Surface ozone and boundary layer observations in the region of Sofia

Grigorieva V.[1], Evgenieva Ts. [1], Kolev N.[1], Donev E.[2], Ivanov D. [2], Danchovski V. [2]

[1]Institute of Electronics, Bulgarian Academy of Sciences, 72, Tsarigradsko shosse Blvd., 1784 Sofia, Bulgaria; Fax: +359 (2) 975 32 01; E-mail: blteam@ie.bas.bg
[2]Department of Meteorology and Geophysics, Faculty of Physics, Sofia University "St. Kliment Ohridsky", Bulgaria

Boundary layer and ozone behavior over Sofia have been investigated with lidar,ceilometer and ozonometers. Analysis of the observations performed in the recent years at three city sites has been made. It was found that at close meteorological situations in autumn period the features of boundary layer development and diurnal ozone variations show the similar behavior from year to year. This founding can be useful when temporal ozone trend and climate change influence on ozone are investigated.

Introduction

Ozone is a small (by concentration), but very active atmospheric constituent. It is one of the main pollutant with harmful effects on the living organisms. Due to its oxidizing ability ozone strongly influences on the proceeding of chemical reactions in atmosphere and thereby influences on the atmospheric chemical composition. Ozone is greenhouse gas and takes part in climate change, which mainly influences on atmosphere temperature and water vapour concentration and they by-turn influence ozone. In low troposphere ozone is the secondary pollutant, which is formed as a result of complex photochemical reactions induced by sun radiation with participation of O_3 precursors – nitrogen oxides NO_x (NO_x :NO+NO_2) and volatile organic components (VOC). Dynamical processes, such as vertical and horizontal advections of ozone-rich air, stratosphere-troposphere exchange also define O_3 pollution near the ground. All these processes strongly depend on meteorological factors (solar radiation, height of mixing layer, wind speed, temperature). So, ozone behavior depends on behavior of the complex system sun-earth-atmosphere. Great number of the processes and factors in considerable degree complicates analysis of the temporal ozone variations. The strong inter-annual ozone variability masks ozone trend and influence of the climate change. Results of the performed in last decade numerous model and experimental investigations corroborate this fact [1]. However, detailed study of ozone behavior observed under special conditions gives an opportunity to identify the impact of individual parameters on ozone state [2,3].

Investigations presented in this paper are extension of our previous observations of the surface ozone behavior in the Sofia boundary layer and deal with the study of inter-annual variability of ozone concentrations. Dynamical processes in the atmospheric boundary layer, such as destruction of the stable layer in early morning hours, development of the mixing layer, which strongly affect ozone state near the ground, were controlled by remote-sensing technique (by aerosol lidar and ceilometer-lidar).

Now it is recognized that synoptic circulation, which greatly varies from year to year, influences the surface ozone state and his inter-annual variations [4]. Taking into account that this influence is more strongly expressed during spring-summer time, when enhanced atmospheric dynamics and photochemical ozone formation take place, we performed analysis of the inter-annual ozone variations in more stable autumn period.

Sites and instruments description

Measurements have been performed at three sites in Sofia (42°39′ N, 23°23′ E, 591 m asl). The site 1 is located at Astronomical observatory, that is situated in the Astronomical Observatory (Borisova Gradina Park), and is surrounded by rich vegetation. The site 2 is located in the urbanized area "Druzhba". This site is administrated by the government /www.sofia.bg/. The site 3 is situated at the territory of the Institute of Electronics, Bulgarian Academy of Sc Astronomical observatory (Borisova Gradina Park) iences and has open terrain with little vegetation covering. Ozone concentrations at site 1 and site 2 were measured by ultra-violet optical absorption photometers, which determine ozone concentration by measuring the attenuation of light at wavelength 254 nm due to ozone absorption in the cell with ambient air. At site 1 photometer model TECO 49 has been used. Due to the inherent stability of the UV adsorption technique it could be considered that the error of ozone concentrations reported here is within +/-5 ppb. Monitoring of the meteorological parameters - total solar radiation, wind speed and direction - has been carried out at 10 m height with using pyranometer (model SP1110, Skye) and wind monitor (model 05103, YOUNG). Air temperature and relative humidity have been measured at 2 m height with HMP45C sensor, manufactured by Vaisala Inc. At site 3 surface ozone concentration was measured with solid-state chemiluminescent ozonometer, model 3-02P developed at the OPTEK Inc. (St.Petersburg, 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 exceeded 15%. The sampling was performed through teflon tubing at a height approximately 12 m above the ground level.

Remote-sensing techniques – ceilometer-lidar and aerosol lidar operated at site 1 and site 3, respectively.

Specifications of the lidar: transmitter – a standard Nd - YAG laser (operational wavelength 532 nm, pulse duration and energy 15–20 ns and 10–15 mJ, repetition rate 12.5 Hz; receiving antenna – a Cassegrainian telescope (main mirror diameter 150 mm, equivalent focal length 2250 mm); photodetector – a PMT with an interference filter (1 nm FWHM); data acquisition and processing set – a 10 bit 20 MHz ADC and a PC.

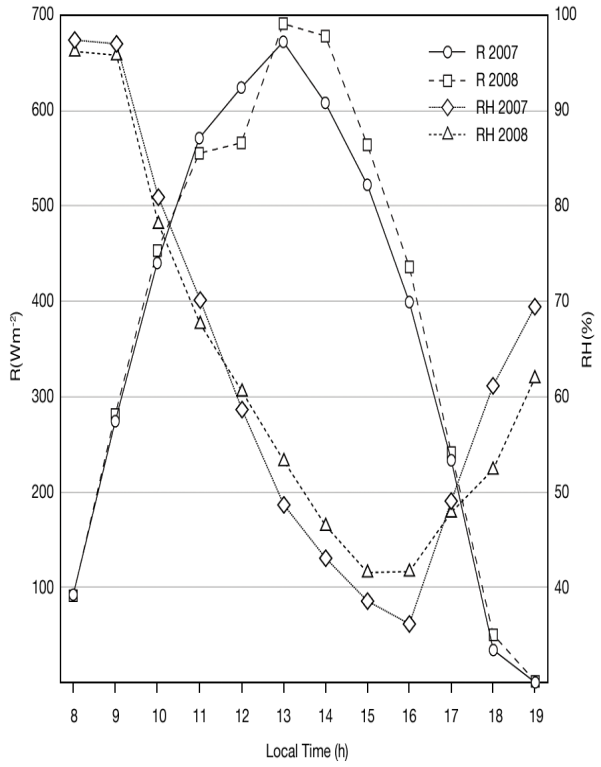

Fig. 1. Diurnal variations of solar radiation and relative humidity, measured in the site 1 on October 4, 2007 and on October 1, 2008.

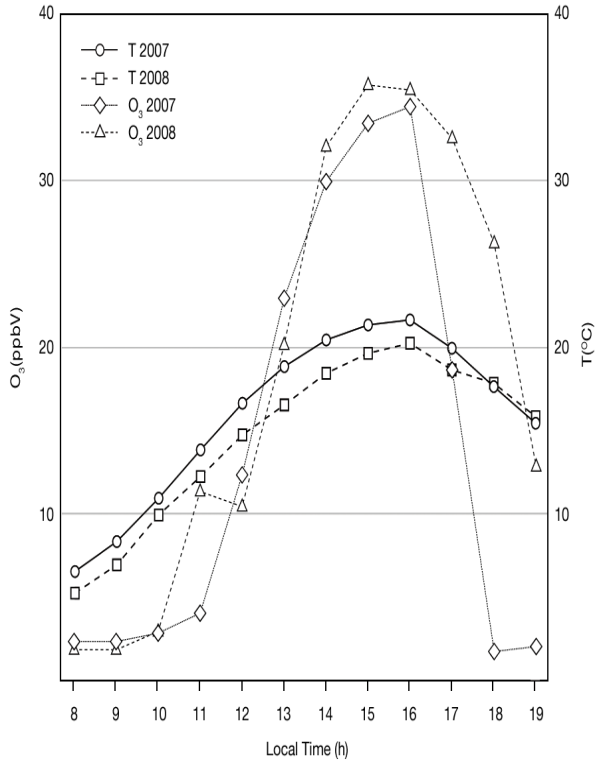

Fig. 2. Diurnal variations of surface ozone concentrations and temperature, measured in the site 1 on October 4, 2007 and on October 1, 2008.

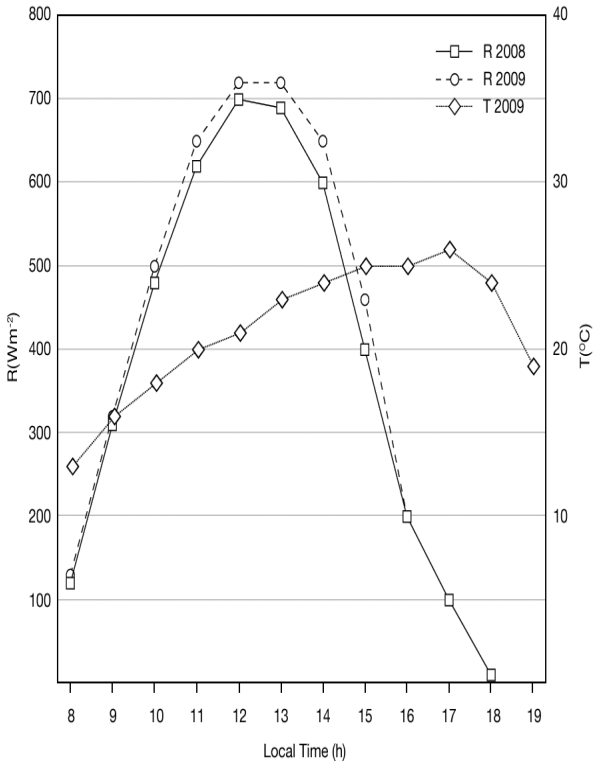

Fig. 3. Diurnal variations of solar radiation measured in the site 2 on October 13, 2008 and on October 8, 2009 and temperature, measured in the site 2 on October 13, 2009.

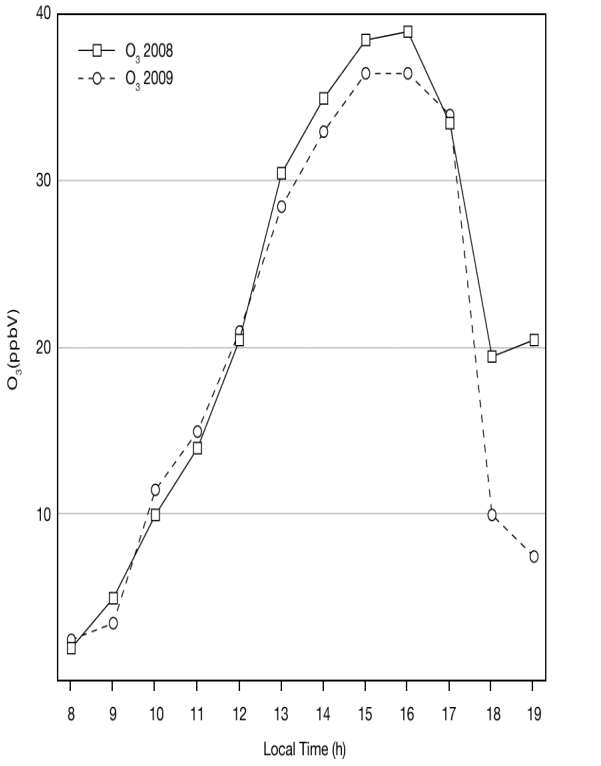

Fig. 4. Diurnal variations of surface ozone concentrations, measured in the site 2 on October 13, 2008 and on October 8, 2009.

Specifications of the ceilometer-lidar: light source - laser protection class 1M under DIN EN 60825-1, measuring range 30-15000m, resolution 15m, measuring time 60s, measuring principle- optical (lidar), wavelength 1064 nm, pulse duration about 1ns, pulse repetition rate 5-7kHz, energy per pulse 8μJ. Commercial ceilometer CHM 15k is manufactured in Germany, by Jenoptic Laser Optik System GmbH.

Results, Discussion, Findings

To reduce the number of factors influencing on ozone variability the experimental observations performed at close meteorological conditions have been analyzed. The examples of such situations are shown in Fig. 1-3. The close values of the main meteorological parameters has been detected on 04.10.2007 and 01.10.2008 at site 1 – Figs. 1, 2 and also on 13.10.2008 and 08.10.2009 at site 2 – Fig. 3.

Detailed analysis of the solar radiation behavior, presented in Fig. 1 and Fig. 3, shows that for every site the peculiarities in the diurnal radiation variations practically doesn't vary from year to year. The maximal values of air temperature at both sites demonstrate time delay (about three hours) relative to those of the solar radiation. Time series of surface ozone concentrations are shown in Fig. 2 and Fig. 4 respectively.

Features of the diurnal surface ozone variations are typical for urban sites with ozone maximum during daytime and minimum during evening and night hours. It must be pointed out that, as Fig.2 and Fig.4 show, ozone demonstrates the striking resemblance in its inter-annual behavior at both sites. In morning hours the increasing solar radiation starts up two processes, which increase ozone concentrations near the ground. The first one is development of the boundary layer, caused by heating of the ground surface and creating turbulent transfer of the warm air to the higher atmospheric layers. This provides the development of the convective mixing layer and following vertical transport of the ozone-rich air from aloft to the ground. The second process is photochemical ozone formation from ozone precursors NO_x and VOC with anthropogenic and biogenic origin. Briefly, the scheme of the photochemical O_3 formation may be described by a chain of next reactions:

$$NO_2 + h\nu \rightarrow NO + O(^3P),\ \lambda \leq 400\ nm \quad (R1)$$
$$O_2 + O(^3P) + M \rightarrow O_3 + M \quad (R2)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R3)$$

M is a random air molecule (N_2 or O_2). The stationary state of this system can be shifted to ozone production by peroxy radicals RO_2, which also can convert NO to NO_2:

$$NO + RO_2 \rightarrow NO_2 + RO \quad (R4)$$
$$RH + OH \rightarrow R + H_2O \quad (R5)$$
$$R + O_2 + M \rightarrow RO_2 + M \quad (R6)$$

In spite of the fact that RO_2 formation is defined by OH radicals, that are produced primarily at the photolysis of the ozone:

$$O_3 + h\nu \rightarrow O(^1D) + O_2,\ \lambda \leq 310\ nm \quad (R7)$$
$$O(^1D) + H_2O \rightarrow 2OH \quad (R8)$$

In the boundary layer RO_2 radicals are performed in result of VOC oxidation by OH radicals, concentration of which in atmosphere is defined by concentration of water vapour. Taking into account that efficiency of the photochemical ozone formation strongly depends on VOC/NO_x ratio, which in many cases are different in various points over large urban area, different levels of ozone concentrations can be detected at monitoring sites. In the evening under developing nocturnal inversion, when processes generating ozone are absent, fast decrease of ozone near the ground is caused by O_3 destruction due to dry deposition and ozone titration with nitric oxide (NO) in accordance with reaction R3. Tne ozone state becomes very sensitive to wind, which generates turbulence (and thereby creates vertical mixing), leads to horizontal advection of ozone-rich air mass and also is responsible for dilution of the air constituents.

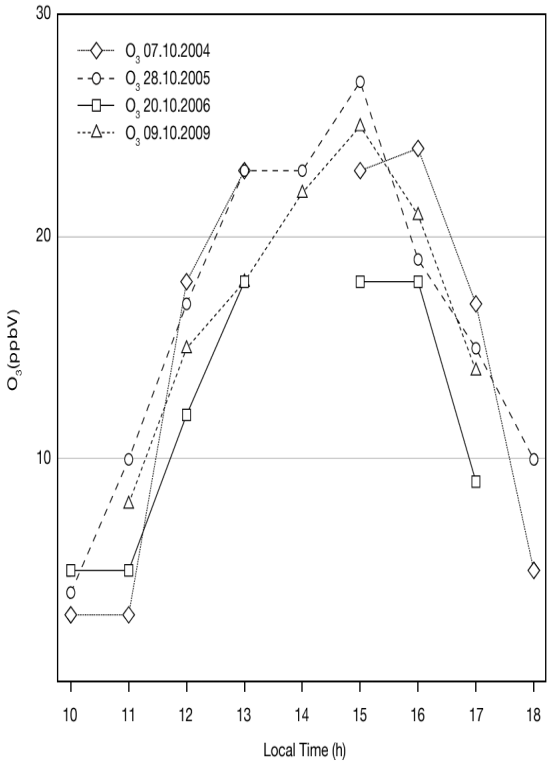

Fig. 5. Inter-annual variations of surface ozone concentrations, measured in the site 3 during October 2004, 2005, 2006, 2009.

Comparison of the time series of the surface ozone concentrations detected at site 3 during some days in October of 2004, 2005, 2006, 2009 is shown in Fig. 5. Observations have been performed at anti-cyclonal conditions in the cloudless days with low wind speed , but the meteorological parameters (radiation, temperature) were not exactly the same. In whole, ozone data received in different years demonstrate a good recurrence (it must be noted that systematic inaccuracy of the measurements was 15%). The lower values of maximum ozone concentrations, which were detected on site 3, in comparison with those at site 1 and site 2 are attributed to its location near the highway. Vehicle exhaust change VOC/NO_x ratio and process (R1-R6) of photochemical ozone formation.

Analysis of the presented observations shows:

1. In spite of the great inter-annual variability, which surface ozone demonstrates in general case, in autumn during anti-cyclonal cloudless weather and at close meteorological conditions (intensity of solar radiation, temperature) the features of diurnal ozone variations (increasing of O_3 concentrations during development of the mixing layer, maximum values and time of its appearance – Fig. 2, Fig. 4, Fig. 5) show stable behavior from year to year. So it can be assumed that boundary layer and ozone precursors concentrations, which involved into photochemical ozone formation in accordance with reactions R1-R6, keep up its state from year to year at mentioned conditions. This fact can be used when temporal ozone trend and climate change influence on ozone are investigated.

2. The discrepancy in the form of ozone increasing from early morning to afternoon at site 1 and site 2 is observed (Fig. 2 and Fig. 4). It reflects difference in the boundary layer development caused by difference in the properties of underlying surfaces at site 1 and site 2. At first site, which is situated in park zone, the great part of incoming solar radiation is spent for evaporation of moisture from vegetation and soil. For this reason development of the mixing layer (and increasing of ozone concentrations) occurs with delay in relation to those at site 2, that is located in more urbanized surrounded by buildings area.

3. Although efficiency of two basic reactions (R1 and R7) in the chain of reactions (R1-R8), forming anthropogenic ozone, strongly depends on the intensity of solar radiation, ozone behavior at site 1 and site 2 shows direct correlation with that of temperature (Fig.2 and Fig. 3, 4), which directly doesn't take part in these reactions. Additional analysis is needed to receive more detailed information about processes, that determine ozone state.

4. Example of the boundary layer observations, performed with aerosol lidar at site 3, is presented in Fig. 6. Lidar data show that mixing layer started to form after 08:30 h. The mixing layer height gradually increased until 11:30 h ,reaching H=400 – 450 m. After this time a rapid growth in the mixing layer height is seen and its height reached H =1200-1400 m at 13:00 h. Fig.7 shows the ceilometer measurements, obtained at site 1. The complex boundary layer structure is observed. On this figure two parts of the residual layer are seen. The first part is observed at height of about H=800m and the second one at height H=1250m. These layers were fully destroyed after 12:00 h. The mixing layer reached its maximum height H=2100m at 16:00 h. The joint interpretation of the mixing layer height data, mixing layer development and the surface ozone concentration data can be summarized as follows: the surface ozone concentration varies in similar manner to the mixing layer development in the three regions of observations. The maximum values of the surface ozone concentration are reached 1-2 hours after mixing layer is fully developed. In the region of the Astronomical observatory (Borisova Gradina Park) – site 1 the mixing layer formation and surface ozone concentration behavior show 1-2 hours delay in comparison with the one in the region of the of the Institute of Electronics – site 3. This discrepancy is caused by difference in characteristics of the underlying surface at site 1 and site 3.

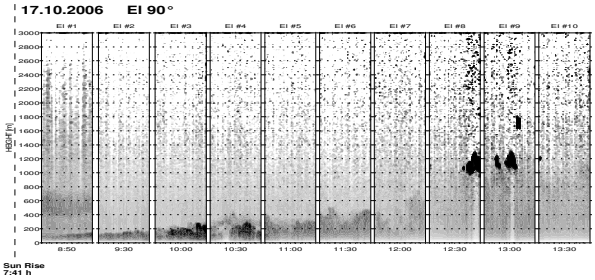

Fig. 6. Height–time indicators constructed from the lidar data obtained on 17.10.2006

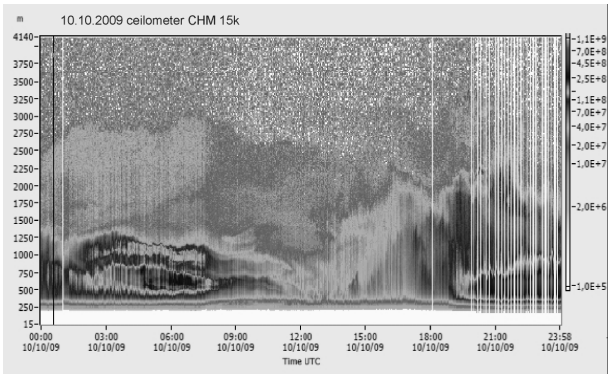

Fig. 7. Height–time indicators constructed from the ceilometer CHM 15k data obtained on 10.10.2009

Summary

Analysis of the surface ozone and boundary layer observations performed in Sofia in recent years at three monitoring sites found that in autumn period at close meteorological conditions diurnal ozone variations show stable behavior from year to year. So it may be assumed that boundary layer and ozone precursors concentrations, which involved into photochemical ozone formation, keep up its state from year to year at mentioned conditions.

Acknowledgements

We would like to thank PhD Ivan Kolev for helpful discussions. Investigations have been performed within the frame of the contract: "City versus Mountain Tropospheric Ozone: The Sofia-Plana region in an air quality and ecological sustainability perspective" (contract DO 02-127/08).

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