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Ozone long-range transport in the Balkans

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ABSTRACT

Based on one year ground level ozone and NOx and six months' CO measurements, two major routes of long-range transported ozone were derived, route 1 from the north–northeast and route 2 from the west, both appearing locally as NE–E winds. During the cold and rainy periods low pressure systems over central Mediterranean in conjunction with highs over central-eastern Europe created strong NE–E winds at our site, route 1. In these periods ozone exhibited little diurnal variation with midday/night ratios 0.97–0.99, NOx less than 3 ppb, while temperature and relative humidity remained rather constant day and night. Less frequently, lows in the Mediterranean without highs over central-eastern Europe, also caused NE–E but weaker winds, which eventually had western origin, route 2. The midday/night ozone ratio was 1.08, and NOx was slightly larger. The stronger the NE–E winds the larger the ozone concentration and the smaller the NOx and CO. In the spring the frequency of lows in the Mediterranean decreased and in the summer stagnating highs prevailed. As a consequence the periods of long-range transport from the north decreased and midday/night ozone ratios varied from 1.2 to 1.3 due to the greater photochemical activity. Still in certain periods under strong northerlies diurnal ozone variation was also small and midday/night ratios dropped to 0.97–0.99. In the warm period air masses were originating mostly from W–NW and ozone and NOx had significant diurnal variation and higher mixing ratios. When transport from the north was indicated air mass back-trajectories were originating mostly in central-eastern Europe, while for transport from the west, back-trajectories were originating in western Mediterranean. Under transport conditions to Patras, ozone levels at Aliartos, 150 km east of Patras, an upwind EMEP site, on the trajectory path from the north, had diurnal ozone variation similar to Patras. In the cold months, ozone values observed at upwind EMEP stations in Bulgaria, Hungary, Slovakia, Poland, Lithuania and Malta were similar if not larger than those measured, under transport conditions, in Patras. In these periods the transported ozone concentration was larger than that due to local formation, whereas in the warm months locally formed ozone was larger. Because long-range transport ozone is very important for rural areas the ozone levels at the Greek EMEP sites were compared to those measured in Patras.

1. Introduction

For the protection of humans and vegetation from the harmful effects of ozone, ambient air quality standards have been set by International and National Agencies. Long-range transport of ozone and its precursors likely impacts attainment status in certain European Union states.

The weather in central Mediterranean is distinguished in the cold (mild) and rainy periods lasting from October/November till March, in a transition period during spring/fall and in hot and dry period June to September. The reason for the rainy period is the passage of low pressure systems, generated in the Atlantic, through the Mediterranean eastwards. When, in conjunction with lows in the Mediterranean, highs are situated over central-eastern Europe then air masses from the north are flowing to the south. In the summer, strong, anticyclonic conditions of long duration, prevail in central Mediterranean, giving the characteristic hot and dry weather. Spring and autumn are transition periods without the prevalence of the characteristic systems of the winter and summer.

Although transport of pollutants from the north to south Balkans is well established for acidic species, SO_2 (Zerefos et al., 2000) and acid rain (Glavas and Moschonas, 2002) relatively few studies exist on the transport of ozone. Two modeling studies found ozone precursor emissions in Bulgaria and Romania to have affected the ozone levels in western Greece (Ganev et al., 2008; Poupkou et al., 2008), although long-range transport was not well characterized by the UAM model (Poupkou et al., 2009). Both examined only summer periods. Field measurements were carried out mostly in eastern Greece (Aegean) in summer periods (Kalabokas et al., 2008) to full year (Gerasopoulos et al., 2005; Kourtidis et al., 2002; Kouvarakis et al., 2002, 2000),

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where also emphasis was placed, with additional campaigns, in the summer months. Thus, the examination of the interesting winter meteorological conditions and their effects on ozone transport were not investigated before. In the previous experimental studies ozone transport was inferred at one point or another.

In the present year long study are examined data pointing to long-range transport of ozone to Patras, on the western coast of Greece. This evidence consists of the special features of the diurnal profile of ozone, the low levels of NOx and of carbon monoxide, under strong wind speeds of characteristic wind direction. These observations are corroborated by the examination of ozone levels from relevant rural EMEP stations, in Greece and other upwind countries, as well as air masses trajectory paths and synoptic weather conditions. Year long ozone and NOx and six months CO measurements along with meteorological parameters are used to establish the necessary conditions for ozone transport.

1.1. Measurement sites and methods

Patras (population 170,000) is situated on the west coast of Greece on the Ionian Sea, 200 km west of Athens. Our measurement site was located at the campus of the University of Patras, 38°15′N 21°44′E, 100 m a.s.l., 10 km NE from the city center, on the foothills of Panachaikon mountain (1928 m) in the south and approximately 0.5 km away from the coast in the north. The University is located in a region covered mostly by olive trees, quickly urbanizing, with no industry except a cement factory, not affecting the air quality of the site. Ozone in Patras was measured at 10 m above ground, with a Dasibi 1008 RS ozone analyzer, NOx with a Thermo Environment 42S high sensitivity NOx analyzer and CO with a Thermo Environment 43C CO analyzer. The instruments were calibrated with the Thermo Environment Dynamic Gas Calibrator 146C, according to US EPA reference methods. Temperature and relative humidity were measured with Rotronic sensors. Wind speed and direction were measured with Vector Instruments sensors. In addition ozone was obtained from the EMEP rural site stations at Aliartos, 38°22′N 23°05′E, 110 m a.s.l., 80 km north of Athens in mainland Greece, Finokalia in Crete, 35°19′N 25°40′E, 150 m a.s.l. as well as other EMEP stations in Europe. In Fig. 1 is shown a map of Europe with the EMEP sites used in this work.

1.2. Selection criteria

The first criterion applied for the selection of time periods when long-range transport was possible, was the exclusion of the site from the Patras' emissions. This occurred under NE–E winds when the site was upwind of Patras. NE–E winds were generally stronger, with mean speeds greater than 3 m s^{-1}, than winds from other directions.

The second criterion was the constant value of ozone day and night. If the maximum value observed at midday, when the larger photochemical formation occurs, is the same as the minimum value during night, when no formation is possible and only destruction occurs, then one may reasonably assume that long-range transport is operating. The location of the origin of the transported ozone is discussed below. Other transport processes, such as the night mountain breeze, possible in our case because of the nearby high mountain, could increase the night ozone levels and affect the day/night ozone ratio, did not occur under the strong NE–E winds. This criterion was quantified by the ratio of the average ozone value from 12 to 15 h in the cold months and 11 to 18 h in the warm ones, to the average ozone from 22 to 04 h. Ozone midday/night ratios varying from 0.96 to 1.07 were taken to hold during assumed transport periods. Transport of ozone during the night may occur either from aloft or horizontal (Eliasson et al., 2003; Reiterbuch et al., 2000; Liu et al., 1990). Although both types of transport

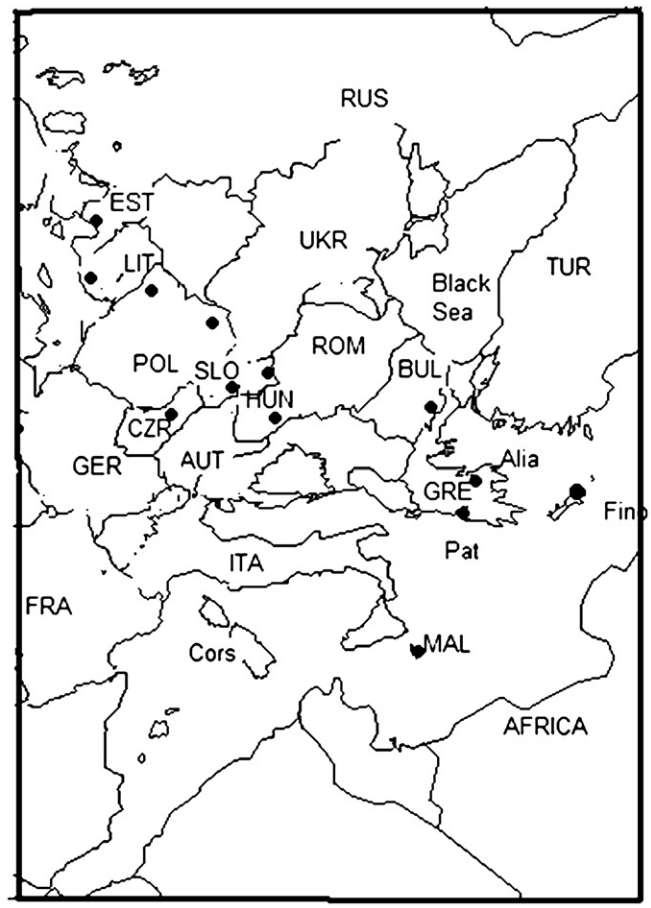

Fig. 1. Map of Europe with relevant EMEP sites, shown as solid circles.

phenomena occurred in this work, the emphasis was placed on the conditions that lead to horizontal long-range transport. An additional observation in favor of transport is that the ozone values remain rather unperturbed even at times when local NO emissions peak, in the morning and late afternoon and may titrate ozone. This is attributed to relatively small emissions, as in our case, in conjunction with strong dispersion.

The third criterion was the levels of NOx ($NO + NO_2$). Because there were no significant NOx sources from NE–E directions and strong NE–E winds dispersed local emissions, due mostly to mobile sources, NOx levels were low. The lower the levels of NOx the greater the probability of long-range transport. Typically NOx values less than 3 ppb were applied.

2. Results and discussion

The study period extended from 1 November 2004 until 31 October 2005. The presence of Panachaikon mountain less than 1 km south of Patras and the monitoring site, as well as several ~1500 m high mountains on the northern side of the narrow, ~1 km wide Gulf of Corinth and the equally narrow Gulf of Patras, near the site, depending on the synoptic weather conditions, create a channeling effect that causes the prevailing local wind directions to be either from NE–E or from SW–W. To the SW–W the Gulf of Patras widens up to several kilometers with no mountains in the vicinity. Sea breeze is also from SW–W. Due to the channeling effect the NE–E winds are generally stronger than those from SW–W directions.

Under NE–E strong winds in time periods lasting from several hours to eight days (only cases with duration greater than 24 h will