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MORNING OZONE BUILDUP DURING SUMMER 2003 EPISODES AND THEIR LINKS WITH SOME RADIOSONDE DATA IN WROCŁAW, SOUTH-WESTERN POLAND

High concentration of ozone, up to 400 μg/m^3, was observed in the air of an urban area during summer 2003 in Wrocław, south-western Poland. In ozone episods, commonly lasting three days, its peak concentration increased from the first to the third day. This coincided with an increasing atmosphere instability near the ground after sunrise and a weaker nocturnal inversion in the following days. Four-hour averaged ozone concentration (09:00–13:00) showed positive association with the height of mixing layer and negative one with the environmental lapse rate in the surface layer at noon. These two independent variables explained 61% of a total variation with a standard error of 26 μg/m^3. It was not a local traffic activity that was responsible for high ozone concentration, but a positive feedback between the weakening of a high-pressure system and the increasing importance of vertical mixing (e.g., higher efficiency of ozone production, vertical transport of aged air masses from upper altitudes), which was supported by well-documented episodes and backward trajectory analysis.

1. INTRODUCTION

Very high levels of surface ozone concentration were recorded in Europe during summer 2003. The "August heat wave" in 2003 and its impacts on ozone levels over some western countries have been investigating in some works (VAUTARD et al. [35], CRISTOFANELLI et al. [7]). Also monitoring stations in south-western Poland reported critical threshold values of both 1 h and 8 h ozone concentration over the period from July to September 2003. In Wrocław, south-western Poland, the highest hourly ozone concentration (400 μg/m^3), exceeding the threshold value (360 μg/m^3, hourly value), was recorded on the 21st September (ZWOŹDZIAK et al. [40]).

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Ozone concentration in urban areas is closely dependent on the emission rates of ozone precursors, photochemistry of the ozone-nitrogen oxides (NO_x)–reactive organic gases (ROG) relationships, and local and synoptic meteorology. These complex interactions are still poorly understood. This is a good cause to undertake the studies on formation mechanisms of ozone within a city as a whole (e.g., SILLMAN [30], LAM et al. [14], KALABOKAS and BARTZIZ [12], TRAINER et al. [34], RAPPENGLUCK et al. [26]) and the impact of urban plumes on the surrounding suburban and rural areas (e.g., JIANG et al. [11], MACDONALD et al. [21], REID et al. [27], LIN et al. [19], MACKENZIE et al. [22], GAFFNEY et al. [10]).

Vertical mixing processes combined with the vertical gradient in pollutant concentration may have a significant impact on near-surface concentration on a diurnal scale. More recent studies by LIN et al. [18], RAO et al. [25], SALMOND and MCKENDRY [28], ZHANG and RAO [37], BERKOWITZ et al. [2] confirmed the importance of pollutant concentration in upper layers on the ground level air quality. According to ATHANASSIADIS et al. [1] the boundary layer evolution and the growth rate of mixing height contribute significantly to the ground level of ozone in the morning hours. The most interesting seems to be the moment of breakdown in the nocturnal boundary layer.

Summer 2003 provided the opportunity to study the short-term ozone behaviour, despite the extreme nature of some episodes (stagnation, radiation and temperature). It was interesting that ozone levels often reached anomalous values before the noon. This suggests that there can be other important contributors to the excess amount of ozone besides its local photochemical production. The present study gives a detailed analysis of two particular data sets and considers mixing processes early in the morning. Wrocław has experienced periodic air pollution episodes lately, and as a result, the local agencies are going to implement the air quality forecast system. Therefore, it is important to develop a good understanding of air pollution episode formation in this region.

2. METHODOLOGY

A homogeneous urban area with rural surroundings constitutes the city of Wrocław. The population is over 700 000. Field observations were conducted at the Air Quality Monitoring Station (51°07' N, 17°02' E, 116 m a.s.l.) of Wrocław University of Technology in July and September 2003 (data were not available for August, 2003, this month was not included in the analysis). The sampling inlet was about 5 m above ground level and at a distance of 15 m from heavy traffic street with four lines.

Surface ozone concentration measurements were carried out by using the UV-photometric analyser (HORIBA Corp., Japan, APOA-360). Zero and span checks were automatically performed every 24 h, while the accuracy and precision reached

±2%. The NO and NO_2 concentrations were measured by means of chemiluminescence methods (HORIBA Corp., Japan, APNA-350E) with daily checking for correct operation.

Meteorological measurements (wind velocity and direction, temperature, relative humidity, pressure and global UVA and UVB radiation) were available from an automatic weather station (Campbell Scientific Ltd) installed near the sampling point.

Sounding data were obtained from the data base of upper air observations of the University of Wyoming, the Departament of Atmospheric Science (http://weather.uwyo.edu). Upper air wind data as well as temperature and relative humidity data from radiosoundings were determined for Wrocław Airport. The airport is located about 7 km to the south-west of the city centre. Soundings are performed twice a day at 00:00 and 12:00 UTC.

A detailed analysis was done for the variability of atmospheric layering up to 3000 meters height. A virtual potential temperature Θ_v describes the atmospheric layering. Based on this parameter it is possible to define the changes in temperature independently of humidity and pressure fluctuations and to give a clear view of atmospheric stability changes at different heights. Potential virtual temperature was computed from the data of temperature, pressure, and water vapour (specific humidity).

Backward air trajectories were calculated using the NOAA HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model (Draxler and Rolph, 2003) to estimate the long-range transport of air masses to Wrocław.

3. RESULTS AND DISCUSSION

3.1. ANALYSIS OF TEMPORAL VARIATIONS IN AIR-POLLUTANT CONCENTRATION

The statistics has revealed rather serious pollution of the Wrocław air with ozone (SÓWKA et al. [31]). Its elevated levels are observed from spring to autumn months. The pattern of ozone and NO_2 pollution is illustrated in figure 1, which shows the time series of half-hourly concentration registered in July and September, 2003. The results clearly demonstrate peaks in ozone concentration with a maximum up to 400 μg/m^3. During episodes the ozone, whose concentration exceeds the European standards (90 ppb, 180 μg/m^3) and sporadically reaches extreme values (360 μg/m^3), builds up in the surface layer.

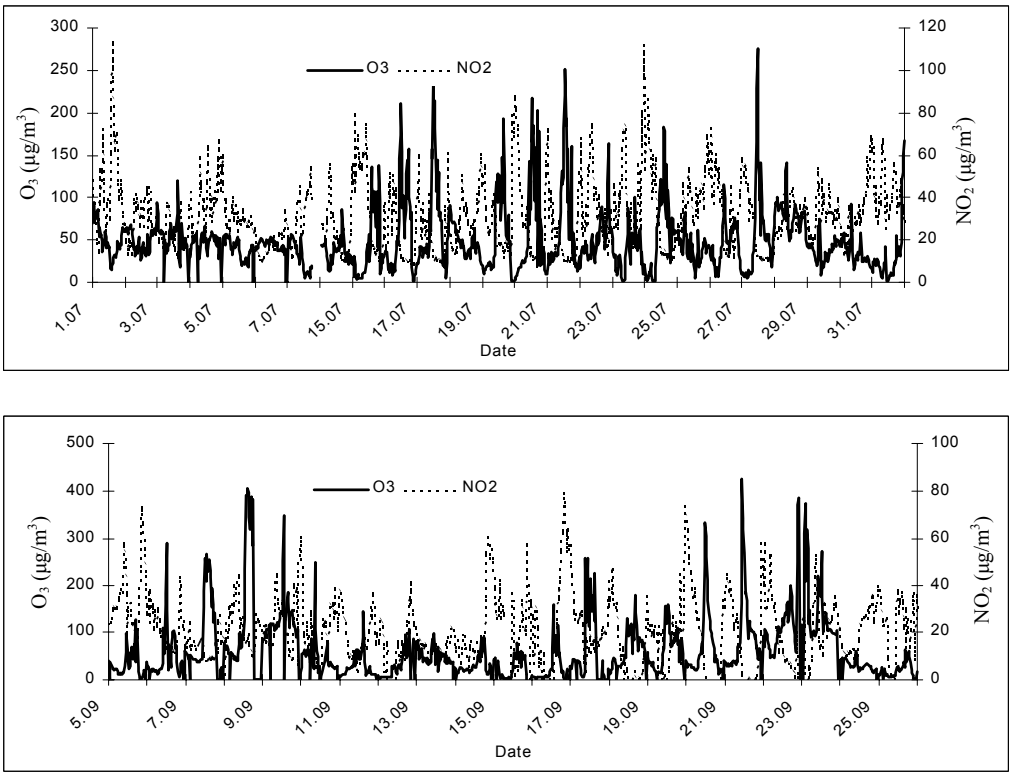

Fig. 1. Time series of half-hourly average O_3 and NO_2 concentration registered in July and September 2003 (the data gaps in July from 8 to 14 are due to data logger damage)

The relationship between ozone chemistry and meteorology has been extensively studied around the world (e.g., ZIOMAS et al. [38], CHEUNG and WANG [4], LEE et al. [15]). The analysis of meteorological data shows that ozone episodes are associated with large-scale stagnation of air, intense solar radiation, downward mixing of ozone-rich air and photochemical reactions. In some instances, however, there should be considered the contribution of local circumstances to air-pollution episodes, e.g., sea-land breezes (TONG et al. [33]; LIU and CHAN [20]), the monsoon system (WANG et al. [36]), stratospheric intrusions (BONASONI et al. [3]). Our results show that ozone episodes in Wrocław are associated with a period of the weakening of a high-pressure system. As an example, the time series of ozone concentration and atmospheric pressure observed in July and September 2003 are shown in figure 2. During a distinct increase in ozone concentration, the high pressure system has just weaken giving way, in our cases, to a depression entering from the west or north-west.

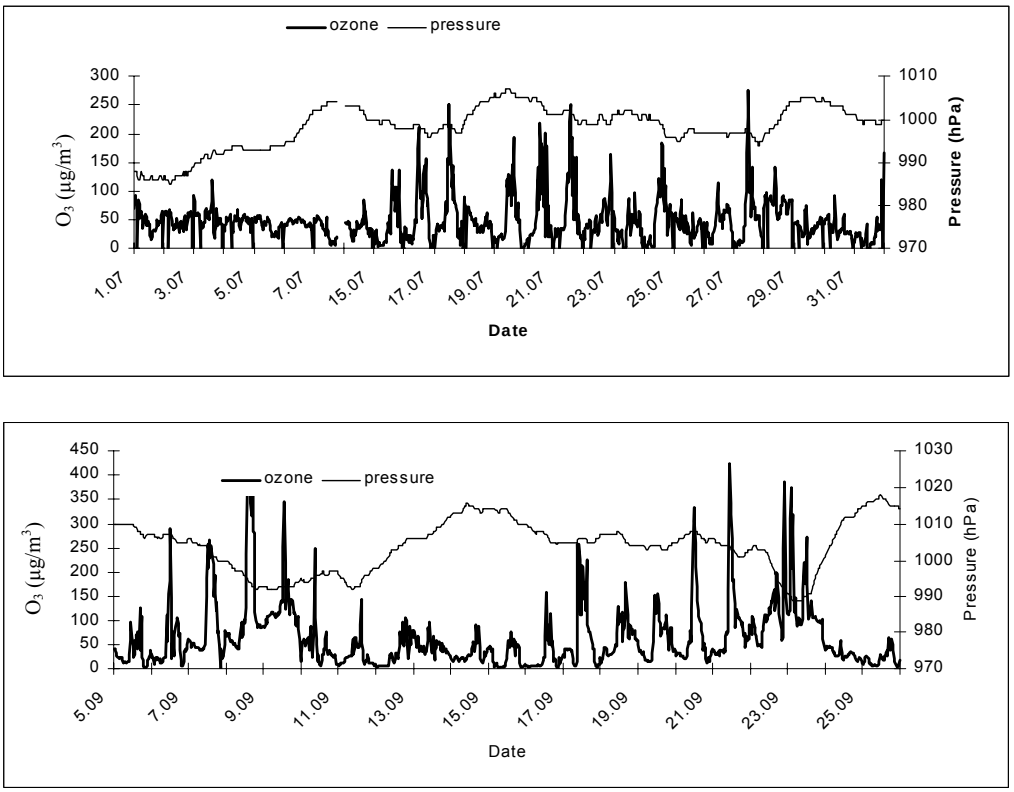

Fig. 2. Time series of half-hourly average O_3 concentration
and atmospheric pressure registered in July and September 2003

In the context of the processes leading to ozone episodes (i.e., solar radiation and NO_2 concentrations), other aspects of these episodes are worth examining. A solar radiation has a significant effect on episode photochemistry, increasing the photolysis rate and hence the ozone concentration. First, as shown in figure 3, a substantial change in ozone level was observed in the days with intensive solar radiation. This statement, however, should not be treated definitely, because there are some days with intense solar radiation and low ozone concentration. The highest levels were registered in September when incoming solar radiation was lower than that during the summer. Comparing ozone and NO_2 concentrations shown in figure 1 we arrive at the conclusion that they are anti-correlated for a number of nights and days. This behaviour is well known and explained in most investigations by the chemistry of reactions. Ozone reacts with locally generated NO which leads to a decrease in ozone concentration in the urban nocturnal boundary layer with a concurrent production of NO_2 and the anti-correlation at night. During the daytime NO_2 is photolyzed rapidly and initiates day-

time chemistry eventually leading to a photochemical ozone production, and also the anti-correlation is observed. A distinct increase in NO_2 concentration (figure 1) is most frequently achieved at nights and early in the morning, not only before the periods of ozone peaks. Thus, there must have been some additional reasons for a very rapid increase in ozone concentration during episodes, in spite of the levels of its local precursors and solar radiation. Therefore, we focus on the transport within the boundary layers (vertical and horizontal) and their influence on the variations in pollutant concentration.

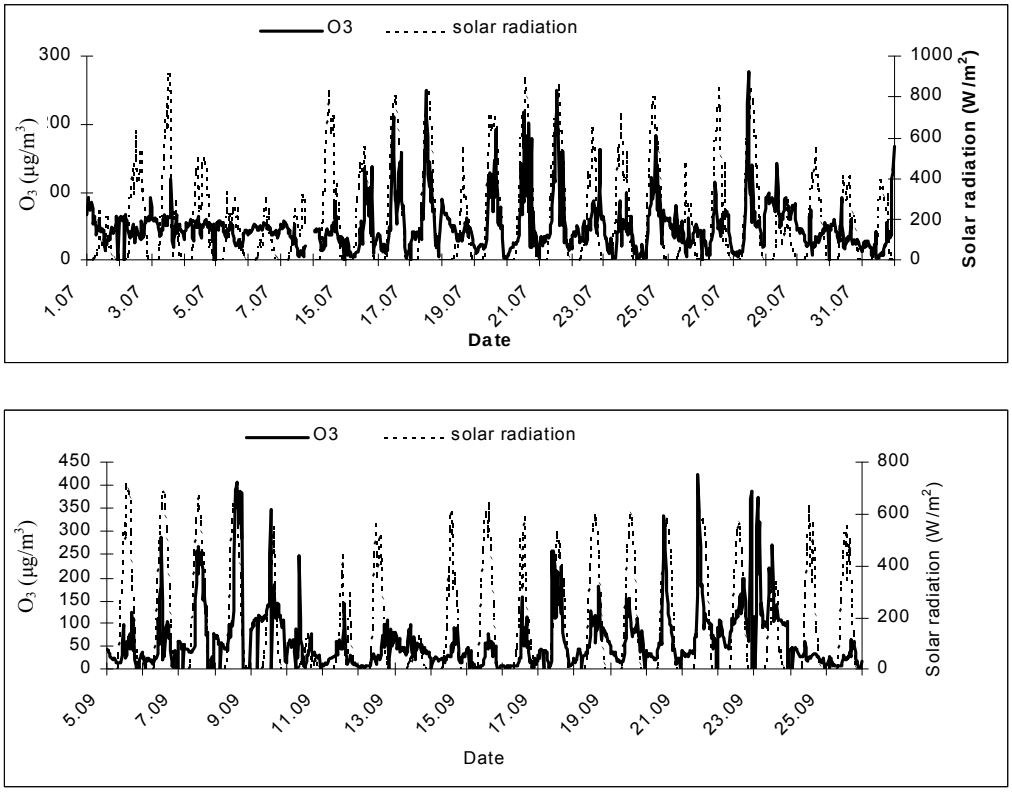

Fig. 3. Time series of half-hourly average O_3 concentration and solar radiation registered in July and September 2003

3.2. METEOROLOGICAL CONDITIONS DURING THE EPISODE

A detailed analysis of daily ozone patterns during summer episodes revealed some consistent trends. The general behaviour of the ozone is characterized by its build up from the first to the third day. Ozone concentration started to increase during the first day of the

episode, was still higher on the second day, and reached the highest level on the third day. In contrary to many other "typical days", the maximum ozone level was very often observed before the noon or just after it and never at the afternoon. This characteristic ozone behaviour is illustrated here with reference to specific case studies carried out between 15 and 17 July 2003 and between 6 and 8 September 2003. Figure 4 displays the half-hourly average ozone, NO and NO_2 concentration time series in downtown Wrocław for these periods. It shows a clear ozone maximum on the third episode day. A very high increase in ozone concentration was recorded between 08:00 and 13:00 LT. This pattern coincides with an increase in solar radiation flux, which testifies to a significant link between photochemical reactions in the air and the variation observed in ozone level. However, this ozone behaviour (the highest concentration on the third day) cannot readily be explained by atmospheric chemistry, since there were no special variations in local concentration of ozone precursors, nor in solar radiation in the succeeding days for each episode. The night-time and morning NO_x concentrations were comparable, in spite of 15 July when NO_2 reached the level of 140 μg/m^3 but ozone concentration was the lowest that day. The highest ozone levels were registered in September when both NO_x concentration and solar radiation were much lower than in July. The temperature reached 30 °C on the 17th July and only 22 °C on the 8th September. This statement allows an examination of other meteorological effects on ozone levels in the city.

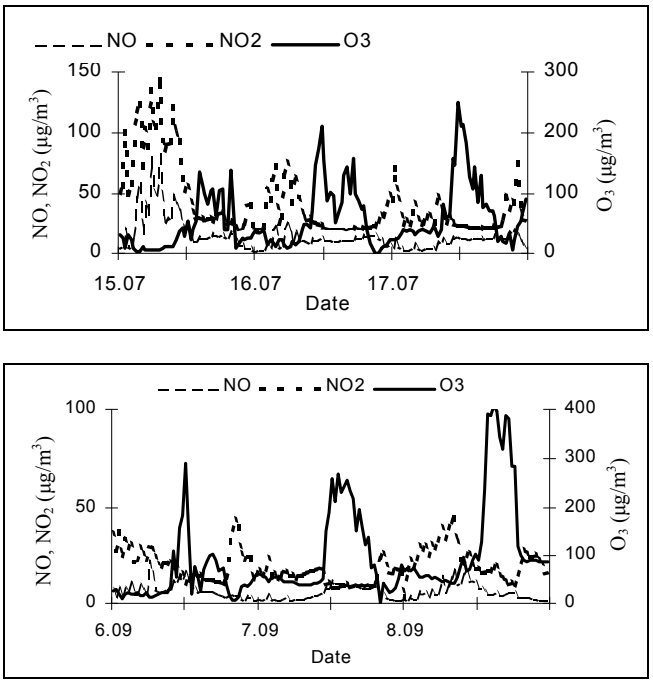

Fig. 4. Half-hourly average NO, NO_2 and O_3 concentration time series in downtown Wrocław

from 15 to 17 July and from 6 to 8 September 2003

To explain why the peak ozone concentration was much higher on the third day than on the first, the importance of the boundary layer structure and its evolution was highlighted. In addition, it has been shown (CHEUNG and WANG [4], ZHANG and RAO [37], LEHNING et al. [16]) that ozone maximum around noon can be related to a morning entrainment. Ozone trapped aloft in the residual layer the previous day mixes downward as the daytime convective boundary layer (CBL) starts to grow in the morning, rising the ground level ozone concentrations. To investigate the relative importance of vertical mixing processes, the profile data of meteorological parameters were used.

The best method for determining the mixing height (MH) is based on the measurements of the vertical distribution of pollutant concentration levels and turbulence profiles (STULL [32]). Since these observations are difficult to obtain on a routine basis, the MH is often estimated from profile data of meteorological variables (e.g., temperature, wind velocity, specific humidity). A review and comparison of different methods for the determination of the MH can be found in SEIBERT et al. [29], MARSIK et al. [23] and LENA and DESIATO [17].

In this study, the profiles of potential virtual temperature have been taken into account. These records proved to be sufficient to study the structure of the boundary layer (STULL [32]). Figures 5 and 6 show the profiles of potential virtual temperature for three days from the 15th to the 17th July, and from the 6th to the 8th September, respectively. It was interesting to find out this, if the differences existed in the temporal evolution of ML during the ozone episode.

Firstly, the mixing height was much greater on the third day than on the first one (e.g., at noon of the 17th July it was ≅1800 m versus ≅1200 m (the 15th July; ≅ 1000 m on the 6th September versus ≅2000 m on the 8th September). The top of the daytime ML manifests itself as a strong temperature inversion.

It would be interesting at this point to compare all the available data for the successive days. For all the nights, the greatest static stability was near the ground, with stability, however, decreasing on the third day. As shown in figures 5 and 6, the strongest temperature inversion was observed to be nearest to the ground on the first day at 00:00 UMT (+7 K in the layer of 160 m a.g.l. on the 15th July compared to +7 K at the depth of 420 m on the 17th July, and +4.4 K in the layer of 122 m a.g.l. on the 6th September compared to +4 K at the depth of 302 m) and probably this inversion has deepened during the night. The strength of a surface inversion is defined as the temperature difference between the top of the inversion and the ground relative to its depth. The top is classified as the level of the highest temperature. Caused by the strong surface inversion and low wind velocity, the dispersion of pollutants was being inhibited and locally produced species started accumulating. Thus, the high NO_x levels observed at that time were the result of pollutant being trapped in the nocturnal boun-

dary layer, which did not mix well due to calm conditions. Ozone displayed an opposite behaviour due to reaction with freshly emitted NO. It is probable that pri-

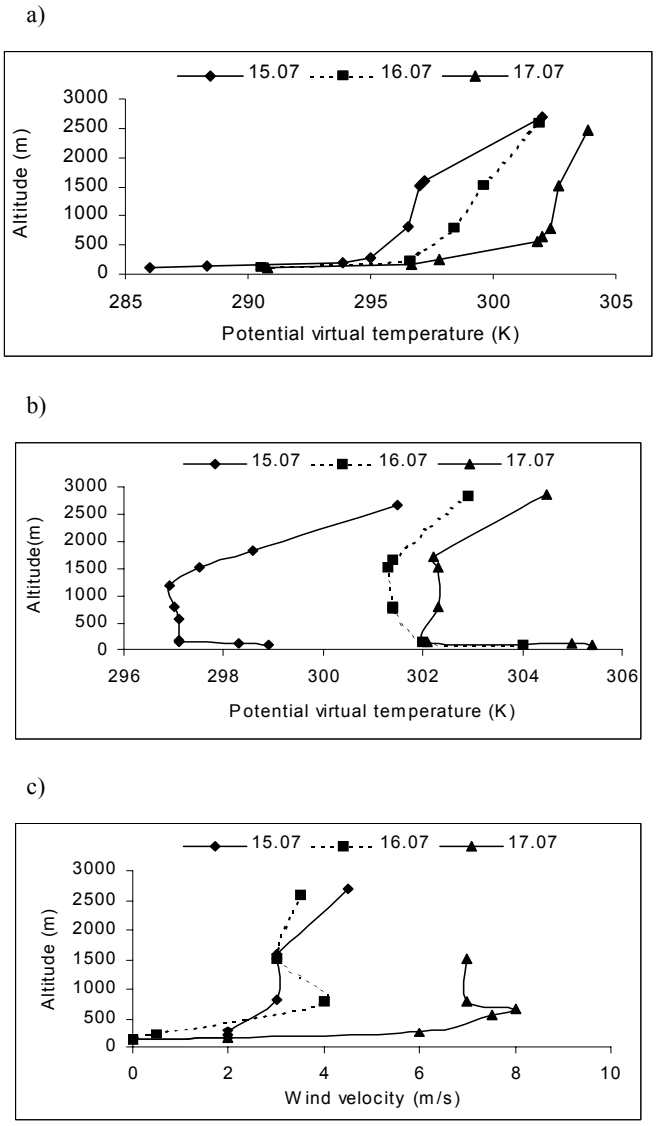

Fig. 5. Profiles of potential virtual temperature at 00:00 UTC (a),
12:00 UTC (b) and wind velocity at 12:00 UTC (c) from 15 to 17 July, 2003

mary pollutants (NO_x and also CO but not shown) occur in high concentration almost up to the time a turbulent ML began to grow quickly in depth. This is manifested itself

as the disappearance of NO_2 and a simultaneous appearance of ozone. The rate of ozone build-up was the highest until 13:00. The hourly growth rate of ground-level ozone concentration, as seen in figure 4, was very high, up to 50 μg/m^{3}h. Thus, an

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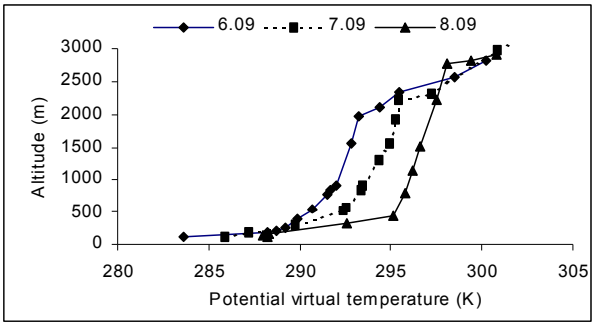

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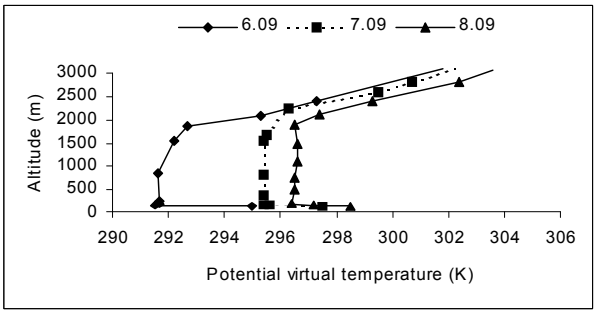

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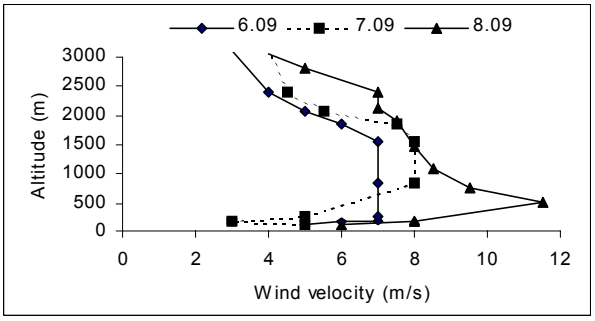

Fig. 6. Profiles of potential virtual temperature at 00:00 UTC (a), 12:00 UTC (b) and wind velocity at 12:00 UTC (c) from 6 to 8 September, 2003

obvious change in the pollutant levels coincides with the changes in mixing

processes late in the morning and the period of increasing photolysis rate (e.g., NO_2 concentration reached a low level at noon, probably due to photochemical loss and an increase in the mixing layer). The sounding made at 13:00 LT on the 15th July revealed that during the daytime the boundary layer was becoming increasingly unstable up to the height 1200 m. The comparison of the MH and environmental lapse rates in the surface layer on the 15th July with those on the 16th and the 17th July allows us to observe a stronger turbulence on the 16th and the 17th July. The surface layer is characterized by a superadiabatic lapse rate which was the highest on the 17th July. Mixing processes caused mainly by turbulent diffusion are vigorous within this layer (STULL [32]). In the second episode, similar relations were observed: the highest MH and environmental lapse rate as well as ozone concentration on the third day, September the 8th. The wind observations show a very similar trend. The wind velocity increases in the day and reaches the highest level at the same time as ozone concentration. Also the wind velocity increased with height on the 8th September which additionally highlights the potential significance of mixing processes at that time.

In order to confirm that some boundary layer factors are involved in the morning ozone build-up in the air of urban area, a simple multivariate linear regression analysis was performed. There were distinguished two independent variables: (1) the height of mixed layer H_M and (2) environmental lapse rate in the surface layer γ_i. The ML is referred to a layer between the ground and the base of capping inversion. As shown in figures 5 and 6, the surface layer, i.e., superadiabatic layer, could be estimated in a relatively simple way from temperature profiles. Because radiosonde measurements are available once a daytime (at noon) at Wrocław airport, we decided not to determine one numerical value of the ozone concentration at noon, but to apply the criterion for averaging ozone concentrations. Ozone values were averaged over the morning hours between 09:00–13:00. During this period the mixing layer growth rate should be the highest, if not, ozone concentration remains low. Slow mixing after sunrise leads to the high content of NO_x and low ozone concentration even later in the morning as was detected on the 15th July. Strong mixing during the morning hours affects considerably the build-up of high concentration of ground-level ozone.

The analytical formula derived for the period from the 1st to the 31st July 2003 was:

$$C_{O_3} = 0.029H_M - 8.77\gamma_i + 13.64\,. \tag{1}$$

Figure 7 shows calculated vs. observed ozone concentrations in July 2003. There is some scatter of results, but the multiple correlation coefficient $R = 0.78$ is quite high. The resulting equation explained 61% of the original variability ($R^2 = 0.61$). An average predicted error approached 26 μg O_3/m^3. Although this calculation makes some crude estimations (no accounting for chemistry), it does indicate that some boundary layer pa-

rameters may contribute significantly to the local ozone budget. Ozone concentration showed a positive association with the height of ML and a negative one with the environmental lapse rate in the surface layer. It should be stressed that under unstable conditions the gradient is negative which means higher ozone concentration.

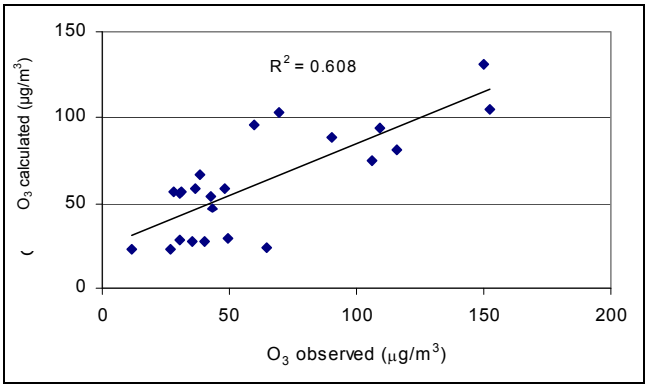

Fig. 7. Observed and calculated 4-hour averaged O_3 concentration (9:00-13:00 LT) in July 2003

Actually, the mixing height can be positively related to the surface ozone concentration which has been presented and discussed by RAO et al. [25], DELCLOO and BACKER [8] and CRISTOFANELLI et al. [7]. It has been suggested that the ozone measured at the surface may be produced in upper troposphere. However, the increase in mixing layer may also be related to the excess amount of ozone produced photochemicalally as photochemical conditions improve with an increase in the mixing depth (higher doses of solar radiation, better dilution of ozone precursors).

Ozone-rich layers in the troposphere have been mentioned in some recent studies (RAO et al. [25], COLETTE et al. [5]). Also our previous measurements (ZWOŹDZIAK et al. [39]) carried out by a DIAL (Differential Absorption Lidar) technique in the valley of the western Sudeten showed the great vertical variations in ozone concentration. Such ozone-rich layers of aged tropospheric air masses are likely to be formed during transport over large distances and, after having undergone mixing with local air, may contribute to the increase in pollutant background concentration. From July 15–17 the effect of high-pressure system over Scandinavian region became limited. The south-western Poland was in the area of weak-pressure gradient between two high- and two low-pressure systems. During these days, the pressure slowly fell. Similar meteorological conditions were observed from 5 to 8 September. Poland was at the edge the Scandinavian High. In the following days, the pressure was slowly decreasing giving way to a depression entering from the west. This situation improved overnight between 17 and 18 July as well as between 8 and 9 September, after the passage of a cold front.

A synoptic anticyclone creates favourable conditions for layering processes and

a longer lifetime of the layers formed, and thus enhanced photochemical ozone production within them. According to the study of CRISTOFANELLI et al. [7], ozone episodes, at the high-mountain station of Mt. Cimone (2165 m a.s.l.), were recorded during August 2003, when air masses travelled within the region, being considered to be the important source of ozone precursors, during the previous 24 h before reaching

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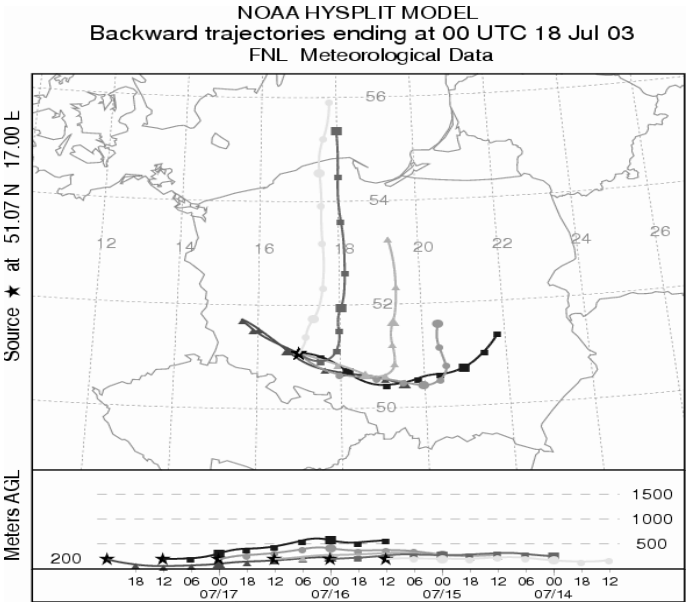

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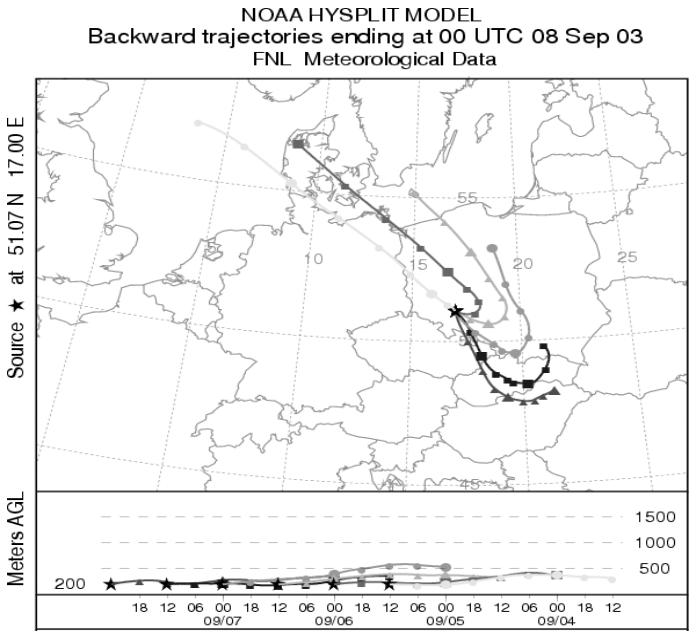

Fig. 8. HYSPLIT 48-h backward trajectories from an altitude of 200 m arriving in Wrocław and calculated for the period of 15–18 July (a) and 5–8 September 2003 (b)

the measuring station. This statement is supported also by our trajectory analysis performed on the respective data in July and September. HYSPLIT backward trajectories calculated for the periods of 16–18 July 2003 and 6–8 September (figure 8) indicate that the air quality has mainly been influenced in those days by air masses arriving from the east and south-east directions. Air masses of the east and south-east origin travelled a considerable time across industrialized and densely populated region which in the last part covers Upper Silesia (July) and Cieszyn Silesia, an industrialized and densely populated region in Poland, and the Czech Republic, ca. 240 km from Wrocław. The average wind velocity (below 3 m/s) was low. Air masses stagnating over this area and slowly pushed by advection towards the west or north-west are likely to undergo some layering processes and chemical transformation during transport due to its long time. These aged air layers focused our attention on the impact of the mixing processes before the noon on high ozone concentration recorded during that time in Wrocław.

4. CONCLUSIONS

The present study examined half-hourly ozone variations in Wrocław during July and September 2003. Ozone concentration was shown to be highly variable in the

surface layer, and the boundary layer evolution could have an important impact on ozone background concentration. It must be stressed that in comparison to a typical set of urban photochemical smog cycle profiles, the ozone concentration was very high relative to the local nitrogen oxide levels, and an ozone maximum quite often did not appear in the late afternoon but around the noon.

These high ozone values can be explained not only by photochemical ozone production directly related to favourable meteorological conditions (stagnation, radiation and temperature), but also by the positive feedback between the weakening of a high-pressure system and ozone production efficiency.

The results suggest that the intensity of mixing processes early in the morning contributed significantly to the morning ozone build-up at this site. The formation of unstable surface layer was confirmed by the environmental lapse rate. The depth of ML could also testify to the air turbulence intensity. If there was little ambient air turbulence and hence the shallower mixed layer, there was no way to dilute some ozone local precursors. The earlier (a weaker nocturnal inversion) and the faster the ML growth (the higher the environmental lapse rate in the surface layer and the greater ML depth at noon), the larger the increase in ozone levels expected around the noon. During the mixing both the downward transport of aged air masses and photochemical processes are very efficient and result in very high ozone concentration.

However, the question arose, where did those ozone-rich layers come from? Combining the results obtained by RAO et al. [25], COLETTE et al. [5], CRISTOFANELLI et al. [7] and others with those found in the present study, it can be suggested that the ozone reservoir could persist aloft for a couple of days under stagnant conditions in Central Europe, its source region could lie several hundreds of kilometres from Wrocław. Even if further analyses will be carried out to evaluate better the downward ozone transport and the origin of ozone-rich layers, this case study shows that in the understanding of the ambient ozone variations, some synoptic and regional phenomena cannot be neglected.

ACKNOWLEDGEMENT

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PORANNY WZROST STĘŻEŃ OZONU PODCZAS LETNICH EPIZODÓW 2003 ORAZ ICH POWIĄZANIE Z WYNIKAMI RADIOSONDAŻY WE WROCŁAWIU, POŁUDNIOWO-ZACHODNIA POLSKA

Podczas lata 2003 obserwowano duże stężenia ozonu, do 400 μg/m^3, w atmosferze Wrocławia, południowo-zachodnia Polska. Epizody te trwały zazwyczaj trzy dni, a maksymalne stężenia wzrastały sukcesywnie od pierwszego do trzeciego dnia. Zachowanie takie było zbieżne ze zwiększeniem się chwiejności atmosfery po wschodzie słońca i słabszą inwersją radiacyjną podczas kolejnych dni. Średnie 4-godzinne stężenie ozonu (09:00 – 13:00) było dodatnio skorelowane z wysokością warstwy mieszania, a ujemnie – z gradientem temperatury w warstwie powierzchniowej w południe. Te dwie zmienne niezależne tłumaczyły 61% całkowitej zmienności stężeń ozonu z błędem standardowym 26 μg/m^3. Wyjaśnieniem dużych stężeń ozonu nie była lokalna emisja gazów spalinowych ze środków transportu, lecz dodatnie sprzężenie między słabnięciem systemu podwyższonego ciśnienia a wzrostem znaczenia procesów mieszania (m.in. wyższa wydajność tworzenia ozonu w atmosferze miejskiej, pionowy transport dojrzałych mas powietrza z dużych wysokości), co zostało potwierdzone przez dobrze udokumentowane epizody i analizę trajektorii wstecznych.