Article

Surface Ozone Pollution: Trends, Meteorological Influences, and Chemical Precursors in Portugal

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Abstract: Surface ozone (O_3) is a secondary air pollutant, harmful to human health and vegetation. To provide a long-term study of O_3 concentrations in Portugal (study period: 2009–2019), a statistical analysis of ozone trends in rural stations (where the highest concentrations can be found) was first performed. Additionally, the effect of nitrogen oxides (NO_x) and meteorological variables on O_3 concentrations were evaluated in different environments in northern Portugal. A decreasing trend of O_3 concentrations was observed in almost all monitoring stations. However, several exceedances to the standard values legislated for human health and vegetation protection were recorded. Daily and seasonal O_3 profiles showed high concentrations in the afternoon and summer (for all inland rural stations) or spring (for Portuguese islands). The high number of groups obtained from the cluster analysis showed the difference of ozone behaviour amongst the existent rural stations, highlighting the effectiveness of the current geographical distribution of monitoring stations. Stronger correlations between O_3, NO, and NO_2 were detected at the urban site, indicating that the O_3 concentration was more NO_x-sensitive in urban environments. Solar radiation showed a higher correlation with O_3 concentration regarding the meteorological influence. The wind and pollutants transport must also be considered in air quality studies. The presented results enable the definition of air quality policies to prevent and/or mitigate unfavourable outcomes from O_3 pollution.

Keywords: cluster analysis; meteorological influence; Multiple linear regression; NO_x influence; Pearson's correlation; rural trends; surface ozone

1. Introduction

With the constant increase of air pollutants emissions since the Industrial Revolution, an increase of ozone (O_3) near the Earth's surface has been observed [1–3]. This pollutant is a powerful oxidant, affecting human health by causing respiratory and cardiovascular diseases [4]. It also affects vegetation and ecosystems, leading to crop yield and biodiversity losses [5,6]. A total value of 769.2 billion USD loss equivalent to decreases in agricultural production and the occurrence of respiratory diseases and mortality could be ascribed to O_3 exposure in China [7].

O_3 is a secondary pollutant resultant of the reaction between nitrogen oxides (NO_x) and volatile organic compounds (VOCs) released to the atmosphere from natural and (mostly) anthropogenic activities [1]. The photochemical regime for surface ozone production determines the sensitivity of O_3 to anthropogenic sources. Usually, urban and suburban zones are VOC-limited due to higher levels of NO_x emissions, while less-populated zones (rural sites) are NO_x-limited [8,9]. Domínguez-López et al. [10] analysed the effect of NO_x (NO_2 and NO) concentrations in surface ozone at different locations through a spatial and temporal variation study. An opposite daily variance was observed between O_3, NO, and NO_2 concentrations in urban and suburban areas. Maximum ozone concentrations

were observed in the early afternoon, while NO_x concentrations usually achieve two peaks (early morning and late afternoon). In rural sites, no hourly peak O_3 or NO_x was observed. Sun et al. [11] showed that rural sites presented O_3 levels (approximately) 30 µg m^{-3} higher than urban regions in the study period of 1990–2019. Therefore, rural and remote areas are the object of many studies, as the highest ozone levels are found there [12,13]. Several factors (such as higher average temperatures and usually lower NO_x emissions) lead to a more significant accumulation of this pollutant in these areas. There is also evidence of the influence of other chemical air pollutants in O_3 tropospheric levels, such as anthropogenic aerosols, that can affect O_3 photolysis rates directly (through earth radiation scattering) and indirectly (due to the formation of clouds), leading to a weaker surface insolation [14,15]. Li et al. [9] found that the increase of O_3 concentrations (predicted due to the decrease in NO_x emissions) was in fact generated by the abrupt decrease in $PM_{2.5}$, resulting in a reduction of aerosols as a sink of HO_2, stimulating the production of this secondary pollutant. O_3 is known for its complex formation, depending on many variables. In addition to chemical precursors, meteorological variables are also considered in studying and predicting ozone levels. In different parts of the globe, Fang et al. [16] and Afonso and Pires [17] reached the same results through correlation analysis: ozone shows a positive correlation with temperature, meaning it increases with the increase of this meteorological parameter, and the opposite with relative humidity, that shows a negative correlation with O_3. Other variables that can lead to the formation or elimination of surface O_3 are air pressure, wind speed, and direction. The same authors also concluded that O_3 has a negative correlation with local air pressure and a positive correlation with wind speed. Being a pollutant resultant of a radiation-induced chemical reaction, O_3 shows higher levels with clear skies, which is also related to the presence of anticyclones. The association of O_3 concentrations with different weather conditions is more detailed in Domínguez-López et al. [10].

In Portugal, surface O_3 pollution has been characterised in many studies [17–21], especially in the northern [17,22–24] and rural regions [13,25,26]. To complete the study area with more recent data and improve O_3 trends' understanding in Portugal, this study aims to (i) determine the evolution of O_3 levels in Portuguese rural stations, focusing on exceedances to legally imposed levels for human and vegetation protection; (ii) compare the relationship between the O_3 concentrations and one of its precursors (NO_x) for different environments; and (iii) evaluate the effect of meteorological conditions in ozone concentrations. This study presents a long-term characterisation (data from more than 10 years) of O_3 concentrations from different environments, including regions in which no similar study was performed yet. In addition, the statistical models were applied to explanatory variables that were selected based on the knowledge of the chemical reactions of O_3 production. This integration enables better performance in predicting O_3 concentrations, allowing, in advance, to prevent and/or mitigate possible unfavourable outcomes.

2. Materials and Methods

2.1. Ozone Concentration Analysis at Rural Stations

For a better understanding of the trends and levels of surface ozone at rural sites, the study period 2009 to 2019 was selected. Table 1 represents the geographical information of the 15 existing rural stations [27]. The minimum distance to the seashore was estimated using a tool available on Google Earth that allows measuring the distance between two points. Figure S1 presents the map with the geographical distribution of the rural sites.

The statistical analyses were performed only for O_3 concentrations recorded at stations with a monitoring efficiency higher than 75%. The temporal trend of O_3 concentrations was assessed by determining the annual average concentration for each station. The exceedances to all thresholds presented in the current legislation were determined: (i) alert (240 µm m^{-3}) and information (180 µm m^{-3}) threshold, (ii) target value for human protection (120 µm m^{-3}), and (iii) AOT_{40}, representative of vegetation protection, as a target value (8000 µg m^{-3} h) and a long-term goal (6000 µg m^{-3} h) [28]. The data collected at

four rural sites from different regions in Portugal were then used to characterise the spatial variability of O_3 concentrations. Histograms with density functions and violin plots were plotted in Python.

Table 1. Geographical coordinates, altitude, and minimum distance to the seashore of the existing rural sites.

Monitoring Stations		Geographical Coordinates	Altitude (m)	Minimum Distance to the Seashore (km)
CH	Chamusca	39°21′15″ N 08°28′03″ W	143	58.5
CR	Cerro	37°18′45″ N 07°40′43″ W	300	21.1
DN	Douro Norte	41°22′17″ N 07°47′27″ W	1086	78.4
ER	Ervedeira	39°55′28″ N 08°53′34″ W	68	4.5
FA	Faial	38°36′18″ N 28°37′53″ W	310	0.7
FD	Fundão	40°13′59″ N 07°17′58″ W	461	133.6
FM	Fornelo do Monte	40°38′39″ N 08°06′00″ W	731	53.4
FP	Fernando Pó	38°38′14″ N 08°41′30″ W	57	25.2
LR	Lourinhã	39°16′48″ N 09°14′04″ W	143	7.6
ML	Minho-Lima	41°48′08″ N 08°41′38″ W	777	14.2
MOV	Montemor-o-Velho	40°12′08″ N 08°40′08″ W	14	17.9
MV	Monte Velho	38°04′37″ N 08°47′55″ W	53	1.2
SN	Sonega	37°52′16″ N 08°43′26″ W	235	1.4
ST	Santana	32°48′28″ N 16°53′11″ W	0	125.1
TR	Terena	38°36′54″ N 07°23′51″ W	187	125.1

Cluster analysis (CA) was applied to the rural stations to evaluate the representativeness of the stations with local O_3 measurement. This analysis aims to group monitoring sites in the same class/cluster according to the observed behaviour (daily concentration fluctuation) of collected O_3 data. A hierarchical clustering method was used, generating solutions with 1 to n clusters. Ward's minimum variance method was used to determine the cluster distance. A dendrogram (or tree diagram—graphical representation of hierarchical CA) was determined for each year. Based on the obtained dendrograms, a matrix of relative frequencies was used to pair each monitoring site in clusters, using measured O_3 concentrations. This matrix enables the definition of the number of different O_3 behaviours in the studied remote areas. Daily profiles of O_3 concentrations were determined for each group of monitoring sites and the daily distribution of the daily maximum values using Microsoft Excel Macros developed by the authors.

2.2. O_3 and NO_x Relationship

For an evaluation of the relationship between O_3 and its chemical precursor (nitrogen oxides, NO, and NO_2), urban (Ermesinde-Valongo, EV), suburban (Mindelo-Vila do Conde, MD), and rural (Douro Norte, DN) stations were selected (see Figure 1). Considering data availability (O_3 and its chemical precursors monitoring efficiency close or higher than 75% for the selected monitoring stations), the studied period was 2019. A correlation matrix (Pearson's Correlation—PC) was obtained with a O_3, NO_2, NO, and NO_2/NO ratio for each monitoring station. Multiple linear regression (MLR) was applied to better understand the NO_x influence in O_3 production. The method aims to develop a linear model to predict the output variable (Y) with several predictor ones (X_i), having each one a regression coefficient (b_i, $i = 1, n$) with b_0 being the Y-intercept, as shown in Equation (1).

$$Y = b_0 + \sum b_i X_i \tag{1}$$

The statistical significance of correlation coefficients and MLR parameters was evaluated by applying a *t*-test with a significance level of 5%.
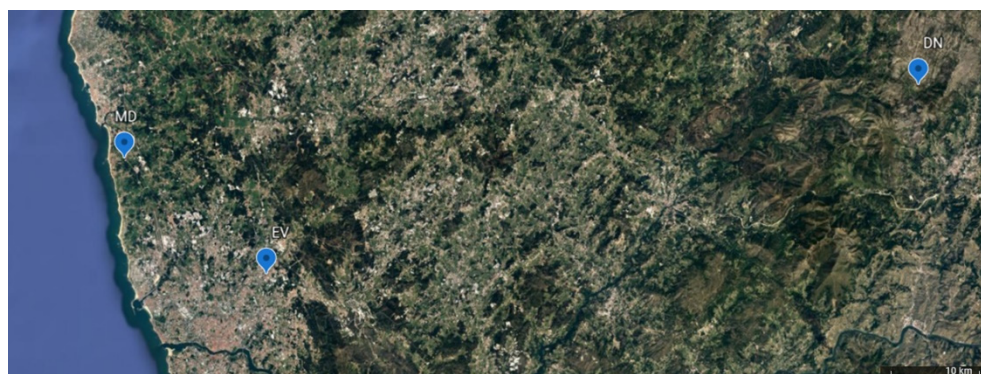
Figure 1. Geographical distribution of O$_3$ monitoring stations EV (urban), MD (suburban), and DN (rural).

2.3. Meteorological Data and O$_3$ Relationship

A similar analysis was performed to assess the effect of meteorological conditions on O$_3$ concentrations using data collected at Pedras Rubras/Aeródromo EMA (Automatic Meteorological Station) and the O$_3$ of Meco-Perafita (MP) and VNTelha-Maia (VNT), which are both suburban stations (Figure 2). The data evaluated corresponds to 2015 (the year in which selected monitoring stations presented a monitoring efficiency close to or higher than 75%). The meteorological data evaluated are mean air pressure (P, in hPa), mean air temperature (T, in °C), relative humidity (RH, in %), wind direction (WD, in degrees), wind speed (WS, in m/s), and solar radiation (SR, in kJ/m^2). The data was provided by the national meteorological, seismic, and oceanographic organisation IPMA (Instituto Português do Mar e da Atmosfera, website: https://www.ipma.pt/en/index.html, accessed on 15 March 2021).
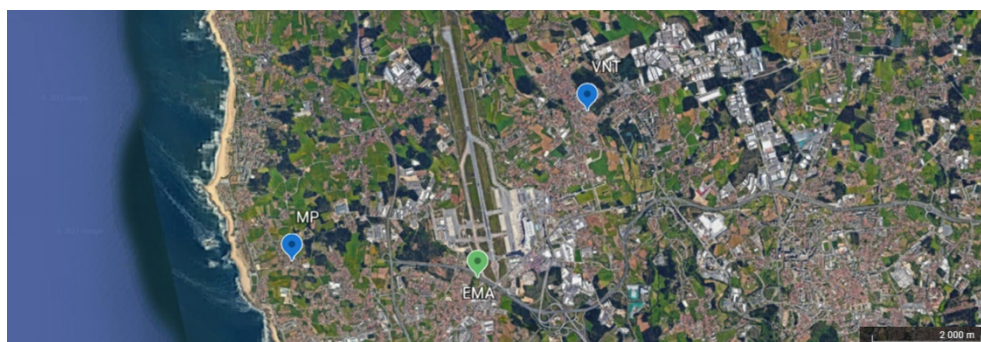

Figure 2. Geographical distribution of the meteorological station (EMA) and O$_3$ monitoring stations, MP and VNT.

The PC and MLR methods were applied to the meteorological parameters (except for wind data) and O$_3$ concentrations for annual quarters. A wind rose was developed to visualise the wind speed and direction registered, resorting to a MATLAB-coded program. To evaluate the wind speed and direction influence on ozone, violin plots were used to represent the frequency of O$_3$ concentration in each wind direction and speed interval considered.

3. Results and Discussion

3.1. Surface Ozone at Rural Stations

Table 2 presents the monitoring efficiency of each station during the study period. Figure 3 shows the annual average O$_3$ concentrations at each monitoring station in the studied period. The highest annual average O$_3$ concentrations were achieved at the DN, CR, SN, FA, FM, and ML sites. The highest values were observed for almost all stations

during the period of 2001–2008 [13], except for the SN station, which shows a significant variance in mean values during the study period (Figure 3b). O_3 concentrations have been decreasing at most stations with rates between -0.12 and -1.35 µg m^{-3} year^{-1}. This behaviour has already been reported at rural Portuguese sites by Pires et al. [13] between 2001 and 2008. The exceptions to this trend are stations ML and SN, with high increase rates of 5.04 and 5.06 µg m^{-3} year^{-1}, respectively, and those with lower increase rates, the MOV (1.26 µg m^{-3} year^{-1}) and FA (0.06 µg m^{-3} year^{-1}) stations. Another study reported similar results for the MOV, FM, and ER stations between 2009 and 2011 [29]. Borrego et al. [22] detected a slight but significant decrease in ozone levels since 2006 in Portuguese rural stations. Yan et al. [30] reported decreases in rural European monitoring stations between 1995 and 2014. In the shorter period of 2000 to 2014, the decrease of O_3 concentrations was also registered by Chang et al. [31] and Proietti et al. [32] in Europe. The latter study reported a more significant decrease rate (-0.22 µg m^{-3} year^{-1}) in Mediterranean Europe.

Table 2. Air quality monitoring efficiency (in percentage) for rural stations.

	CH	CR	DN	ER	FA	FD	FM	FP	LR	ML	MOV	MV	SN	ST	TR
2009	94	0	84	96	44	99	95	99	94	89	94	0	99	0	97
2010	100	19	83	99	89	96	97	98	0	56	99	0	99	0	93
2011	100	40	86	100	98	99	94	96	98	67	100	0	100	0	92
2012	99	99	96	95	91	100	99	99	98	100	99	0	86	0	100
2013	99	87	94	90	98	100	98	93	89	97	92	0	88	0	100
2014	93	88	82	99	94	99	96	91	94	30	99	0	100	0	100
2015	99	97	27	99	99	84	90	100	98	12	99	96	57	0	94
2016	98	89	25	97	93	98	98	99	96	18	68	62	99	99	99
2017	98	88	54	99	100	99	74	98	98	0	100	0	93	100	99
2018	97	94	98	52	99	97	83	98	100	59	78	50	0	100	92
2019	91	95	90	0	100	92	94	100	94	59	0	0	0	100	91

Table 3 shows the exceedances to EU standard values for human protection (alert threshold, information threshold, and target value) during the study period. The alert threshold (240 µg m^{-3}) was exceeded in the DN, FM, and MOV stations. Apart from the TR, CR, ST, and FA stations, the information threshold (180 µg m^{-3}) was exceeded in all others. The highest number of exceedances was determined for the DN station. It is also the station with the highest number of exceedances in the period under study, followed by the FM station. The highest number of exceedances for both standard limits was determined in 2010. Regarding the target value for human health protection (120 µg m^{-3}), DN, CH, and FM were the three stations that recorded the most exceedances (in the respective order). In the Portuguese islands, exceedances to this limit were also observed. However, in ER, LR, SN, CR, TR, ST, and FA stations, exceedances were below 25 on average over 3 years, meaning that their O_3 concentrations were within the legislation requirements. However, none of the stations complied with the long-term objective imposed for human health protection.

Four stations were selected to deeply analyse the O_3 behaviour in different regions of Portugal (representing North, Centre, and South Regions and Islands). A histogram with frequency distribution for 2012 and violin plots representing monthly ozone concentrations are displayed for each selected station in Figure S3. The station located at a higher altitude (DN) presented the highest concentration levels, with more elevated minimum levels. The inner located station (FD) showed significant variation in the ozone concentration, with a maximum value not going far beyond 150 µg m^{-3} unlike DN, whose peak reached 250 µg m^{-3}. The other inland station, located further south (FP), showed similar behaviour to the FD station but reached a higher peak ozone level. All inland stations show peak values in summer, but higher mean concentrations in spring. This characteristic is known in northern hemisphere remote locations, where the peak concentrations can be related to a higher stratosphere-troposphere exchange or be enhanced by increased solar radiation

after winter months with accumulated NO_x and VOC levels [33,34]. In the station at sea level (FA), the lowest ozone concentrations (not surpassing 120 µg m^{-3}) were observed. In all the mentioned stations, the maximum daily concentration occurs at 15 h–16 h, except for the FA station, which shows an almost non-existing daily variation of the concentration. A study conducted in southern Spain also presented that the higher O_3 values appear in high-altitude locations, usually closer to the sea [35]. DN station was the focus of other studies due to register the majority of Portuguese legislated threshold exceedances. Carvalho et al. [25] attribute DN's high levels to long-range transport of pollutants from NE winds, and Borrego et al. [22] showed that background values contribute more than 50% to the local O_3 concentrations.
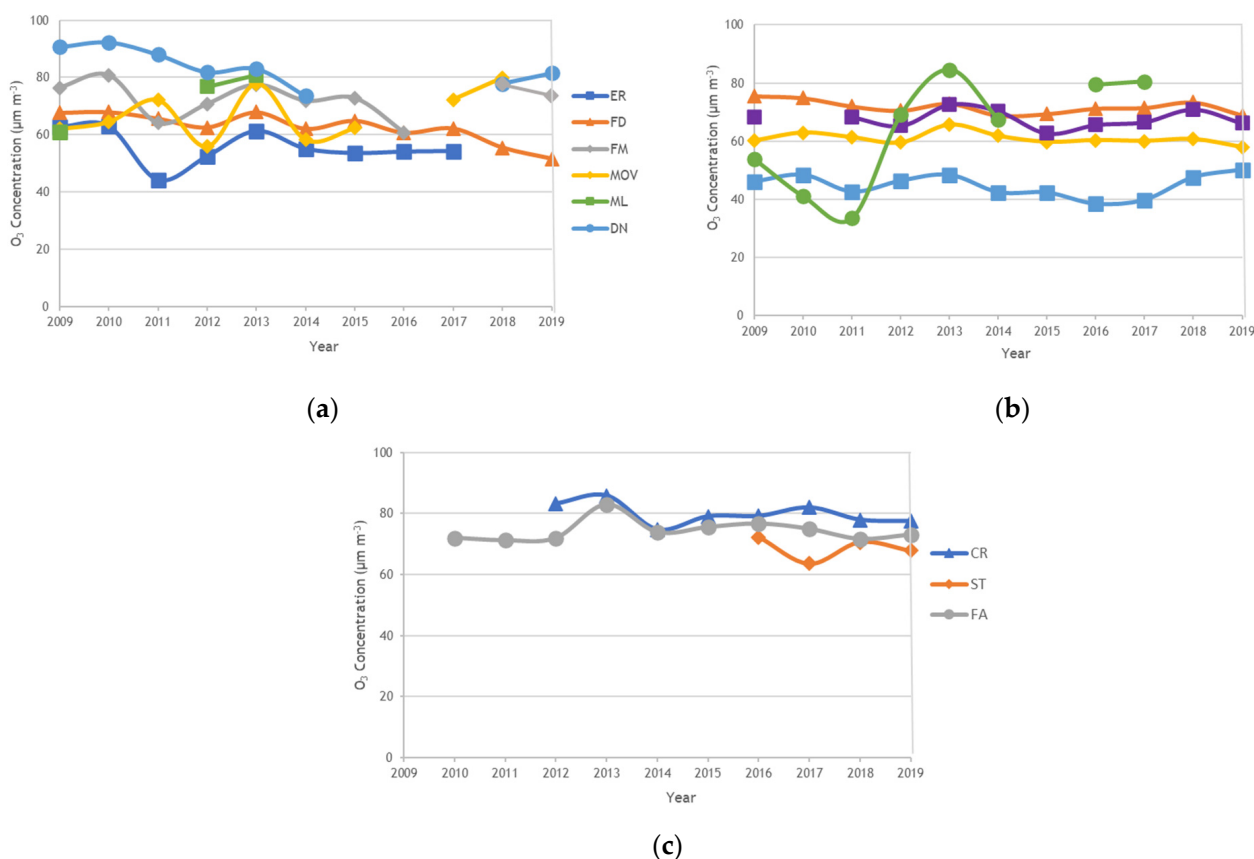

(a)

(b)

(c)

Figure 3. O_3 annual average concentration in each of Portugal's most important regions: (**a**) Regions of North and Centre; (**b**) Regions of Lisbon and Tejo Valley and Alentejo; (**c**) Regions of Algarve and Islands.

Table 3. Exceedances to O_3 alert threshold (AT), information threshold (IT), and target value (TV) for human health protection.

		CH	CR	DN	ER	FA	FD	FM	FP	LR	ML	MOV	SN	ST	TR
2009	AT	0	-	3	0	-	0	0	0	0	0	0	0	-	0
	IT	3	-	37	9	-	0	11	4	0	0	1	0	-	0
	TV	57	-	76	21	-	33	48	32	19	0	24	0	-	0
2010	AT	0	-	4	0	0	0	1	0	-	-	0	0	-	0
	IT	16	-	76	8	0	3	36	1	-	-	9	0	-	0
	TV	55	-	66	29	2	31	66	37	-	-	26	0	-	0

Table 3. *Cont.*

		CH	CR	DN	ER	FA	FD	FM	FP	LR	ML	MOV	SN	ST	TR
2011	AT	0	-	0	0	0	0	0	0	0	-	0	0	-	0
	IT	4	-	30	0	0	0	1	7	0	-	3	0	-	0
	TV	38	-	67	0	0	15	2	27	19	-	53	0	-	0
2012	AT	0	0	0	0	0	0	0	0	0	0	0	0	-	0
	IT	4	0	16	0	0	0	5	0	5	0	0	0	-	0
	TV	36	30	31	7	0	11	22	17	15	28	7	6	-	0
2013	AT	0	0	0	0	0	0	0	0	0	0	0	0	-	0
	IT	2	0	18	0	0	0	8	0	5	1	5	2	-	0
	TV	50	29	37	23	0	22	45	34	31	35	52	53	-	0
2014	AT	0	0	0	0	0	0	0	0	0	-	0	0	-	0
	IT	0	0	0	0	0	0	0	0	0	-	0	0	-	0
	TV	15	5	10	3	0	8	16	12	13	-	3	9	-	0
2015	AT	0	0	-	0	0	0	0	0	0	-	0	-	-	0
	IT	0	0	-	0	0	0	0	0	0	-	0	-	-	0
	TV	24	20	-	3	0	14	20	23	4	-	111	-	-	0
2016	AT	0	0	-	0	0	0	0	0	0	-	-	0	0	0
	IT	6	0	-	3	0	1	1	8	1	-	-	6	0	0
	TV	38	10	-	9	0	9	9	23	12	-	-	50	0	0
2017	AT	0	0	-	0	0	0	-	0	0	-	0	0	0	0
	IT	3	0	-	3	0	0	-	2	0	-	0	10	0	0
	TV	35	11	-	4	1	10	-	15	10	-	30	55	0	0
2018	AT	0	0	0	-	0	0	0	0	0	-	1	-	0	0
	IT	1	0	3	-	0	0	0	0	2	-	3	-	0	0
	TV	26	10	17	-	0	0	20	12	8	-	31	-	0	0
2019	AT	0	0	0	-	0	0	1	0	0	-	-	-	0	0
	IT	0	0	5	-	0	0	5	1	0	-	-	-	0	0
	TV	12	5	36	-	0	0	24	12	8	-	-	-	2	1

The EU legislation presents two different values (AOT_{40}) for the long-term goal and the target value for short-term exposition impact estimations for vegetation protection. Figure 4 presents the calculated AOT_{40} values at each monitoring site, showing the exceedances to these two parameters. Both legislated values were not surpassed at the TR, ST, and FA stations (the last two are in the Portuguese islands).
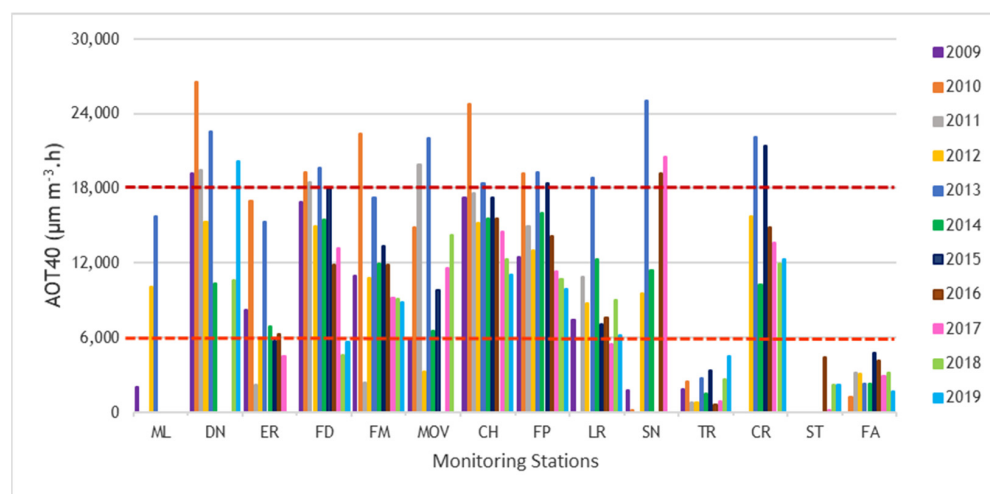
Figure 4. AOT_{40} levels in each station in the study period.

CA was performed to group monitoring stations according to O_3 data for each year. Figure 5 shows, as an example, the dendrogram obtained with data from 2012, forming three groups of stations (dendrograms achieved with the data collected in the remaining years are present in the Supplementary Material. The distribution of stations by these selected clusters was considered for a relationship analysis (Table S1). The frequency with which each pair of stations was grouped in the same class was determined, considering the minimum number of occurrences of stations, i.e., the minimum number of years in which the station is considered. For the final cluster formation, a minimum of 70% of correspondence between stations was considered, resulting in (i) FD, FP, ER, and TR; (ii) DN and FM; (iii) FA and ST; (iv) MOV and LR; (v) ML; (vi) CH; and (vii) SN and (viii) CR. The high number of clusters and the fact that half have only one station assigned are indicative of their importance. Pires et al. [13] also performed CA on Portuguese rural sites, obtaining similar grouping results.
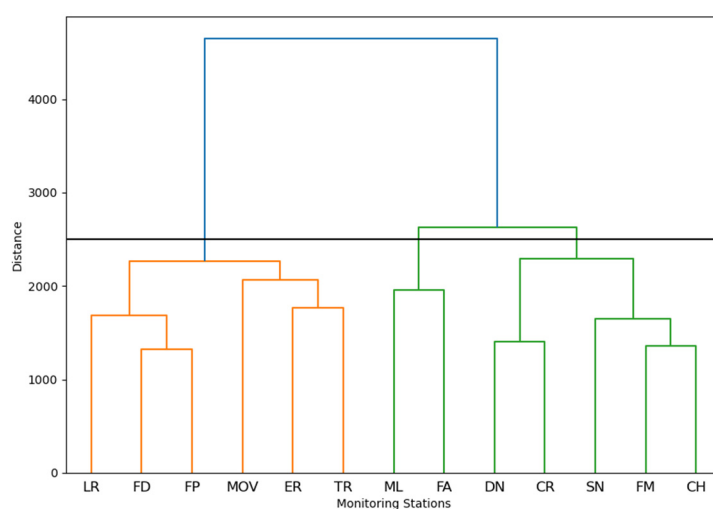

Figure 5. Dendrogram obtained from cluster analysis for 2012.

The daily average ozone concentration profiles (in µm m^{-3}) and the relative frequency (in percentage) of its maximum for the first four clusters are shown in Figure 6. The first cluster shows stations with a higher variation in the O_3 concentration during the day, presenting a decrease in the early morning followed by an increase in the afternoon, with most having their peak at 15 h, as shown in the maximum concentrations profile. In cluster 2, O_3 concentrations have similar behaviours, increasing between 15 h and 16 h. The O_3 concentrations show higher values (and reduced amplitude of values) than those observed in the previous cluster. The stations representing the Portuguese Islands are grouped in cluster 3. They show the lowest concentrations and the shortest variation between the daily minimum and maximum. In the final cluster, the ozone profile in both stations is closer to cluster 1; however, the daily maximum and minimum are lower. Except for stations in cluster 3, a similar daily profile of O_3 concentration was observed in all monitoring stations, the lowest occurring in the morning and the highest in the early afternoon. In FA and ST stations, the peak occurs at night. This event results from the horizontal and vertical transport of ozone and its precursors [13]. Studies of nocturnal ozone concentration increase were developed in the Portuguese continent to explain unexpected ozone levels [21,36]. The ozone enhancement events can be related to transport processes and the related usual meteorological conditions due to the absence of photochemical production. Additionally, vertical mixing was registered in the boundary layer in winter, contributing to surface nocturnal ozone peaks.
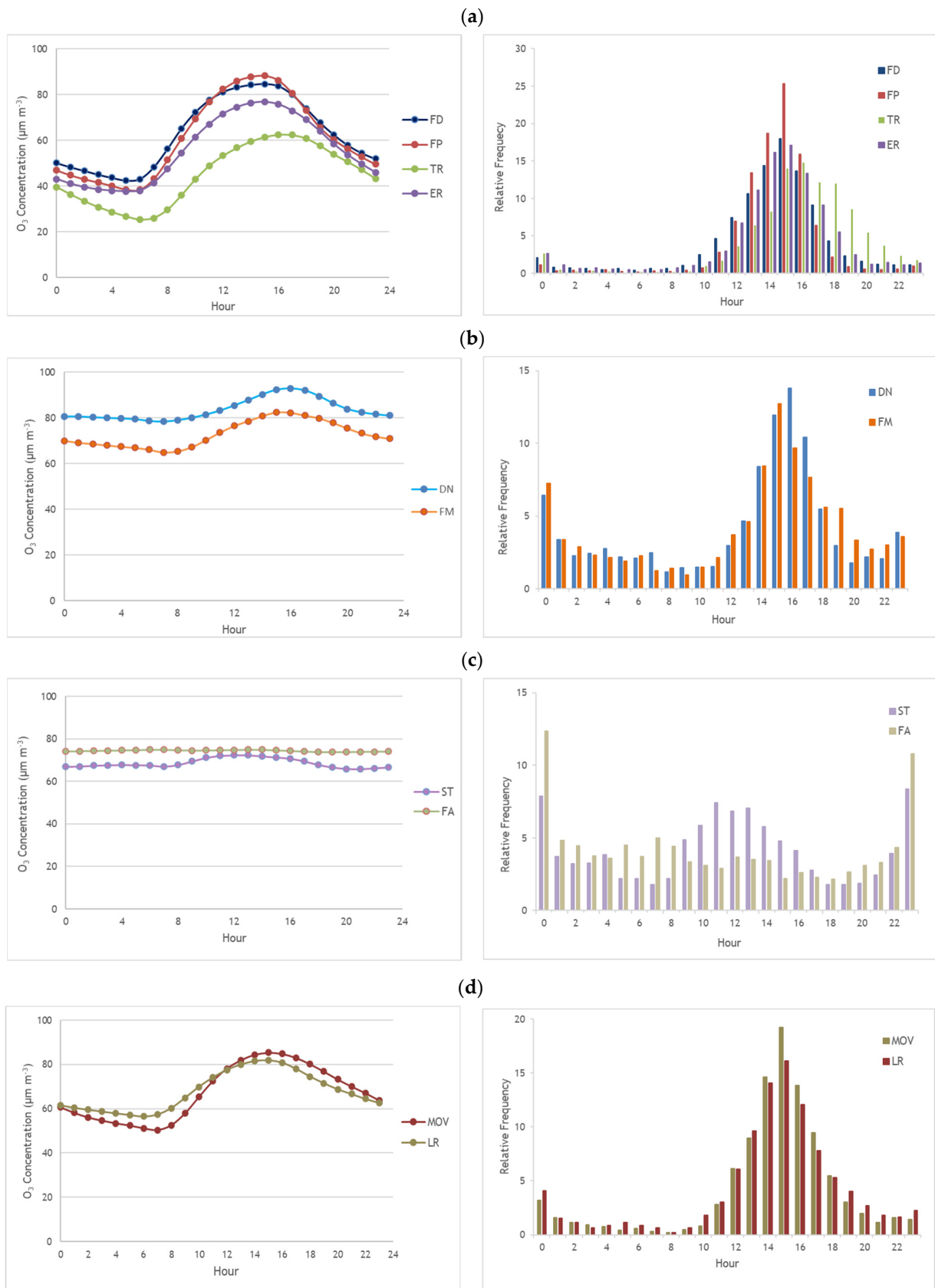
Figure 6. Daily average O$_3$ concentration profile (on the left) and daily evolution of the relative frequency (in percentage) of the daily maximum O$_3$ concentration for the analysed period (on the right), for cluster 1 (**a**), cluster 2 (**b**), cluster 3 (**c**) and cluster 4 (**d**).

3.2. Surface Ozone and NO_x Relation

In suburban and urban areas, surface O_3 concentrations are lower than at rural sites. Figure 7 presents O_3, NO_2, and NO daily average concentrations for the EV, MD, and DN stations in different months. High O_3 concentrations in the DN station can be observed compared with the other two stations. For all stations, high concentrations were observed in the afternoon. As for NO_2 and NO, the concentrations were expectably higher in the suburban and urban areas due to more intensive anthropogenic emission rates. High values observed in the first hours of the day (especially in the NO_2 plot) can be explained by the lack of ozone formation during this period. As expected, the anthropogenic influence in rural stations is weaker, shown by lower levels of NO_x in the DN station (Figure 7h,i). In general, an almost-symmetric daily profile is shown between O_3 and NO_x: in the first hours of the day, NO_x levels are low due to low emissions; in the morning, with the beginning of anthropogenic activities (specifically traffic emissions), there is an increase in NO and NO_2 emissions followed by a decrease in ozone levels due to titration with NO; and during the afternoon, when there is a greater incidence of solar radiation, the NO_2 emitted and formed through the NO present in the air will lead to ozone formation. In the nighttime, ozone levels usually decrease due to the lack of solar radiation. In these conditions, NO_2 photolysis does not occur, and the existing NO can be oxidised back to NO_2 with the reaction with O_3.

Ferreira et al. [37] presented the same connection between O_3 and NO_2 levels in the Lisbon region, registering a higher ozone concentration in the periphery of the urban centre. In the southwest of the Iberian Peninsula, a study of O_3, NO, and NO_2 trends was developed at rural, urban, suburban, and industrial sites by Domínguez-López et al. [10]. According to their reports, most rural sites presented a low and constant NO_x level. In suburban and urban stations, besides the morning NO_x peak, there is a second in the evening due to a decrease in solar activity and an increase in traffic. In the same reference, an analysis of monthly variations showed similar results to the ones shown in Figure 7, with higher ozone levels in the spring and summer for all stations and NO_x levels higher in the autumn and winter for urban and suburban sites, while NO_2 and NO at steady levels during the year were observed at rural sites. In Spain, urban/suburban sites also registered higher NO and NO_2 concentrations and O_3 higher levels in rural/remote regions [35], as shown in a study conducted in the UK too [38].

Considering the ozone concentrations at a chemical equilibrium state, that is, a relation to the NO_2/NO ratio (Equation (2), being *K* the equilibrium constant),

$$[O_3] = [NO_2] \cdot [O_2]/[NO] \cdot K, \qquad (2)$$

Thus, the influence of the NO_2/NO ratio in the O_3 concentration was also included in the PC and MLR analysis. A correlation matrix was obtained (Tables 4–6) to demonstrate the relationship between ozone and its considered precursors in 2019.

Table 4. Pearson's correlation and Multiple Linear Regression results for EV station.

PC	O_3	NO_2	NO	NO_2/NO
O_3	1			
NO_2	−0.611	1		
NO	−0.565	0.846	1	
NO_2/NO	0.353	−0.237	−0.583	1
MLR	b_0	b_1	b_2	b_3
	46.5	−19.8	7.13	8.57

Table 5. Pearson's correlation and Multiple Linear Regression results for MD station.

PC	O_3	NO_2	NO	NO_2/NO
O_3	1			
NO_2	−0.120	1		
NO	−0.188	0.441	1	
NO_2/NO	0.054	0.444	−0.502	1
MLR	b_0	b_1	b_2	b_3
	82.2	-	−4.18	−1.05
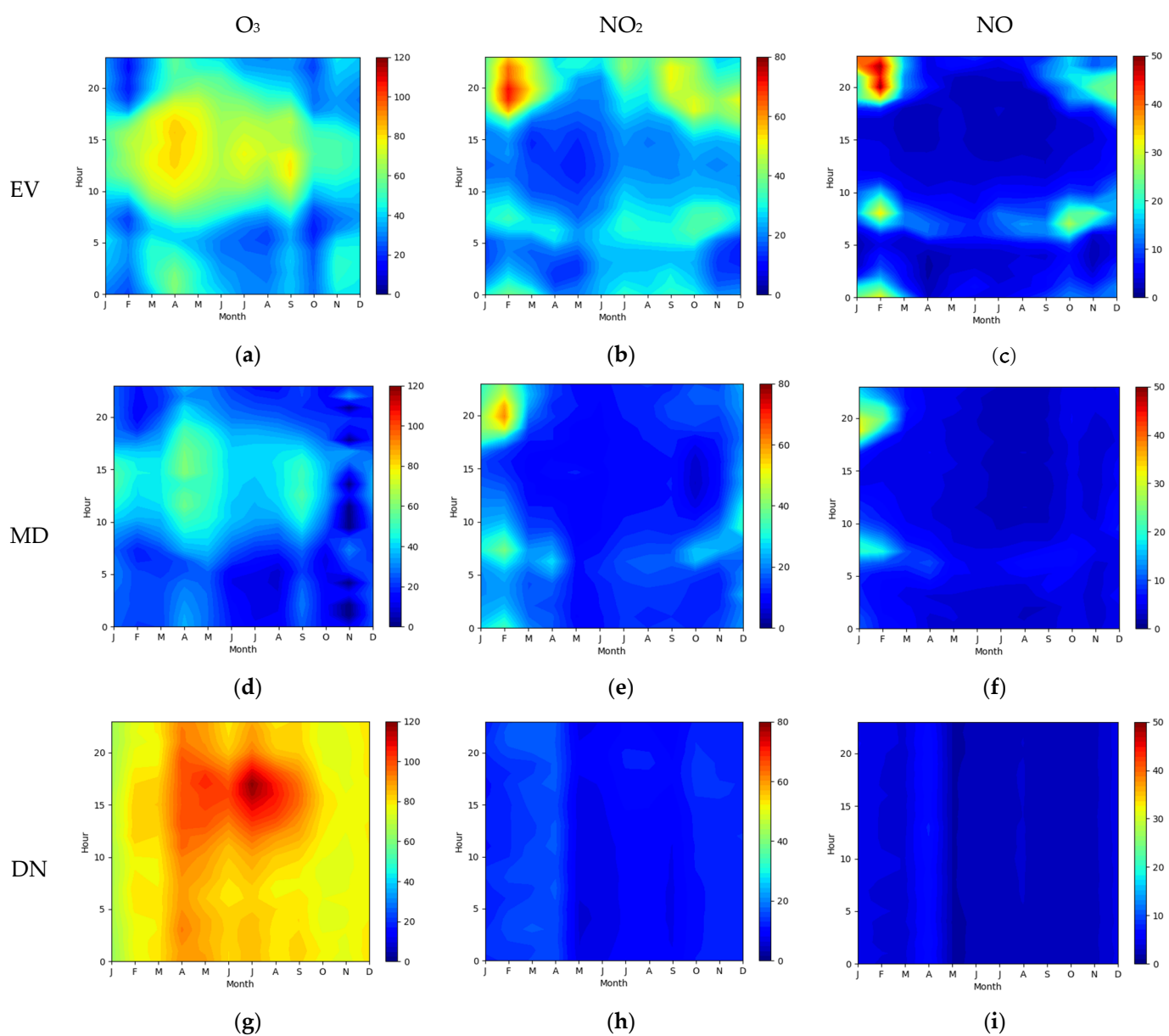
Figure 7. Contour plot of O_3 (**a,d,g**), NO_2 (**b,e,h**), and NO (**c,f,i**) concentrations (in µg m^{-3}) at EV (urban), MD (suburban), and DN (rural) stations.

Table 6. Pearson's correlation and Multiple Linear Regression results for DN station.

PC	O_3	NO_2	NO	NO_2/NO
O_3	1			
NO_2	−0.460	1		
NO	−0.286	0.609	1	
NO_2/NO	−0.075	0.206	−0.213	1
MLR	b_0	b_1	b_2	b_3
	28.8	−8.38	-	0.38

Considering the strength of variables association (see Table S2), Table 4 presents a significant negative correlation between O_3, NO_2, and NO and a medium positive association with NO_2/NO in the urban station (EV), which is what was expected for this type of environment. These results confirm the previous logic of the anti-correlation of ozone and its precursor's daily profile, particularly noticed in the urban sites. Regarding the combined effect of the selected environmental variables, MLR identified a negative relation between NO_2 and O_3 concentrations and a positive with NO, trends also known in other studies in the literature [39].

In the suburban sites (Table 5), a weaker relationship between O_3 and NO_x is expected than in the urban site (Figure 7b). The PC coefficients for O_3 and its precursors obtained are lower than those for the EV station. The NO shows a small correlation with O_3, and the NO_2/NO ratio shows no correlation (coefficient value close to 0). That result is also shown in the smaller b_3 value of MLR, compared to the previous value. The NO_2 shows a small negative association with O_3 and does not show statistical significance to its formation, according to the MLR analysis (b_1 was not considered statistically significant). Table 6 shows the PC and MLR results for the DN station. As is expected, the rural site shows a low (NO_2 and NO) or no relation (NO_2/NO ratio) between O_3 and its chemical precursors. According to the MLR results, NO_2 levels do not influence ozone formation at this site. Contrary to the suburban station, the NO concentration and NO_2/NO ratio have a small negative effect on O_3 levels.

The strength of the association varies with season [40]. The correlation analysis in each season showed negative correlations of O_3 with NO and NO_2 (higher correlation with NO_2 in spring and summer and with NO in the autumn and winter) [41]. This difference can be explained by the interference of meteorological parameters and distinct weather types that affect the pollutants' transport and mixing in the atmosphere.

3.3. Surface Ozone and Meteorological Parameters Relation

The permanence of pollutants in the atmosphere is not only affected by chemical reactions among themselves but also by meteorological conditions, whether at a micro or macro scale. Studying the weather conditions when peak pollutant levels are registered is important to prevent negative effects on humans and the ecosystem. The ozone formation is enhanced by solar radiation and other meteorological parameters. Since these have different levels throughout the year, a quarterly analysis was performed applying PC and MLR to O_3 and the meteorological parameters considered (Tables 7 and 8). The stations under analysis are suburban-type, located in sites with relative anthropogenic influence (e.g., the city airport-related activities). In the MP station, the first quarter presented a medium- (between 0.3 and 0.5) positive correlation with temperature (T) and solar radiation (SR) and a small negative association with relative humidity (RH), meaning that the increase in RH leads to a decrease in ozone (disregarding the results not statistically significant). The MLR, on the contrary, points to a small influence of pressure (P) in the ozone concentration, and relative humidity does not play a role in ozone formation/elimination. A small negative correlation of P and O_3 is pointed to in the second quarter, agreeing with the b_1 value for that period. T and SR show a continuous significant correlation (also seen in the 3rd and 4th

quarters). The RH shows stronger negative correlations in the spring and summer seasons. According to MLR results, the SR has a greater impact in the April–May–June period than the October–November–December period. RH shows a significant negative relation with ozone in the 3rd quarter, and, in the same period, T does not influence O_3 levels.

Table 7. Pearson's correlation and Multiple Linear Regression results for MP station.

PC		P	T		RH	SR
	1st quarter	0.029 *	0.414		−0.177	0.436
O_3	2nd quarter	−0.102	0.426		−0.402	0.472
	3rd quarter	0.012 *	0.441		−0.500	0.465
	4th quarter	−0.412	0.455		−0.288	0.395
MLR		b_0	b_1	b_2	b_3	b_4
1ST QUARTER		52.1	1.25	4.16	-	4.78
2ND QUARTER		60.1	−3.54	2.12	−3.91	8.15
3RD QUARTER		50.7	−2.11	-	−8.41	5.44
4TH QUARTER		36.5	−8.61	2.57	−1.62	7.73

Note: the values with (*) are not statistically significant; $b_0 \rightarrow$ Y-intercept; $b_1 \rightarrow$ regression parameter for pressure; $b_2 \rightarrow$ regression parameter for temperature; $b_3 \rightarrow$ regression parameter for relative humidity; and $b_4 \rightarrow$ regression parameter for solar radiation.

Table 8. Pearson's correlation and Multiple Linear Regression results for VNT station.

PC		P	T		RH	SR
	1st quarter	−0.193	0.435		−0.317	0.484
O_3	2nd quarter	−0.129	0.501		−0.469	0.523
	3rd quarter	0.037 *	0.513		−0.577	0.520
	4th quarter	−0.544	0.542		−0.306	0.407
MLR		b_0	b_1	b_2	b_3	b_4
1st quarter		52.5	−3.30	3.32	-	8.02
2nd quarter		57.9	−4.21	3.04	−4.70	8.56
3rd quarter		47.8	−1.48	1.62	−8.77	4.23
4th quarter		50.9	−3.11	3.04	-	6.55

Note: the values with (*) are not statistically significant; $b_0 \rightarrow$ Y-intercept; $b_1 \rightarrow$ regression parameter for pressure; $b_2 \rightarrow$ regression parameter for temperature; $b_3 \rightarrow$ regression parameter for relative humidity; $b_4 \rightarrow$ regression parameter for solar radiation.

In the VNT station, P presents a higher correlation with ozone in the 4th quarter. The MLR results also show a negative influence of P on ozone levels. In this station, the correlation of T and O_3 presents stronger values, and, except in the 3rd quarter, there is a similar influence level of T in O_3 concentrations. The RH presents a high PC coefficient, but the MLR analysis shows only this parameter influence in the 2nd and 3rd quarters. As for SR, there is a positive correlation with high coefficient values. Ferreira et al. [37] studied the relationship between ozone and some parameters in Lisbon city. Accordingly, daily sea level medium pressure and medium relative humidity negatively influence ozone production in all seasons. As for temperature, the daily medium value only shows a positive (and weak) correlation in the winter months. Pires et al. [24] showed a weak positive correlation of T and a slight negative association of SR and RH with O_3 in a station located in Northern Portugal. The discrepancies between the two applied statistical methods expose the complex task of predicting ozone levels, although, in general, studies applying relationship methods show a positive correlation of O_3 with SR and T and a negative correlation with RH [39,41].

O_3 concentrations can also be influenced by transport and mixing phenomena. Thus, an analyse relating wind direction and speed with O_3 was implemented. Figure S4 presents a wind rose with the wind speed and direction distribution for the year 2015. The most prominent winds were from NW (stronger winds) and E (calmer winds) related to the air

masses from the Atlantic Ocean and Spain that the northern Portuguese region is subjected to. On a macro scale (synoptic weather), it is essential to mention the influence of the Azores anticyclone in Europe [42–44], especially in the Mediterranean [25,35,45–48]. This type of weather system is related to a higher T and low RH and cloud cover (consequently contributing to higher SR activity), enhancing O_3 production. The relatively low wind activity provides the accumulation of this pollutant in the atmosphere.

A more significant contribution of air masses from the Atlantic Ocean for ozone higher concentrations is observed (median values represented in the violin plots, Figure 8). The peak O_3 values are registered for the N-NE and W-NW directions in the MP station. Located closer to shore, the higher concentrations are registered when the wind has lower speed values (more calm weather), which allows the accumulation of ozone. In the VNT station, the peak levels are reached under the North Atlantic air masses influence (NW-N). They are related to faster wind activity, possibly meaning that the high ozone concentrations in this site are associated with the circulation of polluted air masses. Santurtún et al. [48] related ozone trends to weather types in Spain. Accordingly, the stations studied were influenced by the anticyclone system and east and northeast flow (corresponding to the information in Figure S4). Knowing the comparable importance of both chemical and meteorological precursors to ozone formation, Li et al. [49] studied the increase of O_3 pollution in China, concluding that temperature is the meteorological parameter with more influence, but that it is related to anticyclonic conditions. Additionally, the authors pointed to the decrease in $PM_{2.5}$ and the unmitigated emissions of VOCs from anthropogenic sources.
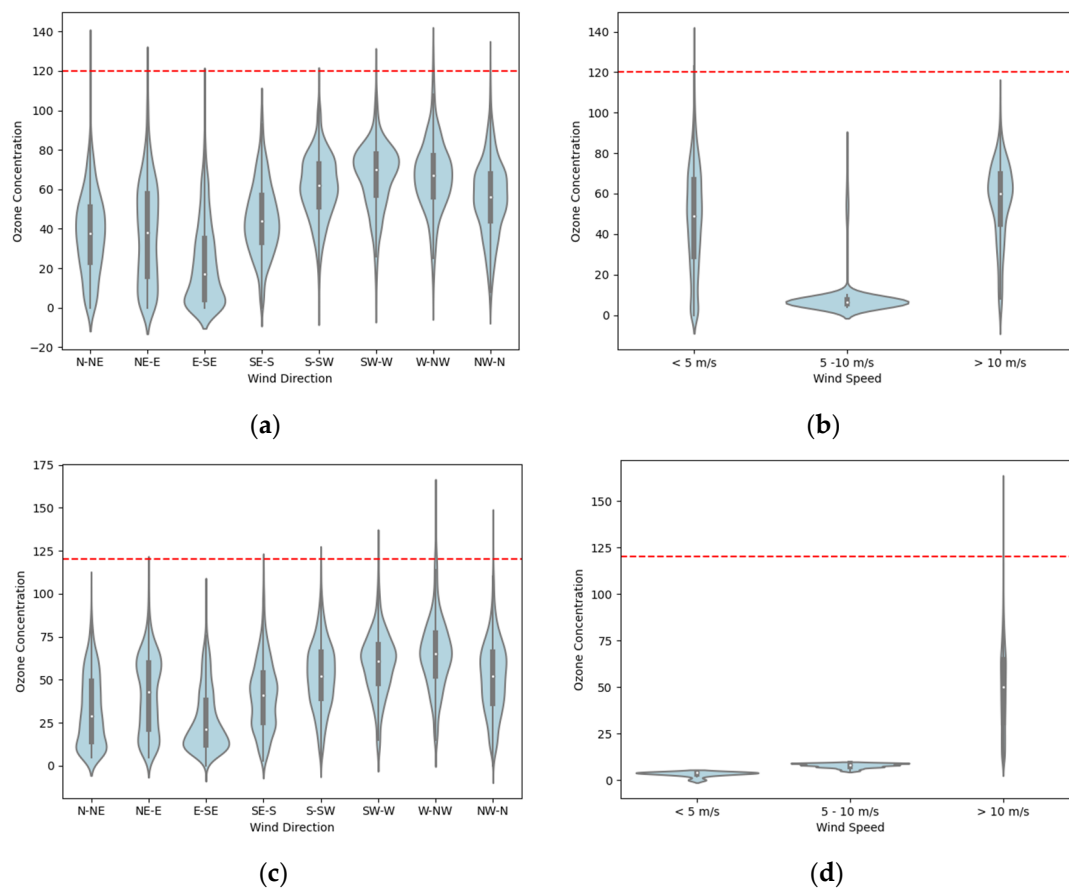

(a)

(b)

(c)

(d)

Figure 8. Relationship between wind direction and speed with ozone levels (in $\mu m\ m^{-3}$) at (**a**,**b**) MP and (**c**,**d**) VNT stations.

4. Conclusions

Annual average O_3 concentrations presented a decreasing trend during the analysed period. However, exceedances to EU legislated values for human health protection were still observed. CA identified several O_3 concentration patterns, showing the effectiveness of the current geographical distribution of the air quality monitoring stations. Negative correlations were determined between NO, NO_2, and O_3 concentrations in urban and suburban stations. The correlation with the NO_2/NO ratio only showed significance in the urban site. As for MLR results, in general, the stronger influence of NO_x levels was expected in the urban station. The O_3 concentrations in both suburban sites showed a strong positive correlation between O_3, T, and SR, a strong negative correlation with RH, and a weaker negative association with pressure. The meteorological parameter that shows a higher contribution in O_3 concentration was solar radiation, showing a stronger influence in the 2nd annual quarter, where the spring high average concentrations are registered. The wind direction distribution showed that the location was under the flow of NW and E-SE winds, related to the Azores anticyclone, and air masses from the Iberian Peninsula, inland.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su14042383/s1, Figure S1: Map with the geographical distribution of Portugal's rural monitoring stations; Figure S2A: Dendrograms for years (a) 2009, (b) 2010, (c) 2011, (d) 2013, (e) 2014 and (f) 2015; Figure S2B: Dendrograms for years (a) 2016, (b) 2017, (c) 2018 and (d) 2019; Figure S3: Annual profile of O_3 concentration ($\mu g\ m^{-3}$) and monthly distribution for 2012 at different stations: (a) Douro-Norte; (b) Fundão; (c) Fernando Pó; (d) Faial; Figure S4: Wind rose with wind direction and speed distribution for the year 2015; Table S1: Matrix of relative frequencies depicting the relationship between the different stations; and Table S2: Guidelines for interpretation of PC coefficient values [50].

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