Understanding the local and remote source contributions to ambient O₃ during a pollution episode using a combination of experimental approaches in the Guadalquivir valley, southern Spain

M. in 't Veld a,b,⁎, C. Carnerero a,b, J. Massagué a,c, A. Alastuey a, J.D. de la Rosa d, A.M. Sánchez de la Campa d, M. Escudero f, E. Mantilla f, G. Gangoiti g, C. Pérez García-Pando h,i, M. Olid h, J.R. Moreta j, J.L. Hernández j, J. Santamaría j, M. Millán f, X. Querol a

a Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Barcelona 08034, Spain
b Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya (UPC), Barcelona 08034, Spain
c Department of Mining, Industrial and ICT Engineering, Universitat Politècnica de Catalunya (UPC), Manresa, 08242, Spain
d Department of Geology, University of Huelva, Huelva 21819, Spain
e Centro Universitario de la Defensa, Academia General Militar, Zaragoza 50090, Spain
f Centro de Estudios Ambientales del Mediterráneo, CEAM, Valencia 46980, Spain
g Department of Chemical and Environmental Engineering, University of Basque Country, Leioa 48940, Spain
h Barcelona Supercomputing Center, BSC-CNS, Barcelona 08034, Spain
i Catalan Institution for Research and Advanced Studies, ICREA, Barcelona 08010, Spain
j Agencia Estatal de Meteorología, AEMET, Madrid 28071, Spain

HIGHLIGHTS
• A complex orographic–meteorological scenario accommodated regional O₃ accumulation.
• The O₃ accumulation increased O₃ with 25–30 ppb due to the recirculating air masses.
• On top of this, local contributions increased O₃ levels up to 20 ppb.
• Abundant agricultural burning increased O₃ with 10 ppb later on the day.
• Source-tracing pollutants were used to associate O₃ peaks to specific sources.

Abstract
The Guadalquivir Valley is one of three major O₃ hotspots in Spain. An airborne and surface measurement campaign was carried out from July 9th to 11th, 2019 to quantify the local/regional O₃ contributions using experimental approaches. Air quality and meteorology data from surface measurements, a microlight aircraft, a helium balloon, and remote sensing data (TROPOMI-NO2-ESA) were used to obtain the 3D distribution of O₃ and various tracer pollutants. O₃ accumulation over 2.5 days started with inputs from oceanic air masses transported inland by sea breezes, which drew O₃ and its precursors from a local/regional origin to the northeastern end of the basin. The orographic–meteorological setting of the valley caused vertical recirculation of the air masses inside the valley that caused the accumulation by increasing regional background O₃ concentration by 25–30 ppb. Furthermore, possible Mediterranean O₃ contributions and additional vertical recirculation through the entrainment zone of the convective boundary layer also contributed. Using particulate matter finer than 2.5 μm (PM₂.₅), ultrafine particles (UPF), and black carbon (BC) as tracers of local sources, we calculated that local contributions increased...
1. Introduction

Tropospheric ozone ($O_3$) is a secondary gaseous pollutant involved with complex chemical processes that affects human health, ecosystems, and climate (Monks et al., 2014, 2015). Its photochemical production, involving the oxidation of non-methane volatile organic compounds (non-methane VOCs), methane (CH$_4$), and carbon monoxide (CO), with the latter two being more relevant for hemispheric transport of $O_3$ (Jacob, 1999a, 1999b), accounts for approximately 90% of global tropospheric $O_3$. Photochemical oxidation produces oxidizing radicals that oxidize nitrogen oxide (NO) into nitrogen dioxide (NO$_2$). The NO$_2$ will then subsequently generate activated oxygen ($O^*$) by photolysis (NO$_2$ = NO + $O^*$), which reacts with molecular oxygen (O$_2$) to generate $O_3$. The remaining ~10% of $O_3$ originates from stratospheric intrusions (Greenslade et al., 2017; Stevenson et al., 2006; Young et al., 2013).

Tropospheric $O_3$ has negative effects on human health, natural vegetation, and crops due to its highly oxidizing nature. It can have acute and chronic effects on pulmonary and cardiovascular morbidity, and can even cause premature mortality (Amann et al., 2008; Lelieveld et al., 2017, 2020). It is therefore considered one of the most harmful air pollutants in the troposphere together with particulate matter (PM) and NO$_2$ (HEI, 2018; WHO, 2016). In 2005, the WHO Air Quality Guidelines (WHOAQG) established a recommended maximum $O_3$ concentration of 100 µg/m$^3$ over an 8-hour period moving average throughout the day (WHO, 2006). This recommendation was not copied by the European Union, which set the limit at 120 µg/m$^3$ over an 8-hour average, with the added condition that the limit cannot be exceeded more than 25 times/year averaged over a three-year period (2008/50/CE) (European Parliament and Council of the European Union, 2008). Additionally, the European standards establish information and alert thresholds at hourly concentrations of 180 and 240 µg/m$^3$, respectively (European Parliament and Council of the European Union, 2008). According to the European Environmental Agency (EEA), between 2013 and 2015 more than 95% of the urban population in EU-28 was exposed to $O_3$ levels exceeding the WHOAQG (EEA, 2018). These exceedances are much more frequent and intense in Southern Europe, where the climate and specific meteorological and orographic patterns, along with intensive emissions of anthropogenic and biogenic precursor emissions, favor $O_3$ formation (Millán et al., 1997, 2002; Millán, 2014; among others).

In recent decades, EU emission abatement policies have had general success in reducing both mean and peak ambient air concentrations of primary PM, VOCs, sulfur dioxide (SO$_2$), and NO$_x$ (NO$_2$ + NO). However, the ambient concentrations of secondary pollutants, such as $O_3$, did not follow a similar trend (Table S2) (Colette et al., 2016; EEA, 2018, 2019; Paolletti et al., 2014; Querol et al., 2014, 2016). In Europe, from 2003 to 2012, the annual mean $O_3$ concentrations increased by 4.1% overall and by 17% in urban areas (Colette et al., 2016; EEA, 2018, 2019), while the frequency and intensity of high $O_3$ episodes decreased by 12% (Colette et al., 2016). The increasing urban $O_3$ concentrations have been attributed to the decrease of NO$_x$ in VOC-dominated environments, and/or to the reduction of NO/NO$_2$ ratios, which reduces the capacity of the troposphere to titrate $O_3$ ($NO + O_3 = NO_2 + O_2$) (Escudero et al., 2014; Massagué et al., 2019; Querol et al., 2016). In Spain, Querol et al. (2016) identified the reduction of NO/NO$_2$ ratios, with a 50–62% decrease in NO concentrations compared to a 31–34% decrease in NO$_2$ concentrations between 2000 and 2015. This resulted in a decreased $O_3$ titration potential, which in turn was identified as the major cause of increasing urban $O_3$ levels (Jhun et al., 2015; Querol et al., 2016). Reducing the tropospheric $O_3$ concentration is quite challenging due to the complex nature of the atmospheric and chemical processes governing its formation:

(I) $O_3$ has a wide variety of precursors (Bergin et al., 1998; Carter, 2000, 2009; Carter et al., 1999).

(II) $O_3$ and some of its precursors have long residence times in the atmosphere, facilitating long-range transport (Dentener et al., 2010).

(III) $O_3$ can accumulate in atmospheric basins under certain atmospheric conditions, due to the combination of topography and specific meteorological patterns (Gangoiti et al., 2001; Millán, 2014; Millán et al., 1997, 2002).

(IV) The reactions of VOCs and NO$_x$ are non-linear (Monks et al., 2015, and references therein).

(V) $O_3$ intrusions can occur from the stratosphere as well as tropospheric influence (Kalabokas et al., 2017).

Reducing the ambient $O_3$ levels is especially challenging in areas of Southern Europe, such as Spain, that are vulnerable due to low precipitation, high insolation, high NO$_2$ pollution, high biogenic VOC emissions, and vertical recirculation of air masses due to orographic features and meteorological patterns (Gangoiti et al., 2001; Millán, 2014; Millán et al., 1997, 2002; Pérez et al., 2004; Querol et al., 2017). Dieguez et al. (2009, 2014) and Querol et al. (2016) identified several atmospheric basins in the northeastern, central, eastern, and southern regions of the Iberian Peninsula, which recorded the most frequent and intense $O_3$ pollution episodes.

Our study focuses on one of these basins, the Guadalquivir Valley (GV), which crosses the southern Iberian Peninsula in a northeastern–southwestern direction (Fig. 1). Prior studies of $O_3$ in the GV (Castell et al., 2009, 2011; Dieguez et al., 2009, 2004; INTA, 2006a) found two urban air quality monitoring stations (hereafter AQMS) with persistently very high $O_3$ concentrations in Córdoba, a city located deep in the valley, suggesting a significant contribution from regional transport; eight stations in the metropolitan area of Seville showed lower $O_3$ concentrations on weekends. The maximum concentrations of $O_3$ during midday and in the early afternoon were hypothesized to have a double origin. First, $O_3$ is formed and transported from the coastal areas of Huelva and Cádiz; second, $O_3$ comes from the recirculated pollution plumes of the city of Seville that originated in previous days. Also, the areas potentially affected most by the pollution plume of Seville were found to be located to the northeast of the city (Adame et al., 2008; INTA, 2006b; Pay et al., 2019). In analyzing the entire Andalusian region, these studies found that the 2000–2008 exceedances of the hourly information threshold (tracing the most polluted $O_3$ episodes) occurred mostly in the western GV (up to 5.3 exceedances per year in Seville). There were neither clear interannual trends nor apparent influences of the average and maximum daily temperatures; the major driver of the exceedances was found to be the number of breezy days.

Adame et al. (2009) studied four stations in Huelva, located at the western end of the GV, and found three important trends. First, southwesternly winds were common during sea breeze circulation in the
summer. Second, the average monthly concentrations were at a maximum of 96–72 μg/m³ in June and July, compared to 62–40 μg/m³ during January and December. Finally, exceedances of the thresholds were frequent, especially at one station located on the coast. Dieguez et al. (2009) attributed the high O₃ concentrations in Seville, which is one of the largest cities in Spain, to the interaction of urban traffic, NOₓ emissions, and VOCs transported by sea breezes from the petrochemical emissions of Huelva. They also noted that when urban plumes are transported, a shift occurs from the usual condition of VOCs-limited O₃ formation to NOₓ-limited conditions.

Pay et al. (2019) studied the sources of O₃ in Spain, which included an urban station in Seville and one rural station near the coast. They concluded that the GV had one of the highest daily O₃ concentrations in Spain, with the largest source of anthropogenic O₃ (approximately 18%) originating from the on-road traffic from Seville, Huelva, and Cordoba; followed by shipping (approximately 17%).
These prior studies were based on air quality data interpretation, but none focused on combining these with airborne measurements during high O₃ episodes to devise a conceptual model for the occurrences and causes of these episodes. In this context, we aim to understand O₃ episodes in the GV, focusing on the Seville metropolitan area, where the most intense O₃ episodes were recorded. To this end, a campaign of land-based and airborne measurements was carried out in the second week of July 2019, when the probability of a high O₃ episode was the highest. This work will provide insight into the phenomenology of O₃ formation in this area, and gives us the ability to quantify the contributions of local and regional sources of O₃ using experimental approaches. We used black carbon (BC), PM finer than 2.5 μm (PM₁₅), and ultrafine particles (UFP; particles of less than 100 nm in diameter) as tracers of different regional/local sources influencing O₃ formation.

2. Methodology

To investigate the phenomenology of high O₃ episodes in the GV, an intensive land-based and airborne O₃, PM₂.₅, BC, and UFP measurement campaign was performed between July 9th and 11th, 2019. The dates of the campaign were selected based on an analysis of an O₃ time series of 24 AQMSs (Table S3) in the GV between 2005 and 2018, which showed the 190th–200th days of the year to be the period with the maximum number of days exceeding an arbitrary hourly O₃ threshold of 150 μg/m³, which occurred mostly around Seville City (in particular, at the Aljarafe AQMS). The campaign was carried out during working days to avoid the typical weekend O₃ drop shown by the data.

The 3D spatial and temporal variability of O₃ concentrations, along with those of other pollutants, and meteorological parameters were measured using airborne instrumentation. Nine free O₃ soundings launched from Mairena del Aljarafe (Fig. 1, yellow star) provided vertical-resolved measurements of O₃ and meteorological parameters. An instrumented microlight plane was used simultaneously to characterize the horizontal variability of O₃, PM₂.₅, BC, UFP, temperature, and relative humidity (RH) across the nine flights covering 250 km each.

These tailored measurements were complemented with surface O₃ concentration measurements from the AQMSs located in the GV from Huelva, in the west, to Jaén, in the east (Fig. 1); meteorological data from the Spanish Meteorological Office (AEMET); NO₂ data from the Tropospheric Monitoring Instrument of the European Space Agency (TROPMI-ESA) satellite measurements; high-resolution outputs from the operational air quality forecast system of Spain (Spanish: CALidad del aire Operacional Para España: CALIOPE); the mesoscale Regional Atmospheric Monitoring System/Hybrid Particle Concentration and Transport (RAMS/HYPACT) modeling system; and the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYPLIT) trajectory model.

2.1. Study area

The GV is located in the southern part of the Iberian Peninsula (Fig. 1), crossing nearly the entire Andalusian territory for 650 km in a northeastern–southwestern direction. In addition to the Guadalquivir River that flows into the GV, the Odriel and Tinto rivers also have estuaries on the Atlantic coast. From its beginning in the Sierra de Cazorla, the GV becomes progressively wider towards the Atlantic Ocean, occupying an approximate area of 57000 km² with widths of more than 150 km. In this paper, altitudes are written in meters above sea level (m a.s.l.), but the elevation of the valley increases from sea level at the Atlantic Ocean coast towards the Sierra de Cazorla. A cross-section of the valley is shown in Fig. S1. At its western end, the Guadalquivir lies at sea level (0 m a.s.l.) at the Atlantic Ocean, near Huelva. Eastward from the coast, the elevation increases to about 200 m a.s.l. at 200 km into the valley. Further eastward, the elevation increases more rapidly towards the mountain ranges of Sierra Mágina and Sierra de Cazorla, to higher than 1000 m a.s.l. Two large mountainous systems surround the GV: the Sierra Morena in the north, which acts as a natural border with the Central Plateau; and the Betic System to the south. Geographical factors of the area, such as the orography and topography, establish some continental climatic regionalization within the dominant Mediterranean climate, with high temperatures, irregular precipitation, and intense heatwaves (Adame et al., 2009; Dieguez et al., 2009). The wide opening of the GV at the Atlantic Ocean has no significant orographic barriers, which favors a relatively humid climate on the coast. Farther into the valley, the wet Atlantic influence weakens, and the continental features increase, bringing less rainfall and more aridity, especially in the upper part of the valley. Intense sea breezes develop quite frequently inside the GV, especially in July, due to the very high inland temperatures (36 °C and 203 °C are the annual average daily maximum and minimum temperatures, respectively, in Seville in July) in contrast with the cooler Atlantic air masses (data accessed from AEMET)1.

The most relevant emission sources in the area are (Fig. 1):

(I) Traffic emissions from the cities of Seville (703,200 inhabitants), Córdoba (328,400 inhabitants), Huelva (148,800 inhabitants), Cádiz (126,800 inhabitants);2 and Jaén (116,500 inhabitants); numerous smaller conurbations; and highly trafficked highways.

(II) Industrial emissions from the large industrial estates of Huelva, which includes one of the largest petrochemical estates in Spain; fertilizer plants; a large copper smelter; and a large industrial harbor, among others, as well as industries of other cities.

(III) Thermal power plants of Arcos (near Cádiz), Huelva, Cádiz, and Córdoba.

(IV) Seville airport.

(V) The dense maritime transport in the Strait of Gibraltar.

(VI) Agricultural, farming, and food industry emissions, which include intense biomass burning throughout the valley and the oil production plants in its central and upper parts.

Apart from these anthropogenic sources of O₃ precursors, there are also significant sources of biogenic VOC precursors in the area, such as large forested areas, crop plantations (citrus and olive groves in the central and upper areas, and fruit trees, including citrus, in the lower areas), and estuarine marshes.

2.2. Surface air quality data, modeling, and satellite data

In order to support interpretations of the airborne measurements carried out during the campaign, we used ground-level measurement data from 55 AQMSs of the Andalusian Regional Government and four AQMSs from the European Monitoring and Evaluation Programme (EMEP) monitoring network, run in this case by AEMET (Table S4). These stations are equipped with instrumentation to measure concentrations of O₃, NOₓ, SO₂, PM₁₀, and PM₂.₅. Furthermore, we used O₃ concentration maps for the Iberian Peninsula from the CALIOPE air quality forecast system at 4 × 4 km resolution (Baldasano et al., 2008, 2011). Tropospheric NO₂ background levels with a resolution of 7.2 × 3.6 km were obtained from the Tropospheric Monitoring Instrument (TROPMI) installed onboard the Sentinel-5 Precursor (SP-5) satellite of the European Space Agency (ESA) (Veekind et al., 2012).

Mesoscale meteorological fields and backward–forward trajectories of tracer particles were generated with the RAMS v6.0 (Pielke et al., 1992) and HYPACT v1.5 models (Tremback et al., 1994), respectively, to interpret the origin of the O₃-enriched free tropospheric layers (Section 3.3) and the contributions of regional background O₃/precursors to the mixing layer along the GV. Three domain grids with increasing resolutions of 48, 12, and 3 km were used following a deployment similar to that in Pey et al. (2008). Similarly, in the vertical direction, 44 levels with variable resolution (30 m at ground level and 1000 m...
in the upper troposphere) were used for all the grids, with a total coverage of 22,400 m. The horizontal boundaries of the largest domain, covering the Iberian Peninsula, Southern Europe, and Northern Africa, were adjusted to the conditions given by the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim reanalysis (Dee et al., 2011) at 00:00, 06:00, 12:00, and 18:00 UTC (0.75° × 0.75° latitude–longitude grid resolution). Four-dimensional data assimilation by nudging was used for the RAMS–HYPACT model run, with Newtonian relaxation around the six-hourly ERA-Interim data. A variable relaxation time was used, with the highest values (weak nudging) at the center of the parent domain, and the lowest values (strong nudging) at the boundaries. Topography and land cover were interpolated from the USGS global 30” database (Gesch et al., 1999). Daily sea surface temperature (SST) data, with an original resolution of 0.25° × 0.25”, were interpolated for this simulation from the Optimum Interpolation SST (OISST) Advanced Microwave Scanning Radiometer with Advanced Very High Resolution Radiometer (AMSR-AVHRR) analysis (Banzon et al., 2016; Reynolds et al., 2007) into the model grids. Our setup of the mesoscale model included a prognostic turbulent kinetic energy (level 2.5) parameterization (Mellor and Yamada, 1982), with modifications for the case of growing turbulence (Helfand and Labraga, 1988), and a full-column two-stream parameterization that accounted for each form of condensate (seven species) for the calculations of the radiative transfer through clouds and gases in the model (Harrington et al., 1999). The RAMS runs from 00:00 UTC on July 4th to 00:00 UTC on July 12th was performed continuously. Hourly meteorological fields estimated by RAMS were forwarded to the HYPACT model to perform the dispersion evaluation of the atmospheric passive tracer.

For the forward trajectories, a total of 17 city-sources of vertical emission lines (0–300 m in height) were selected using a scheme similar to that in Pey et al. (2008). The variable height of the particle selection, from the surface to 300 m a.g.l., accounts for a wide variety of effective emission heights in urban and industrial environments. The selection of coastal Mediterranean, Atlantic, and inland city-sources encompassed an area of diverse weather and wind regimes. This methodology allowed us to simulate different transport mechanisms operating in the area. The sources were grouped into five areas as follows: North-Atlantic (Nantes, Bilbao, La Coruña, Lisbon, Porto), South-Atlantic (Huelva, Seville, Cádiz), North-Mediterranean (Mar- seille, Barcelona, Tarragona), South-Mediterranean (Valencia, Cartagena, Malaga), and Iberian-inland (Madrid, Valladolid, Zaragoza). Particle releases started on July 4th and lasted eight days, and the 3D positions of 384000 particles for each of the 17 city-source simulations were tracked for the whole period until July 12th.

In order to support the interpretations of the airborne measurements along the GV, the dynamics of urban plumes and industrial plumes of the Huelva petrochemical plant were modeled using the HYSLIP model (Draxler and Hess, 1998; Stein et al., 2015) of the National Oceanic and Atmospheric Administration (NOAA). Specifically, behavior was modeled for emissions derived from two plume sources: the CEPSA La Rábida refinery, located in the industrial area of Huelva (geographical coordinates WGS84: 37.2°N, 6.9°W, altitude 140 m a.s.l.); and traffic emissions in a 1 km2 area of Seville (geographical coordinates WGS84: 37.4°N, 6.0°W, altitude 10 m a.s.l.) The HYSLIP model was run through the METEOSIM platform. In the simulations, the meteorological domain used a resolution of 3 km, with data obtained from the Global Data Assimilation System (GDAS) and using a common emission rate of 100 g/s for PM2.5. The duration of the simulation was 12 h, and the distribution of the plume was obtained every hour during the period of the campaign.

2.3 O3 soundings

Vertical variations in O3 concentration and meteorological parameters were measured with nine free O3 soundings, launched every day between July 9th–11th, 2019, at 06:00, 12:00, and 17:00 (UTC), from the El Olivo school 37.3°N, 6.0°W, at 58 m a.s.l, very close to the Aljarafe AQMS, 10 km south of Seville and 25 km from the Guellena airfield (Fig. 1). The instrumentation launched consisted of an R341–SCP (Vaisala) radiosonde combined with an EC–3A O3 sensor (Science Pump Corporation) attached to a helium balloon. The partial pressure of O3, T, RH, GPS location, wind speed, and wind direction were measured at a frequency of 1 s up to an altitude of approximately 30 km, which was reached approximately 2 h after each launch.

2.4 Microlight measurements

The horizontal variation of pollutant concentrations in the lower part of the atmosphere was measured using instrumentation onboard a microlight (single-engine Tecnam P96 Golf) that flew daily at 06:00, 11:30, and 17:30 UTC, with an approximate flight duration of 2 to 2.5 h per flight. The same route (Fig. 1) was repeated for each flight, at an altitude ranging between 150 and 550 m a.s.l.: departing from the Guellena airfield (37.6°N, 6.0°W), heading southbound towards Seville, then to the southwest towards Huelva, with a descent and subsequent ascent upon arrival at the Atlantic coast, a return towards the northeast over Guellena to Lora del Río, and then heading back to Guellena. The measurement devices (Table S5) were placed inside the cabin and connected to an inlet designed for high-speed particle measurement installed in the front ventilaion inlet (Fig. S2).

Black carbon concentrations were measured using a microAeth® aethalometer (Magee Scientific Corporation, 1 min resolution); PM2.5 concentrations with a Dusttraxc DRX aerosol monitor (TSI, 10 s resolution); UFP number concentration and average particle size in the 10–700 nm size range with a diffusion particle size classifier (N and Dp, respectively) (DISCMini; Testo, 1 min resolution); and O3 concentrations with a personal O3 photochemistry monitor (POM; 2B Technologies). The instruments were connected with a Teflon® inlet pointing towards the rear of the aircraft to reduce air flow. In addition, a portable weather monitor for temperature and RH (Kestrel 4500) was installed on the exterior of the aircraft attached to the landing gear and pointing towards the front, and a GPS tracker was placed inside the plane, both with a time resolution of 10 s.

3. Results

3.1. Meteorological context and air mass tracking

The synoptic conditions during the three-day campaign were characterized by the Azores High located west of Iberia and its relative high–pressure area extending eastward, reaching both Southern Europe and the Western Mediterranean region (Fig. 2). Clear skies and surface low–pressure gradients under these anticyclonic conditions developed mesoscale circulations in the lower troposphere of the area. Land–sea breezes in the coastal areas flow inland while the mountain–valley winds give a compensatory flow. This circulation pattern governs the transport of O3 in the lower troposphere of Southern Europe and the Western Mediterranean region, as was first reported by Millán et al. (1997) based on experimental evidence gathered during a series of intensive summer field campaigns in the region, and then by Gangoiti et al. (2001), among others.

The observed low-pressure gradient conditions at lower atmospheric levels contrasted with the rapid evolution at higher atmospheric levels. On July 9th, an upper–level low (marked #1 in Fig. 2b

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4 https://www.ecmwf.int/en/forecasts/datasets/
7 https://www.ncdc.noaa.gov/oisst
8 https://www.meteosim.com/es/
and e) crossed the Iberian Peninsula from southwest to northeast. This low had split from an upper-level trough over the North Atlantic six days before (not shown in the figure) and remained almost stationary during the following days over the west coast of Portugal (Fig. 2). The system brought deep convection and storms on July 8th, ahead of the low over the Iberian landmass. As the low-pressure system #1 moved into the Gulf of Lion and weakened on July 9th, more stable conditions developed over Iberia, with clear skies and northwesterlies (backing to the west in the free troposphere, above 2500–3000 m a.s.l. in the soundings discussed in Section 3.3). These conditions characterized cold advection at the rear of the upper-level low. The northwesterlies, associated with a deep dynamic sinking that affected almost the entire troposphere (Fig. S3, upper-right panel), were responsible for the transport of air masses enriched in O3 from the middle and high troposphere (above 2500–3000 m a.s.l.) into the upper levels of the mesoscale circulations developed in the GV and recorded by the sounding in Seville on July 9th (Section 3.3). Also, based on the RAMS/HYPACT back-trajectories, we found the O3 enriched layers at 3000–4000 m a.s.l. observed in Seville on July 9th to be associated with a tropopause folding following the evolution of the upper level low #1, as shown in Fig. S3b. None of the trajectories ending above 3000 m a.s.l. (3000–4000 m a.s.l.) at the sounding site in Seville between July 9th and 11th were found to be initiated at the boundary layer, after being tracked back to July 4th.

A second upper-level low (marked #2 in Fig. 2a) originated from another upper trough on July 8th in the North Atlantic and moved farther south than the upper low #1, reaching the western coast of Morocco on July 10th (Fig. 2c). This second low triggered important changes in the advection of air masses into the South-Atlantic region. It deepened on July 11th (Fig. 2d) and forced more intense southeasterly winds to veer towards the south and southwest in the free troposphere of the GV (warm advection), with a clear decrease in O3 concentrations above 3000 m a.s.l., as recorded at the sounding site in Seville from July 10th to 11th (Section 3.3). However, these changes during the episode were not observed in the circulation at lower levels in the GV. The

Fig. 2. Left: Climate Forecast System Reanalysis (CFSR): 500 hPa geopotential height (gpdams) and mean sea level pressure (MSLP) contours (hPa) at 06:00 UTC, during the period of July 8th (a), July 9th (b), July 10th (c), and July 11th (d), 2019 (Wetterzentrale, http://www.wetterzentrale.de; last access: March 31st, 2020. The blue circle indicates the study area. Right: ERA-Interim ECMWF reanalysis: winds at 1000 hPa and (right) at 900 hPa, represented with the geopotential height (gpm) of the 1000 hPa surface in shaded colors, and the 1000–500 hPa thickness (gpdams) in contours at 06:00 UTC during the period of the field campaign, July 9th (e), July 10th (f), and July 11th (g), 2019 (ECMWF, https://www.ecmwf.int/en/forecasts/datasets/; accessed 15th January 2020). The red area indicates the study area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
monitoring stations recorded land–sea and mountain–valley breezes with locally developed circulations during the whole period.

In all, the origin of the background air masses incorporated into the basin changed completely from July 9th to July 11th. In the region of the Strait of Gibraltar (including the Gulf of Cadiz and the regions of the Alboran Sea to the west and east of the Strait), alternating easterly and westerly winds typically drive the local meteorology at low levels (Dorman et al., 1995). During the campaign, westerly winds associated with the cold advection on July 9th changed to easterly winds over the following two days (Fig. 2). At surface level (1000 hPa), these changes in the Strait started early on July 11th (following the onset of the mistral in the Gulf of Lion the day before), about 24 h later than at 900 hPa. In Sections 3.3 and 4, we discuss the accumulation of O3 within the GV that occurred from July 9th to 11th, concurrent with the O3 decreases in the free troposphere and the changes in the regional advection at lower layers. The sea breeze prevalence during the measurement campaign is supported by the wind speeds and directions measured at the State Meteorological Agency of Spain(AEMET), Sevilla-Airport, and Bailén (from the coastal area to deep into the GV) reported in Fig. S4, with dominant daylight wind directions of around 250° and very high wind speeds, and light winds from inland with a 45° directional component. The vertical profiles that will be shown in subsequent sections also demonstrate the occurrence of a major sea breeze circulation during the measurement days. The changes in the background pollution inside the GV have been studied using RAMS/HYBFACT forward trajectories for selected cities, as described in Section 2.2. Fig. S5 shows fumigation at low levels of the GV on July 9th of particle tracers released in the Atlantic sector (of the North Atlantic ocean), and the arrival of particle tracers originating in the Mediterranean to the east of the city of Malaga on July 10th and reaching the GV from the southeast, across the southern boundaries of the Betic System. This arrival of pollutants from the east occurred after the described changes in circulation from westerly to easterly 18 h before, which might have also included pollutants from other nearby coastal emissions, including road traffic, industries, and shipping. Interestingly, during the whole episode, most of the tracers were transported below a height of 3000–3200 m a.s.l., which was consistent with the existence of the recorded elevated temperature inversion at that height in the free soundings in Seville (Section 3.3).

Large-scale tropospheric subsidence over the area, which leads to higher O3 concentrations in the boundary layer (see Gaudel et al., 2018 and references therein) might have also contributed to the increase in O3 levels during the campaign. These episodes, associated with large-scale tropospheric subsidence, very frequently occur over the Mediterranean during the warm period of the year, in association with high-pressure systems, and are not always necessarily related to stratospheric intrusions (Coman et al., 2012; Doche et al., 2014; Eremenko et al., 2008; Foret et al., 2009; Richards et al., 2013; Safedidine et al., 2014; Tombrou et al., 2015; Zanis et al., 2014). In fact, the meteorological maps (Figs. 2 and S3) indicate that an extended tropospheric subsidence event probably occurred over the area during the examined episode of July 9th to 11th, 2019.

3.2. Surface O3 and NO2 concentrations

CALIOPE simulated a progressive accumulation of O3 in the southern half of the Iberian Peninsula from July 8th to 11th, with prominent peaks between 12:00 and 20:00 UTC, which gradually became depleted on July 12th and 13th. The accumulation processes of O3 were described in detail by Millán et al. (1997, 2002) and Gangoiti et al. (2001) for the Western Mediterranean area. These papers showed that pollutants are transported inland by sea-breeze and valley circulations caused by weakened synoptic surface circulation and the Iberian and Saharan thermal lows. In the case of the GV, the sea breezes transport air masses inland towards the Sierra de Cazorla mountain range, which creates a chimney/crest effect, injecting polluted air masses up to 2000 to 3000 m a.s.l. In the situation where the boundary layer is below the head of the valley, a pocket is formed that traps the air masses by thermal inversion of the top of the boundary layer, and the air masses are recirculated back towards the ocean. At the ocean, the air masses will sink due to compensatory subsidence. The combination of the recirculation, fumigation, and breeze transport results in accumulation occurring in the valley and generates acute O3 episodes. This process will continue until the synoptic flow intensifies and vents the valley by transporting the polluted air masses to other areas (Gangoiti et al., 2006).

The regional accumulation of O3 until July 11th at 12:00 UTC and the final venting stage of the GV were reproduced with the CALIOPE measurements, as seen in Section 3.3. The modeling also showed that O3 transported from the Cantabrian and Portuguese coasts was channeled into the GV from the Atlantic. Regional O3 formation was widespread between July 8th and 11th, with strong activity not only in the GV but also in the central and eastern parts of Iberia (Fig. S6).

The accumulation over the 3 days was also measured by the AQMSs in the GV during the campaign period. All stations showed a clear increasing trend of maximum daily O3 concentration from July 8th until July 11th, 2019, with an average maximum O3 concentration of 95 μg/m² on July 8th to 138 μg/m² on July 11th (Table S6). At the same time, when looking at certain stations, the hour of the maximum concentration progressively increases from west to east (Fig. S7). From the La Orden station near Huelva to the Las Fuentezuelas station near Jaén, there is a three-to-four hour delay between the hours with the maximum O3 concentrations per day. This trend follows the dynamic of a sea breeze, as explained earlier in this section. Although a few stations do follow this trend, it is important to note that this was only seen at selected stations and not at all stations inside the valley. This trend was also observed at the EMEP AQMSs of Doñana, representing the background GV concentrations in the coastal area (Escudero et al., 2016), which supports the occurrence of vertical recirculation and accumulation during the campaign. The daily progressive accumulation of O3 was more prevalent at the western AQMSs than at the eastern ones, where peak concentrations tended to occur later in the day (16:00–17:00 UTC) due to the transportation of polluted air masses by sea breezes, after the onset of the easterlies at lower atmospheric levels in the Strait of Gibraltar (Section 3.1).

Column NO2 data from TROPOMI (Fig. S8) indicate that the highest levels in the GV were recorded in and around Seville, and not in the industrial area of Huelva. At the same time, there was a significant source of NO2 a few kilometers offshore of the Guadalquivir estuary, due to the intense maritime traffic over the Atlantic in front of the GV (especially on July 11th), which likely favored the formation of O3 production that was then transported inland by the sea breezes.

3.3. Vertical and horizontal O3 profiles

3.3.1. July 9th, 2019

3.3.1.1. Morning. The GV was ventilated well in the days prior to July 9th, 2019 (Section 3.1), resulting in reduced O3 levels in the area, with background O3 being supplied mostly from the Atlantic. At 06:00 UTC (Fig. 3a) on July 9th, 2019, the sounding shows that surface O3 reached the lowest values during the campaign (with titration, ozonolysis, and deposition occurring in a thin mixing layer). Four O3 strata are evident in the profile. Below 600 m a.s.l., where there was a thermal inversion, the atmosphere was characterized by north-northeasterly katabatic winds and a marked O3 reduction all the way down to the surface. The layer between 600 and 1800 m a.s.l. was characterized by northwesterly winds, with increasing RH and constant O3 (around 50 ppb). From 1800 to 3250 m a.s.l., another O3 increase was observed, with moderate and increasing northwesterlies, which backed to the west at higher altitudes. Above 3250 m a.s.l., the troposphere became dryer above a slight thermal inversion, but the westerly circulation was maintained, with a
progressive increase in O₃ of up to 100 ppb at 5000 m a.s.l. This low RH and the very high and thick O₃ layer were likely influenced by the stratospheric O₃ intrusion described above, although stratospheric subsidence might also have contributed to increase O₃ levels. The upper-level low-pressure system located west of Portugal generated a westerly and northwesterly flow at this altitude and transported stratospheric O₃ from higher altitudes during this day. In summary, there was a clear gradual upward increase in O₃ along the profile.

3.3.1.2. Afternoon. At 12:00 UTC (Fig. 3a), surface O₃ increased compared with the morning (<400 m a.s.l.). A second layer persisted on top of the mixing layer (400–1400 m a.s.l.) with a thermal inversion at the top, a nearly constant O₃ concentration of ~45 ppb, a prevalent sea breeze (southwesterly) flow, and a high and increasing RH. From 1400 to 1800 m a.s.l., a transitional O₃ layer was observed, which was the entrainment zone of the convective boundary layer (CBL), limited by two thermal inversions, with a rising O₃ concentration (40 to 70 ppb) and decreasing RH. The top inversion occurred in the morning at 1700–1900 m a.s.l. Above 1800 m a.s.l., a layer with a moderate but increasing O₃ level was detected with northwesterly flow. The top layer was characterized again with a high upward O₃ increase (up to 100 ppb at 5000 m a.s.l.) and a 3900–4100 m a.s.l. thermal inversion. All three O₃ strata above 600 m a.s.l. were similar to those of the morning, but they were now located at lower altitudes. Furthermore, the concentrations of O₃ were high at high altitudes with a northwesterly wind, similar to the 06:00 UTC sounding, as a consequence of the persistence of the contribution from the stratospheric O₃ intrusion, probably with a low incidence of surface O₃.

3.3.1.3. Evening. Three well-defined strata were identified in the 18:00 UTC sounding (Fig. 3a). The lower layer (<350 m a.s.l., limited by a thermal inversion) had a persistent southwesterly sea-breeze flow, but simultaneously O₃ increased to around 40 ppb, similar to its level at 12:00 UTC. Another layer (350 to 2700 m a.s.l.) with northerly and northwesterly winds, high RH, and a homogeneous O₃ concentration of 65 ppb was probably the mixing layer and was associated with the northwesterlies of the cold advection at the rear of the upper-level low #1 (mentioned earlier in Section 3.1) (Fig. S3). This was channeled into the GV and contained a fraction of the pollutants moving inland within the sea breeze at lower levels, and was then transported back to the Atlantic as shown by the wind direction in the vertical profiles (Fig. 3a). Above 2700 m, the high O₃ concentrations from possible stratospheric intrusions or atmospheric subsidence O₃, high-speed westerly flow, and low RH persisted, with an upward increase of O₃ (again up to 100 ppb at 5000 m a.s.l.).

3.3.2. July 10th, 2019

3.3.2.1. Morning. On the morning of July 10th, the four-layer O₃ structure resembled that of the previous morning (Fig. 3b), including the upper layers with O₃ peaks reaching 90 ppb, high and stable wind speeds (7–8 m/s) from the southwest, and very low RH. The low RH and the high O₃ levels were likely associated with the stratospheric intrusion, which was also recorded the day before, but the results of the July 10th measurements showed traces of disruption and a decrease in O₃ compared with the previous day, which is consistent with the transitional character on this day for the stratospheric intrusions reported in Section 3.1.

3.3.2.2. Afternoon. The afternoon atmosphere profile (Fig. 3b) was very similar to the one of the morning sounding, but the layers were at lower altitudes. The thermal inversion was located at 900 m a.s.l., which indicates a much less developed boundary layer compared to the previous day. Below the thermal inversion, northeast to southeast winds prevailed with increasing speeds (2–8 m/s) and decreasing RH (down to 35%). Concentrations of O₃ were higher (55–63 ppb) in this lower layer compared to the morning sounding due to vertical mixing, but also possibly due to local production. Above the thermal inversion, up to 2700 m a.s.l. there was a dominant layer with southeasterly winds (5 m/s), a decrease in RH (down to 10%), and increased O₃ (55 to 85 ppb). Finally, above 2700 m a.s.l. there was a stable southeasterly wind (8–10 m/s), with two high O₃ strata (up to 90 ppb).

3.3.2.3. Evening. Three layers were detected during the evening sounding (Fig. 3b). The lower layer was limited by a thermal inversion at 600 m a.s.l. and characterized by low RH (35%) and southeasterly sea-breeze flows with low wind speeds, with an O₃ increase from 55 to 70 ppb. Similar to the prior day’s sounding, a very well-mixed layer with a homogenous O₃ concentration of about 70 ppb was detected from 600 to 2300 m a.s.l. This layer showed a moderate RH (20 to 40%)
from bottom to top) and northeasterly wind direction, which is consist-
ent with the shift from westerlies to easterlies observed in the morn-
ing sounding. Just as on the previous evening, the northeasterlies transported the pollutants towards the Atlantic Ocean, from which the sea breeze could then carry them into the valley again at lower levels on the follow-
ing morning, as was seen with the increased O₃ concentrations through-
out the day at these altitudes compared with the previous day. Above
2300 m a.s.l., following the warm advection induced by the upper level
low #2, the wind veered from southeast to southwest. Higher wind
speeds were measured around 9 m/s, with low RH, and O₃ increasing
slightly up to about 75 ppb, which was lower than the values attained
in the morning and on previous days.

3.3.3. July 11th, 2019

3.3.3.1. Morning. During the morning of July 11th (Fig. 3c), the three
layers were still persistent, with the bottom layer limited by the thermal
inversion at 500 m a.s.l. The second layer (500–2500 m a.s.l.) was com-
posed of several thinner strata associated with high and increasing O₃
concentrations (from 55 to 75 ppb) and a RH of 25–35%. From bottom
to top, the wind (7–9 m/s with peaks of up to 13 m/s) veered from
northeast to southeast. From 2500 to 5000 m a.s.l., O₃ decreased down
to 50–60 ppb, with winds veering from southeast to southwest (10–12 m/s). There was also an increase in RH with altitude, indicating a
different origin for the air masses that replaced the stratospheric–
intrusion-related O₃ transported from previous days. Also, the northeast
to southeast airflow in the 500–2500 m a.s.l. layer suggests that the
Mediterranean is the origin of the air masses, as described in Section 3.1.

3.3.3.2. Afternoon. The three main layers were still persistent at 12:00 UTC
(Fig. 3c). The lowest and second layers were limited by thermal inver-
sions at 400 and 1600 m a.s.l. The lower level was characterized by low
RH (increasing upward from 20 to 35%) and east-northeasterly winds
(probably driven by the Mediterranean air mass transport) of around
5 m/s. This is similar to the second layer on July 10th, but with a thicker
mixing layer. Interestingly, the O₃ concentration in this layer was higher
than in the layers above, resulting in a 50–60 ppb “hump” in the profile
(more pronounced in the sounding). This hump was likely caused by a
combination of O₃ fumigation from mid-altitude reservoir strata and
the residual layer of locally-produced O₃ from previous days (Escudero
et al., 2019; Querol et al., 2017, 2018), along with O₃ transported from the
Mediterranean. This hump was even more pronounced in the even-
ing profile. In the 1600–5000 m a.s.l. layer, the high-speed (13–20 m/s)
south-southwesterly wind prevailed in an air mass with low RH
(25%) and lower and constant O₃ concentrations (around 50 ppb).

3.3.3.3. Evening. The same three strata were observed in the last sound-
ing (Fig. 3c). In the lower layer, the southwesterly sea breeze was more
intense than on the previous day (7–8 m/s and 40% RH). In this layer, O₃
concentrations increased from 55 to 70 ppb. In the middle layer (400 to
1750 m a.s.l.), a mixing layer with high levels of O₃ up to 75 ppb formed
the aforementioned hump. This layer was driven by very low-speed
east-northeasterly winds (2–4 m/s) originating from the Mediterranean
region. This air mass could also recirculate back into the Atlantic, where
the southwesterly sea breeze could transport it back into the GV at
lower levels. As stated earlier, the effects of the air mass vertical recircu-
lation and the background O₃ concentrations transported from the Med-
iterranean may have been important contributors to the measured O₃
hump. Above 1750 m a.s.l., O₃ concentrations decreased and remained
stable at around 40 ppb. This air mass was affected by high-speed
winds (18–20 m/s) with a constant southwesterly wind. The RH in-
creased from 15 to 40%.

3.3.4. Agricultural biomass burning and African dust outbreak

The morning microlight measurements of July 9th, 2019 (Fig. 4a)
showed a prominent increase in PM₂₅ and BC up to 185 and 1.5 μg/m³,
respectively, in the northeast sector of the flight (Seville-Lora del Rio, in
the green box in Fig. 4d). The UFP data were unavailable from this flight
due to instrument failure. These peaks coincided with widespread agri-
cultural burns in the area (see Fig. S9) and with an O₃ decrease of
15 ppb (down from 45 ppb measured in the other GV areas, Fig. 4a).
We do not have a reference for the timing and frequency of the burns,
but in the early morning the boundary layer was much thinner and the
contaminants from these burns had clearly accumulated and were
consuming O₃ more intensively. Visual observations and RH data also re-
vealed the occurrence of fog over this area. This fog most likely originated
from the wide section of the river, which provides high humidity at the
surface level, in combination with an abundance of irrigated green crops
in this area. Both the fog and the biomass burning might have caused
the O₃ decrease, given the inverse relationship between high RH and O₃
and the emissions of pollutants, with potential O₃ titration and/or
ozonolysis effects (Carter et al., 1999; Granier et al., 2000; Jia and Xu,
2014). Later in the afternoon (Fig. 4b), PM₂₅, BC, and UFP were still de-
tected in the same area (30 and 0.8–1.2 μg/m³, 7000–17000 #/cm³, re-
spectively), but in contrast to the morning, there was a significant
increase in O₃ (by up to 15 ppb, compared with 50–55 ppb background
in other areas) at decreasing altitudes. Thus, biomass burning emissions
and fog caused O₃ depletion during the morning, while the first simulta-
neously provided precursors that generated O₃ at lower altitudes in the
afternoon. During the evening (Fig. 4c), O₃ concentrations were relatively
constant at around 45 ppb, lower than in the afternoon (50–55 ppb). A ho-
ogeneous air mass resulting from convective processes and breeze circu-
lations filled the GV. UFP levels remained relatively high (7500 #/cm³)
over the area where agricultural burns were located, although lower
than during the morning and afternoon flights (10000–14000 #/cm³).
Thus, on this day, agricultural biomass burning contributed to increased
background levels of UFP and O₃ to the northeast of Seville.

During the second day (July 10th, 2019) the impact of biomass burn-
ing on the air quality persisted in the northeast section of the morning
flight (Fig. 5a), with high levels of PM₂₅, BC, and UFP (40 μg/m³,
0.5 μg/cm³, and 6000 #/cm³), and again a decrease of 10 ppb in O₃ with
respect to the surrounding background levels was detected. How-
ever, during the afternoon, the O₃ formation in this northeastern tran-
sect was less pronounced than that of the previous day (Fig. 5b).

During the evening flight (Fig. 6a) of the last day (July 11th, 2019)
the impact of biomass burning over the northeastern transect was evi-
denced again (70 and 2.9 μg/m³ of PM₂₅ and BC, respectively; no UFP
data were available due to an instrument failure). During the evening
flight (green squares in Fig. 6c and f), it was possible to visually identify
an African dust layer that slightly affected the study area (Fig. S10), in-
creasing the PM₂₅ background levels from 20 to 28 μg/m³. This impact
may have been stronger for PM₁₀ than for PM₂₅ (Querol et al., 2019).

3.3.5. Urban and industrial plumes

During the beginning of the afternoon flight on the first day (July
9th, 2019, Fig. 4b), increases in O₃ (up to 15 ppb over a constant back-
ground of 45 ppb) and UFP (10000 #/cm³ over 2000 #/cm³) concentra-
tions were measured on the approach to Seville due to the emissions of
the city, as was confirmed with HYSPLIT modeling (black squares in
Fig. 4e). During the afternoon flight, high levels of pollutants (60 μg/m³
and 30000–100000 #/cm³ of PM₂₅ and UFP, respectively, together
with a slight increase in O₃ of 7 ppb) were also recorded over northeast
Huelva when crossing the plume of the petrochemical plant, as was con-
firmed by HYSPLIT modeling (red squares in Fig. 4e). The evening flight
(Fig. 4c) also measured an 8 ppb O₃ increase when crossing the plume of
the petrochemical plant (red squares in Fig. 4f), while at the same
time significant increases in PM₂₅ and UFP levels were detected
(32–35 μg/m³ and 17000–22000 #/cm³, respectively).

In the morning flight of the second day (July 10th, 2019, Fig. 5a), a
very high peak in UFP (up to 120000 #/cm³) and low BC levels, without
a major effect on O₃, were measured over the southeast of Huelva, coin-
ciding with the petrochemical plume transport (red squares in Fig. 5d).
Fig. 4. Concentrations of O₃, BC, UFP, PM₂.₅, RH, and altitude measured during the: a) morning, b) afternoon, and c) evening microlight flights of July 9th, 2019, and HYSPLIT modeling of the plume transport of the Huelva petrochemical plant and Seville City (d, e, and f) during the respective flights.
Fig. 5. Concentrations of O₃, BC, UFP, PM₂.₅, RH, and altitude measured during the: a) morning, b) afternoon, and c) evening microlight flights of July 10th, 2019, and HYSPLIT modeling of the plume transport of the Huelva petrochemical plant and Seville City (d, e, and f) during the respective flights.
Concentrations of O₃, BC, UFP, PM₂.₅, RH, and altitude measured during the: a) morning, b) afternoon, and c) evening microlight flights of July 11th, 2019, and HYSPLIT modeling of the plume transport of the Huelva petrochemical plant and Seville City (d, e, and f) during the respective flights.
There was also a moderate peak in UFP over Seville (6000 #/cm³) (black squares in Fig. 5d), along with increases in PM$_{2.5}$ and BC (60 and 0.4 μg/m³, respectively), but no significant changes in O$_3$ concentrations. During the afternoon (Fig. 5b), O$_3$ concentrations increased when approaching the plume of Seville (black squares in Fig. 5e), while simultaneously PM$_{2.5}$ and BC concentrations increased to 38 μg/m³ and 0.7 μg/m³, respectively, and UFP concentrations decreased from 26000 #/m³ to 10000 #/m³. A decrease of 10 ppb O$_3$ was measured over the petrochemical plant (red squares in Fig. 5e) along with extremely high peaks of UFP (21000 to 104000 #/cm³) as in the morning, which coincided with higher PM$_{2.5}$ and BC peaks (65 and 1.2 μg/m³). These increases occurred with the rapid descent of the plane to 150 m a.s.l., which might be the cause of the increases and decreases detected. During the evening (Fig. 5c), O$_3$ increased by 25 ppb to the west of Seville (black squares in Fig. 5f). The interesting thing about this increase is that the modeled plume does not coincide with this area but UFP and BC were observed to be 10000 #/cm³ (compared with a background of 2000 #/cm³) and 0.8 μg/m³ respectively, which points towards a local origin from the residual plume of Seville, the Huelva petrochemical plant, or biomass burning. When crossing the plume of Huelva (red squares in Fig. 5f), increased levels of PM$_{2.5}$, UFP, and BC were measured, with concentrations reaching 30 μg/m³, 0.8 μg/m³, and 20000 #/cm³, respectively, but with a decrease of 7 ppb O$_3$. As with the previous flight, this did coincide with a decrease in altitude that might be the cause of these observations, although the concentrations recorded in this plume were comparable to the levels recorded by the AQMSs, even when the plane descended to 200 m a.s.l.

The morning flight on the last day (July 11th, 2019, Fig. 6a) recorded a constant O$_3$ concentration of 65 ppb at 300 m a.s.l., which was higher compared to the morning flights of the previous days (45 ppb). Peak UFP, PM$_{2.5}$, and BC concentrations (47000 #/cm³, and 200 and 1.4 μg/m³, respectively) were measured over the plume of Huelva (red squares in Fig. 6d) due to the rapid decrease in altitude of the plane, which also affected the O$_3$ concentrations. The afternoon flight (Fig. 6b) sampled the highest levels of O$_3$ detected by the flights during the campaign. Background O$_3$ levels of 65–68 ppb were recorded at 300 m a.s.l., and a 20 ppb increase was evident when crossing the plume of Huelva’s petrochemical plant (red squares in Fig. 6e), together with high concentrations of UFP, PM$_{2.5}$, and BC (140000 #/cm³, and 80 and 1.6 μg/m³, respectively). Furthermore, when crossing the plume of Seville (black squares in Fig. 6e), O$_3$ levels also increased by up to 10 ppb, while the rest of the pollutants remained at background levels. The evening flight (Fig. 6c) was affected by the venting meteorological change described in Section 3.1, which caused a decrease in the O$_3$ regional background concentrations (down to 62 ppb of O$_3$ at 300 m a.s.l) compared with the previous flight. Concentrations of O$_3$ were homogeneous throughout the GV without increases associated with urban and industrial plumes (Fig. 6f), but over the Huelva plume, peak UFP and PM$_{2.5}$ concentrations (up to 17000 #/cm³ and 50 μg/m³, respectively) were still recorded.

4. Discussion

Data from the AQMSs showed a progressive accumulation of O$_3$ in the GV from July 9th to 11th, 2019, with the maximum being reported in the hours when fumigation from upper high-O$_3$ strata, O$_3$ formation, and O$_3$ transport by sea breezes were at their maximum. This scenario was similar to those of other locations in Spain, as was described for the Morella-Castelló (Gangoiti et al., 2001), Vic-Barcelona (Millán et al., 2002), and Madrid atmospheric basins (Escudero et al., 2019; Querol et al., 2018).

Three to four O$_3$ layers were identified every day in the first 5000 m a.s.l., with the altitudes of the layers subsiding in the afternoon and evening compared with the morning. This difference is caused under anticyclonic conditions and clear skies, by the lower layers warming up during daytime, and consequently expand in altitude, while during nighttime the lower layers will cool down and shrink. This subsidence intensified from July 9th until 11th as can be seen by the vertical temperature and humidity anomalies in Fig. 3. Fig. 7 shows the evolution of the average O$_3$ concentrations recorded by the soundings for four groups of layers located at different altitudes from July 9th to 11th, according to the morning, afternoon, and evening profiles. The accumulation occurred mainly between 400 and 1850 m a.s.l., where O$_3$ concentrations reached up to 75 ppb during the afternoon and evening soundings of July 10th and 11th, giving rise to a hump-shaped O$_3$ profile (Fig. 5b and c).

We suggest two major processes to be the origin of this hump. First, the surface sea breeze drew O$_3$ and its precursors to the interior of the GV. These pollutants were then injected at mid-altitudes by the higher topography of the upper valley, and were vertically recirculated towards the ocean (Gangoiti et al., 2001; Millán et al., 1997, 2002; Pay et al., 2019). In the GV, airmasses were driven by easterly winds (2–4 m/s and RH < 50%) during July 10th and 11th and were channelled into the GV in a northeast-to-southwest direction during the evening of the campaign. Afterward, the air masses would flow...
over the southwesterlies of the sea breeze after full development of the convective recirculation inside the valley. This situation was similar to the episodes of high O₃ in the Madrid Basin, where the O₃ episodes were generated by the vertical recirculation of air masses, caused when the boundary layer at midday reached a lower altitude than the Sierra de Guadarrama. This trapped regional air masses in the basin, which generated a similar mid-altitude O₃ hump (Querol et al., 2018). Second, the change in the mid-altitude synoptic flow, from westerlies (July 9th) to easterlies (July 10th and 11th), probably contributed to an increase in O₃ concentrations (from the second half of July 10th) by transporting polluted air masses into the region from the Eastern and Southeastern Mediterranean. This accumulation would be enhanced further by a progressive increase in insolation and temperature, with a temperature increase of 8 °C to 10 °C during the campaign, depending on the time of day, promoting additional O₃ formation. Finally, Lefohn et al. (2012), Parrish et al. (2012), Kalabokas et al. (2013, 2015) Zanis et al. (2014), and Akritidis et al. (2016), among others, reported relevant contributions from stratospheric intrusions and tropospheric subsidence to surface O₃ concentrations in the Eastern Mediterranean, Middle East, and United States background O₃ levels. Also in the Western Mediterranean, Kalabokas et al. (2017) reported that during springtime O₃ episodes (April–May), O₃ subsidence from the upper levels may affect the boundary layer as well as the ground surface O₃ concentrations due to vertical mixing through the entrainment zone of the boundary layer (Pay et al., 2019). In the case of the GV, at the highest altitudes (3000–5000 m a.s.l.), O₃ clearly decreased over the three-day period, with the O₃ concentrations being reduced by half on July 11th compared to July 9th in all soundings (morning, afternoon, and evening). This decrease also occurred on the last day for the layers between 1850 and 3000 m a.s.l. This would signify that if stratospheric intrusion occurred, its impact would be less significant over time.

At the surface, O₃ increased in the GV due to surface fumigation from the high-O₃ mid-altitude layer, formation and horizontal transport by sea breezes, and higher temperatures. During the campaign, an accumulation of O₃ occurred over 2.5 days (from July 9th until July 11th), and concentrations increased from 45 to 62 ppb at the surface at Aljarafe Mairena (southwest of Seville), and from 50 to 75 ppb at 400–1850 m a.s.l. during the afternoon soundings. Thus, the increase was mainly due to local and regional causes and was approximately 20 ppb during the study episode. This was also confirmed by airborne measurements carried out simultaneously with the microlight flights, which measured a generalized increase of 20–21 ppb O₃ at 300 m a.s.l. across the GV (Fig. 8).

The combination of decreasing O₃ at highest altitudes and increasing O₃ at lower altitudes, along with the subsidence of the upper layers over the three days and mixing between these layers, resulted in a progressive homogenization of the profiles. For example, on July 9th, the difference increased from around 40 to 100 ppb O₃ between 0 and 5000 m a.s.l., while the difference increased only from 50 ppb to 70 ppb on July 10th. This occurrence is supported by the temperature profiles (Fig. 3), which show a temperature inversion across the top of the boundary layer (Fowler and Brooks, 2006; Kaser et al., 2017), and the inverse trend of the 400–1850 and < 400 m a.s.l. layers, which shows a clear and progressive accumulation of O₃. Thus, without discarding the influence of subsided stratospheric O₃, we believe that the increase in O₃ regional background levels at lower atmospheric levels was mostly driven by other regional atmospheric processes. Large-scale subsidence over the area might have also contributed to an increase in O₃ concentrations in the boundary layer. However, to quantify the proportions of O₃ contributed by recirculation, by formation and transport, and by atmospheric subsidence, only modeling tools are needed, which is beyond the scope of this article. However, on July 11th, the O₃ profiles showed a clear hump into the boundary layer, with minimal O₃ levels above this (2500–3000 m a.s.l., Fig. 3c), pointing to the typical regional episodes described across Iberia by Gangoiti et al. (2001), Millán et al. (1997, 2002), and Querol et al. (2017, 2018), among others.

Furthermore, the microlight flights in combination with HYSPLIT modeling allowed quantification of the O₃ contributions from specific sources (on top of the O₃ background), such as the pollution plumes of the Huelva petrochemical plant and the city of Seville, as well as from the aging of agricultural biomass burning emissions.

Emissions from the early morning agricultural burns on July 9th from Seville to Lora del Río, and the fog in this agricultural area, produced a marked consumption in O₃ of 15 ppb during the morning flights on July 9th and 10th, 2019 (Figs. 4a and 5a). This was also described by Granier et al. (2000), who reported the impact on O₃ formation due to emissions of CO, NOₓ, and hydrocarbons from biomass burning. The
emission of these precursors in the morning might have caused consumption of \(O_3\) by titration of \(O_3\) by NO and the ozonolysis of VOCs. However, in the afternoon the biomass burning yielded an increase in \(O_3\) of 20 ppb (Figs. 4b and 8), together with increases in PM\(_{2.5}\), BC, and UFP. Chen et al. (2017) reported that aging biomass plumes can induce the production of tropospheric \(O_3\) as they contain an excess of \(O_3\) precursors (VOCs, CO, NO\(_x\)), and found \(O_3\) enrichment across China due to biomass burning. This was also reported by Zhu et al. (2014), who reported high concentrations of toluene, isoprene, ethene, propane, and \(n\)-hexane as well as their \(O_3\) formation potential (OFP) in a rural area in Northern China with frequent biomass burns. Jaffe and Zhang (2017) also described delayed \(O_3\) formation from wildfire plumes interacting with NO\(_x\) from urban plumes and attributed the delay to peroxycetil nitrate (PAN) present in the fire plumes.

Concentrations of \(O_3\) in the plumes from Huelva’s petrochemical plant and the city of Seville peaked (simultaneously with those of UFP and PM\(_{2.5}\), and BC in some cases) mainly during the afternoon and evening flights. Thus, the afternoon and evening flights on July 9th measured an increase of 10 ppb \(O_3\) over the regional background levels at 300 m a.s.l. (Fig. 8). An increase of 15 ppb was measured when crossing the Seville plume during the afternoon of July 10th (Fig. 8); finally, an increase of 10 to 17 ppb was measured during the afternoon and evening flights on July 11th through these plumes, reaching a maximum \(O_3\) concentration of 85 ppb, which exceeded an already-high 68 ppb background during the afternoon of the same day (Fig. 8). Thus, both the modeling of the plume transports and the co-measurements of BC, PM\(_{2.5}\), and UFP with \(O_3\) allowed us to quantify the \(O_3\) contribution from the plumes to the regional background \(O_3\) background levels. Indeed, VOC and NO\(_x\) emissions from petrochemical plants may result in high \(O_3\) formation rates. As an example, Fawole et al. (2017) measured peak concentrations ranging from 70 to 115 ppb in instrumented flights when crossing the plumes of a gas flare with high levels of CO and alkanes over the Niger Delta. As another recent example, in Xiong and Du (2020), six sources were identified in the Vancouver metropolitan area as contributing most of the VOC-related OFP, namely fuel production and combustion, fuel evaporation, vehicle exhaust, industrial coatings/solvents, a petrochemical source, and other industrial emissions, with the first three accounting for 68% of the OFP. However, high OFP has been widely reported when urban and industrial plumes interact with air masses containing high levels of biogenic VOCs (see as an example Zong et al. (2018) and references therein).

5. Conclusions

Intensive 3D measurements of \(O_3\), PM\(_{2.5}\), UFP, and BC concentrations, as well as meteorological parameters, were carried out with free soundings and instrumented microlight flights during an \(O_3\) episode affecting the GV (southern Spain) between July 9th and 11th, 2019, to investigate the processes responsible for high \(O_3\) pollution episodes in this region. The results suggest that the episode was caused by 2.5 days of local and regional \(O_3\) accumulation. The main processes causing this accumulation were the:

(I) Transport from the Atlantic sector (western Iberia).

(II) Vertical recirculation of air masses by sea and valley breeze circulations interacting with complex topography.

(III) Locally-formed \(O_3\) in the GV during July 9th and 10th, 2019.

(IV) Trans-basin contribution from Mediterranean \(O_3\) during July 11th, which was initiated during the second half of July 10th.

(V) Possible atmospheric subsidence flows.

Background \(O_3\) in oceanic air masses over the Gulf of Cádiz was transported inland by sea breezes, which drew \(O_3\) and its precursors from the industrial and urban areas of Huelva, Seville, and Córdoba, causing \(O_3\) maxima late in the afternoon–evening at the northeastern end of the GV. In fact, Castell et al. (2011) found the number of consecutive days with sea breezes to be the best predictor of \(O_3\) accumulation processes in eastern Spain. Furthermore, upslping winds at high altitude in the mountains of the eastern GV injected aged air masses into the mid-altitude (400–1850 m a.s.l.) troposphere (generating reservoir layers), which were transported back to the ocean within the northeasterlies, where they subsided and could be recirculated with the sea breezes of the following day (Fig. S11). Furthermore, on July 10th and 11th at this mid-altitude level (400–1850 m a.s.l.), air masses from the eastern to southeastern sectors (of Mediterranean origin) crossed the southern boundaries of the Betic System and reached the GV during the second half of July 10th (Fig. S5), likely bringing an additional supply of \(O_3\). Surface fumigation from the recirculating reservoir layers and those of Mediterranean origin, vertical mixing through the entrainment zone of the convective boundary layer, and local plumes that were transported at lower levels together were the causes of the \(O_3\) pollution episode observed during the field campaign. This resulted in an increase in \(O_3\) over 2.5 days from an initial regional background concentration of 45 ppb on July 9th up to 70–75 ppb during the afternoon of July 11th, 2019.

On top of this gradual \(O_3\) background increase, we quantified, with the support of PM\(_{2.5}\), BC, and UFP measurements and HYSPPLIT modeling, that local contributions increased the \(O_3\) concentration by up to 20 ppb. Although the pollutants have various origins, the relative changes in concentration when crossing the pollution plumes and the agricultural burns made it clear that these were the sources of the observed changes. The attributed sources were agricultural burns and the transported plumes of Huelva’s petrochemical plant and the city of Seville.

In the free troposphere, the stratospheric \(O_3\) intrusion located over the region on July 9th was dispersed during July 10th and 11th, and the high \(O_3\) concentration in the layer at 3000–5000 m a.s.l. followed an inverse trend to that described at the surface, decreasing by half on July 11th compared to July 9th (Fig. 7).

It is important to highlight that, in addition to the \(O_3\) enhancement caused by agricultural burns, very high levels of BC, UFP, and PM\(_{2.5}\) were measured regionally around these areas, especially to the northeast of Seville, which is an area with extensive agricultural practices. During the morning of July 9th and the afternoon of the 11th, abundant agricultural burns were evident, as well as black plumes derived from waste burning (plastics, tires, etc.). During the flights, we were even able to observe that an agricultural burn turned into an uncontrolled fire. We consider it necessary to abate these emissions, which have a strong impact on the air quality of the area.

Our results allowed us to develop a conceptual model of how high \(O_3\) episodes occur in the GV, one of the areas of Spain with the highest \(O_3\) levels after the Madrid and Barcelona regions. The results identified the key spatial patterns that modeling tools can use to accurately reproduce and forecast \(O_3\) concentrations in the area, and to carry out sensitivity analyses to evaluate cost-efficient abatement measures. An important remaining gap in our knowledge is the evaluation of the actual species and concentrations of VOCs across the area horizontally and vertically, to further supply very relevant information to the modeling tools.

CRediT authorship contribution statement

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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