

ATMOSPHERIC BOUNDARY LAYER AND SURFACE OZONE CONCENTRATION STUDY OVER SOFIA AREA BY LIDAR AND OZONEMETER.

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Abstract: The ecological problems caused by the increasing ozone concentration are not easy to be solved because ozone is not directly emitted by certain sources but its concentration is defined by numerous dynamical and chemical processes. Stratosphere-troposphere exchange and subsequent ozone penetration into the boundary layer define the contribution of so-called “natural” ozone to ozone pollution near the ground. The purpose of this research is the studying of the surface ozone concentration behavior during the period of the destruction of stable boundary layer and residual layer and the formation of convective boundary layer, so as the influence of the temperature, the relative humidity and the height of the mixing layer as well as that of the formation of mixing layer in different areas of Sofia, Bulgaria to be determined. The surface ozone concentration in the area of the Institute of Electronics changes synchronously with the development of the mixing layer. The maximum values of the surface ozone concentration are being reached when the height of the mixing layer reached its maximum and afterwards. The maximum growth of the surface ozone concentration is around 11-12:30h local standard time when a fast growth of the mixing layer begins and the complete destruction of the residual layer is observed, i.e. the two processes of mixing layer growing and entrainment of aerosol and ozone from the higher layers of atmosphere boundary layer are observed. The values of the surface ozone concentration during summer months are higher than those during fall.

Keywords: Lidar, Ozonemeter, Planetary boundary layer development, Urban area, Park zone

Introduction

During recent decades the rapid development of transport and industry in certain urban areas causes serious ecological problems in these areas (Gusman and Streit 1993, Cartalis and Varotsos 1994, Varotsos *et al.* 2003). The influence of the ozone and the greenhouse gases on the climate warming is not explained completely so far (Kondratyev and Varotsos 1995). Special attention is to be paid to the ozone, which can be as well harmful as useful both for people and the ecosystems. The situation concerning the concentration of the tropospheric ozone is to be investigated. Experimental data shows decrease of the ozone concentration with time, as well as moving of the maximum of ozone concentration from spring to summer. Despite the many researches of the behaviour of surface ozone, there are issues which are not clear yet, such as the influence of the meteorological parameters and the aerosol over urban area, as well as the influence of the processes, taking place in the Atmospheric Boundary Layer (ABL) in a mountain valley.

The purpose of this research is to study the behaviour of the surface ozone concentration during the period of stable boundary layer (SBL) and residual layer (RL) destruction and ML formation. Further, to determine the influence of the temperature, the relative humidity and the mixed layer (ML) height as well as that of the ML formation over different areas of Sofia, Bulgaria on the surface ozone concentration.

As proposed in our earlier work (Kolev *et al.* 2000) the conceptual model involved is appropriately adapted to the processes influencing the ground level ozone concentration, namely the mixing, entrainment, advection, etc., which result from the interaction between the planetary boundary layer (PBL) development and the mountain-valley circulation.

After sunset the formation of Stable Boundary layer (SBL) and RL begins, which contain aerosol and ozone, which have been in ML before sunset. ML is destroying since no energy to keep it is been supplied. Firstly the layers closest to the Earth's surface are cooling down, while the first temperature inversion is forming. When a SBL develops above an urban area after sunset, one observes a mixing layer formed by the thermal island. In this case NO_x are being dislocated, as in the period between 18:00 h and 20:00 h it is increasing due to the increased traffic, which leads to a decrease in the surface ozone concentration, which, for the dry months of the year, is about $C=5-8$ ppb and as a result of the dry deposition the surface ozone concentration may fall down to about zero, the height of this mixing layer is $\text{HML}=200$ m, where is the first elevated inversion. This elevated inversion separates aerosol and ozone in the residual layer (layers) from the larger concentration of NO_x , (in ML) as a result of the increased traffic (Velasko *et al.* 2008). For this reason the ozone concentration from the day retains during the night.

After sunrise the heating of the Earth's surface begins. The formation of up-slope wind begins at different heights. After about two hours the formation of the mixing layer begins. One well mixed layer of aerosol, moist is being created, from 08:00 h to 10:00 h the increase of NO and NO_x begins, as a result of the developed traffic. The surface ozone concentration has not changed significantly until 08:00h in this period it is resulting from the photochemical processes, because of which there is destruction as well as formation of O_3 , i.e. the surface ozone concentration is being balanced between the formation and the destruction of O_3 . The process of mixing from above does not play significant role until the destruction of the first elevated inversion. During the summer months at about 10:00 h the

mixing layer has destroyed the first elevated inversion. As a result of the up-slope wind in the period from 09:30 to 11:30h begins the actual destruction of the residual layer above. After 11:00-11:30h the intense development of the mixing layer begins. In the period after 11:00-11:30h the rising wind also is influenced due to the different heating of the Earth's surface and the occurring of the up-slope wind and the mountain-valley circulation. During this period, beside the photochemical processes, the mixing processes above begin influencing the surface ozone concentration, the so called process of penetration from upper layers, which are richer in O₃, remaining from the previous day. Thus at 10:30-12:30h often a peak in the surface concentration of O₃ can be observed (Kolev et al. 2008). The solar radiation reaches its maximum and the formation of ozone prevails the destruction, since NO and NO_x decrease as a result of the reduced traffic and the dislocation in altitude. At about 13:00-14:00h the height of the mixing layer reaches its maximum. The behaviour of the mixing layer and the surface ozone concentration during the autumn months of the year is likewise, except that the processes begin later and are not that intensive.

In the following research an attempt is made to examine and explain the influence of some meteorological parameters on the surface ozone concentration.

We shall focus on the relative humidity, the wind velocity and temperature; their influence on the surface ozone concentration will be estimated through the development and height of the mixing layer. The relative humidity at different hours of the day influences in a different way (Markowicz et al. 2003). Usually in the morning hours it has higher values and its appearance can be seen in the low transparency of the atmosphere, as this is usually related to its interaction with atmospheric aerosol. During noon hours it is decreased and around or before the sunset it is increasing again. The second important factor is the speed and the direction of the wind. In any cases when the speed of the wind is growing the surface ozone concentration decreases. In the case of different local sources of ozone the wind could cause a change of the surface ozone concentration by increasing or decreasing it depending on the direction of the wind, to the area in which the measurements are taken, i.e. the advection influence.

The methods employed for the current combined study and the used techniques are described in Section 2. Experimental data is shown in Section 3. The results that revealed the experimental data are discussed in Section 4.

Methods and apparatus

In the present research a lidar and an ozonemeter have been used, which are situated on the territory of the Institute of Electronics (IE) – Bulgarian Academy of Sciences and an ozonemeter and a surface meteorological station situated in the area of the Astronomical Observatory (AO) in the Garden “Borisova”.

IE is located at a distance of about seven kilometres southeast of city centre. The terrain is open with relatively little vegetation covering. The pollutants that affect the ambient air may be mainly associated with road traffic. The air was sampled through teflon tubing at a height approximately 12 m above the ground level. The surface ozone concentration was measured with solid-state chemiluminescent ozonemeter, model 3-02P (Russia). The detection method is based on fast reaction of ozone with sensitive reagent that

produces chemiluminescent radiation. The uncertainty of the measurements was not exceed 15% (Kolev *et al.* 2008).

At the site of AO the total solar radiation, wind speed and direction sensors were located at a height of 10 m; those for determining of the air temperature and humidity – at 2 m height and those for measuring of the precipitation – at 0.5 m. The ground level ozone concentration was measured by TECO 49 UV photometer. Due to the inherent stability of the UV adsorption technique used it could be considered that the ozone concentrations reported here to be within ± 5 ppb. The instrument intake teflon filter was changed approximately every 15 days. The corresponding measuring equipment is summarized in Table 1.

Table 1. Equipment and sensors used at the Astronomical Observatory.

Sensor	Parameter	Units
TECO 49	O ₃	ppb
05103 YOUNG wind monitor	Wind speed and wind direction	m/s
SP1110 Skye pyranometer	Total solar radiation	W/m ²
MRI	Precipitation	mm
Vaisala HMP45C	Temperature	°C
Vaisala HMP45C	Relative humidity	%

Experimental results

6000 profiles were recorded during the lidar observations each for a period of about 9-10 minutes. Batches of 150 profiles were then averaged to increase the signal/noise ratio. The 40 profiles thus obtained were transformed into S-functions for which the standard deviation and the first and second derivatives were calculated; the latter were used to determine the mixing layer height (Kolev 2008).

The results of the lidar observations are presented as height-time indicators (HTI) of the S-functions of the lidar signals calculated for each point along the sounding path. The S-function is used instead of the lidar return itself since the former reveals much better the aerosol structure of the atmosphere. The S-function is being commonly defined as $S = \ln P r^2$.

Lidar measurements – (fall campaign 2006)

Data obtained during two days are presented. On the following HTI data from the experiment on 04 October 2006 are shown (Figure 1a). The sunrise is at 07:26 h. The temperature in the beginning of the experiment was $t \approx 12^\circ\text{C}$ and in the end about it was $t = 28^\circ\text{C}$, respectively the relative humidity was 90% and 35%. The speed of the wind was $V \approx 1-2 \text{ ms}^{-1}$.

(a)

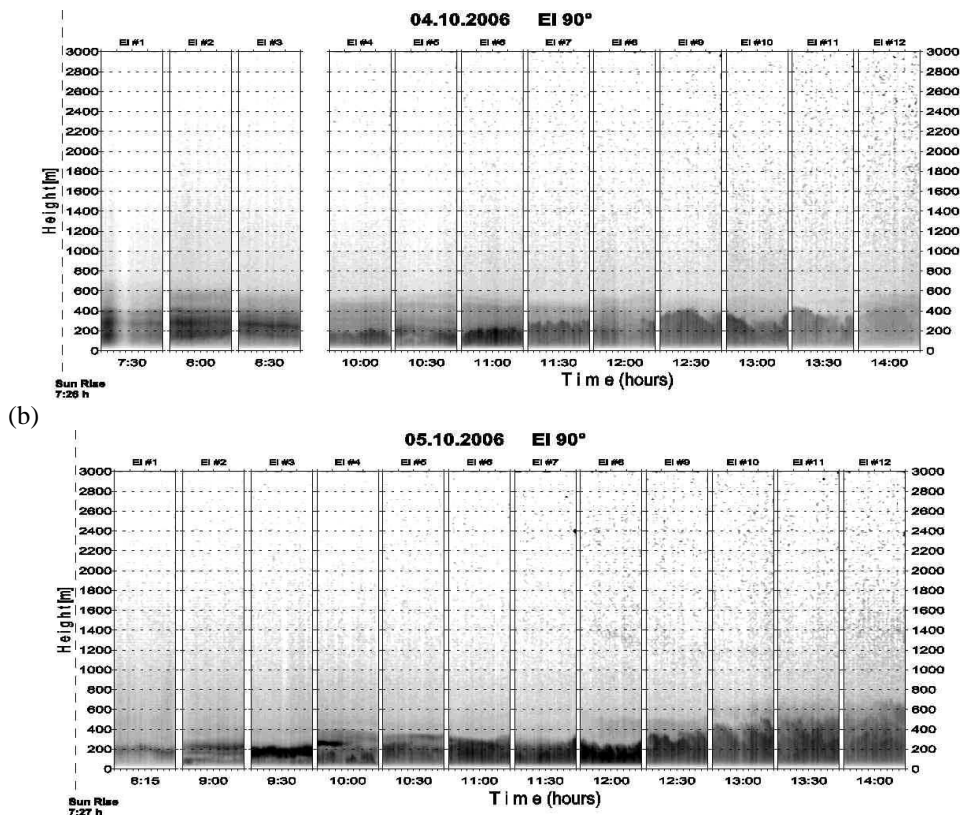


Fig. 1. Height–time indicators constructed from the lidar data obtained on:(a) 04 October 2006, (b) 05 October 2006.

On the figure the first three lidar images show the height of the stable boundary layer $H_{SBL}=400$ m. There are three aerosol layers respectively at heights about $H_1=150$ m, $H_2=250$ m and $H_3=400$ m. The height of the residual layer is about $H_{RL} = 600$ m.

At 10:00h the height of the new mixing layer is $H_{ML}=200$ and it remains like that until 11:00h. At 11:30h the height of the mixing layer reaches $H_{ML}=300$. At 12:00h mixing from above is observed. The residual layer is completely destroyed by the mixing layer at about 12:30h. From 12:00h new layer is observed at height from $H=400$ m to $H=600$ m, which remains like that until 14:00h. In the lidar image obtained at 13:00h certain entrainment can be observed. It can be seen by the lidar image at 13:30h that the mixing layer has reached height $H_{ML}=420$ m, and again there is mixing from above. In the described lidar image the mixing layer reaches $H_{ML}=500-600$ m.

On the next graphic (Figure 1b) lidar data for 05 October 2006 is shown. The experiment started at 08:15h and ended at 14:00h. The sun rises at 07:27h.

On the first lidar image at 07:15h aerosol layer at height of about $H=200$ m is observed. At the second image three layers can be seen. The first aerosol layer is at height

of about $H=100$ m and the next two are close to $H=200$ m. In third lidar image (obtained at 09:30h) a layer at height from $H=100$ m to $H=210$ m, which is quite dense. On the next lidar image at 10:00 h aerosol layer at height of about $H=250$ m is observed, which is dispersed afterwards. On the same image the beginning of the formation of the new mixing layer is observed, which reaches height $H=150$ m.

The residual layer is at height of about $H_{RL}=1000-1200$ m it has less dense part in it at height about $H_{RL}=500$ m to $H_{RL}=600$ m, which is gradually decreasing and at 10:00h the height of the residual layer is $H_{RL}=400-500$ m. At 10:30h the height of the residual layer is $H\approx 330$ m. At 11:00h the mixing layer has reached height $H_{ML}=330$ m and has destroyed the residual layer at this height. According to the lidar data it can be estimated that at height of about $H=300$ m a wind has appeared, which additionally disperses the atmosphere aerosol. Later this can be seen on the image at 12:00h, where above the mixing layer a layer of height 500 is observed. At 12:30 the mixing layer reaches $H=300-400$ m. At 13:00h the upper limit of the mixing layer is about $H\approx 500$ m. At 13:30h the mixing layer reaches $H_{ML}=600-650$ m and at 14:00h $H_{ML}=700$ m. The height of the residual layer remains about $H=1000$ m.

Comparison between the lidar data and model calculations

Figure shows a comparison between the lidar data and calculations about the changes in the heights of ML and RL in time on 04 July 2005. The calculations are made according to the model of Whiteman and McKee (1982). A good correspondence between the theoretical and experimental data is observed in the case also at the value of parameter $k=0.4$. The solar radiation flow is 900 W m^{-2} . The RL descends at approximately 65 m h^{-1} , ML growth speed is about 75 m h^{-1} . The height at which the upper boundaries of those two layers meet at 12:00 h LST is about 400 m. The influence of the mountain-valley circulation on the ML development speed is significantly weaker, so it develops in a "classical" way.

Ozone measurements

This section is concerned about the concentration of the surface ozone obtained during two campaigns performed in 2006 (one from summer and one from fall) are presented.

For the two urban sites which are situated on flat terrain ozone maximum during daytime and minimum during night hours are typical. Features of the diurnal surface ozone variations, to a great extent, reflect processes defining ozone pollution near the ground. After sunrise, the surface heating creates turbulent transfer of the warm air to the higher atmospheric layers. This provides the growth of the convective mixed layer and destruction of the nocturnal stable layer. As a result of the vertical mixing ozone-rich air from aloft penetrates to the ground level and increases surface ozone concentrations.

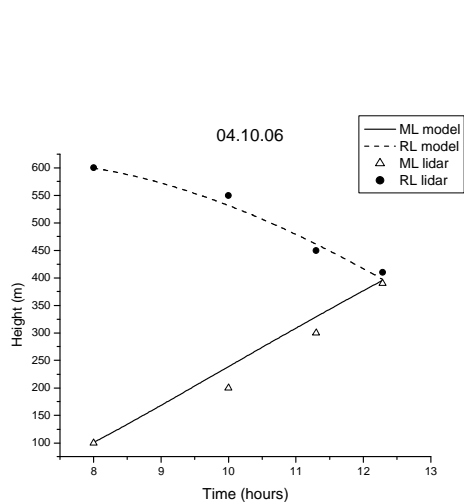


Fig. 2. Comparison between lidar and model data for the ML and RL heights on: 04 October 2006.

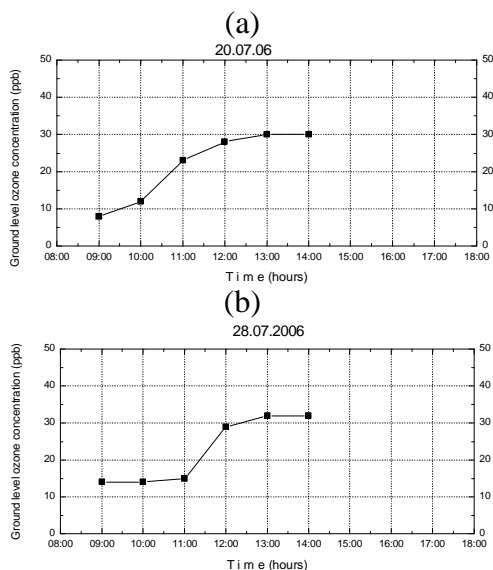


Fig. 3. Variation of the ground level ozone concentration on: (a) 20 July 2006, (b) 28 July 2006.

As sun radiation increases the process of photochemical ozone production from ozone precursors – volatile organic components (VOC) and nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) - becomes more important. Under favourable meteorological conditions (weak wind and clear sky) ozone increase in the early afternoon hours may be significant. In urban area ozone precursors have mainly anthropogenic traffic-related origin, but high reactive biogenic VOC components (in park zone, for example) can also give contribution. Taking into account that efficiency of the photochemical ozone formation strongly depends on VOC/ NO_x ratio and local meteorological factors, which in many cases are different in various points over large urban area, different levels of ozone concentrations can be detected at monitoring sites. After sunset, a stable boundary layer is formed and ozone accumulated above this layer is trapped aloft and forms “ O_3 – reservoir” in the residual layer. On the next day, when convective boundary layer will reach the height of residual layer, this “ O_3 – reservoir” can elevate daytime ozone concentrations. At night, under nocturnal inversion the surface ozone destruction due to dry deposition and ozone titration with nitric oxide (NO) takes place and ozone minimum is observed. It should be noted that, sometimes, ozone concentrations increase to the values typical for daytime hours. This phenomenon can be related to such processes as advection of the ozone-rich air mass from polluted areas or nocturnal low-level jet (Velasko *et al.* 2008).

Ozone measurements (summer campaign 2006)

On the next two graphics data for the surface ozone concentration from the summer campaign of 2006 are shown. On the first graphic (Figure 3a) data from 20 July 2006 is shown.

The experiment started at 9:00h and finished at 14:00h.

In the beginning of the experiment at 09:00h the value of the surface ozone concentration is $C=7$ ppb, at 10:00h it is $C=11$ ppb. At 11:00h and sharp increase of the surface ozone concentration is observed and it reaches $C=23$ ppb. At 12:00h it reaches value $C=28$ ppb. At 13:00h and 14:00h the surface ozone concentration is constant and it has value $C=30$ ppb. After 14:00h there were lots of the clouds and the measurement is stopped.

On the next graphic (Figure 3b) data for 28 July 2006 is presented. The experiment started at 9:00h and ended at 14:00h.

In the beginning of the experiment the value of the surface ozone concentration is large and almost constant. At 09:00h, 10:00h and 11:00h it is respectively $C=13$ ppb, $C=14$ ppb and $C=15$ ppb. At 12:00h the surface ozone concentration is increasing sharply and is $C=28$ ppb. At 13:00h and 14:00h the surface ozone concentration is constant and is equal to $C=32$ ppb.

Ozone measurements in the park region

In this part of the material we shall adduce the data about the surface ozone concentration and the meteorological parameters taken by the surface meteorological station, situated in AO disposed in the park "Borisova Gradina" for the summer campaign of 2006.

On the first graphic (Figure 4a) data obtained on 20 July 2006 are presented. The measurements are made within 24 hours. During the measurement the temperature changes from $t=10^{\circ}\text{C}$ to $t=28^{\circ}\text{C}$, the relative humidity RH changes from 85% at 7:00h to 32% at 13:00h. The maximal solar radiation is 900Wm^{-2} at 13:00h. The wind speed changes within the range of $V \leq 1 \text{ ms}^{-1}$.

The surface ozone concentration at 10:00h is $C=15$ ppb, at 11:00h it remains the same. At 12:00h and 12:00h it is respectively $C=28$ ppb and $C=38$ ppb. At 14:00h and at 15:00h the surface ozone concentration reaches $C=56$ ppb and respectively $C=80$ ppb. Between 16:00h and 21:00h, it varies at about $C=60$ ppb, at 22:00h it is about $C=45$ ppb, at 23:00h about $C=60$ ppb after which it is falling sharply to $C=5$ ppb at 24:00h.

In Figure 4b data obtained on 28 July 2006 are presented.

The air temperature for the time of the measurement changes from $t=15^{\circ}\text{C}$ to $t=31^{\circ}\text{C}$, and the relative humidity at 08:00h is 90% and at 17:00h it reaches its minimum and it is 20%. The solar radiation is maximal at 14:00h and it reaches 900 Wm^{-2} . The speed of the wind changes within the ranges of $V \leq 2 \text{ ms}^{-1}$.

The surface ozone concentration at 11:00h is $C=5$ ppb, at 12:00h it is $C=25$ ppb, at 13:00h it reaches value of $C=49$ ppb, and the maximal value is reached at 14:00h and 15:00h, when it is $C=72$ ppb. After 17:00h the surface ozone concentration falls and at

18:00h it is $C=51$ ppb, and at 19:00h it falls down to $C=25$ ppb, during the night hours it does not exceed $C=10$ ppb.

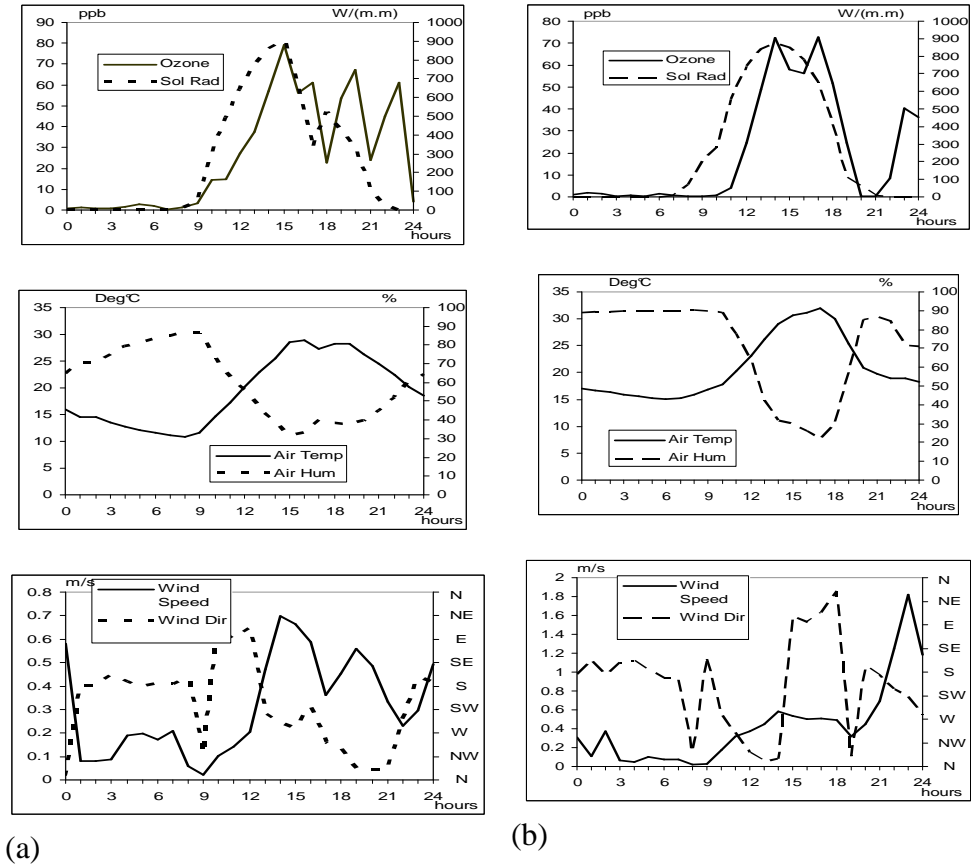


Fig. 4. Variations of the: temperature, air humidity, solar radiation, wind velocity and ground level ozone concentration on: (a) 20 July 2006, (b) 28 July 2006.

In the following three figures data about the surface ozone concentration in the area of the AO during this fall campaign 2006 is presented.

In Figure 5a data for 04 October 2006 is shown.

The air temperature changes from $t=10^{\circ}\text{C}$ at 08:00h to $t=25^{\circ}\text{C}$ at 17:00h. The maximal solar radiation is about 900Wm^{-2} and it is reached at 14:00h. The wind speed does not exceed $V=1\text{ms}^{-1}$.

The surface ozone concentration at 11:00h is about $C=3$ ppb and is gradually growing as at 12:00h it is $C=20$ ppb, and at 13:00h and 14:00h it reaches its maximum and it is about $C=29$ ppb. At 16:00h and 17:00h the surface ozone concentration falls to $C=11$ ppb. For the night hours the values of the surface ozone concentration are very small.

In the next Figure (5b) data obtained on 05 October 2006 are shown.

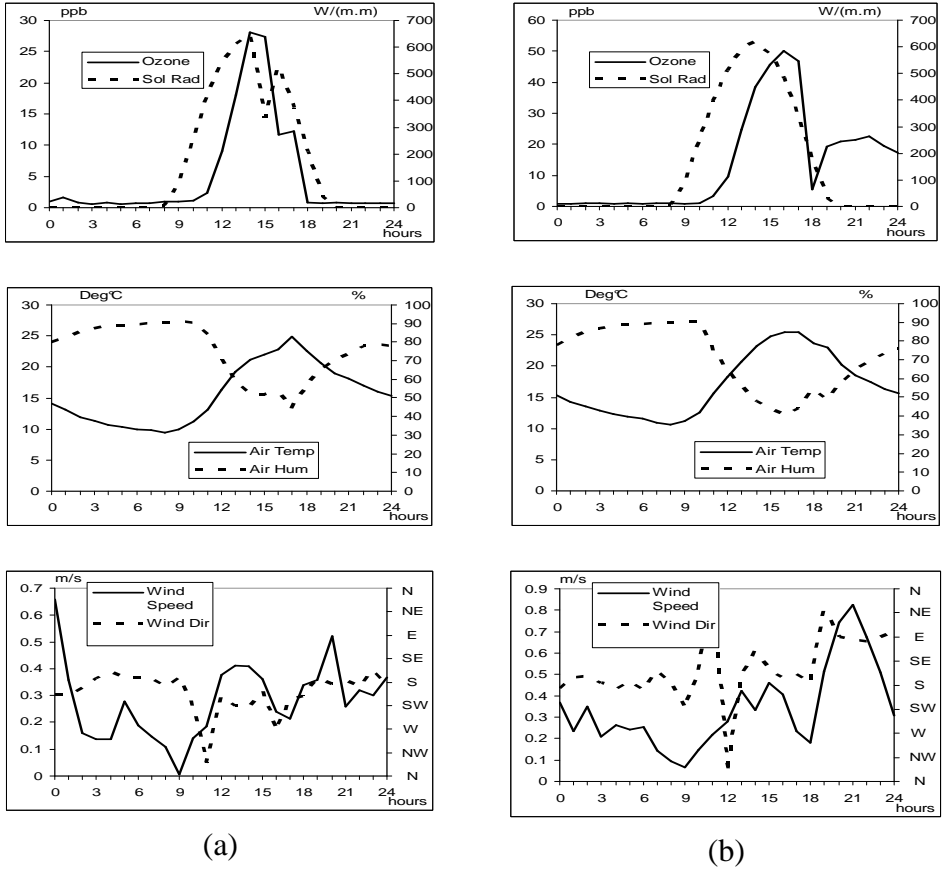


Fig. 5. Variations of the temperature, air humidity, solar radiation, wind speed and ground level ozone concentration on: (a) 04 October 2006, (b) 05 October 2006.

The air temperature changes from $t=10^{\circ}\text{C}$ at 08:00h to $t=25^{\circ}\text{C}$ at 16:00h, the relative humidity RH changes from 90% at 08:00h to 40% at 16:00h. The maximal solar radiation reaches its maximum at 14:00h and it is about 620Wm^{-2} . The surface ozone concentration at 11:00h is $C=5$ ppb, at 12:00h it is $C=10$ ppb, at 13:00h it grows to $C=25$ ppb. At 14:00h, 15:00h and 16:00h the values are respectively $C=40$ ppb, $C=45$ ppb and $C=50$ ppb. At 17:00h the surface ozone concentration starts to fall and it is $C=47$ ppb. At 19:00h the surface ozone concentration is decreasing substantially and reaches value $C=20$ ppb, which remains during the night.

Discussion

Summer measurements (2006)

Summer measurements of the surface ozone concentration in the area of the AO in 2006 show the following. After the sunrise there is constant increase of the surface ozone concentration. The main increase begins after 12:00h and reaches at 14:00h its maximal value for the day (20 July 2006, Figure 4a). The solar radiation reaches its maximal values at 13:00h and reaches 900Wm^{-2} . In the period between 14:00h and 22:00h there are serious fluctuations in the values of the surface ozone. The difference between the maximal and the minimal values of the surface ozone concentration is about three times. This data show that the development of PBL of the atmosphere and the photochemical processes play important role, probably, in this cases these big fluctuations are caused by some other process, e.g. advection.

Data from the second day on 28 July 2006 (Figure 4b) about the behaviour of the surface ozone concentration show more classical pattern. They increase after 10:00h from $C=5$ ppb to $C=72$ ppb at 13:00h. At 14:00h and 15:00h there is slight fall in the values of the surface ozone concentration and at 16:00h the maximal value for the day is reached again $C=72$ ppb, after which it is gradually falling and at 19:00h the surface ozone concentration in this part of the city (in the park) is small.

Autumn measurements (2006)

Lidar data during fall campaign, as we already have discussed it, are two types, in the first case the height of the mixing layer does not exceed $H_{\text{ML}}\approx 600$ (700) m and in the second case the height of the mixing layer reaches $H_{\text{ML}}=1000$ (1200)m.

Data for the surface ozone concentration for 04 October 2006 r. 05 October 2006 for the area of the AO, despite the fact that the full solar radiation is about 600Wm^{-2} , the air temperature and the relative humidity have similar values, they show different behaviour of the surface ozone concentration. For example the maximal concentration on 04 October 2006 is $C=28$ ppb which is reached at 13:00h and 14:00h. On 05 October 2006 the maximal value of the surface ozone concentration is reached at 15:00h and it is about $C=50$ ppb.

Comparing data for surface ozone with the kind of PBL of the atmosphere and its height, it can be said that when the height of PBL grows slowly, the ozone concentration usually (but not always) also grows slowly. In fact the behaviour of the surface ozone concentration in the area of the AO depends on the kind of PBL, but as well on the photochemical processes and transporting.

Lidar data for the next two days from campaign 18 October 2006 and 19 October 2006 show different development of PBL of the atmosphere, closer in value heights of the mixing layer. The surface ozone concentrations are measured in the lidar area (IE-BAS). Because the season is fall and the full solar radiation is weaker (about 600Wm^{-2}), the

maximal ozone concentration is smaller – about $C=17$ ppb. In this case there is certain relation between the behaviour of the ozone and the development of PBL of the atmosphere. In the beginning of the experiment (in the case of mixing layer of low height), the value of the surface ozone concentrations is about $C=5-10$ ppb, and when at 12:00h the mixing layer is growing substantially in height, the surface concentration is also increasing substantially (approximately two times), after which it remains constant after the entire developing mixing layer.

The results for the surface ozone concentration in the area of the AO leads us to the conclusion that they are of local importance, as they are situated in the park, away from sources and are mostly influenced by development of photochemical processes, formation of the mixing layer, and possible advection.

Comparing lidar data for the height of the mixing layer and the indications for the solar radiation, measured in the area of the AO it could be seen, that the maximum height of the mixing layer is reached at about 13:00-13:30h. The maximum values of the solar radiation during summer are about $W=900$ Wm^{-2} . During fall the maximum of the surface ozone concentration is observed an hour or two later than the maximum of the solar radiation, respectively, about an hour later than the time of the maximum height of the mixing layer. The maximum of the surface ozone concentration is in contra phase with the maximum of the relative humidity. It is commonly known that the surface air temperature and the relative humidity change in contra phase as it can be observed. In all measurements in the area of the AO the wind speed was below 2 ms^{-1} , the direction of the wind during the night and the day changes approximately within 180° which lead to changes (fluctuations) in the value of the surface ozone concentration. In the area of the AO the values of the surface ozone concentration in summer are higher than those in the region of IE; this could be assumed to be owing to the fact that AO is situated in a park and there are fewer sources of NO and NO_x which to decrease the surface ozone concentration and ratio VOC/NO_x is higher than that in the area of IE. In fall the values of the surface ozone concentration in the area and of the two experimental zones are lower in comparison with the summer ones because of the decreased solar radiation and are closer in value.

Conclusions

In the present work results from observations of the mixing layer formation and the stable and residual atmosphere layer destruction are presented.

According to the lidar data in clear sunny days (anticyclone) the ABL development over the region of the Sofia city proceeds in three stages. During first one (06:00-08:30h) the ABL development is slow since the main part of the solar radiation is being absorbed by the soil (earth ground) so increasing its temperature. During second one (09:30-10:00h) a slow formation of the new ML starts; its height reaches about 400-600 m. During third stage (11:00-11:30 h) a fast increasing of ML starts and at about 13:00-14:00h it reaches the maximum height. It should be noted that even small changes in synoptical situation and meteorological conditions could lead to changes in different stages. For example, during the first stage a transportation of aerosol from NE is being often observed; similar transport is observed during third stage and after it but at a considerably higher

height. Another often occurring situation is the increasing of the wind speed at the end of the second stage and a rapid development of the mixing layer.

The behavior of the surface ozone concentration in two Sofia areas has been presented: around IE (urban) and in the area of the AO (park). The height of the mixing layer reaches its maximum at about 13:00-13:30h and varies from $H_{ML} = 1400$ m to $H_{ML} = 600$ m during summer and fall. In fall the residual layer is destroyed during intervals 11:00-12:30h at heights in the range of $H_{RL} = 1200$ m to $H_{RL} = 600$ m.

The surface ozone concentration in the area of IE changes synchronically with the development of the mixing layer. The maximal values of the surface ozone concentration are reached, when the height of the mixing layer reached its max and afterwards. The maximal growth of the surface ozone concentration is about 11-12:30h, when fast growth of the mixing layer begins and also the complete destruction of the residual layer is observed, i.e. the two processes of growing of the mixing layer and entrainment of aerosol and ozone from the higher layers of ABL are observed. The values of the surface ozone concentration during summer months are higher than those during fall.

On the grounds of the gained experience, we may make the following conclusion: in the morning hours the photochemical processes play main role because the mixing layer is thin within $H=100-200$ m, up to the first elevated inversion and there is no relation between the residual layer (from the previous day), which contains ozone. In the interval between 08:00 h till 10:00h the surface ozone concentration is usually low or is slowly increasing as the two competing processes are taking place, namely, the formation of ozone due to the photochemical processes and the destruction of the ozone due to the interaction with NO and NO_x, which are in larger amounts because of the bigger traffic in this period.

In the hours between 11:00h and 12:00h an sharp increase in the altitude of the mixing layer begins and during this period the destruction of the residual layer ends.

The surface ozone concentration is growing most fast because of the intensive photochemical reactions and the processes of entrainment, i.e. the entering of aerosol and ozone from higher layers. After reaching maximum altitude of ABL, when the layer is homogeneous throughout its entire thickness, the increase of ozone concentration is due to the photochemical processes again. After the sunset part of this ozone will remain in the new residual layer, which will be formed.

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References

- Cartalis, C. and Varotsos, C., 1994, Surface ozone in Athens, Greece, at the beginning and at the end of 20th-century. *Atmospheric Environment*, **28**, pp. 3-8.
- Gusman, F. and Streit, G., 1993, *Mexico city air quality research initiative, in air pollution'93*, Zannetti, C Billerica (Eds.), (Mass), pp. 599-609.

- Kolev, I., Savov, P., Kaprielov, B., Parvanov, O. and Simeonov, V., 2000, Lidar Observation of the Nocturnal Boundary Layer Formation over Sofia, Bulgaria. *Atmospheric Environment*, **34**, pp. 3223–3235.
- Kolev, N., 2008, Lidar-radiometer investigation in the planetary boundary layer of the atmosphere, PhD dissertation, Institute of Electronics, Bulgarian Academy of Sciences.
- Kolev, N., Savov, P., Kaprielov, B., Grigorieva, V. and Kolev, I., 2008, Influence of the boundary layer development on the ozone concentration over urban area, *International Journal of Remote Sensing*, **29**, pp. 1877-1982.
- Kondratyev, K.Y. and Varotsos, C., 1995, Atmospheric greenhouse effect in the context of global climate change. *Nuovo Cimento della Societa Italiana di Fisica C-Geophysics and Space Physics*, **18**, pp. 123-151.
- Markowicz, K., Flatau, P., Quinn, P., Carrico, C., Falatán, M., Vogelmann, A., Bates D., Lin, M., and Rood, M., 2003, Influence of relative humidity on aerosol radiative forcing: An ACE-Asia experiment perspective. *Journal of Geophysical Research*, **108**, pp. 8662.
- Vaelasco, E., Marquez, C., Bueno, E., Bernabe, R., Sanchez, A., Fentanes, O., Wohnschimmel, H., Cardenas, B., Kamilla, A., Wakamatsu, S., and Molina, L., 2008, Vertical distribution of ozone and VOCs in the low boundary layer of Mexico City. *Atmospheric chemistry and Physics*, **8**, pp. 3061-3079.
- Varotsos, C.A., Efstathiou, M.N. and Kondratyev, K.Y., 2003, Long-term variation in surface ozone and its precursors in Athens, Greece. – a forecasting tool. *Environmental Science and Pollution Research*, **10** (1), pp. 19-23.
- Whiteman, C.D. and McKee, T.B., 1982, Breakup of temperature inversions in deep mountain valleys: part II, Thermodynamic model. *Journal of Applied Meteorology*, **21**, pp. 290–302.

Изследване на атмосферния граничен слой и концентрацията на приземен озон за района на София посредством лидарни и озометрични измервания.

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Резюме: Наличието на разнообразни физични и химични процеси определящи динамиката на атмосферния озон, както и липсата на фиксирани негови източници, поставя проблеми при оценка на екологичното въздействие вследствие нарастване на концентрацията му. Обмена между стратосферата и тропосферата допуска проникване на озон в граничния слой, като това определя приноса на така наречения „естествен“ озон, също и до замърсяване в близост до земната повърхност. Целта на настоящото изследване е да се изучи концентрацията на приземен озон през периодите на разрушаване на стабилния граничен слой, остатъчния слой, формирането на конвективния граничен слой, а също и влиянието на температурата, относителната влажност и височината на слоя на смесване в различни части на София, България. Концентрацията на приземен озон в района на Института по Електроника се променя синхронно с формирането на слоя на смесване.

Максималните стойности на приземен озон се достигат, когато височината на слоя на смесване е най-голяма, а също и след това. Максималният ръст на концентрация на приземен озон е около 11-12:30 часа местно време, когато започва бързо нарастване на слоя на смесване и напълно се разрушава остатъчният слой. Тогава се наблюдават два процеса – на нарастване на слоя на смесване и увеличаване на аерозоли и озон от горните слоеве на атмосферата, като през лятото се наблюдават по-високи стойности на концентрация на озон, отколкото през есента