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ASSESSMENT OF SURFACE OZONE VARIABILITY IN AN URBAN COASTAL AREA AT THE EASTERN MEDITERRANEAN

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ABSTRACT
The surface ozone is a pollutant of major concern due to its impact on receptors, at currently occurring ambient levels in many regions of the world. The aim of this work is to present the results derived from an analysis of hourly surface ozone concentrations, measured at the urban station of Volos, a coastal medium-sized city at the eastern seaboard of Central Greece, during the 8-year period 2001-2008. The regional climate that is characterized by hot and dry summers with intense sunshine plays an important role in the observed exceedances of the air quality ozone limits. The analysis showed that, ozone diurnal patterns depict daytime photochemical ozone built up, during the sunlight hours of the day. It is remarkable that the maximum daily 8-h averages often exceeded the standard value that is assigned by the EU Directive for human health protection, during almost the warm period of the year, mainly at noon and afternoon hours.

KEYWORDS: Surface ozone, temporal variability, trends, Volos, Eastern Mediterranean.

1. INTRODUCTION

Increased ground level ozone concentrations are currently a matter of concern since they have been more than doubled during the last decades (Volz and Kley, 1988; Staehelin and Smith, 1991; Vingarzan, 2004; Lamarque *et al.*, 2005). The importance of surface ozone effects on human health, animal population, plant growth, and its significant role in the energy budget of the troposphere have been reported in the literature (Lippmann, 1991; Brauer and Brook, 1997). The high background ozone values observed in Mediterranean regions may be attributed to the high levels of solar UV in combination with locally emitted anthropogenic ozone precursors. Since weather conditions (sunshine, high temperatures and low winds) significantly affect ozone formation, high concentrations occur mainly during the summer, in urban, suburban and rural areas. A number of scientific works on surface ozone regarding eastern Mediterranean regions underline the problem (Ziomas *et al.*, 1989; Glavas, 1999; Dueñas *et al.*, 2002; Kourtidis *et al.*, 2002; Kouvarakis *et al.*, 2002; Lelieveld *et al.*, 2002; Kalabokas *et al.*, 2000; 2007; 2008; Paliatsos *et al.*, 2006; 2008; Poupkou *et al.*, 2008; Papanastasiou and Melas, 2009). Based on the results reported in these papers, it would be expected that the high rural background ozone levels in the area actually control the surface ozone variability in small cities, in the Mediterranean basin, like Volos.

The main objective of the present study is to reveal the surface ozone temporal variability patterns over the area of Volos, a city of average size on the eastern seaboard of Central Greece. Reasons for the observed temporal variations of ozone levels are discussed. In addition, the data is discussed in relation to the surface ozone thresholds for human health protection set by the European Union.

2. DATA AND METHODOLOGY

In the current work an attempt is made to evaluate the temporal variability of surface ozone in Volos, based on mean hourly surface ozone concentrations recorded at the urban air pollution-monitoring station ($\lambda=22^0$ 57' E, $\phi=39^0$ 22' N, h=2.6 m a.m.s.l.), that started its operation in 2001 and was operating continuously until 2008. The station is provided with fully automated analyzers, that were installed by the Hellenic Ministry of the Environment, Energy and Climatic Change and were operated by the prefecture of Magnesia, in order to measure air pollution levels in Volos, which presents air pollution problems, like most urban areas in the world.

The city of Volos is located in Thessaly region, and extends along the northern part of the cove of the Pagassitikos Gulf on the eastern seaboard of Central Greece (Figure 1). The case of Volos is an interesting example, where the population shifts and the increased industrialization during the last decades have resulted in the degradation of the air quality in the area. Volos is a medium-sized city and has a population of about 120,000 inhabitants (census 2001). This city is a commercial and touristic city, the seaport of Thessaly with a great number of craft-based industrial, and commercial activities, as well as activities, that are related with tertiary sector services. A detailed description of the Volos topography and climate is found in various publications (e.g. Papaioannou *et al.*, 2010).

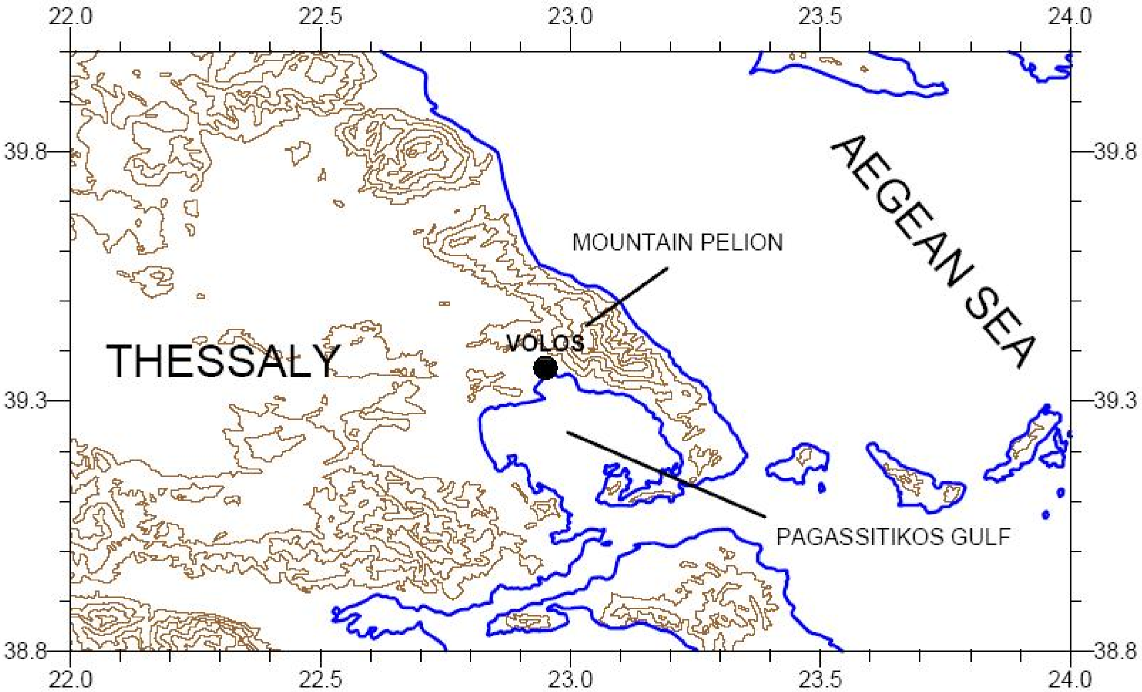

Figure 1. Map of the greater Magnesia's' area with elevation contours at 100 m intervals

The climate of Volos is of Mediterranean type with wet, mild winters and hot, dry summers. The average daily winter (December, January, February) temperature is 8.8 ^{0}C and 26.1 ^{0}C for the summer (June, July, August). The Mediterranean climate is characterized by rainfall deficiency during the warm period of the year. Therefore, from the average annual rainfall that is 420 mm, most occurs in November and during the winter months. The average daily relative humidity varies between 58% in July and 74% in November. The prevailing winds blow from north in early spring, autumn and winter and from south in late spring, summer and early autumn, in the area of Volos (Papaioannou *et al.*, 2010).

The air pollution problems are enhanced by the topography of the area and the city planning. Due to topography, the air masses are trapped within the greater area of Volos, especially during south-south-western wind blow, because of the Pelion Mountain, located to the northeast of the city (Papaioannou *et al.*, 2010). This wind blow is associated with the sea breeze, which occurs mainly during the hot period of the year and during the middle of the day, thus at the time when other parameters (temperature, sunshine duration) facilitate the formation of photochemical pollutants.

3. RESULTS AND DISCUSSION

Mean concentrations were computed for each day, month, and year during the 8-year period 2001-2008. Well-defined seasonal (Figure 2) and diurnal (Figure 3) patterns are revealed. These temporal fluctuations are further discussed.

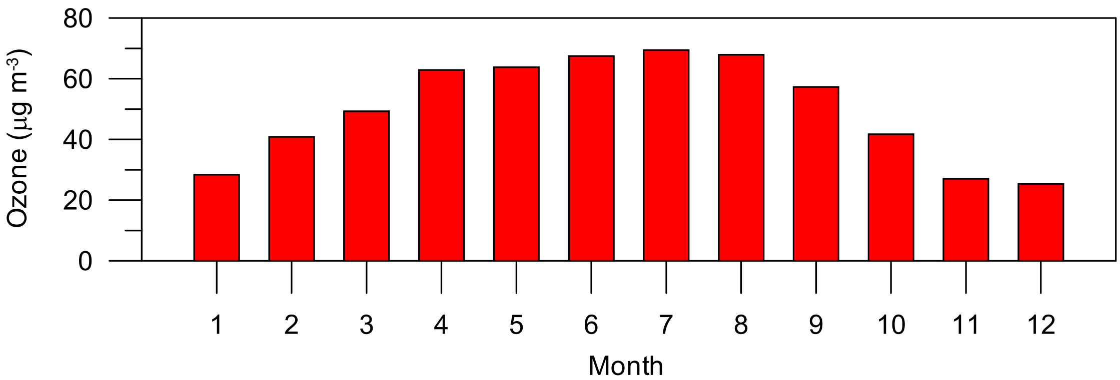

Figure 2. Mean monthly variation of surface ozone concentrations at the measuring site of Volos, from 2001 to 2008

Figure 2 shows the well-defined seasonal cycle of surface ozone concentrations at the urban station of Volos, for the examined 8-year period (2001-2008) with an annual mean value of 51±10 μg m^{-3} (1 standard deviation). The seasonal variation of ozone concentrations is characterized by a maximum during the warm period (April to September) and a minimum during the cold period of the year (October to March). The minimum value observed in December (25±5 μg m^{-3}) and the maximum value in July (69±17 μg m^{-3}) with a ratio 1:2.7.

The ozone concentrations in the troposphere follow a characteristic diurnal course with high concentrations in the early afternoon hours (when radiation and temperature favour ozone formation) and low concentrations during the late night hours until early in the morning (when only ozone destruction takes place). Using data for the period 2001-2008, the mean diurnal variation of surface ozone concentrations, separately during January, April, July and October, at the measuring site of Volos, is shown in Figure 3.

These months were chosen throughout this paper to contrast the surface ozone concentrations patterns from the climatic point of view. This peak is observed between 13:00 - 17:00 LST in January, 11:00-20:00 in April (Figure 3, upper panel), 10:00 - 20:00 in July, and 12:00 - 18:00 in October (Figure 3, lower panel). The amplitude of the diurnal variation ranges from 24 to 61 μg m^{-3}, for January and April respectively. The high amplitude of surface ozone diurnal variation, in July, is probably due to the high photochemical ozone production caused by the high solar insolation during the daytime period. It should be mentioned at this point that the diurnal variation pattern of surface ozone is consistent with the known built-up of ozone in the morning hours, which is caused partly by mixing down of the ozone-rich air from above and later on by photochemical production (Kelly *et al.*, 1984). During the evening and night hour's surface ozone is substantially decreased by chemical destruction and dry deposition (Ziomas *et al.*, 1989). This result emphasizes the strong dependence upon the total UV-solar irradiance reaching the earth of the photochemical surface ozone production. Similar patterns of seasonal variation have also been observed in other Mediterranean sites (Ziomas *et al.*, 1989; Dueñas *et al.*, 2002; Paliatsos *et al.*, 2006; Poupkou *et al.*, 2008).

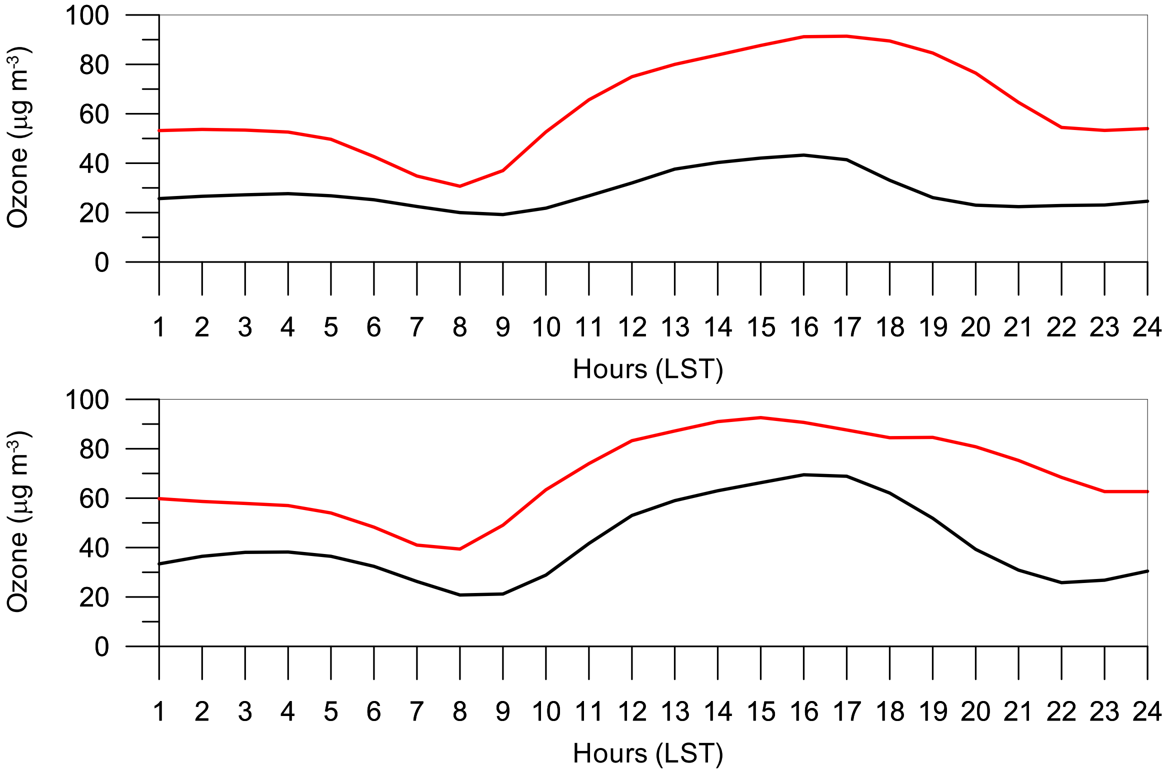

Figure 3. Mean diurnal variation of surface ozone concentrations, for the period 2001-2008, at the measuring site of Volos for January-April (black and red line, respectively; upper panel) and July-October (red and black line, respectively; lower panel)

The urban ozone levels of Volos (especially during the afternoon hours of the warm season) are lower than the corresponding average levels in Athens (Kalabokas *et al.*, 2000), but they are comparable with the corresponding average levels at rural sites such Aliartos (Kalabokas and Repapis, 2004; Paliatsos *et al.*, 2006; 2008).

The maximum daily 8-h moving averages of ozone concentration exceeded the target value of 120 μg m^{-3} for 23, 14, 12, 1 and 4 days in years 2001, 2002, 2003, 2004 and 2005, respectively (Figure 4). This result fulfils the conditions that EU (EU, 2002) determines for the beginning of the year 2010.

Although the primary pollutants were drastically reduced during the last years due to the gradual replacement of old cars with new technology cars (Papaioannou *et al.*, 2010), the ozone levels have not shown the same decreasing trend (Papanastasiou and Melas, 2009). This phenomenon is very likely to be attributed primarily to the preponderant influence of the rural background ozone levels on the measured ozone concentrations inside the urban area of Volos, even if significant reductions of local emissions of photochemical precursors are reported. Kalabokas and Repapis (2004), in a relevant paper, concluded that at the peripheral urban stations of the Athens urban area (with significantly higher emissions than Volos), even during the most favorable conditions for photochemistry, the local ozone photochemical production is only a minority fraction of the total ozone measured, the largest part being attributed to the regional background and transported to the urban area.

The mean annual course of maximum daily 8-h moving averages of surface ozone concentrations for the period 2001-2008 are shown in Figure 5, with vertical lines making the warm period interval. It can be seen that the maximum daily 8-h moving averages often exceeded the thresholdvalue (horizontal line) that is assigned by the EU Directive (EU, 2002) for human health protection, during almost the warm period of the year. This is in agreement with the results of Papanastasiou and Melas (2009) with respect to the area of Volos.

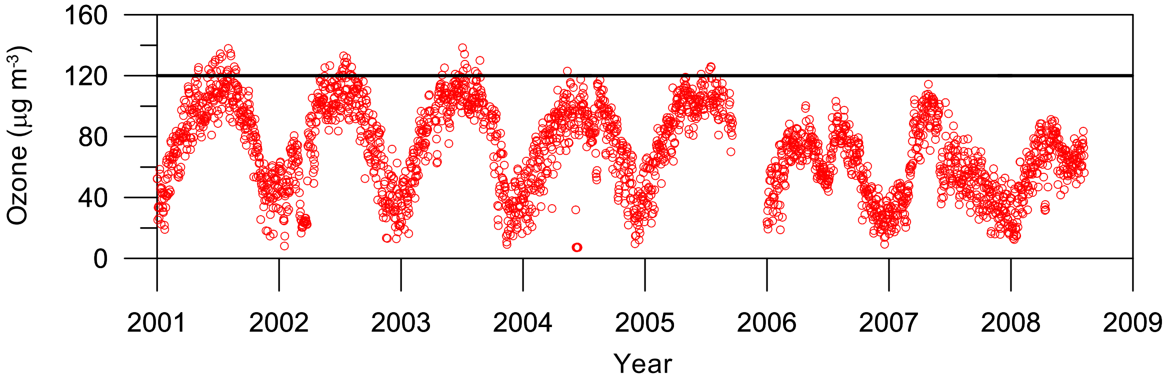

Figure 4. Temporal evolution of surface ozone maximum daily 8-h moving averages at the measuring site of Volos from 2001 to 2008; the horizontal line indicates EU threshold value, 120 μg m^{-3}

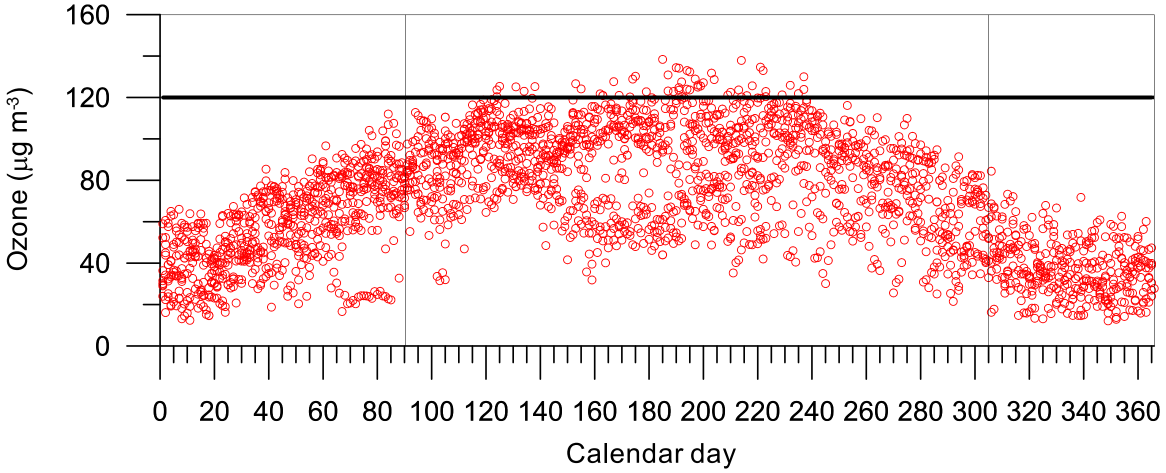

Figure 5. Mean annual variation of surface ozone maximum daily 8-h moving averages at the measuring site of Volos from 2001 to 2008; the horizontal line indicates EU threshold value, 120 μg m^{-3}

The fact that these violations are mainly observed during the warm period of the year is probably attributed more to meteorology (horizontal transport or vertical subsidence) than the photochemical ozone production caused by the high solar insolation during the daytime period of the season. It should be mentioned at this point that, the diurnal variation pattern of surface ozone is consistent with the known ozone built-up in the morning hours, which is caused partly by enriching the air with ozone from above and later on by photochemical production (Kelly *et al.*, 1984; Paliatsos *et al.*, 2008). Most of the violations are observed during the noon and afternoon hours at a station inside an urban area influenced by air of rural origin.

4. CONCLUSIONS

The hourly surface ozone concentrations measured at the urban station of Volos, continuously monitored for the period 2001-2008, were examined in order to study both the seasonal and the diurnal variation. From this analysis the following conclusions can be drawn:

1. The seasonal variation of surface ozone concentrations presents a minimum during the cold period of the year and a maximum during the warm period.
2. The mean diurnal variation of surface ozone concentrations at this rural measuring site has a single peak structure. This peak is observed between 13:00 - 17:00 LST in January, 11:00-20:00 in April, 10:00 - 20:00 in July, and 12:00 - 18:00 in October. The amplitude of the diurnal variation ranges from 24 to 61 μg m^{-3}, for January and April respectively.
3. The maximum daily 8-h moving averages of surface ozone concentration that exceeded the threshold value of 120 μg m^{-3} followed a decreasing during the examined period.

4. The regional climate, which is characterized by hot and dry summers with intense sunshine, plays an important role in the observed exceedances of the 8-h moving averages of surface ozone threshold value (120 μg m^{-3}) for human health protection, during the warm period of the year.

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