Temporal and Spatial Evolution Study of Air Pollution in Portugal

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Abstract — This study provides an analysis of the spatial distribution and temporal evolution of NO, NO_2 and O_3 seasonal and annual concentrations in Portugal during the period 1995-2010. The contribution of nitrogen oxides and several meteorological variables to the variation of O_3 concentration was evaluated with multiple regression analysis in Entrecampos and Douro Norte stations. The variation in NO concentration shows a marked seasonality and presents a significant decreasing annual trend in most of the urban type stations considered, especially those under the influence of road traffic. Despite the downward trend in the concentration of NO, a statistically significant trend in NO_2 concentration is not observed in most of the monitoring stations, except those less influenced by traffic, in which the emission of primary NO_2 is much lower and the reduction in NO emissions leads to less photochemical production of NO_2. The pattern of O_3 concentration is completely opposed to that observed in NO. Several stations showed a significant upward trend in O_3 concentration as a result of the decrease in NO/NO_2 ratio. The correlation between the pollutants and ozone was stronger in Entrecampos than in Douro Norte. In this rural background station, the ozone concentration showed a strong correlation with meteorological variables. In Entrecampos urban station, 68% of the variance in ozone concentration was explained by the variables introduced in the regression model, being the NO_2/NO_X ratio the variable that explained most of the variance. In Douro Norte rural background station, only 43.4% of the variance in ozone concentration was explained by such variables. Therefore, long-range transport, high biogenic volatile organic compounds (BVOCs) concentration and the local geography may play a key role at this station.

Keywords — Portugal, O_3, NO_X, trends

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1 Introduction

Current EU Directive on air quality (2008/50/EC) sets out a number of targets framed within the Thematic Strategy on Air Pollution [COM(2005)446] to improve human health and environmental quality. Ground level ozone and particulate matter ($PM_{2.5}$ and PM_{10}) are the pollutants of most concern in Europe [1].

NO is a primary pollutant, while NO_2 and O_3 are of secondary origin (although a small part of NO_2 in the atmosphere has a primary origin). The main source of nitrogen oxide emissions is road traffic [2]. The implementation of catalytic filters in cars has led to a large reduction not only in the absolute NO concentration, but also in NO/NO_2 ratio, particularly in regions with dense transport networks. However, it is known that the cars using these filters emit NO_2 as primary pollutant [3]. Also, the increased use of diesel cars has led to an increase in primary NO_2 emissions, since they emit a higher fraction of this contaminant than gasoline cars [4]. This results in an increase of NO_2/NO_X ratio.

Recent estimates indicated that stratospheric-tropospheric exchanges are only responsible for 20% of tropospheric ozone, because at present, it is mainly generated by complex photochemical reactions [5]. Ozone is formed by photochemical reactions that involve anthropogenic pollutants (CO, volatile organic compounds-VOCs) and solar radiation, in the presence of nitrogen oxides [6].

Previous studies showed the existence of a NO_X-sensitive regime and a VOC-sensitive regime. In the NO_X-sensitive regime (NO_X is relatively low and biogenic volatile organic compounds - BVOCs - are high, typical of rural regions), O_3 levels are getting higher with increasing NO_X and changes little with respect to VOC. The VOC-sensitive regime (typical of urban areas) exhibits the opposite behaviour [7, 8].

This paper provides an analysis of the spatial distribution of NO, NO_2 and O_3 seasonal concentrations in mainland Portugal during the period 1995-2010, using data obtained from the air quality monitoring network of *Agência Portuguesa do Ambiente*. The temporal evolution of these pollutants was also studied in order to determine the

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statistically significant trend in their concentrations and the year in which new trends started. Furthermore, the contribution of NO, NO_2, NO_X, NO/NO_2 and NO_2/NO_X ratios, SO_2, PM_{10} and several meteorological variables (solar radiation, temperature, pressure and wind speed) to the variation of O_3 concentration was evaluated in a Lisbon urban traffic station and Vila Real background station, during the period 2004-2010.

2 METHODOLOGIES

2.1 Area of study

The field of this study corresponds to mainland Portugal (37-42 °N, 6.5-9.5 ºW), with an area of 8,908,893 ha. Mainland Portugal is covered by a monitoring network for air quality assessment and management purposes. The monitoring network density is greatest in those areas where the protection of human health is critical, corresponding to the urban areas of Lisbon and Oporto, with a population of 2 million and 1.2 million, respectively [9].

At the end of 2010, the *Agência Portuguesa do Ambiente* monitoring network had 91 operational monitoring stations of different types (urban, suburban or rural). These stations reported NO and NO_2 hourly concentrations by chemiluminescence, while O_3 concentrations were obtained by ultra-violet absorption detection, also being reported on an hourly basis. In the first part of this study, data from all these stations that meet the minimum sampling frequency that is required by the air quality Directive 2008/50/EC were used.

Entrecampos station (code 3072) was chosen to assess the contribution of nitrogen oxides and other pollutants, together with several meteorological variables, in the concentration of O_3 on a severely polluted environment. It is an urban traffic station located in Lisbon, with coordinates -9.14889 ° W, 38.7486 ° N and 86 m altitude. Douro Norte station (code 1048) was chosen to assess such contribution in a less polluted environment. It is a rural background station with coordinates -7.7908 ° W, 41.3714 ° N, located at an altitude of 1086 m.

2.2 Data and methods

Annual averages were performed to assess the trend in the concentration of these pollutants by the Mann-Kendall sequential test (SQMK) (rank statistic test) [10] for those stations with continuous data for a minimum of ten years. The SQMK test is a non-parametric test that can be applied to non-normally distributed data with missing points. This test allows us to calculate the year when the trend or change starts. A monotonic trend of increase or decrease is evaluated along with the non-parametric Sens's method for estimating the slope of a linear trend [11].

To analyse the spatial distribution of short term NO, NO_2 and O_3, a seasonal average of concentrations throughout the entire study period was conducted. Subsequently, the results were plotted through Surfer, a contouring and surface modelling package.

Stepwise multiple regression analysis (SMRA) was employed to assess the contribution of NO, NO_2, NO_X, NO/NO_2 NO_2/NO_X ratio, SO_2, PM_{10}, solar radiation, temperature, pressure and wind speed to O_3 levels recorded in Entrecampos and Douro Norte stations (urban traffic and rural background type, respectively) during the period 2004-2010, in order to identify the variables that best predict the variation in the concentration of ozone in each case. The possible existence of multicollinearity between the independent variables by Inflation Factor Variance (VIF) and Condition Index (CI) was previously checked, the latter being one of the most suitable methods for detecting multicollinearity [12]. The presence of multicollinearity in a regression model makes difficult to correctly identify important contributors to a physical process [13], so multicollinearity should be avoided.

3 RESULTS AND DISCUSSION

3.1 Spatial distribution of NO, NO_2 and O_3 concentrations

Seasonal patterns show that the highest NO concentrations are reached during autumn and winter (Fig. 1a), especially in most densely populated areas of Portugal, corresponding to Lisbon and Oporto metropolitan areas. Also, the high concentration registered in Coimbra during these seasons stands out, although it is not a town with a large population density, but it has a dense road network with high traffic. This spatial pattern suggests that the main cause of these high concentrations is road traffic. During these seasons, adverse dispersion conditions and car engine operation, in addition to increased activity in the populated areas, result in an increased emission and accumulation of primary pollutants such as NO [14].

NO_2 concentration pattern (Fig. 1b) shows no marked seasonality as in the case of NO, although concentrations in summer are slightly lower, especially in the more populated coastal areas. The decrease in NO_2 concentration in summer is not as pronounced as in NO. Because NO_2 is mainly a secondary pollutant, the higher solar radiation and temperature during this season accelerates its production, although the emission of their precursors is reduced.

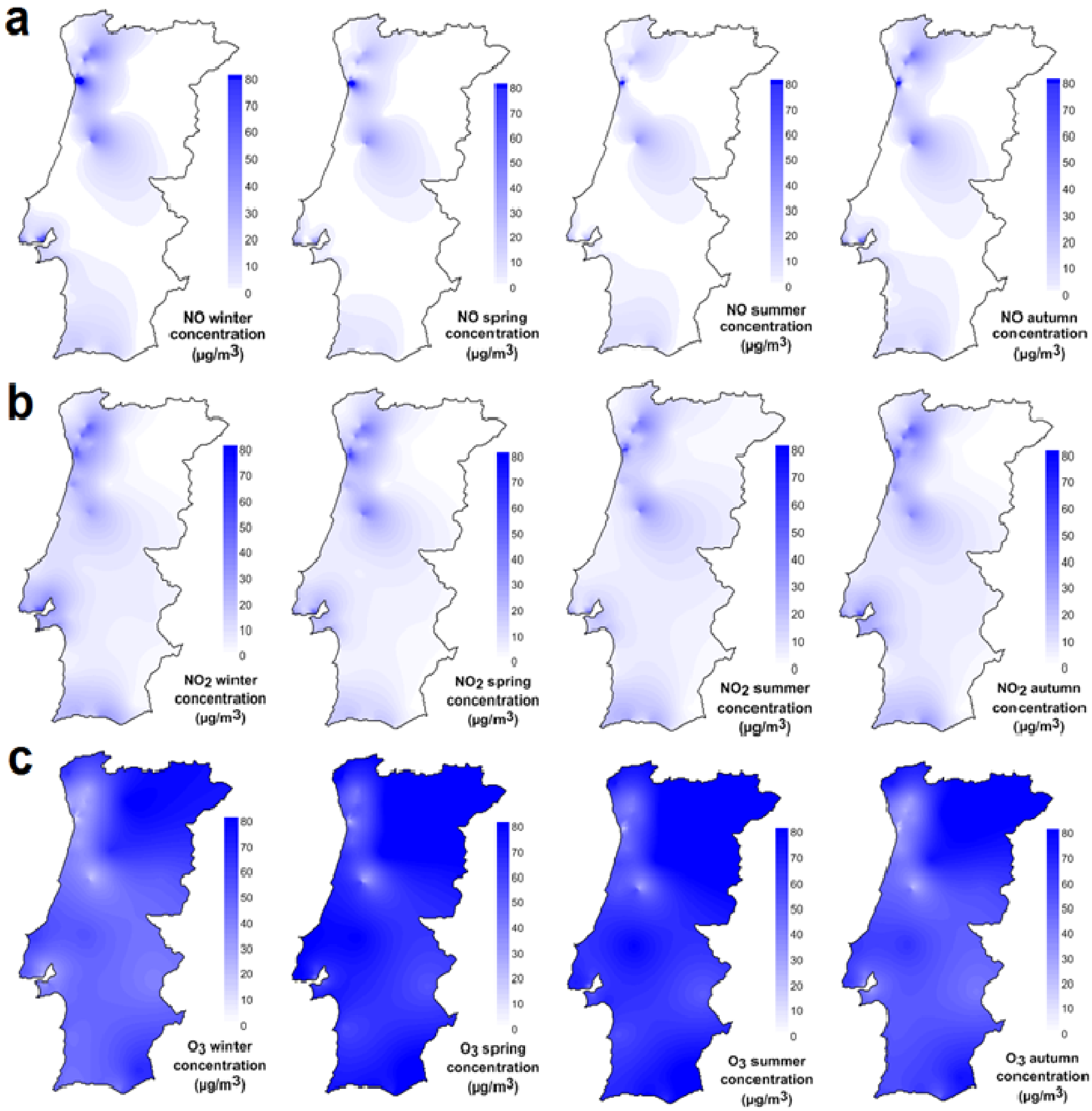

Fig. 1. Seasonally averaged (1995-2010) concentration maps of NO (a), NO_2 (b) and O_3 (c).

The highest O_3 concentrations are reached during the spring and summer (Fig. 1c), thus following a completely opposite pattern of NO. This is because the photochemical activity in these months is high because of the incident solar radiation and the temperature reach their annual maximum. Furthermore, reduction in the emission of primary pollutants (particularly NO) during these months results in an increased accumulation of ozone. Moreover, the high ozone concentration stands out throughout the entire year in Douro Norte monitoring station, located in a mountainous rural area NE of Portugal. This station showed the highest annual average (94.4 µg/m^3) of ozone hourly concentration recorded over the study period. Carvalho et al. [15] highlighted the importance of the long-range transport of atmospheric pollutants or its precursors due to atmospheric flow patterns, mainly from NW of Spain, to the high ozone levels registered in these areas.

3.2 Annual trend of NO, NO_2 and O_3 concentrations

The results obtained by the Mann-Kendall sequential test at 95% level of significance for 29 monitoring stations having a minimum of 10 years in the data series are shown in Table 1.

NO concentration presents a significant decreasing trend ($U < -1.96$) in most of urban and suburban stations. The high decreasing rate of NO concentration in Avenida da Liberdade (U = -3.33, -2.33 µg m^{-3} year^{-1}), Entrecampos (U = -3.60, -2.47 µg m^{-3} year^{-1}) and Mouzinho (U = -3.31, -3.40 µg m^{-3} year^{-1}) urban type stations stands out. These very steep declines of NO concentration in urban type stations can be attributed to the restrictions on the transport sector fuel requirements (Directive 98/70/EC) and the implementation of catalytic filters in vehicles. In contrast, the NO concentration does not show any significant trend in any of the rural stations studied.

Despite the clear downward trend in NO concentration, a significant trend for the NO_2 is not observed in most cases. This absence of trend might be due to the fact that NO_2 is emitted as a primary pollutant because of the implementation of catalytic filters in cars [3]. This behaviour is not observed in Lavradio (U = -3.96, -2.01 µg m^{-3} $year^{-1}$) and Chelas (U = -2.52, -1.40 µg m^{-3} $year^{-1}$) monitoring stations, which show a decreasing trend in NO_2 concentration. The trend starting year is about the same as that pointed out for NO. This behaviour could result from considerably lower NO_2 primary emissions by less traffic. Therefore, a reduction in emissions of NO in the vicinity of this stations, leads to less formation of photochemical NO_2. Moreover, Alto Seixalinho station shows a significant upward trend in the concentration of NO_2 (U = 2.70, +0.82 µg m^{-3} $year^{-1}$) although its NO concentration trend is not significant, despite registering an increase rate of 0.32 µg m^{-3} $year^{-1}$. Again, primary NO_2 plays a fundamental role in this urban traffic station.

Several stations showed a significant upward trend in O_3 concentration, as in the case of Entrecampos (U = 4.86, +2.55 µg m^{-3} $year^{-1}$). This urban traffic station presented a strong downward trend in NO concentration, while NO_2 concentration did not exhibit a significant trend. This results in a decrease of NO/NO_2 ratio and therefore an increase in the availability of ozone. A similar behaviour can be observed in other stations. The rate of increase in O_3 concentration is higher in traffic stations than in industrial or background stations because the rate of decrease in NO concentration is higher at traffic-impacted sites.

3.3 Influence on ozone levels

The independent variables used for studying their contribution to ozone levels recorded during the period 2004-2010 in Entrecampos and Douro Norte monitoring stations were NO, NO_2, NO_X, NO/NO_2 and NO_2/NO_X, SO_2, PM_{10}, solar radiation (SR), temperature (Temp), pressure (P) and wind speed (WS). It was not possible to use relative humidity and wind direction as independent variables due to the lack of data.

Table 1. Sequential Mann-Kendall trend test results (U statistics and trend start year) for NO, NO_2 and O_3 concentration throughout the study period and slope estimation of the linear trend.

			NO			NO_2			O_3		
Monitoring station	Municipality	Type	U	Trend start	µg/m3·year	U	Trend start	µg/m3·year	U	Trend start	µg/m3·year
Laranjeiro	Almada	Urban background	-1.70		-0.5861	0.45		0.2523	3.85	2005	1.7382
Alfragide	Amadora	Urban background				0.14		-0.0759	-2.06	2005	-1.7451
Reboleira	Amadora	Urban background	-1.16		-0.1374						
Alto seixalinho	Barreiro	Urban traffic	1.44		0.3152	2.70	2006	0.8228	2.44	2009	1.8129
Escavadeira	Barreiro	Urban industrial	0.63		0.1457	0.09		0.0755			
Lavradio	Barreiro	Urban industrial	-3.33	2002	-1.5486	-3.96	2001	-2.0111			
Coimbra	Coimbra	Urban traffic				-1.32		-0.8186	0.86		0.6083
Av.24-Espinho	Espinho	Urban traffic	-2.77	2007	-0.8606	0.98		0.2905			
E. Avanca	Estarreja	Rural background				0.08		-0.1498			
E. Teixugueira	Estarreja	Suburban industrial	-2.52	2008	-0.6187	-0.86		0.1557	1.92		1.1197
Pe Joaquim Neves	Gondomar	Urban traffic							2.06	2009	0.9628
Av. da Liberdade	Lisboa	Urban traffic	-3.33	2005	-2.3316	1.08		-0.2622			
Beato	Lisboa	Urban background	-3.42	2004	-0.3846	1.71		0.3067	3.45	2001	1.6611
Chelas	Lisboa	Urban background	-4.14	2000	-1.0820	-2.52	1999	-1.4009			
Entrecampos	Lisboa	Urban traffic	-3.60	2001	-2.4701	0.63		0.4180	4.86	2000	2.5546
Olivais	Lisboa	Urban background	-0.63		-0.1148	1.35		0.4096			
St. Cruz de Benfica	Lisboa	Urban traffic	-2.43	2009	-1.6517	-0.99		-0.0646			
Loures Centro	Loures	Urban background	-0.63		-0.3557						
Don Manuel II	Maia	Urban traffic	-3.66	2004	-1.3649	-0.08		0.0254	1.95		1.2682
VN Telha-Maia	Maia	Suburban background	-2.74	2007	-0.3446	-1.37		-0.1883	0.14		0.1467
Custoias	Matosinhos	Suburban background	-2.74	2008	-1.3432	0.06		-0.3799	1.65		0.6820
Leça do Balio	Matosinhos	Suburban background	-1.70		-0.8023	1.52		0.9135	0.45		0.0609
Mouzinho	Porto	Urban traffic	-3.31	2003	-3.3975	-1.88		-1.5542			
Fco. Sá Carneiro	Porto	Urban traffic							1.52		1.3793
Monte Velho	S. do Cacém	Rural background	-1.34		-0.0790	-0.45		0.0047	0.54		0.0295
Sonega	S. do Cacém	Rural industrial	-1.44		-0.1389	-0.99		-0.0921	-0.86		0.1038
Paio Pires	Seixal	Suburban background	0.23		0.0330	1.32		1.0614	1.95		2.9147
Monte Chaos	Sines	Suburban industrial	-2.34	2008	-0.1037	-1.44		-0.2676	2.34	2009	1.4904
Ermesinde	Valongo	Urban background	-2.41	2008	-0.3487	0.86		0.2787	2.47	2005	0.8332

Pearson correlation test determined that O_3 concentration in Entrecampos station is negatively correlated with NO, NO_2 and NO_X concentration, NO/NO_2 ratio and SO_2 concentration, and positively correlated with NO_2/NO_X ratio and PM_{10} concentration. This is expected since NO and NO_2 are ozone precursors, and therefore a rise in ozone concentrations is associated with a reduction in NO and NO_2 levels [14]. NO and NO_2 enhance ozone's dissociation and production, respectively. Thus, if the NO/NO_2 ratio decreases, ozone concentrations increase [8], which explains the negative correlation between both parameters. For the same reason, if the NO_2/NO_X ratio increases, O_3 concentration also rises. Ozone has a strong positive correlation with solar radiation and temperature, since it is produced through photochemical processes.

In Douro Norte station, the correlation between ozone concentrations with those of most pollutants is significantly weaker than in Entrecampos station, although the direction of the correlations is the same. However, its correlation with solar radiation and temperature is stronger, at the suburban background station with less traffic influence, as previously observed [14].

When two or more explanatory variables in a model are highly correlated in the sample, as in the case of the different nitrogen oxides and their respective ratios, it is very difficult to separate the partial effect of each of these variables on the dependent variable in the regression model. For this reason, the independent variable in relation to nitrogen oxides introduced in the SMRA was NO_2/NO_X ratio, since in both stations it had the strongest correlation with ozone concentration regarding that group of variables. It should be expected that NO_2/NO_X ratio explained a greater proportion of the variance in the ozone concentration. Therefore, the independent variables included in the model were NO_2/NO_X ratio, SO_2, PM_{10}, solar radiation, temperature, pressure and wind speed. Independent variables left in the model were significant at 0.05 level. Those which failed to meet this level of significance were excluded from the model.

The variance inflation factor (VIF) in Table 2 is relatively low for all independent variables at both stations, not being in any case higher than 3. Kleinbaum et al. [16] suggests that there should not be problems with collinearity if the VIFs are less than 10 (tolerance < 0.1). However, other authors, such as O'Brien [17], argue that this rule should be taken with caution, since it may be collinearities not involving all independent variables and therefore not well detected by VIF, among many other reasons. For this reason, we also calculated condition indices (Table 2) for each variable in both stations. Condition indices ranging from 10-30 are associated with a weak collinearity, although they should not present problems, while indices higher 30 can cause a serious problem of collinearity and potential disaster in the regression model [18]. Condition indices did not exceed the value of 15 in both stations, so we can assume that the regression model may be appropriate to elucidate the contribution of the variables considered in the ozone concentration recorded at both stations.

SMRA results for Entrecampos and Douro Norte stations are shown in Table 3. In Entrecampos station, NO_2/NO_X ratio, solar radiation, wind speed, pressure, temperature and PM_{10} remained in the model with the required level of significance (0.05), while the variables that did not meet that requirement were excluded. The value of adjusted R^2 for this station was 0.680, which means that 68 % of the variance in the ozone concentration can be explained by the variables introduced in the model. It is a noticeably high value considering that relative humidity and wind direction were not introduced in the model as independent variables. The NO_2/NO_X ratio explained by itself 55.1 % of the variance in ozone concentration in Entrecampos station. He and Lu [13] also suggested that NO_2/NO_X ratio can be regarded as the dominant precursor of ozone concentration.

In Douro Norte rural station the variables that remained in the model were temperature, solar radiation, NO_2/NO_X, PM_{10} and wind speed. These variables only explained 43.4% of the variance in ozone concentration in this station (37.5 % of the variance was explained by temperature and solar

Table 2. Variance inflation factor and condition index of variables left in SMRA.

Entrecampos	Tolerance	VIF	Dimension	Eigenvalues	Condition index
NO_2/NO_X	0.413	2.419	1	4.551	1.000
SR	0.368	2.716	2	0.468	3.119
WS	0.558	1.792	3	0.298	3.908
P	0.887	1.127	4	0.101	6.715
PM_{10}	0.595	1.680	5	0.058	8.853
T	0.431	2.319	6	0.032	11.926
			7	0.021	14.729
Douro Norte	Tolerance	VIF	Dimension	Eigenvalues	Condition index
T	0.355	2.816	1	5.386	1.000
SR	0.383	2.613	2	0.381	3.759
NO_2/NO_X	0.878	1.139	3	0.267	4.488
PM_{10}	0.883	1.133	4	0.184	5.403
WS	0.921	1.085	5	0.124	6.604
			6	0.031	13.178

Table 3. Stepwise regression model for O_3 concentration in Entrecampos and Douro Norte stations with the variables NO_2/NO_X ratio, solar radiation, wind speed, pressure, PM_{10} and temperature.

Entrecampos	NO_2/NO_X	SR	WS	P	PM_{10}	T
Adjusted R^2	0.551	0.628	0.649	0.660	0.673	0.680
F change	462.402	78.395	23.823	13.077	15.857	8.923
Sig. F change	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.003
Douro Norte	T	SR	NO_2/NO_X	PM_{10}	WS	
Adjusted R^2	0.247	0.375	0.402	0.426	0.434	
F change	124.443	77.487	17.782	16.594	6.445	
Sig. F change	<0.0001	<0.0001	<0.0001	<0.0001	0.012	

radiation). It was noted in section 3.1 that high ozone concentrations recorded at this station may be due to long-range transport from the NW of Spain [15]. The low variance explained by the variables may suggest photochemical production of O_3 from its precursors during transport to this station. Moreover, taking into account that Douro Norte is located in a mountainous area, the amount of biogenic volatile organic compounds (BVOCs) would be significantly higher during the day and consequently contribute to the local photochemical ozone production from transported precursors. In addition, local geography would also play a key role in ozone concentrations recorded at this site. This hypothesis would explain the low correlation between the local ozone concentration and other pollutants, and the strong correlation with both temperature and solar radiation, which are the two factors that explain most of the variance in the regression model.

CONCLUSIONS

Together with meteorological variables, 16 years of NO, NO_2 and O_3 concentrations collected over the period 1995-2010 in several air quality stations of mainland Portugal were analysed. The variation in NO concentration showed a marked seasonal pattern, with the lowest levels occurring during the colder months, especially in the most densely populated areas. The seasonal fluctuations of NO_2 concentrations are not so marked. Despite an overall downward trend in the NO concentration, a statistically significant tendency towards a decrease of NO_2 levels was not observed in most of the monitoring stations. Ozone showed an opposite seasonal pattern to that of NO. Several stations showed a significant upward trend in O_3 level as a result of the decrease of the NO/NO_2 ratio. Long range transport of precursors to mountain sites in the northern region led to frequently high surface O_3 concentrations. A strong correlation between this photochemical pollutant and both solar radiation and temperature was obtained at a representative site of that region. For this rural site, the percentage of variance in O_3 concentrations explained by other pollutants is relatively low. At urban traffic sites, most of the variance is explained by the NO_2/NO_X ratio.

The ozone trends observed in this study in the northern region could be extrapolated to other rural areas of NW Iberian Peninsula, because this geographical area has homogeneous topographical and climatological characteristics. In addition, Galicia and the north of Portugal are affected by similar synoptic circulation patterns.

Taking into account that, in addition to meteorological variability, the O_3 trends are strongly affected by changes in the photochemical precursor emissions, the analysis of future concentration patterns should be very useful to confirm the influence of these factors. Despite the general drop on the NO levels, future long-term trend assessments will be desirable in order to evaluate the effectiveness of both air quality plans and emission control technologies.

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