Atmospheric Environment 185 (2018) 207–220

Contents lists available at ScienceDirect

Atmospheric Environment

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

Spatio-temporal patterns of high summer ozone events in the Madrid Basin, Central Spain

C. Reche[a,*], T. Moreno[a], F. Amato[a], M. Pandolfi[a], J. Pérez[b], D. de la Paz[b], E. Diaz[c], F.J. Gómez-Moreno[c], M. Pujadas[c], B. Artíñano[c], F. Reina[d], A. Orio[d], M. Pallarés[d], M. Escudero[e], O. Tapia[e], E. Crespo[f], R. Vargas[f], A. Alastuey[a], X. Querol[a]

[a] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, c/Jordi Girona 18-26, 08034, Barcelona, Spain
[b] Departamento de Ingeniería Química Industrial y del Medio Ambiente, ETSII, Universidad Politécnica de Madrid (UPM), c/José Gutiérrez Abascal 2, 28006 Madrid, Spain
[c] Joint Research Unit Atmospheric Pollution CIEMAT-CSIC, Department of Environment, CIEMAT, Avenida Complutense, 40, 28040, Madrid, Spain
[d] Ministerio de Agricultura, Alimentación y Medio Ambiente, MAGRAMA, Plaza de San Juan de la Cruz, s/n, 28071 Madrid, Spain
[e] Centro Universitario de la Defensa (CUD) de Zaragoza, Academia General Militar, Ctra. De Huesca s/n, E-50009 Zaragoza, Spain
[f] Consejería de Medio Ambiente, Administración Local y Ordenación del Territorio, Área de Calidad Atmosférica, C/ Alcalá, 16, 28014, Madrid, Spain

ARTICLE INFO

Keywords:
Ozone precursors
Photochemical pollution
Southern Europe
Weekend effect

ABSTRACT

Complex spatial and temporal patterns of ground-level O_3 and NO_2 concentrations have been revealed across an important southern European O_3 exceedance area (Madrid Basin, central Spain). Data were obtained from 102 diffusion tube sites and 49 monitoring stations (25 urban/suburban, 12 urban/suburban-traffic, 7 remote, 3 rural, 2 urban-industrial) located through a wide area inside and beyond the city. This new, high-density database confirms that current locations of monitoring stations in the Madrid networks are well positioned to record representative levels of O_3 across the area. Two air quality monitoring stations were identified as reference measurement points, based on their lower O_3 and NO_2 concentrations, and used as a proxy for regional and hemispheric background levels. Although a main regional contribution was evidenced, emissions of local precursors within the Madrid urban plume play a key role in the generation of O_3 exceedances, which are higher and occur earlier near the city than at rural sites, where the effect of NO titration is lower. Despite the fact that weekend emissions of O_3 precursors in Madrid are typically lower than on weekdays, mainly due to fewer road traffic emissions, there is little difference in average values of weekday and weekend O_3. However, more subtle "weekend effect" differences are revealed by probability density analysis, with high O_3 and low NO_2 at the highest temperature range (30-35° C) at weekends reflecting lower NO titration. This analysis highlights the importance of NO timing with respect to the photochemical activity timing. The complexity of these O_3 pollution patterns in and around the city is dependent on an ever-changing interplay between weather conditions, emission sources, and the timescale required for pollutant transport, chemical processing and recirculation in an evolving contaminated airmass.

1. Introduction

Photochemical pollution is of especial environmental importance in many parts of Southern Europe, typically due to unfavourable combinations of climatic conditions and local geography. The most relevant products of this type of pollution are atmospheric radicals, tropospheric ozone (O_3), secondary particles (nitrates, sulphates, and secondary organic compounds), and the occurrence of ultrafine particles (UFP) nucleation events (Kulmala et al., 2004; Monks et al., 2015).

Tropospheric O_3 produced through the photo-oxidation of nitrogen oxides ($NO_X = NO + NO_2$) in the presence of volatile organic compounds (VOCs) has been estimated to be responsible for 17,000 premature deaths each year in the European Union (EEA, 2016), with a majority of the European population being exposed to O_3 concentrations that exceed WHO health guidelines. Furthermore, it is a greenhouse gas with positive radiative forcing (0.4 ± 0.2 Wm^{-2}, Myhre et al., 2013) that favours global warming, and a powerful oxidant that can damage vegetation and reduce crop productivity (Chuwah et al., 2015). Unfortunately however, control and reduction of ambient levels of O_3 is a difficult challenge due to multiple sources (local, regional and

* Corresponding author. Institute of Environmental Assessment and Water Research, Spanish Research Council (CSIC), c/ Jordi Girona, 18-26, 08034 Barcelona, Spain.
E-mail address: cristina.reche@idaea.csic.es (C. Reche).

https://doi.org/10.1016/j.atmosenv.2018.05.002
Received 20 November 2017; Received in revised form 28 March 2018; Accepted 4 May 2018
1352-2310/

transboundary: Millán et al., 2000; Millán, 2014), the complexity of the meteorological scenarios which produce O_3 episodes (Millan et al., 1997, 2000; EC, 2002, 2004; Gangoiti et al., 2001; Dieguez et al., 2009, 2014; Millán, 2014), as well as to the non-linearity of the chemical reactions which give rise to its formation (Monks et al., 2015).

Current ozone-control legislation tends to reflect the uncertainties and complexity noted above. 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 µg/m^3, for the daily maximum 8 h mean that cannot be exceeded > 25 days/year as a mean of three years (100 µg/m^3 in the WHO guidelines for a maximum value with no exceedances allowed).
- A population information hourly threshold of 180 µg/m^3.
- A population alert hourly threshold of 240 µg/m^3.
- A vegetation protection TV: AOT40 (corrected values), AOT40 (expressed in (µg/m^3) hours) means the sum of the difference between hourly concentrations > 80 µg/m^3 (= 40 parts per billion) and 80 µg/m^3 over a given period using only the 1-h values measured between 8:00 and 20:00 Central European Time each day. Hourly AOT40 from May to July should not exceed 18.000 µg/m^3·h O_3 as a mean for 5 years.

Average O_3 concentrations are generally higher in rural than in urban areas, this being due both to the formation process, which takes time after the emission of urban, industrial and biogenic precursors, as well as to patterns of O_3 consumption, which mainly occurs in urban areas. In recent years an increasing trend of O_3 concentrations at urban and traffic sites has been noted, this likely being linked to a higher relative reduction of NO compared to NO_2 emissions, and therefore to a lower titration of O_3 by NO (Escudero et al., 2014; Querol et al., 2014, 2016; EEA, 2015 and 2016). It has also been observed that O_3 episodes increase markedly during heat waves (EEA, 2016; Diéguez et al., 2009, 2014; Querol et al., 2016). Querol et al. (2016) analysed the occurrence of episodes resulting in exceedances of the European Air Quality (AQ) directive 2008/50/CE information hourly threshold (180 µgm^{-3}) in Spain during 2000–2015, identifying areas such as urban background sites in the Madrid Basin, along the Mediterranean coast and southern Iberia where these episodes are more frequent. Such episodes and exceedances are typically caused by regional ozone plumes generated by road transport and enhanced by meteorological conditions that enhance the recirculation of locally generated "fresh" emissions (Millán et al., 1997, 2000; Gangoiti et al., 2001; Dieguez et al., 2014; Millán, 2014; Valverde et al., 2016; Querol et al., 2017).

In order to design and implement effective pollution abatement strategies, it is important to identify the pollutant sources and understand what are commonly complex distribution patterns of O_3 concentrations in the affected area (Millán et al., 2000; Millán, 2014; Santurtún et al., 2015). In this context, the main goal of the present study is to use a recently generated large database to assess the temporal and spatial variability of O_3 in the Madrid Basin where this pollutant poses a serious problem, together with one of its main precursors (NO_2), in order to clarify the main causes giving rise to acute O_3 episodes. In addition, the database allows us to assess the suitability of the existing AQ station locations with respect to the actual spatial distribution of O_3 concentrations in the area.

2. Methodology

2.1. Study area

The Madrid area is located in the centre of the Iberian Peninsula, on the high Castilian Central Plateau (Fig. 1). The climate is Mediterranean continental, i.e. extreme, with hot, dry summers. The main topographic features are the Tajo valley in the SSE, and the NE-SW trending Guadarrama mountains (2200–2400 m a.s.l.) which bound the metropolitan area of Madrid to the north. The urban area is settled on an uneven plain approximately 700 m a.s.l., with the lowest altitudes of the basin located in the south and southeast, away from the mountains.

During summer, topographical and thermal atmospheric circulations developed on a regional scale and the intense solar radiation trigger the production of secondary photochemically active pollutants, resulting in O_3 episodes that have been recorded in surrounding towns and rural areas in the Madrid air-shed and boundary regions (Plaza et al., 1997). The typical scenario giving rise to exceedances of the hourly O_3 information threshold is driven by summer anticyclonic stagnation episodes, as reported by Millán et al. (1997, 2000) and Gangoiti et al. (2001) in the Mediterranean region, and by Dieguez et al. (2009, 2014) in the study area. The meso-scale re-circulation is characterized by nocturnal air mass drainage flows towards the south and the Tajo valley, and diurnal mountain breezes to the north of Madrid, with a clockwise rotation towards the east during the afternoon, and the restart of the cycle during the night (Plaza et al., 1997; Vivanco et al., 2009; Dieguez et al., 2009, 2014; Millán, 2014). Elevated NO_2 and VOCs emissions from traffic, together with high summer biogenic emissions cause frequent high O_3 episodes in the basin, and these can extend into the city (Dieguez et al., 2009, 2014; Valverde et al., 2016). Querol et al. (2018) described two types of summer O_3 episodes in the Madrid Basin: (a) venting episodes, with more intensive synoptic wind and the top of the PBL usually reaching > 2500 m a.s.l; and (b) accumulation episodes, activated by a relatively thinner PBL (top < 1500 m a.s.l at midday, lower in altitude than the mountain range), together with low synoptic winds.

Recent emission inventories demonstrate that road traffic is the main source of O_3 precursors in the basin, representing 52% and 14% of total NOx and VOCs emissions per year, respectively (Ayuntamiento de Madrid, 2015).

2.2. Online measurements of gaseous pollutants and meteorological parameters

Online measurements of gaseous pollutants were performed at 49 stations (7 remote (RBREM), 3 rural (RB), 25 urban/suburban (UB/SB), 2 urban-industrial (UI), 12 urban/suburban-traffic (UT/ST)) belonging to the regional air quality network of the City Council of Madrid and of the Autonomous Governments of Madrid, Castilla La Mancha, and Castilla León and of the EMEP network managed by AEMET (all these data are included in the National air quality database, http://www.mapama.gob.es/es/calidad-y-evaluacion-ambiental). Information on each station is provided in Table 1, and their spatial distribution is shown in Fig. 2. All of them provided NO_2 and O_3 measurements from 29/06/2016 to 31/07/2016, with data coverage higher than 97%. Measurements were performed at all stations following the EC reference methods for NO_2 (EN 14211: 2012, chemiluminescence) and O_3 (EN 14625: 2012, ultraviolet photometry). Results are expressed in µg/m^3 (20 °C and 101.3 kPa), and were provided by the relevant authorities with an hourly resolution in local time. Meteorological instrumentation for continuous measurements of temperature, solar radiation, wind speed and direction was available and validated at 15 of the selected AQ stations (http://gestiona.madrid.org).

To complement statistical analysis, data for July 2014 and July 2015 from the same air quality stations was evaluated; data coverage ranged between 79% and 100% during these periods.

2.3. Measurements of gaseous pollutants with passive diffusion tubes

Passive diffusion tubes for NO_2 and O_3 (GRADKO Environmental; http://www.gradko.com/environmental/) sampling were deployed at 102 locations during two different and consecutive periods (29/06–13/07/2016 and 13/07–27/07/2016), each tube therefore being exposed for 14 days, and therefore intended for obtaining reliable detailed observation-based air quality maps. The selected locations cover strategic