TRENDS IN OZONE CONCENTRATIONS IN THE IBERIAN PENINSULA BY QUANTILE REGRESSION AND CLUSTERING

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Abstract

In this paper, 10-years of ozone (O_3) hourly concentrations collected over the period 2000–2009 in the Iberian Peninsula (IP) are analyzed using records from 11 background sites. All the selected monitoring stations present an acquisition efficiency above 85%. The changes in tropospheric ozone over the Iberian Peninsula are examined by means of quantile regression, which allows to analyse the trends not only in the mean but in the overall data distribution. In addition, the ozone hourly concentrations records are clustered on the basis of their resulting distributions.

The analysis showed that high altitude stations (> 900 m) have higher background O_3 concentrations (~80 µg.m^{-3}). The same magnitude of background O_3 concentrations is found in stations near the Mediterranean Sea. On the other hand, the rural stations near the Atlantic coast present lower background values (~50-60 µg.m^{-3}) than those of Mediterranean influence. The two sub-urban stations exhibit the lowest background concentrations (~45 µg.m^{-3}). The results of the quantile regression show a very distinct behaviour of the data distribution, the slopes for a fixed quantile are not the same over IP, reflecting the spatial dependence of O_3 trends. Hence the rate of temporal change is not the same for all parts of the data distribution, as implicitly assumed in ordinary regression. The lower quantile (percentile 5) presents higher rates of change than the middle (percentile 50) and the upper quantile (percentile 95). The clustering procedure reveals what has been already detected in the quantile regression. The station with highest rates of decrease on the O_3 concentrations (easternmost station of IP) is isolated and then other clusters are formed among the moderately positive/negative O_3 trends around the IP. The clustering procedure highlighted that the largest trends are found for the lower ozone O_3 values, with largest negative trend at the easternmost station of IP, and also in northern and mainland stations, and an opposite behaviour, with positive O_3 trends, is observed at the Atlantic coast stations.

Keywords: Iberian Peninsula**;** tropospheric ozone; spatial and temporal analysis; quantile regression; cluster procedure

1. INTRODUCTION

Tropospheric ozone (O_3) is a key determinant of the atmospheric oxidation state and a major constituent of photochemical smog which impacts air quality at urban and regional scale. The production of elevated levels of O_3 at ground level is of particular concern because it is known to have adverse effects on human health, vegetation, and a variety of materials (EA, 2010a). There is a high interest in quantifying surface O_3 concentrations and associated trends, as they serve to indirectly quantify the impacts of the anthropogenic precursor reductions and to evaluate the effects of emission control strategies (Tang et al., 2006; Sicard et al., 2009).

There have been a few studies on the analysis of surface O_3 trends in different regions of Europe (Brönnimann et al., 2002, Jenkin, 2008; Sicard et al., 2009). Over the Iberian Peninsula (IP) where high surface O_3 concentrations are monitored each year from April to September (EEA, 2010b), several analyses of surface O_3 concentrations have been carried out. However, they were limited to a single location restricted to a region of the IP and adopting an ordinary regression approach or based on the median/mean and high percentile O_3 analysis (Gimeno et al., 1999; Millán et al., 2002; Ribas and Peñuelas, 2004; Adame et al., 2008).

Observations from background monitoring stations have revealed that baseline surface O_3 concentrations in the northern hemisphere have been increasing over the past three decades (Marenco et al., 1994), with average increases of approximately 0.5–2% per year at northern mid-latitudes (Vingarzan, 2004). The observed increasing trend in baseline O_3 concentrations is believed to be driven by emissions and processing of O_3 precursors on a global scale (Jaffe et al., 2003; Honrath et al., 2004; Derwent et al., 2006, 2007). Although this hemispheric baseline influences O_3 concentrations throughout the IP, the observed concentrations can be further modified by processes occurring on regional- and local-scales, which can both increase and decrease O_3 levels. Therefore such processes occurring on local, regional, and global scales have an influence on whether O_3 air quality standards at a given location are achieved (Jenkin, 2008). Although the progressive control of O_3 precursors emissions -like volatile organic compounds (VOC) and nitrogen oxides (NO_x)- within the European Community since the early 1990s (CEC, 1991) have influenced the magnitude of the O_3 regional- and local- scale effects (Derwent et al., 2003; Jonson et al., 2005; Vautard et al., 2006), the observed O_3 trends is determined from the net trend of the global-, regional- and local-scale effects, the relative contributions of which can vary both spatially and temporally.

Anthropogenic emissions of the main air pollutants across Europe have decreased continuously between 1990 and 2008 in Europe (EEA, 2010a). Reported European emissions of NO_x and NMVOC have both decreased by 39% and 51%, respectively, since 2000. Concerning Spain and Portugal, the O_3 precursor emissions have also been reduced, namely for NO_x (8% and 7%, respectively) and NMVOC (21% and 34%, respectively).

The understanding of the O_3 budget and trends in the troposphere over the IP is required to (a) properly identify the various mechanisms that contribute to the observed hourly average concentration distribution; and to (b) develop and test models capable of simulating and predicting atmospheric chemical and physical processes (Lefohn et al., 2008). It is also important to characterize the changes in the distribution of hourly average O_3 concentrations which provide (a) quantitative feedback on the effects of emission reductions on O_3 concentrations; (b) insights concerning the long-range transport of O_3 outside IP and possible impacts of climate change; and (c) important information on which processes dominate during a specific time of the year and which processes are more likely to influence particular portions of the distribution (Oltmans et al., 2006).

Robust statistical procedures can be applied to investigate the spatial and temporal evolution of the O_3 concentrations over a region from historical datasets. This study adopts the method introduced by Barbosa et al. (2011) which combines quantile regression and clustering procedures in order to better assess the spatial and the temporal evolution of the hourly O_3 measurements over the IP. On the one hand, quantile regression (Koenker and Hallock, 2001) provides the rate of change not only in the mean, as in ordinary regression, but also in all parts of the data distribution. In this sense, the quantile regression quantifies the variability structure of the hourly O_3 concentrations and assesses the changes in the data distribution. On the other hand, cluster analysis is an adequate procedure to spatially characterize the regional variability on the O_3 data and it has been widely used in different analysis of environmental processes (Alonso et al., 2006; Scotto et al., 2009; Barbosa et al., 2011; Carvalho et al., 2011).

This work focuses on investigating the temporal and spatial trends of the hourly surface O_3 concentrations at background environment over the IP for the last decade (2000-2009). The remainder of this paper is laid out as follows. Section 2 discusses the O_3 concentrations acquired at the background monitoring stations used in this study. Section 3 describes the application of the quantile regression approach and the clustering procedure. Results are presented in Section 4. Finally, in Section 5 the results are discussed and main conclusions are summarized.

2. O_3 DATA OVER THE IBERIAN PENINSULA

A total of 11 O_3 monitoring stations within the IP are selected taking into account their background influence and the efficiency data collection (> 85%) during the 10-years period (2000-2009) as shown in Fig. 1 and Table 1. The spatial coverage is suitable over the IP, with two stations located in Portugal and the remaining 9 stations located over Spain.

(Figure 1)

(Table 1)

Ambient O_3 concentrations are reported on an hourly basis and were obtained from the Portuguese Air Quality Database (www.qualar.org) and the EMEP monitoring network (www.emep.int).

Fig. 2 shows the distribution of hourly O_3 concentrations by year. Different groups of stations can be distinguished in terms of background values (median) and minimum/peak values.

(Figure 2)

High altitude stations (> 900 m) (CPB, VIZ and PEN) show high background concentration (~80 $\mu g.m^{-3}$) due to higher O_3 levels in elevated terrains. The same range of background O_3 concentrations are found in stations near the Mediterranean Sea (CCR, ZAR, and TOR). O_3 atmospheric dynamics in the Spanish Mediterranean areas is affected by mesoscale and local meteorological processes but also regional factors, such as (Baldasano et al., 1994, Millán et al., 1997; Toll and Baldasano, 2000; Martin-Vide and Olcina, 2001; Soriano et al., 2001; Pérez et al., 2004): (1) the influence of the Azores high-pressure system, (2) the costal ranges surrounding the Mediterranean coast, (3) the influence of the Iberian and Saharan thermal lows causing weak pressure gradients over the Mediterranean (4) the intense breeze action along the Mediterranean coast favoured by the prevailing low advective conditions, (5) the scarce summer precipitation, and (6) the intense seasonal contrast concerning temperature, humidity and rainfall. All these facts favour the photochemical formation of O_3 and contribute to the accumulation and recirculation of aged air masses which contain O_3. The two rural stations closest to Portugal and located under 506 m of altitude –BAR and SEV – register lower median (~50-60 $\mu g.m^{-3}$) than those of Mediterranean influence, also presenting O_3 peaks (P95) less than 120 $\mu g.m^{-3}$. The NIB station, in the northern IP, also presents low median concentrations along the decade (~50-60 $\mu g.m^{-3}$) due to the influence of large plumes coming from power plants located in northeaster Spain (Pay et al., 2011) containing high NO_x concentration that affects O_3 chemistry in this region. Such episodes happen under the influence of westerly winds which are relatively frequent (Jorba et al., 2004). The two suburban stations (CUS and PP) exhibit the lowest median (~45 $\mu g.m^{-3}$) and the minimum O_3 concentrations (P5) (~ 0 $\mu g.m^{-3}$), explained by the O_3 destruction by NO (emitted by road-traffic and shipping in the urban and suburban areas of Oporto and Lisbon) mainly at nigh-time (Seinfeld and Pandis, 1998).

During the study period the most critical years in terms of O_3 peaks/episodes were 2005 and 2006 for the majority of the stations. The summer period of these two years was characterized by meteorological conditions very favourable for photochemical activity (Monteiro et al., 2005, 2007). The year 2003 was also a particular critical year in terms of photochemical activity (and high O_3 values) due to the occurrence of a strong heat wave over the IP (Ordonez et al., 2010).

3. STATISTICAL METHODS

Quantile regression is a well-defined statistical technique for regression on quantiles rather than regression on the mean. Although it was first introduced in econometrics by Koenker and Basset (1978), quantile regression is being applied in various geoscience contexts (e.g. Koenker and Schorfheide, 1994; Cade and Noon, 2003; Baur et al., 2004; Elsner et al., 2008; Barbosa et al., 2011). We outline here the essential of the quantile regression approach. The starting point is a random variable *Y* with cumulative continuous distribution function $F_Y(y)$ (by definition: FY(y) = P(Y≤y)). The quantile τ is defined as the value $Q_Y(\tau)$ such that P(Y ≤ Qy(τ)) = τ, for 0≤τ≤1. The quantile function $Q_Y(\tau)$ is defined from the cumulative distribution function $F_Y(y)$ as $Q_Y(\tau) = F_Y^{-1}(y)$. Then considering the conditional distribution of Y given X=x, the conditional quantile function Q(Y|X)(τ|x) verifies P(Y ≤ Q(Y|X)(τ|x)|X=x) = τ. Whereas ordinary regression is based on the conditional mean function E(Y|X)=x and minimization of the respective residuals, quantile regression is based on the conditional quantile function and minimization of the sum of asymmetrically weighted absolute residuals $\sum_{i\geq 1}\rho(\tau)(y_i - Q_{(Y|X)}(\tau \mid x = x_i))$, where ρ(.) represents the tilted absolute value function. For further details see Koenker (2005).

The time series clustering procedure proposed to classify the time series of O_3 hourly concentrations based on the corresponding distributions for quantile slopes at lower, middle and upper quantiles is as follows: firstly, for a fixed (but arbitrary) quantile, the algorithm starts with the estimation of the distribution corresponding to quantile slope estimates; second, the corresponding *dissimilarity* matrix is computed. To this extend, an adequate metric between univariate distribution functions is required. In the present setting the weighted L2-Wasserstein distance between two quantile slope distributions is adopted. Finally, a dendrogram based on the application of classical cluster techniques to the dissimilarity matrix is built and that provides the different clusters formed by the distributions of the quantile slopes. In particular, agglomerative hierarchical methods with nearest distance (single linkage), furthest distance (complete linkage) and unweighted average distance (average linkage) are used as grouping criteria. In order to summarise those distributions, the average linkage procedure is applied to obtain dendrograms of slopes for quantiles 0.05, 0.5 and 0.95. Similar conclusions are obtained using the single linkage and the complete linkage methods.

4. RESULTS

In this section, quantile regression is applied for the hourly O_3 concentrations in order to describe the temporal variability of different quantiles of the O_3 distribution over IP. The quantile slopes and corresponding standard errors are derived using the algorithm of Koenker and D'Orey (1987). The clustering procedure is also discussed.

The results for all the stations are shown in Fig. 3, along with the quantile slopes at quantiles 0.05, 0.5 and 0.95, corresponding respectively to the lowest 5%, 50% (median) and 95% of the ordered observations.

(Figure 3)

Several O_3 trends over the last decade can be identified in this group of stations. A significant negative trend is only exhibited by CCR station, especially for lowest quantiles (P5). The same tendency was found by Ribas and Peñuelas (2004) for a coastal station (Begur) in northeastern Spain. CCR is a costal station located in the northeastern extreme of the IP. This site presents strong north-westerly winds (tramontane and mistral) channelled by Pyrenees and Central Massif throughout the Gulf of Lyon. The flow crosses the Carcasone gap into the Mediterranean which can transport new pollutants into the area that are added to local emissions and re-circulated within the coastal breezes at eastern Iberian (Gangoiti et al., 2001). CPB, PEN – located in the northern Spanish plateau – and SEV show a slightly negative slope, mainly for the lower quantiles. BAR and ZAR monitoring sites don't show any significant trend for the three quantiles.

By contrast, the NIB coastal station in the northern IP presents the largest positive trends, even larger for lower concentration (P5). Similar trends are found in TOR and VIZ, sited under the Mediterranean influence, and in a lesser extend at the two suburban stations at Oporto and Lisbon cities (CUS and PP, respectively).

A more complete description of the quantile regression results is displayed in Fig. 4 which displays the quantile slopes and the corresponding standard errors computed for quantiles 0.1 to 0.9 in steps of 0.02.

(Figure 4)

Fig. 4 clearly shows a distinct pattern for the different monitoring sites. However, there are similarities between specific stations in terms of the sign and the distribution over the different quantiles. CCR shows the highest negative slopes over all the analysed sites (from -28 to -19 $\mu g.m^{-3}$/decade), with a higher decrease observed for the lower quantiles. A negative slope over the all ranges of concentrations is also registered for the north mainland stations - CPB, SEV and PEN - with similar magnitudes (around -5 and -10 $\mu g.m^{-3}$/decade) of the quantile distribution pattern. A slight negative slope (> -2.5 $\mu g.m^{-3}$/decade) is also verified for ZAR and BAR, but only for the lower quantiles.

On the opposite, the Atlantic coastal stations - NIB, CUS and PP - have positive slopes over the all concentrations range with the lower increasing at a much faster rate than the middle and upper values. Besides a similar quantile distribution, the magnitude of the slope is significantly different, higher for NIB (> 18 µg.m^{-3}/decade) and lower for CUS and PP (~ 5-15 µg.m^{-3}/decade). Positive slopes are also found for the VIZ and TOR stations (4-12 µg.m^{-3}/decade), both presenting specific and unique quantile distribution.

For all cases the derived slopes vary with the quantiles and are distant to the original ordinary least squares slope, indicating that the distribution of the ozone values is not symmetric and the rate of change is not the same for all parts of the data distribution (lower, middle and upper quantiles behave differently).

In summary over the last decade a group of stations – CCR, CPB, ZAR, BAR, SEV and PEN – registered a decrease mainly on the lower quantiles of O_3 data distribution which reflect the minimum (nocturnal) values over these areas. On the opposite, the rest of the monitoring sites – NIB, PP, CUS, TOR and VIZ – exhibit a high positive slope on these lower quantiles, indicating an increase over the background values of ozone.

Furthermore, the results of the clustering procedure, together with the spatial representation of the quantile slopes, are shown in Fig. 5.

(Figure 5)

The dendrogram for the lower quantile (P5) clearly discriminates three groups: stations with larger negative slopes, ≅ - 28 µg.m^{-3}/decade (CCR), slight negative slopes (BAR, SEV, CPB, PEN and ZAR) and the remaining stations with positive slopes (NIB, PP, CUS, TOR, VIZ). These results corroborate the previous analysis, namely in what concerns the different trend on the background ozone values registered over Iberian Peninsula. The second cluster, with positive slopes, further distinguishes the station with the highest slope, > 18 µg.m^{-3}/decade (NIB) from the other stations. The third cluster, with negative slopes, further subdivides into sites with moderate slopes and stations with very small or non-significant trends (BAR). A similar pattern is found in the dendrogram for the median quantile (P50), with the same groups identified.

The dendrogram for the upper quantile (P95) continues to distinguish the CCR station with the highest negative slopes, > -20 µg.m^{-3}/decade. Within the remaining stations, and differing from the previous dendograms, the major subdivision clusters include (1) the rural stations with positive trend (TOR, NIB and VIZ) and (2) all the other stations with negative slopes and the two suburban stations. This last cluster is then subdivided into two clusters of slight/moderate slopes (ZAR, CUS, BAR and PP) and a cluster of stations with high absolute negative slopes, typically < - 4 µg.m^{-3}/decade (SEV, PEN and CPB).

5. DISCUSSSION AND CONCLUSIONS

Quantile regression and clustering analysis are applied to study changes in hourly O_3 data over the Iberian Peninsula on the last decade (2000-2009). Ozone data was collected from 11 background monitoring stations, spatially distributed along the IP, characterized by different background values that goes from 30 $\mu g.m^{-3}$ (suburban stations on the coast of Portugal) to 80 $\mu g.m^{-3}$ (stations located in centre and east of IP).

Quantile regression allows computing trends at different quantiles of the O_3 data distribution within a well-defined statistical framework. In addition, the classical clustering procedure allows summarising the resulting distributions of sample quantile slopes. As in ordinary regression, the slopes for a fixed quantile are not the same over IP, reflecting the spatial dependence of O_3 trends. The results for all monitoring sites show different slopes for the 5%, 50% and 95% percentiles, indicating a different rate of temporal change for all parts of the data distribution, as implicitly assumed in ordinary regression. Lower (P5), middle (P50) and upper (P95) quantiles behave differently, with the lower quantiles of O_3 data distribution increasing/decreasing at a much faster rate than the middle and higher quantiles.

For example, the CCR station located in the eastern extreme of IP, under influence of different climatic patterns and topographic features, exhibit a very distinct behaviour, with a strong negative trend (< -20 $\mu g.m^{-3}$/decade) over all the data distribution, with a higher decrease observed for the lower quantiles (background values) (~ -28 $\mu g.m^{-3}$/decade). CPB, SEV and PEN – located in the interior north part of IP – show a slight negative slope mainly for the lower quantiles (-10 $\mu g.m^{-3}$/decade). On the other hand, a positive slope (8-18 $ug.m^{-3}$/decade) can be identified for the stations – NIB, CUS and PP – sited over the Atlantic Ocean coast and also TOR and VIZ (4-12 $\mu g.m^{-3}$/decade), sited over the Mediterranean influence, and mainly on the lower quantiles of O_3 data distribution (background values). This larger trend in the lower quantiles than in the central and upper part of the data distribution was not found in studies conducted over North America where higher hourly average O_3 concentrations decrease faster than the mid- and lower-values (Lefohn et al., 2008).

The analysis of the clusters for different quantiles reflects the differences existent mainly between the lower/middle and the upper quantile. The dendrograms for the lower and median clearly discriminate three groups: stations with larger negative slopes (CCR), slight negative slopes (BAR, SEV, CPB, PEN and ZAR) and the remaining stations with positive slopes (NIB, PP, CUS, TOR, VIZ). The dendrogram for the upper quantile displays a distinct picture: continues to distinguish the CCR station with the highest negative slopes, but the remaining stations are classified in several sub-clusters with minor significance. In fact, the minor gradient of spatial variability occurs at the 95% quantile, with slopes ranging from -8 $\mu g.m^{-3}$/decade to 8 $\mu g.m^{-3}$/ decade.

In summary, this complementary analysis pointed out that the largest trends are found for the lower O_3 values, with the largest negative trend at the easternmost station of the IP (CCR), and also in northern and mainland stations (BAR, SEV, CPB and PEN), and an opposite behaviour is detected at the Atlantic coastal stations (NIB, CUS and PP) with positive O_3 trends.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Portuguese 'Ministério da Ciência, da Tecnologia e do Ensino Superior' for the BIOGAIR (PTDC/AAC-AMB/103866/2008) project, for the Ph.D grant of Isabel Ribeiro (SFRH/ BD/60370/2009) and the post-doc grant of Alexandra Monteiro (SFRH/BPD/63796/2009). The acknowledge is extended to the CRUP and the Ministerio de Ciencia e Innovación of Spain by the support of the Integrated Action E 122-10/PT2009-0029. The Spanish Ministry of Science and Innovation is also thanked for the Formación de Personal Investigador (FPI) doctoral fellowship held by María Teresa Pay (CGL2006-08903).

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Table captions

Table 1. Selected O_3 background monitoring stations over the IP.

Figure captions

Figure 1. Map of the IP showing the locations of the background monitoring stations considered in the present analysis (Table 1). The bullet size indicates the altitude and the round/square shape the type of the background station (rural/suburban).

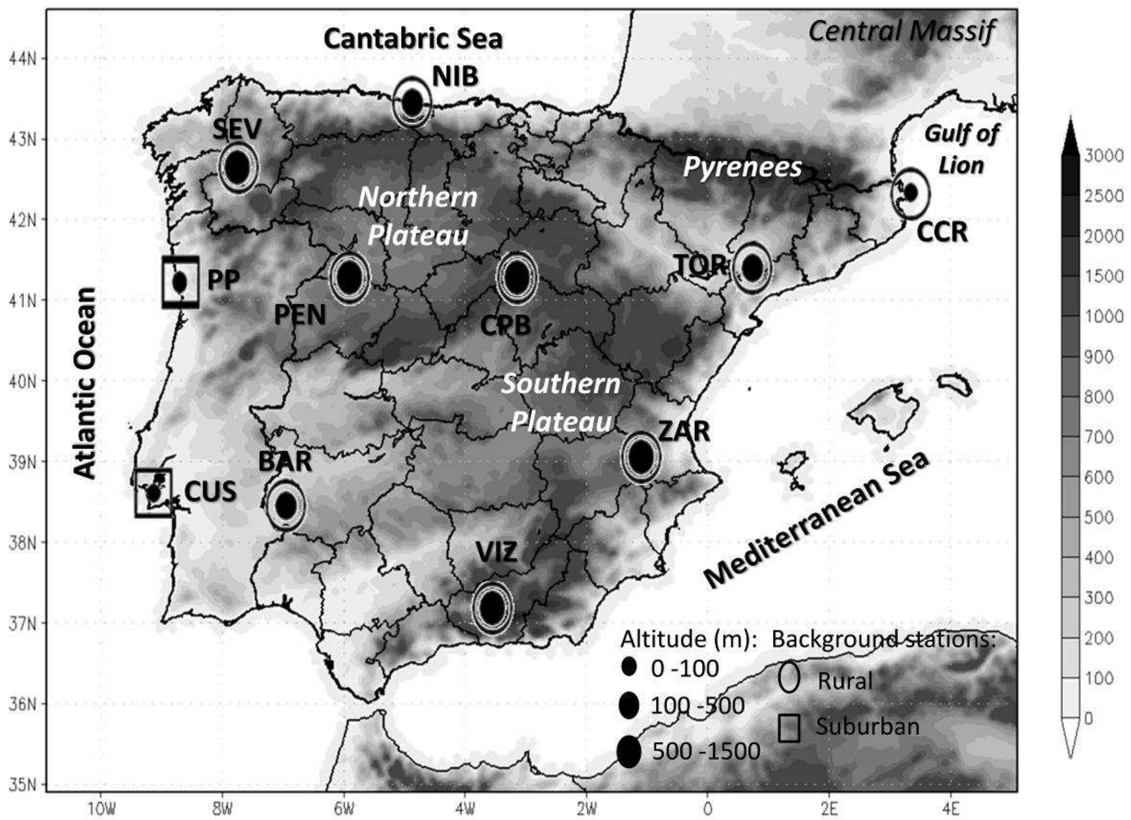
Figure 2. Whisker plots of the hourly O_3 concentrations, measured at the selected sites over the IP, depicting the median (P50), the P5-P95 range and the non-outliers range.

Figure 3. Time series of hourly O_3 concentrations changes per decade ([$\mu g.m^{-3}$]/decade) (solid grey line) and trends for quantiles 0.05 (dashed line), 0.5 (solid line) and 0.95 (dotted line).

Figure 4. Quantile slopes (O_3 concentration [$\mu g.m^{-3}$]/decade) and corresponding standard errors for the selected group of stations. The horizontal dashed line represents the usual ordinary least squares slope.

Figure 5. Dendrogram for 5%, 50% and 95% quantile slopes (right) and the spatial representation of the quantile slopes (left).

Figure1



Cantabric Sea
Central Massif
NIB
SEV
Gulf of Lion
Pyrenees
Northern Plateau
CCR
PP
TOR
PEN
CPB
Atlantic Ocean
Southern Plateau
ZAR
BAR
CUS
Mediterranean Sea
VIZ
Altitude (m):
0 -100
100 -500
500 -1500
Background stations:
Rural
Suburban
44N
43N
42N
41N
40N
39N
38N
37N
36N
35N
10W
8W
6W
4W
2W
0
2E
4E
3000
2500
2000
1500
1000
900
800
700
600
500
400
300
200
100
0

Figure2

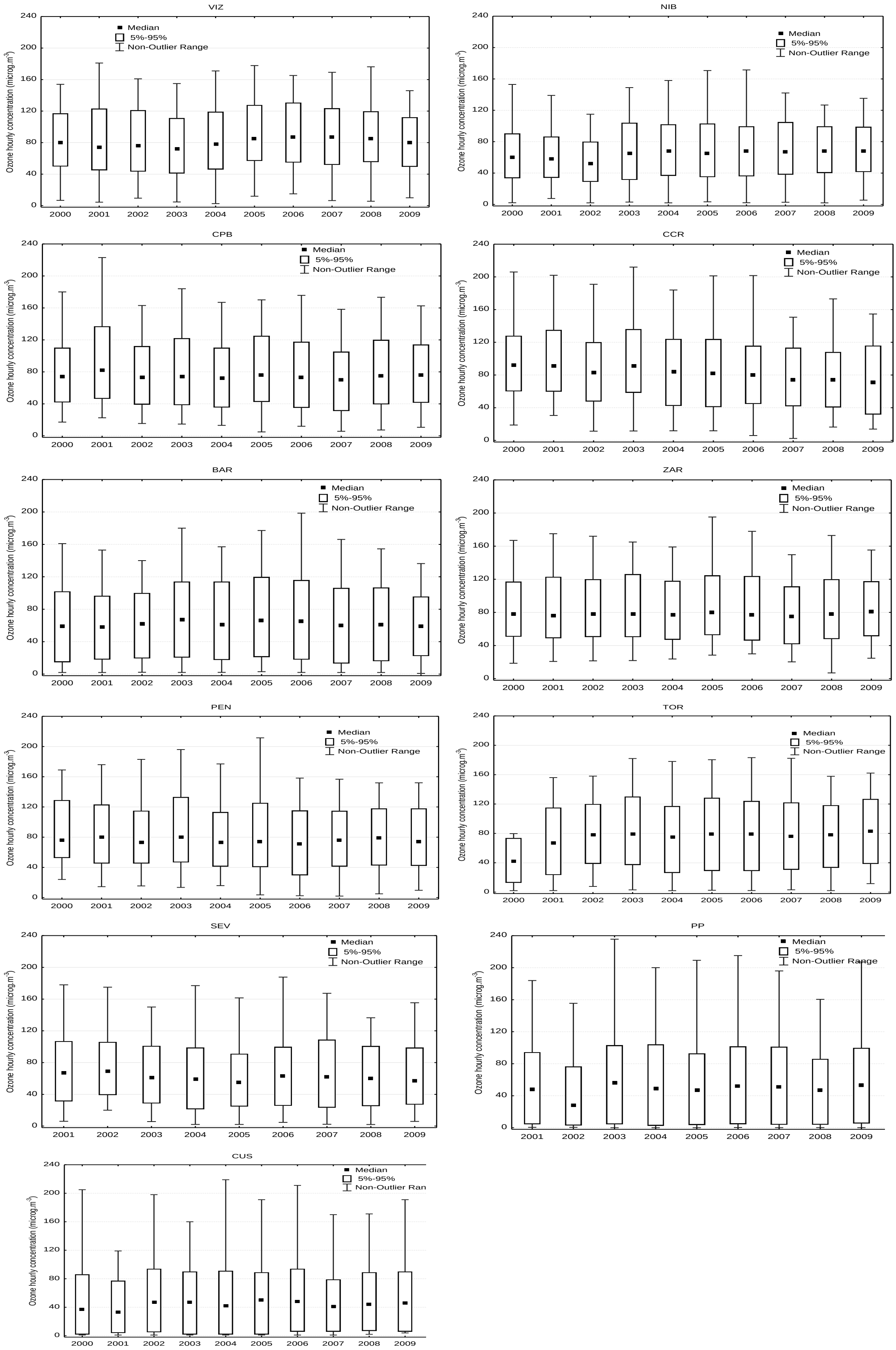
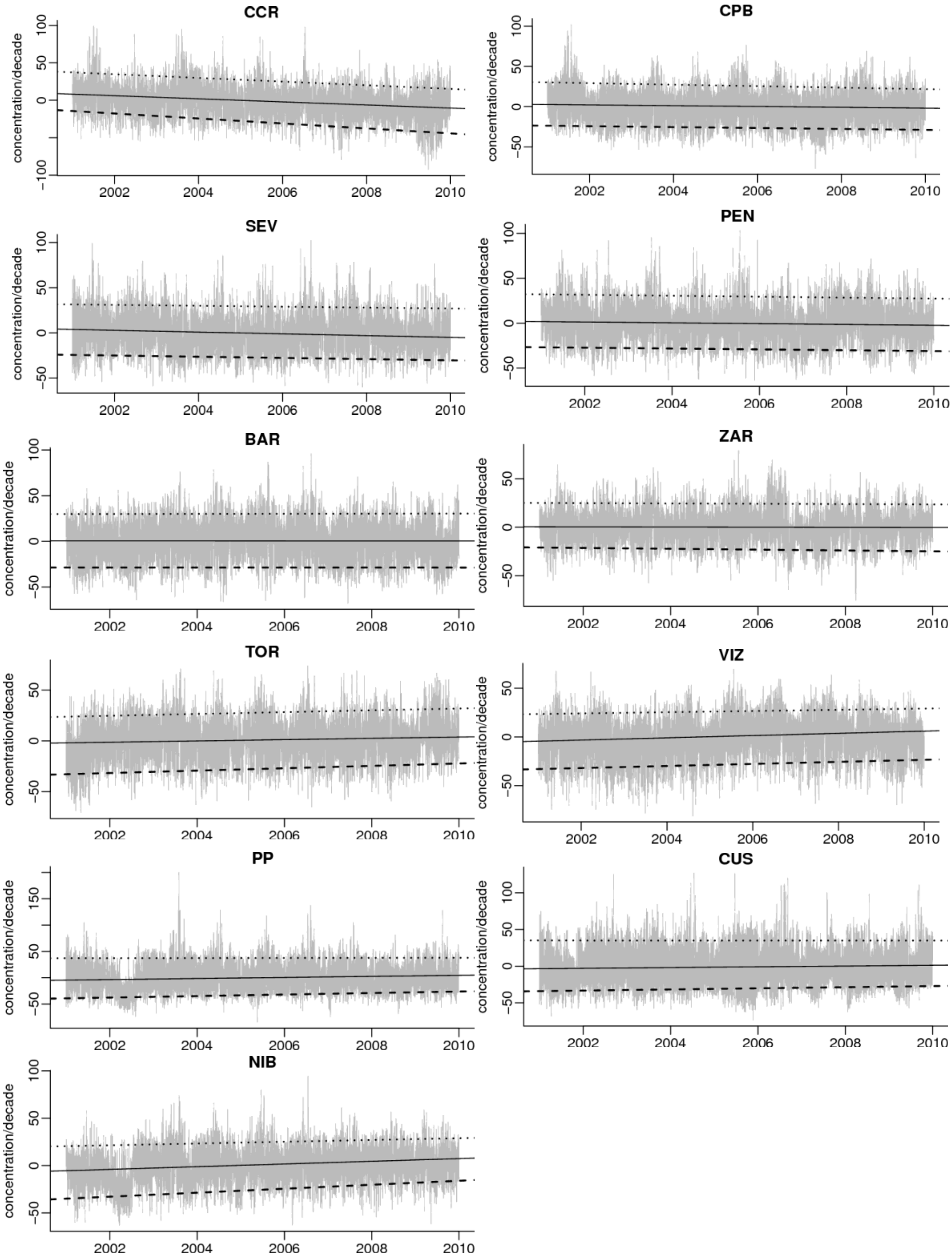

VIZ
NIB
CPB
CCR
BAR
ZAR
PEN
TOR
SEV
PP
CUS
Median
5%-95%
Non-Outlier Range
Ozone hourly concentration (microg.m-3)
240
200
160
120
80
40
0
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009

Figure3



CCR
CPB
SEV
PEN
BAR
ZAR
TOR
VIZ
PP
CUS
NIB
concentration/decade
2002
2004
2006
2008
2010

Figure4

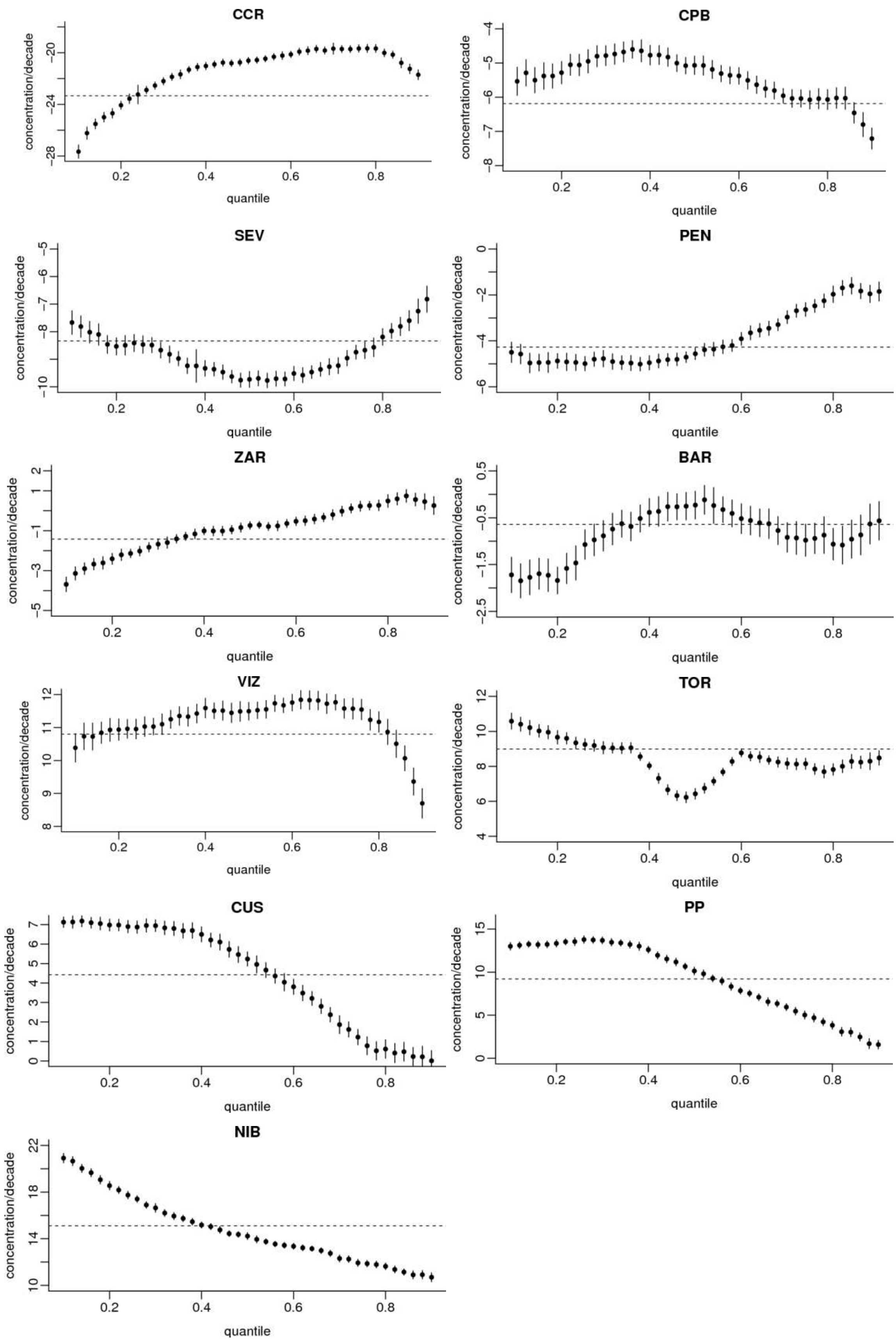

CCR
concentration/decade
-28
-24
-20
0.2
0.4
0.6
0.8
quantile
CPB
-8
-7
-6
-5
-4
SEV
-10
-8
-7
-6
-5
PEN
-6
-4
-2
0
ZAR
-5
-3
-1
1
2
BAR
-2.5
-1.5
-0.5
0.5
VIZ
8
9
10
11
12
TOR
4
6
8
10
12
CUS
0
1
2
3
4
5
6
7
PP
0
5
10
15
NIB
10
14
18
22

Figure5

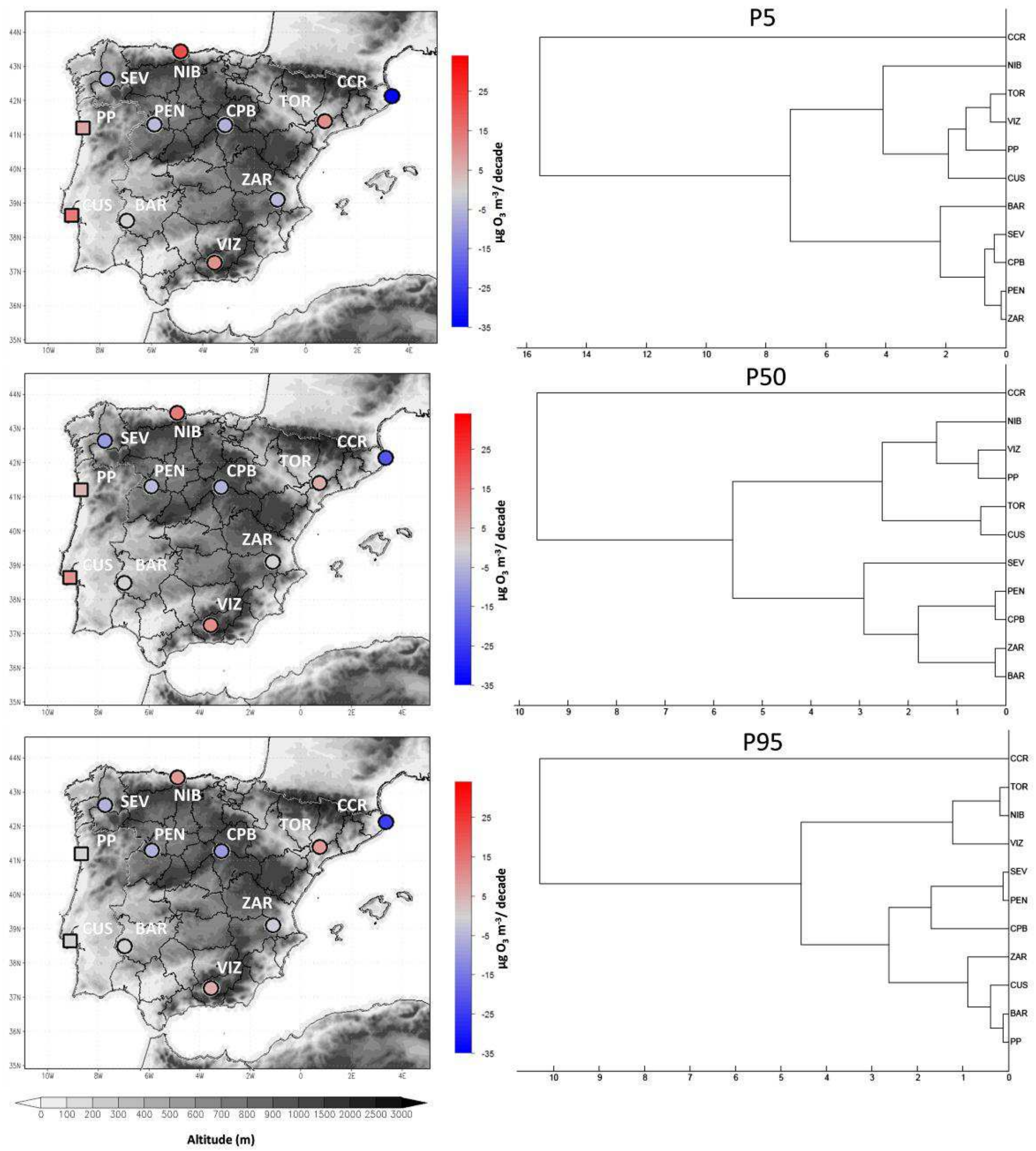

P5
P50
P95
CCR
NIB
SEV
PP
PEN
CPB
TOR
ZAR
CUS
BAR
VIZ
µg O3 m-3/ decade
Altitude (m)

Table1

Click here to download Table: Table 1.doc

Code	Station name	Country	Lat	Lon	Type	Data collection (%)	Altitude (m)
CUS	Custóias	Portugal	41.21	-8.65	Suburban	89.2%	100
PP	Paio Pires	Portugal	38.63	-9.08	Suburban	89.3%	46
VIZ	Víznar	Spain	37.23	-3.53	Rural	97.2%	1265
NIB	Niembro	Spain	43.44	-4.85	Rural	97.6%	134
CPB	Campisábalos	Spain	41.28	-3.14	Rural	95.5%	1360
CCR	Cabo de Creus	Spain	42.32	3.32	Rural	96.6%	23
BAR	Barcarrota	Spain	38.48	-6.92	Rural	97.0%	393
ZAR	Zarra	Spain	39.08	-1.10	Rural	96.8%	885
PEN	Peñausende	Spain	41.28	-5.87	Rural	91.9%	985
TOR	Els Torms	Spain	41.40	0.72	Rural	89.7%	470
SEV	O Saviñao	Spain	42.64	-7.71	Rural	85.0%	506