A Review of Surface and Lower Troposphere Ozone Concentration Characteristics Around the Urban Area of Athens, the Aegean Sea and at the Central and Eastern Mediterranean

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Abstract During the last 20 years, systematic studies of the variability of ozone concentrations by analyzing surface ozone measurements at peripheral Athens stations and at rural sites at Central Greece, the Aegean Sea and the Central and Eastern Mediterranean have been carried out. Also, ozone, humidity and carbon monoxide summertime vertical profiles collected over some Aegean and Eastern Mediterranean airports within the MOZAIC project have been analyzed. Special focus was given to the study of atmospheric circulation in the European/N. African sector by using composite synoptic meteorological maps during high and low summer ozone episodes. It comes out that for the examined area in the lower troposphere and in the boundary layer the role of the synoptic weather conditions and the associated large-scale transport of air masses seem to be more important for the ozone variability than the local or regional short-term ozone photochemical production. The highest ozone concentrations are associated with large scale tropospheric subsidence of ozone rich air masses under prevailing anticyclonic conditions (N. Africa) while the lowest ozone concentrations are associated with low pressure prevailing conditions (N. Europe) inducing a strong westerly flow of Atlantic air masses poor in ozone and rich in humidity to the Mediterranean basin.

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1 Introduction

Atmospheric ozone plays an important role in the physico-chemical processes of the troposphere, it is also an important greenhouse gas and it may cause damages to humans, animals and vegetation. About thirty years ago it was realized that increased surface ozone levels is an hemispheric or global scale phenomenon especially in the northern hemisphere (Volz and Kley 1988). Until the mid-90s there was a lack of systematic ozone measurements, especially in rural areas in south-eastern Europe and the eastern Mediterranean basin, where high background ozone levels are observed (Lelieveld et al. 2002; Zerefos et al. 2002).

In this work, a review of the research results on surface, boundary layer and tropospheric ozone characteristics carried out essentially at the Research Center for Atmospheric Physics and Climatology of the Academy of Athens during the last 20 years is presented. Special focus was given to the investigation of the meteorological and air pollution factors leading to high and low ozone levels in the boundary layer and the lower troposphere around the urban area of Athens, the Aegean Sea and at the Central and Eastern Mediterranean.

2 Data and Methodology

The analysis of surface ozone measurements in Athens was based at first at two peripheral monitoring station of the Athens urban area located to the E-NE at 10 km from the city center and to the N-NW at 12 km respectively. The data of an Athens urban background station have also been used. The Athens data were screened for cases of strong airflow from rural areas (only measurements under strong northerly winds were taken into account). Also, data from the Mediterranean rural stations of Aliartos (Central Greece), Finokalia (Crete), Gozo (Malta) and Ag. Marina (Cyprus) were also processed.

In addition Vertical MOZAIC (Measurement of Ozone and Water Vapor by Airbus in Service Aircraft; Marenco et al. 1998) profiles (1994–2008) from ascending and descending flights over the Aegean airports of Heraklion and Rhodes as well as the Mediterranean airports of Antalya, Cairo and Tel-Aviv have been analyzed. The analysis is focused on summertime (June to August) profiles. The analyzed parameters are: Ozone, carbon monoxide, relative humidity, temperature, and wind speed. The set of collected profiles is classified into groups of 7 % highest and lowest ozone levels for two vertical layers, 1.5–5 km representing the lower free troposphere, and 0–1.5 km representing the boundary layer.

In order to proceed to a detailed investigation of the atmospheric conditions prevailing during the ozone episodes, composite reanalysis maps covering Europe and North Africa of several meteorological parameters corresponding to the days with the highest and lowest ozone concentrations observed in the lower troposphere and the boundary layer over the Aegean and the Eastern Meditteranean airports

have been plotted. The maps were constructed from NCEP/NCAR reanalysis on a 2.5° × 2.5° grid at 850 and 700 hPa for the days of the ozone measurements and the preceding 3 days following the procedure of Kalnay et al. (1996). They include the following meteorological parameters: geopotential height, geopotential height anomaly, vertical velocity omega, vertical velocity omega anomaly, specific humidity anomaly, precipitable water anomaly, air temperature anomaly and vector wind. The anomalies are calculated as differences to the climatological mean 1981–2010.

Also, for the determination of the air-mass origin, the Lagrangian particle dispersion model FLEXPART (version 6.2; Stohl et al. 2005) was used in backward mode. The model was initialized by release of 20,000 particles from grid boxes of 0.5° × 0.5° horizontally and 100 m vertically centred on the MOZAIC profiles.

3 Results

Based on a series of ozone sounding over Athens (12/1991–03/1992), winter tropospheric ozone concentrations were higher by about 20 % in the lower and 10 % in the higher troposphere than corresponding measurements in N. Europe. Also, the March tropospheric average ozone concentrations were constantly higher by 10–15 ppb than in December through the whole troposphere (Varotsos et al. 1993).

Surface ozone measurements at a peripheral site at the NE edge of the Athens basin showed that summer ozone averages by about 60–65 ppb were higher when the wind was originating from the "clean" NE sector, if compared with the "polluted" SW sector (Kalabokas et al. 1996; Kalabokas and Bartzis 1998).

The rural ozone levels at the periphery of the urban area of Athens show a clear seasonal variation with maximum values in summer, followed by spring. The long-term rural summer afternoon average concentrations (12:00–18:00) are comparable (at 60 ppb) at two peripheral Athens stations as well as at a rural station in Central Greece at distances up to 80 km (Kalabokas et al. 2000).

Under the frequent summer strong northerly winds (the Etesians) the long-term average ozone concentrations at an urban background station in Athens are comparable with the corresponding concentrations at the peripheral upwind site. During the 1987–1999 period the average ozone levels under these conditions at both stations remained almost constant at 60–65 ppb (Kalabokas and Repapis 2004).

Under southerly winds (mainly sea-breeze), when both stations are located downwind of the urban area, the concentrations at the urban background station increased by about 20 ppb (or 35 %) and at the peripheral station located about 10 km downwind from the city center the average concentrations increase by about 30 ppb (or 50 %) relatively to the rural background concentrations measured upwind (Kalabokas and Repapis 2004; Kalabokas et al. 2006).

The measured summer afternoon rural and marine ozone levels, in Central Greece and on Crete Island, are quite comparable while they are significantly higher (15–20 %) than the corresponding levels in Malta and Cyprus. After investigating

the characteristic meteorological conditions associated with high and low rural and marine surface ozone concentrations, it appears that an important factor leading to high tropospheric ozone values in the Eastern Mediterranean area is the anticyclonic influence of the high-pressure domination over the Central Mediterranean and the Balkans. On the other hand, the lowest ozone levels, particularly in the Crete and Cyprus stations, are associated with an extension to the west of the Middle-East low pressure and also weak pressure gradients over the Eastern Mediterranean and an upper air trough in the North Eastern Europe (Kalabokas et al. 2008; Kleanthous et al. 2014).

Vertical ozone profiles measured in the period 1996–2002 in the framework of the MOZAIC project (Measurement of Ozone and Water Vapor by Airbus in Service Aircraft) for flights connecting Central Europe to the Eastern Mediterranean basin (Heraklion, Rhodes, Antalya) were analyzed in order to evaluate the high rural ozone levels recorded in the Mediterranean area during summertime. The average summer vertical ozone profiles showed substantially (10–12 ppb, 20–40 %) enhanced ozone mixing ratios in the lower troposphere over the Eastern Mediterranean frequently exceeding the 60 ppb, 8-h EU air quality standard, whereas ozone between 700 hPa and 400 hPa was only slightly (3–5 ppb, 5–10 %) higher than over Central Europe. Analysis of composite weather maps, corresponding to high and low ozone episodes, show that the synoptic conditions influence greatly the ozone concentration variability. The differences between highest and lowest ozone levels in the boundary layer remain about the same also in the lower troposphere (at 20–30 ppb). In addition, analysis with the FLEXPART back-trajectory model shows that strong subsidence is observed during the highest ozone cases (Kalabokas et al. 2007).

From the analysis of MOZAIC vertical ozone profiles over the Middle-Eastern Mediterranean airports of Cairo and Tel-Aviv, it turns out that the lower-tropospheric ozone variability over the eastern Mediterranean area is controlled mainly by the synoptic meteorological conditions, combined with local topographical and meteorological features. In particular, the highest ozone concentrations in the lower troposphere and subsequently in the boundary layer are associated with large-scale subsidence of ozone-rich air masses from the upper troposphere under anticyclonic conditions while the lowest ozone concentrations are associated with low pressure conditions inducing uplifting of boundary-layer air, poor in ozone and rich in relative humidity, to the lower troposphere (Kalabokas et al. 2013; Doche et al. 2014).

During the 7 % highest ozone days at the 0–1.5 km layer over Cairo, very high ozone concentrations of about 80 ppb on average are observed from the surface up to 4–5 km altitude. The difference in ozone concentrations between the 7 % highest and lowest ozone days reaches maximum values around 60 ppb close to the ground. During the highest ozone days for both 1.5–5 and 0–1.5 km layers, there are extended regions of strong subsidence in the eastern Mediterranean but also in eastern and northern Europe and over these regions the atmosphere is dryer than average. The detailed examination of three characteristic highest ozone profiles confirms that tropospheric subsidence is a major source for the high ozone

background at the surface in the region. This could be due to either deep or shallow tropospheric subsidence associated with different meteorological conditions. During deep tropospheric subsidence and on a few days timescale, transport is clearly predominant while during conditions of shallow subsidence associated with extended stagnant conditions and pollutants accumulation as well as high temperatures, ozone photochemical production could be important as well. The day with the highest ozone values at the 0–2 km layer over Cairo (about 90 ppb, well above the 60 ppb EU standard) a combination of both types of deep and shallow subsidence is observed (Kalabokas et al. 2015).

4 Conclusions

Combining the above observations, it appears that ozone variability over the urban area of Athens, the Aegean Sea and the Eastern Mediterranean in the boundary layer as well as at the surface is significantly influenced by tropospheric transport with a strong vertical component, which is associated with certain mesoscale synoptic meteorological conditions. As a consequence of this important tropospheric ozone influence, high summer ozone background levels are observed within the boundary layer and at the surface, which might be further enhanced by the photochemically produced ozone from local or regional pollutant emissions under the favorable meteorological conditions prevailing during Mediterranean summers.

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