

# Ozone source apportionment during peak summer events over southwestern Europe

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**Abstract.** It is well established that in Europe, high O<sub>3</sub> concentrations are most pronounced in southern/Mediterranean countries due to the more favorable climatological conditions for its formation. However, the contribution of the different sources of precursors to O<sub>3</sub> formation within each country relative to the imported (regional and hemispheric) O<sub>3</sub> is poorly quantified. This lack of quantitative knowledge prevents local authorities from effectively designing plans that reduce the exceedances of the O<sub>3</sub> Target Value set by the European Air Quality Directive. O<sub>3</sub> source attribution is a challenge because the concentration at each location and time results not only from local biogenic and anthropogenic precursors, but also from the transport of O<sub>3</sub> and precursors from neighbouring regions, O<sub>3</sub> regional and hemispheric transport and stratospheric O<sub>3</sub> injections. The main goal of this study is to provide a first quantitative estimation of the contribution of the main anthropogenic activity sectors to peak O<sub>3</sub> events in Spain relative to the contribution of imported (regional and hemispheric) O<sub>3</sub>. We also assess the potential of our source apportionment method to improve O<sub>3</sub>. Our study applies and thoroughly evaluates a countrywide O<sub>3</sub> source apportionment method implemented in ~~a Chemical Transport Model (CTM)~~ the CALIOPE air quality forecast system for Spain at high resolution (4 x 4 km<sup>2</sup>) ~~over the Iberian Peninsula (IP) to understand and quantify the origin of peak O<sub>3</sub> events~~ over a 10-day period ~~covering the most a frequent synoptic~~ characterized by typical summer conditions in the Iberian Peninsula (IP). The method tags both O<sub>3</sub> and its gas precursor emissions from source sectors within one simulation and each tagged species is subject to the typical physical processes (advection, vertical mixing, deposition, emission and chemistry) as the actual conditions remain unperturbed. We quantify the individual contributions of the largest NO<sub>x</sub> local sources to high O<sub>3</sub> concentrations compared to the contribution of imported O<sub>3</sub>. We show for the first time that imported O<sub>3</sub> is the largest input to the ground-level O<sub>3</sub> concentration in the IP, accounting for 46% to 68 % of the daily mean O<sub>3</sub> concentration during exceedances of the European Target Value. The hourly imported O<sub>3</sub> increases during typical northwestern advections (70-90%, 60-80 µg/m<sup>3</sup>), and decreases during typical stagnant conditions (30-40%, 30-60 µg/m<sup>3</sup>) due to the local NO titration ~~effect~~. During stagnant conditions, the local anthropogenic precursors control the O<sub>3</sub> peaks in areas downwind of the main urban and industrial regions (up to 40% in hourly peaks). We also show that ground-

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level O<sub>3</sub> concentrations are strongly affected by vertical mixing of O<sub>3</sub>-rich layers present in the free troposphere, which result from local/regional layering and accumulation, and continental/hemispheric transport. Indeed, vertical mixing largely explains the presence of imported O<sub>3</sub> at ground level in the Iberian Peninsula. Our results demonstrate the need for detailed quantification of the local and remote contributions to high O<sub>3</sub> concentrations for local O<sub>3</sub> management, being the O<sub>3</sub> source apportionment an essential analysis prior to the design of O<sub>3</sub> mitigation plans in any non-attainment area. ~~To Achieving~~ the European O<sub>3</sub> objectives in the southern Europe and after the estimated relative importance of the imported O<sub>3</sub> to local generation from anthropogenic precursors, requires not only strong ad hoc local actions should be complemented by but also decided national and European-wide strategies.

## 1 Introduction

10 Tropospheric ozone (O<sub>3</sub>) is an air pollutant of major public concern as it harms human health (WHO, 2013) and sensitive vegetation (Booker et al., 2009), and contributes to climate change (Jacob and Winner, 2009). O<sub>3</sub> is formed in the atmosphere through nonlinear photochemical reactions among carbon monoxide (CO), peroxy radicals generated by the photochemical oxidation of volatile organic compounds (VOC), and nitrogen oxides (NO<sub>x</sub>) (Crutzen, 1973). Therefore, meteorological stagnation, high temperature, and low precipitation enhance tropospheric O<sub>3</sub> formation (Demuzere et al.,  
15 2009; Otero et al., 2016). Atmospheric circulation also controls the short and long-range transport of O<sub>3</sub> affecting its lifetime in the atmosphere (Monks et al., 2015). For example, the transport of precursors emitted in urban and industrialized areas may cause O<sub>3</sub> production downwind (Holloway et al., 2003).

20 According to the European Environmental Agency (EEA) around 95-98% of the population in Europe during 2013-2015 were exposed to O<sub>3</sub> concentrations that exceeded the guidelines of the World Health Organization (WHO) (EEA, 2017). These guidelines establish a maximum daily 8-hour averaged (MDA8) O<sub>3</sub> concentration of 100 µgm<sup>-3</sup> never to be exceeded. The European Air Quality Directive (2008/50/EC) is less restrictive as it sets an O<sub>3</sub> Target Value of 120 µgm<sup>-3</sup> for the MDA8 concentration, which can be exceeded up to 25 days per calendar year averaged over three years.

25 Southern European countries around the Mediterranean Basin are particularly exposed to exceedances of the O<sub>3</sub> Target Value in summer due to the influence of frequent anticyclonic and clear-sky conditions that favour photochemical O<sub>3</sub> formation in the troposphere (EEA, 2017). In addition, its geographic location also makes the Basin a receptor of the long-range transport of pollution from Europe, Asia and even North America (Lelieveld et al., 2002; Gerasopoulos, 2005). The importance of long-range transport on surface O<sub>3</sub> has been studied in the Mediterranean Basin, indicating that the emission  
30 sources within the Basin have a dominating influence on surface O<sub>3</sub>, while remote sources are more important than local sources for O<sub>3</sub> mixing ratios at higher altitudes (Richards et al., 2013; Safieddine et al., 2014). Recent studies suggest that the upper O<sub>3</sub>-rich air masses could increase the surface O<sub>3</sub> concentration in the Mediterranean Basin (Kalabokas et al., 2017;

Querol et al., 2018). Further detailed and quantitative studies on the mechanism linking upper O<sub>3</sub>-rich layer with increases of the ground-level O<sub>3</sub> concentration in episodes need further clarification particularly regarding the contribution of O<sub>3</sub> transported at regional and hemispheric scales.

5 Several studies in the Iberian Peninsula (IP) have addressed the causes of O<sub>3</sub> episodes looking at the circulation of air masses (Millán, 2014, and references therein). In the Atlantic region, the blocking anticyclones over Western Europe favour the inter-regional transport of O<sub>3</sub> in the area and its accumulation for several days during the most severe episodes (Alonso et al., 2000; Gangoiti et al., 2002, 2006; Valdenebro et al., 2011; Saavedra et al., 2012; Monteiro et al., 2016). On the other hand, in the Mediterranean coast, the typical summer synoptic meteorological conditions with a lack of strong synoptic advection, 10 combined with the orographic characteristics and the sea and land breezes, favour episodes where high levels of O<sub>3</sub> are accumulated by recirculation of air masses loaded with O<sub>3</sub> precursors (Millán et al., 1997 and 2000; Toll and Baldasano, 2000; Gangoiti et al., 2001; Pérez et al., 2004; Jiménez et al., 2006; Gonçalves et al., 2009; Millán, 2014, Querol et al., 2017; Querol et al., 2018). The coupling between synoptic and mesoscale processes governing the levels of O<sub>3</sub> in the Western Mediterranean Basin need further research in order to understand the O<sub>3</sub> intercontinental contribution. Furthermore, from our 15 understanding there is a lack of research quantifying the contribution of the activity sources to the O<sub>3</sub> local formation during peak events in this region.

O<sub>3</sub> analyses in the Western Mediterranean Basins show that regional background O<sub>3</sub> levels have remained high without significant changes (EEA, 2016; EMEP-CCC, 2016; Querol et al., 2016). However, they have increased at traffic and urban 20 background sites (EEA, 2016; Querol et al., 2016; Sicard et al., 2016; Saiz-Lopez et al., 2017). ~~The reasons behind the urban O<sub>3</sub> upward trend are not clear yet due to the complex VOC-NO<sub>x</sub> regime; part of the O<sub>3</sub> increase may have resulted from the reduction of NO emissions relative to  $\text{NO}_2/\text{NO}_x$  and therefore to a lower NO titration effect in VOC-limited situations. The reasons behind the urban O<sub>3</sub> upward trend are not clear yet; it might be a result of the reduction of NO emissions relative to NO<sub>2</sub> and therefore a lower NO titration effect or the fact that urban O<sub>3</sub> formation is VOC-limited, and a reduction in NO<sub>x</sub> emissions might enhance O<sub>3</sub> formation.~~ The most intense O<sub>3</sub> events in the last decade, measured by the number of exceedances of the O<sub>3</sub> Target Value are recorded over areas downwind of large urban and industrial hot spots (Monterio et al, 2012; Querol et al., 2016; EEA, 2016). Overall, the number of these type O<sub>3</sub> events occur in June-July and during summer 25 heatwaves (i.e., 2003 and 2015).

30 According to the European Air Quality Directive, in zones exceeding the O<sub>3</sub> Target Value, Member States must develop plans to attain compliance by reducing the emission of O<sub>3</sub> precursors. Abatement of tropospheric O<sub>3</sub> concentration in the Western Mediterranean Basin has been insufficient so far (Querol et al., 2018). Effective planning requires an accurate quantitative knowledge of the sources of these precursors and their respective contributions to the exceedances of the O<sub>3</sub> Target Value (Querol et al., 2016; Borrego et al., 2015). However, source attribution of surface O<sub>3</sub> concentration remains a

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challenge, because the concentration at each location and time results not only from local biogenic and anthropogenic precursors, but also from the transport of O<sub>3</sub> and its precursors from neighbouring regions, O<sub>3</sub> hemispheric transport (UNECE, 2010), and stratospheric O<sub>3</sub> injections (Monks et al., 2015).

- 5 At present, there are no methods based on observations that distinguish the origin of O<sub>3</sub>. Despite their inherent uncertainties, Chemical Transport Models (CTMs) allow apportioning the contribution of any source (by sector and/or region) to O<sub>3</sub> concentrations. The most widely used approach is the “brute force” method, which consists on running an ensemble of simulations zeroing out the sources one by one and then comparing them with a baseline simulation that accounts for all of the sources. Several O<sub>3</sub> source apportionment studies at European scale have applied the brute force method to quantify the contribution of one or two emission sectors. For example, road transport emissions with the EMEP model (Reis et al., 2000), biogenic and anthropogenic emissions with the Polyphemus model (Sartelet et al. 2012), transport-related emissions including road transport, shipping, and aviation with the WRF-CMAQ model (TRANSPHORM, 2014), and ship emissions with CAMx (Aksoyuglu et al., 2016). ~~This approach~~ **Brute force** is simple to implement, as it does not require additional coding in the CTM. However, as it quantifies the contribution of each source based on its absence, it does not reproduce actual atmospheric conditions, and therefore it is susceptible to inaccuracies in the prediction of O<sub>3</sub> peaks under non-linear regimes (Cohan and Napelenok, 2011). Actually, brute force is not suitable to retrieve source contributions when the relationship between emissions and concentration is non-linear. ~~Despite these limitations, brute force but it~~ is useful for analysing the concentration responses to emission abatement scenarios (Clappier et al., 2017).
- 20 Recently, CTMs include algorithms that tag multiple pollutants by source (region and/or sector) all the way through the pollutant’s lifetime, from emission to deposition. This integrated source apportionment approach has several advantages. First, it allows identifying the main sources contributing to high O<sub>3</sub> levels under actual atmospheric conditions, which is a preliminary step towards designing refined and efficient emission abatement scenarios. Second, as we show below, it supports enhanced model evaluation and therefore potential model improvements by identifying problems in emission estimates (sectors or regions) or chemical boundary conditions. The Integrated Source Apportionment Method (ISAM) within the Community Multiscale Air Quality (CMAQ) model has shown promising results for O<sub>3</sub> tagging, exhibiting less noise in locations where brute force results are demonstrably inaccurate (Kwok et al., 2013, 2015). Recent ISAM experiments have quantified that the contribution of traffic in the cities of Madrid and Barcelona to the daily O<sub>3</sub> peaks downwind of the urban areas is particularly significant (up to 80-100 µgm<sup>-3</sup>) (Valverde et al., 2016a). O<sub>3</sub> tagging methods are also included in other regional and global models applied over Europe (Karamchandani et al., 2017; Butler et al., 2018).

The integrated source apportionment tools combined with high-resolution emission and meteorological models can help unravelling the sources responsible for peak summer events of O<sub>3</sub> in the Western Mediterranean Basin. Quantifying the contribution of emission sources during acute O<sub>3</sub> episodes is a prerequisite for the design of future mitigation strategies in the

region. In this framework, the main goal of this study is to provide a first quantitative estimation of the contribution of the main anthropogenic activity sectors compared to the imported concentration (regional and hemispheric) to peak O<sub>3</sub> events in Spain. We also assess the potential of our source apportionment method to improve O<sub>3</sub> modelling. Our study applies for the first time a countrywide O<sub>3</sub> source apportionment at high resolution over the (IP) Iberian Peninsula to investigate the local sources responsible for high O<sub>3</sub> concentration compared to the imported (regional and hemispheric) O<sub>3</sub> during a typical summer episode. Our analysis focuses on over the period between July 21<sup>st</sup> and 31<sup>st</sup>, 2012, which is representative of the typical summer synoptic conditions in the region. We use the CMAQ-ISAM within the CALIOPE air quality forecast system for Spain ([www.bsc.es/caliope](http://www.bsc.es/caliope)), which runs at 4-km horizontal resolution of 4x4 km<sup>2</sup> over the IP. The system is fed by the HERMESv2.0 emission model, which provides disaggregated emissions based on local information and state-of-the-art bottom-up approaches for the most polluting sectors.

The paper is organized as follows. In Section 2 we introduce the CALIOPE system, the set-up of ISAM and the HERMESv2.0 emission model for O<sub>3</sub> source apportionment studies, and the methodology used to quantify evaluate the model. In Section 3 we demonstrate the representativeness of the selected episode, we evaluate the model, and we provide an analysis of the source-sector contribution to the Spanish O<sub>3</sub> under the different synoptic patterns occurring during the study period. In Section 4, we discuss our findings, the regulatory implications, and future research.

## 2 Methodology

### 2.1 Air quality model

We used the CALIOPE air quality modelling system ([www.bsc.es/caliope](http://www.bsc.es/caliope)) to simulate the O<sub>3</sub> dynamics over the IP during the selected episode. CALIOPE is described elsewhere (Baldasano et al., 2008; Pay et al., 2014; Valverde et al., 2016a; and reference therein). The system consists of the HERMESv2.0 emission model (Guevara et al, 2013), the WRF-ARWv3.6 meteorological model (Skamarock and Klemp, 2008), the CMAQ v5.0.2 chemical transport model (Byun and Schere, 2006) and the BSC-DREAM8bv2 mineral dust model (Basart et al., 2012). CALIOPE first runs over Europe at 12-km resolution (12x12 km<sup>2</sup>, named EU12 domain) and then over the IP at 4-km resolution (4x4 km<sup>2</sup>, named IP4 domain) (Fig. S1). In the present work, the system is configured with 38 sigma layers up to 50 hPa, both for WRF and CMAQ. The planetary boundary layer is characterized with approximately 11 layers, where the bottom layer's depth is ~39 m. The EU12 domain uses meteorological initial and boundary conditions from the Final Analyses provided by the National Centers of Environmental Prediction (FNL/NCEP) at 0.5° by 0.5°. The first 12 h of each meteorological run are treated as cold start, and the next 23 h are provided to the chemical transport model. Boundary conditions for reactive gases and aerosols come from the global MOZART-4/GEOS-5 model at 1.9° by 2.5° (Emmons et al., 2010). CMAQ uses the CB05 gas-phase mechanism with active chlorine chemistry, an updated toluene mechanism (CB05TUCL; Whitten et al., 2010; Sarwar et al., 2012), and the sixth generation CMAQ aerosol mechanism including sea salt, aqueous/cloud chemistry and the ISORROPIA II

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thermodynamic equilibrium module (AERO6; Reff et al., 2009; Appel et al., 2013). **Table S1** depicts the remaining CALIOPE configuration options.

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For the IP4 domain, HERMESv2.0 estimates emissions for Spain with a temporal and spatial resolution of 1 h and up to 1 km by 1 km, according to the Selected Nomenclature for Air Pollution (SNAP), which are then aggregated to ~~4 km~~ 4-km resolution (Guevara et al., 2013). HERMESv2.0 is suitable for source apportionment studies thanks to its level of detail in the calculation of the emission fluxes by source (Guevara et al., 2014). HERMESv2.0 is currently based on 2009 data, which is the ~~most recent~~ closest year with updated information on local emission activities in HERMES at the time this work started. For neighbouring countries and international shipping activities, HERMESv2.0 uses the annual gridded national emission inventory provided by the European Monitoring and Evaluation Programme (EMEP) disaggregated to 4-km resolution using a SNAP-sector-dependent spatial, temporal and speciation treatment (Ferreira et al., 2013). ~~The VOC and NO<sub>x</sub> emissions from vegetation, which are critical in the formation of O<sub>3</sub>, are estimated with the Model of Emissions of Gas and Aerosols from Nature (MEGANv2.0.4) (Guenther et al., 2006) using temperature and solar radiation from the WRF model. HERMESv2.0 is suitable for source apportionment studies thanks to its level of detail in the calculation of the emission fluxes by source (Guevara et al., 2014).~~

HERMESv2.0 integrates the Model of Emissions of Gas and Aerosols from Nature (MEGANv2.0.4; Guenther et al., 2006) to estimate VOCs and NO<sub>x</sub> emissions from vegetation, which play a major role on O<sub>3</sub> photochemistry, using temperature and solar radiation from the WRF model. Note that we configured MEGAN to compute VOC emissions from cultivated crops; the agriculture emission module in HERMESv2.0 estimates the VOC from manure management and field burning of agricultural residues. In this study, we have updated MEGANv2.0.4 with emission factors from ~~last~~ MEGANv2.1 (<http://lar.wsu.edu/megan/guides.html>). In Sect. 2 of the supplement, we provide a comparison with measurements from the DAURE campaign (Pandolfi et al., 2014) showing the reasonably good behaviour of our modelled isoprene.

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Urban VOC emissions could be a relevant source ~~offer~~ O<sub>3</sub> concentration. Over Spanish urban areas, HERMESv2.0 estimates VOC emissions from road transport and the use of solvents (Fig. 1) following bottom-up approaches (Guevara et al., 2013). However, uncertainties in the estimation of urban VOC emission inventories, as stated recently by several works (Pan et al., 2015; Liu et al., 2017; McDonald et al., 2018; Lewis, 2018) makes uncertain the urban VOC contribution to tropospheric O<sub>3</sub> concentrations. In order to overcome this problem, continuous monitoring of urban VOC should be performed in Spanish cities, following the example of other regions in which O<sub>3</sub> is also a major problem such as Mexico City (Jaimes-Palomera et al., 2016). In addition, the use of formaldehyde satellite observations to constrain urban VOC emissions could be also pointed out as a future task to improve the representativeness of urban emission inventories (Zhu et al., 2014).

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## 2.2 Ozone source apportionment method

We applied ISAM to quantify contributions from different SNAP categories to the surface O<sub>3</sub> over the IP. The ISAM O<sub>3</sub> tagging method is a mass balance technique that tags both O<sub>3</sub> and its gas precursor emissions (NO<sub>x</sub> and VOC) from each source sector within one simulation (Kwok et al., 2013, 2015). Each tagged species undertakes typical physical processes (advection, vertical mixing, deposition, emission and chemistry) without perturbing the actual conditions. The O<sub>3</sub> rate of change for each tag in any grid cell is calculated as follows (Eq. 1):

$$\frac{dC_{tag}}{dt} = P_{tag} - D \frac{C_{tag}}{\sum_{tag} C} \quad (1)$$

Where C<sub>tag</sub> represents the O<sub>3</sub> concentration related to a tagged source of interest, P<sub>tag</sub> is the chemical production rate of O<sub>3</sub> formed by the precursors emitted for each tag, and D is the total chemical destruction rate of O<sub>3</sub> in this grid cell. Different ratios of NO<sub>x</sub>/VOC cause the formation of O<sub>3</sub> in each grid cell, which is controlled either by NO<sub>x</sub>- or VOC-limited conditions. ISAM uses the ratio H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub> to determine whether O<sub>3</sub> is NO<sub>x</sub>- or VOC-sensitive (above or below 0.35, respectively) (Zhang et al., 2009). The bulk O<sub>3</sub> concentration in each model grid cell (P<sub>bulk</sub>) is equal to the sum of O<sub>3</sub> tracers that were produced in either NO<sub>x</sub> or VOC-sensitive conditions (Eq. 2),

$$P_{bulk} = \sum_{tag} P_{tag} = \sum_{tag} P_{tag}^N + \sum_{tag} P_{tag}^V \quad (2)$$

where P<sub>tag</sub><sup>N</sup> and P<sub>tag</sub><sup>V</sup> are the O<sub>3</sub> produced under NO<sub>x</sub>- and VOC-limited conditions, respectively according Eqs. 3 and 4:

$$P_{tag}^{N,new} = P_{tag}^{N,old} + P_{bulk}^{new} \frac{\sum_x NO_{x,tag}}{\sum_{tag} \sum_x NO_{x,tag}} \quad (3)$$

$$P_{tag}^{V,new} = P_{tag}^{V,old} + P_{bulk}^{new} \frac{\sum_y VOC_{y,tag} \times MIR_y}{\sum_{tag} \sum_y VOC_{y,tag} \times MIR_y} \quad (4)$$

NO<sub>x,tag</sub> and VOC<sub>y,tag</sub> are the concentrations of the x nitrogen and y VOC species in CB05 that participate in the photochemical O<sub>3</sub> formation for each source sector tag and grid cell. MIR<sub>y</sub> is the maximum incremental reactivity factor of each y species of VOC emitted by each source sector tag, corresponding to the O<sub>3</sub> generating potential of each single VOC species (Carter, 1994).

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### 2.3 Ozone tagged species

Table 1 summarizes the O<sub>3</sub> tagged sources in the present study and Fig. 1a depicts the HERMESv2.0's estimates of the contribution by each SNAP category to the total emissions of O<sub>3</sub> precursors in Spain. The largest NO<sub>x</sub> sources are road transport (SNAP7; 42%), non-road transport (SNAP8; 19%), manufacturing industries (SNAP34; 16%), and energy production (SNAP1; 16%). VOC are dominated by biogenic sources (SNAP11; 70%) and to a lesser extent by the agricultural sector (SNAP10; 11%), solvent and other product uses (SNAP6; 9%) and road transport (SNAP7; <7%). The selected (tagged) SNAP categories in this study are the energy, industrial, road transport and non-road transport sectors (Fig. 1b), which account for the 92% of the total NO<sub>x</sub> emissions in Spain. An additional tracer (OTHR) gathers the remaining emission categories that were not explicitly tracked (i.e., SNAP2, 5, 6, 9, 10 and 11).

In addition to the selected sources, we tracked the contributions of the chemical boundary conditions (BCON) and the initial conditions (ICON). BCON represents both the O<sub>3</sub> directly transported through the IP4 domain boundaries and the formation of O<sub>3</sub> resulting from precursors that are also transported through the boundaries. BCON O<sub>3</sub> comes from the EU12 parent domain, which includes the O<sub>3</sub> produced in Europe and the O<sub>3</sub> transported at global scale (both tropospheric and stratospheric O<sub>3</sub>) provided by the MOZART-4/GEOS model (Fig. S1). Hereinafter, we name BCON O<sub>3</sub> as the imported O<sub>3</sub> to the IP4 domain. Tagging the O<sub>3</sub> initial allows quantifying the number of spin-up days to minimize the impact of model initialization. For the present run, we required 6 days of spin-up to set the contribution of initial conditions to less than 1% of the net hourly O<sub>3</sub> concentration over 95% of the available O<sub>3</sub> stations.

### 2.4 Evaluation method

We evaluate the simulated concentrations against air quality measurements from the Spanish monitoring stations that are part of the European Environment Information and Observation Network (EIONET; <https://www.eionet.europa.eu/>). The EIONET network provides a relatively dense geographical coverage of the Spanish territory. During the July 21<sup>st</sup>-31<sup>st</sup> episode we used the measurements from 347 stations for O<sub>3</sub> and 357 stations for NO<sub>2</sub> with a temporal coverage above 85% on an hourly basis. Fig. S2 shows the distribution of the stations for O<sub>3</sub> and NO<sub>2</sub>.

The evaluation based on discrete statistics includes the correlation coefficient (*r*), Mean Bias (MB), Normalized Mean Bias (NMB) and the Root Mean Square Error (RMSE) (Appendix B). We used the package "openair" (Carslaw and Ropkins, 2012) for R (v3.3.2; R Core Team, 2016) to compute the statistics. We calculate statistics on an hourly basis for O<sub>3</sub> and NO<sub>2</sub>, as well as for the regulatory MDA8 in the case of O<sub>3</sub>. The evaluation also takes into account the station type, following the categories established by the EEA (i.e., rural background, suburban background, urban background, industrial and traffic).

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There are no direct evaluation methods for apportioned pollutants. Instead, we designed a diagnostic plot for source apportionment analysis at each individual receptor, including a time series of measured and observed O<sub>3</sub> and NO<sub>2</sub> concentrations together with the simulated tagged sources. In addition, this plot includes the simulated wind speed and direction. These plots are helpful as they compare the modelled O<sub>3</sub> and NO<sub>2</sub> with the observations, while highlighting the sources and circulation patterns at least partly responsible for the model behaviour. This work will only discuss in detail the source apportionment plots at key O<sub>3</sub> receptor regions, given the high number of stations (260) that simultaneously measure O<sub>3</sub> and NO<sub>2</sub>.

Evaluation results will be discussed together with the source apportionment results. On the one side, the interpretation of the source apportionment results benefits from model evaluation. On the other side, the source apportionment results support enhanced model evaluation as it allows identifying potential errors in emission estimates for specific sectors and/or in the chemical boundary conditions.

### 3 Results

#### 3.1 Description of the ozone episode

In 2012, the largest O<sub>3</sub> episode in Europe occurred between July 21<sup>st</sup> and 31<sup>st</sup>. That period alone comprised 33% of the total number of exceedances of the information threshold, and 12% of the number of exceedances of the O<sub>3</sub> Target Value in 2012 (EEA, 2013). In Spain, around 60% of the annual exceedances also occurred during this period. (As shown in Querol et al. (2016) July is typically the month with the highest number of O<sub>3</sub> exceedances in Spain.) The episode affected the central and north of the IP (Fig. 2c), in particular the 90<sup>th</sup> percentile of the MDA8 O<sub>3</sub> concentration exceeded the Target Value at the surroundings of the Madrid Metropolitan Area (MMA), and an area located north of the Barcelona Metropolitan Area (BMA), which correspond to hotspots and the tail end of large urban and/or industrial plumes.

Figure 2a shows the observed MDA8 O<sub>3</sub> concentrations trends at the Spanish EIONET stations during the (extended) summers (i.e., from April to September) from 2000 to 2012, together with the values recorded during the selected episode.

We have categorized the MDA8 O<sub>3</sub> concentrations by station type. Rural background stations show the highest MDA8 O<sub>3</sub> concentrations during the episode followed by industrial, traffic and urban stations, which is consistent with the observed previous summer patterns. More specifically, the episode shares a similar 75<sup>th</sup> percentile (75p) of the MDA8 O<sub>3</sub> concentrations at rural background stations above the Target Value with the particularly severe summer of 2003 (Solberg et al., 2008). Note that the MDA8 O<sub>3</sub> concentrations at rural and urban background sites barely changed between 2000 and 2012, which suggests that the benefits from European emission controls may have been significantly counterbalanced by increasing background O<sub>3</sub> (Monks et al., 2015). In contrast, the MDA8 O<sub>3</sub> concentrations at TR and IN sites slightly

increased, likely because of a lower O<sub>2</sub> titration due to the preferential abatement of NO vs. NO<sub>2</sub>. However, we need more research on O<sub>3</sub> source apportionment to confirm this hypothesis (Querol et al., 2016; Sicard, et al., 2016).

Our first estimation of the origin of peak O<sub>3</sub> events in Spain focuses on the episode July 21st -31st, 2012. Figure 2a illustrates the relevance of the episode showing the observed MDA8 O<sub>3</sub> concentrations trends at the Spanish EIONET stations during the (extended) summers (i.e., from April to September) from 2000 to 2012, together with the concentrations recorded during the episode. Although the selected episode is not the most severe between 2000 and 2012 at national scale, it comprises a period with high MDA8 O<sub>3</sub> concentrations measured at rural background stations, actually the 75<sup>th</sup> percentile of those values were above the Target Value, similar to the particularly severe summer of 2003 (Solberg et al., 2008).

This episode is also interesting because it was widespread and affected big parts of Europe (EEA, 2013). Only during this period 33% and 12% of the total number of exceedances for the information threshold and the Target Value in 2012, respectively, were measured. The O<sub>3</sub> regional context of the episode allows us to study the influence of the imported O<sub>3</sub> to Spain.

The maps of the 90th percentile of the measured MDA8 O<sub>3</sub> concentrations over Spain (Fig. 2b) show high concentration spots all over the domain. The exceedances of the Target Value were found in the surroundings of large urban areas (Madrid, Barcelona, Valencia, Seville) and along Spanish valleys (i.e., Ebro Valley, Guadalquivir Valley).

Figure 2b shows the number of observed exceedances of the O<sub>3</sub> Target Value per day during the selected episode. There were more than 100 exceedances of the O<sub>3</sub> Target Value in most of the days during the episode, with relative maxima on July 25<sup>th</sup>, 28<sup>th</sup> and 31<sup>st</sup> attributed to the change in the synoptic conditions (Fig. S3). Figure 3 shows the meteorological patterns (2m temperature, 10m wind, precipitation, mean sea level pressure and geopotential height at 500 hPa) modelled by WRF-ARW during the three distinctive days over the outer EU12 domain.

Our characterization of the study period is based on the circulation type classification performed proposed in Valverde et al. (2014), who developed an objective synoptic classification method over the period 1983–2012, specifically designed to study air quality dynamics over the IP. Stagnant conditions and northwestern advections are the most frequent summer synoptic circulation patterns over the IP, occurring ~44% of the days in a year (Jorba et al., 2004; Valverde et al., 2014). Stagnant conditions are characterized by reduced surface pressure gradients and weak synoptic winds, intense solar radiation, and the development of the Iberian Thermal Low (ITL). The ITL forces the convergence of surface winds from the coastal areas towards the central plateau enhancing sea breezes and mountain-valley winds and subsidence over the Western Mediterranean Basin as described by (Millán et al., 1997, 2000; Millán 2014). In contrast, northwestern advections (NWad) transport air masses from the Atlantic towards the north and west of the IP and they are characterized by atmospheric

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instability and intense ventilation. Periods of accumulation and venting of pollutants follow the same sequence of pressure ridging and throughing respectively, of the lower and middle troposphere of the IP during the warm season (Querol et al., 2017; 2018). According to the circulation type classification in Valverde et al. (2014), the selected episode started with the development of an accumulation-the ITL period (July 21<sup>st</sup>-25<sup>th</sup>), followed by a NWad-venting period (July 26<sup>th</sup>-29<sup>th</sup>) and ended with the development of another ITL (July 30<sup>th</sup>-31<sup>st</sup>).

Figure 4 shows the 90<sup>th</sup> percentile (90p) of the simulated hourly O<sub>3</sub> and NO<sub>2</sub> concentrations corresponding to the three distinctive days with the relative maxima of exceedances. In the northern Spanish Mediterranean areas, intense O<sub>3</sub> episodes often affect the plains and valleys located 60 km north of the to the north of the BMA- Barcelona Metropolitan Area (BMA) in summer (Toll and Baldasano, 2000; Gonçalves et al., 2009; Valverde et al., 2016a; Querol et al., 2017). High NO<sub>x</sub> concentrations from the BMA combined with high summer-biogenic VOC levels are driven inland by mesoscale processes (sea breezes and mountain-valley winds) sea-breezes and mountain valley winds, channelled by north-south valleys towards an-intra mountain plains located 60 km north of the BMA. This happened on July 31<sup>st</sup> when the highest 90p of the hourly O<sub>3</sub> concentrations (160-180 µgm<sup>-3</sup>) in Spain occurred over the N-north and NW-northwest of the BMA. Occasionally, as it happened on July 25<sup>th</sup>, anticyclonic winds over the western Mediterranean Sea deflect the sea-breeze flow enriched with precursors from the BMA towards the Gulf of Lion where it reaches the highest 90p of the hourly O<sub>3</sub> concentrations (160-180 µgm<sup>-3</sup>) in the IP Mediterranean region. Eastern Spanish Mediterranean areas show similar O<sub>3</sub> dynamics, with inland regions depicting the highest O<sub>3</sub> peaks (140-160 µgm<sup>-3</sup>) when low-pressure gradientsstagnant conditions cover central and eastern IP.

In the centre of the IP, intense O<sub>3</sub> episodes occurred during the development of the ITL, where the affected area depends on the synoptic conditions (Querol et al., 2018). Under the absence of synoptic forcing (e.g., July 25<sup>th</sup>), the MMA had the highest 90p of the hourly O<sub>3</sub> concentrations (~140-160 µgm<sup>-3</sup>). In contrast, when mountain valley winds are reinforced with synoptic westerlies (e.g., July 31<sup>st</sup>) (Fig. 3) the urban NO<sub>x</sub> plume is channelled along the mountain ranges in Madrid towards the northeast and the highest 90p of the hourly O<sub>3</sub> concentrations are found along the valley (~140-160 µgm<sup>-3</sup>).

In the north and northeast of the IP, the 90p of the hourly O<sub>3</sub> concentrations show a significant increase when the blocking anticyclone over Western Europe is combined with the development of the ITL (e.g. July 25<sup>th</sup>). The stagnant conditions favour the accumulation of O<sub>3</sub> precursors around main cities and industrial areas and enhance the local O<sub>3</sub> formation.

The NWad pattern (e.g., July 28<sup>th</sup>) significantly decreases the 90p of the hourly O<sub>3</sub> concentrations in the centre and north of the IP. The northwesterly winds decrease the temperature and therefore the O<sub>3</sub> formation. As consequence, O<sub>3</sub> levels are reduced in the plumes from the BMA and the MMA, although they are still significant in the latter. Overall, the

90p of the hourly O<sub>3</sub> concentrations during the NWadv pattern were ~100 µgm<sup>-3</sup> in most background areas. In contrast, during the ITL it was above 120 µgm<sup>-3</sup>.

### 3.2 Statistical evaluation

CALIOPE has been evaluated in detail elsewhere (Pay et al., 2014 and references therein). ~~Furthermore, the system has been evaluated using the DELTA-Tool (Thunis and Cuvelier, 2014) tool developed by the Forum for Air Quality Modelling in Europe, named DELTA Tool (Thunis and Cuvelier, 2014) to support and harmonize the model evaluation in the frame of the Air Quality Directive. Valverde et al. (2015; 2016) used the DELTA-Tool v4.0 and showed that the CALIOPE system accomplishes the quality objectives as defined in the Air Quality Directive for 78% of the NO<sub>2</sub> and 91% of the NO<sub>2</sub> and O<sub>3</sub> monitoring stations in summer conditions during the summer of 2012.~~ Here, we evaluate the updated version of CALIOPE using ISAM to quantify the system's ability to reproduce O<sub>3</sub> and NO<sub>2</sub> concentrations during the selected episode. Table 2 compiles the quartiles of the statistics calculated by station type. ~~(Note that there are stations not fitting any of the four categories (i.e., IN, TR, UB and RB), so the exceedance/station numbers in the IN/TR/UB/RB rows do not sum up to the numbers in the "ALL" rows.)~~

The model slightly overestimates the average hourly and MDA8 O<sub>3</sub> concentrations with MB of +12 µgm<sup>-3</sup> and +6 µgm<sup>-3</sup>, respectively. The *r* is above 0.6 in more than 50% of the stations and above 0.7 in 25% of them. The MB for average hourly and MDA8 O<sub>3</sub> concentrations are lower at RB stations (±4 µgm<sup>-3</sup>) than at IN, TR and UB stations (between +6 and +16 µgm<sup>-3</sup>) in 50% of the stations. As expected, the highest number of exceedances of the O<sub>3</sub> Target Value was recorded at RB stations (260 exceedances) followed by IN stations (204 exceedances).

At RB stations, average hourly O<sub>3</sub> is overestimated (+4 µgm<sup>-3</sup>) and MDA8 O<sub>3</sub> is underestimated (-4 µgm<sup>-3</sup>), which indicates that nighttime O<sub>3</sub> is overestimated. The nighttime overestimation is a common feature of CTMs and it is typically attributed to the underestimation of vertical mixing during nighttime stable conditions and to underestimation of the O<sub>3</sub> titration by NO (Bessagnet et al., 2016; Sharma et al., 2017).

CALIOPE underestimates the average hourly NO<sub>2</sub> concentrations with -7 µgm<sup>-3</sup> at TR stations and -2 µgm<sup>-3</sup> at RB stations. This partly explains the high overestimation of the average hourly and MDA8 O<sub>3</sub> concentration at TR and UB stations, as well as the systematic overestimation of average hourly O<sub>3</sub> concentration at nighttime (due to a lack of O<sub>3</sub> titration by NO). The average hourly NO<sub>2</sub> concentration at TR stations feature the highest *r* (with 25% of stations above 0.6), which proves the reasonably accurate representation of temporal emission in urban areas by the HERMESv2.0 (Guevara et al, 2014; Baldasano et al., 2011). In contrast, the RMSE is highest at TR stations, which results from the underestimation of NO<sub>2</sub> peaks during traffic rush hours. Underestimation of NO<sub>2</sub> traffic peaks is a common problem in Eulerian mesoscale models (Pay et al., 2014), as emission heterogeneity is lost in the grid cell-averaging process, which is especially critical in urban

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areas. Next generation microscale models will potentially solve this problem (Lateb et al., 2016). Besides the dilution of the emission in the grid, meteorology also may play an important role in the low performance of NO<sub>2</sub> and O<sub>3</sub> in hotspot areas. Several inter-comparison studies (e.g., EURODELTA and AQMEII) agree on the limitations of models to simulate meteorological variables that affect the average hourly NO<sub>2</sub> temporal variability, which controls model performance for O<sub>3</sub> in high NO<sub>x</sub> environments and areas downwind (Bessagnet et al., 2016; Solazzo et al., 2017).

Figure 5 classifies the average hourly and MDA8 O<sub>3</sub> concentrations at the air quality stations into four MB categories that account for the 93% of the stations. There are two categories with the lowest hourly O<sub>3</sub>-MB ( $\pm 10 \mu\text{g m}^{-3}$ ): type A with a MDA8 O<sub>3</sub>-MB between -40 and -10  $\mu\text{g m}^{-3}$  and type B with MDA8 O<sub>3</sub>-MB of  $\pm 10 \mu\text{g m}^{-3}$ . There are two categories with the highest hourly O<sub>3</sub>-MB (between 10 and 40  $\mu\text{g m}^{-3}$ ): type C with a MDA8 O<sub>3</sub>-MB of  $\pm 10 \mu\text{g m}^{-3}$  and the type D with MDA8 O<sub>3</sub>-MB between 10 and 40  $\mu\text{g m}^{-3}$ . In addition, Fig. S2 depicts the MB, RMSE and *r* for hourly and MDA8 O<sub>3</sub>, and hourly NO<sub>2</sub> concentrations. The best performances for O<sub>3</sub> (type B) are found at the 28% of the stations, located in the surroundings of the MMA, the BMA and most of the northern Mediterranean stations, which is consistent with the highest *r* ( $0.6 < r < 0.9$ ) found in the center and north of the IP (Fig. S3 Fig. S4). The highest O<sub>3</sub> overestimations (type D) are present at 36% of the stations, mainly located in highly industrialized areas in Spain (Guadalquivir Basin Valley, Strait of Gibraltar, Valencia) and inside the MMA. Next sections analyze the origin of these O<sub>3</sub> biases using the source apportionment time series.

The comparison with previous CALIOPE studies (Baldasano et al., 2011; Pay et al., 2014) indicates that *r* is in the same range for O<sub>3</sub> (0.6-0.7) and NO<sub>2</sub> (0.4-0.5) at individual stations; the same applies to the RMSE (15-29  $\mu\text{g O}_3 \text{ m}^{-3}$  and 10-20  $\mu\text{g NO}_2 \text{ m}^{-3}$ ). Modelled O<sub>3</sub> shows higher performance at traffic stations in large cities, since stations influenced by road transport emissions (i.e., high-NO<sub>x</sub> environments) are better characterized with a more pronounced daily variability (Baldasano et al., 2011). At European scale, several model intercomparisons (Giornado et al. 2015; Bessagnet et al., 2016) indicate that O<sub>3</sub> concentrations in summer agree with the surface observations with *r* between 0.5 and 0.6. NO<sub>2</sub> hourly variability is overall underestimated due to uncertainties in the emission estimates, and meteorological modelling input and model resolution. These studies highlight the limitations of models to simulate meteorological variables that affect the NO<sub>2</sub> hourly variability, and therefore the model performance for O<sub>3</sub> in high-NO<sub>x</sub> environments and downwind. The comparison with previous CALIOPE studies (Baldasano et al., 2011; Pay et al., 2014) indicates that *r* is in the same range for O<sub>3</sub> (0.6-0.7) and NO<sub>2</sub> (0.4-0.5) at individual stations; the same applies to RMSE (15-29  $\mu\text{g O}_3 \text{ m}^{-3}$  and 10-20  $\mu\text{g NO}_2 \text{ m}^{-3}$ ). Modelled O<sub>3</sub> shows higher performance at traffic stations in large cities, since stations influenced by road transport emissions (i.e., high-NO<sub>x</sub> environments) are better characterized with a more pronounced daily variability (Baldasano et al., 2011).

Section S4 in the supplement discusses the meteorological evaluation results and their impact on the pollutant concentrations. Not surprisingly, temperature shows the best behaviour when compared with observations (Table S2). The modelled wind speed is overestimated, particularly during nighttime (Fig. S5), coincident with low level wind speed. The

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nighttime overestimation of wind is a source of ~~large error compensation for the modelling error of~~ simulated  $\text{NO}_2$  and  $\text{O}_3$  nighttime concentrations (Vautard et al., 2012; Bessagnet et al., 2016).

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### 3.3 Source-sector ozone contributions during peak episodes

Figure 6 shows the 90p of the average hourly  $\text{O}_3$  concentration over the IP tagged by source type (Table 1) for different days (July 25<sup>th</sup>, 28<sup>th</sup> and 31<sup>st</sup>). ~~(Fig. S3-Fig. S6 in the supplementary material shows similar plots for  $\text{NO}_2$ .)~~ The imported  $\text{O}_3$  is by far the largest contributor showing a 90p ranging from 70 to 120  $\mu\text{g m}^{-3}$  in the east/north/centre of the IP on July 25<sup>th</sup> /28<sup>th</sup> /31<sup>st</sup>, respectively ~~(Fig. 6)~~. The imported  $\text{O}_3$  enters the study domain through the IP4 domain boundaries and it can only be transported, scavenged deposited or depleted by  $\text{O}_3$  precursors. Therefore, areas with low imported  $\text{O}_3$  concentrations ( $< 50 \mu\text{g m}^{-3}$ ) are good indicators of (1) the accumulation of specific  $\text{O}_3$  precursors that deplete imported  $\text{O}_3$ , and (2) the subsequent  $\text{O}_3$  photochemical production that occur mostly under stagnant conditions and around the largest industrial/urban areas. The 90p of the hourly imported  $\text{O}_3$  concentration shows the lowest values in two different conditions and regions. ~~First, on~~ July 25<sup>th</sup> in the northwestern IP and Portugal, ~~extremely low winds~~ stagnant conditions allow the accumulation of local pollutants that titrate imported  $\text{O}_3$  concentrations down to 30-70  $\mu\text{g m}^{-3}$ ; ~~at~~ At the same time  $\text{O}_3$  is locally produced due to traffic emission downwind of major northern cities (La Coruña, Gijón, Bilbao) (60-120  $\mu\text{g m}^{-3}$ ), shipping activities (up to 40  $\mu\text{g m}^{-3}$ ) and the generation of energy and industrial processes (10-20  $\mu\text{g m}^{-3}$ ). ~~Second, on~~ July 31<sup>st</sup> in the northeast ~~of the~~ IP, when the pollutants transported from the Gulf of Lion and Catalonia towards the Mediterranean act as a sink of imported  $\text{O}_3$  reducing its concentration down to 60  $\mu\text{g m}^{-3}$ . As a result, there is a local  $\text{O}_3$  formation up to 120-160  $\mu\text{g m}^{-3}$  along the Ebro Valley and the Lleida Plain. ~~Borrego et al. (2016) in a source attribution study over northern Portugal Borrego et al. (2016) also found~~ thea reduction of imported  $\text{O}_3$  and the subsequent  $\text{O}_3$  formation by local sources under similar meteorological conditions.

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After the imported  $\text{O}_3$ , the largest contributor to  $\text{O}_3$  is the road transport sector. Downwind of the major urban areas in Spain (i.e., Madrid, Barcelona, Bilbao, ~~Sevilla~~ Seville, Valencia, ~~Gijon~~, Pontevedra), on-road traffic contributed to the 90p of the hourly  $\text{O}_3$  concentrations as much as 60-120  $\mu\text{g m}^{-3}$ , and affected different areas depending on the synoptic/mesoscale regimes (Fig. 6). In the ~~northern~~ of the BMA, the 90p of the hourly  $\text{O}_3$  concentration from the road transport sector reaches its maximum when the stagnant conditions affects the centre and eastern IP (e.g., July 31<sup>st</sup>). As noted above, mesoscale winds carry traffic  $\text{O}_3$  precursors from the BMA inland, channelled by north-south valleys towards the intra-mountain plain in the north. Over the MMA, the 90p of the hourly  $\text{O}_3$  concentration from the road transport sector showed the maximum when the ITL was combined with the synoptic westerlies (e.g., July 31<sup>st</sup>), carrying high  $\text{O}_3$  as far as to the Ebro Valley, as shown in Fig 4.

Regarding the contribution from the non-road transport sector, the Atlantic regions of the IP show the highest 90p of the average hourly  $\text{O}_3$  concentration (25-40  $\mu\text{g m}^{-3}$ ) on July 25<sup>th</sup>. The stagnant condition favoured the accumulation of precursors

from the Atlantic shipping route and the formation of O<sub>3</sub> within the region. The Spanish Mediterranean region shows the highest 90p of the average hourly O<sub>3</sub> concentrations from the non-road transport sector in front of the southeastern coasts of the IP (~180 µgm<sup>-3</sup>) when the westerlies in the Strait of Gibraltar injected precursors from international shipping into the Mediterranean Basin (e.g., July 28<sup>th</sup> and 31<sup>st</sup>). Note that during days with high 90p of the average hourly O<sub>3</sub> concentration from non-road transport, the imported O<sub>3</sub> concentration shows the lowest 90p due to the NO titration effect over emission areas.

The elevated point source emission sectors (i.e., energy and industry) contributed less to O<sub>3</sub> than the traffic sector, but their contributions were significant reaching 15-25 µgm<sup>-3</sup> of the 90p of the average hourly O<sub>3</sub> concentrations (Fig. 6). The north and northeastern of the IP, the Mediterranean coast, and the Guadalquivir Valley are the most affected regions under stagnant conditions.

The contribution of the remaining sectors (OTHR) to the 90p of the average hourly O<sub>3</sub> concentrations was similar to that of the elevated point sources (15-25 µgm<sup>-3</sup>), but it reached up to 30 µgm<sup>-3</sup> in areas downwind of Oporto and Lisbon (Fig. 6). OTHR includes the formation of O<sub>3</sub> from the remaining anthropogenic and biogenic sources (accounting for less than 8% of total NO<sub>x</sub> emissions, but 93% of total VOC). The high OTHR concentration around the biggest cities in Portugal may be related to precursors emitted by the residential sector (SNAP2 and 9) and biogenic emissions, as found in other source apportionment studies over Portugal (Borrego et al., 2016; Karamchandani et al., 2017).

### 3.4 Regionalization of source-sector contributions

~~The analysis of the source-sector contributions to O<sub>3</sub> allowed~~ We have identified ~~ten O<sub>3</sub> receptor regions with similar characteristics in terms of meteorological and O<sub>3</sub>-geographical patterns, O<sub>3</sub> dynamics and main source contributors~~ main source contributors and geographical patterns (Figs. 4 and 6). ~~The receptor regions defined in this work are consistent with Diéguez et al. (2014) and Querol et al. (2016), who proposed a similar regionalization based on observations from air quality stations.~~ Figure 7c shows the location of the air quality stations belonging to each receptor region corresponding to the ~~central of the~~ IP (CIP), the east ~~of the~~ IP (EIP), the Ebro Valley (EV), the Guadalquivir Valley (GV), the Mediterranean Sea (MED), the northeast ~~of the~~ IP (NEIP), the north ~~of the~~ IP (NIP), the northwest ~~of the~~ IP (NWIP), the south ~~of the~~ IP (SIP) and the west ~~of the~~ IP (WIP). ~~The O<sub>3</sub> receptor regions are consistent with Diéguez et al. (2014) and Querol et al. (2016), who proposed a similar regionalization based on observations from air quality stations.~~

Figure 7a shows the absolute O<sub>3</sub> contribution of each tagged source at air quality stations by region along with the modelled and observed daily mean concentration during exceedances of 120 µgm<sup>-3</sup> of the observed MDA8 ozone. ~~Note that differences between sectors are more evident in the when normalized contribution~~ (Fig. 7b). ~~(Table S3 compiles de numerical values of Fig. 7.)~~ Figure 7 indicates that during exceedances of the MDA8 target value there is a good agreement

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( $r = 0.79$ ) between the sum of apportioned  $O_3$  and the observed concentrations over the receptor regions. Fig. 7b shows the respective fractional mean  $O_3$  contribution. (Table S2 compiles de numerical values of Fig. 7.) We have excluded the ICON  $O_3$  in Table S2 because its contribution is negligible after six days of spin-up. The spatial  $r$  between modelled and observed daily mean  $O_3$  concentration during exceedances of the MDA8 target value is 0.79, which indicates that CALIOPE is able to reproduce reasonably well the spatial variability of  $O_3$  during peak episodes in Spain.

The MED region ~~represented by stations in the Balearic Islands~~ shows the highest imported  $O_3$  contribution (76%) because it is relatively far away from important anthropogenic  $NO_x$ +VOC sources in the IP. Under the ITL influence (July 25<sup>th</sup> and 31<sup>st</sup>), MED received air masses enriched with on-road traffic precursors from southern France and the NEIP, which enhanced  $O_3$  production up to 7%. Shipping emissions in the MEDMediterranean region contributed up to 8% of the total  $O_3$ .

After MED, there is a cluster of regions along the Spanish Mediterranean coast (i.e., NEIP, EV and EIP) showing imported  $O_3$  contributions between 60 and 68 % of the daily mean  $O_3$  under exceedances. This is explained by their proximity to the eastern boundary and the frequent mesoscale phenomena enhancing the recirculation and accumulation of imported  $O_3$  along the Spanish Mediterranean coasts. The contribution of road and non-road transport is similar (~11-16%) because these regions have both important roads and maritime trade routes. -Note that the SIP region, which is also located in the Spanish Mediterranean coast, shows a daily mean imported  $O_3$  concentration lower than the regions along the Spanish Mediterranean coast ~~other Mediterranean regions~~ (~57%) and the highest non-road transport contribution in Spain (19%). The main sink of imported  $O_3$  are precursors resulting from dense shipping traffic through the Strait of Gibraltar, which have substantial impact in the  $O_3$  production downwind (either in the Alboran Sea or the Gulf of Cadiz).

The regions including the largest metropolitan areas in Spain are the CIP (Madrid) and the NEIP (Barcelona). Both regions show an imported  $O_3$  contribution of ~60% and a similar contribution from the road transport sector (18 and 16%, respectively). However, the NEIP shows a slightly higher contribution from non-road transport (13 vs 10%) due to the influence of international shipping near coastal areas.

The northern and northwestern regions of the IP (NIP and NWIP) had relatively lower imported  $O_3$  contributions (56-59%). The contribution of non-road transport was ~10-12%, slightly lower than in the Mediterranean coast, and that of road transport was also significant (~14-15%). The contribution from the industrial sector was one of the highest in the country (~5%) ~~due probably related~~ to the influence of the large industrial facilities located in several areas of ~~Galicia, Cantabria, Asturias, and the Basque Country~~ the north of Spain. The contribution from the energy sector in the NWIP region was the highest in Spain (~5%) due to emissions from large coal-fired power plants ~~located in the area, including As Pontes, Meirama, Aboño, Guardo, and Compostilla~~.

The WIP had the lowest daily mean O<sub>3</sub> concentrations during days exceeding the O<sub>3</sub> Target Value (93.5 µg m<sup>-3</sup>) and a high imported O<sub>3</sub> contribution (~63%). NO<sub>x</sub> emissions in the WIP region are moderate (Fig. 4), which could explain the low daily mean O<sub>3</sub> concentration. There is a significant contribution from traffic (14% for road transport and 11% for non-road transport) and industrial and energetic sectors (7%) to the daily mean O<sub>3</sub> concentrations. These anthropogenic contributions suggest that O<sub>3</sub> in the WIP ~~may be produced~~<sup>is produced</sup> by precursors transported from the surrounding cities (OpPorto, Lisbon and Madrid) and the highly industrialized areas in the NWIP and the NIP (Fig. 6).

The Guadalquivir Valley had the lowest imported O<sub>3</sub> contribution of the IP (~46%) and the highest daily O<sub>3</sub> concentration during days of exceedance. ~~The relatively low imported O<sub>3</sub> contribution resulted from the titration effect driven by the high NO<sub>x</sub> emissions from industrial and urban hotspots in the region.~~ The on-road traffic was the highest anthropogenic contributor to O<sub>3</sub> (~18%) due to the emissions from three major cities (SevillaSeville, Huelva, and Cordoba). Although O<sub>3</sub> in Huelva may be overestimated (as discussed later), shipping is the second most important contributor to O<sub>3</sub> in the Guadalquivir Valley (~17%) ~~due probably link to~~ the important fluvial transport along the Guadalquivir Rriver. (The Guadalquivir River is one of the most important routes for merchandise transport in Europe.) In fact, the non-road transport sector is the highest contributor (~17-19%) in sSouthern Spain, both in the Guadalquivir Valley and the SIP, also due to the dense maritime routes across the Strait of Gibraltar.

~~The following sections analyse the source apportionment results eight stations located in key regions (see Fig. 5). We analyse two regions with high on-road traffic contribution (CIP and NEIP), and two regions with high contribution from industry and energy production (NWIP and Guadalquivir Valley).~~

~~The following sections analyse the source apportionment results at key-regions with a high on-road traffic contribution (i.e., CIP and NEIP) and a high contribution from industry and energy production (i.e., NWIP and Guadalquivir Valley).~~

#### 3.4.1 ~~The centre of the~~ Central Iberian Peninsula

Figure 8 show the source apportionment time series of the average hourly O<sub>3</sub> and NO<sub>2</sub> concentrations at two stations ~~in the CIP~~, an urban station in Madrid (station 1 in Fig. 8a), and another one located in Guadalajara (station 2 in Fig. 8a8b), which is a medium size city affected by Madrid's urban plume. ~~The model reproduces reasonably well the main processes and source contributions, with a significant imported O<sub>3</sub> contribution in both stations.~~

~~At the urban station, the model reproduces the O<sub>3</sub> traffic cycle ( $r = 0.66$  and  $MB=22.5 \mu\text{g m}^{-3}$ ) featuring the typical low O<sub>3</sub> concentrations ( $< 40 \mu\text{g m}^{-3}$ ) in the early morning and in the afternoon due to O<sub>3</sub> titration (Fig. 8a). However, O<sub>3</sub> was overestimated (MB type D) during daytime peaks due to the overestimation of the NO<sub>2</sub> morning peaks during stagnant conditions, coincident with the highest road transport contribution for both pollutants. The results point towards a poor~~

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representation of the meteorological conditions in the city during the stagnant conditions as shown in the meteorological evaluation (Sect. 4 in the supplement).

At the urban station downwind (Fig. 8b) the modelled  $O_3$  shows a positive bias (MB type B) due to the underestimation of  $NO_2$  concentration. Note that the uncertainty of traffic- $NO_2$  traffic emissions in medium size cities is larger than in the largest urban areas (i.e. Madrid, Barcelona) because data is generally not available and emissions are estimated using emission factors that depend on population density (Baldasano et al., 2011).

Despite the limitation, the source apportionment results show that imported  $O_3$  is the main contributor in both stations, but  $O_3$  formation from traffic increases significantly during peaks in both stations. The highest  $O_3$  concentrations ( $\sim 160 \mu g m^{-3}$ ) are modelled when westerly winds channelled along the Tajo valley carry the polluted air masses in a NE direction through the Tajo Valley. This, which results in a  $O_3$  contribution of  $\sim 70 \mu g m^{-3}$  from the road transport sector in areas downwind (see wind vectors in Fig. 8b on July 28<sup>th</sup> and 31<sup>st</sup>). The  $O_3$  contribution from the industrial sector (whose precursors could come from facilities in the south of the MMA, Fig. 4) reinforces the  $O_3$  peaks up to  $\sim 10 \mu g m^{-3}$ , meanwhile the contribution from non-road transport increases systematically the background  $O_3$  concentration by  $\sim 15 \mu g m^{-3}$ . The  $O_3$  contribution from non-road transport in this region may arise mainly from the Madrid's airports and the agricultural machinery operating in the surrounding rural areas.

In Madrid, the model reproduces the  $O_3$ -traffic cycle featuring the typical low  $O_3$  concentrations ( $< 40 \mu g m^{-3}$ ) in the early morning and in the afternoon due to  $O_3$  titration (Fig. 8a). However,  $O_3$  was overestimated (MB type D) during daytime peaks due to the overestimation of the  $NO_2$  morning peaks during stagnant conditions. The  $NO_2$  overestimation correlates with the highest road transport contribution. The  $NO_2$  overestimation in Madrid is inconsistent with the overall underestimation of  $NO_2$  in urban areas due to the dilution effect. The results point towards a poor representation of the vertical mixing during the stagnant conditions. In urban areas downwind (Fig. 8b) the modelled  $O_3$  shows a positive bias (MB type B) due to the underestimation of  $NO_2$ . While traffic- $NO_2$  emissions in the largest urban areas (i.e. Madrid, Barcelona) are estimated at the road link level using specific data such as daily average traffic, mean speed circulation and real world vehicle fleet composition profiles, in medium size cities this information is not available and traffic emissions are estimated using emission factors that depend on population density (Guevara et al., 2013), which implies having a larger uncertainty in the results.

The  $O_3$  contribution from the industrial sector (whose precursors could come from facilities in the southern MMA, Fig. 4) reinforces the  $O_3$  peaks up to  $\sim 10 \mu g m^{-3}$ , meanwhile the contribution from non road transport increases systematically the

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background  $O_3$  concentration by  $\sim 15 \mu\text{g m}^{-3}$ . The  $O_3$  contribution from non-road transport in this region may arise from the Atlantic shipping route, Madrid's airports and the agricultural machinery operating in the surrounding rural areas.

Figure 8a and 8b also shows that the urban  $O_3$  plume presents different intensity and distribution depending on the meteorological pattern. Downwind of Madrid (Fig. 8b), stagnant conditions favour  $O_3$  peaks exceeding  $120 \mu\text{g m}^{-3}$  and on-road transport contributes up to  $20\text{--}30 \mu\text{g m}^{-3}$  (e.g., July 25<sup>th</sup>). The highest  $O_3$  concentrations ( $\sim 160 \mu\text{g m}^{-3}$ ) are modelled when westerly winds channelled along the Tajo valley carry the polluted air masses in a NE direction through the Tajo Valley, which results in a  $O_3$  contribution of  $\sim 70 \mu\text{g m}^{-3}$  from road transport sector in areas downwind (see wind vectors in Fig. 8b on July 28<sup>th</sup> and 31<sup>st</sup>).

#### 3.4.2 The northeast of the North-Eastern Iberian Peninsula

Figure 8c and 8d show the source apportionment time series at two stations in the NEIP, an urban station in Barcelona (station 3) and a remote rural area downwind (station 4). ~~In Not surprisingly, at the urban station,  $\text{NO}_2$  levels of up to  $100 \mu\text{g m}^{-3}$  affect  $O_3$  concentrations by titration during traffic peaks. In contrast, the rural station downwind depicts a higher  $O_3$  and lower  $\text{NO}_2$  concentration than the urban station. Absolute  $O_3$  biases in both stations are  $\sim 10 \mu\text{g m}^{-3}$  (MB type B).~~

~~Absolute  $O_3$  biases in both stations are  $\sim 10 \mu\text{g m}^{-3}$  (MB type B). In the urban area, the modelled  $O_3$  concentrations are in agreement with the observations. As at Madrid urban station, The model suggests that  $O_3$  mostly results from import and from the  $\text{NO}$  titration effect due to local road transport and industrial sources (Fig. 8c). However, the  $O_3$  diurnal cycle in the NEIP urban areas of the NEIP is less marked than in the CIP due to persistently high  $O_3$  concentration at night ( $\sim 60 \mu\text{g m}^{-3}$ ). The breezes and mountain-valley winds contribute to the accumulation and recirculation of pollutants in this region. However, the model presents some under/overestimation at nighttime, which could result from the  $\text{NO}_2$  underestimation and complex mesoscale phenomena not captured by the model. Note that the  $O_3$  diurnal cycle in the NEIP urban areas is less marked than in the CIP due to persistently high  $O_3$  concentration at night ( $\sim 60 \mu\text{g m}^{-3}$ ). The breezes and mountain-valley winds contribute to the accumulation and recirculation of pollutants in this region.~~

~~At the rural station, Despite of the slight overestimation of  $\text{NO}_2$  concentration in rural areas, modelled  $O_3$  peaks ( $> 120 \mu\text{g m}^{-3}$ ) are highly correlated in a good agreement with observations (Fig. 8d), which suggests that overall the model reproduces the main transport paths, photochemical processes, and relative contributions from different sources. Imported  $O_3$  is one of the main contributors to ground-level  $O_3$  (from  $40$  to  $100 \mu\text{g m}^{-3}$ ), but during peaks the on-road traffic contribution sharply increases up to  $80 \mu\text{g m}^{-3}$ .~~

The  $O_3$  concentration from the road transport sector arriving at rural areas in the NEIP, mainly comes from the Barcelona and surroundings as a result of the afternoon sea breezes (see wind vectors in Fig. 8c and 8d). However, under specific

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meteorological patterns these winds also carry precursors from other cities located in the NW Mediterranean Basin. For example, on July 28<sup>th</sup> both the model and observations show that O<sub>3</sub> exceeded 120 μgm<sup>-3</sup> in both urban and rural areas and the model attributed ~60% of it to regional anthropogenic sources (non-imported O<sub>3</sub>). In the morning, two main meteorological phenomena favoured the transport of precursors towards the Western Mediterranean. First, the North African Thermal Low reinforced the sea breezes in the NEIP coast. Second, NW synoptic winds channelled between the Pyrenees and the French Central Massif towards the Gulf of Lion transported precursors from urban areas upwind (e.g., Marseille, Toulouse). In the afternoon, the sea breezes transported air masses enriched with O<sub>3</sub> and precursors inland. Other authors (Gangoiti et al., 2001) have hypothesized that high O<sub>3</sub> concentration in the Western Mediterranean Basin is influenced by transport from France via the Carcassonne gap. The present experiment cannot quantify the contribution of French cities to the O<sub>3</sub> concentration over the NEIP, but future studies could explicitly tag the emission from the French regions.

### 3.4.3 Guadalquivir Valley

The largest modelled O<sub>3</sub> overestimations are found in the Guadalquivir Valley (MB type D). Precursors emitted along the Guadalquivir Valley arise from large industrial facilities and a coastal power plant (Fig. S3), a few densely populated cities (notably Sevilla and Cordoba with more than 700,000 and 320,000 inhabitants, respectively), and the navigable river. The airflow in the region is controlled by the Atlantic synoptic conditions, the development of breezes in the coast of the Gulf of Cadiz and the channelling through the Guadalquivir Valley (Adame et al., 2008).

We have selected two stations along the Guadalquivir Valley to evaluate O<sub>3</sub>, one in the urban area of Sevilla-Seville (station 5 in Fig. 9a), and one in a rural coastal area (station 6 in Fig. 9b). The contribution of anthropogenic sources to NO<sub>2</sub> at the coastal rural background station is low but still significant. The contribution of non-road transport is due the influence of one of the largest Spanish harbours. The contribution of the energy sector to the O<sub>3</sub> concentration is also noticed (e.g., July 25<sup>th</sup>). As expected, the urban station (Fig. 9a) shows a high NO<sub>2</sub> concentration dominated by on-road traffic. NO<sub>x</sub> from traffic is the main sink of O<sub>3</sub> in the city and the model reproduces the titration effect in agreement with observations (e.g., July 28<sup>th</sup>-31<sup>st</sup>).

High O<sub>3</sub> overestimations (10-30 μgm<sup>-3</sup>) at both stations (Fig. 9a and b) were detected during July 25<sup>th</sup>-28<sup>th</sup> which corresponds to intense and persistent SW winds transporting air masses from the Atlantic Sea along the Guadalquivir Valley, as shown by the wind vectors in Fig. 9a and b. Although the model overestimates O<sub>3</sub> concentrations, it reproduces the temporal variability.

Our results suggest that the non-road transport sector is a significant contributor along the Guadalquivir Valley during these days. The impact of shipping emission on O<sub>3</sub> in the Guadalquivir Valley region is mainly evidenced by the relative high NO<sub>x</sub> from ship exhaust (Fig. S3). NO<sub>2</sub> time series at the coastal station (Fig. 9b) indicates that the model overestimates NO<sub>2</sub> concentrations in hours where the NO<sub>2</sub> contribution from non-road transport is the highest. The unrealistic NO<sub>2</sub> peaks from non-road transport suggest that shipping emissions are overestimated in the HERMESv2.0 model, which HERMESv2.0 uses

the EMEP gridded emission ~~database-inventory~~ at 50 km x 50 km horizontal resolution to estimate shipping emissions and spatially distributes them to the 4-km model domain using the marine routes reported by Wang et al. (2008).

5 A recent review on the state-of-the-art of marine traffic emissions (Russo et al., 2018) indicates that STEAM appears as the most reliable and detailed emissions inventory since it is based on Automatic Identification System data and specific vessel information, with a resolution of 2.5 x 2.5 km<sup>2</sup> (Jalkanen et al., 2016). A comparative analysis indicates that EMEP gridded inventories are overestimated, in particular over hotspots in the Mediterranean shipping routes, and underestimated in secondary routes. Marine traffic emissions estimated with current state-of-the-art methods, such as the use of data provided by Automatic Identification System (AIS), show large discrepancies with the reported CEIP-EMEP gridded inventories both in term of totals and spatial distribution (Jalkanen et al., 2012), suggesting that uncertainties associated to current official emissions may be large. This factor, added to the 15% decrease of NO<sub>x</sub> shipping emissions observed in Europe between 2009 (HERMESv2.0 base year) and 2012 (EMEP CEIP, 2019<sup>http://www.ceip.at</sup>) could ~~can at least partly~~ explain the discrepancies observed.

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15 O<sub>3</sub> peaks are highly biased (by ~40-50 µg m<sup>-3</sup>) during stagnant conditions on July 28<sup>th</sup>-31<sup>st</sup>, especially in the urban station (station 5). During these days, measured NO<sub>2</sub> daily peaks increased up to 40 µg m<sup>-3</sup>. Although the model reproduces the variability, it overestimates the concentration due to an excessive on road transport contribution. As discussed for the CIP, under low dispersion conditions NO<sub>2</sub> concentrations are difficult to model due to complex mixing regimes.

#### 3.4.4 The Northwestern ~~northwest of the~~ Iberian Peninsula

20 Figures 9c and 9d show the source apportionment time series at one urban (station 7) and one rural (station 8) background station in the NWIP. The urban station (Fig. 9c) located in Santiago de Compostela, a medium size city with ~100,000 inhabitants, shows a high NO<sub>2</sub> concentration with a dominant contribution from the road transport sector. Traffic NO<sub>2</sub> is the main sink of urban O<sub>3</sub> via titration. Because NO<sub>2</sub> is underestimated, especially during stagnant conditions (July 24<sup>th</sup>-27<sup>th</sup>), O<sub>3</sub> concentrations are overestimated (MB category C).

25 In rural background areas (Fig. 9d), ~~Despite the O<sub>3</sub> biases during stagnant conditions,~~ the modelled O<sub>3</sub> concentration is in general agreement with observations at the rural background station (Fig. 9d)(MB category B), but the model tends to underestimate the observed concentrations, particularly under weak winds. NO<sub>2</sub> is likely to be underestimated due to missing traffic emissions. As noted previously, traffic emissions are poorly constrained in small and medium size cities; due to a lack of detailed information. There is also additional uncertainty in the precursors emitted from the large coal power plants and industries in the region (Valverde et al., 2016b). Our study uses emissions for 2009, and it has been estimated that between 2009 and 2012 energy production in coal-fired power plants increased from 13.1% to 19.4% (UNESA, 2012), ~~which. This implies~~ <sup>implied</sup> an increase of ~~in~~ NO<sub>x</sub> emissions from the power industry sector of around 19.5% (EMEP CEIP, 2019).

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~~Despite the O<sub>3</sub> biases during stagnant conditions, t~~The time series show that ~~the~~ model reproduces reasonably well the observed O<sub>3</sub> variability under different synoptic conditions. O<sub>3</sub> reaches the highest concentration (~100/150 µgm<sup>-3</sup> in urban/rural areas) under stagnant conditions (July 24<sup>th</sup>-27<sup>th</sup>) when the contribution of anthropogenic sources from all activity sectors is the highest (60-70%). O<sub>3</sub> concentrations decrease down to ~70 µgm<sup>-3</sup> under NW advective conditions (e.g., July 28<sup>th</sup>-30<sup>th</sup>) when the imported O<sub>3</sub> shows the highest contribution (80-90%). Saavedra et al. (2012) found that stationary anticyclones ~~over the NWIP~~~~over the northern~~ play an important role in the occurrence of high O<sub>3</sub> concentrations ~~over the NWIP~~. Our results show that under these stagnant conditions O<sub>3</sub> concentrations are due largely to in situ production (photochemistry) from on-road traffic, shipping, power plants, and industry in almost the same proportion.

### 3.5 Imported ozone

~~These O<sub>3</sub> source apportionment results~~~~The results presented before~~Our results indicate that imported O<sub>3</sub> represents the highest contribution to ground-level O<sub>3</sub> concentration in southwestern Europe. Imported O<sub>3</sub> enters the IP4 domain through the boundaries; it includes the contribution of O<sub>3</sub> from the EU12 domain, which in turn includes the contribution of hemispheric O<sub>3</sub> from the MOZART-4 global model. The imported O<sub>3</sub> is as large as the background O<sub>3</sub> regionally produced within the IP. ~~We~~Note that the small biases at rural background stations obtained in the evaluation section indicate an overall high performance of the modelled background O<sub>3</sub> in the IP4 domain (Fig. S1). Given ~~its importance~~~~the important implications and robustness of this results~~, ~~this section is devoted to analyse the importance of the imported O<sub>3</sub> in southwestern Europe~~~~we further analyse this contribution below~~. In particular, we aim to understand its high contribution within the IP, ~~even~~, far from the model domain boundaries.

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Figure 10 shows the vertical cross-sections at 6, 12, and 18 UTC for O<sub>3</sub> and NO<sub>2</sub> at a constant latitude (40.38° N) on July 25<sup>th</sup>, 28<sup>th</sup> and 30<sup>th</sup>. ~~It helps to understand the vertical variability of both pollutants with the PBL dynamic as schematized by Millán et al. (1996)~~. The model predicts a pronounced O<sub>3</sub> vertical gradient above a height of 4 km above sea level (asl), showing that O<sub>3</sub> in the free troposphere is, to a large extent, imported to the IP4 domain (Safieddine et al., 2014). As expected, NO<sub>2</sub> mixing ratios show a negative gradient with altitude as it is mainly emitted at the surface. In the morning, the sun starts to heat up the ground, producing convective thermals and forcing the growth of the mixing layer. At noon, the mixing height reaches its maximum, being the highest in the CIP (2-4 km) and decreasing towards the coast (< 1 km) (Fig. 10). At the mixing layer top the O<sub>3</sub>-enriched air aloft is entrained into the mixing layer, mixing with O<sub>3</sub> and other pollutants produced locally within the mixing layer. When the mixing height decreases, O<sub>3</sub> is left in the free troposphere forming high O<sub>3</sub> residual layers (Gangoiti et al., 2001) that contribute to the regional transport. Over the following days, these residual layers (composed of imported O<sub>3</sub> and local O<sub>3</sub> produced within the domain over previous days) can be entrained by fumigation into the mixing layer to reach the surface. This fumigation effect, previously described in the eastern USA

(Zhang and Rao, 1999; Langford et al., 2015) and in the Western Mediterranean Basin (Kalabokas et al., 2017; Querol et al., 2018), leads to a rapid increase in O<sub>3</sub> concentrations at ground level. The accumulation and recirculation of air masses is intensified along the Eastern Mediterranean coast (Millán et al., 1996, 2000; Gangoiti et al., 2001; Querol et al., 2017) by the action of the breezes and mountain-valley winds. Furthermore, the small deposition velocity of O<sub>3</sub> over the sea and its high atmospheric lifetime in the free troposphere contributes to enrich the O<sub>3</sub> background concentration (c.a. several weeks, Monks et al., 2015; Seinfeld and Pandis, 2016).

The O<sub>3</sub> fumigation effect was particularly intense on July 30<sup>th</sup>-31<sup>st</sup>, when a high O<sub>3</sub> levels are found in the free troposphere compared to previous days (Fig. 10). The analysis of the O<sub>3</sub> concentration map with the imported O<sub>3</sub> contributions (Fig. 6) indicates that ground-based O<sub>3</sub> is neither advected nor titrated; therefore, it can only result from vertical mixing. The high O<sub>3</sub> mixing ratio in the free troposphere was mainly due to O<sub>3</sub> advection entering the Atlantic boundary driven by westerlies (Fig. 3). We hypothesize that two events may have contributed to the increase of the O<sub>3</sub> concentration by long-range transport. First, a low-pressure system in the British Islands on July 28<sup>th</sup> could have transported significant O<sub>3</sub> amounts from the stratosphere to the free troposphere (Fig. S4 Fig. S7). Second, O<sub>3</sub> episodes generated in mid-July over the Eastern USA predicted by the MOZART-4 model could have contributed to an increase in the O<sub>3</sub> transported from N America to Europe by the action of the prevailing westerlies (Fig. S7 Fig. S4) associated with cyclonic systems along the “warm conveyor belt” (Pausata, et al., 2012; Derwent et al., 2015).

#### 4 Discussion and conclusions

Our study has provided a first estimation of the main sources responsible for high O<sub>3</sub> concentration in the Western Mediterranean Basin during the episode period July 21<sup>st</sup> -31<sup>st</sup>, 2012. We used the Integrated Source Apportionment Method (ISAM) within the CALIOPE system to estimate the contribution of the main anthropogenic activity sectors compared to the imported concentrations to peak O<sub>3</sub> events in Spain compared to the imported O<sub>3</sub>. In addition, the use of ISAM has allowed an in-depth evaluation of the applied modelling system the model, and has provided a perspective on about its potential use for regulatory studies in non-attainment regions.

The results demonstrate that the O<sub>3</sub> problem over the Western Mediterranean Basin is local, regional, and hemispheric. Long-range transport of O<sub>3</sub> from beyond the IP domain is the main contributor to the ground-level daily mean O<sub>3</sub> concentration (~45%) during peak episodes. The imported O<sub>3</sub> contribution ranges from 40% during O<sub>3</sub> peaks to 80% at night or during well-ventilated conditions. The absolute imported O<sub>3</sub> is higher in the NEIP than in the central-CIP due to the recirculation and accumulation of pollutants along the Mediterranean. The high imported O<sub>3</sub> at the surface far away from the model boundaries is consistent with the high levels of O<sub>3</sub> in the free troposphere (resulting from local/regional layering and accumulation, and continental/hemispheric transport) along with intense vertical mixing during the day.

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Our results support the European Commission (EC, 2004) in pointing out that the effectiveness of abatement strategies for achieving compliance with the European air quality standards in southern Europe might be compromised by the long-range transport of O<sub>3</sub>. This is especially true in Mediterranean regions (i.e., NEIP, EV and EIP) where the contribution of imported O<sub>3</sub> is particularly dominant (60-68% of the daily mean O<sub>3</sub> concentration ~~in episodes~~) as a result of the accumulation and recirculation of pollutants over the Mediterranean Basin. In those areas, if the long-range transport of O<sub>3</sub> is not reduced, the mean background level will not decrease making it more vulnerable to exceedances of the O<sub>3</sub> target values by enhanced local production under stagnant conditions.

During high O<sub>3</sub> events, the imported O<sub>3</sub> is added to the formation from local and regional anthropogenic sectors. The road transport is an important contributor to the O<sub>3</sub> concentration in rural areas downwind of the large cities in Spain. It contributed up to 16-18% of the daily mean O<sub>3</sub> concentration under exceedances of the target value for human health protection, and up to 70 µg m<sup>-3</sup> on an hourly basis downwind of Barcelona and Madrid.

The non-road transport sector (including international shipping, airport and agricultural machinery) is as significant as road transport inland (10-19% of the daily mean O<sub>3</sub> concentration during the peaks). There is a high influence of international shipping (13%), affecting the coastal areas in the Mediterranean and the south of the IP (along the Strait of Gibraltar) with contributions of up to ~20 and ~30 µg/m<sup>3</sup>, respectively. Although the non-road transport contribution was found to be overestimated in coastal areas in the south of the IP in the present experiment, it cannot be neglected and actions controlling international shipping should be considered as important as those related with road transport especially in regions with big harbours (e.g., Huelva and Barcelona). Dalsøren et al. (2010) indicated that annual O<sub>3</sub> concentration is increasing yearly in a range of 0.5-2.5 ppb in areas impacted by shipping activities. Recent studies indicate that shipping emissions are projected to increase significantly due to increases in transportation demand and traffic. As the Strait of Gibraltar is the only shipping route connecting the Atlantic Ocean with the Mediterranean Basin, the regulation of these emissions is key in order to control O<sub>3</sub> exceedances in Spain and the Mediterranean Basin. Shipping emissions can be regulated by each country within 400 km of coastlines, but policy-induced controls for offshore emissions are very dependent on the success of adopted and proposed regulations within the International Maritime Organization.

The energy and industrial sectors contribute ~6-11% of the daily mean O<sub>3</sub> concentration during the peaks and over all the receptor regions. As they ~~usually~~ are usually injected in high altitudes, their contribution extends way beyond their surroundings. The energy combustion sector (3%) and industrial and non-industrial combustion sectors (3%) have a mean contribution of 2-4 µg m<sup>-3</sup>, going up to 4-6 µg m<sup>-3</sup> in NO<sub>x</sub>-limited areas (i.e., the western IP). In highly industrialized regions (i.e., Guadalquivir Basin and northwestern IP), abatement strategies affecting all sectors at regional scale could contribute to

decrease the local formation of O<sub>3</sub> as the regional/local anthropogenic contribution can be greater than 50% during several days.

In the Barcelona Metropolitan Area the contribution from energy and industrial sectors to the NO<sub>2</sub> concentrations can be in the same range than the contribution from road transport (~40-60%, Fig. 8c). In contrast, in areas downwind Barcelona the contribution from energy and industrial sectors to O<sub>3</sub> concentrations is relatively low compared with the contribution from road transport (Fig. 8d). The different contribution to O<sub>3</sub> concentration might be related to the different reactivity of VOC for O<sub>3</sub> formation. Each VOC emission source emits a different mix of VOC, which makes a different contribution to photochemical ozone formation. For example, in the UK, Derwent et al. (2007) showed a higher photochemical O<sub>3</sub> creation potential for road transport emissions than for production processes and combustion. Future national policy actions to control the emissions of VOC should tackle the sources that contribute more to photochemical O<sub>3</sub> formation.

The remaining sectors (i.e., SNAP 2, 5, 6, 9, and 11, see Table 1), are the fourth main contributors to the daily mean O<sub>3</sub> concentration during the days exceeding the target value (~2-8%). Future work should tag the biogenic sources as an individual sector as it is the main contributor to VOC emissions in Spain (i.e., ~70% in 2009 according to HERMESv2.0 model).

~~According to the model uncertainty, the~~ air quality and meteorological evaluation ~~of the model~~ indicate that uncertainties in our model are in the same range as the most recent inter-comparison studies using state-of-the-art air quality models. In addition, our model evaluation together with the source apportionment results has allowed a better understanding of the origin of model errors related to the emission estimates. Our methodological choice has been to use a detailed bottom-up emission inventory instead of a typical top-down regional emission inventory. Bottom-up emissions, estimated using source-specific emission factors and activity statistics, accurately characterise pollutant sources and allow obtaining more realistic results than the ones reported by top-down or regional emission inventories. To understand the impact of the use of 2009 data to study year 2012, we revised the EMEP Centre on Emission Inventories and Projections (EMEP-CEIP), which collects and reviews the national emission inventories from Parties to the Convention on Long-range Transboundary Air Pollution. Between 2009 and 2012, total NO<sub>x</sub> and NMVOC emissions in Spain decreased by -10.6% and -10.7%, respectively (EMEP CEIP, 2019). For NO<sub>x</sub>, around 80% of this reduction is linked to a reduction of road transport emissions, whereas in the case of NMVOC ~50% of the reduction is due to a decrease in industrial emissions. For our modelling study, we consider these differences as small and acceptable, and not creating any major inconsistency. The difference of 10-15 % in emissions for certain precursors between 2009 and 2012 is within the typically larger ranges of uncertainty in emission inventories.

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Another relevant and uncertain source for  $O_3$  concentration is the urban VOC emitted in urban areas emissions. Future tasks should be devoted to the continuous monitoring of urban VOC and take advantage of satellite observations to improve speciation and spatial variability of urban VOC emissions.

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We have identified two sources of uncertainty in the modelling estimation of the imported  $O_3$  concentration. First, it depends on both the performance of the CALIOPE system over EU12, and on MOZART-4 at global scale. The small biases at rural background stations support an overall high performance baseline background  $O_3$  in the IP4 domain (Fig. S1). Second, our set-up involves some uncertainty in the estimation of the imported contribution of  $O_3$ . In reality, there is a fraction of the imported  $O_3$  that may have been generated within the IP4 domain before the period of simulation (including the spin-up). We have assumed that this fraction is negligible and future works should check to what extent this assumption is correct.

For regulatory applications, further source apportionment studies should target not only emissions from activity sectors, but also the source regions where the emission abatement strategies should be applied. In addition, future studies should preferentially cover multiple summer periods in order to improve representativeness. We note that our results cannot predict whether emission abatement will have either a positive or negative effect in  $O_3$  changes due to the non-linearity of the  $O_3$  generation process. Subsequent source sensitivity analyses tailoring the identified main contribution sources could predict how  $O_3$  will respond to reductions in precursor emissions, which are essential to define the most efficient  $O_3$  abatement strategies in the Western Mediterranean Basin.

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Overall, we find that the imported  $O_3$  is the largest input to the ground-level  $O_3$  concentration in the IP during the studied episode. However, during stagnant conditions, the emission from local anthropogenic activities in the IP control the  $O_3$  peaks in areas downwind of the main urban and industrial regions. Furthermore, ground-level  $O_3$  concentrations are strongly affected by vertical downward mixing of  $O_3$ -rich layers in the free troposphere, which result from local/regional layering and accumulation, and continental/hemispheric transport. The importance of both imported and local contributions to the  $O_3$  peaks in the IP demonstrates the need for detailed quantification of both contributions to high  $O_3$  concentrations for local  $O_3$  management. Furthermore, the influence of local sources and topographical and meteorological conditions in the high  $O_3$  concentration indicate the importance of designing  $O_3$  abatement policies at local scale.

This work has identified and quantified the local and imported contributions to  $O_3$  concentration during an episode in a particular area in southwestern Europe. In addition, we have provided a perspective about the potential use of source apportionment method for regulatory studies in non-attainment regions. However, further  $O_3$  source apportionment studies targeting other non-attainment regions in Europe covering different episodes are necessary prior to defining local mitigation

~~measurements that complement national and European-wide abatement strategies to reach the efforts. European O<sub>3</sub> objectives.~~

~~We investigate the origin of ground-level O<sub>3</sub> concentration over southwestern Europe during the episode July 21<sup>st</sup>–31<sup>st</sup>, 2012. The period includes the two most frequent summer synoptic circulation patterns over the region: stagnant conditions with development of the Iberian Thermal Low (ITL) and North-Western Advection (NWAd). We used the Integrated Source Apportionment Method (ISAM) within the CALIOPE system to estimate the main sources responsible of the high O<sub>3</sub> concentrations in receptor regions over the IP compared to the imported (regional and hemispheric) O<sub>3</sub> contribution. In addition, the source apportionment method has allowed an in-depth evaluation of the modelling system applied. Below, we summarize the new findings from the source attribution study, we discuss the model uncertainties and we give a perspective on some of the regulatory implications, which may be applicable to other non-attainment regions.~~

#### ~~4.1 Source apportionment results~~

~~The results demonstrate that the O<sub>3</sub> problem over the Western Mediterranean Basin is local, regional, and hemispheric. Long-range transport of O<sub>3</sub> from beyond the IP domain is the main contributor to the ground-level daily mean O<sub>3</sub> concentration (~45%) during peak episodes. The imported O<sub>3</sub> contribution ranges from 40% during O<sub>3</sub> peaks to 80% at night or during well-ventilated conditions. The absolute imported O<sub>3</sub> is higher in NEIP than in the central IP due to the recirculation and accumulation of pollutants along the Mediterranean. The high imported O<sub>3</sub> at the surface far away from the model boundaries is consistent with the high levels of O<sub>3</sub> in the free troposphere (resulting from local/regional layering and accumulation, and continental/hemispheric transport) along with intense vertical mixing during the day.~~

~~During high O<sub>3</sub> events, the imported O<sub>3</sub> is added to the local and regional anthropogenic contributions. The road transport is an important contributor to the O<sub>3</sub> concentration in rural areas downwind of the large cities in Spain. It contributed up to 16–18% of the daily mean O<sub>3</sub> concentration under exceedances of the target value for human health protection, and up to 70 µg m<sup>-3</sup> on an hourly basis downwind of Barcelona and Madrid. The non-road transport sector is as significant as road transport inland (10–19% of the daily mean O<sub>3</sub> concentration during the peaks). There is a high influence of international shipping (13%), affecting the coastal areas in the Mediterranean and the southern IP (along the Strait of Gibraltar) with contributions of up to ~20 and ~30 µg/m<sup>3</sup>, respectively. The energy and industrial sectors contribute ~6–11% of the daily mean O<sub>3</sub> concentration during the peaks and over all the receptor regions. As they usually are injected in high altitudes, their contribution extend way beyond their surroundings. The energy combustion sector (3%) and industrial and non-industrial combustion sectors (3%) have a mean contribution of 2–4 µg m<sup>-3</sup>, going up to 4–6 µg m<sup>-3</sup> in NO<sub>x</sub> limited areas (i.e., the western IP). The OFHR tag, which lumped the remaining sectors (i.e., SNAP 2, 5, 6, 9, and 11, see Table 1), is the fourth main contribution to the daily mean O<sub>3</sub> concentration during the days exceeding the target value (~2–8%). Future work~~

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should tag the biogenic sources as an individual sector as it is the main contributor to VOC emissions in Spain (i.e., ~70% in 2009 according to HERMESv2.0 model).

#### 4.2 Model uncertainty

The modelled concentrations present uncertainties that are in the same range as the most recent inter-comparison studies using state-of-the-art air quality models. Our results show a good agreement between the modelled and observed  $O_3$ , which provides confidence in our source apportionment results.

In addition, our model evaluation together with the source apportionment results has allowed a better understanding of the origin of model errors. Under stagnant conditions, the model shows lower performances: in coastal areas, this may be related to a poor representation of mesoscales processes such as sea breezes and recirculation; in Madrid,  $NO_2$  overestimations may be due to a poor representation of the vertical mixing. There is likely an overestimation of shipping emissions, and an underestimation of road transport emissions in medium size cities.

Overall, the estimated imported  $O_3$  depends on both the performance of the CALIOPE system over EU12, and on MOZART 4 at global scale. The evaluation of model in the EU12 domain using the European EIONET stations (not shown here) showed good skills for  $O_3$  and its precursors. Furthermore, the source apportionment results have shown that  $O_3$  local production could be as large as the imported  $O_3$ , so the small biases at rural background stations indicate an overall high performance baseline background  $O_3$  in the IP4 domain (Fig. S1). This study has not evaluated MOZART 4, but there are many studies supporting its good performance. Several inter-comparison studies (e.g., EURODELTA and AQMEII) also found the importance of chemical boundary conditions to reproduce the  $O_3$  background concentrations (Giordano et al., 2015; Bessagnet et al., 2016; Solazzo et al., 2017).

Our set up involves some uncertainty in the estimation of the imported contribution of  $O_3$ . In reality, there is a fraction of the imported  $O_3$  that may have been generated within the IP4 domain before the period of simulation (including the spin up). We have assumed that this fraction is negligible and future works should check to what extent this assumption is correct.

#### 4.3 Regulatory implications

Our study has identified the main sources responsible of high  $O_3$  in receptor regions in the Western Mediterranean Basin, but cannot predict whether emission abatement will have either a positive or negative effect in  $O_3$  changes due to the non-linearity of the  $O_3$  generation process (Monks et al., 2015 and papers therein). Subsequent source sensitivity analysis tailoring the identified main contribution sources could predict how  $O_3$  will respond to reductions in precursor emissions. Future source sensitivity studies are essential to define the most efficient abatement strategies to reduce high  $O_3$  concentrations in the Western Mediterranean Basin. Complementarily, it would be important to know where the emission

abatement strategies should be applied. To answer this question further source apportionment studies should be conducted tagging both source activities and source regions.

5 This case study supports a relatively old conclusion by the European Commission (EC, 2004) pointing out that the effectiveness of abatement strategies for achieving compliance with the European air quality standards in southern Europe might be compromised by the long range transport of  $O_3$ . This is especially true in Mediterranean regions (i.e., NEIP, EV and EIP) where the contribution of imported  $O_3$  is particularly dominant (60-68% of the daily mean  $O_3$  concentration in episodes) as a result of the accumulation and recirculation of pollutants over the Mediterranean Basin. In those areas, if the long range transport of  $O_3$  is not reduced, the mean background level will not decrease making it more vulnerable to  
10 exceedances of the  $O_3$  target values by enhanced local production under stagnant conditions.

Reduction of the background  $O_3$  concentration can be achieved by decreasing the concentrations of  $O_3$  and precursors aloft. Given the polluted dome aloft the Western Mediterranean Basin during a typical  $O_3$  episode, which may result from local/regional layering and accumulation, and continental/hemispheric transport, it will necessary and important to  
15 implement emission reduction strategies on the hemispheric and continental scale. There is an urgent need of international collaboration at European and hemispheric level to reduce  $O_3$  and its precursors. High background contribution to Iberian  $O_3$  could represent a substantial future challenge to the attainment of  $O_3$  limit values, which requires controlling hemispheric  $O_3$  (EC, 2004; Fowler et al., 2013).

20 Besides the long range transport contribution,  $O_3$  peaks during episodes result from the local/regional photochemical formation from the transport and industrial sectors, and therefore regional emission reduction strategies are also urgent. The contribution from road transport determines  $O_3$  peaks in rural areas (up to  $70 \mu\text{g}/\text{m}^3$ ) downwind of the main Spanish Metropolitan Areas (i.e., Madrid and Barcelona). To reduce  $O_3$  peaks downwind of the Madrid city, a decrease of road transport emissions in the urban area would be effective. However, to reduce  $O_3$  peaks downwind of the Barcelona city, the  
25 reduction of road traffic emission in the city should be complemented with abatement strategies in other Mediterranean cities, especially in Southern France.

In the BMA the contribution from energy and industrial sectors to  $\text{NO}_2$  concentration can be in the same range than the contribution from road transport (~40-60%, Fig. 8c). In contrast, in areas downwind of the BMA the contribution from energy and industrial sectors to  $O_3$  concentrations is relatively low compared with the contribution from road transport (Fig. 8d). The differences contribution to  $O_3$  concentration might link with the different reactivity of VOC for  $O_3$  formation. Each VOC emission source emits a different mix of VOC, which makes a different contribution to photochemical ozone formation. For example, in the UK, Derwent et al. (2007) showed a higher photochemical  $O_3$  creation potential for road

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transport emissions than for production processes and combustion. Future national policy actions to control the emissions of VOC should tackle the sources that contribute more to photochemical O<sub>3</sub> formation.

Although the non road transport contribution was found to be overestimated in coastal areas in the south of the IP in the present experiment, it cannot be neglected and actions controlling international shipping should be considered as important as those related with road transport especially in regions with big harbours (e.g., Huelva and Barcelona). Dalsøren et al. (2010) indicated that annual O<sub>3</sub> concentration is increasing yearly in a range of 0.5–2.5 ppb in areas impacted by shipping activities. Recent studies indicate that shipping emissions are projected to increase significantly due to increases in transportation demand and traffic. As the Strait of Gibraltar is the only shipping route connecting the Atlantic Ocean with the Mediterranean Basin, the regulation of these emissions is key in order to control O<sub>3</sub> exceedances in Spain and the Mediterranean Basin. Shipping emissions can be regulated by each country within 400 km of coastlines, but policy induced controls for offshore emissions are very dependent on the success of adopted and proposed regulations within the International Maritime Organization.

In highly industrialized regions (i.e., Guadalquivir Basin and northwestern IP), abatement strategies affecting all sectors at regional scale could contribute to decrease the local formation of O<sub>3</sub> as the regional/local anthropogenic contribution can be greater than 50% during several days.

Overall, we find that the imported O<sub>3</sub> is the largest input to the ground level O<sub>3</sub> concentration in the IP during episodes. In addition, during stagnant conditions, the emission from local anthropogenic activities in the IP control the O<sub>3</sub> peaks in areas downwind of the main urban and industrial regions. Furthermore, ground level O<sub>3</sub> concentrations are strongly affected by vertical downward mixing of O<sub>3</sub> rich layers in the free troposphere, which result from local/regional layering and accumulation, and continental/hemispheric transport. The importance of both imported and local contributions to the O<sub>3</sub> peaks in the IP demonstrates the need for detailed quantification of both contributions to high O<sub>3</sub> concentrations for local O<sub>3</sub> management. Furthermore, the influence of local sources and topographical and meteorological conditions in the high O<sub>3</sub> concentration indicate the importance of designing O<sub>3</sub> abatement policies at local scale.

This work has identified local and imported contributions to O<sub>3</sub> concentration during an episode in a particular area in southwestern Europe. However, further detailed and longer O<sub>3</sub> source apportionment studies targeting other nonattainment regions in Europe are necessary prior to define local mitigation measurements that complement national and European-wide strategies to reach the European O<sub>3</sub> objectives.

### Data availability

Air quality measurements are available at the EIONET database (<https://www.eea.europa.eu/data-and-maps/data/airbase-the-european-air-quality-database-7>). The CMAQ code is available at the <https://www.cmascenter.org/>. The WRF-ARW code is available at [http://www2.mmm.ucar.edu/wrf/users/download/get\\_source.html](http://www2.mmm.ucar.edu/wrf/users/download/get_source.html). Download Mozart-4 outputs are available at <http://www.acd.ucar.edu/wrf-chem/mozart.shtml>. The program that generates CMAQ boundary conditions from MOZART-4 output is available at: <http://www.camx.com/getmedia/a0c2d710-6187-47bb-af3f-bd9b4a4d19bb/mozart2camx-12jul17.tgz>. The HERMESv2 outputs are available upon request. The modelled data in this study are available upon request from the corresponding author.

## 10 Appendix A

Table 1A shows the acronyms used in the text.

|        |   |
|--------|---|
| BCON   | Chemical boundary conditions to IP4, also named as imported O <sub>3</sub> contribution             |
| BMA    | Barcelona Metropolitan Area   |
| CIP    | Central Iberian Peninsula   |
| CMAQ   | Community Multiscale Air Quality model  |
| EIP    | Eastern Iberian Peninsula   |
| EU12   | European domain at 12-km horizontal resolution (12x12 km <sup>2</sup> )                             |
| EV     | Ebro Valley   |
| GV     | Guadalquivir Valley   |
| IP     | Iberian Peninsula   |
| IP4    | Iberian Peninsula domain at 4-km horizontal resolution (4x4 km <sup>2</sup> )                       |
| ISAM   | Integrated Source Apportionment Method  |
| MDA8   | Maximum daily 8-hour average concentration  |
| MMA    | Madrid Metropolitan Area  |
| MED    | Mediterranean Sea   |
| NEIP   | Northeast of the <del>thern</del> Iberian Peninsula   |
| NIP    | North of the <del>thern</del> Iberian Peninsula   |
| NWIP   | Northwest of the <del>thern</del> Iberian Peninsula   |
| SIP    | South of the <del>thern</del> Iberian Peninsula   |
| SNAP1  | Emission sector on combustion in energy   |
| SNAP34 | Emission sector on combustion and processes in industry   |
| SNAP7  | Emission sector on road transport, exhaust and non-exhaust  |
| SNAP8  | Emission sector on non-road transport (international shipping, airport and agricultural machinery ) |
| WIP    | West of the <del>thern</del> Iberian Peninsula  |
| WRF    | Weather Research and Forecasting Model  |

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## Appendix B

Definition of the discrete statistics used in the evaluation: correlation coefficient ( $r$ , Eq. B1), mean bias (MB, Eq. B2), normalized mean bias (NMB, Eq. B3) and root mean squared error (RMSE, Eq. B4). Where  $C_m(x, t)$  and  $C_o(x, t)$  are the modelled and observed concentrations at a location ( $x$ ) and time ( $t$ );  $N$  is the number of pairs of data.  $\overline{C_m}$  and  $\overline{C_o}$  are the modelled and observed mean concentrations over the whole period, respectively.

$$r = \frac{\sum_{i=1}^N (C_m(x,t) - \overline{C_m})(C_o(x,t) - \overline{C_o})}{\sqrt{\sum_{i=1}^N (C_m(x,t) - \overline{C_m})^2} \sqrt{\sum_{i=1}^N (C_o(x,t) - \overline{C_o})^2}} \quad (\text{B1})$$

$$MB = \frac{1}{N} \sum_{i=1}^N (C_m(x, t) - C_o(x, t)) \quad (\text{B2})$$

$$NMB = \frac{\sum_{i=1}^N (C_m(x,t) - C_o(x,t))}{\sum_{i=1}^N (C_o(x,t))} \times 100 = \left(\frac{C_m}{C_o} - 1\right) \times 100 \quad (\text{B3})$$

$$RMSE = \frac{1}{N} \sqrt{\sum_{i=1}^N (C_m(x, t) - C_o(x, t))^2} \quad (\text{B4})$$

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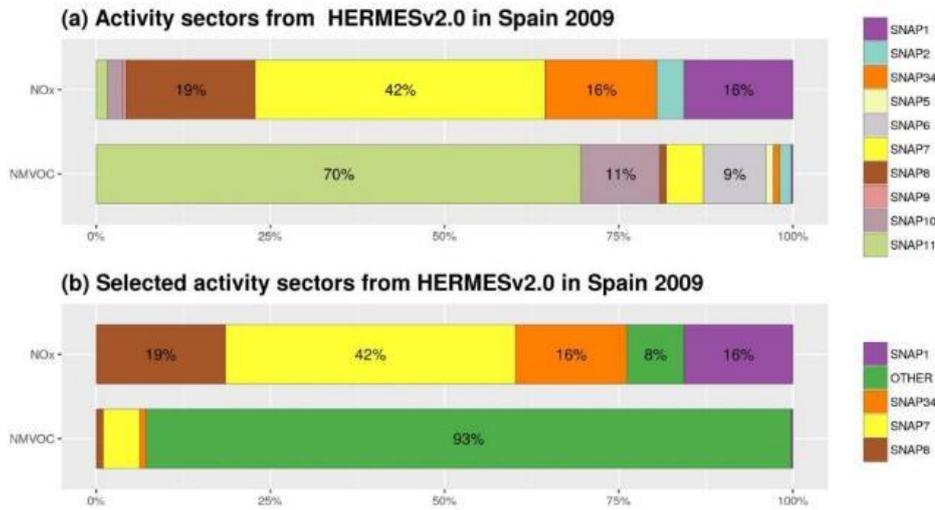


Figure 1: Percentage of the contribution of emissions to total annual emissions by SNAP sector calculated by HERMES for Spain 2009 (a) and for the selected SNAP sector accounting for more than 90% of NO<sub>x</sub> total emission to be tracked with ISAM (b). "OTHER" compiles the SNAP categories 2 (Residential combustion), 5 (Fugitive emissions from fuels), 6 (Solvent use), 9 (Waste management), 10 (Agriculture) and 11 (Other sources).

5

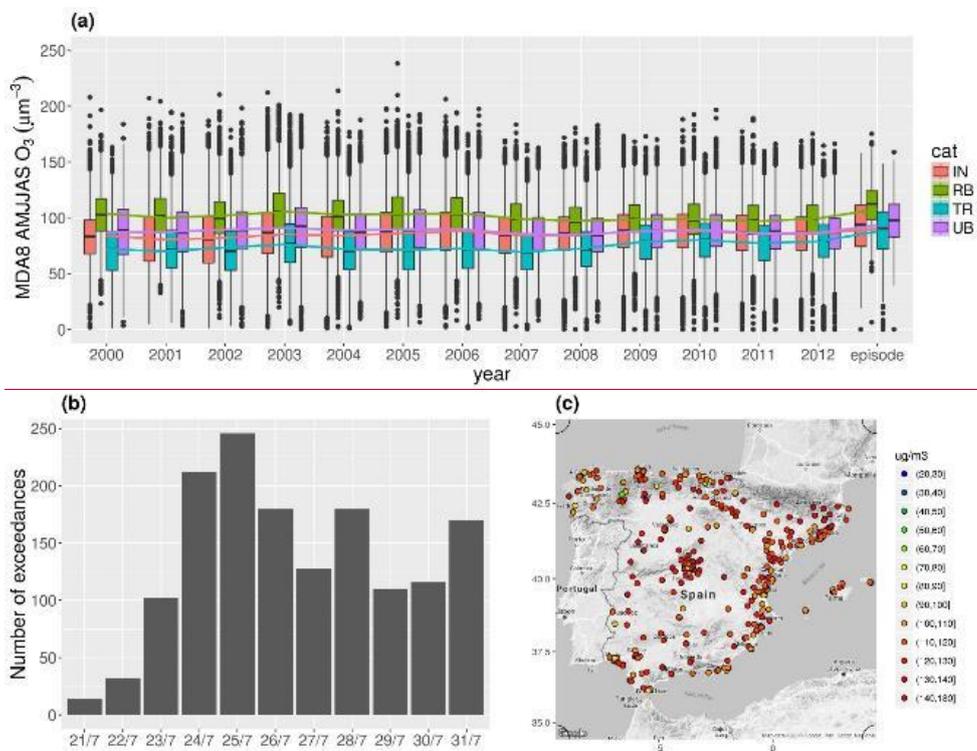
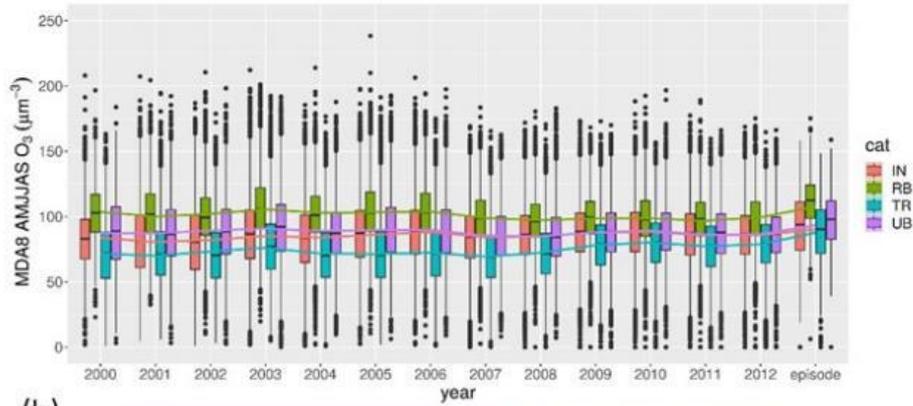


Figure 2: (a) Temporal distribution of the MDAS O<sub>3</sub> concentration during the extended summer (from April to September, AMJJAS) at the Spanish EIONET stations for the period 2000-2012 and the episode (from 21/07/2012 to 31/07/2012) by station type: IN (industrial), RB (rural background), TR (traffic) and UB (urban background). (b) Number of days exceeding the O<sub>3</sub> Target Value (120 µg/m<sup>3</sup>) by each day of the episode. (c) 90<sup>th</sup> percentile of the MDAS O<sub>3</sub> concentration at the Spanish EIONET stations during the

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episode-

(a)



(b)



Figure 2: (a) Temporal distribution of the MDA8 O<sub>3</sub> concentration during the extended summer (from April to September, AMJJAS) at the Spanish EIONET stations for the period 2000-2012 and the episode (from 21/07/2012 to 31/07/2012) by station type: IN (industrial), RB (rural background), TR (traffic) and UB (urban background). (b) 90<sup>th</sup> percentile of the MDA8 O<sub>3</sub> concentration at the Spanish EIONET stations during the episode. Numbers indicate the stations cited in section 3.4.

5 3.4.

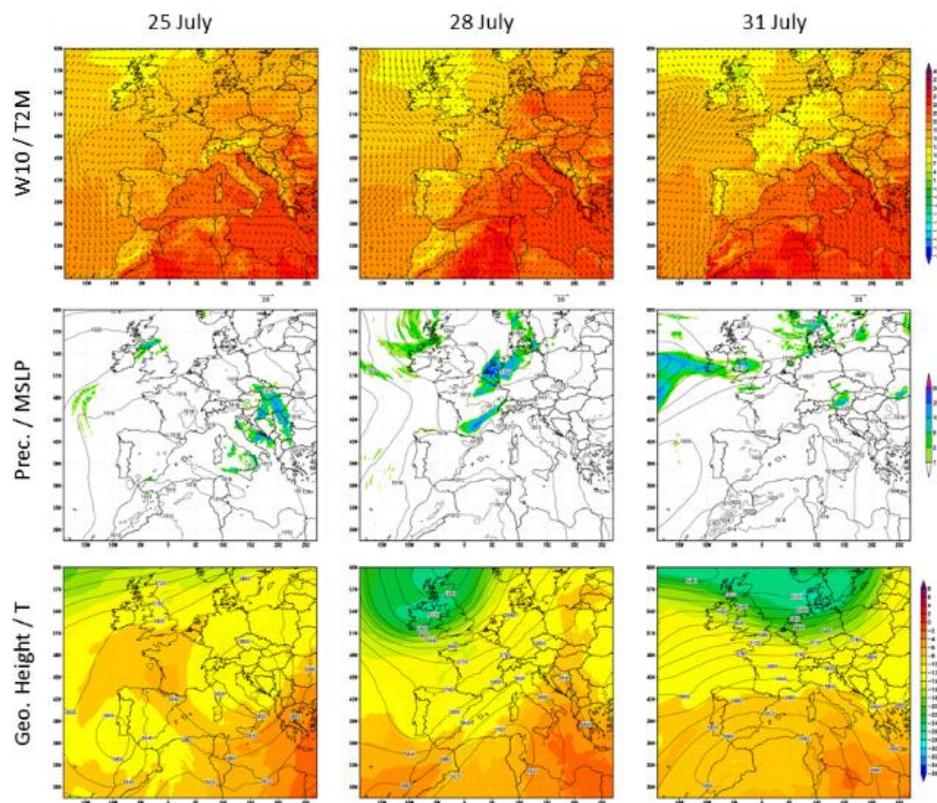


Figure 3: WRF-ARW meteorological fields at 6 UTC for July 25<sup>th</sup>, 28<sup>th</sup> and 31<sup>st</sup> in the EU12 domain: 10-m wind speed (W10,  $\text{ms}^{-1}$ ), 2-m temperature (T2M, C), 6 h accumulated precipitation (Prec., mm), mean sea level pressure (MSLP, hPa), 500-hPa geopotential height in contours (Geo. Height, m), and 500-hPa temperature in shaded colors (T, °C).

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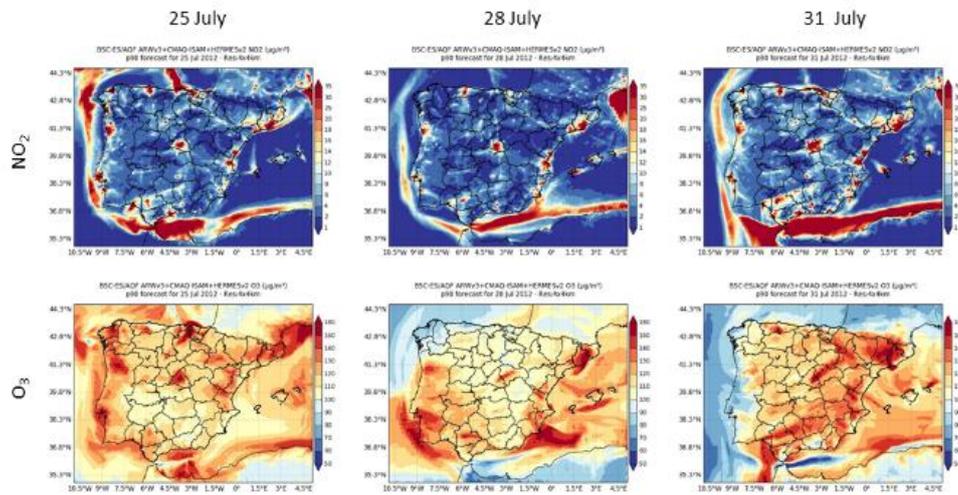
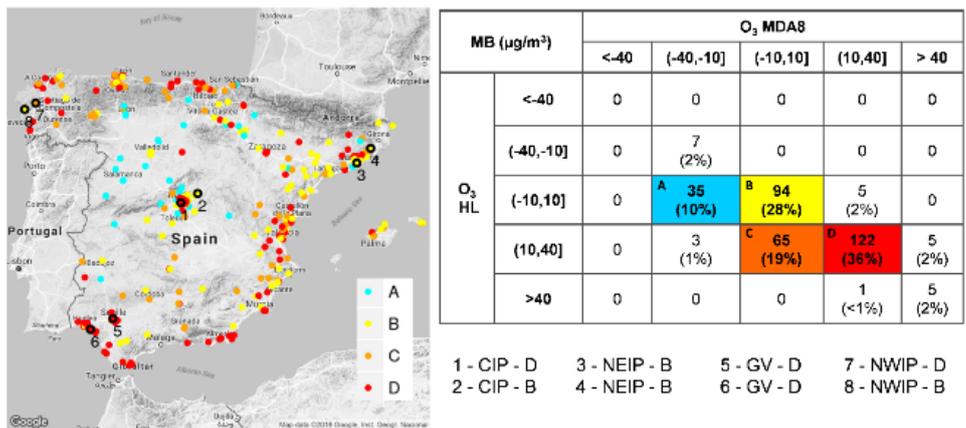


Figure 4: Ground-based concentration maps (in  $\mu\text{g}/\text{m}^3$ ) for  $\text{NO}_2$  (first row) and  $\text{O}_3$  (second row) corresponding to the 90<sup>th</sup> percentile of the average hourly concentrations on 25<sup>th</sup> (first column), 28<sup>th</sup> (second column) and 31<sup>st</sup> (third columns) July 2012.



5 Figure 5: Air quality stations classified by both mean bias (MB, in  $\mu\text{g}/\text{m}^3$ ) for average hourly and MDA8  $\text{O}_3$  at the Spanish EIONET stations and lumped by categories (A, B, C, and D). Numbered black circles indicate stations under study in Central IP (CIP; station 1 and 2), Northeastern IP (NEIP; station 3 and 4), Guadalquivir Valley (GV; station 5 and 6), and Northwestern IP (NWIP; station 7 and 8).

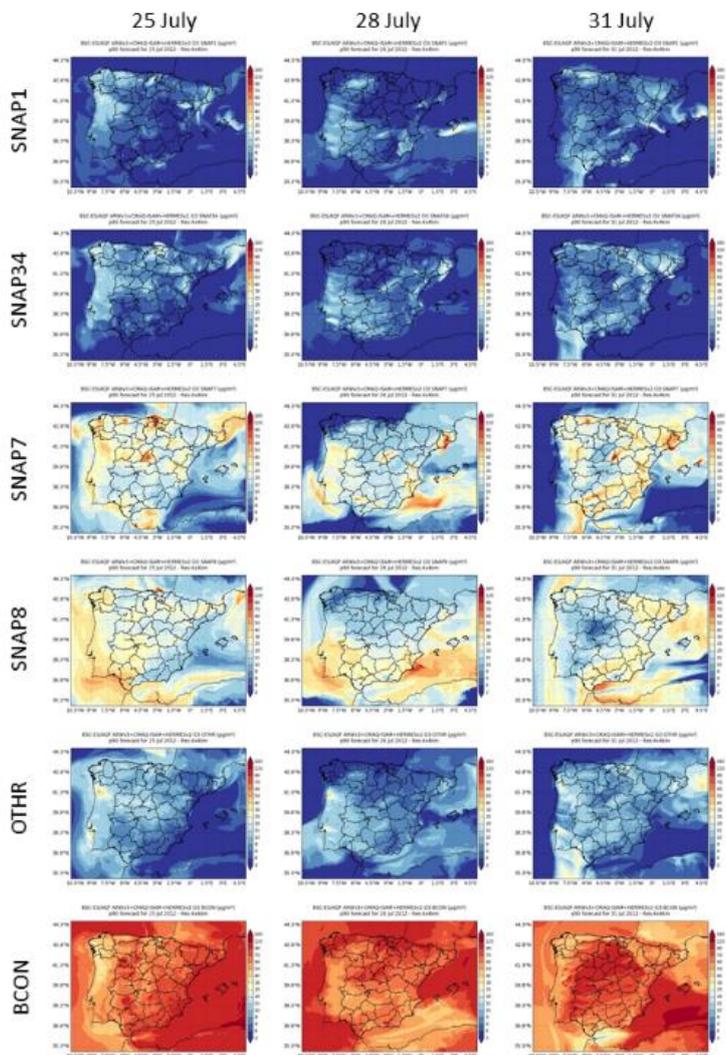
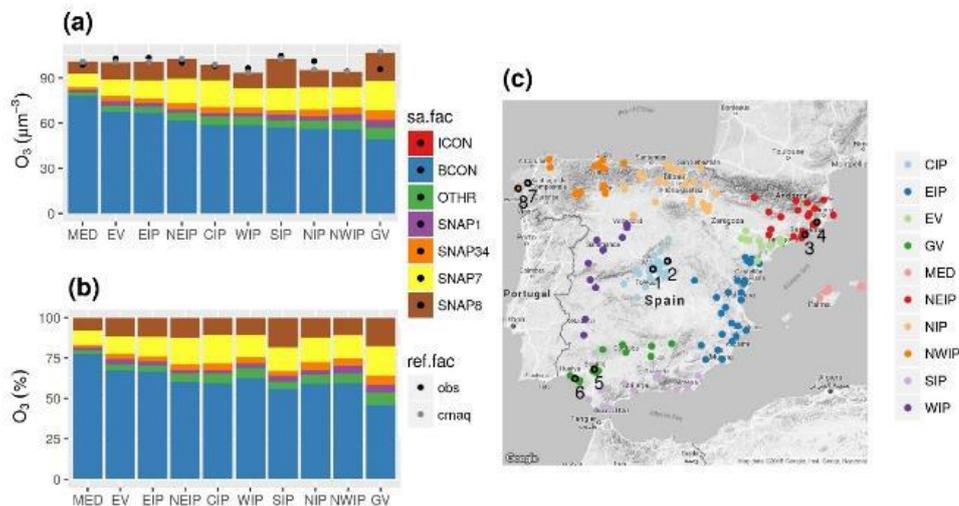


Figure 6: Tagged O<sub>3</sub> concentrations (in μg<sub>m</sub><sup>-3</sup>) corresponding to the 90<sup>th</sup> percentile (90p) of the average hourly concentrations: SNAP1, SNAP34, SNAP7, SNAP8, OTHER, and BCON for July 25<sup>th</sup> (first column), 28<sup>th</sup> (second column) and 31<sup>st</sup> (third columns) in 2012.



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Figure 7: Daily mean contribution in μg<sub>m</sub><sup>-3</sup> (a) and in percentage (b) of tagged sources to O<sub>3</sub> during exceedances of the observed 120 μg<sub>m</sub><sup>-3</sup> for MDA8 O<sub>3</sub> averaged by the identified receptor regions (c). Black and grey dots represent observed and modelled daily mean concentration during exceedances of 120 μg<sub>m</sub><sup>-3</sup> of the observed MDA8 O<sub>3</sub>. Regions correspond to the Center of the IP (CIP), the Eastern of the IP (EIP), the Ebro Valley (EV), the Guadalquivir Valley (GV), the Mediterranean Sea (MED), the North-Eastern of the IP (NEIP), the Northern of the IP (NIP), the North-Western of the IP (NWIP), the Southern of the IP (SIP) and the Western of the IP (WIP). Numbered black circles indicate stations under study CI (1-2), NEIP (3-4), GV (5-6) and NWIP (7-8).

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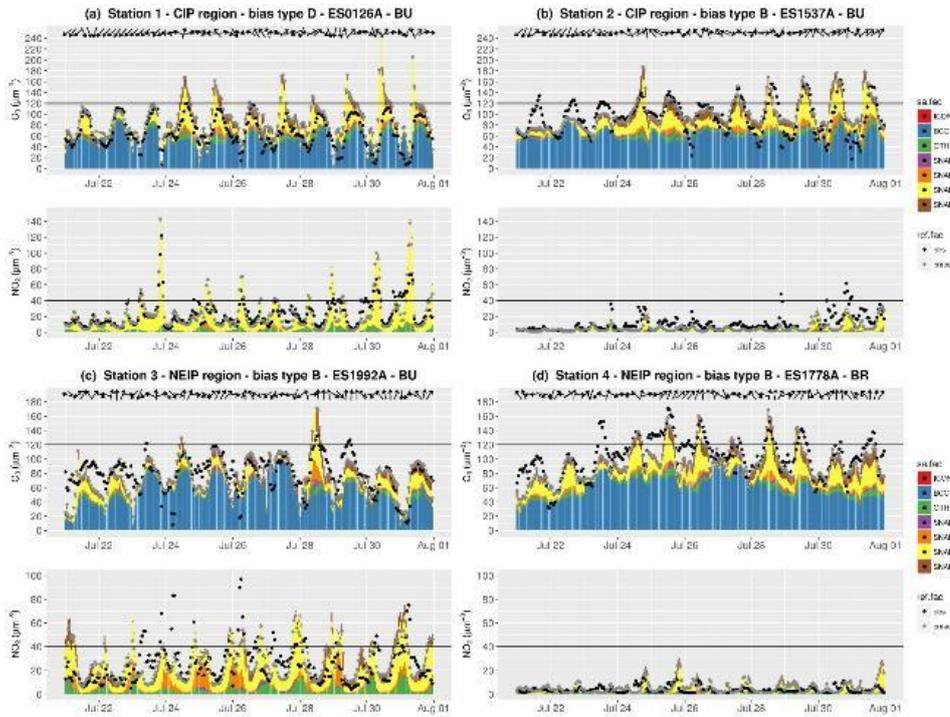


Figure 8: Source apportionment time series for  $O_3$  and  $NO_2$  concentrations (in  $\mu g m^{-3}$ ) in the episode at the selected stations in the **C**entral-**c**enter of the IP (CIP) region (a,b), and in the **N**orth-**E**astern of the IP (NEIP) (c,d). Color bars (sa.fac) indicate the  $O_3$  tags. Black and grey dots (ref.fac) indicate the observed and modelled concentrations, respectively. Black horizontal lines represent  $O_3$  target value ( $120 \mu g m^{-3}$ ) and  $NO_2$  limit value ( $40 \mu g m^{-3}$ ) as a reference. The location of the stations is shown in Fig. 7

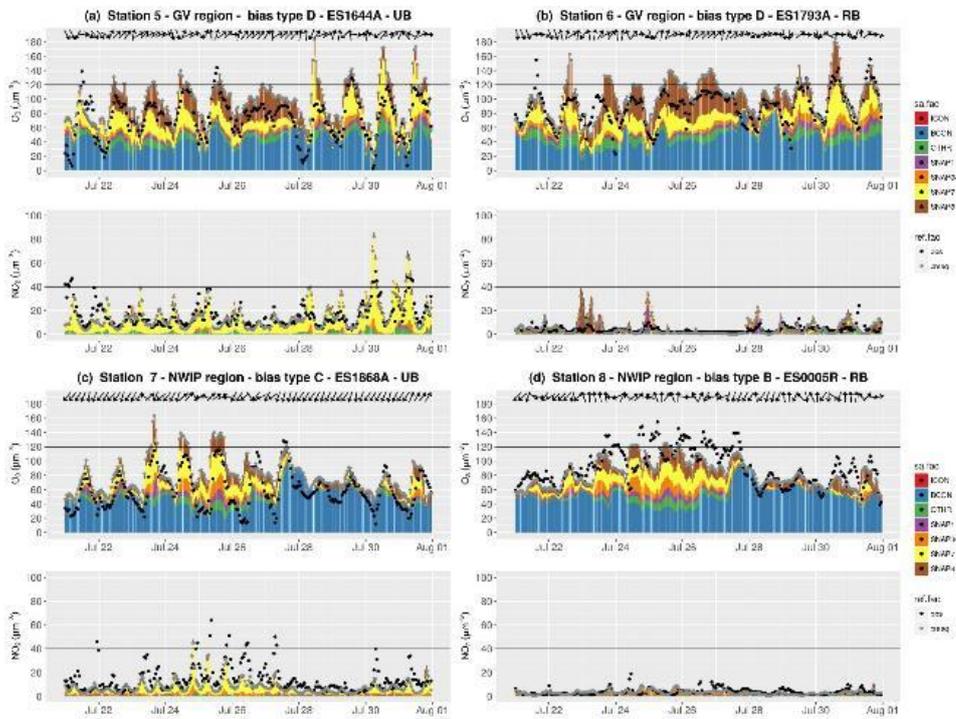


Figure 9: Source apportionment time series for  $O_3$  and  $NO_2$  concentrations (in  $\mu\text{g}\text{m}^{-3}$ ) in the episode at the selected stations in the Guadalquivir Valley (GV) (a,b), and in the northwest of the IP (NWIP) (c,d). Color bars (sa.fac) indicate the  $O_3$  tags. Black and grey dots (ref.fac) indicate the observed and modelled concentrations, respectively. Black horizontal lines represent  $O_3$  target value ( $120 \mu\text{g}\text{m}^{-3}$ ) and  $NO_2$  limit value ( $40 \mu\text{g}\text{m}^{-3}$ ) as a reference. The location of the stations is shown in Fig. 7 by the corresponding numbers.

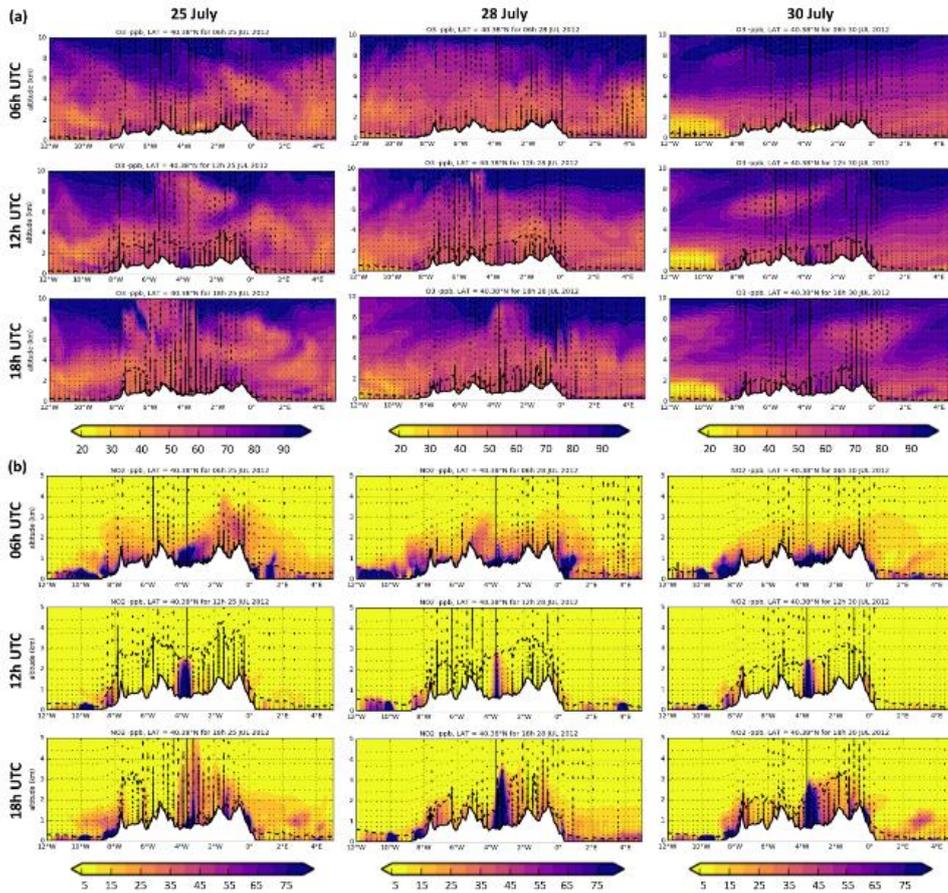


Figure 9: Cross section of modelled mixing ratios (in ppb) for O<sub>3</sub> (a) and NO<sub>2</sub> (b) at a constant latitude (Latitude = 40.38°, Madrid city) of the daily Iberian Thermal Low circulation, equivalent to the conceptual scheme of Millán et al. (1996) for July 25<sup>th</sup> (first column), 28<sup>th</sup> (second column) and 30<sup>th</sup> (third column) at 06, 12 and 18 UTC. Dot lines indicate the boundaries of the planetary boundary layer height. Vertical arrows indicate the vertical wind. Up arrows depict positive winds. Note the different scale for the y-axis between O<sub>3</sub> and NO<sub>2</sub>.

**Table 1: Description of the O<sub>3</sub> tagged sources in the present study.**

| ISAM tag* | Emission by SNAP category                                | Description  |
|-----------|--|--|
| SNAP1     | SNAP1  | SNAP1: Energy industry   |
| SNAP34    | SNAP34   | SNAP34: <a href="#">Manufacturing Industries</a> (combustion and processes-)   |
| SNAP7     | SNAP7  | SNAP7: Road transport, exhaust and non-exhaust   |
| SNAP8     | SNAP8  | SNAP8: Non-road transport (international shipping, <a href="#">airport and agricultural machinery</a> )  |
| OTHR      | SNAP2 + SNAP5 +<br>SNAP6 + SNAP9 +<br>SNAP10 +<br>SNAP11 | SNAP2: residential and commercial/institutional combustion<br>SNAP5: Fugitive emissions from fuels<br>SNAP6: Product use including solvents<br>SNAP9: waste management<br>SNAP10: Agriculture<br>SNAP11: Other sinks |
| BCON      | -  | Chemical boundary conditions to IP4 domain from the EU12 simulation which includes the contribution from Europe and international contribution from MOZART-4. O <sub>3</sub> external contribution                   |
| ICON      | -  | Initial chemical condition of the domain IP4   |

\*Each ISAM tag is applied to O<sub>3</sub> and its precursor species in the CB05 (NO<sub>x</sub> and VOCs). NO<sub>x</sub> species contributing to O<sub>3</sub> formation involve (9 species): NO, NO<sub>2</sub>, nitrogen trioxide (NO<sub>3</sub>), dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), nitrous acid (HONO), peroxyacyl nitrates (PAN), higher peroxyacyl nitrates (PANX), peroxyxynitric acid (PNA), and organic nitrates (NTR). VOC species contributing to O<sub>3</sub> formation include (14 species): acetaldehyde (ALD2), higher aldehydes (ALDX), ethene (ETH), ethane (ETHA), ethanol (ETOH), formaldehyde (FORM), internal olefin (IOLE), isoprene (ISOP), methanol (MEOH), olefin (OLE), paraffin (PAR), monoterpene (TERP), toluene (TOL), and xylene (XYL).

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Table 2: Statistics for average hourly O<sub>3</sub>, MDA8 O<sub>3</sub>, and average hourly NO<sub>2</sub> concentrations in the episode as a function of the station type. Exceedances indicate the number of exceedances of the European Air Quality Directive Standards for hourly O<sub>3</sub> (180 µgm<sup>-3</sup>), MDA8 O<sub>3</sub> (120 µgm<sup>-3</sup>) and average hourly NO<sub>2</sub> (200 µgm<sup>-3</sup>). N indicates the number of monitoring stations used in the statistics calculation. MO and MM depict the measured and modelled mean concentrations, respectively. Statistics are calculated by considering more than 75-% of the hours in a day, as established by Directive 2008/50/EC. The statistics correspond to following quantiles 50<sup>th</sup> (25<sup>th</sup>, 75<sup>th</sup>) by station. Type indicates the station categories in the calculation of statistics: all the stations (ALL), industrial (IN), traffic (TR), urban background (UB), suburban background (SB) and rural background (RB) stations. **Note that there are stations that do not fit in any of these four classifications.**

| Pollutant              | Type                | Exceedances: |          | N   | MO<br>(µgm <sup>-3</sup> ) | MM<br>(µgm <sup>-3</sup> ) | MB<br>(µgm <sup>-3</sup> ) | NMB<br>(%)             | RMSE<br>(µgm <sup>-3</sup> ) |                              |
|------------------------|---------------------|--------------|----------|-----|----------------------------|----------------------------|----------------------------|------------------------|------------------------------|------------------------------|
|                        |                     | Observed/    | Modelled |     |                            |                            |                            |                        |                              |                              |
| Hourly O <sub>3</sub>  | ALL                 | 26/216       |          | 348 | 77.3<br>(66.7,86.5)        | 89.9<br>(83.5,95.6)        | 12.6<br>(4.4,20.2)         | 16.8<br>(5.1,29.2)     | 26.7<br>(21.5,32.1)          | 0.60.65<br>(0.60,57.0-70.72) |
|                        | IN                  | 5/23         |          | 106 | 74.1<br>(62.2,83.2)        | 82.2<br>(83.4,94.5)        | 14.1<br>(4.5,21.5)         | 19.8<br>(5.5,34.7)     | 26.8<br>(21.1,32.8)          | 0.70.66<br>(0.60,56.0-70.73) |
|                        | TR                  | 0/58         |          | 70  | 68.4<br>(57.1,76.7)        | 83.8<br>(74.4,89.2)        | 15.9<br>(8,21.8)           | 23.4<br>(10.1,38.5)    | 28.8<br>(24.5,33.9)          | 0.60.63<br>(0.50,54.0-70.70) |
|                        | UB                  | 0/78         |          | 56  | 74.8<br>(64.1,80.0)        | 89.4<br>(81.4,94.5)        | 15.6<br>(7.8,21.3)         | 22.1<br>(10.2,31.1)    | 28.2<br>(24.5,33.5)          | 0.70.65<br>(0.60,60.0-70.70) |
|                        | SB                  | 4/48         | 44       |     | 83.2<br>(78.1,87.2)        | 93.5<br>(88.2,97.3)        | 10<br>(4.6,14.6)           | 12.9<br>(5.4,17.5)     | 25.1<br>(21.4,29.3)          | 0.66<br>(0.60,0.72)          |
|                        | RB                  | 17/9         |          | 66  | 91.2<br>(80.9,97.1)        | 96.2<br>(92.6,99.6)        | 4.5<br>(-3.3,14.7)         | 4.8<br>(-3.2,17.2)     | 21.2<br>(18.3,28.0)          | 0.70.67<br>(0.60,57.0-70.72) |
|                        | MDA8 O <sub>3</sub> | ALL          | 751/822  | 348 |                            | 101<br>(91.0,113.4)        | 106.2<br>(101.8,113.2)     | 5.7<br>(-3.7,16.9)     | 5.5<br>(-3.3,17.4)           | 17.9<br>(13.5,25.4)          |
|                        | IN                  | 204/187      |          | 106 | 96.7<br>(88.9,109.5)       | 104.8<br>(99.4,109.2)      | 5.7<br>(-2.9,16.5)         | 5.7<br>(-2.9,17.8)     | 17.0<br>(13.0,24.5)          | 0.70.68<br>(0.50,48.0-80.82) |
|                        | TR                  | 62/145       |          | 70  | 92.7<br>(83.6,99.9)        | 104.1<br>(98.3,110.2)      | 13.3<br>(4.6,23.8)         | 15.1<br>(4.6,27.2)     | 21.2<br>(15.2,31.2)          | 0.50.54<br>(0.30,27.0-80.76) |
|                        | UB                  | 86/174       |          | 56  | 100.0<br>(89.3,105.5)      | 107.6<br>(102.2,122.8)     | 14.1<br>(2.1,21.7)         | 14.8<br>(2.1,22.5)     | 22.6<br>(15.6,28)            | 0.60.59<br>(0.30,34.0-80.77) |
|                        | SB                  | 139/131      | 44       |     | 110.7<br>(99.8,118.5)      | 110.0<br>(105.5,119.2)     | 3.1<br>(-6.2,10.5)         | 2.9<br>(-5.4,10.1)     | 16.9<br>(13.6,22)            | 0.5<br>(0.31,0.67)           |
|                        | RB                  | 260/185      |          | 66  | 113.1<br>(104.9,119.9)     | 108.6<br>(104.5,113.2)     | -3.7<br>(-11.1,5.5)        | -3.3<br>(-9.1,5.1)     | 15<br>(11.8,20.2)            | 0.70.72<br>(0.60,60.0-70.72) |
| Hourly NO <sub>2</sub> | ALL                 | 3/0          |          | 358 | 14.0<br>(8.4,21.2)         | 9.9<br>(4.4,16.2)          | -4.1<br>(-8.4,-0.5)        | -31.9<br>(-54.2,-4.9)  | 12.8<br>(8.2,17.6)           | 0.40.43<br>(0.30,29.0-60.55) |
|                        | IN                  | 0/0          |          | 120 | 11.5<br>(7.9,16.3)         | 8.8<br>(3.8,14.7)          | -3.0<br>(-6.6,0.2)         | -28.6<br>(-55.0,1.1)   | 11.0<br>(7.9,15.6)           | 0.40.40<br>(0.30,26.0-40.42) |
|                        | TR                  | 3/0          |          | 95  | 22.9<br>(17.7,28.7)        | 14.1<br>(8.7,21.6)         | -7.4<br>(-13.9,-2.6)       | -35.2<br>(-58.1,-14.3) | 18.4<br>(14.1,23.1)          | 0.40.42<br>(0.30,28.0-60.57) |
|                        | UB                  | 0/0          |          | 63  | 17.0<br>(13,21.2)          | 13.2<br>(7.8,18.4)         | -4.0<br>(-8,-0.3)          | -26.9<br>(-47.4,-2)    | 14.1<br>(10.5,17.3)          | 0.50.49<br>(0.40,36.0-60.63) |
|                        | SB                  | 0/0          | 33       |     | 12<br>(8.2,14.6)           | 7.6<br>(4.8,11.1)          | -2.8<br>(-6.5,0.8)         | -34.4<br>(-48.6,7.5)   | 6.4<br>(7.9,13.6)            | 0.5<br>(0.41,0.65)           |
|                        | RB                  | 0/0          |          | 41  | 4.3<br>(3.5,9.3)           | 2.8<br>(1.6,4.0)           | -2.0<br>(-5.3,-0.3)        | -49.5<br>(-72.3,-9.7)  | 4.4<br>(2.7,7.1)             | 0.30.34<br>(0.20,24.0-40.42) |

