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On the origin of the highest ozone episodes in Spain

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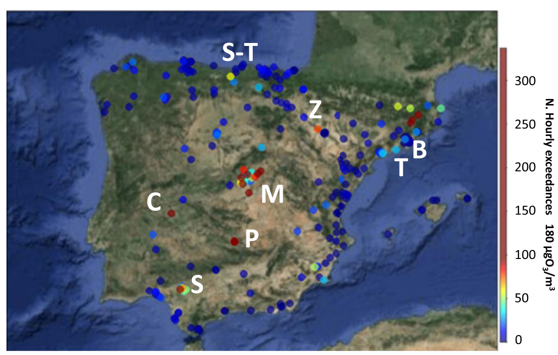
HIGHLIGHTS

- A 2000–2015 evaluation of the occurrence and origin of the highest ozone pollution episodes in Spain
- We consider here all episodes exceeding the information target value.
- These occur mostly around specific large urban and industrial agglomerations.
- In addition of the regional origin the local emission of precursors clearly contributes to generate the highest episodes.

GRAPHICAL ABSTRACT



Number of hourly exceedances of the ozone information threshold in Spain during 2000–2015.

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ABSTRACT

The 2000–2015 occurrences of the highest ozone (O_3) pollution episodes in Spain were evaluated to investigate their origin. To this end, data series available for urban and regional background (UB and RB), traffic (TR) and industrial (IN) sites were analysed separately and intercompared. Results evidenced that during these 16 years mean O_3 levels in the RB sites did not change significantly, and remained constantly high. However, there is a clear increase at the TR and UB sites. Although sensitivity analysis is needed to interpret the cause of this increasing trend, this might be caused probably by the lower O_3 titration intensity due to the preferential abatement of NO vs NO_2, as supported from the neutral trend of O_X ($NO_2 + O_3$) at these sites. We found that the exceedances of the hourly information threshold for O_3 (>180 μg/m^3) are recorded mostly at UB and IN sites located in seven areas of Spain (specific hotspots or at the tail end of large urban plumes), and that these increased during summer heatwaves (i.e. 2003 and 2015).

Although the external contribution of regional-to-subcontinental transported O_3 might be relevant during the highest O_3 episodes in the Western Mediterranean, our results evidenced that in the above specific areas, regional-local O_3 production decisively contributes to the exceedances of the information threshold. Also that the human protection threshold and the AOT40 are more frequently exceeded in the Central, Southern and Mediterranean sides of the Iberian Peninsula.

The design of effective episode abatement measures is quite complex in those conditions, due to both the nonlinearity of the chemical processes of O_3 formation and destruction, and to the interplay with the complex

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meteorological setting, causing frequent recirculation and in situ aging of air masses. However, the combination of meteorological forecasting of the main recirculation processes and sensitivity analysis of NO_X/VOC emission abatement measures might be powerful tools to evaluate the effectiveness of potential O_3 mitigation strategies. Finally we would like to highlight that the current UB, RB, IN and TR classification (somewhat subjective) is not adequate to interpret the origin of O_3 exceedances in complex areas of Southern Europe. Thus, a UB station recording exceedances, and located in a small city in the tail end of an urban plume of a large city, receives not only the contribution from its own UB, but mainly from the specific high O_3 RB caused by the urban plume transport.

1. Introduction

Tropospheric ozone (O_3) is a secondary atmospheric pollutant with complex mechanisms of formation and reaction processes, transport, and deposition (see recent review by Monks et al., 2015 and references therein). Therefore it is also complex to design effective air quality (AQ) policies to efficiently abate the ambient air concentrations of this pollutant. In the Western Mediterranean region this policy complexity arises from three main circumstances.

The firsts are of a scientific/technical nature: (i) the complex non-linear reactions between nitrogen oxides ($NO_X = NO + NO_2$) and volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts, 1993; Pusede et al., 2015, among others); (ii) the huge diversity of the VOC precursors implied, and the involvement of biogenic VOCs (BVOCs) in O_3 formation and destruction (Hewitt et al., 2011; Whalley et al., 2014; Sahu and Saxena, 2015; Sahu et al., 2016); and (iii) the complexity of the atmospheric recirculation patterns during O_3 episodes in this region of the Mediterranean, that allows for O_3 accumulation and continuous vertical recirculation into a specific basin (Millán, 1994, 2009; Millán et al., 1991, 1996a, 1996b, 1997, 2000; Gangoiti et al., 2001; EC, 2002; Gonçalves et al., 2009; Dieguez et al., 2009, 2014).

The second are strategical: (i) Transboundary air masses with relevant concentrations of O_3 and its precursors are contributing to increase O_3 levels (mainly background levels, UNECE, 2010) with different relative proportions across the European regions; (ii) in spite of the EU effort to reduce NO_X emissions, ambient concentrations in urban areas did not follow a proportional decreasing trend (EEA, 2015); (iii) O_3 concentrations are higher in rural areas, where local O_3 abatement plans will be mostly ineffective since emission of precursors occur mostly in large urban and industrial agglomerations.

The third are climatic and geographic: (i) At European scale, the highest O_3 concentrations occur in Southern Europe (EEA, 2015), with peculiar climatic, geographic and meteorological patterns: high insolation and temperature, low precipitation, vertical recirculation of air masses in the warm seasons, and a geographical setup characterised by surrounding mountain ranges (Betic, Iberian, Catalan Ranges, Atlas, Alps and Apennines) that favour stagnation-recirculation episodes (Millán et al., 2000; EC, 2002, 2004, Millán, 2009; Dieguez et al., 2009, 2014); (ii) high BVOCs emissions in spring and summer as compared with other regions of Europe (Seco et al., 2011); (iii) the complex orography and the meso-meteorological circulations that develop from late spring to the end of summer (AMJJAS). These are intimately linked and facilitate the penetration of air masses via the river basins that drain into the Mediterranean, all the way from the sea to their headwaters along the European continental divide during summer (Millán et al., 2000 and Millán, 2014). This penetration takes place under a very confined boundary layer, of normally <250 m deep (EC, 2002), extending all the way from the coast to the mountain tops, and limiting the vertical dispersion of pollutants in the air mass. Those mesoscale systems combine themselves to give semi-closed vertical re-circulations, yielding to the accumulation of pollutants, secondary PM and O_3 precursors and water vapour over the Western Mediterranean Sea (Millán, 2014). Finally, (iv) the high density of Mediterranean cities and industrial settlements accounts for the concentration of emissions in specific areas, e.g., coastal, generating urban and industrial plumes with high concentrations of O_3 precursors. The huge increase in population and traffic due to tourism in summer months adds another ingredient to this already complex setting.

O_3 is one of the key AQ pollutants as far as human and ecosystem health is concerned. Thus, according EEA (2015) around 97% of the European population is exposed to levels of O_3 that exceed the WHO guideline for the protection of the human health.

In Europe the AQ directive 2008/50/CE sets the following AQ objectives for O_3.

- A human health target value (TV) fixed at 120 $\mu g/m^3$, for the daily maximum 8 h mean that cannot be exceeded >25 days/year as a mean of three years (100 $\mu g/m^3$ in the WHO guidelines for a maximum value with no exceedances allowed).
- A population information hourly threshold of 180 $\mu g/m^3$.
- A population alert hourly threshold of 240 $\mu g/m^3$.
- A vegetation protection TV: AOT40 (corrected values), AOT40 (expressed in ($\mu g/m^3$) hours) means the sum of the difference between hourly concentrations >80 $\mu g/m^3$ (=40 parts per billion) and 80 $\mu g/m^3$ over a given period using only the one-hour values measured between 8.00 and 20.00 Central European Time each day. Hourly AOT40 from May to July should not exceed 18.000 $\mu g/m^3 \cdot h$ O_3 as a mean for 5 years.

Another O_3 metric frequently used to evaluate population exposure is SOMO35 that represents the sum of means over 70 $\mu g/m^3$ (daily maximum 8-h).

In spite of the evidences of the effect of O_3 on health and ecosystem (WHO, 2013a, 2013b, 2016, and WGE, 2013) there is a lack of well-defined and structured national action plans in Europe to avoid exceedances of the above TVs. The following major reasons for this are adduced: (i) O_3 is a transboundary problem and measures at EU level, even at UNECE level, are required; (ii) climate and AQ measures for other pollutants will contribute to abate O_3 levels; (iii) given the complexity of the O_3 formation and the lack of linearity with precursors it is difficult to apply effective measures.

This article evaluates the whole set of AQ data concerning O_3 levels recorded in the Spanish AQ monitoring networks in the period 2000–2015 with the aim of giving light on the causes of high O_3 episodes, and give scientific basis for possible future implementation of specific O_3 plans.

2. Methodology

To this end 245 data series from currently operating AQ monitoring stations were selected for the 2000–2015 analysis (see location in Fig. 1). Main constrains for this selection were fixed as follows: (i) availability of a minimum of 10 years of data in the study period; (ii) >85% of valid data during the summer period; (iii) data available for 2014–2015; (iv) data used, at least one year, to officially report on O_3 to the European Commission (EC); and (v) only sites from the continental Spain and Balearic Islands were included. From these, 70 were classified as urban background (UB), 77 industrial (IN), 41 regional background (RB) and 57 traffic (TR) according to the specific AQ networks. In all