



## Air pollution in the plateau of the Iberian Peninsula



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### ABSTRACT

To assess the air pollution in the central Iberian Peninsula, NO, NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub> and PM10 hourly data were collected at eight air quality stations (urban and suburban) belonging to the Air Quality Network of Castilla-La Mancha (Spain) during the 2008–2011 period. Weather conditions and air mass patterns were investigated, and three atmospheric transport patterns were identified. The mean levels of O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub> and PM10 ranged between 51 and 64, 12 and 25, 2 and 7 and 23 and 34 μg m<sup>-3</sup>, respectively, although some peaks of O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub> exceeded the thresholds defined in the European Directives. Monthly and daily variations showed typical cycles, with SO<sub>2</sub> peaks in industrial areas, or high ozone levels in downwind zones strongly affected by traffic emissions. The weekend effect was observed mainly for NO<sub>2</sub> and PM10, while there was a low effect for ozone and NO effect for SO<sub>2</sub>. Dependence of NO, NO<sub>2</sub> and O<sub>3</sub> with the NO<sub>x</sub> levels was also investigated through oxidant concentrations OX (O<sub>3</sub> + NO<sub>2</sub>). NO<sub>x</sub>-independent regional contribution to the oxidant levels showed a strong seasonality and high values. Maximum values of OX concentrations at low levels of NO<sub>x</sub> were found in areas strongly affected by urban plumes, whereas maximum OX levels at high NO<sub>x</sub> values indicated the influence of local sources. The studied area can be divided into three groups, that located downwind of strong traffic emissions, that influenced by industrial emissions (in these two zones the main air pollution problems are focused) and finally that group conditioned by local sources.

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### 1. Introduction

Air pollution emissions in industrial and urban areas, linked to weather conditions, can affect regional or even global scales (e.g. Stohl et al., 2002; Varotsos et al., 2012). Particulate matter (PM) from anthropogenic and biogenic emissions, or formed in the troposphere by condensation of photo-oxidized vapour of semivolatile organic aerosols (e.g. Mallet et al., 2003; Kumar et al., 2010; Szmigielski et al., 2010; Huang et al., 2011), have an important effect in human health (e.g. Chan and Yao, 2008). Besides, anthropogenic emissions of SO<sub>2</sub> damage ecosystems

and form sulfate aerosols that have a significant effect on global and regional climate (Smith et al., 2011). On the other hand, volatile organic compounds (VOC) and nitrogen oxides, NO<sub>x</sub> (NO + NO<sub>2</sub>), emitted mainly by industries and vehicles, are precursors of photochemical ozone and other smog pollutants which have an adverse impact on human health (e.g. Duan et al., 2008; Jerrett et al., 2009; Wu et al., 2012), vegetation (e.g. Fishman et al., 2010) and materials (Tzanis et al., 2009).

In urban areas, emissions of NO<sub>x</sub>, CO, PM10 and VOCs are lower at weekends than in weekdays because of the decrease of the human activity. However, O<sub>3</sub> levels measured on weekend are very similar or even higher than those measured on weekdays in many sites. This phenomenon known as “weekend effect” (Finlayson-Pitts and Pitts, 2000; Seinfeld and

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Pandis, 2006) has been studied in Europe or Asia and most extensively in the USA (see for example references cited by Stephens et al., 2008 or Koo et al., 2012).

The region of Castilla-La Mancha (14% of the total extension of the Iberian Peninsula) is affected by both local and long-range transport pollution, where intense summer heat induces alternating wind currents, which move towards the interior during the day and back to the coast during the night (Millán et al., 1997; Millán et al., 2002). This long-range transport pollution is also observed in other rural sites of industrialized countries (e.g. Varotsos et al., 2001, 2003). Although the limits established by the European Directive on Air Quality for ozone (European Directive, 2008) to protect human health were exceeded in many occasions (Saiz-Lopez et al., 2009; Adame et al., 2012; Notario et al., 2012a, 2012b, 2013a, 2013b, 2013c), or the AOT40 limits to protect vegetation and trees (Notario et al., 2012a, 2012b, 2013b), no studies covering the entire region or by a prolonged period of years were carried out. Only few studies were performed, and they were made in specific cities: Ciudad Real (Saiz-Lopez et al., 2006), Puertollano (Moreno et al., 2006; Saiz-Lopez et al., 2009; Adame et al., 2012; Notario et al., 2013a, 2013b, 2013c), and rural environments near Cabañeros National Park (Notario et al., 2012a, 2012b, 2013b).

The main goal of this work is to perform an overview of the air pollution situation in the centre of Spain. With this aim, a meteorological overview has been shown in Section 3.1, analysing the annual values of meteorological parameters and air mass typology. Air pollutants values are presented in Section 3.2 while the monthly and diel variations are depicted in Section 3.3. Section 3.4 is focused on the analysis of the daily variation differences on weekdays and weekend to investigate the weekend effect. A detailed study to know the link between NO–NO<sub>2</sub>–O<sub>3</sub> and NO<sub>x</sub> along with the levels and variability of OX (NO<sub>2</sub> + O<sub>3</sub>) has been carried out and stated in Section 3.5. Finally, the main conclusions are remarked.

## 2. Area description, instrumentation and air masses

The region studied is surrounded by important mountain chains, dominating the plain of the rest of the territory (Fig. 1). Eight monitoring stations from the Air Quality Network of the Environmental Department of the Regional Government were selected for continuous monitoring of O<sub>3</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub> and PM10 during 2008–2011, five of them situated at the five capitals corresponding to the provinces administratively divided the region: Ciudad Real (CIR), Toledo (TOL), Albacete (ALB), Cuenca (CUE) and Guadalajara (GUA). The other three stations were placed in the cities of Puertollano (PUE), Talavera de la Reina (TAL) and Azuqueca de Henares (AZU) in the provinces of Ciudad Real, Toledo and Guadalajara, respectively.

In Ciudad Real, with 75,000 inhabitants, the traffic is likely to be the most important source of air pollution. Puertollano with 52,000 inhabitants is located at 40 km south of Ciudad Real, and it has the highest concentration of heavy industry in the centre of the Iberian Peninsula. Guadalajara and Azuqueca de Henares, with 85,000 and 34,000 inhabitants respectively, are located at ~50 km NE from Madrid in the “Henares corridor”, one of the most industrialized areas of Spain. Toledo approximately 70 km south from Madrid and with a population of 83,000 inhabitants is one of the most

important touristic cities in Spain, and Talavera de la Reina at 114 km southwest from Madrid and with 89,000 inhabitants is the second in population in this region; traffic is likely to be an important source of air pollution in these two cities. Cuenca with 57,000 inhabitants is located in an abrupt succession of landforms, 163 km southeast from Madrid. Albacete is the most populous city in the region (171,000 inhabitants). It is situated 250 km southeast from Madrid, and 190 km southwest from Valencia, an important touristic and industrial area of the Mediterranean coast.

Experimental data of air pollutants were extracted from the air pollution stations. Hourly averaged values have been obtained from 10 minute data, applying quality criteria of 75%. The methods used to analyse the different air pollutants O<sub>3</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub> and PM10 are those defined by European Directive (2008/50/CE) as reference methods. Ozone measurements were carried out by ultra-violet absorption and SO<sub>2</sub> by ultra-violet fluorescence. The uncertainty and detection limit for ozone and SO<sub>2</sub> is 1 ppb (1.96 µg m<sup>-3</sup> for O<sub>3</sub> and 2.62 µg m<sup>-3</sup> for SO<sub>2</sub>). NO and NO<sub>2</sub> data were recorded using a chemiluminescence method, where a pre-reactor separates the NO–NO<sub>2</sub> reaction from the background chemiluminescence, allowing accurate auto-zeroing of the analyser. The uncertainty and detection limit for NO–NO<sub>2</sub> is 1 ppb (1.27 µg m<sup>-3</sup> for NO and 1.88 µg m<sup>-3</sup> for NO<sub>2</sub>). Particulate PM10 were monitored using beta radiation absorption. The equipment was submitted to a rigid maintenance program being tested and calibrated periodically.

The weather conditions in this region were analysed with the meteorological information on surface (10 m agl) available in the air quality stations as well as with a classification of the air masses to identify the atmospheric transport patterns. Air masses were analysed using back trajectories from HYSPLIT model (Draxler and Rolph, 2013). The input meteorological fields used in this study were the ERA Interim from the global model ECMWF (European Centre for Medium Range Weather Forecasts). Daily 3-D kinematic back trajectories have been calculated, at 12:00 UTC and in a height of 100 m, using the vertical wind component given by the ERA Interim meteorological files. 48 hour backward trajectories from the five stations have been simulated since they cover the Iberian Peninsula and its surroundings and were long enough to identify air patterns. HYSPLIT model includes a tool which allows the grouping of back trajectories into clusters (Stunder, 1996). Five clusters were selected as the optimal number in all the stations, since it is a number sufficient to collect the air pattern variability.

## 3. Results

### 3.1. Meteorological overview

In the centre of Spain the winter months (Dec, Jan and Feb) are cold and relatively dry, monthly values of temperature are between 4 and 9 °C and relative humidity oscillates between 56 and 69%. During the spring period (Mar, Apr and May) the temperature starts to increase, with values between 7 and 15 °C, while the humidity decreases, with monthly levels between 41 and 53%. Summer (Jun, Jul and Aug) is hot in this region, with average values from 17 to 22 °C with maximums up to 40 °C, and therefore humidity is low, between 24 and 47%. In the autumn season (Sep, Oct and Nov) the temperature begins to

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