Temporal patterns of surface ozone levels in different habitats of the North Western Mediterranean basin

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Abstract

A systematic temporal analysis of surface ozone observations in four sites representative of the main types of habitats: coast, mountain, inland and urban in the North Western Mediterranean basin is presented here for the period between 1994 and 2001. Concentrations were relatively high, especially in the coastal site where the European human and plant protection thresholds were surpassed an average of 54 and 297 days per year, respectively. We observed a 22% decrease in the ozone concentrations along the past decade in the coastal site, a 14% increase in the mountain site, and no significant change in the inland and urban sites. The annual cycle of ozone in the coastal site (maximum concentrations in spring) was typical of areas with higher influences of background ozone, whereas in the other sites, the broad spring–summer maximum indicated dominance of local photochemical production. The site differences were also evident in their diurnal cycles, which were very evident in all sites except in the coastal one. There was thus significant variability among the monitoring sites, due to both the influence of local and background sources and the complex orographic and meteorological conditions of this region.

1. Introduction

In Europe, increasing ozone concentrations are observed from Scandinavia and Britain to south-central Europe (Beck and Grennfeld, 1993; Lelieveld et al., 2002). The high levels of solar irradiation observed in the Mediterranean, in combination with the anthropogenic and biogenic ozone precursors, favor photochemical ozone production. There are many rural air-pollution monitoring stations in central and northern Europe providing a satisfactory picture of the spatial distribution of surface ozone concentrations but there are fewer systematic measurements for the Mediterranean basin (Glavas, 1999; de Leeuw, 2000). Previous measurements have shown high ozone concentrations in this Mediterranean region (Gimeno et al., 1995; Ziomas et al., 1998; Ribas and Peñuelas, 2000; Sanz et al., 2000), but they are still scarce and need detailed temporal and spatial analysis, specially in Spain, where the experimental evidence of oxidants and precursors is limited (Dueñas et al., 2002).

Chemistry transport model simulations (Lelieveld and Dentener, 2000) suggest that in the free troposphere, on average, 20–40% of the O3 originates from the stratosphere. The rest is photochemically produced within the troposphere, and about half of this latter ozone is anthropogenic. In the boundary layer in the Mediterranean region during summer, about 90% of the O3 is formed in situ, with an anthropogenic fraction of about 75% (Lelieveld et al., 2002). On Northern mid-latitudes, and until last decade an increase of about 10% per decade in ground-level ozone concentration has been reported (London and Liu, 1992). This increase was
attributed primarily to the increase of anthropogenic ozone precursors (Volz and Kley, 1988; Staehelin et al., 1994).

The photochemical origin and the reactive nature of ozone produce large temporal and spatial variations in its ambient concentrations (PORG, 1997). Ozone is a reactive atmospheric chemical that is influenced in many ways by its sources, sinks, and chemical reactions. As a result of those complex series of reactions enhanced by temperature and sunlight, ozone exhibits significant variations in space and time (hourly, daily, seasonally, and annually). Chemical reactions involving ozone formation and removal occur within a time scale of a few hours, over corresponding spatial scales of tens of kilometres. Ozone lifetime is typically a few weeks in summer and a few months in winter, during which ozone can be transported hundreds to thousands of kilometres. Measurements of surface ozone clearly show an annual cycle with a distinct maximum usually in spring-summer. Annual variation in ozone concentration apparently depends on a multitude of factors, such as proximity to large source areas of ozone precursors (mainly NOx and volatile organic compounds (VOCs)), geographical location and meteorological factors (Logan, 1985). The annual cycle of ozone over mid-latitudes shows two main kinds of seasonal behaviour, with either a broad summer maximum typical of populated and industrialised areas, or with a spring maximum typical of remote regions and associated to background conditions (Monks, 2000). The broad summer maximum is generally attributed to local photochemical production (Lefohn, 1992; Logan, 1985) whereas the spring maximum origin is more controversial, although it is increasingly attributed to enhanced photochemical activity resulting from increased solar radiation acting upon a pool of NOx and VOCs accumulated during the winter period (Simpson, 1995). The magnitude of the annual maximum seems to have increased in certain locations of Europe over the last couple of decades (Monks, 2000).

A good way of unravelling the dynamics of ozone is by examining its diurnal pattern. The diurnal cycle of chemical formation and destruction is driven by the pattern of NOx and HC emissions (Peleg et al., 1997), as well as by solar radiation. In rural areas, photooxidant (NO2 + O3) levels depend on NOx emissions (Silman et al., 1990), even linearly in some cases (Wang et al., 2001). By contrast, the photochemistry over a large city mostly exhibits a negative response to NOx emissions, although there are also meteorological conditions, those in which the dispersion plays a key role, under which the photochemistry becomes positively related to NOx emissions (Honéré et al., 2000).

Controlling air quality has turned out to be of primary importance as many sites violate air quality standards, especially with respect to photo-oxidant (NO2 and O3) levels. Atmospheric ozone guidelines or standards are proposed or are already in effect in several countries. In Europe, the critical levels are calculated on the basis of the World Health Organisation instructions. Currently, critical level for protection of human health is 110 µg m⁻³ for 8-h mean concentration (European Parliament Council Directive 2002/3 EC, Official Journal of the European Communities L67/14 09.03.2002). For plant protection, the accepted threshold value is 65 µg m⁻³ for 24-h mean concentration. However, accumulated exposure thresholds such as AOT40 (accumulated over threshold 40 ppbv) of 3000 ppbv h (for O3 1 ppbv = 1.96 µg m⁻³ at 20°C and 101.325 kPa) during daily hours for 3 consecutive months in growing season are more commonly used for agricultural and semi-natural vegetation (Kärenlampi and Skärby, 1996).

We aimed to study in detail the surface O3 concentrations in Catalonia as representative of the Mediterranean North Western Mediterranean basin region. We focused on the temporal patterns (diurnal, annual, and decadal) and the description of typical habitats (coast, mountain, inland and urban) patterns. An additional aim was to investigate the number of days exceeding the European thresholds for human and plant protection in the studied sites of this region.

2. Material and methods

We analysed 8-year half-hourly ozone data recorded in Catalonia (NE Iberian Peninsula) between 1994 and 2001. We selected four monitoring stations: Begur, Bellver, Juneda and Barcelona, as representative of the main types of stations: coastal, mountain, inland and urban (Fig. 1). They cover a variety of environmental conditions ranging from sea level (Barcelona, 41°25'N, 2°11'E) to 1040 m of altitude (Bellver 42°22'N, 1°46'E) and from sea shore (Begur 41°57'N, 3°12'E) to 200 km inland (Juneda 41°33'N, 0°49'E) (Fig. 1).

These stations are operated by the Department of Environment of the Generalitat (Catalan Government) as part of a network to monitor background air pollution. The ozone measurements are conducted with MCV 48 AUV analysers which use absorption of 253.7 nm radiation. The detection limit of the instrument is 2 µg m⁻³ and the precision is ±2% with a signal to noise level of 2 µg m⁻³.

All data analyses in this paper are based upon the hourly averaged data. Site mean and maximum daily ozone values were averaged for each year, and month. For the daily profile study, we calculated the seasonal average for each hour of the day through 1996. The number of days with an average 8-h value higher than 110 µg m⁻³ ozone concentrations (days with risk of human incidence) and average 24-h value higher than 33.3
65 μg m⁻³ (days with risk of plant incidence) were also calculated. For statistical analyses (linear regression analyses, ANOVAs and Tukey HSB post-hoc test), we used the statistical package Statistica 6.0 (StatSoft Inc., Tulsa, USA).

3. Results

3.1. Temporal and habitat patterns

The averaged values ranged between ca. 30 μg m⁻³ in the urban site and ca. 90 μg m⁻³ in the coastal site (Fig. 2A). The mean maximum daily values ranged between ca. 60 in the urban site and ca. 115 μg m⁻³ in the coastal site (Fig. 2B). The annual average and the mean of maximum daily ozone concentrations increased throughout the decade in the mountain site (approximately 14% in the 8-year period). On the contrary, mean O₃ concentrations decreased ca. 22%, and maximum daily concentrations decreased 17% in the coastal site (Fig. 2). Ozone concentrations in the inland and urban sites remained constant throughout the years.

Summer–spring values were almost twice greater than autumn and winter concentrations. There was a spring (April) maximum which was followed by another peak in July (except for the coastal site, Begur, where ozone concentrations slightly decreased in summer). The minimum mean values were observed in December (Fig. 3A). Similar trends were observed for the maximum monthly values, although in this case the peak concentrations occurred most clearly in July except for the coastal site. It was also in July when the differences within sites were minimum (Fig. 3B).

The lowest concentrations occurred at night, with a minimum at 8:00 (Fig. 4). After that, a sharp rise started in the morning, a maximum was reached in the afternoon, and a drop followed until sunset. For all seasons there was a strong diurnal variation, which became more distinct in spring–summer, when the afternoon values were almost 2.7 times higher than the...
nocturnal ones (1:7 for urban; 1:4.2 for mountain; 1:2.3 for inland and 1:1.2 for coastal sites). The nocturnal values did not vary strongly from one season to the other. This was not the case for the afternoon values, which had a spring–summer/autumn–winter ratio of the order of 2, with the summer concentrations varying between 80 and 110\,\mu g\,m^{-3} for about 7\,h (8–15\,h, solar time). Begur station presented the smallest diurnal variation in all seasons. This lack of great day–night contrast in this coastal site was more pronounced in spring and summer when the ozone concentration remained at almost constant 100\,\mu g\,m^{-3} throughout the whole day. Daily values (night included) measured at this coastal site were, moreover, systematically the highest values in the studied sites.

3.2. Thresholds exceedances

The number of human health protection exceedance days, i.e. days with an 8-hr average ozone concentration of more than 110\,\mu g\,m^{-3}, the threshold value for protection of human health under the current European ozone Directive (92/72/EEC), was exceeded mainly in the spring–summer season and in the rural areas (an average of 54 days per year in the coastal site). The plant protection threshold (65\,\mu g\,m^{-3} as mean of 24-h) was exceeded up to an average of 297 days per year also in the coastal site (Fig. 5). In the urban site, however, on average, this plant protection threshold was exceeded 14 days per year and the human protection threshold was exceeded an average of 3 days per year (Fig. 5). Fig. 5 shows the time-course evolution of the number of exceedances along past decade for the studied four sites. A significantly decreasing trend has been observed in coastal site ($r^2 = 0.69$ and 0.81 for human and plant exceedances). For the rest of sites no significant patterns have been found. However in the mountain site, the trend tended to be opposite to the coastal site; it tended to increase along the decade as it significantly happened with the average concentrations (Fig. 2).
4. Discussion

Scheel et al. (1997) described average O$_3$ concentrations over Europe as a gradient from the northwest to the southeast ranging from 19 to 27 ppb (38–54 mg m$^{-3}$) over the continent in wintertime, and from 39 and 56 ppb (78–108 mg m$^{-3}$) in summertime. Similar ranges were observed in this North Western Mediterranean region. Mean monthly ozone concentrations at the studied sites (excluding the urban site) for the months April–September ranged from 50 to 100 mg m$^{-3}$, which is also comparable to the higher average ozone levels at rural stations in south-central Europe (Emerson et al., 1996; Kalabokas et al., 2000) and to values reported in other Mediterranean regions (Kalabokas et al., 2000; Gangoiti et al., 2001; Lelieveld et al., 2002; Nali et al., 2002).

The ozone concentrations increased throughout the years only in the mountain site which may have received increasing pollutant charge linked to increasing tertiary activity in the area (Departament de Treball, Industria, Comerç i Turisme of Generalitat de Catalunya, http://www.gencat.es/tict/). Instead, there was a significant decrease trend of ca. 20% for the maximum diurnal and seasonal values in the coastal site. These decreases have been detected in different countries since the late 1980s (PORG, 1997; de Leeuw, 2000). Emissions of ozone precursors have decreased since the mid-1980s in Western and Northern Europe due to control strategies and in Eastern European regions due to modernisation or shutdown of air-polluting industrial branches, whereas in the Mediterranean region the decrease is somewhat smaller or has started later than in Central Western Europe (de Leeuw, 2000; Brönnimann et al., 2003). No decadal trend was found in the other two sites: the inland and the urban ones. Thus, it is difficult to conclude which is the general pattern at regional scale, much less at global scale. One reason is the non-linearity of chemical ozone production with respect to precursor emissions. This non-linearity suggests that to achieve a considerable reduction of ozone levels, precursor emissions could have to be cut down by a disproportionately large amount. In the rural sites, O$_3$ levels are often found to linearly depend on NO$_x$ emissions (Wang et al., 2001). By contrast in the large cities there is often a negative relationship with NO$_x$ emissions that can also occasionally switch to positive under particular meteorological conditions (Honoré et al., 2000).

The spring maximum is formed partly from enhanced photochemistry after a wintertime accumulation of air pollutants (Penkett and Brice, 1986) and partly from a stratospheric flux of ozone (Viezee et al., 1983). The summer maximum is produced in areas with large...
pollutant sources (Logan, 1985). The shift of the ozone maximum from spring to summer is a signal that the photochemical production of ozone due to the emissions of the manmade ozone precursors is the determining factor in the tropospheric ozone budget (Gimeno et al., 1999). All our sites except the coastal site, had a maximum concentration summer peak, which coincides with south and central Europe trends described by Esser (1993) and Monks (2000) and which suggests high concentrations of anthropogenic ozone precursors (Logan, 1985). The spring maximum and the subsequent decrease of ozone concentrations in the coastal site are indicative of a higher influence of background ozone. This is also the site with an interannual decreasing trend (Fig. 3) as in many other European sites (PORG, 1997; de Leeuw, 2000).

The chemical emission-dependent production (concentrations above 100 μg m⁻³) varies from year to year, but the repetitive annual pattern of all sites emphasises that meso-meteorological processes dominate the O₃ cycles. These data document the existence of persistent medium-to-high O₃ levels, as compared with peak-type episodes in central and northern Europe (Sanz and Millán, 2000).

The variation of ozone within a day may be helpful in delineating the processes responsible for ozone formation or loss at a particular location. Significant differences were found between the diurnal cycles in the different sites. The coastal site showed very small differences between day and night. This is a site with very strong northwesterly winds (tramontana and mistral) that strongly determine the air flow of this region (Gangoiti et al., 2001). These winds disturbance of the vertical stability (Kalabokas et al., 2000) likely greatly account for the O₃ uniform diurnal profile of this site in all seasons (Fig. 3). Besides, over the sea surface, deposition of ozone is slow while little quantities of NOₓ are injected into the atmosphere. The combination of these factors results in much less ozone being destroyed during night over the sea than over the continent, and as a consequence high ozone levels are observed at night (PORG, 1997). This is also observed in short-term measurements in Eastern Mediterranean coasts (Peleg et al., 1997; Kalabokas et al., 2000).

Also in the coast, but in a strongly urban environment, Barcelona site presents a typical profile of large urban locations with substantial car traffic (Chameides and Lodge, 1992). The lowest values occurred about 08:00 h. That was probably caused by a reaction of ozone with nitric oxide produced by the early morning traffic (Blum et al., 1997). Such low concentrations are a feature typical of urban sites and sites close to major roads. However, even though local sources of nitric oxide lead to local ozone depletion, the daily maximum still achieved high concentrations during episode conditions, with values as large as 240 μg m⁻³ recorded during 1994. Toll and Baldasano (2000) explain that the city of Barcelona can reach high levels of ozone in spring and summertime because Barcelona has a complex situation in which the mesoscale wind flows and the local emissions (basically from road traffic) are crucial in the production and transport of O₃ in the area.

Juneda and Bellver, the two inland sites, although not influenced by the sea breeze, also presented a marked diurnal variation. However, their maximum O₃ concentrations were reached at different times. While in the plain inland Juneda site, maximum values occurred in the afternoon, in the mountain Bellver site, the maximum values occurred earlier, at midday. Differences in VOCs summer concentrations between these two sites (Peñuelas et al., 1999) and their role into O₃ formation (Ryerson et al., 2001; Peñuelas and Llusia, 2003) might account at least partially for their differences.

These different O₃ cycles are typical of the western Mediterranean basin, where O₃ cycles strongly depend on the topographic location and its relationship to the reservoir layers, the atmospheric circulations involved, and the chemical processes along each path (Sanz and Millán, 2000; Gangoiti et al., 2001). Thus, no single station can be considered representative of region processes, and much less of the whole situation (Sanz and Millán, 2000).

4.1. Final remarks

These results suggest the existence of different trends for different locations (emission types) and different weather conditions, similar to what has been found in other European countries (de Leeuw, 2000). There were no clear increases in background ozone levels throughout the last decade. In fact, the most significant trend was a decrease in the concentrations of the coastal site probably due to the decrease of precursor substances in Europe, again similar to what has been described in other European countries (Pleijel, 2000; Brönnimann et al., 2003). In any case, the human health protection threshold has been exceeded an average of 54 days per year in the coastal site and 3 days in the urban site, and the plant protection threshold was exceeded an average of 297 days per year in the coastal site and 14 days in the urban site. Therefore, and according to recent literature on critical levels (Pleijel, 2000), the observed values in Catalonia could have thus negative effects on human and plant life.

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