Science of the Total Environment 476–477 (2014) 677–687

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

On the temporal and spatial variation of ozone in Cyprus

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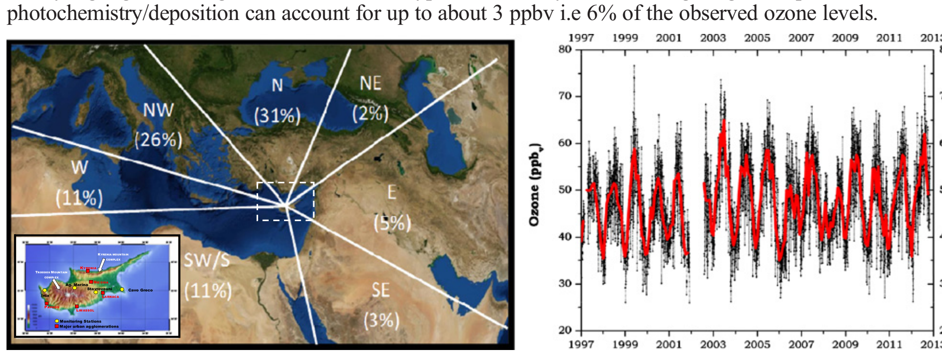
HIGHLIGHTS

- More than sixteen years of ozone observations at a rural station in Cyprus (Agia Marina) were statistically analyzed.
- The observations revealed the presence of a prominent seasonality with the maxima observed during summer.
- A non-significant (a < 0.05) upward trend over the 16 years equal to 0.11±0.12 ppbv y^{-1} has been computed.
- Concurrent observations at three remote sites suggest that high ozone levels are mostly linked to long-range-transport.
- The local photochemistry/deposition can account for up to ~3 ppbv i.e 6% of the observed ozone levels.

GRAPHICAL ABSTRACT

The left panel shows the location of Cyprus in the East Mediterranean region and the major wind sectors, including their relative annual frequency during the period 1997–2012. A fraction of 11% (not shown here) is attributed to air masses of local/mixed origin. The right panel depicts the daily (in black) and monthly (in red) means of ozone concentrations observed at the rural Agia Marina station for the period 1997–2012. Our work clearly highlights that high ozone levels over Cyprus are directly linked to long-range-transport and that local photochemistry/deposition can account for up to about 3 ppbv i.e 6% of the observed ozone levels.



ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form 20 December 2013
Accepted 21 December 2013
Available online 7 February 2014

Keywords:
Ozone observations
East Mediterranean
Cyprus
Transported pollution
Spatiotemporal variability
Long-term air quality observations

ABSTRACT

More than sixteen years (1997–2013) of continuous ozone concentrations at the rural Agia Marina (EMEP, 532 m a.s.l.) station in Cyprus, together with a number of ancillary chemical and meteorological parameters have been analyzed on a multiannual, annual and diurnal basis. The observations reveal a) the presence of a prominent seasonality with maxima observed during summer (54 ± 5 ppb_v) and the minima in winter (39 ± 3 ppb_v) b) a relatively small diurnal variability with the noon levels (50 ± 9 ppb_v) being higher by ~4 pbb_v compared to nighttime (46 ± 9 ppb_v) and c) a non-significant upward trend over the 16 years of 0.11 ± 0.12 ppb_v y^{-1}. To assess the spatial variability over Cyprus, simultaneous measurements in 2011–2012 have been performed at Inia, Stavrovouni and Cavo Greco, three remote marine monitoring sites located to the west, central and the east of the Island, respectively. Our results show that ambient ozone levels over Cyprus are mostly influenced by regional/transported ozone while the local precursor emissions play a minor role in ozone formation. On an annual basis a net ozone reduction of 1.5 and 1.0 ppb_v occurs when the air masses originate from northerly and westerly directions, respectively, while this is 2.4 ppb_v during southerly wind. This suggests continuous net ozone loss controlled by surface deposition and photochemical destruction, and highlights the importance of long-range transport in controlling ozone levels in Cyprus.

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http://dx.doi.org/10.1016/j.scitotenv.2013.12.101

1. Introduction

Ozone is an important greenhouse gas (e.g. Roelofs et al., 1997) and a noxious air pollutant (Seinfeld and Pandis, 2006) with an impact on human health, agriculture and ecosystems (Brönnimann et al., 2002; Wang et al., 2003). Tropospheric ozone levels are controlled by photochemical production processes, including reactions of precursor species of anthropogenic and natural origin, such as volatile organic compounds (VOC) and nitrogen oxides (NO_x) in the presence of solar radiation and by the downward transport of stratospheric ozone through the free troposphere, sometimes even reaching the surface (Crutzen et al., 1999; Trainer et al., 2000; Monks, 2000; Kalabokas et al., 2013).

The importance of increasing ozone relates to a) air quality as a secondary pollutant gas and b) inducing climate change as a potent greenhouse gas altering the radiative budget of the atmosphere, underscores the necessity of performing both large scale and local long-term ozone measurements in order to understand its spatial distribution, temporal variability, and production and destruction rates. These are key issues for environmental policy definition. Especially for the Mediterranean region, an area characterized by relatively strong photochemical activity and frequent biomass fires (Lelieveld et al., 2002; Pace et al., 2005; Amiridis et al., 2012) and influenced by air masses of various origin and chemical composition (Vrekoussis et al., 2005; Ladstätter-Weissenmayer et al., 2007; Kanakidou et al., 2011) the above are of particular importance. The Mediterranean encounters the highest background ozone levels in Europe exceeding 60 ppb_v in summer across the entire basin (Kalabokas et al., 2008). High rural background ozone levels have been observed at urban peripheral sites in Athens, Greece (Kalabokas et al., 1999, 2000) and other rural stations in Greece (Kalabokas and Repapis, 2004). Several studies have been conducted at the remote Finokalia station in Crete, Greece (Mihalopoulos et al., 1997). Kouvarakis et al. (2000) presented the first year-round observations of background ozone for the period 1997–1999 reporting the presence of elevated summertime levels of up to 80 ppb_v. Gerasopoulos et al. (2005) extended this analysis for a 7 year period (1997–2004). They reported mean ozone levels of 49 ± 11 ppb_v and a declining trend of 1.64 ± 0.15 $ppb_v\ y^{-1}$ attributing this decrease to the reduced emissions in Europe. Another study at Finokalia by Gerasopoulos et al. (2006) showed that the role of local photochemistry is limited contributing to less than 4% of the observed ozone levels. Kouvarakis et al. (2002) performed spatial ozone measurements over the Aegean on board the "El-Greco" vessel. They found no statistically significant latitudinal gradient over the Aegean Sea, indicating that most of the observed ozone above this area is of regional scale originating from long-range transport. Similar findings have been reported from the long-term measurements of ozone (1997–2006) conducted at Gozo Island in Malta (Saliba et al., 2008). The authors attributed the high mean ozone values (50.2 ppb_v) to transported polluted air masses and to high regional pollution by ship emissions. Furthermore, free tropospheric ozone measurements were performed at the Mt. Cimone (2165 m a.s.l.) in Italy (Bonasoni et al., 2000) for the period 1996–1998. The yearly mean value of 53 ± 8 ppb_v is in close agreement with the surface ozone values of the previously mentioned studies in Malta and Greece. The authors highlighted that during the warm period, polluted air masses are the main contributors of the high non-background ozone values at the Mt. Cimone station while the lowest ozone values were related to air masses flowing from low latitudes and in particular from the Saharan Desert.

The present study builds on the above reports by taking into account the most extended, to our knowledge, record of ozone data in the Eastern Mediterranean region. The measurements were conducted at the EMEP Agia Marina station (1997–2012); our analysis provides novel information on the multiannual (Section 3.1), seasonal (Section 3.2) and diurnal variability (Section 3.3) of ozone in Cyprus. The findings are supported by a number of ancillary chemical observations and meteorological parameters. Section 3.4 of this paper focuses on the spatial variability of ozone in Cyprus based on information provided by the analysis of ozone, chemical and meteorological observations conducted at three monitoring stations placed to the west (Inia), central (Stavrovouni) and east (Cavo Greco) of the Island. From the above results and together with the climatological analysis of the winds' origin, the combined impact of the local emissions and the surface deposition on the observed ozone levels is examined.

2. Measuring sites location and instrumentation

Cyprus is an island country in the Eastern Mediterranean Sea covering an area of 9250 km^2 and a coastline of 648 km. The region is in the crossroads of transported air parcels of different origin thus different chemical composition; on an annual basis the north-easterlies and the northerlies prevail followed by westerlies and southerlies (Fig. 1, left panel). The main cities of the Island are the capital Nicosia (400k citizens), Limassol (235k), Larnaca (140k), Paphos (66k) and Kyrenia (62k) (Fig. 1, right panel). Geographically, the Island is divided by two mountain complexes, the Troodos Mountains and the Kyrenia Mountains.

Data from four monitoring stations of the network of the Air Quality Section of the Department of Labour Inspection (http://www.airquality.dli.mlsi.gov.cy/) have been used in this study. The stations are a) the rural inland Agia Marina station (35.04N–33.06E, 532 m a.s.l.), b) the rural-marine Inia (34.99N–32.40E, 672 m a.s.l.) to the east of Cyprus,

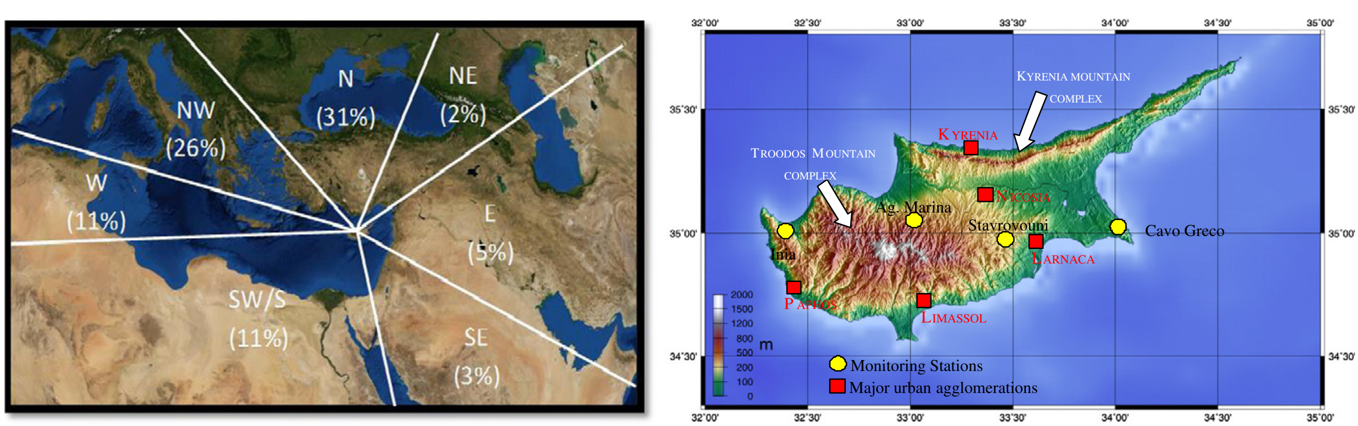

Fig. 1. The location of Cyprus in the East Mediterranean region and the major wind sectors, including their relative annual frequency during the period 1997–2012. A fraction of 11% (not shown here) is attributed to air masses of local/mixed origin. The right panel shows a) the location of the DLI monitoring stations (yellow circles), i.e. the rural Agia Marina station (35.04N–33.06E, 532 m a.s.l.), the rural-marine Inia station (34.99N–32.40E, 672 m a.s.l.), the rural-marine Cavo Greco station (35.02N–34.09E, 23 m a.s.l.) and the rural-Stavrovouni station (34.89N, 33.44E, 650 m a.s.l.); b) the five major urban agglomerations (red squares) Nicosia, Limassol, Larnaca, Paphos and Kyrenia; and c) the Troodos and Kyrenia mountain complexes.