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RESEARCH ARTICLE

Daily, seasonal and monthly variations in ozone levels recorded at the Turia river basin in Valencia (Eastern Spain)

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Abstract
Introduction The Turia river basin, located in the east of the Iberian Peninsula, drains into the Mediterranean Sea near the city of Valencia (population, 814,208). The predominance of sea-breeze fluxes favours the inland transport of pollutants from the city up the basin where ozone concentrations exceeding the threshold for protection of human health are systematically recorded during the summer months.
Methods This work analyses the variability in ozone levels by examining their spatial and temporal distribution in a Mediterranean river basin downwind from a city within the period 2005–2008. Orographic determinants and atmospheric fluxes induce strong variations in ozone measurements, even on relatively close locations.
Conclusions Results show a different behaviour of the monthly means and the daily cycles depending on the season of the year and the measuring environment, with summer/winter ratios ranging from 2.4 in cities to 1.6 inland, and mean values always higher in the interior of the basin. Daily cycles show significant summer/winter differences related to the predominant situations of anticyclonic stability in winter, which limit ventilation, and the predominant breeze circulations in summer. Results also show a "weekend effect" at urban and medium-distance stations. At the most inland station, the weekend/weekday behaviour differs according to the season of the year; weekend ozone levels are higher in spring, autumn and winter, and lower in summer, coinciding with the predominance of local wind cycles that favour air mass penetration inland from the coast.

Keywords Ozone · Nitrogen oxides · Daily and seasonal variations · Weekend effect · Western Mediterranean

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1 Introduction

Ozone is a secondary pollutant formed in the atmosphere by means of photochemical reactions in which nitrogen oxides and volatile organic compounds participate as the main precursors. Tropospheric ozone plays a crucial role in atmospheric chemistry as it is one of the main precursors of the hydroxyl radical (OH), which controls the atmospheric oxidant potential (Logan et al. 1981; Thompson 1992). The level of OH in the atmosphere has an impact on concentrations of other pollutants such as CH4, CO and SO2 (Poulida et al. 1991). Ozone is also a greenhouse gas (IPCC 2001).

Besides its important role in the physical–chemical processes that take place in the atmosphere, ozone is considered a pollutant due to its strong oxidant properties, which have been documented to cause adverse effects on humans and vegetation. Exposure to certain ozone concentrations affects the structure and function of the respiratory tract, and epidemiological studies give evidence of damage in individuals doing exercise during episodes of high ozone levels (Carlisle and Sharp 2001; McConnell et al. 2002). Photochemical pollution has also been associated with increases in the number of asthma cases (Cody et al. 1992; McConnell et al. 2002).

With the aim of mitigating ozone pollution and informing the public on high-ozone days, European Union Directive (2008) has established information (180 μg/m^3 measured as hourly average) and alert (240 μg/m^3 measured as hourly average) thresholds, as well as an objective value for the protection of human health (120 μg/m^3 as 8-h average). This objective value should not be exceeded on more than 25 days as a 3-year average from 2010 on.

Although high ozone concentrations can be recorded in cities, the highest values normally occur in locations downwind from them, due to the transport of precursors. Depending on weather conditions, ozone precursors can be transported over long distances and originate ozone formation in locations far from their sources.

Several studies highlight the importance of meteorological factors in ozone formation and transport (Laurila 1999; Thompson et al. 2001; Millán et al. 2000). An increase in ozone concentrations has been observed with increasing temperatures and solar-radiation intensities (Olszyna et al. 1997; Garcia et al. 2005; Castell et al. 2008).

The special climatic conditions of the Western Mediterranean Basin (high temperatures and intense solar radiation) favour ozone formation, especially in June, July and August. Add to this both the higher frequency of anticyclonic atmospheric conditions in summer, during which the region stays under the influence of the Azores High, and the formation of relative thermal lows due to intense land warming and weak pressure gradient conditions over the Iberian Peninsula, which favour the development of a daily cycle of local winds and allow air mass recirculation (Millán et al. 1991, 1996, 2000; Gangoiti et al. 2002). Moreover, the combination of a low frequency of fronts during summer and a high number of days with local wind fluxes results in a long residence time of the air mass; this favours air-mass ageing, i.e., a gradual rise in ozone levels and the maintenance of moderately high concentrations in summer, and leads to the systematic exceeding of the objective value for the protection of human health during the summer months (Castell et al. 2010).

In addition, the topography of the Turia basin, which extends perpendicularly inland from the Mediterranean coastline, favours air mass channelling between the coast (where the main anthropogenic emission sources are located) and the areas inland. And the high predominance of mesoscale circulations and high radiation index characteristic of summer cause these valleys to become natural photochemical reactors (Millán et al. 2000).

In the Western Mediterranean Basin, processes have been documented in which east-facing mountainsides favour an early beginning of the slope winds that intensify the coastal breezes, combining into the so-called "combined breezes". Furthermore, these mountain slopes act as orographic-convective chimneys that favour vertical injections of air into the breeze front. When the breeze is fully developed vertical injections can reach heights up to 3–4 km. In this way, a connection between surface inland winds and higher-altitude return fluxes to the sea is established, with implications in pollutant transportation and dynamics (Millán et al 1996, 2000).

A consequence of this situation is the high spatial and time variability observed in ozone records, where daily and seasonal behaviours are characterised in terms of location relative to the emission sources, distance to the coast and height above terrain level (Millán et al. 2000; Castell et al. 2008).

A singular aspect of this variability, also observed in other European and American urban areas, is an ozone-level time pattern characterised by systematically higher concentrations on weekends than on weekdays, known as "weekend effect" (Lebron 1967). The exact mechanisms that cause this behaviour have not yet been clearly established, but four potential causes of this weekend effect have been suggested in different studies (Heuss et al. 2003; Altshuler et al. 1995; Marr and Harley 2002a, b):

1. A decrease in NO_x emissions during weekends which would reduce ozone titration;
2. A change in the time pattern of NO_x emissions during weekends that would allow a more efficient ozone production;
3. An increase in the amount of incident solar radiation caused by a reduction in the quantity of anthropogenic source particles in the air;
4. A reduction in NO_x emissions that would favour a change from NO_x-sensitive conditions to VOC sensitive conditions.

The present study analyses historical ozone records at seven measurement stations along the Turia basin. All seven are under the influence of the same atmospheric dynamics determined mainly by the development of local circulations along the basin and making it act as a transport route for coastal emissions.

In this context, we analyse not only the seasonal variations in ozone concentrations, but also the influence of the type of day (weekday or weekend) on these daily and seasonal variations.

1.1 Description of the study area and the measurement locations

The Turia river basin is situated in eastern Spain, and at its mouth is located the Mediterranean city of Valencia, with a population of 814.208. The river's source is located in the Montes Universales, at the southwestern boundary of the Iberian System, with peaks between 1,600 and 1,935 masl. The Turia river has a length of 280 km, and the basin covers a surface of 6,400 km^2. Figure 1 shows the topographic map of the study area, with marks at the measurement locations.

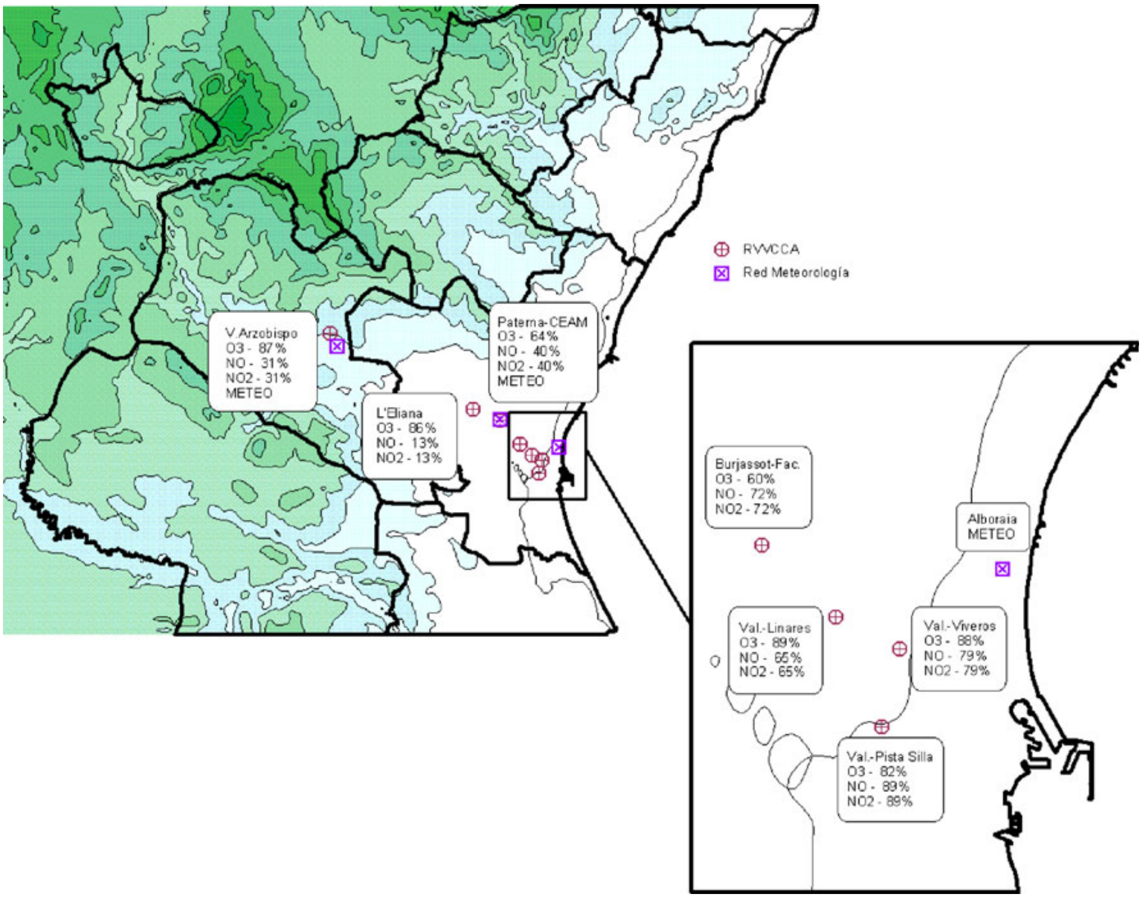


Fig. 1 Relief map of the Turia basin and location of the air quality stations (*circles*) and weather stations (*squares*). Percents correspond to the fraction of available data within the period 2005–2008

The air quality network has measurement stations distributed from Valencia City to the municipality of Villar del Arzobispo, located at a distance of 50 km from the city, on the left side of the Turia river. All the monitoring stations are equipped with a SIR S5014 UV photometry analyser for measuring ozone, with 1-ppb precision in the 0–1,000 ppb range, and a SIR S5012 chemiluminescence NO_x analyser, with a limit of detection of 0.4 ppb in the 0–500 ppb range. Measurements are averaged and stored every 10 min. In addition to ozone, continuous recording of other pollutants (NO_x, SO_2, CO and PM) and of several weather parameters (wind, temperature, radiation, rainfall and relative humidity) is also carried out in the basin. The air quality measurement stations belong to the Valencia air quality monitoring network, and the weather stations belong to the Mediterranean Center for Environmental Studies Foundation (CEAM). For this study, we used the ozone data recorded at seven points classified as coastal-urban, mid-distance-residential and inland-rural, as well as the weather data recorded at three points representative of coastal, mid-distance and inland locations, all of which was collected during a period of 4 years (2005–2008).

Weather and pollution data have been appropriately validated; furthermore, for hourly averages, 8-h averages and daily maxima calculations, we imposed a 75 % minimum data availability requirement for valid data.

The study area is included in Mediterranean climate. In Valencia City, the mean annual temperature is 17.8 °C, and ranges between 11.5 °C in January and 25.5 °C in August. Sunshine hours reach 2,660 per year. Heat waves, with abnormally high temperatures, occur frequently in summer in episodes that normally last at least 3 days (AEMET 2010).

Figure 2 shows averaged daily cycles for several parameters at different stations located in the basin, segregated by season of the year. The daily thermal curve is clearly defined, with the daily oscillation being a reflection of the station's degree of continentality. At the coastal stations, and especially in summer, the chilling effect of the sea breeze is clearly noticeable as a curve that flattens out during the central hours of the day, effect that disappears at inland locations (Villar del Arzobispo).

Wind averages also highlight the summer predominance of local breeze circulations with a well-defined daily wave. The high frequency of this kind of cycles cause the mean

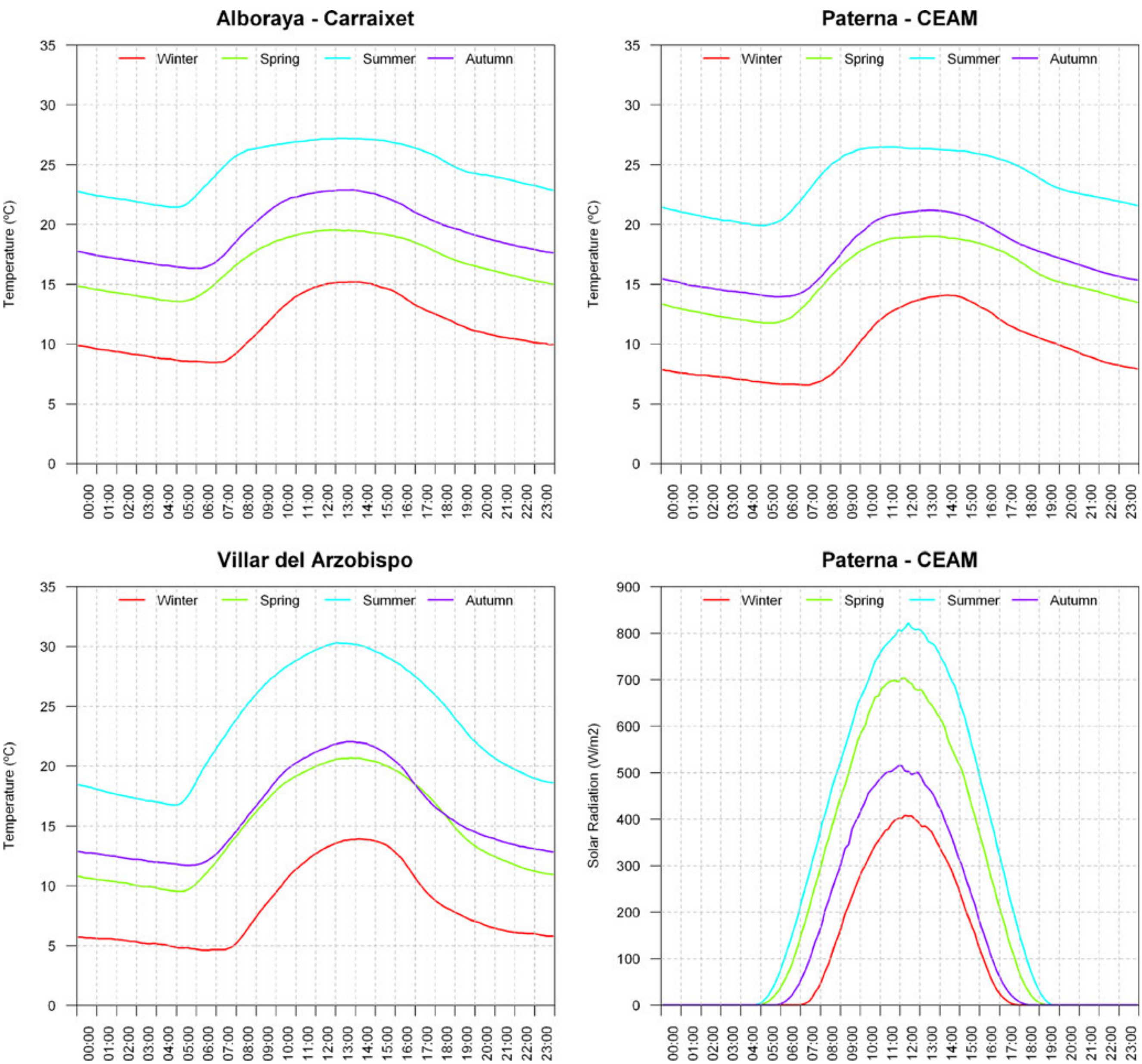


Fig. 2 Average daily cycles of temperature and wind speed and wind direction at Alboraya-Carraixet (*coastal*) and Villar del Arzobispo (*interior*) and solar radiation and temperature at Paterna (*mid-distance*)

wind intensities in summer to be higher than on winter days, even though stronger winds are recorded (but much less frequently) during the cold season, due to large-scale circulation situations. The same origin would justify higher nocturnal intensities in winter time, as opposed to the weak land winds recurrent during summer nights.

Figure 3 shows the seasonal wind roses for the measurement points at Alboraya-Carraixet (coastal) and Villar del Arzobispo (inland). At the coastal station the frequency of calms ranges from 7 to 11 %, with the highest value in winter. At the inland station, calms represent a higher rate, between 22 and 32 %, with their peak in summer.

Also during summer, wind speed exceeds the value of 8 m/s less frequently, due to the lower occurrence of western synoptic winds and the higher predominance of local circulations during this season.

Both stations show clear seasonal differences with respect to wind pattern. In winter, western winds predominate (WSW-WNW, with a percentage of 38 % at the coast and 43 % inland), which highlights the importance of synoptic fluxes during those months. In spring, a significant eastern flux (between ENE and ESE) appears at the coastal location, reaching a rate of 35 % in summer while the rate of western fluxes is reduced to 15 %. Butterfly-wing shapes during

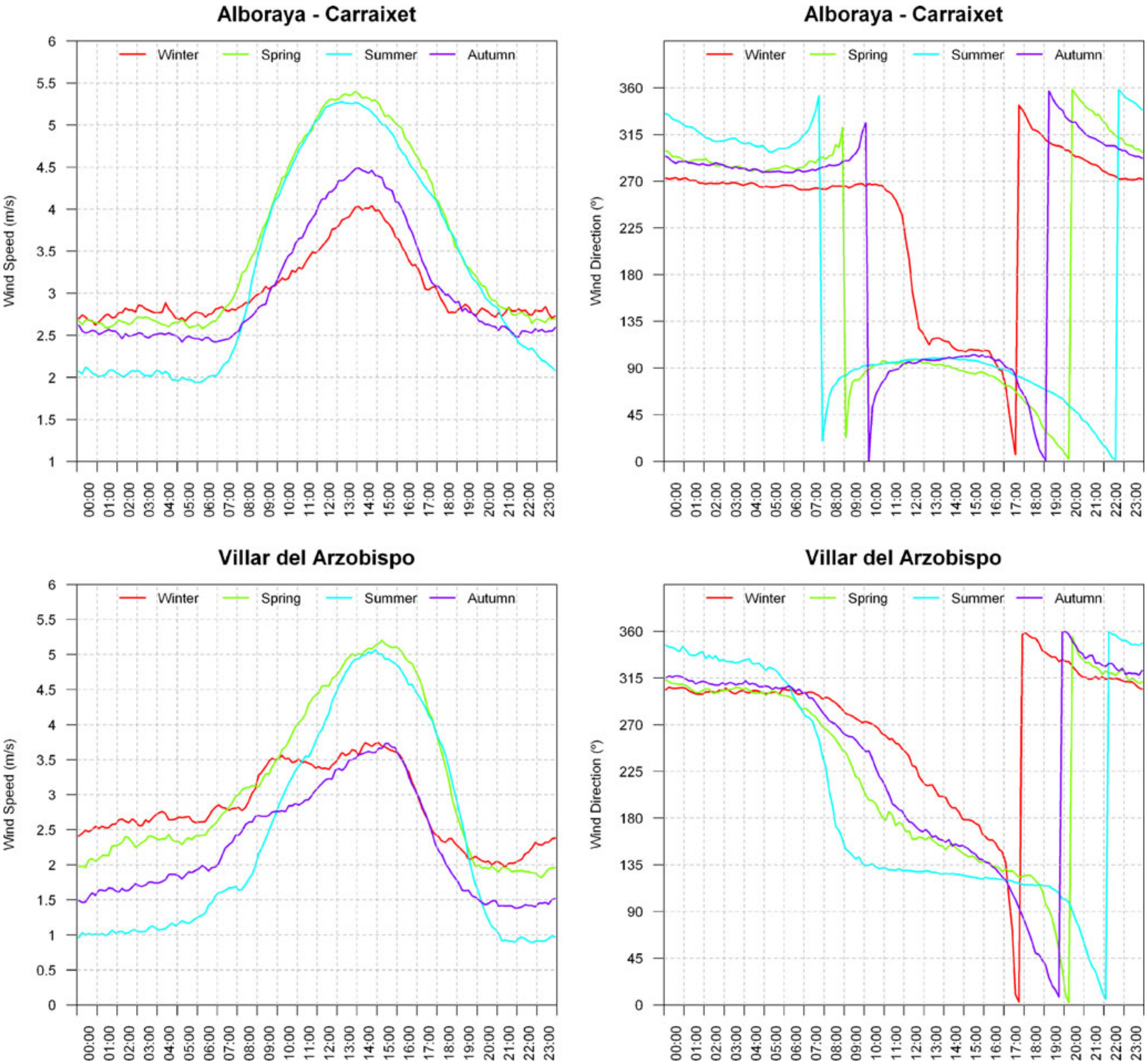


Fig. 2 (continued)

spring and summer months confirm the importance of breeze fluxes within these seasons. At the Villar del Arzobispo station, a significant ESE-SE flux (20 %) appears in spring, reaching a frequency of 37 % in summer. WSW-WNW fluxes inland are reduced to 13 % in summer.

Different meteorological analyses highlight the importance of local breeze cycles, especially in the summer season. During the central months of the year, the predominance of sea winds places the seven measurement stations under the influence of the plume generated in Valencia City. The frequent development of breeze cells, with diverse degrees of penetration, favours transportation of the polluted air mass from coastal areas to inland locations. This dynamics, which involves dispersion and photochemical transformation of the emitted species, is mainly responsible for the different ozone-concentration behaviour patterns, as recorded at measurement stations and discussed within the following sections.

2 Results

2.1 Seasonal variations

Table 1 shows the averaged ozone values for the selected 4-year period (2005–2008). A strong seasonal variation is

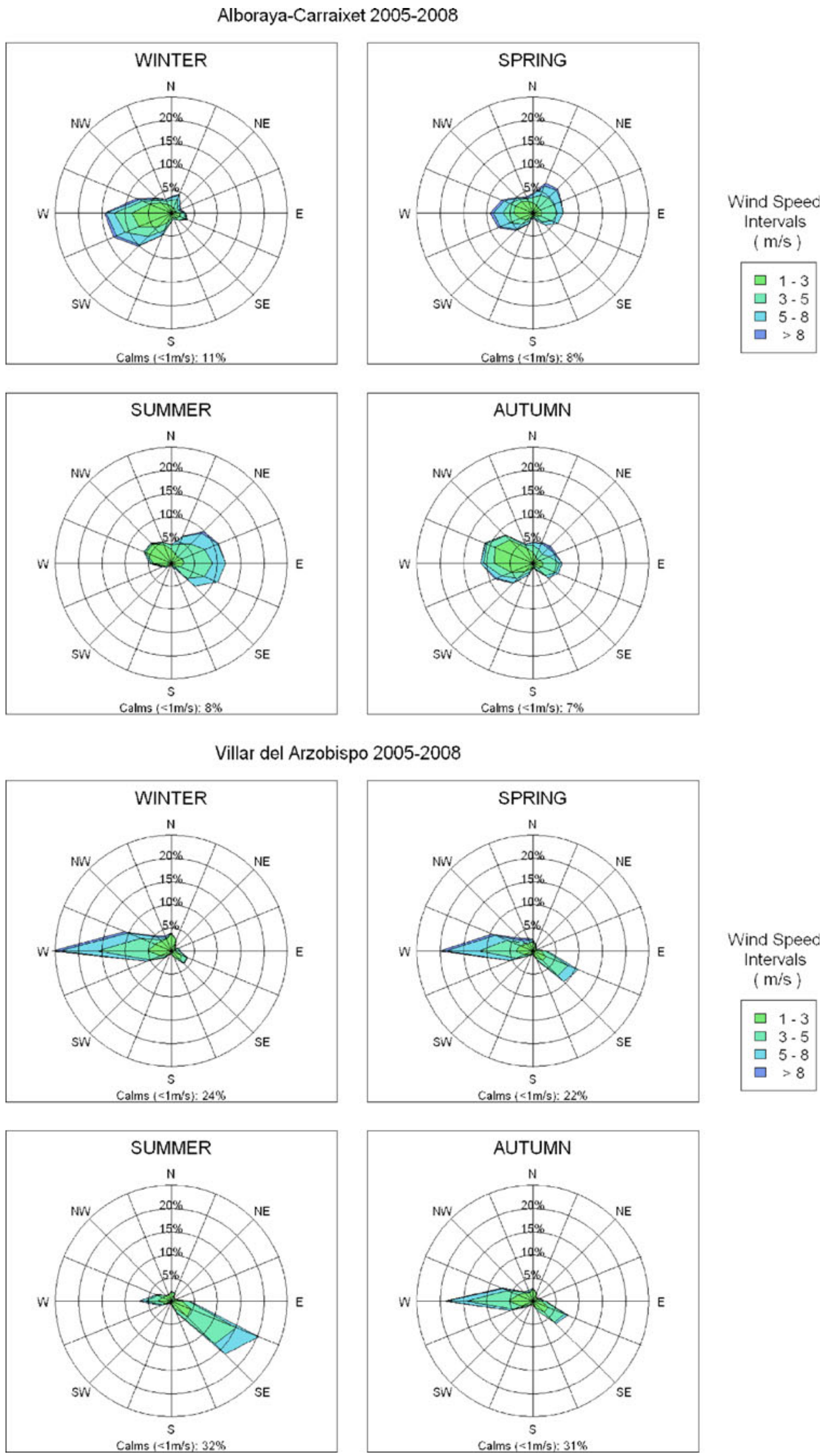


Fig. 3 Seasonal wind roses at Alboraya-Carraixet (*coastal*) and Villar del Arzobispo (*inland*)

Table 1 Average ozone concentrations (in microgrammes per cubic metre) at the Turia basin stations in winter, spring, summer and autumn within the period 2005–2008

Location	Winter	Spring	Summer	Autumn
Valencia-Viveros	22.5	53.3	54.9	31.8
Valencia-Linares	13.8	32.7	37.6	21.5
Valencia-Pista Silla	15.8	32.1	39.5	24.2
Burjassot-Facultats	29.8	59.6	65.3	39.6
Paterna-CEAM	34.0	62.0	69.5	44.4
L'Eliana	30.4	65.8	69.3	43.0
Villar del Arzobispo	52.8	79.0	80.7	58.5

observed, with ozone concentrations twice as high in summer as in winter. The highest variability is recorded at the urban station of Valencia-Linares, with a summer/winter ratio of 2.7 while the lowest variability is found at Villar del Arzobispo, with a ratio of 1.6. The fact that ozone formation is mainly triggered by the incidence of solar radiation explains why ozone concentrations experience this seasonal variation. Furthermore, additional forcings superimposed on the normal cycle can substantially modulate ozone concentrations and introduce strong variations between nearby locations.

Ozone formation and accumulation along the basin respond to three factors:

1. Presence of precursors due to emissions in the basin and possible transport from other areas.
2. Favourable weather conditions, which can be summarised as high insolation and high temperatures.
3. Synoptic situations unfavourable for atmospheric cleaning, with anticyclonic conditions and a weak pressure gradient, predominance of mesoscale cycles and occurrence of air mass recirculation processes and vertical reserve layer formation.

Even though a seasonal pattern can be observed for some emissions, e.g. those related to heating systems (higher in winter) and vegetation (higher in summer), this pattern is not so obvious in traffic-related emissions, which represent the highest fraction of NO_x emissions in the Turia basin. Therefore, the seasonal differences in ozone concentrations (Table 1) observed in this area must originate in meteorological and atmospheric conditions which inhibit or encourage chemical reactions and limit or favour atmospheric dispersion. The observed seasonal trend in ozone is in good agreement (in terms of summer/winter ratio) with that reported for several Mediterranean locations (Adame-Carnero et al. 2010; Kouvarakis et al. 2000)

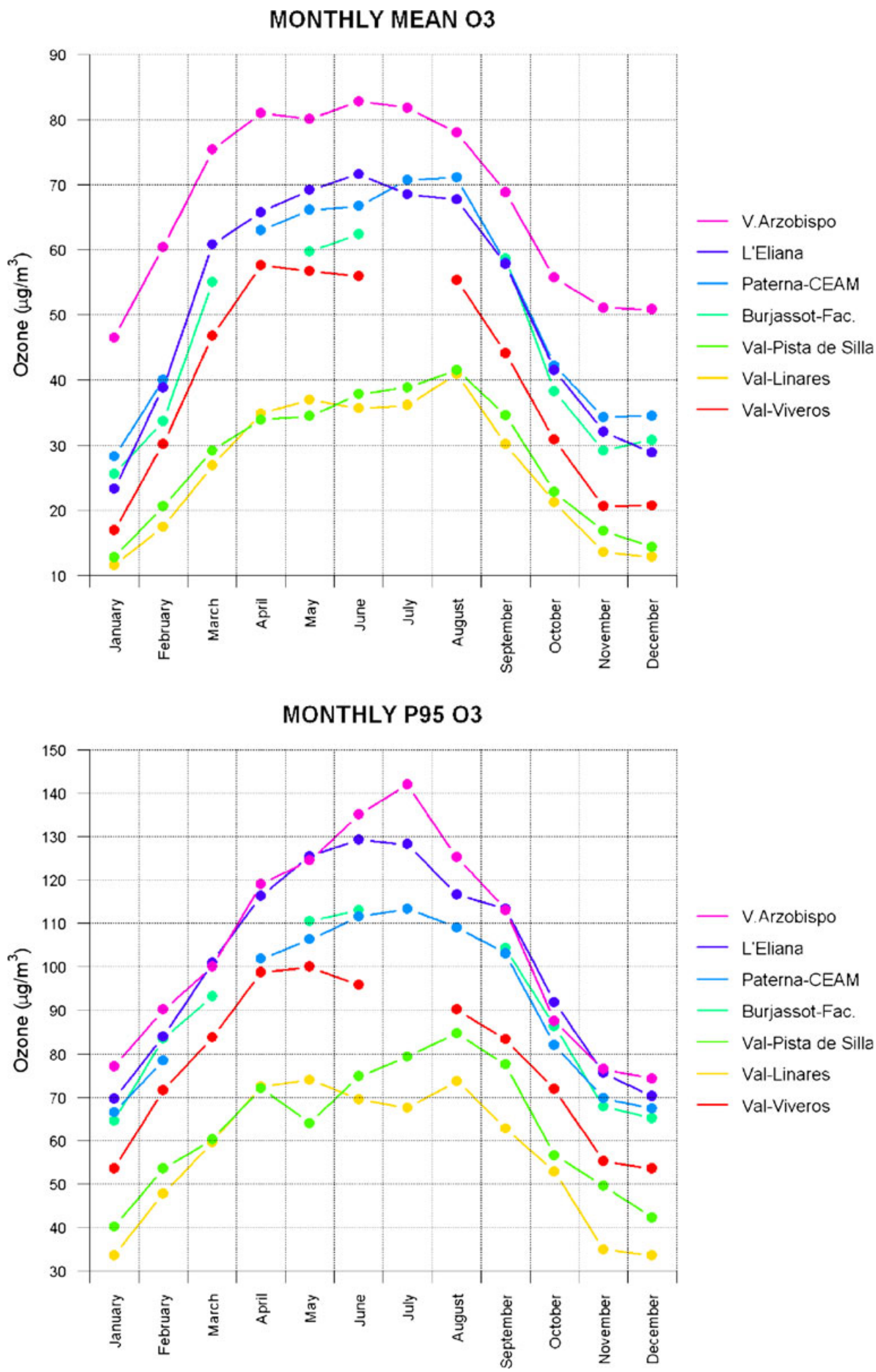
Figure 4 shows the yearly evolution of the mean monthly ozone concentrations and the monthly 95th percentile of the ozone concentrations. A hill-shaped evolution can be seen in the monthly averages plot, showing a gradual rise in mean concentrations from January to March, stable high values from April to August (though with occurrence of absolute maxima at some of the stations), and a drop from September to November, finally reaching a new plateau between November and January. From April to August, the average values and their standard deviation are 80.7±1.9 μg/m^3 at Villar del Arzobispo, 68.6±2.1 μg/m^3 at L'Eliana and 56.4±1.0 μg/m^3 at Valencia-Viveros while the yearly average standard deviation reaches values that range from 10 to 18 μg/m^3. A similar behaviour has been documented in the southwestern Iberian Peninsula (Adame-Carnero et al. 2010).

Also significant is the presence of a spatial gradient, as a function of the station's location in the basin, with lower values at the coastal stations and higher values towards the interior, reaching the highest monthly averages at the inland station of Villar del Arzobispo. The stations of Paterna and L'Eliana, both located at a mid-distance from the sea, register similar mean ozone concentrations, even though the 95th percentile is considerably higher at L'Eliana. In fact, the 95th percentile values at L'Eliana are comparable to those recorded at the inland station of Villar del Arzobispo, although the latter shows a higher peak in July. This behaviour may be due to the fact that Villar del Arzobispo represents a more rural environment, less subjected to ozone destruction reactions (especially during night-time), as opposed to the L'Eliana location, which is more highly influenced by nearby emission sources. This could explain why the average ozone level is higher at Villar, but not its 95th percentile since both stations are in the same section of the daily ozone formation curve during the day, without remarkable differences related to distance between them, except for the months with the highest insolation when higher values are registered at Villar del Arzobispo. A detailed description about the relation between ozone and its precursors in urban and polluted rural environments can be consulted in Sillman (1999).

A specific aspect of the spatial gradient is the differences observed in relation to proximity to anthropogenic sources. At urban stations located closer to this kind of emission, such as Valencia-Linares and Valencia-Pista de Silla, with yearly average values of 25–28 μg/m^3, lower average values are recorded during the whole year than at urban locations farther from direct emission sources, such as Valencia-Viveros (located in a park inside the city), with yearly averages of 39 μg/m^3.

In addition, from the observed monthly distribution of ozone concentrations we can see that the highest values occur inland during June and July (Fig. 4, yearly evolution of monthly 95th percentile). Therefore, at Villar del Arzobispo during the months of June and July, the 95th percentile curve moves away and takes higher values than the L'Eliana curve (as an example, in July, a 95th

Fig. 4 Average evolution of monthly mean ozone concentrations (*left*) and 95th percentile (*right*), calculated over hourly values within the period 2005–2008, at the Turia monitoring stations



percentile value of 142 µg/m^3 was recorded at Villar del Arzobispo, as opposed to the 128 µg/m^3 value recorded at L'Eliana while both stations had shown a 95th percentile value of 120 µg/m^3 in May). This suggests that ozone formation reaches its peak at relatively short distances downwind from Valencia almost all year round (justifying the absence of significant differences between the peaks at L'Eliana and Villar del Arzobispo); however, during the summer months, peak ozone formation occurs more inland (with Villar generally showing higher peak values within this period).

A particular case of the time distribution of monthly average concentrations and 95th percentiles involves the peaks observed in August at the urban stations of Valencia-Linares and Valencia-Pista de Silla. These can be explained by the reduction in traffic emissions that characterise a typical holiday month such as August. This would cause the "weekend effect" to extend to the whole month, i.e. a "holiday effect", making an increase in average concentrations likely for the same reasons argued in the introduction for the weekend effect. The effect of holidays in air pollution has also been identified in the city of Taiwan; the study found that NO_x, CO, NMHC, SO_2 and PM_{10} were lower in the Chinese New Year (CNY) than in the non-CNY period while the variation in the concentration of O_3 was reversed, which was mainly due to the NO titration effect (Tan et al. 2009).

Our results agree with those obtained in other Mediterranean basins which, as indicated in the introduction, found differentiated seasonal behaviours depending on location relative to emission sources, distance to the coast, and height over terrain level (Millán et al. 1996, 2000; Castell et al. 2008).

Figure 5 shows the frequency of occurrence of the different ozone concentration ranges (calculated over hourly and 8-h daily maxima, as these values are related to legislated thresholds) for the four seasons of the year within the period 2005 to 2008.

Differences in the shapes and central values of the distributions depend on the station environment. Thus, stations located far from anthropogenic emission sources show higher central values, for the hourly values as well as for the 8-h averages, than the ones located closer to the emission sources. As an example, for the whole year, the mean value and standard deviation recorded at Villar del Arzobispo are 99.85±28.53 μg/m^3 and 89.88±24.27 μg/m^3 for hourly and 8-hour maxima respectively, as opposed to the values of 70.11±23.52 μg/m^3 and 60.25±24.03 μg/m^3 recorded at Valencia-Viveros for the same parameters.

Likewise, frequency distributions also show differences depending on the season of the year. High peak concentrations are recorded in summer, spring, autumn and winter, in that order. For example, at the Valencia-Viveros station, the average maximum hourly value in summer is 87.32 μg/m^3 while in winter it is 48.71 μg/m^3; at the Villar del Arzobispo station, the average maximum hourly value is 127.75 μg/m^3 in summer and 73.56 μg/m^3 in winter. Moreover, peak concentrations above the averaged yearly maximum value, calculated over the 2005–2008 period, are measured more frequently in summer than in winter. Therefore, in summer the occurrence frequency for values above the yearly average is 90 % at Valencia-Viveros and Villar del Arzobispo, for hourly and 8-hour average concentrations while in winter these values are reduced to a 12 % frequency at Valencia-Viveros and a 2 % frequency at Villar del Arzobispo.

Regarding the legislated values, Villar del Arzobispo is the only station where the information threshold is exceeded, though with a very low frequency (2.44 % in summer). The alert threshold was never reached during the period of study. On the other hand, the threshold for the protection of human health was frequently exceeded at the stations of Villar del Arzobispo and L'Eliana, with 33 and 20 % respectively in summer. This threshold was also exceeded in summer at Burjassot-Facultats (7.4 %) and Paterna-CEAM (2.33 %) while it was only exceeded in spring at the urban station of Valencia-Viveros (0.33 %). A similar analysis performed in Málaga (Spain) showed a different pattern. In that study a similar percentage of exceedances of the human health protection threshold was registered at two urban and rural sites during summer and exceedances of the information threshold was registered only at the urban station (Dueñas et al. 2004). The topography of the Turia basin plays an important role in the location of the maximum ozone levels.

2.2 Daily variations

Studying the diurnal distribution of O_3 and NO_x concentrations makes it possible to analyse the joint contribution of emissions, atmospheric dynamics and chemical transformation to the measured pollution concentrations. The ozone daily cycle shape is directly linked to its precursor levels, as well as to the evolution of weather conditions (temperature, solar radiation and wind speed and direction). Figure 6 shows seasonal averaging for ozone, NO and NO_2 daily cycles, within the period 2005 to 2008.

The following facts can be observed:

- Patterns in O_3, NO and NO_2 daily curves:

  – Well-defined daily cycles are observed during the whole period, with seasonal and locational variations.
  – Ozone curves show a morning minimum, occurring at 7 UTC in winter and at 5 UTC in summer, at all the stations in the basin. This minimum is linked to fresh road traffic emissions of NO_x associated with the rush hour. This behaviour is similar to the one observed at other Mediterranean locations (Dueñas et al. 2002).
  – Hourly maximum takes place at 13–15 UTC, in all seasons of the year and at every measurement point. Therefore, the maximum occurs 1 or 2 h after peak solar radiation. Moreover, seasonal patterns are observed in the ozone curves. For example, at Villar del Arzobispo a

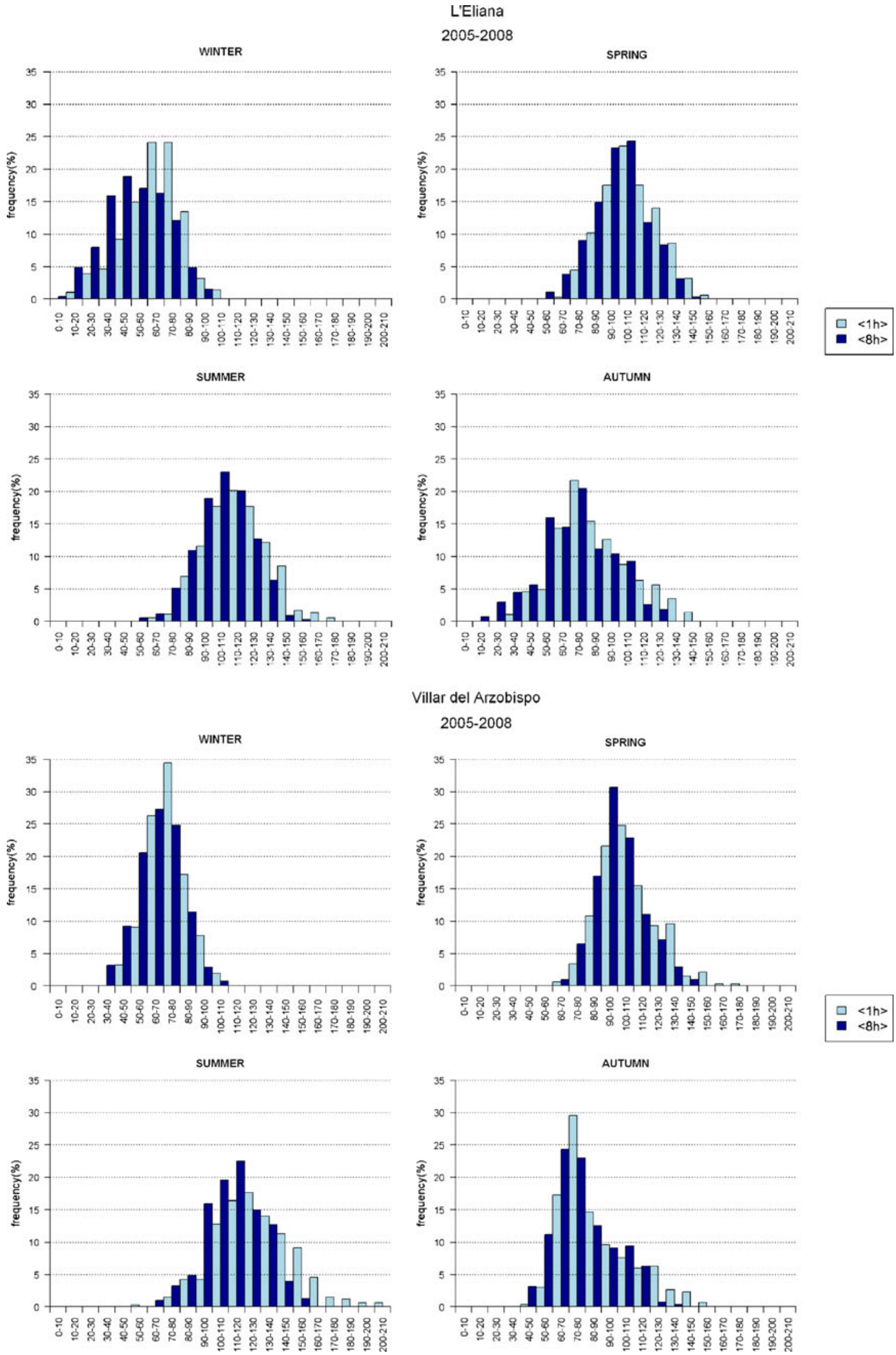
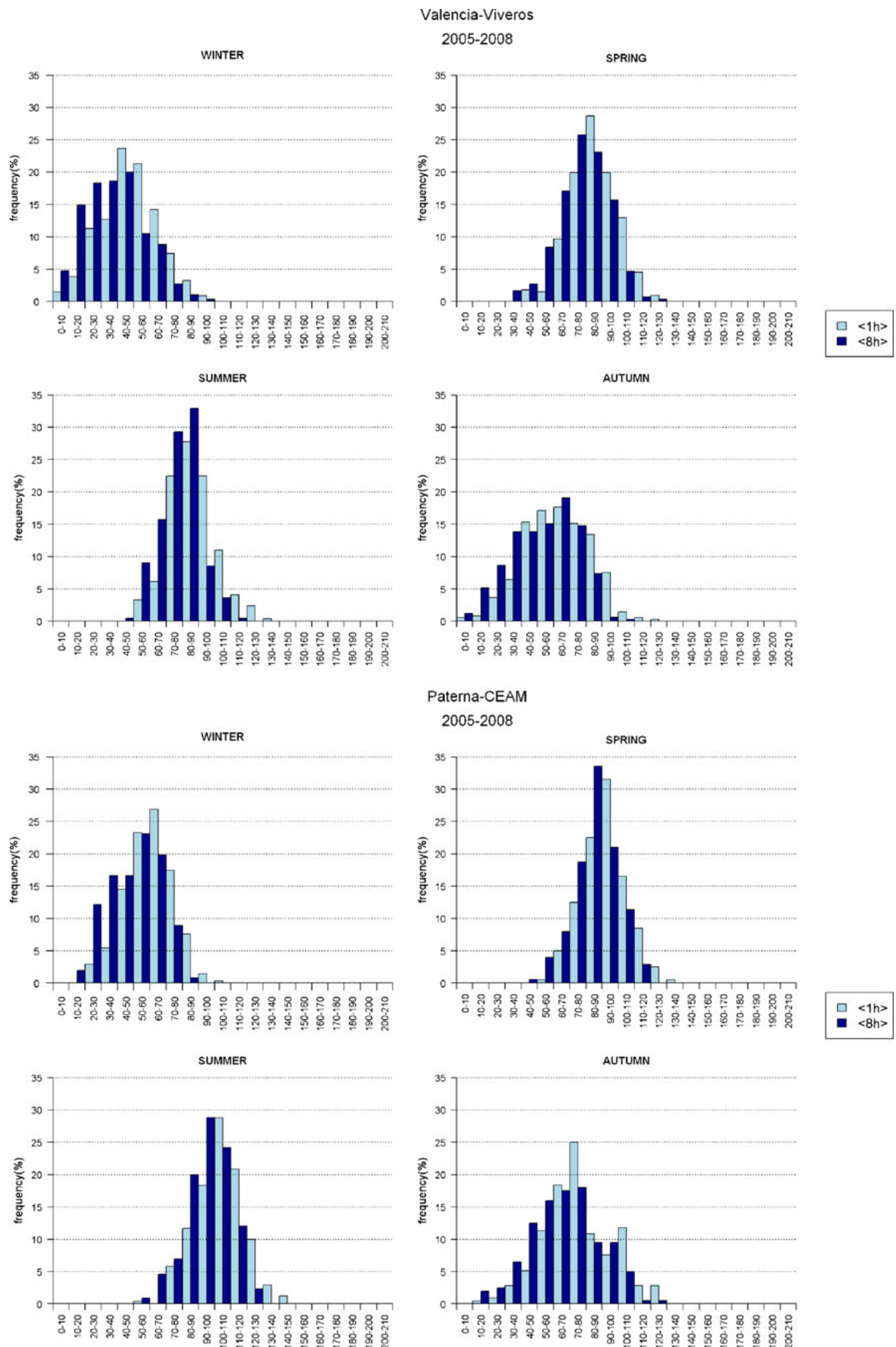


Fig. 5 Histograms of daily maximum hourly and octo-hourly concentrations (in microgrammes per cubic metre) during the period 2005–2008, at the monitoring stations in the Turia basin



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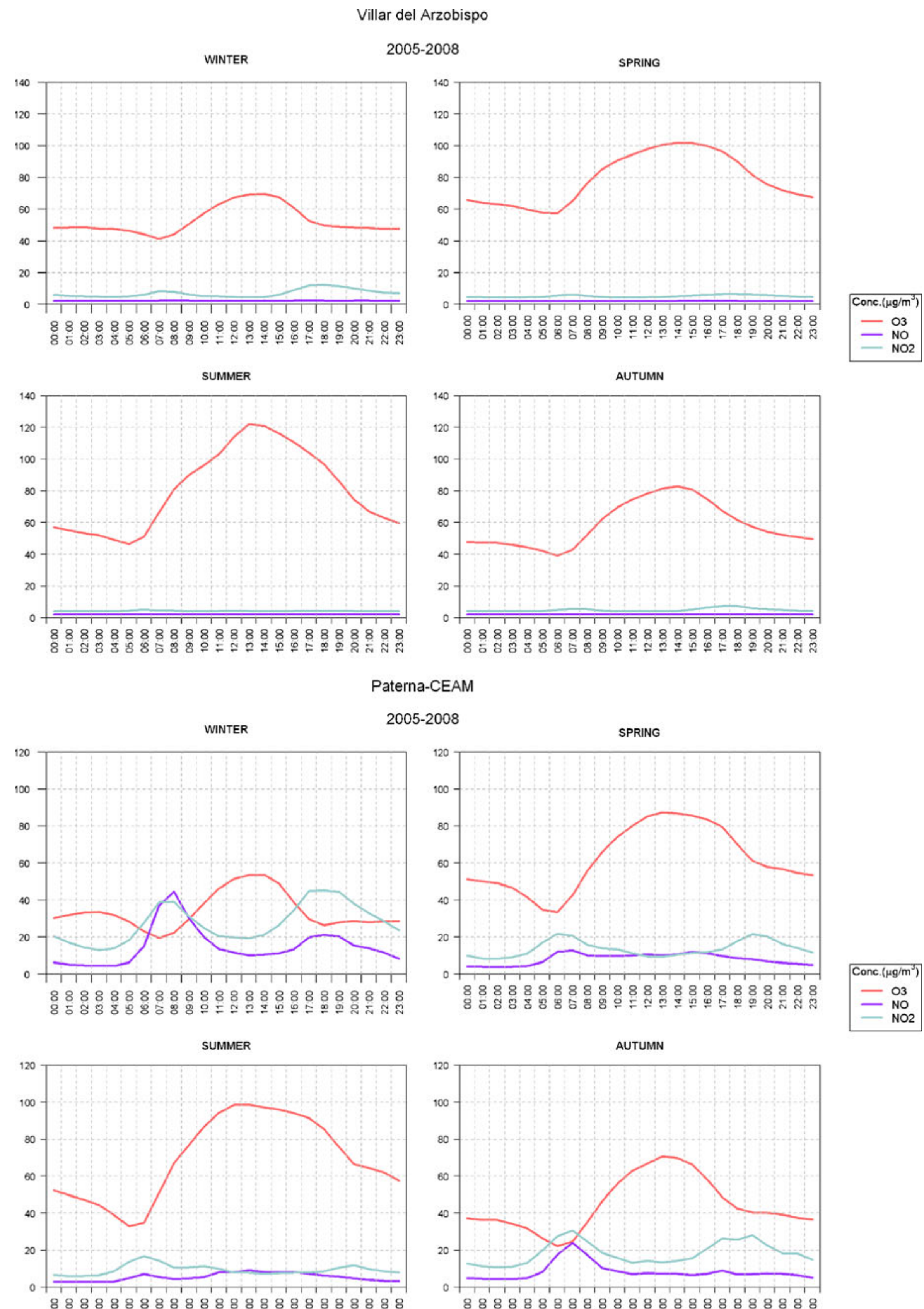

Fig. 6 Average ozone and nitrogen oxide daily cycles (in microgrammes per cubic metre) for winter, spring, summer and autumn data within the period 2005–2008, at the analysed stations in the Turia basin

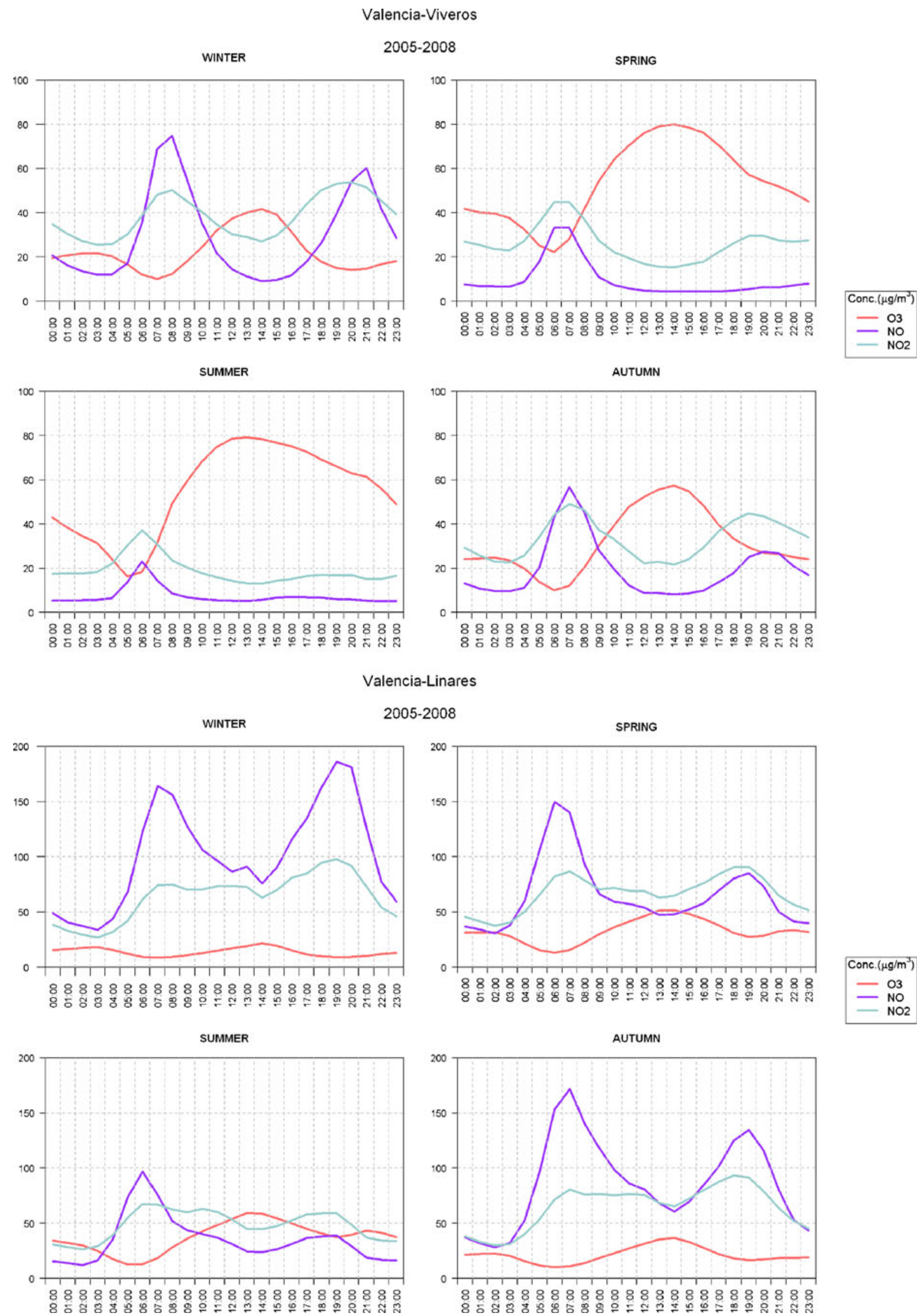

Fig. 6 (continued)

double wave appears in summer, caused by the superposition of sea and valley breezes, with the latter beginning earlier.

- Daily curves of NO and NO_2 show two peaks, one in the early morning (6–8 UTC) and the second in the evening (18–19 UTC). These two peaks are linked to rush hours.
- At midday, NO and NO_2 curves show a valley, not a peak reflecting the traffic increase typical of these hours. This is due to the fact that there is greater ventilation during the central hours of the day. This effect can also be reinforced by chemical activity linked to ozone formation.

• Average daily cycles show differences due to the station location in the basin:

- A spatial gradient is observed in ozone concentrations, with higher values at inland stations, and lower values in the urban area. This pattern is a reflection of ozone production during its upstream transportation.
- NO and NO_2 daily curves show higher values at the coast (urban stations) and lower values in the interior (areas far from the emission sources). This pattern is exclusively a function of distance to emission sources.

• Ozone, NO and NO_2 daily cycles show variations over the general pattern depending on the season of the year.

- NO and NO_2 concentrations are higher in winter and reach their minima in summer. This effect is mainly related to ventilation. In winter atmospheric dispersion is limited by the predominant situations of anticyclonic stability while in summer breezes predominate, favouring air mass ventilation (the morning peak takes place before breeze fluxes are established).
- While in winter NO and NO_2 morning and evening peaks have similar values, in summer the evening peak is considerably lower, due to a higher ventilation linked to breeze circulations, as discussed in the previous point.
- Ozone concentrations show a reverse pattern to NO and NO_2 ones, with higher values in summer, when the photochemical processes that lead to ozone formation are favoured by weather conditions.
- During summer and spring, nightly ozone concentrations are higher than in winter and autumn, at both inland and coastal stations. This is due to a higher ozone formation during daylight hours in summer, which leaves a higher remainder after the nocturnal destruction processes.
- At stations less influenced by anthropogenic emissions, the day/night oscillation in ozone levels becomes more pronounced in summer, due to a higher contrast in production processes.
- At locations closer to anthropogenic sources, two minima on the ozone curves are observed in winter, both clearly associated with morning and evening NO_x consumption. In summer, the evening consumption is not noticeable at the Paterna-CEAM station, not even at the Valencia-Viveros station while the morning one maintains its shape. This is because of the better ventilation in the evening, associated with more intense breezes. In the morning, the breezes are still not developed, and dispersion is more limited, favouring ozone destruction.
- At the urban station of Valencia-Linares, a decrease in ozone levels is observed in the evening due to titration, but immediately afterwards ozone concentrations rise again. The daily ozone evolution often experiences nightly rises at stations under the influence of nearby emissions, and the daily curve reflects this behaviour in a smoothed-out way due to averaging. Our plots seem to show that the efficient ozone destruction during the night under the influence of fresh emissions (or the advection of a polluted air mass) causes a strong decrease in ozone levels, and then when nightly background levels are recovered an increase is observed.

2.3 Weekly variations. Weekend effect

Figure 7 shows the seasonal variation in hourly ozone concentrations on weekdays and weekends. Anomalies are calculated as the difference between the weekend average (Saturday and Sunday) and the ozone concentration for each weekday.

At the urban (figure only shows Valencia-Viveros) and mid-distance stations (L'Eliana and Paterna-CEAM) a clear weekly pattern is observed, where average ozone concentrations are higher on weekends that on weekdays. This behaviour is repeated during the four seasons of the year, and it is also observed in the average daily maxima (computed over hourly values; figure not shown). Likewise, at the inland station of Villar del Arzobispo, the pattern of lower ozone concentrations on weekdays than on weekends (i.e. "the weekend effect" typical of urban areas) is also observed most the year, although it is not so pronounced as at the other stations studied (resulting in smaller anomalies, of 5 $\mu g/m^3$ at most). Nevertheless, in summer and only at this monitoring station, a different pattern is observed: ozone concentrations are below the weekend average from Wednesday to Friday, and above it on Mondays (slight variation is found on Tuesdays in average). This response is also observed when averaging daily maxima computed over 8-hourly values, and it is reinforced by the fact that the differences between weekdays and weekends are slightly significant in winter, spring and autumn (figure not shown).

This behaviour at the Villar del Arzobispo station could be related to wind patterns, considering that the predominance of western synoptic winds in winter,

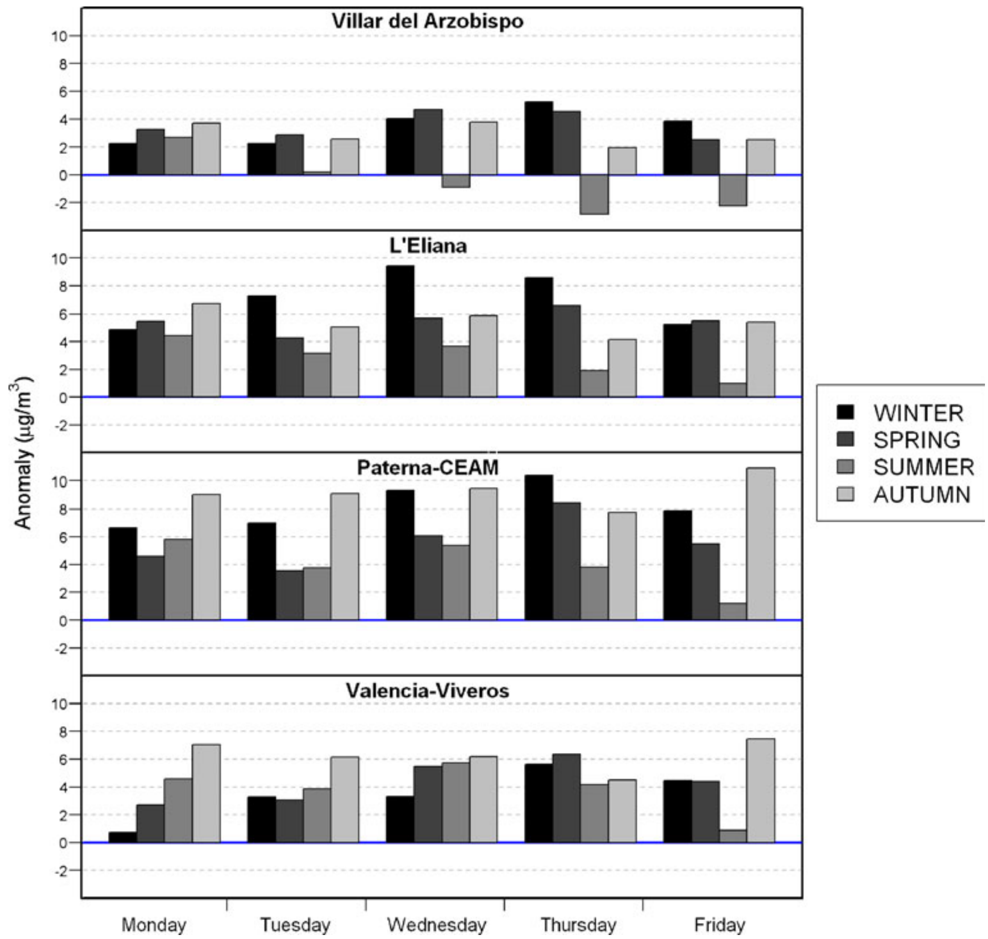

Fig. 7 Bar diagram of weekday–weekend anomalies for winter, spring, summer and autumn data within the period 2005–2008, at the analysed stations in the Turia basin. Positive values show higher weekend concentrations

spring and autumn leaves the station isolated from local processes in the basin while in summer the predominant mesoscale SE-ESE winds connect the station with the emissions transported and chemically transformed along the basin from the coastal area.

Figure 8 shows the average daily cycle of the differences between the average weekend values and the average weekday values for NO, NO_2 and O_3, by splitting the total data base (2005 to 2008) into seasonal subsets. The variations in the daily cycles of weekend–weekday differences can be seen to depend on the season of the year and the measurement environment.

Urban stations (represented by Valencia-Viveros) generally register higher NO_x concentrations on weekdays, with the exception of the 00–04 UTC time interval when weekend concentrations can be slightly higher. A pronounced drop is observed in the NO and NO_2 level of the morning peak on weekends, with the drop being more noticeable on NO than on NO_2 (decrease of 60 % on NO and 40 % on NO_2 between 06 and 09 UTC, considering the whole year). This reduction coincides with the peak at the beginning of the working day. Seasonally, the morning peak of NO shows higher differences over a longer time period in winter than in summer, reaching 70 % in winter against 56 % in summer (between 06 and 09 UTC) while differences in NO_2 follow the reverse pattern, with higher variations in summer (42 %) than in winter (35 %). In contrast, differences in the evening peak are not so significant, and NO variations from 18 to 20 UTC are between 38 and 46 % in winter, spring and autumn, descending to 23 % in summer while NO_2 differences stay at values from 16 % in winter and 36 % in spring, for the same time period.

Ozone concentrations at urban stations follow a reverse pattern to the NO_x one, with higher concentrations during the weekend; the positive peak observed between 6 and 9 UTC is linked to less ozone titration on Saturdays and Sundays. In the evening, differences between weekdays and weekends are less highlighted, and even though an evening peak (17–18 UTC) is observed in winter and autumn, it disappears in spring and summer. This evening maximum takes place earlier that the NO_x evening peak, which occurs between 18 and 20 UTC. Also, variations between weekends and weekdays are smaller in summer and spring. Therefore, within the whole day, ozone concentrations are higher on weekends than on weekdays, with rates of 21 % in autumn, 16 % in winter, 8 % in spring and 7 % in summer. During the central hours of the day (12 to 16 UTC) ozone concentrations are 3 % higher in summer,

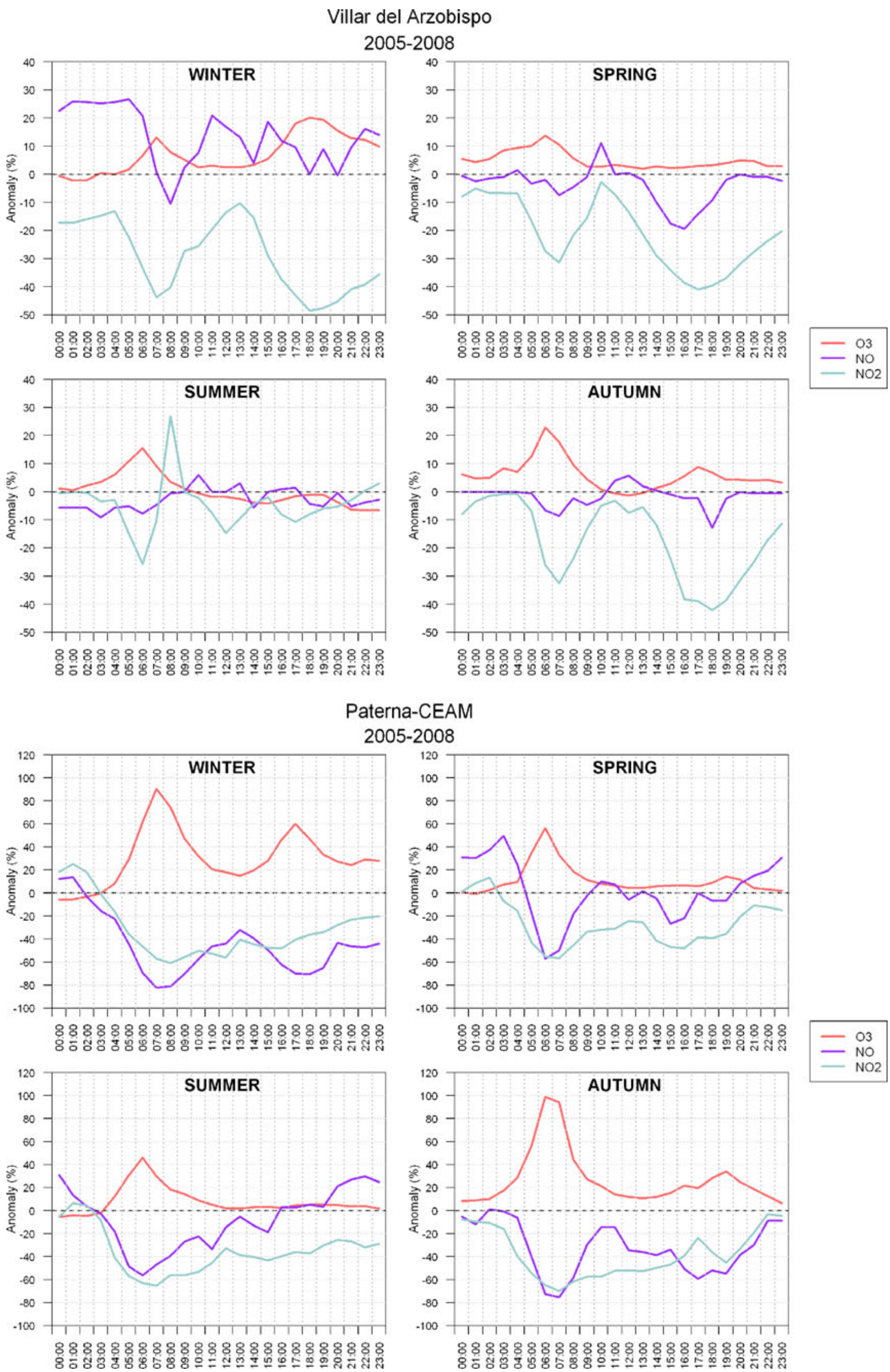

Fig. 8 Anomaly (in per cent) of the hourly differences between average O_3, NO and NO_2 concentrations on weekends and weekdays. Positive values show higher weekend concentrations

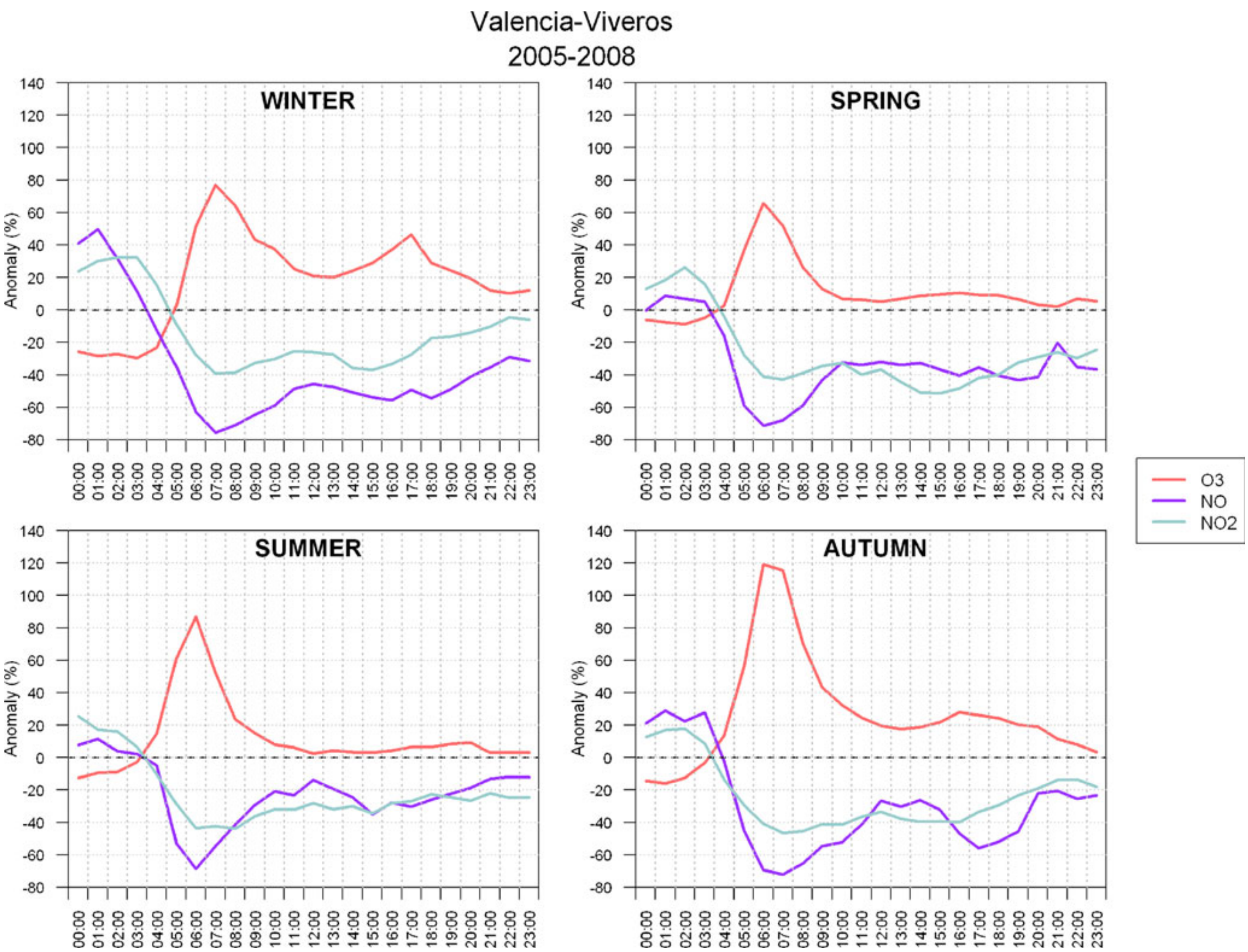

Fig. 8 (continued)

against 25 % in winter. This could be caused by the predominance in urban areas, during winter, of chemical reactions directly dependent on the amounts of NO and NO_2 present in the air (for example, ozone titration) while the weekend reduction in emissions strongly limits these reactions. In summer, however, factors independent of the weekly cycle, such as higher dispersion and weather conditions favourable to ozone formation, take on an important role.

The Paterna-CEAM station also shows the influence of traffic on the differences between weekends and weekdays. Its seasonal and daily patterns are fairly similar to those found at the Valencia-Viveros station, with ozone concentrations 13 % higher on weekends, and lower NO and NO_2 concentrations, 37 and 36 %, respectively (considering the whole period in all cases).

At the Villar del Arzobispo station, the differences in O_3 and NO_x daily cycles are observed as a function of the season of the year, and are also noticeable in the seasonal averages illustrated in Fig. 7. During winter, autumn and spring, the daily cycles of the differences show similarities to the ones recorded in urban areas, with negative NO_x peaks in the morning (06–08 UTC) and in the evening (18–19 UTC), both associated with rush hours. Higher differences are observed in NO_2 than in NO, unlike the urban station where the larger variations correspond to NO. Also unlike urban areas, the evening peak is higher than the morning one; for example, NO_2 in the period 06–09 UTC is 26 % lower at weekends while in the period 18–20 UTC the ratio is 39 %, considering in both cases the whole period 2005–2008. In contrast, NO is 2.2 % lower in the morning peak and 1.9 % lower in the evening one.

Regarding ozone, at the station of Villar del Arzobispo, concentrations are higher at weekends during winter, spring and autumn months, with respective values of 7, 5 and 5 %. As at the urban stations, morning and evening peaks are observed.

On the contrary, daily cycles at Villar del Arzobispo in summer are totally different from the other stations in the basin. Until 8 UTC the pattern is similar to the rest of the year, with higher ozone values at weekends (9 % between 6 and 8 UTC), but from 8 UTC on, the pattern is reversed, and the observed ozone concentrations are lower at weekends than on weekdays, with a 2 % variation between 8 and 18 UTC, reaching 3 % during the central hours (12–16 UTC).

Summarising, results show that at the station located in the interior of the Turia basin (Villar del Arzobispo), in summer, when local winds that transport the air mass inland from the coast (diurnal breezes) are developed, ozone levels experience a drop as a consequence of traffic emissions in the city of Valencia and its metropolitan area.

The weekend effect, defined as an increase in ozone concentrations despite a decrease in its precursors, is observed in the Turia basin not only at urban stations but also at mid-distance stations located in areas far from direct traffic emissions.

As argued in the introduction, one of the possible causes of the weekend effect is a decrease in NO local emissions on weekend mornings. This would lead to a smaller consumption of ozone, with the result that the ozone formed later would not be totally consumed during the day, and as a result more ozone would be accumulated. In this sense, Atkinson-Palombo et al. (2006) suggest that the main cause of the higher ozone concentrations recorded during weekends is the reduction in NO_x levels, and therefore in ozone titration, produced by decreased traffic emissions. At the Turia basin stations a positive ozone peak is observed to coincide with negative NO and NO_2 peaks, highlighting that, on weekends, the reduction in emissions at 6–7 UTC leads to an ozone increase at the same hours. However, in summer, from 10 UTC on, there is no noticeable difference in ozone concentrations between weekends and weekdays, unlike in winter and autumn when a higher ozone accumulation is observed on weekends.

Likewise, the change in the time pattern of NO_x emissions during the weekend has been related to weekend ozone increases (Heuss et al. 2003). Using numerical modelling techniques, Marr and Harley (2002b) observed that changes in emission patterns have an influence on the weekend effect, although lesser than reductions in NO_x emissions. At the Turia basin stations a pronounced reduction in NO and NO_2 levels is observed at weekends, but the daily cycle follows the same time pattern on holidays and weekends. However, traffic data would be required to be able to relate weekend variations to changes in traffic patterns. It is not the aim of our work to deal with these aspects.

Another possible cause of the weekend effect lies in the differences in the weekend reductions of NO_x and VOC emissions, which would produce variations in VOC/NO_x ratios between weekdays and weekends. Since ozone formation depends on NO_x and VOC concentrations as well as the VOC/NO_x ratio, this change at the weekend could cause a higher proportion of VOCs, which in VOC-sensitive conditions (characteristic of urban areas) would favour a higher ozone formation. Altshuler et al. (1995) suggest that this difference in NO_x and VOC reductions is the main cause of the weekend effect in the San Francisco Bay area. Likewise, Marr and Harley (2002a) point out that the weekend effect in California is due to NO_x reduction and VOC sensitivity. Unfortunately, there are no available VOC or chemical indicator measurements in the Turia basin during the period 2005–2008.

Other authors propose that the lower solar radiation absorption due to a reduced presence of small particles in the atmosphere (which reflect and diffuse solar radiation) favours ozone formation during weekends. This hypothesis has not been explored in the present work.

3 Conclusions

The aim of this work is to highlight and analyse the temporal variations in ozone levels observed at various measurement points, within a typical Mediterranean river basin, subjected to similar atmospheric dynamics (dominated by breeze regimes) and anthropogenic emissions (basically urban). The results obtained have allowed us to extract the following conclusions relative to ozone dynamics in the Turia basin:

(a) The occurrence of the ozone monthly peak depends on the measurement station environment, and a possible link to the intensity of the breeze cell is observed. When the sea breeze penetrates further inland, maxima occur farther from the coastal area; on the other hand, when the inland extension of the sea breeze is limited, peaks occur closer to the coast.

(b) An ozone peak is observed in August in urban areas. This peak is probably linked to a reduction in city traffic, giving rise to a “holiday effect”.

(c) Urban stations show a secondary ozone maximum during the night, probably linked to a recovery of levels after the nocturnal ozone consumption, under the influence of fresh emissions or the advection of a polluted air mass.

(d) Daily NO and NO_2 cycles show morning and evening peaks associated with traffic increases. A seasonal variation is observed in these peaks, with the evening peak being noticeably lower than the morning peak during the summer months, due to the more intense ventilation. NO_x concentrations are: (a) higher in winter and lower in summer as a consequence of greater ventilation within the summer months and (b) higher at the coast that in the interior due exclusively to the distribution of the emission sources.

(e) A weekend effect, with a rise in ozone concentrations despite the reduction in NO_x levels, is observed at urban and mid-distance stations during the entire year. At the inland station, the weekend effect is observed in winter, autumn and spring, but not in summer, when ozone levels show a reduction during the weekend. This may be due to the predominance of local circulations in summer—which allows this station to become coupled to the urban plume of Valencia—in contrast with the western synoptic winds that predominate during the rest of the year.

The results obtained in this work highlight the different seasonal dynamics of ozone concentrations, which are linked to the development of local wind cycles during the summer. A particular effect derived from this fact is the difference between weekday–weekend dynamics observed at Villar del Arzobispo in summer (predominance of local winds) and winter (predominance of synoptic winds).

Significant seasonal variations have been observed in O_3 and NO_x daily cycles for weekends and weekdays, especially the more pronounced weekend effect, with higher differences in ozone concentrations, found in winter and autumn.

These results can be helpful in the design of effective abatement strategies to reduce the number of exceedances of the ozone target value, one of the main problems in the Turia basin. These results also show the necessity of exploring the influence of the breeze cycles, due to their importance in ozone dynamics in summer (when higher levels are recorded). It is also advisable to widen the study of the chemical processes involved in ozone formation, especially those contributing to the weekend effect, because of their relevance in strategies to reduce ozone pollution.

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