

Analysis of tropospheric ozone concentration on a Western Mediterranean site: Castellon (Spain)

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Abstract Ozone dynamics in our study area (Castellon, Spain) is both strongly bound to the mesoscale circulations that develop under the effect of high insolation (especially in summer) and conditioned by the morphological characteristics of the Western Mediterranean Basin. In this work we present a preliminary analysis of ozone time series on five locations in Castellon for the period 1997–2003. We study their temporal and spatial variations at different scales: daily, weekly, seasonally and interannually. Because both the O₃ concentration and its temporal variation depend on the topographic location of the observing station, they can show large differences within tens of kilometer. We also contrast the variation in the ozone concentration with the variations found for meteorological variables such as radiation, temperature, relative humidity and recirculation of the air mass. The link between elevated ozone concentrations and high values of the recirculation factor ($r = 0.7 – 0.9$) shown the importance

of recirculating flows on the local air pollution episodes.

Keywords Ozone time series · Mesoscale circulations · Meteorological variables · Recirculation factor

Introduction

Pollution by ozone is the result of a complex process that involves chemical reactions between nitrogen oxides, volatile organic compounds and oxygen in the presence of solar light. The highest surface ozone concentrations occur mainly in the seasons of the year with greatest insolation and are usually associated with poor-ventilation situations. The meteorological conditions favouring these situations reduce the dispersion of the polluting agents and thus increase the probability that they will react.

Pollution on a local or regional scale is determined by a great number of factors that can be combined into three large groups: orographic, meteorological and precursor sources. The Mediterranean area is located in subtropical latitudes. In the case of Castellon, a strong altitudinal gradient is registered, from 0 to 1,500 m in 100 km. Also characteristic of the zone is the complexity of its topography, abounding in river channels that provide penetration paths for the coastal

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flows and the sea-mountain breeze systems. The different land-use types range from semi-arid to Mediterranean forest zones. Their influence on ozone dynamics is reflected in biogenic emissions, elimination by dry deposition and forcing of the meteorological processes. With respect to source distribution, in the case of Castellon the most extensive population centres and industrial zones are located primarily in the coastal zone.

To characterize the dynamics of pollutants in the Mediterranean basin and to compose a mosaic of the atmospheric circulations involved, the European Commission (EC) supported the following projects: (1) meso-meteorological cycles of air pollution in the Iberian Peninsula (MECAPIP), 1988–1991, intended to document the atmospheric circulations over the Iberian Peninsula (Millan et al. 1992); (2) regional cycles of air pollution in the west central Mediterranean area (RECAPMA), 1990–1991, which extended the characterization from the Atlantic coast of Portugal to Italy (Millan et al. 1997); and (3) south European cycles of air pollution (SECAP), 1992–1995, for the whole of the basin (Millan et al. 1997; Kallos et al. 1998).

These projects have shown that stacked layer systems form along the Spanish Mediterranean coasts, 2–3 km deep and more than 300 km wide, with the most recent layers at the top and the older ones near the sea. These act as a reservoir for aged pollutants to reenter land the next day, and tracer experiments have shown that turnover times are from 2 to 3 days. During the night, part of this system drifts along the coast. Under strong insolation these circulations become large natural photochemical reactors, where most of the NO_x emissions and other precursors are transformed into oxidants, acidic compounds, aerosols, and O_3 (exceeding some EC directives for several months) (Millan 2003; Gangoiti et al. 2001; Millan et al. 1998).

The links between atmospheric circulations from the local, through the regional, to the sub-continental scales have been documented in these European projects. The available information includes the circulation structure, its diurnal evolution and, in minor degree, its seasonal and annual variation.

In this work we present a preliminary analysis of ozone time series for five locations in Castellon. These are located at various altitudes and distances from the coast, and illustrate the observed variability within a 100 km square. The years of the study go from 1997 to 2003. The temporal and spatial variations at different scales: daily, weekly, seasonally and interannually, are examined.

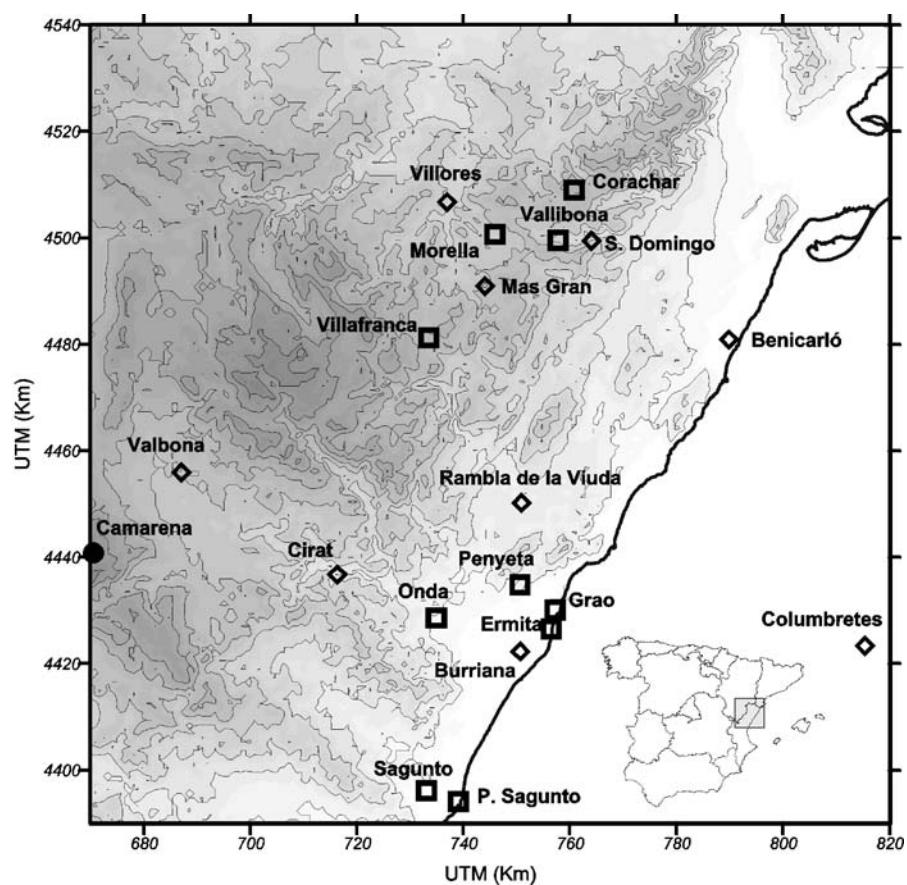
Methodology

Our analysis is based on measurements from the Generalitat Valenciana air pollution monitoring network. Concretely, we have used the data from five monitoring stations: Morella, Vilafranca, Onda, Penyeta, Ermita and Grau. These stations are characteristic of five different location-types in terms of their relative position within the river basin: mountain inland, upper-valley floor, valley floor, height at coast, and coastline, respectively (Millan et al. 1997). Figure 1 shows the location of the monitoring stations. Table 1 lists the sites, their coordinates, and the altitudes. Both meteorological and ozone measurements are made continuously at all sites.

The principal sources of anthropogenic ozone precursors are located in the coastal zone. The largest city is Castellon de la Plana (2 km from Grau), with a population of 147,000 inhabitants, Onda has 20,000 residents. The population density in inland areas is considerably low: Morella and Vilafranca have 2,700 and 2,500 inhabitants, respectively. The highway is located along the coast, and in summer it has an approximate average daily traffic of 20,000 vehicles per day. Around Onda area are located the industries dedicated to the ceramic sector, and close to Grau are placed several chemical industries, one refinery, and a power plant. The main air pollutants emitted are VOCs, NO_x , CO, CO_2 , SO_2 , and particulate matters.

The three stations near the city of Castellon de la Plana (Ermita, Grau and Penyeta) are intended to provide links between ozone concentrations measured near the coast and those inland. Penyeta is located on the side of a steep mountain at some 250 m above the coastal plain. Because

Fig. 1 Location of the monitoring stations. Stations of Morella (mountain inland); Vilafranca (upper-valley floor); Onda (valley floor); Penyeta (height at coast); Ermita and Grau (coastline)



the ground-based nocturnal inversion over this coastal plain in summer was known to be on the order of 100–150 m or less (Millan et al. 1992), it would remain above the stable surface layer during the night.

All calculations are based on hourly averages for the summers (months of June, July and

August) of 1997 to 2003. During this season of the year, enhanced insolation favours photochemical ozone formation; thus, in these months there is a great probability of high ozone concentrations that systematically surpass the thresholds of protection to vegetation and health defined in European Directives.

Table 1 Monitoring sites used in this study

Station	X coordinate (UTM) (km)	Y coordinate (UTM) (km)	Altitude (MSL) (m)	Distance to sea (km)
Ermita	756.4	4,426.5	21.0	1.0
Grau	755.9	4,426.5	2.0	0.0
Penyeta	750.5	4,434.8	250.0	7.0
Onda	734.8	4,428.6	167.0	20.0
Vilafranca	733.9	4,477.9	1,125.0	48.0
Morella	745.7	4,503.2	1,150.0	50.0

Coordinates are on the Universal Transverse Mercator (UTM) grid, Zone 30. MSL indicates above mean sea level.

Results and discussion

Diurnal ozone trends

Figure 2 shows the variation in ozone cycles with orography. This variation is directly linked to the daily ozone-maximum distribution (Fig. 3). The most notable features are the changes in shape from the sites at the coast to those at the mountain tops. At the mountain station (Morella) the concentrations do not drop below 80–90 $\mu\text{g}/\text{m}^3$. The nocturnal maximum is probably due to the fact that the station remains in contact with residual-reservoir layers. These layers may have been formed by orographic and/or deep convective injection (Millan et al. 1997). The high mountain stations may also show a minimum in the morning, at about the same time that a strong rise in ozone is observed at the stations located on the valley floor below. Both of the above are indicative of the development of convective mixing processes along the sun-heated valley walls. These processes include two complementary mechanisms: the mixing of ozone-depleted air from the valley bottom with the layers aloft, and the fumigation to the valley floor of ozone-enriched air from reservoir layers trapped within the valley during the night. The Vilafranca station shows two maxima: the first

due to ozone fumigation from the reserve layers and the second due to the arrival of the breeze with fresh ozone. Vilafranca, unlike Morella, is located in the nitrogen oxide (NO_x)-limited region. During the day it is within the path of the pollutants coming from the coast. At the Onda station a marked cycle is observed, with a diurnal maximum due to local production. At the Penyeta station, located on a high coastal site, a minimum is observed to coincide with the maximum convective activity registered during the arrival of the breeze, and then a sharp maximum during the breeze period. At the coastal stations (Ermita and Grau) a large-amplitude wave is observed, showing maxima in the central part of the day and a nocturnal minimum of nearly zero due to chemical depletion (these stations are close to important anthropogenic NO_x sources).

Figures 4 and 5 shows the maximum ozone frequency during the week. Figure 4 includes all months from January to December for the years 1997 to 2003, whereas Fig. 5 includes only the summer months (June, July and August). These graphs emphasize the different frequency allocation of the maxima for both periods. When we consider the whole year, we observe an increasing tendency as the week progresses, with the weekly maximum occurring on Friday or Saturday. On

Fig. 2 Ensemble averages of the ozone diurnal cycles for June, July and August, 1997, at five stations located at various altitudes and distances from the Spanish Mediterranean coast

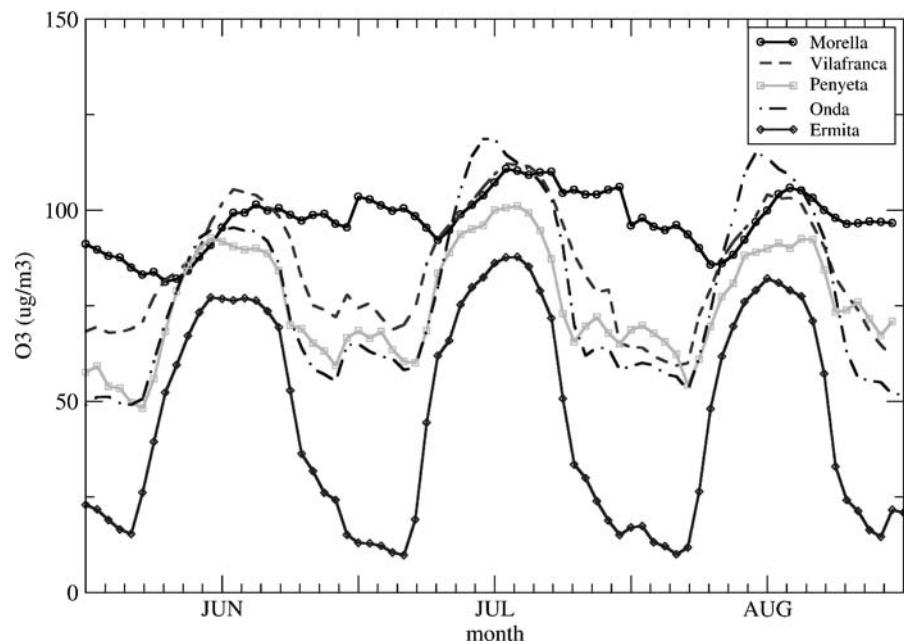
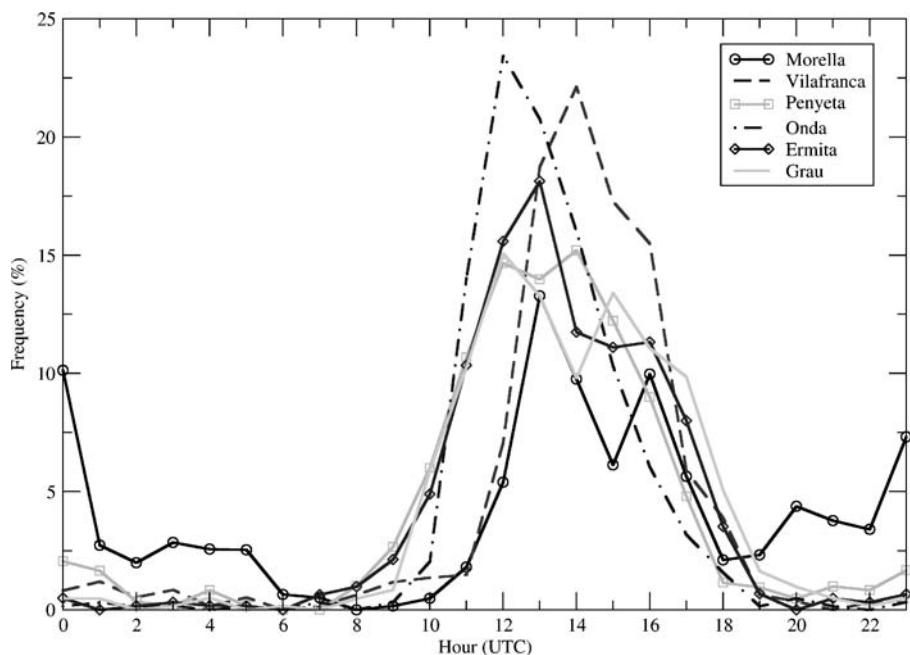


Fig. 3 Daily peak ozone distribution during the summers (June, July and August) of 1997 to 2003



Sunday, we observe a decrease in the frequency, as a result of reductions in primary emissions. The high mountain station (Morella) is the only station showing an increase in maximum ozone frequency on Sunday. When we consider only the summer period (Fig. 5), we also observe the Sunday reduc-

tion in maximum ozone frequency, again with the exception of the Morella station. However, the tendency towards increased ozone peaks as the week progresses is lost in the summer period. Mondays show the maximum frequency, whereas the remaining days show similar frequency values.

Fig. 4 Weekly distribution of peak ozone concentrations from January to December of 1997–2003

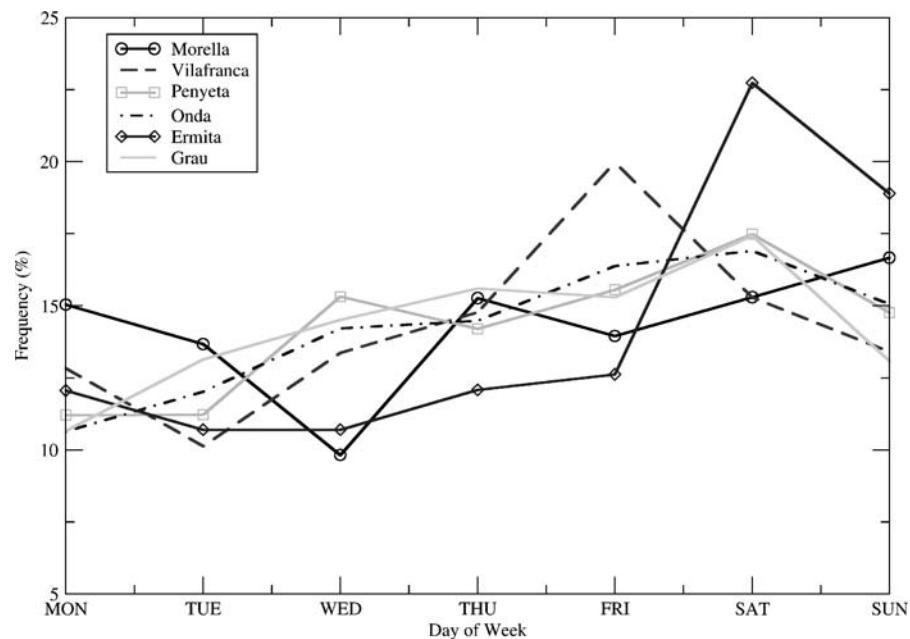
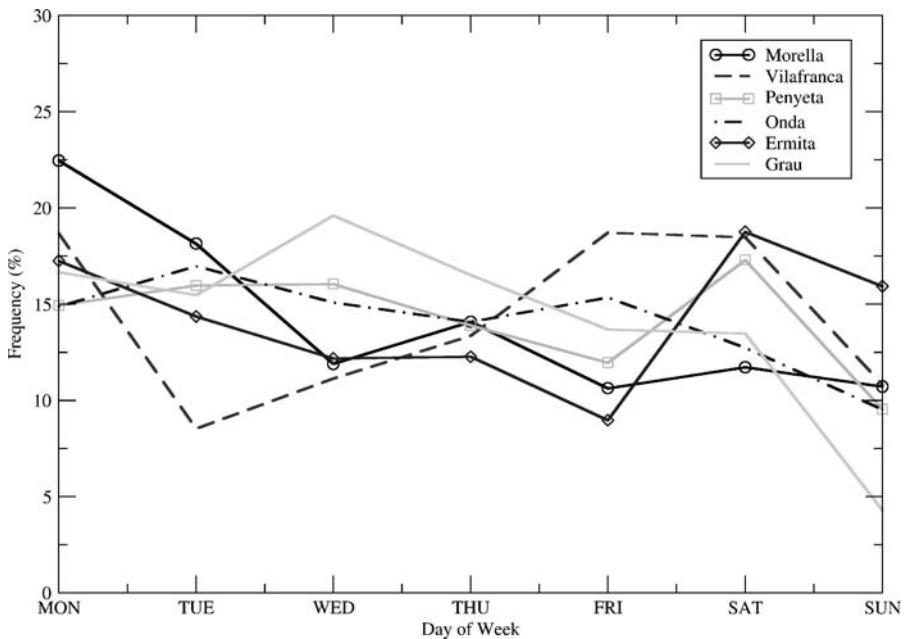


Fig. 5 Weekly distribution of peak ozone concentrations during the summers (June, July and August) of 1997–2003



In the seasonal variation average the appearance of a spring maximum is observed at the coastal stations (Fig. 6). At the stations located inland the spring maximum is secondary, with the main maximum being registered during the central months (summer) of the year. The spring maximum may be explained by the smaller

spatial development of the breeze cell during these months, i.e., levels stay confined relatively close to the production areas (Castell and Mantilla 2005).

In the interannual variation, showed in Fig. 7, the 5 and 98 quantiles and percentiles show no clear tendency; nevertheless, in some years an

Fig. 6 Seasonal variation average of ozone concentrations from January to December of 1997–2001

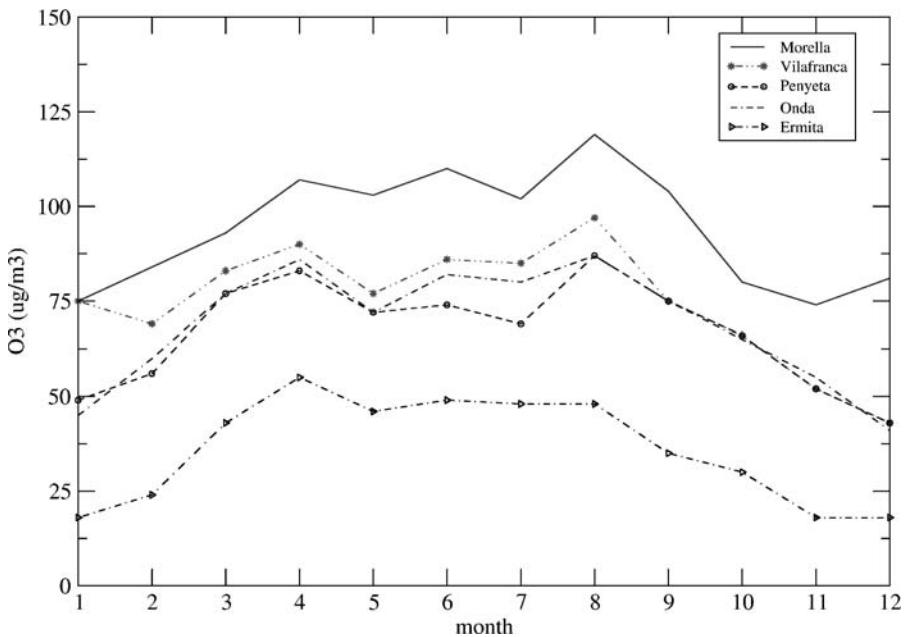
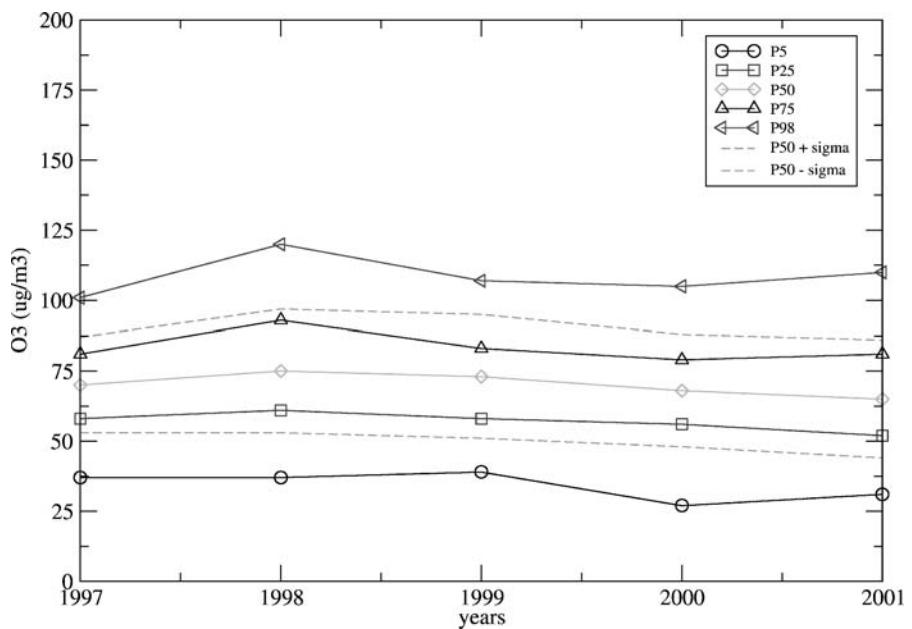


Fig. 7 Interannual variation of ozone concentrations in Penyeta from 1997–2001



increase can be observed in percentile 50 of up to $10 \mu\text{g}/\text{m}^3$. These specific increases can be explained by the meteorological conditions characteristic of each year (years more/less warm, more/less dry, etc.) (Castell and Mantilla 2005).

Effects of meteorological conditions on ozone concentrations

Meteorological conditions play an important role in the formation and destruction of ozone. Millan et al. (2000) provides an interpretation of the diurnal cycles of the averaged wind parameters, that is, direction and speed, and its relation with the O_3 evolution at Castellon for July. They conclude that mesometeorological processes are the dominant cause of the shape of the observed diurnal cycles of O_3 in summer.

In this section we present a preliminary analysis of the correlation between temperature, radiation, relative humidity and recirculation factor, and the daily ozone maximum concentrations in June, July and August, 1997–2003.

Figure 8 shows the correlation between maximum ozone concentrations and maximum temperatures. In general, the ozone concentration increases with increasing temperature; the correlation coefficient is higher for the inland stations

($R = 0.58 – 0.53$) than for the coastal stations ($R = 0.27 – 0.24$). This result supports the notion that ozone formation kinetics intensifies with increasing temperature. Figure 9 shows the correlation between the hourly ground-level ozone concentrations and the eight-hour maximum radiation ($R = 0.37 – 0.31$). Ozone is a photochemical air pollutant, and it is produced in the troposphere from reactions between ozone precursors in the presence of sunlight.

Humidity is another factor that influences ozone formation. Water vapour in the atmosphere

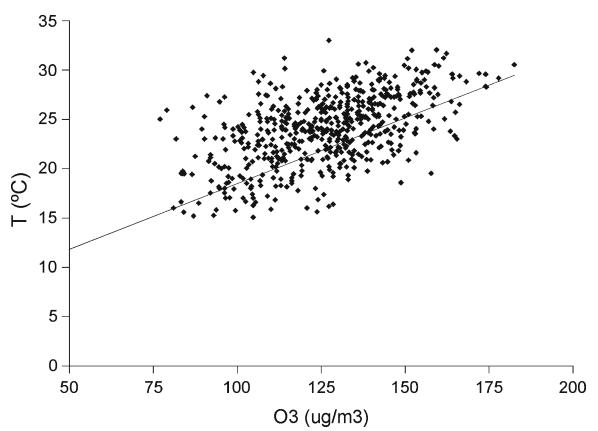


Fig. 8 Ozone concentrations versus temperature in Morella during summer: 1997–2003

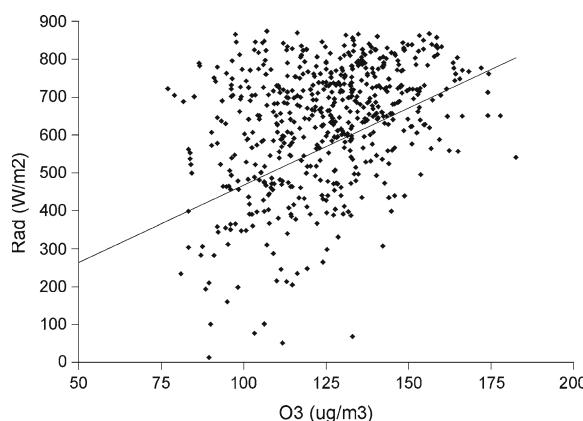


Fig. 9 Ozone concentrations versus radiation in Morella during summer: 1997–2003

can enhance the removal of short-lived and highly reactive radicals (ie., $\text{HO}_x = \text{HO} + \text{HO}_2$), which are important precursors of ozone formation. Some studies have shown that HO_2 decreases dramatically with increasing water vapour concentration, and this is consistent with the reaction: $\text{H}_2\text{O} + 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{H}_2\text{O}$. Figure 10 illustrates the relationship between ozone concentration and relative humidity. We have found that the coefficient correlation is better for the inland stations ($R = -0.46, -0.43$) than for the coastal stations ($R = -0.14, -0.07$).

The fact that correlations at inland stations are better than ones at the coastal stations may be explained by the influence of anthropogenic emissions. Both, the temporal distribution and the

total contribution of human emissions have an impact on maximum ozone. The contribution of human activity is larger in the coastal zone, because the location of most extensive cities, highways and industries, than inland. The inland monitoring stations are mainly influenced by biogenic emissions. Anthropogenic emissions, unlike biogenic ones, aren't strongly influenced by meteorological conditions. Nevertheless, further research is needed before a firm conclusion can be drawn.

In the Western Mediterranean area, high ozone concentrations are often associated with synoptic-scale high-pressure systems and the formation of thermal lows. The low pressure system induces flow convergence at the peninsular scale and forces the sea breeze to flow along the Mijares River for most of the solar day. Figure 11 shows the scatterplot between the recirculation factor and maximum ozone concentrations. The recirculation factor r gives an indication of the presence of local recirculations. When r is equal to 0, straight-line transport has occurred with no recirculation; when r is equal to 1, zero net transport has occurred over the time interval (24 hours in our case), and there has been a complete recirculation in which the air parcel has returned to its origin (Allwine and Whiteman 1994). We found a greater density of days with elevated ozone concentrations between recirculation factors, $r = 0.7 – 0.9$. Millan et al. showed the importance of meso-meteorological cycles and air-mass recirculations in the Western Mediterranean area. Our

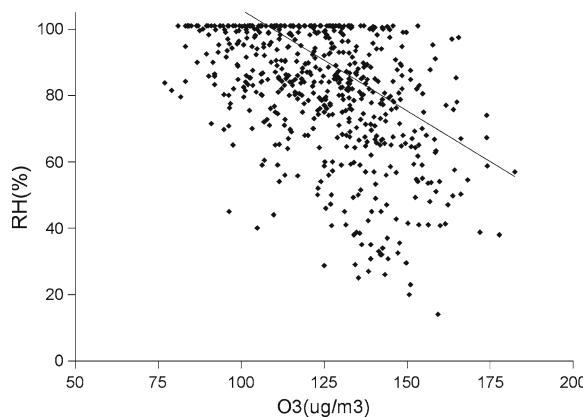


Fig. 10 Ozone concentrations versus humidity in Morella during summer: 1997–2003

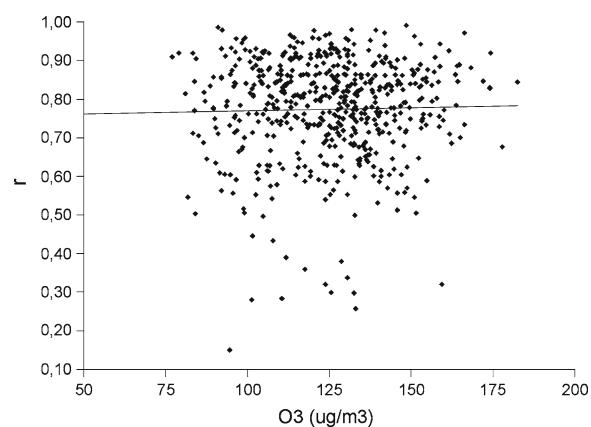


Fig. 11 Ozone concentrations versus recirculation factor in Morella during summer: 1997–2003

results agree with previous studies (Millan et al. 2000; Gangoiti et al. 2001) and support the role of meso-meteorological cycles and air-mass recirculation in Castellon ozone dynamics.

Conclusions

In this work we show how the observed ozone time series depend on the topographic location of the observing station. Both the surface ozone concentration along the day and the temporal allocation of the ozone peak, show large differences in observing stations located in a 100 km square. This means that no single station can be considered representative of the average regional processes.

The correlation between ozone and meteorology is better inland (high mountain and valley) than on the coastal sites. It may be explained by the fact that coastal monitoring stations are strongly influenced by anthropogenic emissions (like big cities, highways and industries), whereas inland sites are not. Human emissions suppose a new variable that affects the ozone cycles independently of the ambient meteorology. However, additional research is needed before a firm conclusion can be drawn.

Elevated ozone concentrations are linked with high recirculation factors. This indicates that local air pollution episodes originate via oscillatory or recirculating flows on the mesoscale.

These results are important in atmospheric dispersion modelling on a Mediterranean coastal site, where it is necessary to take into account the mesoscale processes that can act on inland locations as far as 100 km from the coast. This further emphasises the point that to properly address atmospheric pollution problems in southern Europe, the diffusion-transport scenarios and transformation mechanisms must be well understood at their relevant time and space scales.

Due to the lack of meteorological and ozone vertical profiles, it is not possible to monitor the pollutants transport by the sea breeze and its

injection into the reservoir layers. Future works must include the use of photochemical models that allow to study the ozone behavior in the Mediterranean atmospheric dynamics, both in surface and in height.

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