Meteorol. Zeitschrift, N.F. 7, 15-18 (Februar 1998)

Diurnal courses of ozone in an inner urban park

A. STRASSBURGKR **and W.** KUTTLER, **Essen**

Summary. The aim of the investigation was the analysis of diurnal courses of **O3** concentrations in a large inner urban green area. For that purpose, 10 field experiments with durations of up to 54 hours were carried out in the Grugapark (70 ha) in the city of Essen (Ruhr, Germany) between May 1995 und August 1996 during calm clear weather conditions in summer. 50 % of the diurnal courses showed two **O3** maxima. In the daytime the **O3** concentrations were higher than at reference stations at the outskirts on the leeside of Essen and in the highlands (Eifel) in 30 % of the cases. The observed nocturnal **O3** maxima occurred during stable atmospheric conditions in the second half of the night. Distinct increases in air temperature of up to 3 K near the surface were found at the same time. This is an indication of vertical **O3** transport from the urban residual layer to the ground level, which may be induced by increased turbulence after the development of a nocturnal low-level jet. The horizontal transport of 0_3-rich air masses from the cooler rural area by a country breeze can be excluded in this connection.

Ozontagesgänge in einem innerstädtischen Park

Zusammenfassung. Ziel der hier vorgestellten Untersuchung war die Analyse von Ozontagesgängen in einer großen **Urbanen** Grünfläche. Dazu erfolgten 10 Meßkampagnen von bis zu 54 h Dauer im Grugapark (70 ha) der Stadt Essen (Ruhrgebiet, Deutschland) im Zeitraum von Mai 1995 bis August 1996 während sommerlichen austauscharmen Strahlungswetters. 50 % der gemessenen Tagesgänge wiesen zwei Ozonmaxima auf. Tagsüber wurden in 30 % der Fälle höhere Ozonimmissionen gemessen als an Referenzstationen am leeseitigen Stadtrand von Essen und im Mittelgebirge (Eifel). Die nächtlichen Ozonmaxima traten bei stabiler atmosphärischer Schichtung in der zweiten Nachthälfte auf. Zeitgleich wurden in Bodennähe deutliche Temperaturanstiege von bis zu 3 K festgestellt. Das weist auf einen Vertikaltransport des Ozons aus der städtischen Reservoirschicht in bodennahe Schichten hin. Dieser Transport kann durch Turbulenzanregung nach Ausbildung eines nächtlichen Grenzschichtstrahlstroms induziert werden. Ein Horizontaltransport ozonreicher Luft aus dem kühleren Umland — etwa durch einen Flurwind — ließ sich in diesem Zusammenhang ausschließen.

1. Introduction

Mean diurnal courses of ground-level O3 concentrations are characterized by a main maximum in the day and a minimum in the night during summer weather conditions with low wind velocities and high radiation fluxes. Moreover nocturnal secondary maxima can occur. The amplitude of the daily course of O3 concentrations at ground level is determined by the interaction of O3 sources (NO2, volatile organic Compounds), O3 sinks (chemical reactions, deposition) and meteorological conditions [radiation intensity (NO2 photolysis: $\lambda < 420$ nm), air temperature, horizontal and vertical exchange processes]. Large cities and areas on their leeside are characterized by relatively high O3 maxima during the day **(FABIAN** et al. 1993) and a strong fall in concentrations during the night **(BAUMBACH** 1993). In comparison, a typical diurnal course of O3 concentrations in regions remote from emissions, especially high in the mountains, has medium O3 concentrations with low or even no daily amplitude (e.g. **MAYER** et al. 1994). In the case of a diurnal O3 course with two maxima (e.g. **SAMSON** 1978), the main maximum usually occurs in the afternoon, the secondary maximum in the night. Nocturnal O3 maxima were observed for example in the Hamburg area after at least six hours of negative radiation balance **(WlNKLER** 1980). According to **JACOBI** and **ROTH** (1995) it can be assumed that an increase in turbulence can be caused by growing shearing stress between the ground-level layer and the upper limit of the temperature inversion following the development of a nocturnal low-level jet. This may be due to vertical mixing of O3 from the residual layer down to the ground level, as observed by **CORSMEIER** et al. (1997) in a rural area. In an attempt to clarify the structure of diurnal O3 courses in an inner-city park, measurements were made in the city of Essen.

2. Investigation area

Field experiments were carried out in the Grugapark, the largest park in the city of Essen between May 1995 and August 1996. The park has an area of 70 ha and attracts about 1 million visitors per year. The land-use structure of the park is mainly determined by small woods (29 %) , grass areas (28 %) , flower beds, shrubs (6%) as well as pavements, buildings and sports facilities (37%). A motorway is located to the south of this urban green area, and there is a busy main road to the east (about 50 m and 250 m from the park boundary respectively).

0941-2948/98/0007-0015 $ 01.80

3. Methods

The measurements of diurnal courses of air pollutants in the Grugapark were carried out by a mobile laboratory of the University of Essen. A total of 10 measurements with a duration of up to 54 hours were made. The instruments of the laboratory van allow the registration of the atmospheric trace-gas concentrations of O_3 (UV absorption), NO, NO_x (chemiluminescence), non-methane hydrocarbons (GC-FID) and CO (IR absorption) as well as the meteorological parameters: global radiation, UV radiation (295–385 nm), radiation balance, wind direction and velocity, air temperature and humidity.

The measurements were carried out mainly during calm clear weather conditions in the summer (maximum global radiation intensities > 670 W m^{-2}, mean wind velocities < 2 m s^{-1}).

4. Results

The results showed diurnal courses of O_3, characterized by a main and a secondary maximum in 50 % of the 10 measurements (Weather conditions: 26.06.95 HB, 06.06.96 BM, 21.07.96 HM, 22.07.96 HM, 08.08.96 HFa). The diurnal course of O_3 concentrations was marked by ascending concentrations in the morning which reached maxima over 128 µg m^{-3} in the afternoon or in the early evening (mean maximum value for the diurnal courses with two maxima: 168 ± 38 µg m^{-3}). This was followed by a distinct decrease in O_3 concentrations of at least 58 µg m^{-3} (mean value: 16 ± 25 µg m^{-3}). The nocturnal secondary maximum is caused by a distinct increase in O_3 concentrations which occurred after midnight (time of maximum concentration values: 1:50 CET ± 1:10 h). In our investigations the nocturnal maximum reached more than 31 % (mean value: 75 ± 14 µg m^{-3}) of the maximum in the daytime in each measurement. Fig. 1 shows an example of a diurnal course of O_3 concentrations of this type.

4.1. Main maxima in the daytime

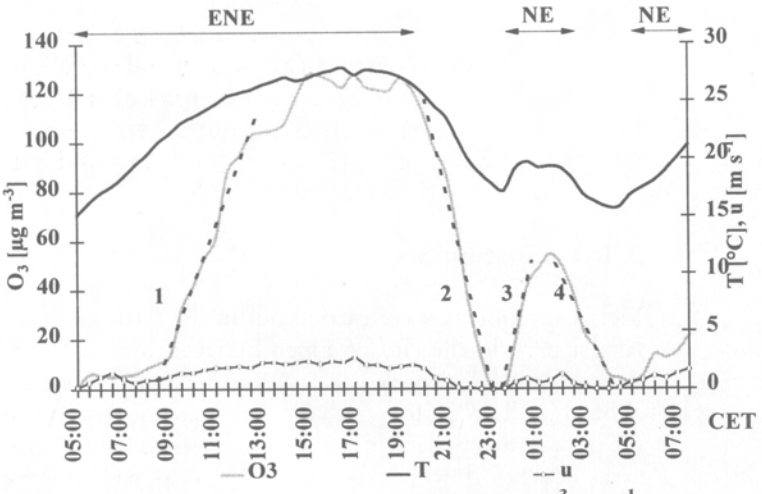
The comparison of the specific results of summer measurements in the Grugapark with data of the official network of the North Rhine-Westphalia State Environment Agency located at the outskirts on the leeside of Essen and in the highlands (Eifel) showed distinct differences (Fig. 2). The amplitudes of the diurnal courses within the park and on the outskirts of the city are higher than in the highlands. There is a significant time lag between the increase in O_3 concentration in the park and on the outskirts of the city. This may be due to the transport of O_3 formed in the city to the outskirts to the leeside of the city.

Three of the 10 measurements carried out in the park indicated higher main O_3 maxima in some cases (up to 40 %) than on the outskirts or in the highlands. The question as to why O_3 values in the Grugapark may be higher in some cases than those at the reference stations during weather conditions with high radiation intensities has not yet been solved.

In general, the following processes have been discussed as possible causes of O_3 concentration maxima during the day:

— The maximum may be caused both by horizontal and vertical transport. As regards vertical transport it is suggested that 50–70 % of the maximum may be due to convective mixing of O_3 from the previous day stored in the residual layer (NEU et al. 1994).

— Moreover, local chemical processes may be important for



Rates of O_3 increase: **1: + 0.42 µg O_3 m^{-3} min^{-1}**
3: + 0.69 µg O_3 m^{-3} min^{-1}

Rates of O_3 decrease: **2: - 0.65 µg O_3 m^{-3} min^{-1}**
4: - 0.48 µg O_3 m^{-3} min^{-1}

Fig. 1. Example of a diurnal course of O_3 concentration: 30-min mean values of O_3 concentration as well as wind velocity (u) 10 m above ground level and air temperature (T) 2 m above ground level in the Grugapark, Essen (26./27.06.1995, data base: 10-s-values).

Abb. 1. Beispiel für einen O_3-Tagesgang: 30-min-Mittelwerte der O_3-Immissionen sowie zeitlicher Verlauf von Windgeschwindigkeit (u) in 10 m Höhe ü. Gr. und Lufttemperatur (T) in 2 m Höhe ü. Gr. im Grugapark, Essen (26./27.06.1995, Datengrundlage: 10-s-Werte).

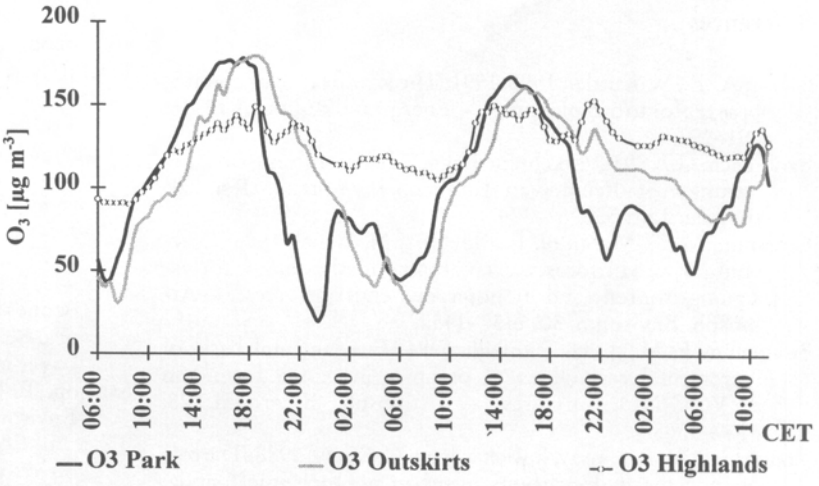


Fig. 2. Comparison of a diurnal course of O_3 (30-min mean value) in the Grugapark (110 m NN), Essen, with data of the official network of the North Rhine-Westphalia State Environment Agency on the outskirts of Essen (153 m NN, 2.4 km to the Southwest of the Grugapark, Essen) and in the highlands (Eifel, 572 m NN, 110 km to the Southwest of Essen) (21.–23.07.1996, data base: 10-s-values resp. 1-min-values).

Abb. 2. Vergleich eines O_3-Tagesganges (30-min-Mittelwerte) des Grugaparks (110 m NN), Essen, mit TEMES-Daten des Landesumweltamtes NRW einer Stadtrandstation (Essen, 153 m NN, 2,4 km südwestlich des Grugaparks) und einer Mittelgebirgsstation (Eifel, 572 m NN, 110 km südwestlich von Essen) (21.–23.07.1996, Datengrundlage: 10-s-Werte bzw. 1-min-Werte).

O_3 formation. Especially in large urban park areas there is a certain possibility that local anthropogenic and biogenic precursors may contribute to this phenomenon (BOWMAN and SEINFELD 1994, TAHA 1996, CORCHNOY et al. 1992). For example, CHAMEIDES et al. (1988) calculated the oxidation potential caused by biogenic hydrocarbons at 30 % referred to the total hydrocarbons in Atlanta. In the state of Baden-Württemberg up to 18 % of the O_3 may be produced by biogenic precursors (VOGEL et al. 1995).

As regards estimates of biogenic volatile organic compounds it should be mentioned that there are several uncertainties with respect to the emission rates of plants. The data available have been obtained by measurements made on a variety of plant species in different vegetation zones using different types of measurement equipment (FEHSENFELD et al. 1992). For example, for liquidambar (*Liquidambar styraciflua*), emission rates ranging from 3.5 to 35.3 µg g(dry mass)$^{-1}$ h^{-1} were measured (BENJAMIN et al. 1996). For this reason, the share of biogenic hydrocarbons in O_3 formation should not be estimated solely using numerical models based on emission rates. Such estimates should be supported by appropriate field measurements of biogenic emissions and ambient air concentrations.

4.2. Nocturnal secondary maxima

In view of the lack of solar radiation, the nocturnal O_3 increase is purely a meteorological phenomenon not affected by photochemical processes. There are two theoretical explanations for this phenomenon: firstly vertical transport of O_3 to the ground from the residual layer located over the ground inversion by an occasional breakdown of stability (e.g. WINKLER 1980); secondly local wind systems, e.g. a country breeze (BARLAG and KUTTLER 1990/1991, KUTTLER 1996), that is a horizontal ground-level cold air flow, can transport air rich in O_3 from the cooler rural area into the warmer city.

With respect to our measurements, horizontal O_3 transport by country breezes from rural areas cannot be assumed as a possible cause. In view of the distinct increase in wind velocity and air temperature near the surface (ΔT = 3 K) during the secondary O_3 maximum in the park it can be assumed that this O_3 may descend from the urban residual layer as a result of increased turbulence.

In general, the decrease in O_3 concentrations may be caused by deposition and by reactions of O_3 with NO and NO_2 forming NO_2 and NO_3 respectively (GÜSTEN et al. in press). In contrast to the fall in O_3 concentration in the evening the nocturnal decrease is a slower process (Fig. 1: *evening*: rate of O_3 decrease: –0.65 µg m^{-3} min^{-1} (mean value for the diurnal courses with two maxima: –0.57 ± 0.25 µg m^{-3} min^{-1}), NO_x concentrations: NO: 57 µg m^{-3} (24 ± 24 µg m^{-3}), NO_2: 75 µg m^{-3} (61 ± 42 µg m^{-3}), *night*: rate of O_3 decrease: –0.48 µg m^{-3} min^{-1} (–0.26 ± 0.18 µg m^{-3} min^{-1}), NO_x concentrations: NO: 2 µg m^{-3} (1 ± 1 µg m^{-3}), NO_2: 40 µg m^{-3} (27 ± 22 µg m^{-3})).

The O_3 decrease in the evening may be mainly the result of reaction due to the relatively high NO_x concentrations. For the depletion of the secondary maximum after vertical transport in the night at comparatively low NO_x concentrations, deposition may play a certain role in addition to chemical reactions (HARRISON et al. 1978).

Acknowledgements

This work was supported by the Forschungsvereinigung Automobiltechnik e.V. (FAT), Frankfurt/Main, within the framework of the project "Analysis of automobile caused air pollutants in inner urban traffic and green areas" and by the research pool of the University of Essen as a part of the project "Horizontal concentration profiles of ozone precursors between urban traffic and green areas". The authors wish to thank A. SCHMIDT (laboratory technician) and R. ZIMMERMANN (technical assistant) for their effective help with the field experiments.

References

Barlag, A.-B., W. Kuttler, 1990/1991: The significance of country breezes for urban planning. — Energy and Buildings 15-16, 291-297.

Baumbach, G., 1993: Verkehrsbedingte Schadstoffimmissionsbelastung in Städten und an Autobahnen. — Staub - Reinhaltung der Luft 53, 267-274.

Benjamin, M. T, M. Sudol, L. Bloch, A. M. Winer, 1996: Low-emitting urban forests: a taxonomic methodology for assigning isoprene and monoterpene emission rates. •— Atmosph. Environm. 30,1437-1452.

Bowmann, F. M., J. H. Seinfeld, 1994: Fundamental basis of incremental reactivities **of** organics in ozone formation on VOC/NOx mixtures. — Atmosph. Environm. 28, 3359-3368.

Chameides, W., R. Linsay, J. Richardson, C. Kiang, 1988: The role of biogenic hydrocarbons in urban photochemical smog: Atlanta case study. — Science 241, 1473-1475.

Corchnoy, S. B., J. Arey, R. Atkinson, 1992: Hydrocarbon emissions from twelve urban shade trees of the Los Angeles, California, Air Basin. — Atmosph. Environm. 26B, 339-348.

Corsmeier, U., N. Kalthoff, O. Kolle, M. Kotzian, F. Fiedler, 1997: Ozone concentration jump in the stable nocturnal boundary layer during a LLJ-event. — Atmosph. Environm. 31, 1977-1989.

Fabian, R, G. Jakobi, C. Haustein, H. Mayer, B. Rappenglück, P. Suppan, 1993: Erfassung von human-biometeorologisch relevanten Photooxidantien und deren Vorläufern in einem Ballungsraum. — GSF-Ber. 31, 57-73.

Fehsenfeid, F., J. Calvert, R. Fall, P. **Goldan,** A. B. Guenther, C. N. Hewitt, B. Lamb, S. Liu, M. Trainer, H. Westberg, P. Zimmermann, 1992: Emission of volatile **organic Compounds** from **Vegetation and** the **implication** for atmospheric chemistry. — Global Biogeochemical Cycles 6, 389-430.

Güsten, H., G. Heinrich, D. Sprung, in press: Nocturnal depletion of ozone in the upper Rhine valley. — Atmosph. Environm.

Harrison, R. M., C. D. Holmann, H. A. McCartney, J. F. R. Mcllvern, 1978: Nocturnal depletion of photochemical ozone at a rural site. — Atmosph. Environm. 12,2021-2026.

Jacobi, C., R. Roth, 1995: Organisierte mesoskalige Störungen in der stabilen planetaren Grenzschicht. — Meteorol. Z. N.F. 4, 150-161.

Kuttler, W, 1996: Aspekte der Angewandten Stadtklimatologie. — Geowissenschaften 14, 221-228.

Mayer, H., J. Schmidt, A. Matzarakis, 1994: Lufthygienische Kennzeichen von stadtnahen Wäldern. — Wetter und Leben — Z. f. Angew. Meteorol. 46, 49-65.

Neu, U., T. Künzle, H. Wanner, 1994: On the relation between ozone storage in the residual layer and daily **Variation** in the near-surface ozone concentration - A case study. — Bound. Layer Meteorol. 69, 221-247.

Samson, P. J., 1978: Nocturnal ozone maxima. — Atmosph. Environm. 12, 951-955.

Taha, H., 1996: Modeling impacts of increased urban Vegetation on ozone air quality in the South Coast Air Basin. — Atmosph. Environm. 30, 3423-3430.

Vogel, B., F. Fiedler, H. Vogel, 1995: Influence of topography and biogenic volatile organic Compounds emissions in the State of Baden-Württemberg on ozone concentrations during episodes on high air temperatures. — J . Geophys. Res. 100, 22,907-22,928.

Winkler, P, 1980: Störungen der nächtlichen Grenzschicht. — Meteorol. Rdsch. 33, 90-94.

Dipl.-Chem. ANJA STRASSBURGER
Prof. Dr. rer. nat.
WILHELM KUTTLER
Institute of Ecology
Department of Landscape Ecology
University of Essen
D-45117 Essen
E-mail:
a.strassburger@uni-essen.de
w.kuttler@uni-essen.de

Received 31 March 1997, in revised form: 8 August 1997