorološki povoljnih uvjeta za izgradnju u ozon (O₃) česte su u Beogradu i okolici. Mjerenja, za godišnja doba 1993 do 2004 nastupila na tri različita sučelja unutar grada, otkrila dva glavna obrazaca fotokemijskih smog događaja u Beogradu površina: progresivni porast i akumulacija fotokemijskih oksidants tijekom razdoblja topla i stabilna vremenska sa čestim visoke dnevne ozon koncentracije i lokalno prijevoz oksidants s visokim koncentracijama ozon mjestimičan sporadino tijekom noći. U većini slučajeva diurnalni koncentracijama ozon pokazao općenito tipičnom obrascu foto-smog formation; strm uspon ozon ujutro, a najviše u ranim poslijepodnevni satima (ponekad sa 1-h ozon razina veća od 110 ppb) i brzo smanjenje navečer. Tijekom takvih događaja bili su uglavnom noćni ozon kao niskim koncentracijama od 10 do 20 ppb (ispod razine pozadini), ali u nekim slučajevima su

se kao visok kao 80 ppb. Ove varijacije koncentracije ozon su ascribed to transporta onečišćujućih, ozon osiromašeni kemija (uglavnom s NE dušikova monoksida u noći) i poboljšane depozicijskih za ozon na mokrim površinama pri visokom vlagom. Snažna anticorrelation je pronađena između noćni visina koncentracije ozon i relativna vlažnost vjerojatno utjecati na malim, lokalnim porast temperature.

Ključne riječi: *visoka dnevna ozon, voda pare, ozon noćni događaje.*

INTRODUCTION

Ground level ozone (O₃) and other photochemical oxidants have become pollutants of concern because elevated concentrations are known to cause detrimental effects and threaten human health and vegetation. Moreover, for some years there have been numerous reports of an association between increases in particle air pollution (PM₁₀) and increases in ozone concentration (e.g. Atkins, 1972; Finlayson-Pitts and Pitts, 1997; Meng et al., 1997; Mulholland et al., 1998; Rizzo et al., 2002; Ying and Kleeman, 2003; Rappenglück et al., 2004). High ozone levels are mainly observed during periods with warm and sunny weather in combination with stagnant air masses and the build-up of precursor substances such as nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs).

Meteorological conditions favorable for the build up of ozone are frequent, in Belgrade and the surrounding area, from early spring to early autumn. During this period photochemical smog events often show different features and are difficult to assign to a particular pattern.

Although, ozone levels were being measured in Belgrade sporadically during early 80-ties and each season starting from 1991, few of these data have been published and the information is scant and difficult to find (e.g. Vukmirović et al., 1987; Mičić et al., 1998). Air quality measurements for the city of Belgrade consist of a very limited data base. Therefore we consider it useful to present the more complete results of our measurements for the seasons 1993-2004 stressing the main characteristics of the photochemical episodes recorded in the Belgrade area. Since ozone concentration measurements from this area are very limited and not included in the reports published by the European Environment Agency (EEA), see for example EEA 2003, we also intend to increase the geographical coverage of the current state of knowledge with respect to ozone seasonal cycles in the troposphere over Europe.

In this paper we report the results for NO₂ (nitrogen dioxide), O₃ and some relevant meteorological parameters obtained at three different sites in Belgrade (Serbia) during three sampling periods over the last decade. This is the earlier data set for these compounds in this city and consequently important information about the local air quality.

EXPERIMENTAL

Starting in 1993, NO₂ concentrations were measured, using a Dasibi M 2108 NO_x chemiluminescence monitor (USA) calibrated via a NO₂ permeation tube. The ozone concentration (1993 to 1997) was evaluated from the total oxidants data obtained from a home-made electrochemical cell calibrated on an ozone generator by a KI colorimetric method (Katz, 1977). Starting in 1998 continuous ozone measurements were made on a Dasibi AH 1008 ozone UV monitor (USA). These readings were occasionally compared with those using a Monitor Labs Ozone Analyzer 8810 with an internal ozone generator. Both instruments were in agreement within $\pm 15\%$. Accompanying continuous measurements of the major meteorological parameters (temperature, relative humidity, wind speed and direction, precipitation and solar radiation) were made on an automatic meteorological station (Met One Instruments USA) at three sampling sites. The first site (1993-1997) was in the lowest part of the city (below 100 m a.s.l.) at the meteorological and ecological station in the open area of a park (1), flanked on two sides by large boulevards. Although screened by vegetation from the main traffic artery, it may be classified as a street station. The second measurement site (1998/99) was removed some 8 km SE at one of the highest city point on top of a hill (Zeleno brdo, 243 m a.s.l.) and may be

classified as a semi-urban background station. During the summer and autumn of 1999 urban ozone and relevant meteorological data were recorded at this place (2). The third measurement site (2001 and onwards) was located on the banks of the river Danube (3) some 6 km NW from the first site and was isolated from the main city traffic artery (Fig. 1). Sporadic measurements were taken in Belgrade's downtown area.

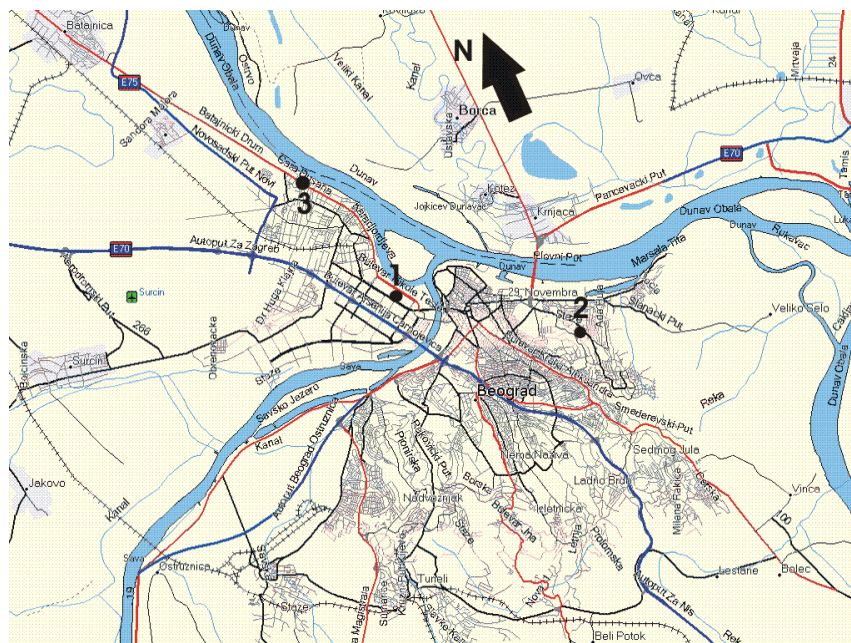


Figure 1: Location of measurement sites across Belgrad
Slika 1: Položaj mjernih lokacija diljem Belgrad

RESULTS AND DISCUSSION

Ozone production in photochemical smog events and its spatial and temporal distribution depends on several variables but mostly on the concentration ratio of precursors (NO_x , VOC), meteorological conditions and the height of the mixed layer (Pagnotti, 1990; Rao and Zurbenko, 1994; Sillman, 1995; Hjorth et al., 2001; Buffoni, 2002). The influence of the concentration ratio of precursors is not linear because different limiting conditions are set depending on the value of this ratio (Sillman, 1995; Finlayson-Pitts and Pitts, 1997; Hjorth et al., 2001). The concentration of VOC has never been systematically measured in Belgrade (before 2004) and such data are not available. The concentrations of NO_2 and NO_x (mostly colorimetric before 2004) are determined by some public health institutions in Belgrade for their own purposes and are expressed as average daily (24 hour) values. We have carried out continuous measurements of NO_2 in periodic episodes since 1993 (Mičić et al., 1998), and the analysis of most recorded profiles of NO_2 concentration changes showed the characteristic urban surroundings pattern (Mestayer et al., 2003) in which traffic plays a major role regarding NO_x emissions. On weekdays, the morning level of NO_2 concentration rose slowly, as the result of oxidation of an abundance of morning NO . Lower concentrations of NO_2 late in the afternoon were expected as a result of less traffic and NO_2 depletion in which O_3 and RO_2 radicals play an important role at this time of day. A new rise of NO_2 concentration was clearly seen during the evening rush hours. The traffic rush hour is expected to occur at the same time as the morning and evening peaks of NO_2 . In the late evening NO_2 concentrations decreased in accordance with the reduction in traffic density and usually stayed low during the night (Fig. 2 a). Nighttime loss of NO_2 via formation of N_2O_5 and its adsorption on aerosols is an important process and should be considered in the NO_2 budget (Neftel et al, 2002). On Saturday and Sunday NO_2 concentrations were usually smaller and any variations less pronounced (Fig. 2 b). Away from busy traffic streets, in residential areas, the concentrations of NO_2 were substantially lower and the diurnal variation remained more or less similar.

The variations in the average height of the mixed layer over Belgrade can be evaluated from data in the literature (Vukmirović and Vukmirović, 1984; Vukmirović et al., 1987; Vukmirović et al., 1990). Satisfactory agreement between the calculated and measured diurnal course of the boundary layer height was observed in a typical photochemical smog episode in Belgrade. In the late summer months the boundary layer showed evolutions with heights varying from a nocturnal minimum of 150 m to a daytime maximum of 1400 -1600 m above the ground (Vukmirović et al., 1990). Under such features of the Belgrade urban troposphere, which plays a primary role in determining the type, duration and intensity of photochemical smog episodes, we noticed two main patterns of photochemical smog events in the Belgrade area:

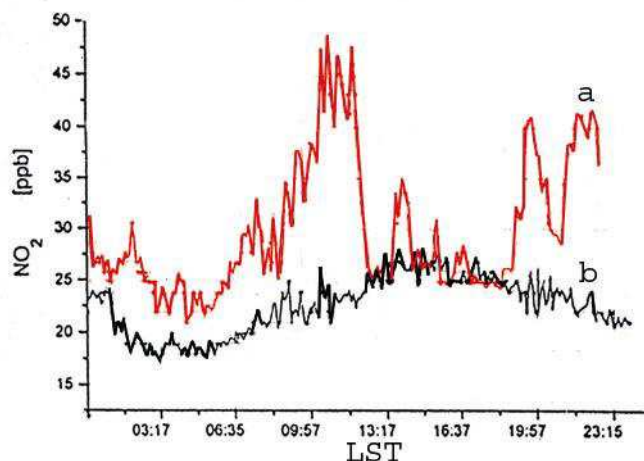


Figure 2: Typical NO₂ profiles observed in the Belgrade troposphere: a) work-day (tuesday) (11. Nov. 1997, average concentration NO₂ = 30 ppb), b) Sunday (11. May 1997, average concentration NO₂ = 22 ppb).

Slika 2: Tipične No₂ profila promatrana u Beogradu troposfera: a) radnog dana (utorak) (11. Studeni 1997, prosječna No₂ koncentracija = 30 ppb), b) Nedjelja (11.. Svibanj 1997, prosječna No₂ koncentracija = 22 ppb).

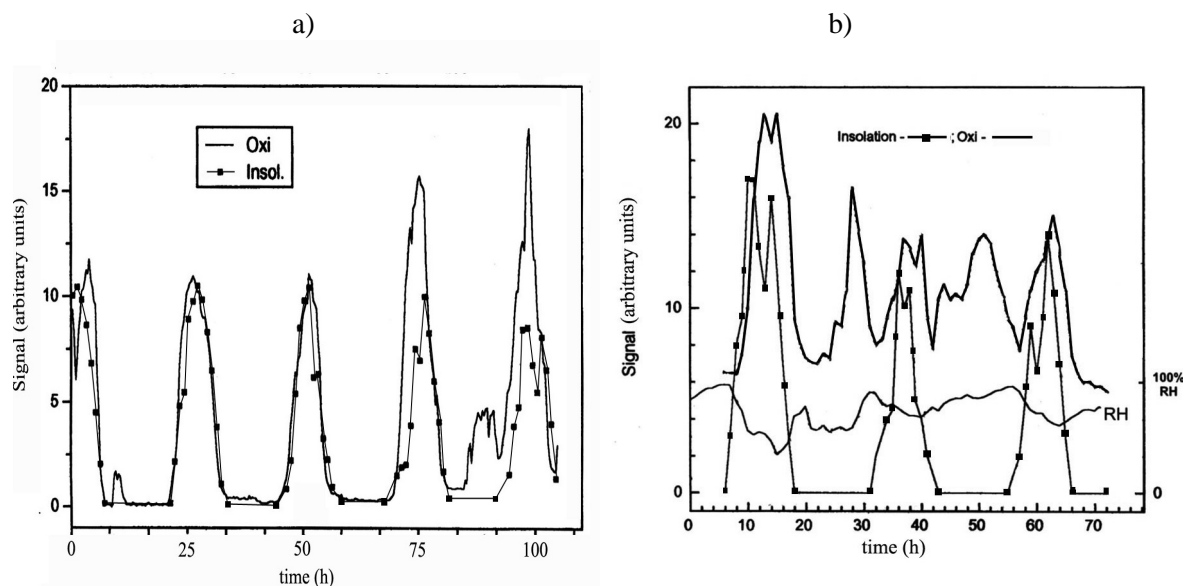


Figure 3: a) The oxidants (full line) and solar radiation (dots-line) data for 24 to 28 Sept. 1994, b) The oxidants (full-line), solar radiation (dots-line) and relative humidity (RH) data for 28 to 30 Sept. 1993.

Slika 3: a) oxidants (puna linija) i solarnog zračenja (točkice-line) Podaci za 24 do 28 Sept 1994 b) oxidants (full-line), solar radiation (točkice-line), a relativna vlažnost (RH) Podaci za 28 do 30 Sept 1993.

A progressive increase of the daily oxidants maximum over periods of typically 3 to 5 days) and accumulation of photochemical oxidants during warm, sunny and stable weather (Fig. 3 a) assigned as

local ozone production pattern. This can be recognized at the beginning and end of episodes in July/August 2003. (Fig. 6).

Regional/local oxidant transport with frequently occurring unusually high levels of ozone detected during the night, with a change in synoptic conditions, associated with altered wind speed and direction (Fig. 3 b) assigned as an imported ozone pattern. This was noticed during the last few days of July 2003 and at the very end of the episode on 13/14 August 2003 (Fig. 6).

These assignments are based on the observation that ozone concentration peaks appear frequently during the night if ozone excess is attributed to imported pollutants, while maxima associated with locally generated ozone would be expected to occur during mid- and late-afternoon (Fuentes and Dann, 1994). During the night, NO₂ formation does not take place and therefore ozone production rate is zero (Shetter et al., 1983). It is clear, that increased oxidant concentrations during the night are due to the local/regional transport of air masses from areas where ozone had accumulated during previous days. It rained before dawn on September 29, with changes in wind speed and direction, which led to a significant decrease of oxidant concentration. With the cessation of rain and the increase of solar radiation the oxidant concentration rose and reached its daily maximum in the early afternoon hours, at a lower level than the maximum recorded the night before. This was not unexpected, because the passage of frontal systems accompanied by precipitation usually ends an ozone episode. It should be noted that the occurrence of increased ozone concentrations during the night is accompanied with a noticeable decrease of relative humidity (RH). Lower RH and elevated ozone nighttime concentration could be associated with downward mixing of ozone from the reservoir layer and this possibility will be discussed later. A similar pattern was repeated in the subsequent few days and many times afterwards.

Since 1998, the measuring site was situated about 8 km to SE towards the border of the urban center, and ozone was measured on an automatic UV monitor instead of an electrochemical sensor. At the same site the monitoring station of the Federal Hydro-Meteorological Institute supplied us with meteorological data (temperature, pressure, solar radiation, relative humidity, precipitation and wind speed and wind direction). At this monitoring site, extensive measurements of ozone were made from August 16 to November 12 1999. During this campaign three periods with different characteristics occurred. The first period (Aug. 16 – Sept. 8) was characterized by high (and very high) maximal daily temperatures (MDT from around 21 to above 33°C) and increased ozone concentrations with maximal daily values from around 60 to almost 100 ppb (pattern 1; Fig. 4).

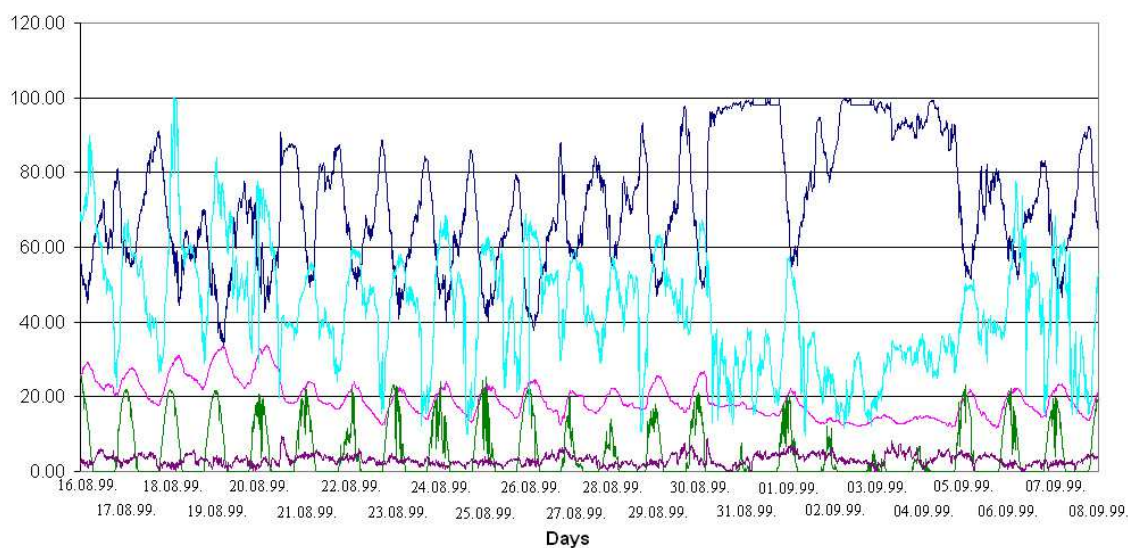


Figure 4: Ozone (ppb, light blue line), RH (%), temperature (°C, pink line), solar radiation (Wm⁻², green line) and wind speed (m s⁻¹, violet line) data for 16 Aug. to 8 Sept. 1999 at the No 2 measuring site.

Slika 4: ozona (ppb, svjetlo plava linija), RH (%), temperaturu (oC, roza linija), sunčevom zračenju (W m⁻², zelena linija) i brzine vjetra (m s⁻¹, ljubičasta linija) podatke o Aug 16 do 8. rujna. 1999 No 2 na mjerenoj mjestu.

Data analysis showed close correlation between the concentration of ozone, temperature and intensity of solar radiation. Ozone concentration followed the solar radiation curves with a time lag of approximately two hours. Nighttime peaks of elevated ozone concentration (≥ 50 ppb) happened frequently (Fig. 4). Near the end of this period a short episode of rather cool (MDT around 14°C) and wet (RH nearly 95%) weather, with maximal daily ozone concentrations less than 40 ppb, disturbed the photochemical cycle of ozone, which emerged again during the last three days of the measuring period. On cloudy days, when the level of solar radiation was lower and the relative humidity higher, the photolytic cycle was not clearly displayed (Sept. 2 -4).

The daily RH fluctuations presented in Fig. 4. followed changes of temperature and solar radiation (Lopez et al., 2001). Ozone is strongly negatively correlated with wind speed and humidity (Mulholland et al. 1998) but its nighttime increase was accompanied with an decrease or delay in RH increase (August 21/22, 22/23, 24/25, 28/29).

The second (autumn) measuring period (Oct.8 - 22) also revealed a strong negative correlation between RH and ozone concentrations (Fig.5). This period had sporadically high concentrations of ozone (O_3 max. about 60 ppb), but proceeded further with a decrease of temperature, progressive RH increase and a gradual decline of maximal daily ozone concentrations to about 40 ppb. We also noticed that, occasionally, the nocturnal ground level ozone concentration may increased, sometimes more than 40 ppb, usually followed by a decrease of RH. The end of this period, between 19 and 22 October, was characterized with high RH, low temperature and enhanced wind, which completely impaired the pattern of the photochemical ozone cycle, similarly to the end of the previous period. The last measuring campaign (Oct. 26 onward) was characterized by daily temperature maxima well below 20°C , daily ozone maxima between 30 and 50 ppb and a high RH level except for 28/29 October when a high nocturnal ozone concentration was recorded. Generally, strong seasonal variation of ozone was observed. Summer-August values were almost twice as great as Autumn-November concentrations.

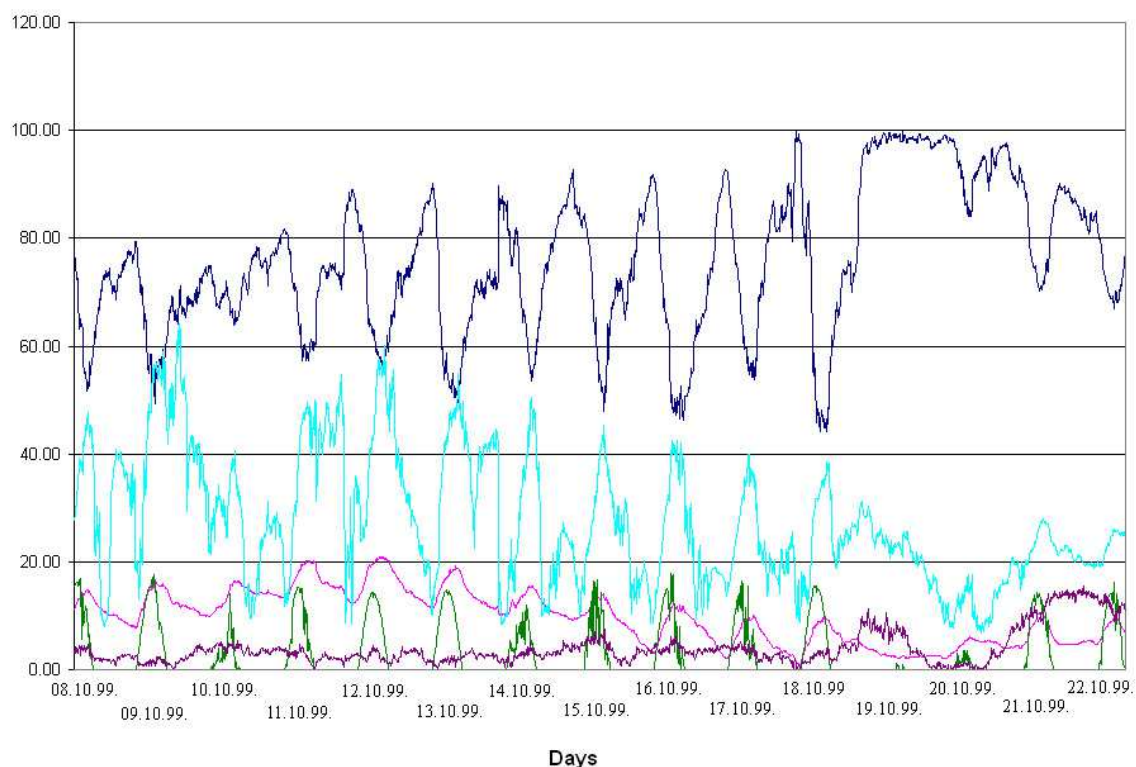


Figure 5: Ozone (ppb, light blue line), RH (%), temperature ($^{\circ}\text{C}$, pink line), solar radiation (Wm^{-2} , green line) and wind speed (m s^{-1} , violet line) data for 8 to 22 October 1999 at the No 2 measuring site.

Slika 3: a) oxidants (puna linija) i solarnog zračenja (točkice-line) Podaci za 24 do 28 Sept 1994 b) oxidants (full-line), solar radiation (točkice-line), a relativna vlažnost (RH) Podaci za 28 do 30 Sept 1993.

The influence of temperature, solar radiation, RH and other meteorological parameters on ozone production and the daily profile of its ground level concentration has been recognized for a long time and was examined in detail by Vukovich and Sherwell (2003). A strong negative influence of RH on ozone concentration was clearly shown by Thompson et al. (1992) and Mulholland et al. (1998). Ozone adsorption is known to be enhanced on wet vegetation (leaves, grass) which increases its rate of deposition. At high humidity, open stomata enhance the amount of air pollutants taken up by vegetation (Thompson et al., 1992). Dry deposition velocity is increased when condensed water or rain is deposited on vegetation. The fastest deposition velocity was observed in the morning when maximal daily RH values were recorded due to dew deposition but also because of partial closure of stomata in the afternoon (Lopez et al., 2001). Thus in the presence of a water vapor gas phase ozone loss was significant.

We noticed that a RH decrease occurred during the rise in nocturnal ozone concentration (Fig. 3. b, Fig. 4). A drop in RH during the night is rather unusual. Examples of this type of event were found in summer in 2003, i.e. from July 25 through August 14, 2003 (Fig 6). This period included a 21-day episode with some peak 1-h ozone levels greater than 110 ppb (27 July, 2 and 14 August). Our measurements showed clearly that the sharp increase of ozone concentration before dawn on July 29, from about 10 ppb to almost 70 ppb, was simultaneously accompanied by a 30 % decrease of RH. The rise in ozone concentration was preceded by an increase of wind speed from 3 and 8 m/s (in the two previous days) to more than 16 m/s from SSE direction ($130-150^{\circ}$, city center) and a slight fluctuation in temperature. After approximately 3 hours, the ozone concentration steeply declined to about 30 ppb while the RH returned nearly to its former high value. In the proceeding days the dominant wind direction was WNW and the diurnal ozone concentration showed the typical pattern of photo-smog formation (Mestayer et al, 2003). A similar occurrence was recorded during the next night. Repeated measurements between 13 and 15 August revealed the same behavior. During the night of August 14/15, the ozone concentration reached its highest nocturnal level of 80 ppb, an increase of about 70 ppb over the lowest level that night. A drop in RH happened regularly with high nocturnal ozone. Accordingly, without a doubt, there was a trend for a substantial decrease of RH as ozone increased during the night. Usually, a small fluctuation of temperature was noticed during such an event (from zero to 1.7 °C rise lasting for only 1-2 hours). Transported air could be a little warmer and the temperature may have risen at the measuring location during nocturnal transport of air masses.

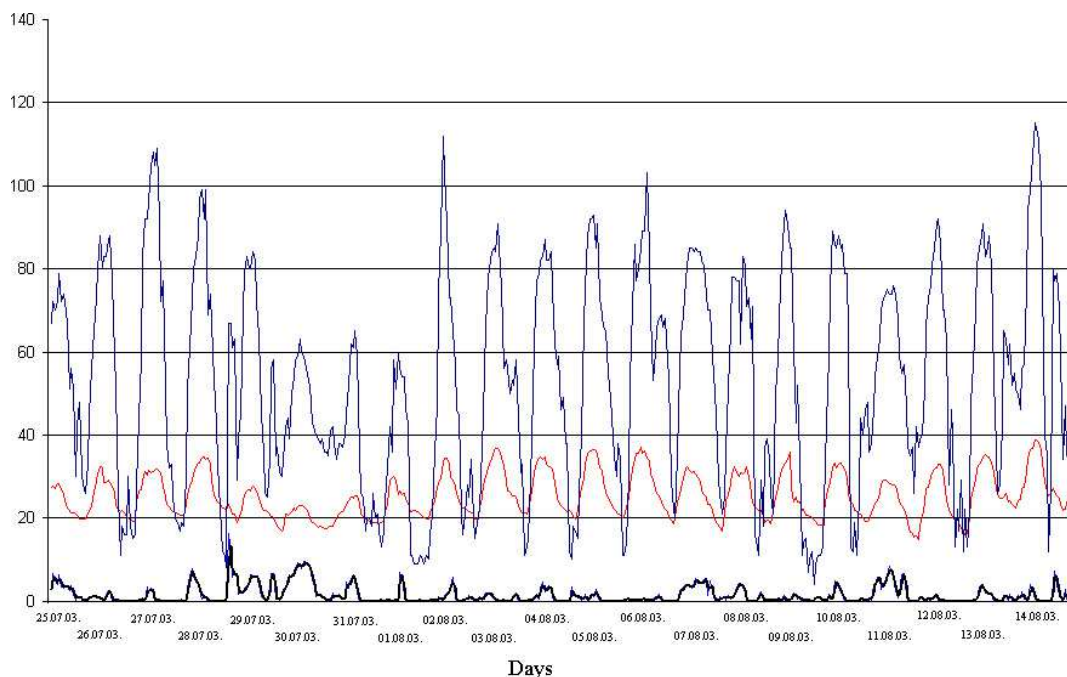


Figure 6: Ozone (ppb, dark blue line), temperature (°C, red line) and wind speed (m s^{-1} , black line) data for 25 July to 14 August 2003 at the No 3 measuring site.

Slika 6: ozona (ppb, tamno plava linija), temperaturu (oC, crvena linija), a brzina vjetera (m s^{-1} , crna linija) Podaci za 25 srpnja do 14 kol, 2003 No 3 mjerenja na mjestu.

Similar behavior was noticed during the Berlioz field campaign (Rappenglück et al., 2004) when an unusually high level of nocturnal ozone (88 ppb) was detected. At the same time increasing temperature, increasing wind speed and decreasing RH were recorded. Analyses revealed that this pollution had its origin in the Netherlands and the southern United Kingdom about two days before, showing that regional air quality can be influenced by transport of air masses from remote regions. Apart from a certain similarity, this situation is not the same as with our measurements. Several days with low maximal concentrations in the range of 35 and 40 ppb preceded the episode of high levels of night ozone recorded in Berlin on 7 August 1998, while in our case several days with ozone concentrations of the order of 100 ppb preceded the high levels of night ozone in 2003.

In order to explain these high nocturnal levels of ozone we can suppose two possibilities: 1. that local (regional) air quality can be affected by pollution transport from some other (remote) regions or 2. downward-mixing of O₃ from higher altitudes (reservoir layer).

1. Synoptic conditions (Case study for 27 July 2003)

GENERAL WEATHER SITUATIONS

The weather over the Balkan Peninsula in the summer is very often under the influence of subtropical high pressure. The Azores High may extend over North Africa towards the Mediterranean Sea and Balkan Peninsula, as on 27 July 2003. The surface pressure and absolute topography of 500 hPa is shown in Fig. 7. This synoptic situation was characterized by surface pressure only slightly above the average mean sea level pressure (Fig. 8). The non-existing surface pressure gradient was associated with weak air movement in the lower troposphere. The sky was cloudless and the surface maximum temperatures were high. The strong insolation allowed the formation of mesoscale circulation over the central Balkan Peninsula (Serbia). Winds near surface were light east-southeasterly and at upper level somewhat stronger northwesterly (Fig. 9).

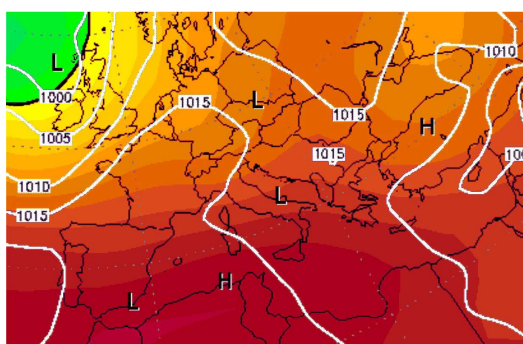


Figure 7. Slika 7.

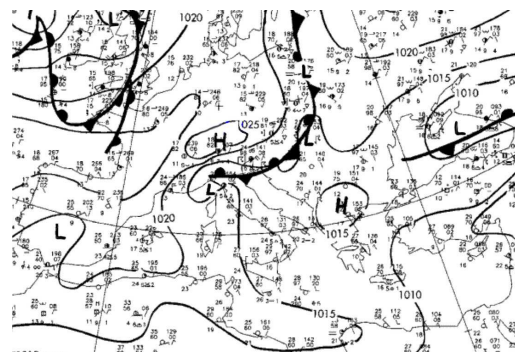


Figure 8. Slika 8.

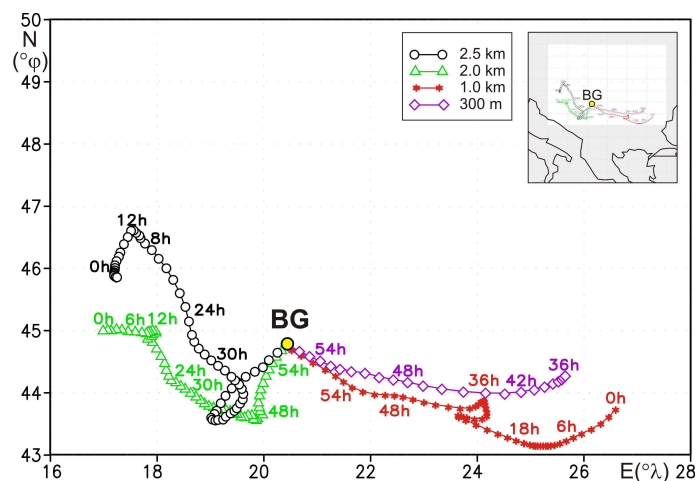


Figure 9. Slika 9.

Figure 7. The sea level pressure (full line on every 5 hPa) and 500 hPa geopotential (shaded, in gpm) for 1200 UTC 25 July 2003. The L and H depict low and height values respectively.

Slika 7. Razina mora tlaka (puna linija na svakih 5 hPa) i 500 hPa geopotential (hladu, u gpm) za 1200 UTC 25. srpnja 2003. The L i H prikazu visina i niske vrijednosti respektivno.

Figure 8. Surface weather situation over Europe for 1200 UTC 29 July 2003. The sea level pressure (full line on every 5 hPa) and subjective surface analysis of fronts, with wind and other observed meteorological parameters are shown. Obviously, the light wind and height pressure dominate in the vicinity of Belgrade.

The cold front on northwest is passed over Belgrade in the night between 29 and 30 July.

Slika 8. Površina vremenska situacija nad Europe za 1200 UTC 29. srpnja 2003. Razine mora tlaka (puna linija na svakih 5 hPa) i subjektivna analiza površine pročelja, s vjetrom i ostalih meteoroloških parametara promatrane su prikazani. Očito, svjetla visina dominantan vjetar i tlak u blizini Beograda. U hladni front prošao na sjeverozapadu Beogradu je u noći između 29. i 30. srpnja.

Figure 9. The backward trajectories tracked 60 hours from position of Belgrade (BG) at 1200 UTC 27 July 2003. The successive positions of air parcels are shown after every one hour for levels 2.5; 2.0; 1.0 and 0.3 km above surface

Slika 9. Zadnje trajektorie gusjenični poziciju od 60 sati od Beograda (BG) at 1200 UTC 27. srpnja 2003. Sukcesivnom pozicijama zraka parcela prikazane su nakon svake razine za jedan sat 2,5, 2,0, 1,0 i 0,3 km iznad površine.

In association with mesoscale anticyclonic circulation a high concentration of O_3 occurred in the area of Belgrade (the capital of Serbia). The cold front shown in Fig. 8 passed over Belgrade between 29 and 30 July. It caused the rain in some part of Serbia. After that we had low values of O_3 for the next three days. Next days the surface pressure is increased over Belgrade area. In association with very slow horizontal air motions during day-time the concentration of O_3 tend to increase.

AIR TRAJECTORY

To investigate the origin of the polluted air mass over Belgrade we constructed a Lagrangian trajectory from three-dimensional velocity fields derived from the mesoscale model (Curic et al., 2006) at several successive times separated by one hour. Construction of three-dimensional air parcel trajectories provides a valuable diagnostic tool for studying three-dimensional flow fields and associated transports. The trajectories were tracked backward in time 60 hours from positions in Belgrade ($\lambda = 20^\circ 28'$, $\varphi = 44^\circ 48'$). Figure 9 shows a set of trajectories whose end point lies at four heights over Belgrade (2.5, 2.0, 1.0 and 0.35 km). The backward simulation started at Belgrade on 27 July 2003, 00 UTC. It is easy to see that the horizontal displacement of the particles was very slow. The two upper trajectories were mainly from NW towards SE, changing the direction of displacement, while the two lower trajectories were from E towards W. All trajectories slowly descended towards Belgrade in the cloud-free region.

Clearly, the light wind in low level, and very slow descending motion of air suggest that height production of O_3 were induced by local factors (mainly by traffic). It has already been stated that we recorded several days with very high ozone levels from July 25 to August 14, 2003. In the same interval there were also 12 days with 1-h ozone levels equal to or greater than 90 ppb (EU information threshold). In the same year, from May 25 to June 8 we recorded 9 days with 1-h ozone equal to or greater than 90 ppb and 2 days with 1-h ozone concentrations equal to or greater than 120 ppb (EU threshold value). Episodes with high ozone concentrations reoccurred during the following years through 2006. These high ozone levels are of critical interest for local air quality.

NOCTURNAL OZONE

The morning maximum of ozone on July 29, 2003 is coincides with thunderstorm activities during the cold front passage. Namely, in region of large-scale ascent near front developed deep convective

clouds. Deep convective cells in various stages produce lightning frequently. The meteorological observer at main Meteorological Observatory in Belgrade reported thunder and strong lightning within a few hours period prior and after of the time of morning ozone maximum occurrence. The surface time series of meteorological observations shown in Fig. 10. indicate the passage of cold front too. Temperature dropped and the pressure rose. The most pronounced shift in the wind (from WNW to SSE) is occurred.

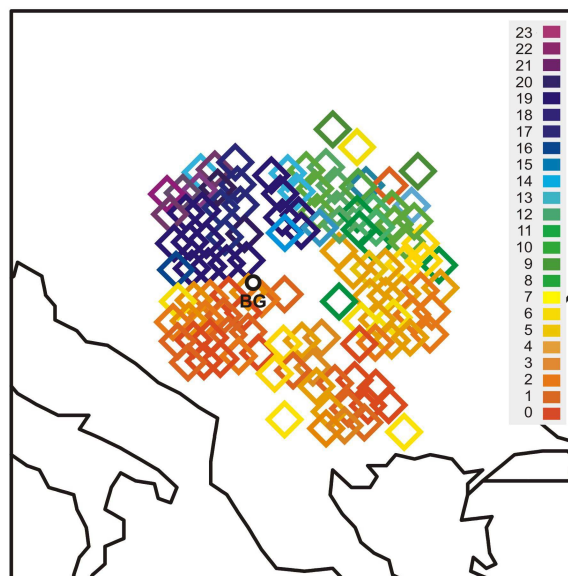


Figure 10. Composite satellite imagery of lightning flashes for July 29, 2007 up to 2300 UTC.
The site of ozone measurement in Belgrade is indicated by the bold black circle.

Slika 10. Kompozitna satelitska krpovi od munje trepće za 29. srpnja 2007 do 2300 UTC.
Stranice ozon mjerenja u Beogradu je označen podebljano po crnom krugu.

The lightning flashes observed from satellite shown in Fig.10 confirms the existence of persistent band of deep convection which is coincident with advancing of cold front. All of these meteorological events suggest that the morning maximum of ozone is induced by the thunderstorm activities during the cold front passage.

Acknowledgments and disclaimer

This research was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia, Grants No. 141012 and 1727. Mention of trade names or commercial products does not constitute endorsement or recommendation for their use.

REFERENCES

1. Atkins, D.H.F., Cox, R.A., Eggleton, A.E.J., 1972. Photochemical ozone and sulphuric acid aerosols formation in the atmosphere over southern England. *Nature* 235, 372-376.
2. Buffoni, A., 2002. Ozone and nitrogen dioxide measurements in the framework of the National Integrated Programme for the Control of Forest Ecosystems (CONECOFOR). *Journal of Limnology* 61, (suppl.1) 69-76.
3. Curic, M., Janc, D., Vuckovic, V., 2006. Seeding agent dispersion within convective cloud as simulated by a 3-D numerical model. *Meteorology and Atmospheric Physics* 92, 205-216.
4. European Environment Agency, 2003. Air Pollution by ozone in Europe in summer 2003, Topic report No 3/2003. (www.eea.eu.int).
5. Finlayson-Pitts, B.J., Pitts, J.N. Jr., 1997. Tropospheric Air- Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons and Particles. *Science* 276, 1045-1051.
6. Fuentes, J. D., Dann, T. F., 1994. Ground-Level Ozone in Eastern Canada: Seasonal Variation, Trends, and Occurrences of High Concentrations. *Journal of Air & Waste Management Association* 44, 1019-1026.

7. Hjorth, J., Dell'Acqua, A., Duane, M., Larsen, B.R., Maggi, C., Perrone, M.G., Poma, B., Putaud, J.P., Rembets, D., Roselli, D., Van Dinigenen, R., 2001. Aerosols and photochemistry: Field observation in Northern Italy, July 2000. Results of the Y2K campaign at JRC Ispra (Italy). "A Changing Atmosphere", 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants 17-20 Sept., Torino, Italy, AP73. (www.ei.jrc.it/ap/events/torino_2001).
8. Katz, M., (Ed.), 1977. Methods of Air Sampling and Analysis. American Public Health Association, Washington, 2nd edition, pp. 556-559.
9. Lopez, A., Fontan, J., Corraja, A., 2001. Quantification and Parameterization of the Vertical Fluxes of Ozone at the Interface Vegetation-Atmosphere. EUROTRAC-2 BIATEX-2 Annual Report 1998/99, GSF-Munich, pp 73-78.
10. Meng, Z., Dabdub, D., Seinfeld, J.H., 1997. Chemical Coupling between Atmospheric Ozone and Particulate Matter. *Science* 277, 116-119.
11. Mestayer, P., Almbauer, R., Tchepel, O. 2003. Urban field campaigns, Air quality in cities, N. Moussiopulos, editor. Springer Verlag Berlin Heidelberg (ISBN 3-540-00842-x), 2003, pp.51-89.
12. Mičić, M., Marković, D., Stamatović, A., Vukelić, N., 1998. Characterization and Trends in NO₂ Diurnal Concentration Profiles in Belgrade Troposphere during autumn 1997. The Proceedings of the EUROTRAC-2 Symposium 98., WIT Press, Southampton, pp. 847-850.
13. Mulholland, J.A., Butler, A.J., Wilkinson, J.G., Russell, A.G., 1998. Temporal and Spatial Distributions of Ozone in Atlanta: Regulatory and Epidemiologic Implications. *Journal of Air & Waste Management Association* 48, 418-426.
14. Neftel, A., Spirig, C., Beekmann, M., Dommen, J., Hjorth, J., Volz-Thomas, A., Winiwarter, W., 2002. Limitation of Oxidant Production, Chapter 9, www.gst.de/eurotrac/indexsubprojects.html
15. Pagnotti, V., 1990. Seasonal Ozone Levels and Control by Seasonal Meteorology. *Journal of Air & Waste Management Association* 40, 206-210.
16. Rao, S.T., Zurbenko, I.G., 1994. Detecting and Tracking Changes in Ozone Air Quality. *Journal of Air & Waste Management Association* 44, 1089-1092.
17. Rappenglück, B., Forster, C., Jakobi, G., Pesch, M., 2004. Unusually high level of PAN and ozone over Berlin, Germany, during nighttime on August 7, 1998. *Atmospheric Environment* 38, 6125-6134.
18. Rizzo, M., Scheff, P., Ramakrishnan, V., 2002. Defining the Photochemical Contribution to Particulate Matter in Urban Areas Using Time-Series Analysis. *Journal of Air & Waste Management Association* 59, 593-605.
19. Shetter, R.E., Stedman, D.H., West, D.H., 1983. The NO/NO₂/O₃ Photostationary State in Claremont, California. *Journal of the Air Pollution Control Association* 33, 212-214.
20. Sillman, S., 1995. The Use of NO_y, HCHO, H₂O₂ and HNO₃ as indicators of O₃-NO_x-hydrocarbon sensitivity in urban location. *Journal of Geophysical Research* 100, 14175-14188.
21. Thompson, C.R., Gerrit, K., Olszyk, D.M., Adams, C.J. 1992. Humidity as a Modifier of Vegetation Response to Ozone: Design and Testing of a Humidification System for Open-Field Chambers. *Journal of Air & Waste Management Association* 42, 1063-1066.
22. Vukmirović, D., Vukmirović, Z., 1984. Analysis of probability of photooxidants high concentrations occurrence in Belgrade in dependence on the lower troposphere structure. *Zeitschrift fur Medizin-Meteorologie, MED-MET* 2, 23-24.
23. Vukmirović, Z., Spasova, D., Marković, D., Veselinović, D., Vukmirović, D., Stanojević, Č., Popović, M., Hadžipavlović, A., 1987. Some characteristics of oxidant occurrence in the atmosphere of Belgrade. *Atmospheric Environment* 21, 1637-1641.
24. Vukmirović, Z., Vukmirović, D., Slavić, D. Merkle, M., 1990. Pollutant Transport Parameterization for Urban Areas including Heat Island Effect. EUROTRAC Annual Report 1989, Part 5, ISS Garmish-Partenkirchen, pp 75-80.
25. Vukovich, F.M., Sherwell, J., 2003. An examination of the relationship between certain meteorological parameters and surface ozone variation in the Baltimore-Washington corridor. *Atmospheric Environment* 37, 971-981.
26. Ying, Q., Kleeman, M.J., 2003. Effect of aerosol UV extinction on the formation of ozone and secondary particulate matter. *Atmospheric Environment* 37, 5047-5068.