Regional responses of surface ozone in Europe to the location of high-latitude blocks and subtropical ridges

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Abstract. This paper analyses for the first time the impact of high-latitude blocks and subtropical ridges on near-surface ozone in Europe during a 15-year period. For this purpose, a catalogue of blocks and ridges over the Euro-Atlantic region is used together with a gridded dataset of maximum daily 8-hour running average ozone (MDA8 O_3) covering the period 1998–2012. The response of ozone to the location of blocks and ridges with centres in three longitudinal sectors (Atlantic, ATL, 30º–0º W; European, EUR, 0º–30º E; Russian, RUS, 30º–60º E) is examined. The impact of blocks on ozone is regionally and seasonally dependent. In particular, blocks within the EUR sector yield positive ozone anomalies of ~5–10 ppb over large parts of central Europe in spring and northern Europe in summer. Over 20 % and 30 % of the days with blocks in that sector register exceedances of the 90th percentile of the seasonal ozone distribution at many European locations during spring and summer, respectively. The impacts of ridges during those seasons are subtle and more sensitive to their specific location, although they can trigger ozone anomalies of ~5–10 ppb in Italy and the surrounding countries in summer, eventually exceeding European air quality targets. During winter, surface ozone in the northwest of Europe presents completely opposite responses to blocks and ridges. The anticyclonic circulation associated with winter EUR blocking, and to a lesser extent with ATL blocking, yields negative ozone anomalies between -5 ppb and -10 ppb over the UK, Northern France and the Benelux. Conversely, the enhanced zonal flow around 50˚–60˚ N during the occurrence of ATL ridges favours the arrival of background air masses from the Atlantic and the ventilation of the boundary layer, producing positive ozone anomalies above 5 ppb in an area spanning from the British Isles to Germany. This work provides the first quantitative assessments of the remarkable but distinct impacts that the anticyclonic circulation and the diversion of the zonal flow associated with blocks and ridges exert on surface ozone in Europe. The findings reported here can be exploited in the future to evaluate the

modelled responses of ozone to circulation changes within chemical transport models (CTMs) and chemistry-climate models (CCMs).

1 Introduction

Air pollution results from a combination of elevated emissions and unfavourable weather conditions. One of the air pollutants of most concern for public health is surface ozone (O_3). Ozone in the troposphere is formed by photochemical reactions involving non-methane volatile organic compounds (NMVOCs), carbon monoxide (CO) and nitrogen oxides ($NO_x \equiv NO + NO_2$). The oxidation of methane (CH_4) also contributes to tropospheric ozone formation at the global scale. Another source of tropospheric ozone is the injection of O_3 from the stratosphere, while dry deposition to the Earth's surface and chemical loss provide the main sinks. Ozone is known to be detrimental not only to humans' health (e.g. Brunekreef and Holgate, 2002) but also to ecosystems, reducing plant primary productivity and crop yields (e.g. Ashmore, 2005). Moreover, tropospheric O_3 is a greenhouse gas. The past increase in tropospheric O_3 is estimated to have contributed 0.40 (0.20 to 0.60) W m^{-2} to direct radiative forcing (RF) since the pre-industrial era (Myhre et al., 2013). There is also robust evidence of indirect radiative effects of tropospheric ozone (Sitch et al., 2007) although quantitative estimates of the associated RF are still uncertain (Myhre et al., 2013).

A large number of observational studies have established statistical relationships between near-surface ozone concentrations and meteorological variables at the local and regional scales for over two decades (e.g. Bloomfield et al., 1996; Tarasova and Karpetchko, 2003; Ordóñez et al., 2005; Camalier et al., 2007; Seo et al., 2014). Comprehensive summaries can be found in the reviews by Jacob and Winner (2009) and Fiore et al. (2012). While ozone is favoured by elevated temperatures and regional stagnation in summer (e.g. Jacob and Winner, 2009), stable weather conditions generally accelerate the loss of ozone close to the surface in winter through the enhanced effect of dry deposition and reaction with nitrogen monoxide (NO) to form nitrogen dioxide (NO_2), a process known as ozone titration (e.g. Laurila et al., 1999; Ordóñez et al., 2005).

Some studies have addressed the connection of tropospheric ozone with circulation patterns, but the few analyses available for Europe are often restricted to specific regions. As an example, some studies have established objective links between circulation weather types (CWTs) and surface ozone in western Iberia (Carvalho et al., 2010; Russo et al. 2014) as well as in northwest and central Europe (e.g. Demuzere et al., 2009, 2011). Furthermore, past research efforts have traditionally been focused on the export of pollution from North America and the injection of stratospheric ozone into the troposphere (see e.g. Monks et al., 2009, 2015, and references therein), as well as on the impact of the North Atlantic Oscillation (NAO) regimes (Hurrell, 1995; Jones et al., 1997). Creilson et al. (2003) suggested that during positive phases of the NAO, characterized by stronger than usual Azores high and Icelandic low, the enhanced westerlies across the North Atlantic lead to increased springtime ozone in western Europe as a consequence of the long-range transport of pollution plumes from North America. More recently, Pausata et al. (2012) showed that the commonly used NAO index (NAOI) is able to capture the link existing

between atmospheric dynamics and European surface ozone concentrations in winter and spring, while a modified NAO index is needed to detect the atmospheric circulation - ozone relationship in summer.

The NAOI, like any other teleconnection index associated with large-scale circulation patterns, can explain intra- and inter-annual fluctuations of the intensity of the zonal flow, but such one-dimensional monthly-based approaches limit our understanding of the complex spatial patterns occurring at intra-monthly time scales (e.g. Sousa et al., 2106a). Therefore, the day-to-day variability of the O_3 concentrations at the regional scale may be better captured by analysing the occurrence, persistence and position of specific synoptic-scale weather patterns. For example, some attention has already been paid to the role of frontal passages associated with mid-latitude cyclones as well as to the relative position and strength of meteorological systems in Europe (e.g. Ordóñez et al., 2005; Doche et al., 2014). During summer the first days after a frontal passage are usually accompanied by an increase in temperature and stagnation of the air masses, leading to elevated ozone concentrations over central Europe, while the opposite effect can be observed in winter as the stability favours the ozone loss by titration and dry deposition (Ordóñez et al., 2005). The relative position and strength of the Azores anticyclone and Middle Eastern depression (Doche et al., 2014), as well as the subsidence of ozone-rich air masses from the upper troposphere and lower stratosphere (e.g. Doche et al., 2014; Zanis et al., 2014), also influence the variability of lower tropospheric ozone over the Mediterranean in summer. Many studies have highlighted the complexity of the ozone dynamics in the Mediterranean region, where the interaction between the synoptic scale and mesoscale circulations needs to be considered. A number of sub-synoptic processes such as land-sea breeze and channelling effects due to terrain features which favour the re-circulation of air masses and the formation of ozone reservoir layers, vertical mixing along the sloped terrain, and subsidence are known to be relevant in the region (e.g. Millán et al., 2000; Gangoiti et al., 2001; Cros et al., 2004; Drobinski et al., 2007; Flocas et al., 2009; Velchev et al., 2011; Kalabokas, 2013). This study will be focused only on the role of the synoptic scale.

Comprehensive analyses of the impact of synoptic patterns on surface ozone in Europe, considering their seasonal effects and temporal scales larger than those of episodic cases, are not common. Among the synoptic features which are expected to impact surface ozone and other air pollutants one can mention the frequency and persistence of high pressure systems with an anticyclonic circulation such as high-latitude blocks and subtropical ridges. These systems are often associated with stable weather conditions in all seasons and above normal temperatures in summer under the anticyclonic centre, thus setting favourable conditions for the formation of ozone in that season. There are conceptual differences in the definition of blocking and subtropical ridge patterns although sometimes they induce similar anomalies in the surface climate (e.g. Barriopedro et al., 2010b; Sousa et al., 2016a). Atmospheric blocking is associated with persistent, slow-moving high pressure systems that interrupt the prevailing westerly winds of middle and high latitudes, and therefore the eastward progress of extratropical storm systems (Christensen et al., 2013). Changes in the frequency and duration of blocking events have a significant impact on temperature and precipitation in winter (Fraedrich et al., 1993; Trigo et al., 2004; Masato et al., 2012; Sousa et al., 2016a). Atmospheric blocking has also been associated with temperature extremes in Europe, including heat waves (Matsueda, 2011; Katsafados et al., 2014) and cold spells (Buehler et al., 2011; Cattiaux et al., 2010), presenting

stronger links with collocated warm temperature extremes than with collocated cold extremes over mid to high latitude land regions (Pfahl and Wernli, 2012). On the other hand, subtropical ridges are low latitude structures characterized by positive geopotential height anomalies extending from sub-tropical latitudes towards extra-tropical regions such as southern Europe (e.g. Sousa et al., 2016b) and by northward displacements of the Atlantic eddy-driven jet stream (Woollings et al., 2011).

5   The occurrence of strong and persistent mid-latitude anticyclonic ridges over the Eastern North Atlantic plays a key role in triggering precipitation extremes in western Iberia during winter (Santos et al., 2009a, 2009b). Moreover, Santos et al. (2015) found that temperature extremes in Iberia during summer 2003 were associated with enhanced anticyclonic circulation over northern Africa and the western-central Mediterranean, extending as a ridge towards northern France and diverting the westerly flow to northern Europe. García-Herrera et al. (2010) also showed that the atmospheric conditions

10   during the 2003 "mega-heatwave", which triggered strong air pollution episodes over large areas of western Europe, did not display the typical signatures of canonical blocking patterns. Finally, recent analyses have documented the distinctive regional responses of European temperatures to both blocking and subtropical ridges (Sousa et al., 2016b). However, the impact of these synoptic patterns on surface air quality (AQ) on multiannual time scales has not been assessed yet.

In this study we conduct the first comprehensive analysis of the seasonal impacts of high-latitude blocks and subtropical

15   ridges on near-surface ozone. A recent 15-year gridded dataset of daily ozone mixing ratios over Europe is used for this purpose. Section 2 describes the ozone and meteorological data used as well as the methodology applied to build the catalogue of high-latitude blocks and subtropical ridges. The impact of blocks and ridges on ozone is separately examined for the seasons with the highest levels of this pollutant (spring and summer) in Sect. 3 and for winter in Sect. 4. Finally, Sect. 5 summarises and discusses the main results, while Sect. 6 outlines some of the implications of our findings.

20   **2 Data and methods**

2.1 Ozone and meteorological data

We use an interpolated dataset of observed maximum daily 8-hour running average near-surface ozone (MDA8 O_3) over Europe during the period 1998–2012. These gridded data have been created with the objective mapping algorithm of Schnell et al. (2014, 2015), who compiled and merged hourly observations from the European Monitoring and Evaluation

25   Programme (EMEP) and the European Environment Agency's air quality database (AirBase) to calculate hourly surface ozone averaged over 1° x 1° grid cells. This product has been initially used by Schnell et al. (2014, 2015) to evaluate global chemical transport models (CTMs) and chemistry–climate models (CCMs). More recently, this dataset has been proved to be useful for the examination of the influence of atmospheric circulation and meteorological conditions on extreme ozone concentrations in Europe (Otero et al., 2016). Overall, seasonal linear trends of MDA8 O_3 are small for most regions during

30   the period of analysis. The main exception is the Balkans, which presents significantly positive ozone trends at the 5 % level and will be omitted from the regional analyses presented here.

Daily geopotential heights at 500 hPa (Z500) from the NCEP/NCAR meteorological reanalysis dataset at 2.5°×2.5° horizontal resolution (Kalnay et al., 1996) are employed for the detection of high-latitude blocks and subtropical ridges (see Sect. 2.2). Daily mean sea level pressure (MSLP) and 850 hPa wind fields from this reanalysis dataset are also used to compare the low level flow patterns associated with ridges and blocks, and assess their impacts on MDA8 O_3.

5   Before introducing the methodology used for the detection of blocks and ridges, we will briefly discuss some of the main climatological features found in the 15-year MDA8 O_3 dataset. This will help interpret the impacts of these synoptic patterns on ozone in the following sections. In this paper seasons are defined as follows: spring (March, April, May; MAM), summer (June, July, August; JJA), autumn (September, October, November; SON) and winter (December, January, February; DJF). For the sake of brevity, autumn will be omitted from our analyses, as O_3 mixing rations are not particularly high in this

10   season and the features that blocks and ridges imprint on surface ozone are weaker than those in the other seasons (not shown).

Figure 1 illustrates the seasonal climatology of MDA8 O_3 (shaded areas), MSLP (black contour lines) and 850 hPa winds (arrows) in spring (top), summer (middle) and winter (bottom) during the 1998–2012 period. On average over the European continent, surface MDA8 O_3 mixing ratios are somewhat higher in spring (~41 ppb) than in summer (~39 ppb). This is not

15   surprising as a distinct spring maximum has been observed at many locations of the northern hemisphere. The spring ozone maximum is likely a result from the combination of dynamical/transport processes and photochemistry at relatively unpolluted locations (Monks, 2000), while polluted sites exhibit a double peak or a wide spring-summer maximum, with the summer maximum being more pronounced at daytime and hence attributed to photochemical processes (Monks et al., 2015). Observational studies have also shown that the Mediterranean region presents a marked summertime ozone maximum (e.g.

20   Richards et al., 2013, and references therein). Actually, in summer there is a strong north-south gradient, with low mixing ratios in the UK and most of Scandinavia and high in southern Europe, including the areas around the Mediterranean coast (Figure 1, middle). During this season, ozone levels in northern (central-southern) Europe are lower (higher) than those registered in spring. The highest MDA8 O_3 mixing ratios in summer (average seasonal values above 55 ppb) are found for the Po Basin, where very high levels of ozone and other photooxidants both at the surface and within the boundary layer

25   have been reported in previous field experiments (e.g. Martilli et al., 2002; Neftel et al., 2002; Thielmann et al., 2002; Steinbacher et al., 2005; Liu et al., 2007). The picture in winter is completely different as the European continent is predominantly a sink for ozone during this season (Laurila, 1999). Cold temperatures, low radiation and short days in winter inhibit ozone formation, while shallow mixing layers favour the accumulation of pollutants close to the surface and therefore the depletion of surface ozone by reaction with NO as well as dry deposition. The bottom panel of Figure 1 highlights that

30   such processes take place over most of the continent, in particular in regions of elevated emissions such as the Benelux and the Po Basin. Winter surface ozone presents the highest levels over the northern and western coasts as these are directly under the influence of maritime air masses into the European continent advecting background ozone, which has undergone relatively low loss by dry deposition and photochemical processes. This is favoured by the zonal westerly flow prevailing over northern Europe, as can be inferred from the MSLP and wind fields in the figure.

2.2 Climatology of high-latitude blocks and subtropical ridges

We use the same catalogue of high-latitude blocks and subtropical ridges as Sousa et al. (2016a, 2016b). Blocks are detected by applying a simplified version of the method described by Barriopedro et al. (2006) on the NCEP/NCAR reanalysis. By definition, blocks are defined as large-scale departures of Z500 above a seasonally varying threshold and must fulfil some conditions on extension and minimum duration; for this study we have considered that blocks must have a minimum horizontal extension of $2 \cdot 10^6$ km^2 during their whole lifetime and a minimum duration of 5 days. To identify ridges and avoid their overlap with blocks, the detection algorithm sets some north/south boxes (black squares in Figure 2) whose latitudinal limits move according to the season (e.g. the maximum latitude for the detection of ridges is 45º N in winter and 50º N in summer). Two conditions are imposed for the detection of subtropical ridges: a ridge is detected in a south box if (i) at least 75 % of the grid points are above the 80th percentile of the Z500 climatology of the specific month during the period 1950-2012 and (ii) no more than 50 % of the grid points of the north box are above the same threshold.

Three longitudinal sectors of 30˚ width with two boxes each (north/south) are used to catalogue high-latitude blocks and subtropical ridges regionally according to the position of their centres (Figure 2): Atlantic (ATL, 30º–0º W), European (EUR, 0º–30º E), and Russian (RUS, 30º–60º E). Note that some blocks and ridges can have their centres in more than one sector during their lifetimes, since they tend to move eastwards. The total number of days in which block and ridge centres have been identified over each sector and season are displayed in Table 1 and Table 2, respectively. As more than one block and ridge can be simultaneously identified within different sectors on the same day, the total number of days with blocks and ridges in the region of study does not coincide with the totals shown in the tables. During the 5479 days of the 1998–2012 period, we have computed a total number of 1609 days with at least one block in any of the three sectors, 1871 days with ridges, and 3153 with blocks and/or ridges. Therefore, more than half the days register at least the occurrence of a block or a ridge anywhere in the whole region.

The seasonal composites of daily Z500 anomalies (with respect to the climatology) and absolute values, considering days with blocking and ridge centres in each sector for a ~60-year period, can be found in Sousa et al. (2016a, 2016b). For illustration purposes, only the composites of daily Z500 for block and ridge centres over the EUR sector during the 1998–2012 period are shown in Figure 3, while Supplementary Figures S1 and S2 display the results for the ATL and RUS sectors, respectively. Stippling indicates statistically significant anomalies at the 5% level (two-sided t-test). The highest values of the absolute Z500 field (black contour lines) and the positive Z500 anomalies (shaded areas) are centred in the respective sector. Significantly positive anomalies dominate the northern latitudes in the case of blocks and the low latitudes in the case of ridges, being the largest found for blocks as well as in winter for all sectors. Another feature that can be seen on the plots is the northward displacement of the atmospheric circulation from spring to summer, as indicated by the position of the 560 dam isohypse in those seasons (thick back contour lines).

Some of the analyses in the following sections are also based on seasonal composites of MDA8 O_3 over Europe. For each season, composite differences are calculated between days with blocks or ridges whose centres are in a specific sector (ATL, EUR or RUS) and days without blocks or ridges in that sector. Moreover, to better quantify the impact of blocks/ridges on key European regions, probability density functions (PDFs) of MDA8 O_3 have been computed for the grid cells within the

5   grey boxes in Figure 2 (from west to east and from north to south: 'UK/North Fr', 'Central/North EU', 'NE Scandinavia', 'Iberia', 'Central/South EU', 'East EU') under different weather regimes. The PDF plots will display ozone data in a given region and season, separately for the whole 1998-2012 climatology and for the days with blocks/ridges in each of the three sectors. The two-sample Kolmogorov-Smirnov test (two sample K-S test; see e.g. Wilks, 2011) has been used to determine whether the distribution of the daily O_3 mixing ratios averaged over such regions on days with blocks/ridges differ from

10 those of the seasonal climatology; we will discuss the situations when the distributions are statistically significant at the 0.1 % level, which may seem too stringent but ensures that only the most relevant changes in the O_3 distributions are identified. Finally, to assess the potential implications of blocks and ridges on the occurrence of ozone extremes, days with high ozone extremes are identified locally over each grid cell of the O_3 dataset as those when the MDA8 O_3 mixings ratios exceed the 90th percentile of the distribution during the corresponding season, while days with low ozone extremes are those below the

15 seasonal 10th percentile.

3 Impact of high-latitude blocks and subtropical ridges on MDA8 O3 during summer and spring

3.1 Regional responses to high-latitude blocks

First, we focus on the impact of blocks on ozone. From the three 30º longitude sectors used in this study, blocking over the EUR sector has the strongest impact on ozone both in spring and summer. On average for the 15-year period of analysis,

20 MDA8 O_3 mixing ratios increase by 5–9 ppb over large areas of central Europe in spring (Figure 4, upper-left) and by 5–11 ppb over northern Europe in summer (Figure 4, upper-right) on days with EUR blocking, which is broadly consistent with the anticyclonic circulation and continental advection observed over those regions. If in the calculation of the composites we only consider days when blocking centres have stayed over the EUR sector for at least 3 days, the extension of the regions with anomalies higher than 5 ppb increases and there are larger areas where they exceed 10 ppb (Figure 4, bottom panels).

25 This minimum number of 3 days is somewhat arbitrary, but it has been chosen to illustrate that the persistence of blocks over a given area favours the photochemical build-up of O_3 both in spring and summer. The strongest positive anomalies cover large areas of the continent (40º–60º N) in spring and are located in the north (50º–70º N) during summer, season in which weaker negative anomalies are also found in southern Europe. The differences in the latitudinal position of the positive anomalies are due to the northward displacement of the atmospheric circulation from spring to summer (see e.g. position of

30 the 560 dam isohypses in Figure 3). Another factor that might contribute is the fact that the days are long in summer at high

latitudes, which would favour the photochemical build-up of ozone under blocking conditions, but further analyses would be needed to corroborate this hypothesis.

The PDFs of MDA8 O_3 are illustrated in Figure 5 for both spring (upper panels) and summer (bottom panels). The percentage frequency of all the MDA8 O_3 data polled over each region in a given season during the 15-year period is represented by the grey bars, while data on days with ATL, EUR and RUS blocking are represented by the blue, red and green solid lines, respectively. The vertical dotted lines indicate the 10th and 90th percentiles of the climatology, while the short vertical coloured lines on the top of the plots correspond to the values of the 10th and 90th percentiles for the data under the influence of blocking. Figure 5 highlights the increase in the percentage occurrence of high ozone levels over a number of regions in spring and only over the northern regions in summer on days with EUR blocking (red lines), which is consistent with the results from Figure 4. The largest increases in the 90th percentile of the ozone volume mixing ratios occur under the influence of EUR blocking for 4 out of 6 boxes in spring and for the 3 northernmost boxes in summer, the differences with the climatology being around 5–10 ppb (compare short solid red lines on top of the panels with the vertical dotted lines). These changes are mainly due to a shift and to some extent also a broadening of the frequency distribution for EUR blocking days. The results from the two-sample K-S test reveal that the O_3 distribution on days with EUR blocks differs from that of the seasonal climatology (at the 0.1% level) for all regions except Iberia in spring and for the three northern regions in summer. Another emergent feature is the increase in the occurrence of MDA8 O_3 mixing ratios within the range 35–55 ppb over 'UK/North Fr' in summer on days with ATL blocking (blue line); however, the two-sample K-S test does not indicate significantly different distributions at the 0.1% level for this particular case because of the small sample size (only 27 days with ATL blocks in summer, see Table 1). Additional analyses have confirmed that this O_3 increase is mainly due to the contribution of days with blocking centres over a narrow longitudinal sector within the East Atlantic (15°–0° W), when the British Isles are under the influence of an anticyclone (supplementary Figure S3). This synoptic situation, albeit relatively uncommon (only 13 days identified in summer during the whole 15-year period), is also associated with weak negative ozone anomalies in southern Europe, in particular over Italy. Overall, RUS blocking does not seem to be closely related to changes in the PDF of ozone for any region.

The previous analyses have illustrated that significant changes in the mean distribution of MDA8 O_3 occur mainly in northern and central Europe on days with EUR blocking during summer and spring, respectively. We have also evaluated the evolution of the occurrence of above average O_3 mixing ratios and extreme ozone days under the influence of EUR blocking. In particular, during summer the extension of the areas with positive ozone anomalies above 5 ppb increases day after day when block centres are in the EUR sector (Figure 6). On average for all blocks remaining in that sector, the fifth day registers the maximum anomaly over any given $1° \times 1°$ cell in the domain (~23 ppb) as well as the maximum extension of anomalies above 5 ppb (~4×10^6 km^2). Moreover, the maximum extension of the areas exceeding the 90th percentile is found for that day as indicated by the grey open squares in the figure. Note, however, that only 7 blocks have been considered for the calculation of anomalies on the fifth day compared to 32 on the first day (see numbers in brackets on the top of the panels); the reason for this is that blocks do not necessarily stay over the same sector during their lifetime. A similar

evolution has been found for spring, although the overall magnitude of the anomalies and the total area exceeding the 90th percentile are smaller in that season (not shown).

To better illustrate how EUR blocking impacts the occurrence of extremes in summer and spring, we have calculated the percentage of EUR blocking days with MDA8 O$_3$ values above the 90th percentiles of those seasons. Figure 7 indicates the likelihood that EUR blocking is collocated with exceedances of the 90th percentile in summer (top) and spring (bottom). The results at any location can be compared with what would be expected by random chance (i.e. only 10 % of exceedances of the 90th percentile). More than 30 % of the EUR blocking days concur with exceedances of the 90th percentile over large parts of Scandinavia, the North Sea as well as the north of the UK in summer. Note however that as ozone levels are low in northern Europe during summer (see middle panel of Figure 1) these events do not often result in exceedances of the EU target value for maximum daily 8-hour mean ozone (120 μg m^{-3}, approximately 60 ppb; EEA, 2015). The impact is smaller in spring, when 25 % of the EUR blocking days are coincident with exceedances of the 90th percentile over large parts of Germany, north-eastern France, the Benelux and the North Sea. Therefore, EUR blocks increase the occurrence of ozone extremes over some regions mainly in summer but also in spring.

The use of 30° longitude sectors, as done throughout most of this work, is useful to generalise the interpretation of the impacts of blocks on ozone, but one could expect the occurrence of extremes to be higher for some areas of the continent if we only considered blocks with centres over narrower longitudinal sectors. In fact, the areas with the highest occurrence of extremes in Figure 7 move westward/eastward when block centres are considered within the west (0° –15° E) / east (15° – 30° E) flanks of the EUR sector and the percentage of occurrence of extremes also increases over those areas (not shown).

3.2 Regional responses to subtropical ridges

The impact of subtropical ridges on surface MDA8 O$_3$ during spring and summer is considerably smaller than that of blocking for most of the regions considered in this study. The fact that ridges (582 in spring and 649 in summer) are more frequent than blocks (534 in spring and 283 in summer) during the 15-year period of analysis might explain to some extent that a weaker signal has been found for ridges in summer. Nonetheless, the signal of ridges on ozone is even smaller in spring, the season in which the catalogue contains a similar number of days with ridges and blocks, in particular over the EUR and ATL sectors. Only the most relevant results for regions where the signal of ridges is strong enough are discussed here, separately for spring and summer.

The PDFs of MDA8 O$_3$ for days with ridges in the ATL, EUR and RUS sectors resemble that of the climatology for most regions in spring and summer (Supplementary Figure S4). The only case that stands out during spring is the Iberian Peninsula under the influence of Atlantic ridges, when the Azores high moves eastwards and has its centre of action close to Iberia, resulting in an increase in the frequency of events with MDA8 O$_3$ above 50 ppb but not in a statistically significant change in the distribution at the 0.1 % level (this particular case is included with a blue dashed line in the upper panel of Figure 5). Our findings illustrate that the regional responses of surface ozone to subtropical ridges in spring and summer are

generally more localized than those of blocks and hence they are smoothed if large longitudinal sectors are considered for the analyses. Thus, when ridge centres are located over a narrower 15° sector covering the East Atlantic (15°–0° W; see Figure 8, left), the centre of the anticyclone is particularly close to Iberia and the isobaric gradient is stronger than the climatology in the north, yielding moderate positive ozone anomalies of up to ~5 ppb over Iberia and small negative

5 anomalies in northern Europe.

The most prominent feature in summer is the shift towards higher values of MDA8 O_3 in the PDF for the 'Central/South EU' box with the presence of ridges in the European sector (red dashed line in lower panel of Figure 5, significantly different from the climatology at the 0.1% level). Again, the maximum positive anomalies in that region are observed when ridge centres are located over a narrow sector that covers western Europe (0°–15° E; Figure 8, right). Despite the lack of a strong

10 link between subtropical ridges and the highest percentiles of the summer ozone distribution within the whole region, the seasonal anomalies are above 5 ppb in Italy and surrounding countries, exceeding 10 ppb in some areas of the Po Basin. As this region registers average MDA8 O_3 mixing ratios of ~55 ppb in summer, the occurrence of ridges within 0°–15° E pushes the ozone levels high enough so that more than 60 % of the days with this synoptic situation breach the 60 ppb target over the whole Po Basin. Moreover, under this synoptic situation ozone mixing ratios can be well above 60 ppb at some major

15 towns in the region. For instance, Figure 9 (left) shows the time series of ozone (medians ± interquartile ranges) for the grid cell covering Milan, pooled separately over the days before and after the appearance of ridges in western Europe. Even though the presence of ridges is already preceded by above normal ozone levels at this specific location, they contribute to yielding mixing ratios over 75 ppb after a few days. As the ozone dataset is averaged over 1° x 1° grid cells, some urban areas are likely to have higher ozone levels.

20 **4 Impact of high-latitude blocks and subtropical ridges on MDA8 O_3 during winter**

As introduced in Sect. 2 and also documented by previous analyses (Laurila, 1999), during winter predominantly westerly winds from the Atlantic advect background ozone into the European continent, which is a net sink region for ozone. As a consequence, the impact of blocking on surface ozone is expected to be the opposite of that found in summer. Blocking situations divert the western zonal flow and are associated with stagnation, which impedes the arrival of ozone-rich

25 background air masses from the Atlantic and favours the accumulation of pollutants in the boundary layer, reducing surface ozone levels. This can be seen over the northwest of the continent in the composites of winter MDA8 O_3 anomalies for blocking centres remaining in the ATL and EUR sectors (Figure 10, upper and middle panels), and over central Europe for blocking centres in the RUS sector (Figure 10, bottom panel). The anticyclone located above the British Isles under ATL blocking situations (Figure 10, upper panel) diverts the typical westerly flow that is present in the climatology (Figure 1,

30 bottom panel), although only relatively small negative anomalies of up to around -5 ppb are found in that region as well as in other countries of western Europe. The impact of EUR blocking over the UK, Northern France and the Benelux is stronger, yielding MDA8 O_3 negative anomalies of up to around -10 ppb (Figure 10, middle panel). This occurs because under the

influence of ATL blocking north-western Europe is exposed to air masses which re-circulate over the Atlantic, whilst the position of the EUR blocking high better shields the arrival of maritime air masses and it is concomitant with weak winds which transport ozone-depleted continental air masses to those regions.

The PDFs of MDA8 O_3 in winter (Figure 11) also highlight the increase in the number of low ozone events within the 'UK/North Fr' and 'Central/North EU' boxes under EUR blocking (red solid lines), and to a lesser extent in the 'UK/North Fr' box when blocking centres are located over the ATL sector (blue solid line). The three distributions differ significantly from the climatology at the 0.1 % level (two-sample K-S test). In particular, the percentage of the ozone occurrences below 20 ppb (10 ppb) in 'UK/North Fr' associated with ATL and EUR blocking is 24 % and 24 % (25 % and 39 %), respectively. Similarly, there is a shift to the left of the MDA8 O_3 PDF over the 'Central/North EU' and 'NE Scandinavia' boxes on days with blocking centres over the Russian sector (green lines, Figure 11), this change being significant at the 0.1 % level only for the latter region. This situation is mainly found with blocking centres over the west flank of that sector (30º–45º E), which divert the westerly flow and result in weak winds that transport continental air masses from the south to those regions (Figure 10, bottom). The blocking-related decreases in surface O_3 over northern Europe concur with an overall reduction of the winter total ozone column (TOC) as reported by Barriopedro et al. (2010a). Their results obey to different mechanisms, as they found that blocking substantially increases the frequency of extremely low TOC values and ozone mini-holes mainly due to the combined effect of horizontal transport of ozone-poor air and vertical motions in the lower stratosphere.

While the overall response to winter blocking is characterized by O_3 decreases, it is worthwhile to mention several regions that actually experience rising levels of MDA8 O_3. For example, ATL blocking is associated with a shift to the right in the PDF of MDA8 O_3, resulting in statistically significant changes with respect to the climatology at the 0.1 % level, for the two eastern boxes ('NE Scandinavia' and 'East EU', Figure 11). This is particularly the case for the 'East EU' box, as it is often under the influence of westerly flow which is expected to bring ozone-depleted continental air masses (Figure 1, bottom panel) while it is more exposed to background air masses from the ocean under ATL blocking (Figure 10, upper panel).

The responses of some regions to ATL and EUR ridges in winter are more noticeable than those previously found for summer and spring (see PDFs for all regions in Supplementary Figure S5). In addition, unlike in the warm seasons, during winter the effects of ridges in northern regions of Europe tend to be the opposite to those of blocks. As an example, Figure 12 (left) illustrates the MDA8 O_3 responses to ATL ridges. Iberia is under the influence of the Azores high and the isobars are tightly packed over the UK and downwind regions. The stable weather conditions in Iberia result in moderate negative ozone anomalies, while the strong zonal flow in the north brings background air masses into the continent and ventilates the boundary layer, yielding ozone increases in excess of 5 ppb over the UK, Northern France and the Benelux. Anomalies of that magnitude become more widespread, extending to larger areas of northern France and most of Germany, when only ridges which have remained at least three days over the Atlantic sector are considered for the calculation of the composites (Figure 12, right). This result stresses again the importance of synoptic weather persistence on the surface O_3 responses. Similar features, with moderate ozone decreases in the south (not only 'Iberia' but also the 'Central/South EU' box) and increases in the north ('UK/North Fr' and 'Central/North EU' boxes), are patent when ridge centres are located over the

EUR sector. The shift towards higher MDA8 O_3 mixing ratios within the 'UK/North Fr' and to a lesser extent in the 'Central/North EU' boxes under the influence of subtropical ridges with centres over the ATL and EUR sectors can also be seen in Figure 11 (blue and red dashed lines). The four distributions are statistically different from that of the respective climatology at the 0.1 % level. In particular, the PDFs become much narrower and are displaced to the right for the

5 'UK/North Fr' box. From the visual inspection of the PDFs it is also evident the completely opposite impact of ATL and EUR ridges (blue and red dashed lines, O_3 increase) compared to that of ATL and EUR blocks (blue and red solid lines, O_3 decrease) over that area.

The different regional responses of near-surface ozone to blocks and ridges found here for winter are not observed in other seasons. This is in line with the results of Sousa et al. (2016b), who found that while near-surface temperatures increase over

10 different parts of Europe with the presence of both blocks and ridges in summer, they decrease/increase under the influence of blocks/ridges over large parts of the continent in winter. This opposite response also manifests in the exceedance of low and high ozone extremes (10th and 90th percentiles of the winter distribution, respectively) as well as in the evolution of ozone under the influence of these synoptic patterns. Figure 13 shows that more than 30 % of the winter days with EUR blocking are associated with ozone levels below the 10th percentile over England and Northern France, while over 20 % of

15 the days with ATL ridges are concurrent with exceedances of the 90th percentile over the British Isles, the Benelux and the west of Germany.

Finally, we have explored the surface ozone responses to blocking and ridges at several European locations in order to frame them into the previous larger scale analysis. As an example, we illustrate here the day-to-day ozone decrease/increase under the influence of winter blocks/ridges at Amsterdam (Figure 9, right), which is located between the 'UK/North Fr' and

20 'Central/North EU' boxes. The local time series of winter ozone (medians ± interquartile ranges) were pooled separately over the days before and after the appearance of blocks in the EUR sector (red) and ridges in the ATL sector (blue). The median values are well below the climatological median and get close to the 10th percentile after a few days when blocks stay in the EUR sector, while they are above the climatological median and approach the 90th percentile on the days with ridges in the ATL sector. Similar results have been found for other major towns in the northwest of Europe such as London,

25 Brussels and Berlin.

5 Summary and discussion

We have used a catalogue of high-latitude blocks and subtropical ridges occurring in three distinct 30˚ longitudinal sectors (ATL, EUR, RUS) covering the Euro-Atlantic region, together with a 15-year gridded European surface O_3 dataset, to examine the regional responses of MDA8 O_3 to the occurrence, position and persistence of blocks and ridges. The maximum

30 ozone anomalies often follow the longitudinal position of the block and ridge centres. As both synoptic patterns disrupt the atmospheric circulation over large areas far from their centres of action, they also exert a moderate influence on the surface ozone levels in distant regions.

Overall, we have found a stronger impact of blocks than that of ridges on O_3 during spring and summer. In particular, EUR blocking is associated with ozone increases over large areas of Europe in both seasons, with anomalies around 5–10 ppb within the 40˚–60˚ N latitudinal band in spring and further north (50˚–70˚ N) in summer. In addition, over 20 % and 30 % of the days with blocks in the EUR sector are concurrent with exceedances of the 90th percentile of the ozone distribution in
5   those regions during spring and summer, respectively. Blocks within the ATL sector also yield moderate ozone increases over the UK in summer.

The impact of subtropical ridges is small in the warm seasons, with the exception of the positive ozone anomalies above 5 ppb found in summer for a region in central/southern Europe – including Northern Italy, Switzerland and Austria – when ridge centres are located over the west flank of the EUR sector. These anomalies reach 10 ppb over the Po Basin, yielding
10   MDA8 O_3 mixing ratios well above the 60 ppb AQ target. Our analyses have not revealed strong signals of either blocks or ridges on surface ozone over southern Europe during spring and summer, apart from the mentioned increases around Northern Italy, although it is worthwhile to indicate that the 15-year gridded ozone dataset used here does not include data in southern Italy. Other datasets of shorter duration but improved coverage over that region, such as the 10-year gridded ozone fields produced by Schnell et al. (2014) or time series at selected sites, could be helpful to investigate this more in detail. In
15   addition, the joint examination of synoptic and mesoscale weather patterns is needed to better understand the localized impact of circulation on surface ozone in the Mediterranean.

It is well known that anticyclonic conditions, which occur both with high-latitude blocking episodes and under the influence of subtropical ridges, trap pollutants close to the surface in winter, yielding ozone decreases through the enhanced effect of titration and dry deposition. However, this study has revealed that blocks and ridges produce very different responses in
20   surface ozone over the northwest of Europe during this season. The anticyclonic circulation associated with ATL blocking results in moderate ozone decreases over the UK, whereas the response to EUR blocking is stronger (with negative anomalies between -5 ppb and -10 ppb) over the UK, Northern France and the Benelux. With the latter synoptic situation, the air masses are re-circulating around the European continent, which acts as an ozone sink during this season. Conversely, ATL and EUR ridges yield positive winter ozone anomalies in northern Europe, with values exceeding 5 ppb over the British
25   Isles, Northern France, the Benelux and Germany. Whilst moderate ozone decreases are found in some southern areas of the continent, these synoptic situations, in particular ATL ridges, are associated with strong MSLP gradients and enhanced zonal flow around 50˚- 60˚ N, favouring the arrival of background air masses from the Atlantic and the ventilation of the boundary layer. Moreover, while 30 % of the winter days with EUR blocks record ozone levels lower than the 10th percentile in England and Northern France, above 20 % of the days with ATL ridges coincide with exceedances of the 90th percentile in
30   the British Isles and the Benelux. Thus, during winter, blocks and ridges lead to opposite effects in both surface ozone mean anomalies and extremes, particularly in northern countries. These findings might not look relevant from the AQ perspective as threshold values for this pollutant are rarely exceeded at most mid-latitude locations in winter. However, these results have potential implications for primary pollutants and particulate matter (PM), whose response is expected to be the opposite to that of ozone. We anticipate that blocking will result in elevated NO_2 and PM levels in north-western Europe during

winter, and that the changes in the circulation at those latitudes introduced by the influence of subtropical ridges will ventilate the west of the continent and transport these pollutants from inland regions further into the continent. This should be looked at in detail in the future.

6 Implications and future directions

5   A warming climate is expected to increase peak levels of O_3 in polluted regions, an impact that has been referred to as a climate change penalty on AQ. The response of ozone to temperature changes as modelled by both CCMs and CTMs relies on the parameterisation of a number of processes whose temperature dependence is uncertain (e.g. biogenic emissions, which also depend on other environmental factors) or difficult to quantify in practice (e.g. extra evaporation of anthropogenic NMVOCs under high temperatures). Moreover, in regions with a significant contribution of biogenic
10   emissions, ozone-temperature relationships are strongly affected by major uncertainties in the chemistry of isoprene within the models, in particular the isoprene nitrate yields and the fate of these nitrates. Further details on these and other issues can be found e.g. in Vautard et al. (2005), Jacob and Winner (2009), Fiore et al. (2012), Fu et al. (2015) and Zhang and Wang (2016). In addition, it is important to quantify the contribution of both thermodynamic (temperature and specific humidity) and dynamic (circulation) effects to future climate changes (e.g. Shepherd, 2014; Horton et al., 2015). Taking all this into
15   account, future air pollution episodes cannot be modelled as all else being equal except for a uniform temperature shift. As a consequence, the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC) indicates that projecting AQ empirically from a mean surface warming using observed correlations of air pollutants with temperature may be problematic, while establishing relationships with synoptic conditions may be more robust (Kirtman et al., 2013).

Following the IPCC's recommendations, the results from this work provide observational constraints for the process-
20   oriented evaluation of modelled O_3 to changes in the occurrence and position of two types of synoptic patterns of great relevance for the weather and climate at the mid-latitudes. It should be borne in mind that a number of studies have shown that climate models often underestimate blocking activity in different regions of the Northern hemisphere (e.g. Scaife et al., 2010; Barriopedro et al., 2010c; Barnes et al. 2012; Anstey et al., 2013; Dunn-Sigouin et al., 2013), with potentially different origins of the model biases depending on the region and season (e.g. Vial and Osborn 2012; Zappa et al., 2014). The ability
25   of some models to simulate blocking is improving, but future trends in blocking are still uncertain (Christensen et al., 2013). To the authors' knowledge, there have been no attempts to evaluate ridge activity over the North Atlantic European region in climate models.

Despite the mentioned uncertainties, our results provide quantitative assessments of the response of surface ozone to circulation changes which can be easily exploited to evaluate CTMs, as these are driven by meteorological reanalyses like
30   the one used in this work. In this context, the problem with the underestimation of blocking activity in climate models can also be overcome to some extent by the use of ensembles of historical CCM simulations, which would provide a high enough number of blocking/ridge events whose impacts on surface ozone could be compared with our observational

assessments. The analyses conducted here for European ozone can also be extended to other mid-latitude regions and other pollutants like PM in a relatively easy manner. Future efforts in this direction, in combination with improvements in the representation of blocking and ridge activity in climate models, will help understand the contribution of dynamic effects to near-term projections of AQ.

7 Data availability

The data can be obtained from the authors of this paper.

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Table 1: Total number of days with blocking centres identified over each sector (Atlantic, ATL, 30º–0º W; European, EUR, 0º–30º E; Russian, RUS, 30º–60º E) and season (winter, DJF: December, January, February; spring, MAM: March, April, May; summer, JJA: June, July, August; autumn, SON: September, October, November) during the 5479 days of the 1998–2012 period.

	ATL	EUR	RUS	Total
DJF	228	151	75	454
MAM	200	203	131	534
JJA	27	91	165	283
SON	103	169	93	365
Total	558	614	464	1636

Table 2: As Table 1 but for ridges.

	ATL	EUR	RUS	Total
DJF	183	202	191	576
MAM	172	230	180	582
JJA	217	228	204	649
SON	178	168	180	526
Total	750	828	755	2333

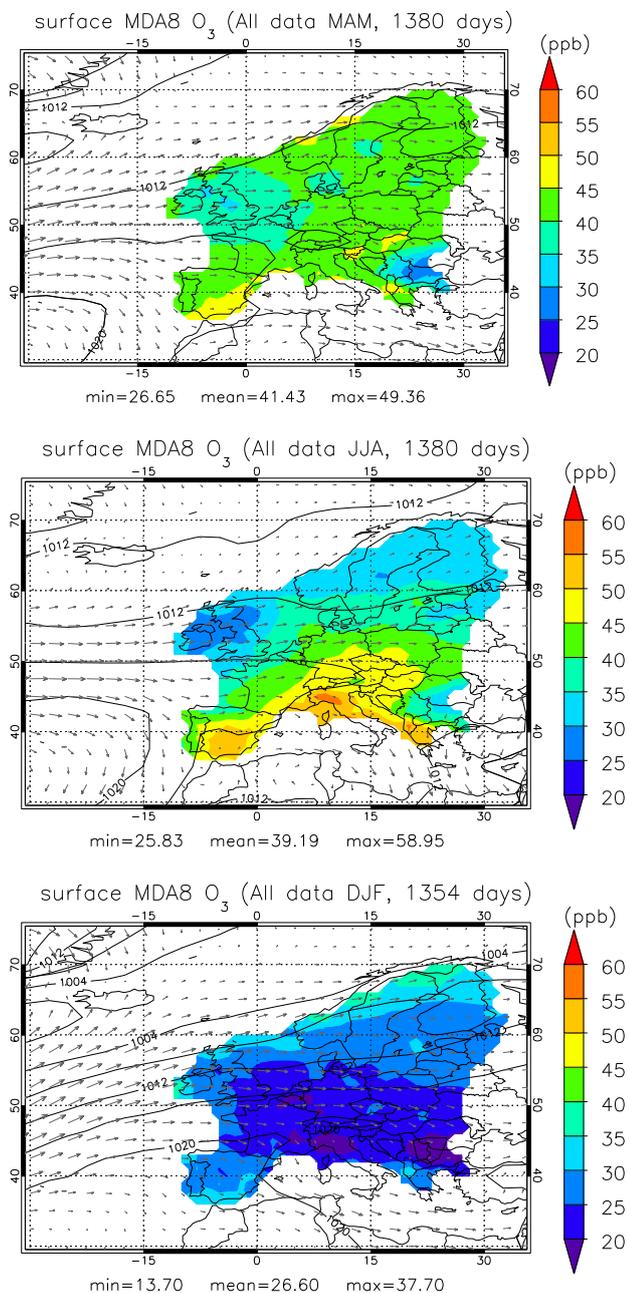
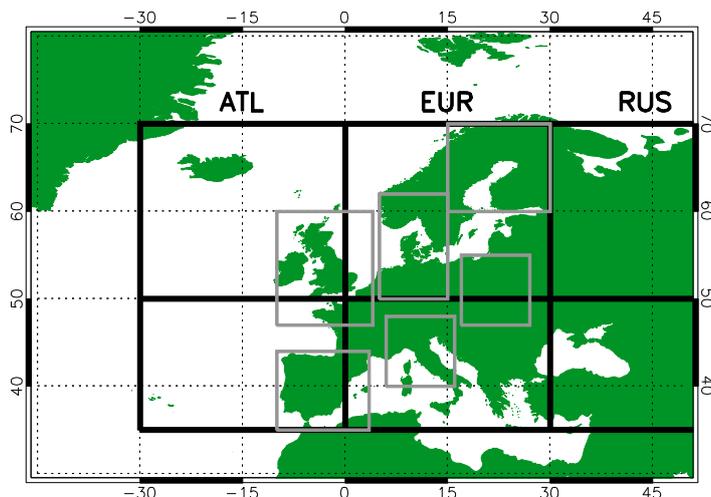



Figure 1: Composites of the seasonal means of maximum daily 8-hour running average near-surface ozone (MDA8 O₃) expressed in parts per billion by volume (ppb, shaded areas) in spring (top), summer (middle) and winter (bottom) during the 1998–2012 period. The black contour lines depict the mean sea level pressure (MSLP) for the same period, expressed in hPa. Arrows indicate horizontal winds at 850 hPa. The total number of days considered is indicated on the top of each panel.

5 **Figure 2: Longitudinal sectors considered for the identification of the centres of high latitude blocks (northern black boxes) and subtropical ridges (southern black boxes): Atlantic (ATL, 30º–0º W), European (EUR, 0º–30º E) and Russian (RUS, 30º–60º E, only partially shown). Grey boxes identify the geographic areas considered in the regional assessment performed in Sections 3 and 4. The regions considered, from west to east and from north to south, are 'UK/North Fr', 'Central/North EU', 'NE Scandinavia', 'Iberia', 'Central/South EU' and 'East EU'.**

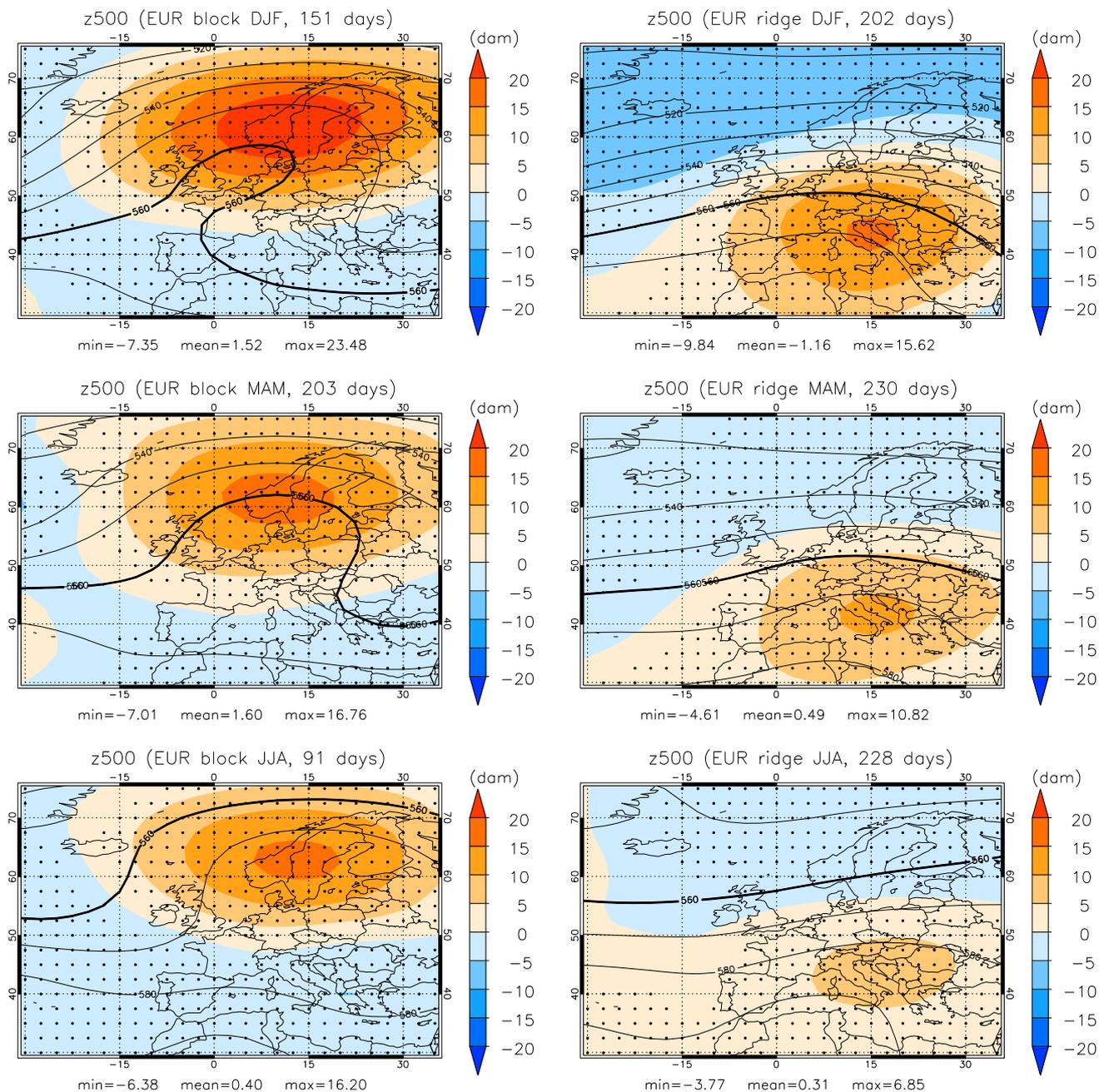



Figure 3: Composites of the daily anomalies with respect to the 1998–2012 climatology (shaded areas) as well as absolute values (black contour lines) of 500 hPa geopotential height (Z500) for blocking (left) and ridge (right) centres within the European sector in winter (top), spring (middle) and summer (bottom). Stippling indicates statistically significant anomalies at the 5% level (two-sided t-test). All values are in decametres (dam) and the thick line represents the 560 dam isohypse. The total number of days considered is indicated on the top of each panel.

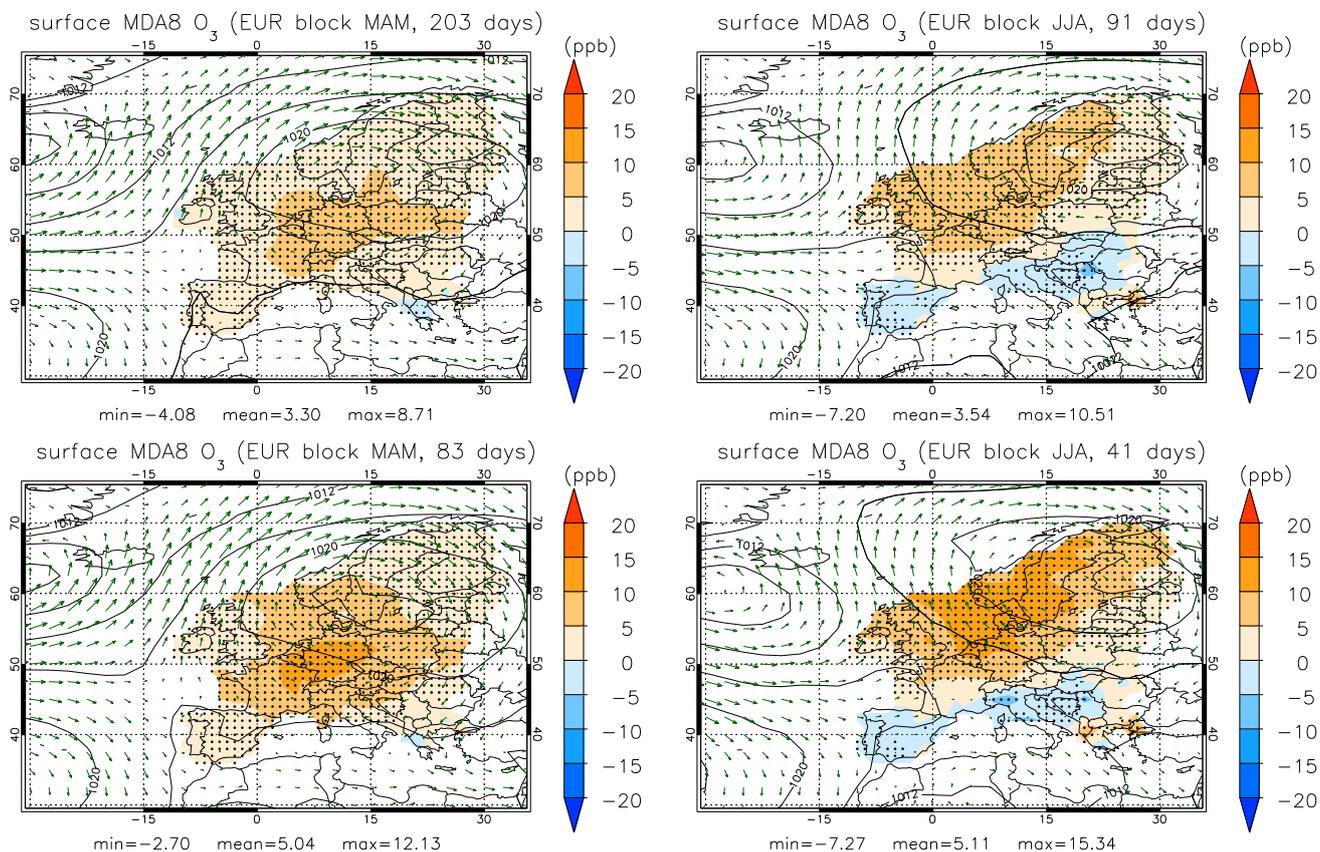



Figure 4: Composites of the seasonal anomalies of surface MDA8 O₃ (ppb) for days with blocking centres over the European sector (EUR, 0°–30° E), during spring (left) and summer (right). Anomalies have been calculated with respect to the MDA8 O₃ mixing ratios on days without EUR blocking in that season during the 1998–2012 period. Only days when blocked areas with a minimum horizontal extension of 2·10⁶ km² and centres remaining over 0°–30° E for at least one (top) and three (bottom) days have been taken into account for the calculation of the ozone anomalies. Stippling indicates statistically significant anomalies at the 5 % level (two-sided t-test). The black contour lines depict the composites of MSLP (hPa) for those days. Horizontal wind fields at 850 hPa are displayed by arrows. The total number of days considered is indicated on the top of each panel.

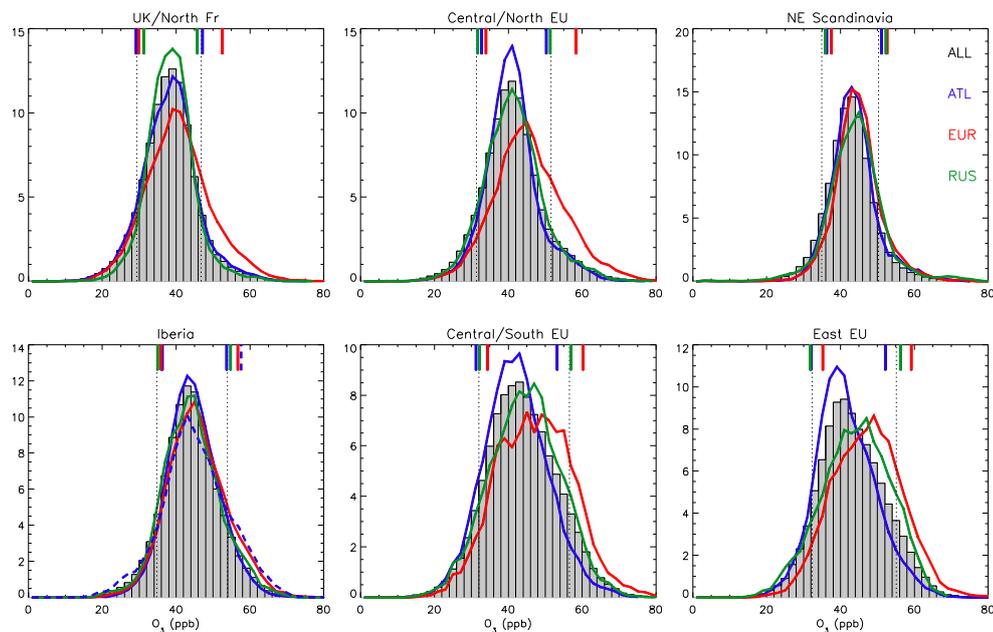
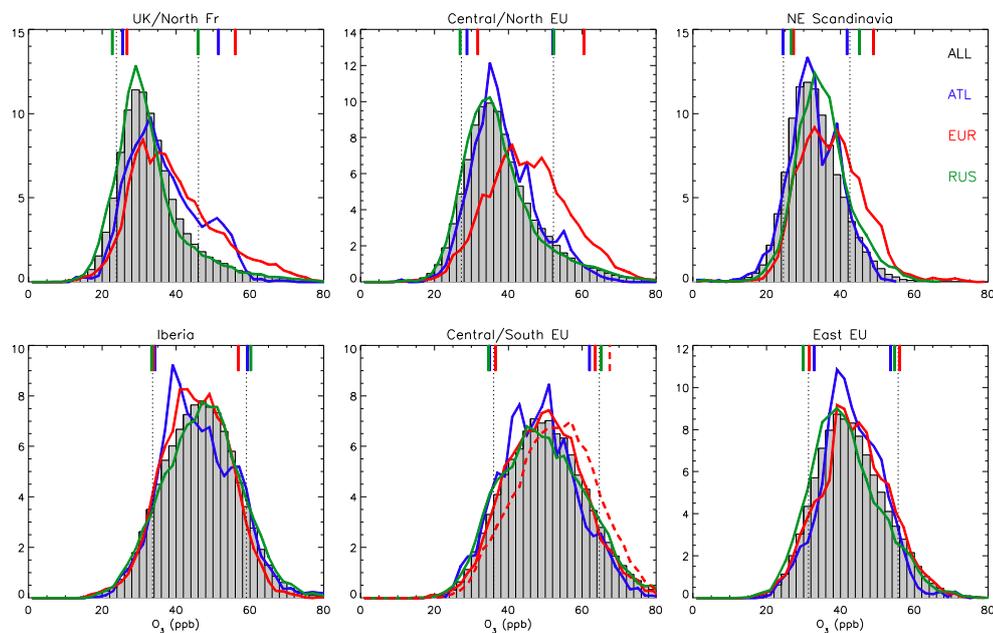
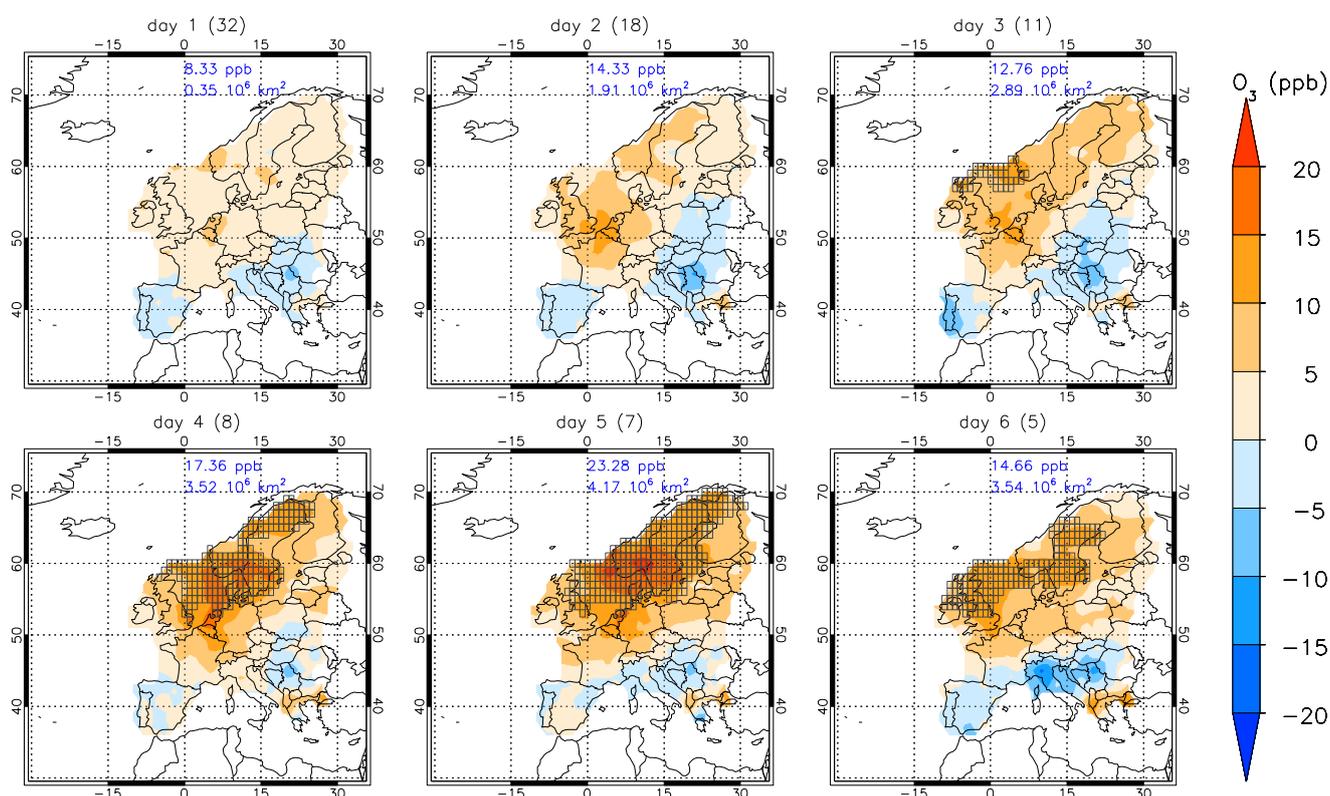
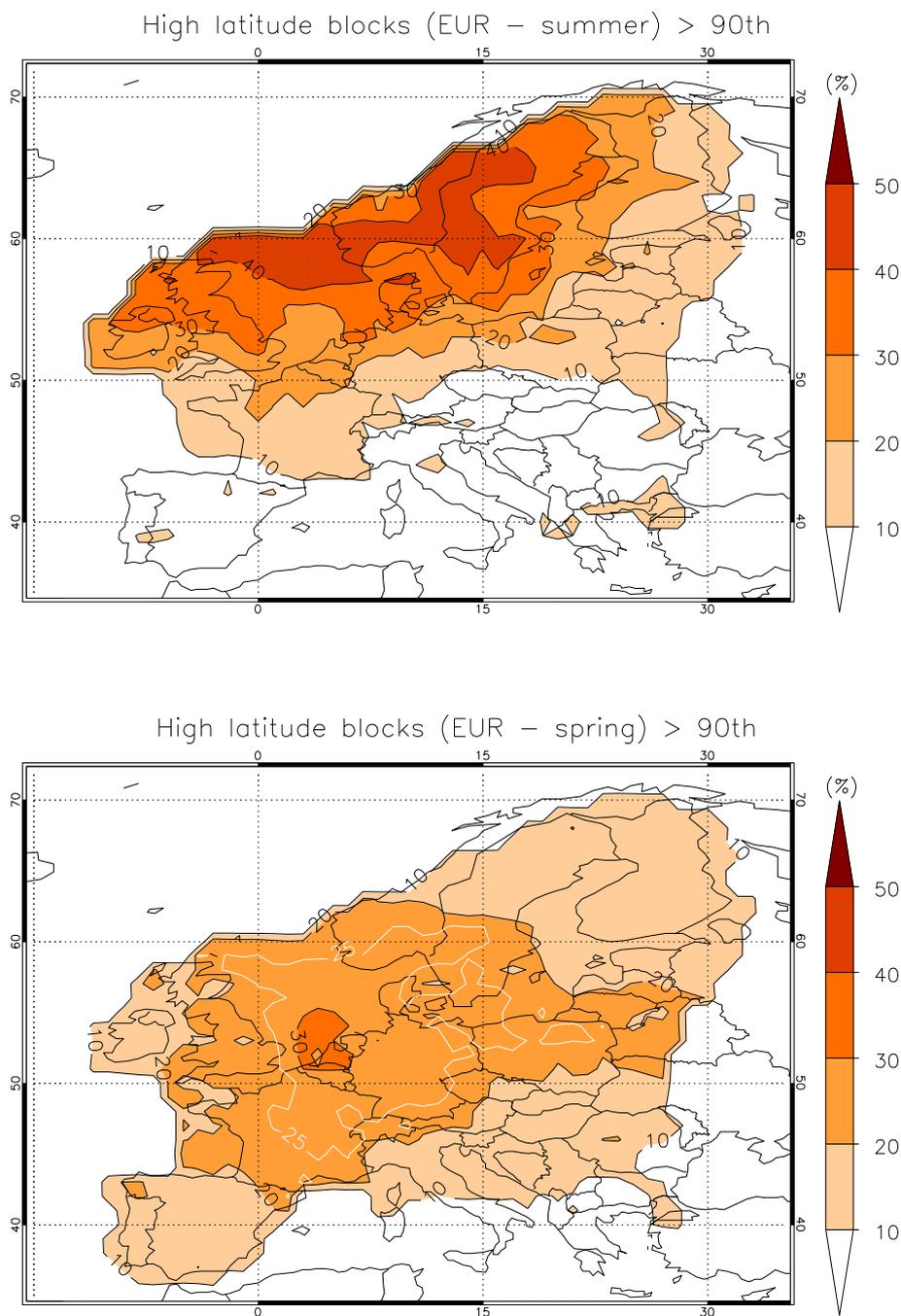



Figure 5: Spring (upper panels) and summer (lower panels) probability frequency distributions (%) of MDA8 O₃ for the six regional boxes presented in Figure 2 under different synoptic situations. Grey bars denote the 1998-2012 seasonal climatology. Solid lines correspond to days with block centres over the Atlantic (blue), European (red) and

Russian (green) sectors. Blue and red dashed lines also represent the frequency distributions for data within the 'Iberia' box when ridge centres are located over the ATL sector in spring (upper panel) and the 'Central/South EU' box when ridge centres are located over the EUR sector in summer (lower panel), respectively. The width of the bins is 2 ppb. The horizontal position of the vertical dotted lines represents the 10th and 90th percentiles of the climatology,

5 **while the short vertical lines on the top of the plots indicate the values of the 10th and 90th percentiles under the influence of ATL, EUR and RUS blocking. The 90th percentiles of the data with ridges are also displayed as dashed lines when they are above those with blocking.**

10 **Figure 6: Evolution of MDA8 O₃ anomalies under the influence of EUR blocking in summer. The panels show, from left to right and from top to bottom, the average anomalies on the first six days a block is in the sector. The total number of blocks considered is given in brackets on the top of each panel. The maximum anomaly found (ppb) and the total area with anomalies higher than 5 ppb (km²) are also indicated in blue colour. Grey open squares indicate grid cells where the ozone composite under blocking exceeds the 90th percentile of the summer distribution.**

5 **Figure 7: Percentage of EUR blocking days in summer (top) and spring (bottom) with MDA8 O$_3$ above the 90th percentile of its seasonal distribution.**

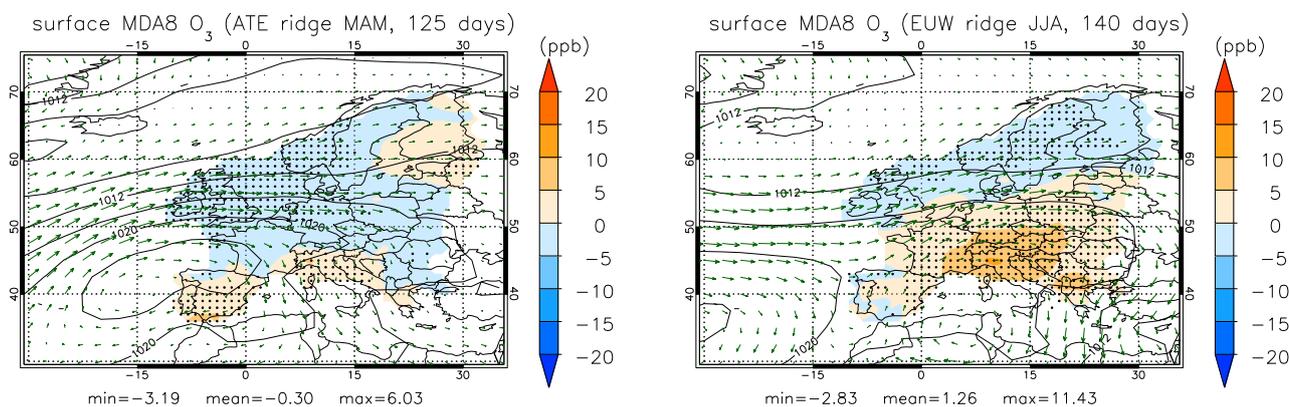



Figure 8: As Figure 4 but for subtropical ridges with centres over the East Atlantic (15°–0° W) in spring (left) and western Europe (0°–15° E) in summer (right).

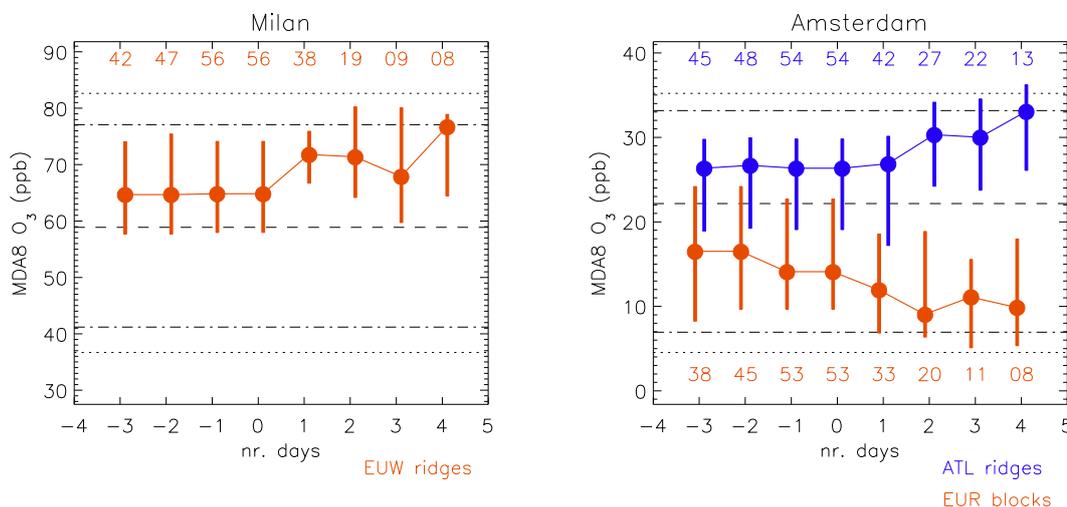



Figure 9: Time series of the average evolution of MDA8 O₃ within the grid cells covering (left) Milan when ridge
10 **centres are within 0-15º E during summer as well as (right) Amsterdam under the influence of EUR blocking (red) and ATL ridges (blue) in winter. The ticks on the x-axis represent the last three days before a block/ridge is present in a given sector (-3, -2, -1), the first day it is in the sector (0) and the four following days it remains in that sector (1, 2, 3, 4). The closed circles and bars correspond to the medians and interquartile ranges of the ozone data for those days. The numbers in red and blue indicate the total number of days analysed for EUR blocks/ridges and ATL**
15 **ridges, respectively. Horizontal lines correspond to the 5ᵗʰ, 10ᵗʰ, 50ᵗʰ (i.e. median), 90ᵗʰ and 95ᵗʰ percentiles of all the MDA8 O₃ data for that grid cell during the corresponding season within the 1998–2012 period.**

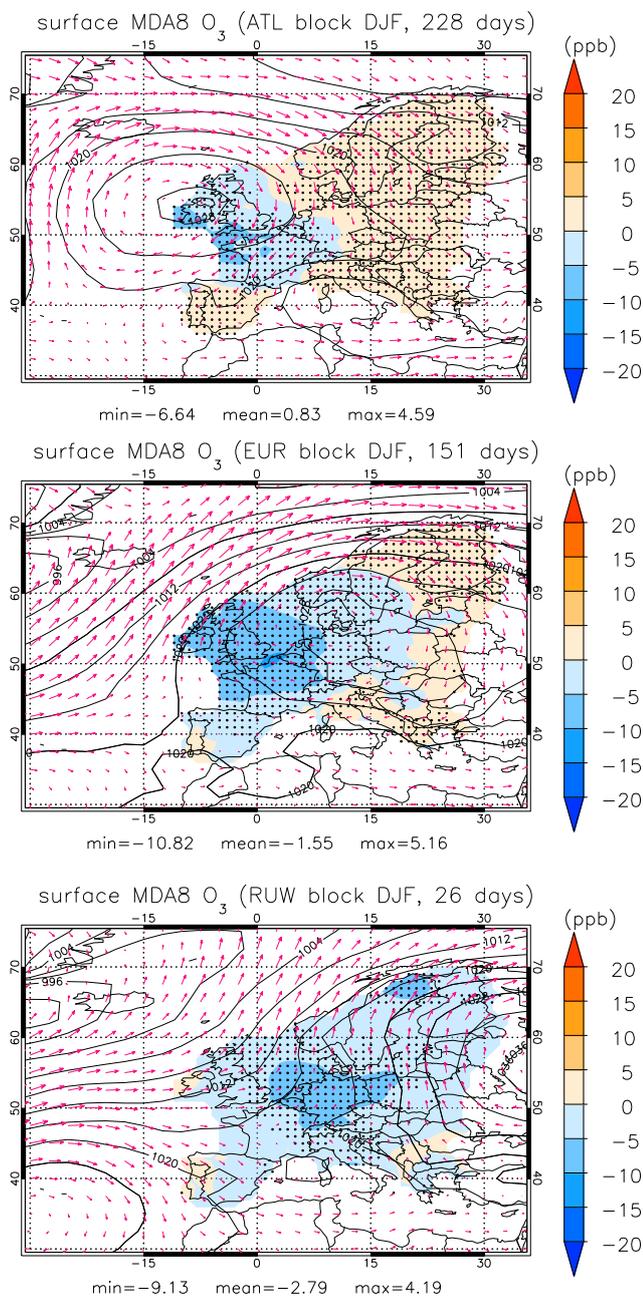



Figure 10: As Figure 4 but for blocking centres remaining in the Atlantic (30°–0° W, top) and European (0°–30° E, middle) sectors as well as in the west flank of the Russian sector (30°–45° E, bottom) in winter.

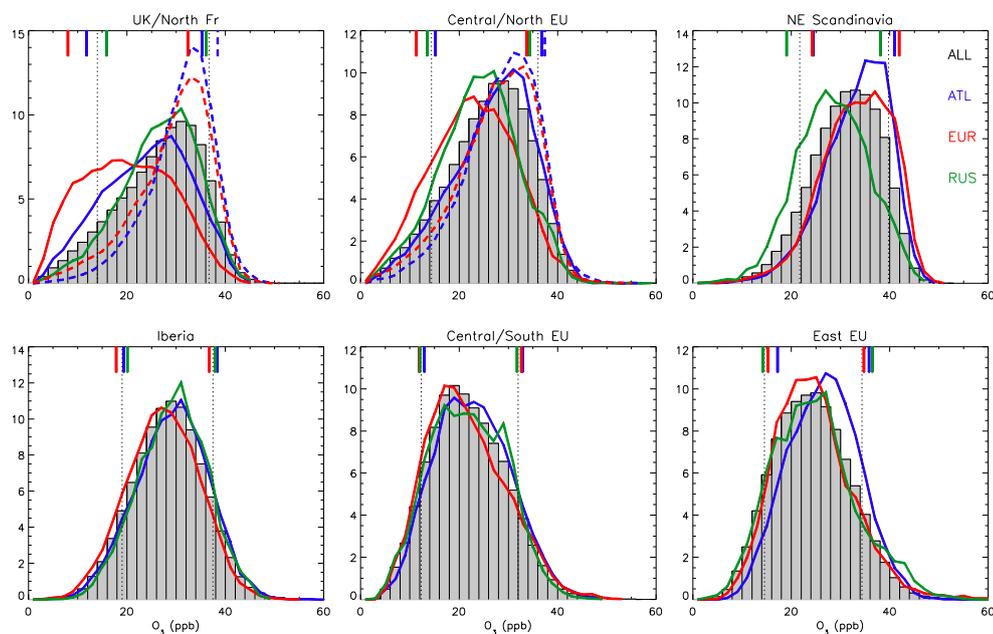



Figure 11: As Figure 5 but for winter blocking. Note that blue and red dashed lines have been added to represent the frequency distributions of the data within the 'UK/North Fr' and 'Central/North EU' boxes when ridge centres are located over the ATL and EUR sectors, respectively.

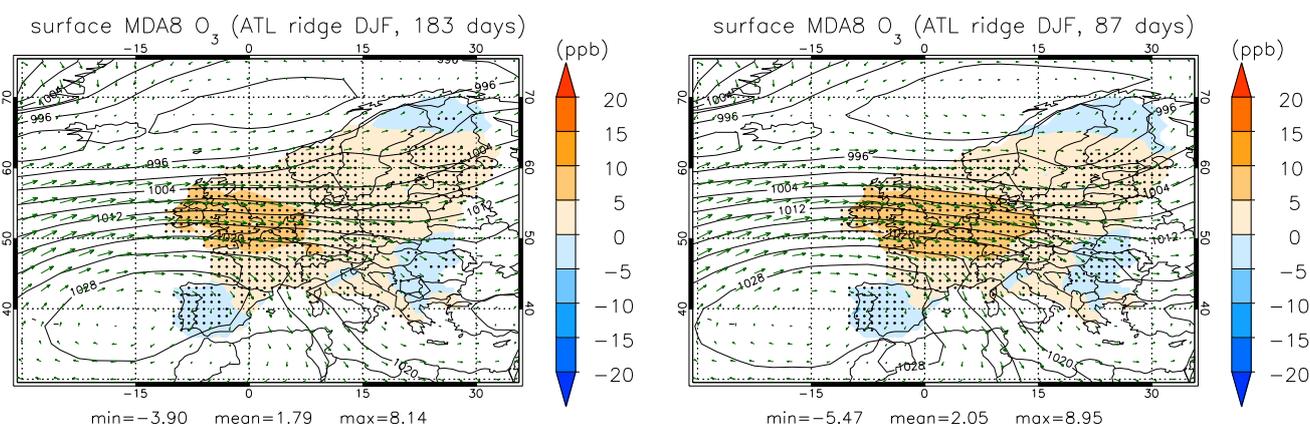



Figure 12: As Figure 4 but for subtropical ridges with centres remaining in the Atlantic (30˚–0˚ W) for at least (left)
10 **one and (right) three days in winter.**

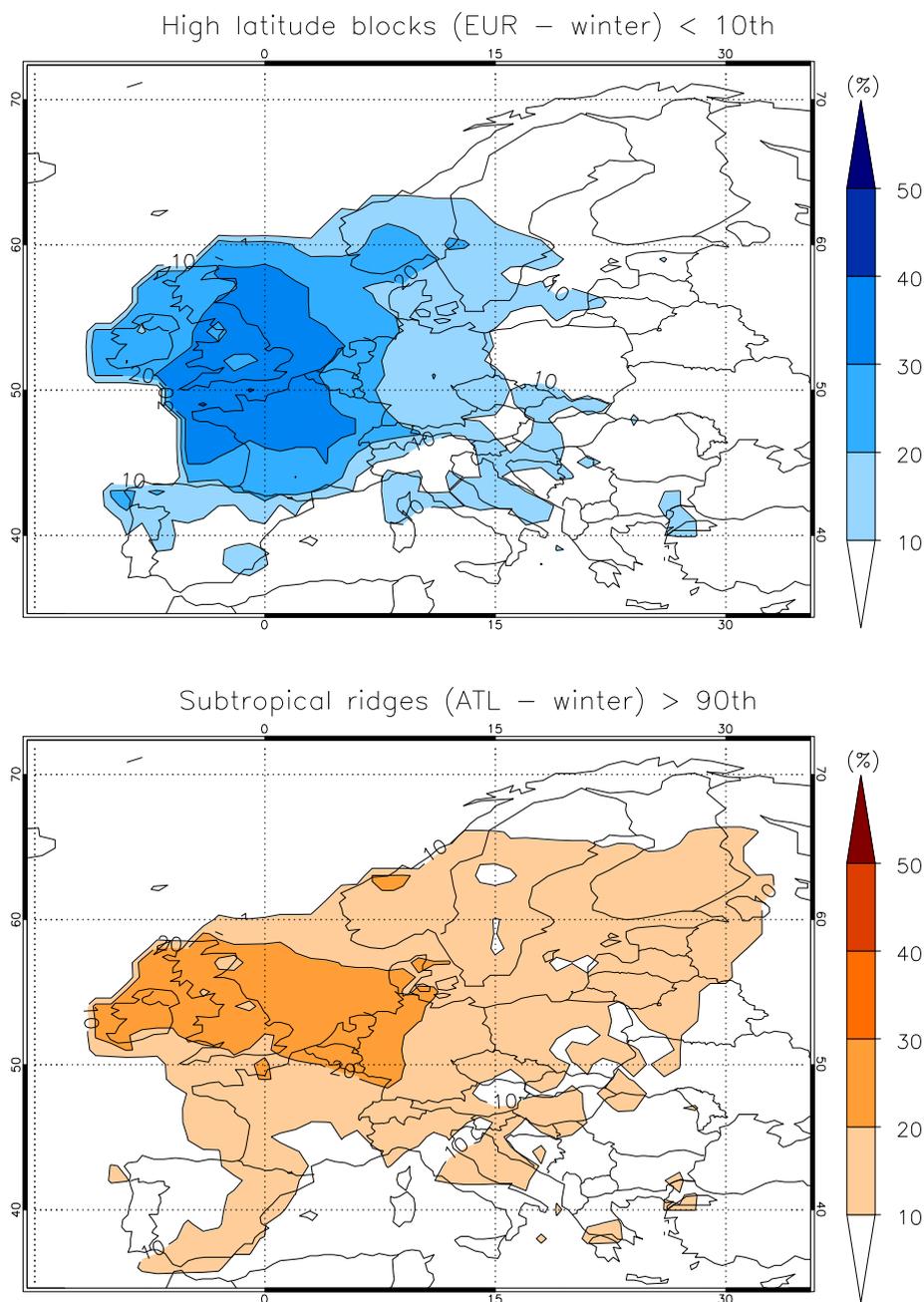



Figure 13: Percentage of EUR blocking days with MDA8 O₃ below the 10th percentile (top) and ATL ridge days above the 90th percentile (bottom) of its seasonal distribution in winter.