Correlation between urban early ozone minimum and solar radiation
J.C. Guerra, S. Rodríguez, J.P. Díaz & A. Díaz.
Physical Atmosphere and Environmental Group
Department of Physics, University of La Laguna
38071, La Laguna, S/C Tenerife, Canary Islands, Spain

Abstract

The surface ozone concentration measured in urban and semiurban atmospheres shows in its daily pattern an early morning minimum and an afternoon maximum. In some cases, it can be observed a second minimum after sunset. These variations can be attributed to the daily pattern of other pollutants. After the first minimum in O3 daily variation, the increment of ozone concentration can be attributed to photochemical formation and to the transport from the higher layer, when the boundary layer is raised. In all cases the driver of both process is the solar radiation, therefore it should be a direct relation between them. We have find in our preliminary studies that the early morning ozone minimum has a seasonal variation in its time of occurrence. This variation can be attributed to some causes. A natural causes is the variation of level of radiation that reach the surface, which displace the balance between the mechanism of destruction and production of ozone in urban and semiurban areas.

Introduction

The surface ozone concentration measured in urban and semiurban atmospheres shows the direct influences of local pollution. One of this effects appear in the daily pattern, which are characterized by an early morning minimum and an afternoon maximum. In some cases, it can be observed a second minimum after sunset (Guicherit R. [1]). These variations can be attributed to the daily pattern of other pollutants, mostly
nitric oxide and VOCs. Also there are important differences between the weekdays and the weekends.

After the first minimum in \( O_3 \) daily variation, the increment of ozone concentration can be attributed to photochemical formation and to the transport from the higher layer, when the boundary layer is raised (Logan et al. [2]). In all cases the driver of both process is the solar radiation, therefore it should be a direct relation between them.

**Site description and instrumentation**

The concentration of tropospheric ozone and solar radiation used in this paper were measured in a small town, La Laguna (Tenerife, Canary Islands, 28° N & 16° 3' W)) situated under the inversion layer, at an altitude of approximately 550 meter at sea level. The station is placed on a building roof, close to a highway with heavy traffic at peak hours (principally at about 08 and 20 local official time on working days), therefore local pollution must be noted.

In the La Laguna university station a UV spectrophotometer DASIBI #1108 has been used since November 1990. This instrument was calibrated against the USA-NBS by S. Oltmans [S. J. Oltmans, private communication]. Periodically we compare and calibrate our spectrophotometer with the instruments at Izaña (Díaz A. Et al. [3]) whose calibration is tied to the U.S. National Institute of Standards Technology reference \( O_3 \) photometer. This analyzer has been completely automated (Guerra J. C. et al [4]) by using the RS-232C interface incorporated in the Dasibi #1108.

The values of irradiance had been measured with a piranometer which work in the espectral range of 350-1100 nm.

**Surface ozone concentration in La Laguna**

The \( O_3 \) concentrations measured at LLO, show the direct influence of local pollution sources, specially the vehicular traffic emission (some recent studies give values less than 0.01% for VOCs and a 0.05% for NOx industry emissions (Corine Program [5]) in La Laguna). The influence of the traffic emissions over the \( O_3 \) in La Laguna appear
clearly in the daily variation. Standard diurnal variation, that is to say the mean monthly values for each hour of the day, were computed for weekdays and weekends, due to the different behavior of the primary components sources. The results show minimums at 08 hours during the weekdays and everyday at 20 hours (Fig.1). This behavior is closely related to road traffic density. Our study found that the typical daily pattern of road traffic for weekdays has two important maximums at 8 and 20 local time. Also we can see that this daily pattern is different on the weekends, which is characterized by only a broad maximum at 20 local time (Guerra et al. [6]).

![Graph showing diurnal variation of surface ozone in La Laguna during 1992 calculated for weekdays.](image)

**Fig. 1a.-** Standard diurnal variation of surface ozone in La Laguna during 1992 calculated for weekdays.

Other evidence about this minimum origin, appear clearly in the representations (Fig.2b). We can see that the bottom of the valley (specifically the first minimum) is not fixed at the same time. We observed that during some months (April-September) the minimum is an hour before with respect to the rest of the year. This is only a result due to the change in local time (Daylight Savings Time) that occurs every year in Spain, which delays the peak density of traffic.
Surface ozone concentration and solar radiation

The daily variation of surface ozone in urban-semiurban atmospheres are usually characterized by an afternoon maximum, due to diurnal photochemical production and by an early morning minimum (we named as "Minimum Laguna"), due to nocturnal destruction process from precursors constituents (NOx, VOCs, etc.) (Bowman F.M. et al [7], Cox R. A. [8]). The minimum O$_3$ value reached in the morning must be temporarily located at the time when the destruction and production process of ozone are balanced. After this moment the photochemical production and upper transport produce a displacement of this balance and lift the ozone concentration until the observed maximum.

This temporal dependence of the early morning O$_3$ minimum with the balance of the process of destruction and production can be observed when we correlated the time of occurrence of this minimum with the level of solar radiation measured. When the only mechanism that can produce a displacement of this equilibrium is the seasonal variation of level of radiation, we must find that the time of occurrence of the
minimum move according with the hour in that a threshold of radiation it reached.

Fig. 2a.- Time of occurrence of the early morning surface ozone minimum and the threshold of 100 Wm$^2$ from April to August 1992.

To study this point we have analysed ozone concentration (10 minutes averages values) and measures of radiation in La Laguna during the year 1992. We have divide the study in temporal interval when we can guarantee that the only variation in the balance between destruction and production process of ozone is attributed to the variation of level of solar radiation during the year (we had see that the early morning O$_3$ minimum in La Laguna has a variation due to changes in local time).
We have studied the period from April to August, when we find the summer solstice, and a second period from October to February when we find the winter solstice. In both cases the local time don’t change.

Fig. 2b.- Time of occurrence of the early morning surface ozone minimum and the threshold of 100 Wm\(^2\) from October 1992 to February 1993.

In the figure 2a and 2b we show the hour when the ozone minimum is reached and the hour when an arbitrary threshold of radiation (100 Wm\(^2\)) is measured. We have selected this level of radiation by simplicity. The time of occurrence (ordinate variable in Fig. 3a and Fig. 3b) has in all cases a seasonal variation according to the daily variation in the sunrise time during the year. We can see that the time of occurrence presents a minimum in the summer solstice while a maximum is detected in the winter solstice.
Results and conclusion

The early morning urban ozone minimum has a seasonal variation in its time of occurrence. This variation can be attributed to some causes. A natural cause is the variation of level of radiation that reach the surface, which displace the balance between the mechanism of destruction and production of ozone in urban and semiurban areas.

References