Increasing interannual and altitudinal ozone mixing ratios in the Catalan Pyrenees

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ABSTRACT

Interannual, seasonal, daily and altitudinal patterns of tropospheric ozone mixing ratios, as well as ozone phytotoxicity and the relationship with NOx precursors and meteorological variables were monitored in the Central Catalan Pyrenees (Meranges valley and Forest of Guils) over a period of 5 years (2004–2008). Biweekly measurements using Radiello passive samplers were taken along two altitudinal transects comprised of thirteen stations ranging from 1040 to 2300 m a.s.l.. Visual symptoms of ozone damage in Bel-W3 tobacco cultivars were evaluated biweekly for the first three years (2004–2006). High ozone mixing ratios, always above forest and vegetation protection AOT40 thresholds, were monitored every year. In the last 14 years, the AOT40 (Apr–Sept.) has increased significantly by 1047 m2gm−3/h per year. Annual means of ozone mixing ratios ranged between 38 and 67 ppb v (38 and 74 ppb v during the warm period) at the highest site (2300 m) and increased at a rate of 5.1 ppb v year−1. The ozone mixing ratios were also on average 35–38% greater during the warm period and had a characteristic daily pattern with minimum values in the early morning, a rise during the morning and a decline overnight, that was less marked the higher the altitude. Whereas ozone mixing ratios increased significantly with altitude from 35 ppb v at 1040 m–56 ppb v at 2300 m (on average for 2004–2007 period), NO2 mixing ratios decreased with altitude from 5.5 ppb v at 1040 m–1 ppb v at 2300 m. The analysis of meteorological variables and NOx values suggests that the ozone mainly originated from urban areas and was transported to high-mountaine sites, remaining aloft in absence of NO. Ozone damage rates increased with altitude in response to increasing O3 mixing ratios and a possible increase in O3 uptake due to more favorable microclimatic conditions found at higher altitude, which confirms Bel-W3 as a suitable biomonitor for ozone concentrations during summer time. Compared to the valley-bottom site the annual means of ozone mixing ratios are 37% larger in the higher sites. Thus the AOT40 for the forest and vegetation protection threshold is greatly exceeded at higher sites. This could have substantial effects on plant life at high altitudes in the Pyrenees.

1. Introduction

During the pre-industrial period ozone concentrations were approximately 10–15 ppb v (Finlayson-Pitts and Pitts, 1997). However, these concentrations rapidly increased when NOx emissions became more intense due to the switch to fossil fuels that took place in the industrial revolution (Finlayson-Pitts and Pitts, 1997). Nowadays, the annual average background ozone concentrations over the mid-latitudes of the Northern Hemisphere ranges approximately between 20 and 45 ppb v, with variability depending on location, atmospheric elevation and distance to other pollutants’ emission sources (Finlayson-Pitts and Pitts, 2000).

Overall, in mountainous areas ozone mixing ratios seem to rise with increasing altitude (Aneja et al., 1994a,b; Skelly et al., 1997; Cooper and Peterson, 2000; Ribas and Peñuelas, 2006; Sanz et al., 2007). Higher solar radiation (Volz and Kley, 1988), local air recirculation linked to orographic systems (eg. valley-mountain systems or mixing boundary layers) (Lefhon, 1992; Sanz and Millán, 2000), ozone intrusions from the stratosphere (Viezee et al., 1983) and less chemical ozone loss under low NO concentrations (Naja et al., 2003) are all factors which contribute to high ozone mixing ratios at high altitude. Moreover, stomatal conductance is found to increase with rising altitude (Wieser et al., 2000), since trees rarely have the need for restricting water loss at high altitudes (Tranquillini, 1979). Therefore, vegetation at higher altitudes can be more easily affected by ozone toxicity than at lower sites (Ribas and Peñuelas, 2006).
The distribution of ozone in mountainous regions has been studied in Europe in the Alps (Chevalier et al., 2007) and the Carpathian Mountain Range (Manning et al., 2002) and, in North America in the White Mountains, Adirondack Mountains (Aneja et al., 1994a, b), Appalachian Mountains (Skelly et al., 1997), San Bernardino Mountains (Arbaugh et al., 1998, 2003; Bytnerowicz et al., 2007), Sierra Nevada (Arbaugh et al., 1998), Wasatch Mountains (Wager and Baker, 2003) and in the mountains around Mexico City (De Bauer et al., 1985). Although ozone concentrations have been studied in the Mediterranean area (Gimeno et al., 1995; Ziomas et al., 1998; Sanz et al., 2000; Ribas and Péñuelas, 2000, 2004), no thorough studies have been conducted in the mountain ranges of the Mediterranean region in Europe. In this region, preliminary studies have indicated high ozone mixing ratios which are often above the human and vegetation protection threshold and strong interannual, seasonal and daily variations (Ribas and Péñuelas, 2006).

The aim of this study was to describe the interannual, seasonal and daily pattern of distribution of ozone in the mountains of the European Mediterranean area by monitoring ozone concentrations along two altitudinal gradients in the Pyrenees during a period of five years. We also studied ozone phytotoxicity in order to discern the suitability of Bel-W3 for biomonitoring ozone mixing ratios in long-term studies and the relationship between ozone mixing ratios and variations in NOx precursors, as well as meteorological variables with the aim of determining the possible source of ozone in this area.

2. Material and methods

2.1. Field monitoring set up

From 2004 to 2007, during the whole year, and in 2008, during summer, thirteen sites were studied along two altitudinal gradients: one from 1040 m a.s.l. to 2300 m a.s.l. on the south-facing slopes of Puigpedrós (Meranges transect) and the other one from 1300 m a.s.l. to 2200 m a.s.l. facing north-east (Gulls transect). Both were in the La Cerdanya county, located in the Central Catalan Pyrenees (Bellver 42° 22’N, 1° 46’E). The sampling sites were located approximately every 200 m in altitude (Fig. 1) in a forested area dominated by Pinus uncinata. Ozone mixing ratios and their phytotoxicity, as well as NOx mixing ratios were measured at all stations every two weeks in the warm period and once a month in the cold period. Phytotoxicity was measured during the warm period from 2004 to 2006 at all sampling sites except the highest one at 2300 m since the irregularity of terrain hindered the installation of plants and the weather was excessively cold for the tobacco plants used as biomonitors.

2.2. Physico-chemical measurements

Radiello radial symmetry passive samplers (Cocheo et al., 1996) were used to analyze ozone and nitrogen dioxide at all sampling sites. The use of these samplers is very common in studies conducted in remote areas (Cooper and Peterson, 2000; Krupa and Legge, 2000) where logistic limitations such as power supplies make it difficult to accurately quantify spatial patterns.

At 1040 m a.s.l., at Bellver, the lowest valley-bottom site of the south-facing transect, and at 1500 m a.s.l., in the village of Meranges, ozone measurements were also performed with a Thermo 49i analyzer (Thermo, Franklin, USA) in the first station and with a SIR S-5014 analyzer (SIR, Madrid, Spain) in the latter. NOx levels were determined by using chemiluminescence with a Casella Monitor ML9841B (Casella Measurement Ltd., Bedford, UK) in Bellver and a SIR S-5012 (SIR, Madrid, Spain) in Meranges. These two sites are part of a regional network of rural monitoring stations run by the Department of the Environment and Housing of the Government of Catalonia (Generalitat de Catalunya) that consists of a network of ozone monitors and meteorological stations. The second station (Meranges, at 1500 m a.s.l.) was monitored with a mobile unit only during summer 2008.

Intercalibrations were made between passive samplers and monitors at these points. As in other previous works (Krupa and Legge, 2000; Skelly et al., 2001), close relationships were found between passive and active measurements (Ozone mixing ratio-

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p_{\text{passive sampler}} = 0.9468 \times \text{Mixing ratio}_{\text{monitor}} + 7.4734, R^2 = 0.73, p < 0.0001.
\]

Nitrogen dioxide from passive samplers was also significantly correlated with NO2 active measurements (Mixing ratio_{passive sampler} = 0.5958 \times \text{Mixing ratio}_{\text{monitor}} + 1.8214, R^2 = 0.65, p < 0.001).

Temperature and humidity were measured at six of the sampling sites by means of a weatherproof Temperature/RH Datalogger (HOBO Pro, Sistemas y Instalaciones, Madrid, Spain), with sensors located at 1500, 2100 and 2300 m a.s.l. in the south-facing transect, and at 1300, 1800 and 2200 m a.s.l. in the north-east transect. These parameters in addition to wind direction and speed were also available for the valley-bottom station (1040 m a.s.l.) and Meranges mobile unit (1500 m a.s.l.) operated by the Department of the Environment and Housing of the Government of Catalonia. Extrapolations from linear models for each biweekly period were used to estimate the temperature for the rest of sites.

2.3. Description of ozone phytotoxic levels: active bioindication

Phytotoxic effects were evaluated in terms of the ozone damage present in sensitive tobacco (Nicotiana tabacum) cultivars Bel-W3.

![Fig. 1. Map of the altitudinal transect sites studied in the region of La Cerdanya in the central Catalan Pyrenees.](image-url)
and the resistant cultivar Bel-B that are commonly used in ozone bio-indicator programs (Heggestad, 1991; Klumpp et al., 2002). Tobacco seeds were germinated in ozone-free conditions to obtain homogeneous plants, thereby avoiding any possible early ozone contamination. When seedlings were at the fourth leaf stage, they were transplanted to 8 L pots filled with 25% peat, 25% vermiculite, 25% perlite and 25% sand. The soil pH of these pots was adjusted to 6.0 by adding CaCO₃. An NPK 15:11:13 slow-release fertilizer (Osmocote plus) was also added. A self-watering system was used in which each pot was placed above individual self-watering reservoirs connected by two wicks. Every fortnight, from May to September/early October, we used six new plants in each one of the stations (Fig. 1). Phytotoxic levels were defined according to the percentage of damaged leaf area in the Bel-W3 cultivar (Bytnerowicz et al., 1993; Ribas and Penuelas, 2003, 2006). After each fortnight, the percentage of ozone-induced lesions on the oldest four leaves was visually recorded. These percentages were estimated in 5% intervals.

3. Results

3.1. Meteorological variables

The expected decrease in temperature with increasing altitude was observed along the transects. During the study period (2004–2008) biweekly average temperature ranged from 12 to 14 °C (at 1040 m and 1300 m a.s.l. in the Meranges and Guils transect respectively) and from 5.6 to 7.8 °C (at 2300 m and 2200 m a.s.l. in the Meranges and Guils transect respectively), that is, temperatures decreased by approximately 0.5–0.7 °C per 100 m altitude. Average values of relative humidity for 2004 in the Meranges transect were as follows: 71.9% at 1040 m, 63.4% at 1500 m, 68.48% at 2200 m and 65.84% at 2400 m; nevertheless, these differences were not statistically significant. The prevalent winds at the Meranges site during the period monitored (summer 2008) were from N (23% frequency) and SE (21%) (Fig. 2). Winds blowing from the south and west summed a total frequency of 50%, and had the highest wind speed and ozone averages (2.39–3.55 m s⁻¹ and 44–48 ppbv, respectively). These winds typically blew from 09:00 to 21:00 (local time) (Fig. 3).

3.2. O₃ threshold excess

The vegetation protection threshold has been set at AOT₄₀ = 6000 μg m⁻³ h by the Directive 2002/3/EC of the European Parliament relating to ozone in ambient air, where AOT₄₀ is defined as the sum of the diurnal hourly ozone concentration exceeding the threshold of 40 ppbv over the period 1 May - 31 July. This threshold has been exceeded every year since 1994 in the valley-bottom site (data from monitor in Bellver station, Fig. 4). The highest AOT₄₀ (May–July) value was reached in 2006 (6 times higher than the protection threshold). The forest protection threshold (AOT₄₀ = 20000 μg m⁻³ h, calculated over the period 1 April - 30 September) has also been exceeded every year since 1994 (Fig. 4). The highest AOT₄₀ (Apr–Sept.) value was reached in 1998 (2.3 times greater than the protection threshold for forests). There has been a statistically significant increasing trend over time in the AOT₄₀ (Apr–Sept.) of 1047 μg m⁻³ h year⁻¹ (p < 0.05, R² = 0.30).

3.3. O₃

Ozone mixing ratios increased with altitude in both transects: from an annual mean (for the 2004–2007 period) of 35 ppbv, measured at the lowest site studied (1040 m a.s.l.), to 56 ppbv, at the highest site (2300 m a.s.l.) in the Meranges transect (Fig. 5). Thus, mean ozone mixing ratios for the whole period in the valley-bottom site (1040 m a.s.l.) were 37% smaller than in the highest site (2300 m a.s.l.). The increase in ozone mixing ratios was 1.6 ppbv per every 100 m of altitude. This increase was less clear along the intermediate altitudes of the Guils transect. There, ozone mixing ratios ranged from 46 ppbv at 1300 m a.s.l. to 48 ppbv at 2200 m a.s.l. (Fig. 5). Even though the difference between the ozone mixing...
ratios at the lowest and highest site in the Guils transect are smaller than those in the Meranges transect, there was a significant relationship between ozone mixing ratios and site altitude in the Guils transect for data gathered between 2005 and 2007 (\[O_3\] mixing ratios = 36.749 + 0.007\text{altitude}, \(R^2 = 0.77, p < 0.05\)).

Yearly variations were found in both altitudinal gradients (Fig. 5). Ozone mixing ratios in 2004 were on average 31% and 28% smaller than the average values for 2004–2007 in the Meranges and Guils transects, respectively. The highest annual values were found in 2007 in the Meranges transect and in 2005 in the Guils transect (21% and 12% greater than the average value for 2004–2007 in Meranges and Guils transects, respectively). On average, the Guils transect had ozone mixing ratios 11% greater than the Meranges transect. Even though the AOT40 (April–September) has been increasing significantly since 1994, we have not detected a significant increasing trend in the annual means of ozone mixing ratios in the valley-bottom station (Bellver, 1040 m a.s.l.) (Fig. 4). At the highest site (2300 m), annual means of ozone mixing ratios ranged between 38 and 67 ppbv (38 and 74 ppb, during the warm season) and increased 5.1 ppb, per year during the period sampled (2004–2007).

The seasonal pattern of ozone mixing ratios occurred as expected being on average 35% and 38% greater during the warm period (April–September) than during the cold period (October–March) in the Meranges and Guils transect, respectively (Fig. 6A and C).

Average daily patterns of ozone mixing ratios for years 2004–2007 in the valley-bottom site (Fig. 7) showed the characteristic pattern of minimum values in the early morning, a significant rise during the morning with increasing solar radiation (which coincided with the NO\textsubscript{2} minimum), peaking in the afternoon between 13:00 and 15:00 (local time) and then declining during the night (probably due to NO titration) (Fig. 7). Nevertheless, this daily pattern faded with altitude. Only a small daily variation was found at the Meranges station (1500 m a.s.l.), where ozone mixing ratios were also very high during the night-time (Fig. 8).

3.4. NO\textsubscript{2} and NO

We found no significant increasing or decreasing trend over time for NO\textsubscript{2} and NO mixing ratios recorded since mid-February 2004 in the Bellver station (1040 m a.s.l.) (data not shown).

Yearly variations of NO\textsubscript{2} mixing ratios were minimal in both altitudinal gradients. Mean NO\textsubscript{2} mixing ratios over 2004–2006 remained at approximately 1–2 ppb, in all sites in both altitudinal transects. Only at the lowest sites, in the town of Bellver (5.5 ppb\textsubscript{v}) and in the town of La Tor de Querol (2.5 ppb\textsubscript{v}, Guils transect), did NO\textsubscript{2} exceed 2 ppb\textsubscript{v} (Fig. 5).

NO\textsubscript{2} mixing ratios followed the expected seasonal pattern with higher values during the cold period than during the warm period, especially in those sites with nearby human activity.
NO₂ and NO maximum mixing ratios were recorded in the morning before ozone mixing ratios rose and at the beginning of the night when human activity increases (Figs. 7 and 8), a pattern that became more accentuated during the cold period (Fig. 7). Mixing ratios in Meranges mobile station (1500 m a.s.l.) during summer 2008 were very low and close to the limit of instrument accuracy, showing no peak comparable to those found in Bellver.

3.5. Phytotoxic levels: spatial variation of leaf damage

Phytotoxicity increased with altitude and it was on average greater in the Meranges transect than the Guils transect (Fig. 9). Substantial ozone injury symptoms were found at all altitudes on the Bel-W3 tobacco plants exposed to the ambient air, although damage was more intense in the plants at greatest altitudes (Fig. 10). More than 30–40% of the surface area of Bel-W3 was affected at all sites in the Guils and Meranges transects, although at the highest sites (2200 m in the Guils transect and 2100 m a.s.l. in the Meranges transect) the mean damaged leaf area was 60–80% in the sensitive Bel-W3 tobacco plants and 16–40% in the Bel-B resistant cultivar. The resistant cultivar (Bel-B) was less affected overall and damaged leaf areas ranged from 5 to 15% in the remaining sites (Fig. 10).

The percentage of ozone-induced damaged leaf area in the sensitive Bel-W3 cultivar had a significant quadratic relationship (Damaged leaf area Bel-W3 (%) = 213.29 – 8.03(Ozone mixing ratio) + 0.08(Ozone mixing ratio)², R² = 0.68, p < 0.03, Fig. 11).

4. Discussion

Yearly exceedance of the AOT40 threshold for forest and vegetation protection has also been reported in other areas of the Mediterranean basin (Nali et al., 2002a; Klumpp et al., 2006; Ferrecci et al., 2007; Paolleti et al., 2007; Saliba et al., 2008). Likewise, typical O₃-induced injuries in vegetation have been positively related to O₃ exceeding the critical level with a variable degree of intensity (Nali et al., 2002b; Cvitas et al., 2006; Calatayud et al., 2007; Waldner et al., 2007). Hence, our data provide evidence of an O₃ risk also for the vegetation of the high mountain areas of this Mediterranean region.

The ozone mixing ratios we measured fall into the highest range of the average ozone levels recorded in non-mountainous areas (1000 m, 1500 m and 2100 m at Bellver town, Meranges village, and Malniu mountain refuge, respectively) (Fig. 6B).
from the Mediterranean basin (Kalabokas et al., 2000; Lelieveld et al., 2002; Nali et al., 2002a) and they are similar to measurements reported by previous studies in valley sites (Ribas and Peñuelas, 2004). Mean growing season values of 31–41 ppb_v and maximum hourly values of 84–118 ppb_v monitored in our valley-bottom site since 1994 are also close to the O_3 mixing ratios reported in high mountain ecosystems in the European Alps and in the Carpathian mountains, where mean growing season values of 40–50 ppb_v (Bytnerowicz et al., 2004; Wieser et al., 2006) and O_3 maximum hourly values of 105–107 ppb_v (Bytnerowicz et al., 2004) have been reported. These data thus document the existence of persistent medium-to-high O_3 levels that contrast with the peak-type episodes found in central and northern Europe (Sanz and Millán, 2000).

Ozone mixing ratios increased with altitude along the transects studied (Fig. 5), a phenomenon which also has been reported in other mountainous regions (Stockwell et al., 1997; Peterson et al., 1999; Cooper and Peterson, 2000; Sanz et al., 2007). The average rate of ozone mixing ratio increase in the Meranges transect (1.6 ppb_v per 100 m of altitude, 0.3 in Guils transect) is quite close to the 1.3 ppb_v reported in the western Washington Mountains (USA) (Cooper and Peterson, 2000). A positive correlation has been found between ozone mixing ratios and solar radiation (Dueñas et al., 2002), the latter tending to rise with increasing altitude. Nonetheless, in our study the altitudinal variations in ozone mixing ratios seem to be more related to air pollutant transport and diminished loss processes rather than to increased irradiance with altitude. Firstly, at mid-elevation sites (Meranges, 1500 m a.s.l.), solar radiation does not differ statistically from the values recorded in the valley-bottom site (Bellver de Cerdanya, 1040 m a.s.l.), where the average values from 08:00 to 19:00 are 457 and 464 W m^{-2} in Meranges and Bellver, respectively. Secondly, 50% of the wind blows from S and W, corresponding to the areas from which ozone precursors have most probably originated (main urban areas and roads). These winds blow during the daytime and they have the highest ozone concentrations. This suggests that they are probably carrying the ozone produced in the urban areas and roads where they come from. Furthermore, NO_2 and NO production is very low at the valley-bottom site in comparison with urban areas (mean annual concentrations of 2 ppb_v of NO and 5 ppb_v of NO_2 in Bellver versus 23 ppb_v and 22 ppb_v in several urban sites in Catalonia (data not published, courtesy of the Department of the
Environment and Housing) and they become even lower at Meranges site (1500 m a.s.l., Fig. 5). Thus, the low NO mixing ratios found at the Meranges site (and probably at higher altitudes as well) could explain the high night-time mixing ratios of ozone that contribute to enhancing the overall mean ozone mixing ratio. In effect, some of the highest ozone mixing ratios ever detected are at high-altitude rural sites (Brace and Peterson, 1998), where local production of NO is minimal and ozone night losses are low (Lefhon, 1992). Nonetheless, further research should be done in order to clarify how much stratospheric intrusions of O$_3$ and how much lower vertical mixing contributes to the increasing ozone mixing ratios found with rising altitude.

The AOT40 (Apr–Sept.) at the Bellver site (1040 m a.s.l., Fig. 4) has increased 1047 m$^{-3}$ h per year since the measurements started in 1994 (Fig. 4). Nevertheless, the annual mean of ozone mixing ratios does not necessarily follow AOT40, as can be seen in 2007. In that year the AOT40 was relatively low in comparison with the previous years (Fig. 4), while the annual mean ozone mixing ratio reached its highest value in the whole period 2004–2007 (Fig. 5). Therefore, special attention should be paid to AOT40 measurements, which give a more realistic estimation of the potential risk for vegetation than annual means and, as we have seen, it can differ significantly from the annual means calculated for the same period.

In our case study, higher ozone mixing ratios in the warm period are probably a result of anabatic transport of photochemically produced ozone in nearby urban areas during the daytime. This process has been reported in other regions of the Mediterranean basin (Milla´n et al., 2000; Duen ˜as et al., 2002; Gonçalves et al., 2009). Even though anabatic and katabatic winds are formed all year long, the photochemical production of ozone is greater during the warm period due to higher temperatures, which explains the higher ozone mixing ratios found during this period. However, other factors like stratospheric ozone flux during early spring (Viezee et al., 1983) or excess hydrocarbons released during bud break (Aneja et al., 1991) could contribute to the observed seasonal variability.

Ambient conditions at Meranges station (1500 m a.s.l.) followed the typical daily pattern of high altitude sites. During the day, the valley floor warms up and the air rises up the slopes of the surrounding mountains (anabatic wind or valley breeze). These winds (blowing from S and W, Fig. 3) transport the ozone produced photochemically in urban areas to the reservoir layer, the highest ozone concentration being reached at mid-afternoon (15:00 local time, Fig. 8). After that, ozone mixing ratios start to decrease very slowly but still remain high over night (Fig. 8), as has been recorded in other high altitude sites (Millán et al., 2000). Indeed, the reservoir ozone layer created the day before can continue to cover high altitude sites the next day (Millán et al., 2000). Katabatic winds (also called mountain breeze and, in this case, blowing from N, Fig. 3), which are usually very gentle (<2 m s$^{-1}$ in Meranges, Fig. 3), keep the reservoir layer almost stagnant, thus maintaining elevated
ozone concentrations during the night. Moreover, NO mixing ratios at Meranges station are so low or even inexist (around 1 ppbv, Fig. 8) that they could hardly contribute to ozone depletion. The diurnal minimum in Meranges takes place in the morning, probably when the onset of anabatic winds occurs, bringing O₃-depleted and/or NO enriched air from the valley or other more urbanized areas to the mountain tops, as has been reported in previous studies (Millán et al., 2000).

Similarly, Gonçalves et al. (2009) found that in the North-Eastern Iberian Peninsula the maximum contributors to ozone surface were net transport and vertical diffusion. High ozone mixing ratios were not produced in situ, but came from horizontally advected flows during the morning and gas-phase chemical contributions. During the afternoon and dusk, vertical advective flows injected pollutants in layers above the atmospheric boundary layer, which accumulated due to stagnant conditions and contributed positively to surface concentrations the following day (Gonçalves et al., 2009).

Annual means of NO₂ mixing ratios recorded by passive methods during 2004–2006 (Fig. 5) and by monitoring in Bellver station since 2004 (data not shown), did not present a statistically significant trend. This is despite the fact that NO₂ emissions have apparently decreased since the mid–1980s in Western and Northern Europe and even in the Mediterranean region, although in the latter the decrease of NO₂ emissions was smaller and it started later than in the rest of Europe (De Leeuw, 2000; Brönnimann et al., 2003).

The daily pattern of NO₂ mixing ratios at Bellver station suggests that local photochemical production of ozone takes place in the morning since NO₂ mixing ratios start to drop precisely when ozone mixing ratios start to increase, coinciding with increasing solar radiation (Fig. 7). Conversely, the low or even inexistent levels of NO₂ and NO recorded at higher altitude, in Meranges (Fig. 8), could indicate again that the variations of ozone mixing ratios in this station are probably a result of net transport and vertical diffusion rather than local photochemical production and/or NO titration.

In the tobacco plants, the percentage of leaf area which was damaged increased with altitude (Figs. 9 and 10) in response to increasing O₃ mixing ratios and likely increases in NO titration with greater altitude (Kaufmann, 1976; Wieser et al., 1999). In effect, there was a postive relationship between damaged leaf area of Bel-W3 and ozone mixing ratios (Fig. 11) which also has been reported in previous studies (Ribas and Peñuelas, 2006). The intense damage response found in these mountain sites is probably because the sensitivity threshold for the Bel-W3 cultivar (40 ppbv, Heggestad, 1991) was frequently exceeded. This was coupled to micrometeorological conditions such as high irradiation or humidity that enhance stomatal conductance and ozone uptake (Kaufmann, 1976; Peñuelas et al., 1999). These results confirm the value of tobacco plants as good biomonitor tools for ozone concentrations and phytotoxicity in the Catalan Pyrenees during summer time whereas the use of passive samplers is probably more appropriate for long-term monitoring of ozone mixing ratios in mountainous areas with hard winter conditions.

It should be highlighted that the AOT40 threshold for plants’ and forests’ protection has been greatly exceeded every year since 1994 in the valley-bottom site, where ozone mixing ratios are on average 37% smaller than in the higher sites. Therefore, the AOT40 for vegetation and forest protection is even more exceeded at high altitudes which, in accordance with recent literature on critical levels (Pleijel, 2000; VanderHeyden et al., 2001), could have negative effects on plant life at high altitude sites in the Pyrenees.

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