OZONE EPISODES OVER THE SOUTHEAST IBERIAN COAST: ORIGIN AND RECYCLING BETWEEN TWO SEAS

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ABSTRACT

Episodes of high tropospheric ozone concentration in the southeast coast of Iberian Peninsula during 2015 were identified together with associated synoptic conditions, and their most probable origins were determined by means of different atmospheric modelling simulations and data analysis. Most of episodes in this study were associated with high pressures and temperatures, not only over the southeast coast but also over the whole southern Iberian region, which are favourable to the ozone photochemical production. The tropospheric ozone levels detected are mainly due to the transport of ozone from the Eastern Iberian coast. However, Atlantic winds through the Strait of Gibraltar also produce recycling over the study region, and locally increase the ozone levels over the southeast coast of the Iberian Peninsula.

Keywords: tropospheric ozone, air quality modelling, photochemistry, recycling.

1 INTRODUCTION

At the Iberian Peninsula, tropospheric ozone is detected in all regions and, particularly, in the Mediterranean and other coastal areas. This is related to industrial development, road traffic increase, and the high insolation in central, east and south regions. However, ozone levels distribution is very heterogeneous between regions, because of their strong differences in climate patterns, emissions profiles and, even, possible external apportioning.

From the Iberian regions, Mediterranean has been the most widely studied, because emissions and high insolation are usually high, especially during summertime. Works of Millán et al. [1] and Gangoiti et al. [2] explained the influence of both synoptic and local coastal patterns in the ozone levels at this region. Other authors supported their studies in this region with photochemical modelling [3], [4]. Finally, several studies were focused in topographic and land use effects, including sea breezes [5], [6]. Some of their results were extended to the Cantabric [2] and Atlantic coasts [3], focusing in the Lisbon urban area, Cantabric coast is also a region with significant ozone levels, mainly because the transboundary transport of ozone from the East (Central Europe). Some studies were focused in the meteorological patterns associated to ozone peaks. Following this approach, the origin of ozone peaks at the Northwest of Iberian Peninsula related to the synoptic patterns over the Iberian Peninsula [7] was carried out; and, air quality simulations of the most typical ozone episodes in this region [8]–[10].

Most of these studies were performed by a combination of observations and models results analysis. In general, large scale wind patterns can produce persistent high level ozone conditions over these regions, while local coastal peaks are usually related to sea breezes effects over the ozone produced at the same region at its surroundings.

In this work, both observations and different modelling results were analysed to explain the origin of ozone peaks observed at a less populated southeast Iberian coastal area; as the local photochemical ozone production in this study region is limited by low emissions of precursors (NO_X); even though local coastal recycling could increase these ozone levels.

WIT Transactions on Ecology and the Environment, Vol 230,
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/AIR180441

Figure 1: Study region covering the southeast coast of the Iberian Peninsula and surrounding areas, in order to consider possible ozone transport from them. Also, 11 Andalusia air quality network sites considered to identify and analyse ozone episodes are shown as green named circles.

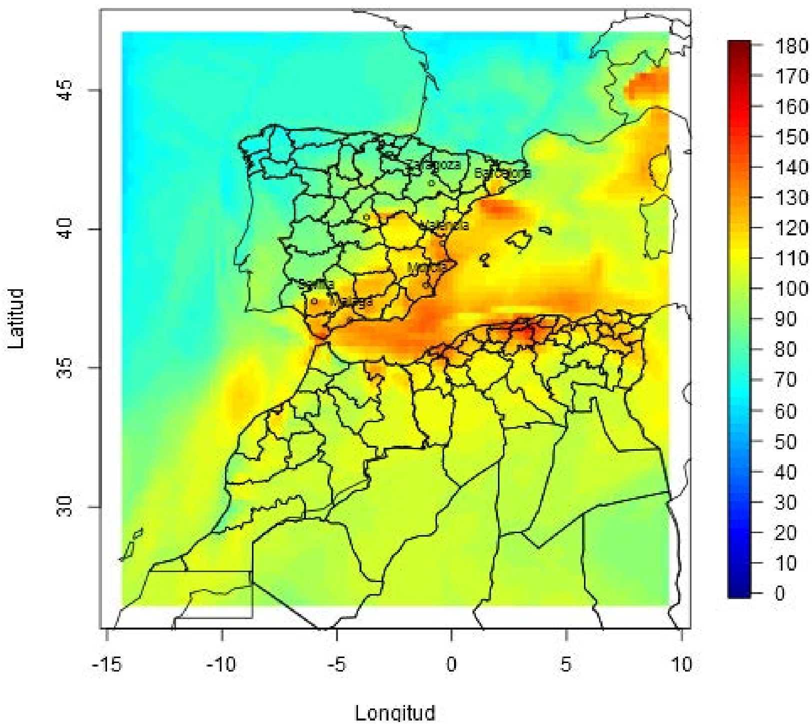


Figure 2: Air quality modelling simulation domain applied in the analysis of ozone episodes observed in Almeria province, at the southeast coast of the Iberian Peninsula. Coloured scale corresponds to 8-hr average ozone ground level concentrations calculated by the air quality model, in g·m-3.

2 OZONE EPISODES

High and persistent tropospheric ozone levels over different air quality sites at the Southeast coastal area of the Iberian Peninsula are observed, especially during spring and summer periods; also, in less populated areas, as Almeria province, where road traffic and industrial NO_x emissions are lower than in surrounding regions.

Therefore, Almeria province was selected as case study (Fig. 1), but larger domains around it were also analysed in order to consider possible external ozone contributions, as it is shown in Fig. 2 for the air quality modelling domain.

In order to identify and analyse the ozone episodes over the study region, tropospheric ozone hourly ground level concentrations (glc) observed along 2015 at 11 surface sites were collected. These sites (Fig. 1) belong to the Andalusia Air Quality Network, and they are located all over the province. As the least populated coastal province in this region, local emissions influence over the ozone levels should be lower; however, high and persistent ozone levels are usually observed during spring and summer periods.

From these glc observations, 8-hours average ozone concentrations were calculated too and both, hourly and 8-hours average concentrations, were compared to the legal thresholds included in BOE [11]. Particularly, the first health goal threshold for 8-hours average, 120 $\mu g \cdot m^{-3}$, was exceeded in several sites in the study region during several periods between March and November 2015, showing conditions that keep high and persistent ozone levels.

Table 1 shows the number of exceedances per site in 2015. Bedar and Rodalquilar sites show the highest ozone levels; in fact, in most of the periods with exceedances include at least one of both sites as exceedance site.

In order to analyse these exceedances and their probable origin, they were classified by time periods, taking into account the meteorological conditions during them. A total of 10 different periods were considered, as it is shown in Table 2, also including the sites with exceedances per period. Most of exceedances are associated to summer periods, with more sites affected and longer; although spring periods exceedances are also significant. Again, Bedar inland site and Rodalquilar coastal site are the most frequently affected by high ozone levels.

Table 1: Number of exceedances of 8-hr average ozone glc over the first health goal threshold (120 $\mu g \cdot m^{-3}$) at each site of the Andalusia air quality network in Almeria province (eastern and western sites), along 2015.

Site	Number of exceedances	Location at Almeria province
Benar	54	eastern
Benahadux	14	western
El Boticario	27	western
Campohermoso	15	eastern
El Ejido	12	western
Fernán Pérez	1	eastern
La Granatilla	16	eastern
La Joya	9	eastern
Mediterráneo	0	western
Mojácar	33	eastern
Rodalquilar	46	eastern

Table 2: Periods with exceedances of 8-hr average ozone glc over the first health goal threshold (120 g·m-3) at the Andalusia air quality network in Almeria province, along 2015; also showing the sites with exceedances per period.

Period	Sites with exceedances
March, 11–13	Rodalquilar, La Joya, Mojácar, Fernán Pérez
April, 30–May, 1	Bedar, Rodalquilar, La Joya
May, 7–20	Bedar, Rodalquilar, El Boticario, Campohermoso, La Joya, Mojácar
May, 23–30	Bedar, Rodalquilar, El Boticario, Campohermoso, Mojácar
June, 2–4	Bedar, Rodalquilar, Boticario, Campohermoso, Mojácar
June, 7–11	Bedar, Rodalquilar, Boticario, Mojácar
June, 16–July, 10	Bedar, Rodalquilar, Boticario, Mojácar, Campohermoso, La Joya, Benahadux, El Ejido
July, 18–August, 15	Bedar, Rodalquilar, Boticario, Mojácar, El Ejido, Benahadux, La Granatilla
September, 11–13	Bedar, Boticario, La Granatilla, Rodalquilar
November, 2–3	Rodalquilar

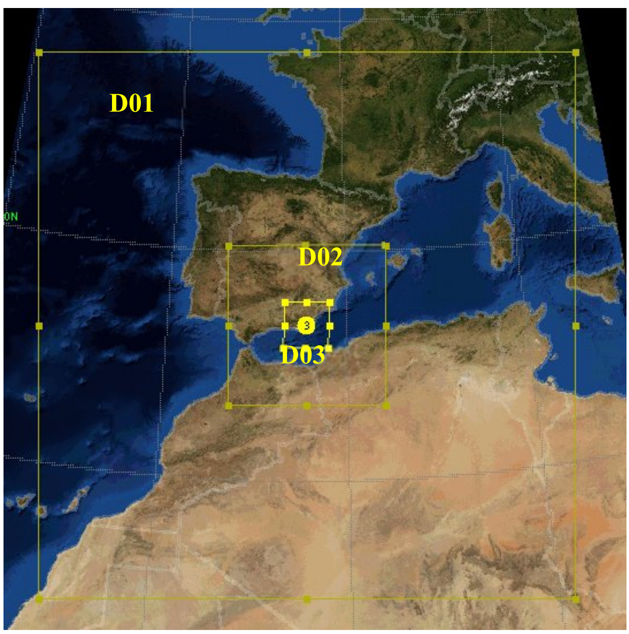


Figure 3: WRF-ARW model nested grids applied in the simulation of mesoscale meteorological conditions, for the analysis of ozone episodes in the study. Horizontal resolution: D01: 27 km; D02: 9 km; D03: 3 km.

3 MATERIALS AND METHODS

As a secondary pollutant, ozone production involves both physical and chemical atmospheric phenomena. Therefore, in order to analyse the origin and dynamics of ozone episodes, different datasets must be considered and, specially, modelling have to be applied to take into account the interactions between precursors emissions (mainly, NO_2), meteorology, and other pollutants and atmospheric components.

In this work, apart from the observed air quality time series to identify the ozone peaks, the following datasets were applied,

a) Synoptic maps, namely, 850 and 500 hPa maps from the GFS (Global Forecast System) model NCEP reanalysis over Western Europe [12]. These maps provide a qualitative analysis of the influence of meteorological conditions over the ozone local photochemical production, and possible ozone transport from the surrounding areas. High temperature and clear skies (related to high solar radiation) jointly to calms are favourable conditions to photochemical ozone production; and large-scale wind patterns can help to consider possible ozone transport.
b) Back trajectories, with origin in the sites with the highest ozone peaks along each episode. These back trajectories were calculated using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trayectory) model [13], using as input the results of WRF-ARW meteorological model [14] simulations over a nested grids domain at 27, 9, and 3 km horizontal resolutions (Fig. 3). The largest domain, D01, includes the Iberian Peninsula, most of the eastern North Atlantic Ocean, the main western Mediterranean basin [15], and the north western African region; in order to consider possible influence of any surrounding area.
c) Initial and boundary conditions for D01 domain were provided by the GFS model reanalysis from the NCEP [16] at 0.25º of horizontal resolution.
d) Air quality modelling simulations results, using the CHIMERE photochemical transport model [17] with three nested grids inside de corresponding nested grids applied in the WRF-ARW model (see Fig. 3). EDGAR-HTAP anthropogenic emissions inventory [18] was applied as main emission dataset, and biogenic emissions were calculated using the MEGAN model [19]. As chemical mechanism, SAPRC7 [20] was selected, as the newest mechanism included in CHIMERE model, that demonstrated its ability to represent ozone photochemical production in lab experiments.
e) CHIMERE model results were compared to the observed ozone episodes time series at different sites in the study region, in order to assess the quality of this model results to be applied in the episodes analysis.

4 RESULTS

All the datasets previously described were systematically analysed in the different ozone episodes identified, in order to determine the different contributions to the ozone glc measured in the sites at the study region. As a result, Table 3 summarizes the main conclusions of the analysis for each ozone episode.

From this episode's analysis, the origin of most of the ozone peaks observed at the study region during 2015 is the transport of ozone from the Eastern coast. This is a region previously characterized as highly ozone polluted, including not only ozone photochemical production due to human activities precursors emissions (mainly NO_x, from road traffic, industry and, also, domestic sources), but also local coastal recycling, namely "mirror effect" [1], as Valencia, Barcelona, Alicante and Castellon provinces are also affected by this effect; but in those cases, the precursors emissions mainly come from the own cities/industries. Also,

Table 3: Summary of the analysis of each ozone episode along 2015 in the study area, considering synoptic maps, backtrajectories simulations, and air quality simulations.

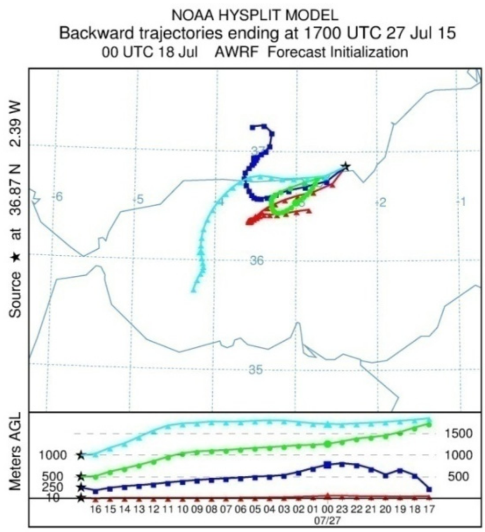
PERIOD	SUMMARY
March 11–13	High temperature/radiation. Back trajectories: WSW to ENE. Main ozone origin: Local photochemical production.
April 30–May, 1	High temperature/radiation. Back trajectories: Variable, recycling. Main ozone origin: Local photochemical production.
May 7–20	High pressure and temperature. Back trajectories: From the Eastern coast. Main ozone origin: Aloft ozone transport from the East, mixed to the surface level.
May 23–30	High pressures. Strong aloft-surface ozone mixing. Backtrajectories: From the Eastern coast. Main ozone origin: Aloft ozone transport from the East, mixed to the surface level.
June 2–4	High pressures. Low East winds. Some aloft-surface ozone mixing. Persistent ozone. Backtrajectories: From the Eastern coast. Main ozone origin: Slow and persistent aloft ozone transport from the East, mixed to the surface level.
June 7–11	High pressures. High basal ozone concentrations, with some NO local impacts. Aloft-surface ozone mixing. Backtrajectories: (a) From the Eastern coast, (b) Variable (E-W) with recycling from the Straits of Gibraltar. Main ozone origin: Ozone transport from the East, also with recycling from the Straits of Gibraltar.
June 16–July, 10	High temperatures, due to African influence over the Peninsula. High basal ozone concentrations, with fluctuations in 5 sites due to the local NO_x. Back trajectories: From the Eastern coast, except at Bedar site (from the southwest). Main ozone origin: Aloft transport from the East.
July 18–August, 15	High pressures. First mid-period: West flow, with aloft-surface ozone mixing. Strong sea breeze influence. Second mid-period: East flow, stratified. Low basal ozone levels, with high fluctuations: Back trajectories: (a) First mid-period: West flow, with recycling. (b) Second mid-period: East flow, ending with West flow. Two different origins: (a) First mid-period: Western ozone transport, with high local influence (also, sea breezes). (b) Second mid-period: Eastern coastal transport.
September 11–13	Low pressure over the region. Strong aloft wind from the West. High ozone fluctuations. Local influence of NO_2 over the ozone in 3 sites. Aloft-surface ozone mixing, high surface ozone levels. Back trajectories: From the WSW, also African coast at the Straits. Main ozone origin: From the Straits of Gibraltar, including both European and African coasts.
November 2–3	Low pressure over the Iberian Peninsula. Local influence of NO_x over the observed ozone. No aloft-surface mixing. Backtrajectories: From WNW, but no ozone transport. Main ozone origin: Local ozone production, at the site affected.

this phenomenon was identified in other Iberian coastal regions, as over Lisbon and Porto areas [3].

Following this mirror effect, precursor emissions at a coastal region and its surroundings can produce ozone due to favourable photochemical conditions, which is transported to the sea in the morning, but this ozone is also carried inland due to the afternoon sea breezes, adding to new produced ozone.

However, over the study region lower precursor emissions is observed, so low local ozone production is possible; otherwise, Eastern produced ozone is carried hundreds of km along

(a)



(b)

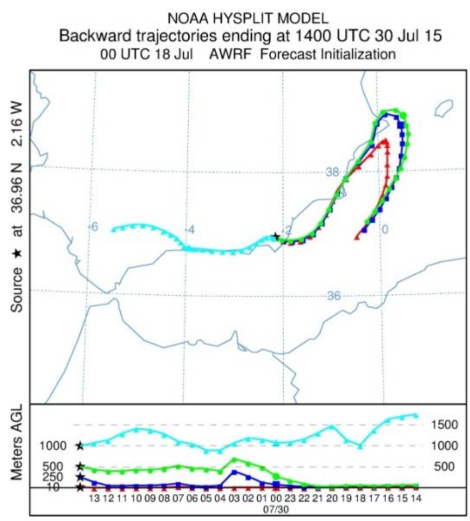


Figure 4: Backtrajectories calculated using the HYSPLIT model, over the study region: (a) July 27th, 2015; (b) July 30th, 2015. Origin: Peak ozone sites, at four different levels: 10, 250, 500 and 100 agl-m.

the coast to the study region, increasing the local ozone levels also due to the favourable vertical mixing conditions. In addition, some of the ozone episodes includes coastal recycling of the carried ozone, either from the Eastern coast or from the Strait of Gibraltar (including both European and African coasts are possible origins). This recycling is not produced by sea breezes, otherwise it is an influence of the two-faced coasts, European and African, over the study region.

As an example of this feature, Fig. 4 shows back trajectories calculated by HYSPLIT model at July 27th, 2015 and July, 30th 2015, at four different vertical levels. The early day back trajectories come from the west, but different and complex recycling close the study region is observed. The latter day most of them come from the east, but with a large recycling along the eastern coast; with the highest back trajectory from the west.

Considering the synoptic conditions, western local flows from the Strait of Gibraltar dominated this period until 27th, when they went a bit lighter due to a small low pressure condition; therefore, and opportunity to the Eastern winds came in the following days, but still aloft western winds keeps, producing the large recycling observed in the 30th the lowest back trajectories parallel to the coast; with the highest back trajectory showing the effect of the aloft western wind. Therefore, in this study region it is possible that western winds from the Strait of Gibraltar and Eastern coastal winds from other Mediterranean more polluted areas, collaborating to recycle the ozone received from different origins to increase the ozone levels over the study region. As strong Strait winds are singular from the two continents proximity, this effect cannot be observed in other regions of the Iberian Peninsula.

Apart from this singular effect, ozone peaks at the study region are usually produced by either Eastern or Western straight ozone transport along the coast. During the period July 18th -August 15th, high ozone levels at 7 different air quality sites were observed; but ozone origin changes along that period, because of changes in the mesoscale flow affecting the study region.

This feature can be observed in Figs 5 and 6 from the analysis 8-hours average ground level concentrations obtained from the CHIMERE model simulation results along the whole period. Considering these results, two different mid-periods can be identified,

a) A first mid-period (Fig. 5), until August 1st, when west winds from the Straits of Gibraltar are carrying ozone from the Straits to the study region, including ozone produced along the coastline.
b) A second mid-period (Fig. 6), from August 2nd to the end of the period, when eastern Mediterranean winds are carrying highly ozone polluted air from the Mediterranean Sea through the Straits of Gibraltar, passing over the study region.

Between these two mid-periods, a transition sub-period between July 27th and August, 1st is observed, as explained before. Changes in ozone patterns at both Strait of Gibraltar sides are apparent due to the encounter between the western winds from the Strait and eastern winds from the Mediterranean Sea; both carrying air to the study region and producing mesoscale ozone recycling over it. However, the origin of ozone is mainly the Atlantic Iberian coast when western winds are stronger (including Portuguese coastline), and the Mediterranean Sea (including the Mediterranean Iberian coastline) when eastern winds dominates lighter western winds. In fact, in this domain strong western winds produce higher ozone levels at western air quality sites (see Table 1); while stronger eastern Mediterranean winds increase the ozone levels at eastern air quality sites.

This mesoscale feature is very different than typical coastal recycling produced by local sea breezes in other Iberian coastal sites close to urban concentrations (Valencia, Barcelona, Lisbon, Porto, …), previously named as “mirror effect”.

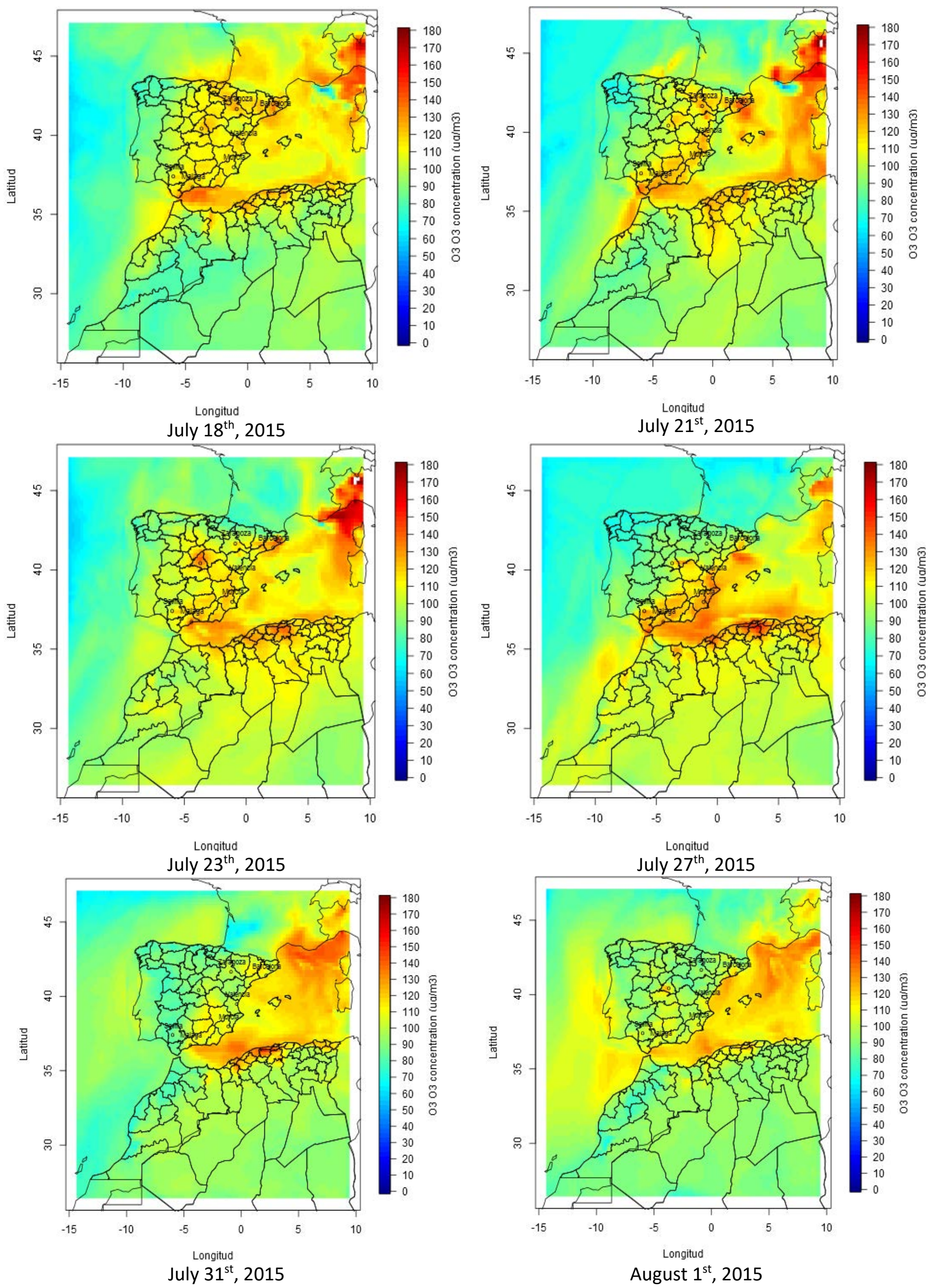


Figure 5: Different 8-average ozone daily peaks (g·m-3) calculated from the hourly results of the CHIMERE model simulation along the period July 18th–August 1st, 2015. Only starting and ending dates results, and dates when significant changes in ozone patterns at both Strait of Gibraltar sides, are shown.

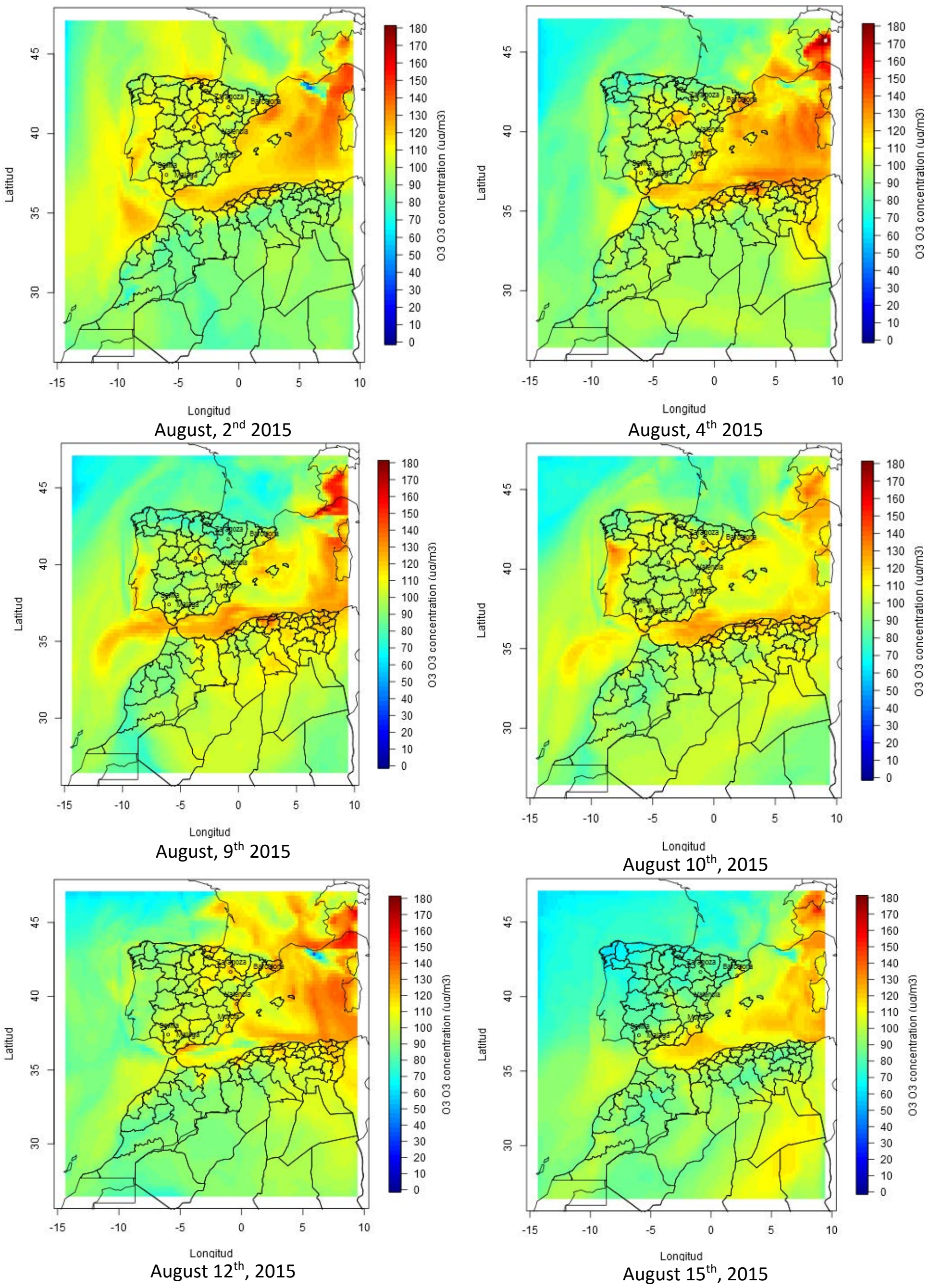


Figure 6: Different 8 hr-average ozone daily peaks (μg·m^{-3}) calculated from the hourly results of the CHIMERE model simulation along the mid-period August 1st–15th 2015. Only starting and ending dates results, and dates when significant changes in ozone patterns at both Strait of Gibraltar sides, are shown.

5 CONCLUSIONS

In this work, ozone peaks episodes observed along 2015 in the southeast coast of the Iberian Peninsula were identified and analysed. Most of these episodes are related to the eastern winds along the Mediterranean coastline, carrying ozone from more populated coastal eastern regions and, also, from the West Mediterranean core. However, in other episodes western winds crossing the Strait of Gibraltar can also carry ozone, from the Atlantic Iberian coastline.

As a singular feature, during summertime when mesoscale Atlantic flows crossing the Straits are opposite to Mediterranean eastern flows, mesoscale recycling over the study region can increase the ozone levels, as the mesoscale wind direction changes daily. This feature is quite different than the local "mirror" effect previously characterized in both Mediterranean and Atlantic Iberian coastal regions, close to high populated cities, when sea breezes can recycling the ozone from the sea back to the coast. However, mesoscale flows changes can also be so powerful in recycling coastal ozone, when two continents are close and those flows are strong enough.

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