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Nitrogen oxides and ozone in Portugal: trends and ozone estimation in an urban and a rural site

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Abstract This study provides an analysis of the spatial distribution and trends of NO, NO_2 and O_3 concentrations in Portugal between 1995 and 2010. Furthermore, an estimation model for daily ozone concentrations was developed for an urban and a rural site. NO concentration showed a significant decreasing trend in most urban stations. A decreasing trend in NO_2 is only observed in the stations with less influence from emissions of primary NO_2. Several stations showed a significant upward trend in O_3 as a result of the decrease in the NO/NO_2 ratio. In the northern rural region, ozone showed a strong correlation with wind direction, highlighting the importance of long-range transport. In the urban site, most of the variance is explained by the NO_2/NO_X ratio. The results obtained by the ozone estimation model in the urban site fit 2013 observed data. In the rural site, the estimated ozone during extreme events agrees with observed concentration.

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Introduction

Human exposure to outdoor air pollution can be particularly problematic primarily in areas where pollution levels tend to be high due to poor dispersion and high density of emission sources (Marenco et al. 1994). In this sense, urban and suburban areas, in addition to recording the highest concentration of industrial activity and road traffic, are densely populated. Therefore, these areas will be a priority in the monitoring activities of environmental quality due to their high pollution levels, which result in high impact on human health.

WHO Air Quality Guidelines provide a uniform scientific basis for protecting public health from the adverse effects of air pollutants. In this sense, the guidelines offer background information and guidance to national and local authorities in making risk assessment and risk management decisions. The epidemiological evidence indicates that the possibility of adverse effects remains even if the guideline values are achieved, and some countries may select even lower levels for their standards. Evaluation and prediction of air quality are useful tools that can be used to determine the magnitude of the air pollution risks faced by the population.

High concentrations of gaseous pollutants, such as nitrogen oxides and ozone, may induce acute respiratory infections and cardiovascular disease in humans (Monsalve et al. 2013), as well as damage to vegetation, such as lesions on leaves, lower crop yields and changes in sensitivity to the stress caused by several biotic and abiotic factors (López and Ballesteros 2003; Alvim-Ferraz et al. 2006). Therefore, assessment of the nitrogen oxides and ozone levels is essential especially in urban-industrialized areas (Melkonyan and Kuttler 2012).

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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 (Colvile et al. 2001). The implementation of catalytic converters in cars (particularly in gasoline cars) has led to a large reduction not only in the absolute NO concentration, but also in the NO/NO_2 ratio (Carslaw and Rhys-Tyler 2013). This is especially relevant in regions with dense transport networks. On the other hand, the increased use of modern diesel cars with after-treatment technologies such as diesel particulate filters (DPF) has led to an increase in primary NO_2 emissions (Keuken et al. 2012). This results in an increase of the NO_2/NO_X ratio (Alves et al. 2015).

Recent estimates indicate that stratospheric-tropospheric exchanges only account for 20 % of tropospheric ozone, because, at present, it is mainly generated by complex photochemical reactions (Marenco et al. 1994) involving anthropogenic pollutants (CO, volatile organic compounds (VOCs)) and solar radiation, in the presence of nitrogen oxides (Alvim-Ferraz et al. 2006).

The main reactions involving NO, NO_2, O_3 and VOC chemistry in the troposphere are compiled and explained in the Online Resource (Appendix A).

In Portugal, several research studies have focused on the spatial distribution of several pollutants, such as the experimental campaign of sulphur dioxide, nitrogen dioxide and ozone, which covered the entire Portuguese continental territory over a short period of time (Ferreira et al. 2001). Carvalho et al. (2010) conducted an analysis of the high ozone levels registered in the northeast of Portugal. The association between the spatial distribution of various pollutants and circulation weather types in some monitoring stations was also studied during the period 2002–2010 by Russo et al. (2014). Other research studies in Portugal aimed at ascertaining the influence of several variables on ozone levels (Alvim-Ferraz et al. 2006) or modelling ozone concentration among other pollutants throughout the entire territory of Portugal (Monteiro et al. 2007).

The objectives of this paper are as follows:

- To analyze the spatial distribution of NO, NO_2 and O_3 seasonal concentrations in the more densely populated areas of Portugal with the highest spatial coverage of the air quality monitoring network in the period 1995–2010.
- To determine the statistically significant trends of NO, NO_2 and O_3 concentrations and the year in which those trends started.
- To develop an ozone estimation model based on the contribution of nitrogen oxides, SO_2, PM_{10} and several meteorological variables to the variation of O_3 concentration in the period 2004–2010, in an urban and a rural environment with the highest ozone levels in Portugal.

Study area and data collection

The study area corresponds to mainland Portugal (37–42° N, 6.5–9.5° W), with an area of 8,908,893 ha. Mainland Portugal is covered by a monitoring network for air quality assessment and management purposes (Fig. 1). The monitoring network density is greater in those areas where the protection of human health is critical, corresponding to the urban areas of Lisbon and Porto, with a population of 2 million and 1.2 million, respectively (Borrego et al. 2009). Therefore, most of the air quality monitoring stations are located along the coastline, next to the most industrialized and urbanized areas.

At the end of 2010, the *Agência Portuguesa do Ambiente* monitoring network had 86 operational stations on mainland Portugal (Appendix B in the Online Resource and summarized in Table 1) of different types (urban, suburban and rural). These stations reported NO and NO_2 hourly concentrations by chemiluminescence, while O_3 concentrations were obtained by ultra-violet absorption detection on an hourly basis. Data from all these stations which meet the minimum sampling frequency required by the air quality Directive 2008/50/EC were used to analyze the spatial distribution and trends of these pollutants.

The Entrecampos station was chosen to assess the contribution of nitrogen oxides and other pollutants, together with several meteorological variables, to the concentration of O_3 on a severely polluted environment located near the coastline. It is an urban traffic station
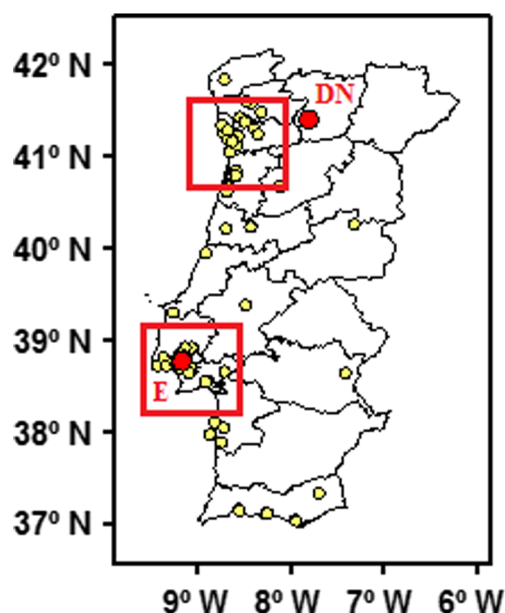

Fig. 1 Air quality monitoring stations considered; in *red*, "Entrecampos" urban station (E) and "Douro Norte" rural station (DN). Air quality stations framed within the *top* and *bottom squares* correspond to the ones located in the most densely populated regions (Porto and Lisbon, respectively)

Table 1 Operational air quality monitoring stations of mainland Portugal at the end of 2010

Station	Long (°)	Lat (°)	Station	Long (°)	Lat (°)
Afonso Henriques (Ut)	−8.58	41.20	Ílhavo (SUb)	−8.67	40.59
Afonso III (Ut)	−7.94	37.02	I.G. de Coimbra (Ub)	−8.41	40.21
Alfragide (Ub) (L)	−9.21	38.74	João G. Laranjo (Ut) (P)	−8.66	41.19
Alto Seixalinho (Ut)	−9.06	38.65	Joaquim Magalhães (Ub)	−7.93	37.02
Alverca (Ub) (L)	−9.04	38.90	Laranjeiro (Ub) (L)	−9.16	38.66
Arcos (Ub)	−8.89	38.53	Lavradio (Ui) (L)	−9.05	38.67
Augusto Gomes (Ut)	−8.68	41.19	Leça do Balio (SUb) (P)	−8.63	41.22
Av.24/Espinho (Ut)	−8.64	41.01	Loures-Centro (Ub) (L)	−9.16	38.83
Aveiro (Ut)	−8.65	40.64	Lourinhã (Rb)	−9.25	39.28
Av. Casal Ribeiro (Ut)	−9.14	38.73	Malpique (Ub)	−8.25	37.09
Av. da Liberdade (Ut) (L)	−9.15	38.72	Meco-Perafita (SUi) (P)	−8.71	41.23
Avintes (Ub) (P)	−8.56	41.10	Mem Martins (Ub) (L)	−9.35	38.79
Beato (Ub) (L)	−9.12	38.89	Mindelo (SUb) (P)	−8.72	41.31
Benfica (Ut)	−9.20	38.75	Minho-Lima (Rb) (P)	−8.69	41.80
Burgães (Ub) (P)	−8.46	41.35	Monte Chãos (SUi)	−8.84	37.95
Calendário (SUb)	−8.53	41.39	Monte Velho (RRb)	−8.80	38.08
Câmara Municipal (Ut)	−9.07	38.66	Montemor-o-Velho (Rb)	−8.68	40.18
Camarinha (Ub)	−8.87	38.53	Mouzinho (Ut)	−8.63	41.16
Cascais-Mercado (Ut) (L)	−9.42	38.70	Município (Ut)	−8.23	37.09
Cerro (RRb)	−7.68	37.31	Odivelas (Ut) (L)	−9.18	38.80
Chamusca (RRb)	−8.47	39.35	Olivais (Ub) (L)	−9.11	38.77
Chelas (Ub)	−9.11	38.75	Paços de Ferreira (Ub) (P)	−8.38	41.27
Coimbra (Ut)	−8.40	40.21	Paio Pires (SUb) (L)	−9.08	38.62
Cónego (Ut) (P)	−8.30	41.45	Paranhos (Ut)	−8.61	41.18
Custóias (SUb) (P)	−8.64	41.20	Pe Joaquim Neves (Ut)	−8.55	41.19
David Neto (Ut)	−8.54	37.14	Pe Moreira Neves (Ut) (P)	−8.34	41.21
D. Manuel II (Ut) (P)	−8.62	41.24	Pontal (Ub)	−8.53	37.13
Douro Norte (RRb) (P)	−7.79	41.37	Quebedo (Ut) (L)	−8.89	38.52
Entrecampos (Ut) (L)	−9.15	38.75	Quinta do Marquês (Ub) (L)	−9.32	38.70
Ermesinde (Ub) (P)	−8.55	41.21	Reboleira (Ub) (L)	−9.23	38.75
Ervedeira (RRb)	−8.89	39.92	Restelo (Ub) (L)	−9.21	38.71
Escavadeira (Ui) (L)	−9.07	38.66	Rua da Prata (Ut)	−9.14	38.71
Estarreja/Avanca (RRb)	−8.57	40.81	Rua dos Bragas (Ut)	−8.62	41.15
Estarreja/Teixugueira (SUi)	−8.57	40.76	Sta. C. de Benfica (Ut) (L)	−9.20	38.75
Fernando Pó (RRb) (L)	−8.69	38.64	Santiago do Cacém (Ui)	−8.70	38.02
Fidalguinhos (Ub) (L)	−9.05	38.65	Santo Tirso (Ub)	−8.47	41.35
Formosa (Ut)	−8.61	41.15	Sines (SUt)	−8.85	37.95
Fornelo do Monte (RRb)	−8.10	40.64	Sobreiras (Ub) (P)	−8.66	41.15
Fr. Bartolomeu (Ut) (P)	−8.41	41.55	Sonega (RRi)	−8.72	37.87
Fco. Sá Carneiro (Ut) (P)	−8.59	41.16	Terena (Rb)	−7.40	38.62
Frossos (SUb) (P)	−8.46	41.57	Vila do Conde (SUt)	−8.72	41.31
Fundão (RRb)	−7.30	40.23	Vila Nova de Gaia (Ut)	−8.61	41.13
Hospital Velho (Ut)	−9.07	38.65	VN Telha (SUb) (P)	−8.66	41.25

The typology of each station is designed by letters within the first brackets (*U* urban, *SU* suburban, *R* rural, *RR* regional rural, *t* traffic, *b* background, *I* industrial). The letters within the second brackets designate the two areas of interest that are relevant to the subsequent analysis: Porto (P) and Lisbon (L)

located in Lisbon, with coordinates 9.15° W, 38.75° N and 86-m altitude. Douro Norte station was chosen to assess such contribution in a less polluted rural environment in a mountainous area. It is a rural background station with coordinates 7.79° W and 41.37° N, located at an altitude of 1086 m.

Meteorological data (except solar radiation) were provided by the *Instituto Português do Mar e da Atmosfera* (IPMA) on an hourly basis. Solar radiation data were obtained every hour from HelioClim-3 Database of Solar Irradiance (derived from satellite data), provided by Transvalor S.A.

Methodologies

Trend calculations

Annual averages of NO, NO_2 and O_3 concentrations for the period 1995–2010 were used to assess the trend in the concentration of these pollutants using the Mann-Kendall sequential test (SQMK) (Sneyers 1990) for those stations with uninterrupted data for a minimum of 10 years. The SQMK test is a non-parametric test which can be applied to non-normally distributed data with missing points. This test also estimates the year when the trend or change starts.

Furthermore, a monotonic trend of increase or decrease is evaluated along with the non-parametric Sen's method for estimating the slope of a linear trend (Sen 1968).

More details about both statistical methods are provided in the Online Resource (Appendix C).

Contour maps of spatial distribution

In order to analyze the spatial distribution of NO, NO_2 and O_3 concentrations in the areas around Lisbon and Porto, where the density of the air quality monitoring network is higher, a seasonal study of hourly concentrations throughout the entire study period was conducted. For this purpose, an average of the pollutant concentrations registered hourly at each monitoring station for each of the seasons during the period 1995–2010 was computed, thereby obtaining a result for each pollutant at each monitoring station and season for the entire period. Subsequently, the results were plotted through Surfer12, a contouring, gridding and surface mapping package. The interpolation method used was ordinary kriging with a linear semivariogram model.

Stepwise multiple regression analysis and generalized linear model

Stepwise multiple regression analysis (SMRA) (Hocking 1976) was employed to assess the contribution of NO, NO_2, NO_X, NO/NO_2, NO_2/NO_X, SO_2, PM_{10}, temperature, pressure, relative humidity, wind speed, wind direction, solar radiation, dew point and precipitation to the O_3 levels recorded in the Entrecampos urban station and the Douro Norte rural station in the period 2004–2010, in order to identify the variables that best predict the variation in the ozone concentration in each case. VOC-related variables were not employed in the

analysis due to the lack of recorded concentrations in the monitoring stations of Portugal during the study period. The adjusted R-squared ($adjR^2$) diagnostic criterion was employed to determine which model was more appropriate. Using this technique, the model with the largest $adjR^2$ was declared the best linear model (Beal 2007).

The possible existence of multicollinearity between the independent variables by variance inflation factor (VIF) and condition index (CI) was previously checked, the latter being one of the most suitable methods for detecting multicollinearity (Judge et al. 1985). The presence of multicollinearity in a regression model makes it difficult to correctly identify important contributors to a physical process (He and Lu 2011), so multicollinearity should be avoided.

Once the independent variables explaining more variation in ozone concentration were identified, excluding previously the existence of multicollinearity problems, a generalized linear model (GLM) was used to describe the relationship between ozone concentration and the set of independent variables by a prediction equation. A log-link function was used to specify the relationship between the expected response and the linear predictor because that function is the most appropriate one for predicting ozone concentration (Camalier et al. 2007).

Moreover, as wind direction is a circular variable, a linear-circular statistics is required to calculate the correlation between wind direction and the rest of variables in the SMRA. This linear-circular correlation coefficient (Mardia 1976) is defined as the multiple correlations between a linear variable and the sine and cosine of a circular variable.

Details of the previous methods are shown in the Online Resource (Appendix D) and summarized in Table 2.

Results and discussion

Spatial distribution and seasonal patterns of NO, NO_2 and O_3 concentrations

Seasonal patterns over the study period 1995–2010 for the two Portuguese areas with a great spatial coverage of the air quality monitoring network show that the highest NO concentrations are reached in autumn and winter (Table 3(A)), especially near the most densely populated areas, corresponding to Lisbon and Porto (Fig. 2a). This spatial pattern suggests that one of the main causes of these high concentrations could be road traffic. During these seasons, adverse conditions in dispersion 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 (Mavroidis and Ilia 2012). Moreover, in the most populated areas of Portugal, there is a great influence of biomass burning heating systems in winter (Gonçalves et al. 2012), which can lead to

Table 2 Statistics and equations of the statistical methods presented in this section

Statistical method	Statistic parameter	Equations[a,b,c,d]
Multicollinearity analysis	Variance inflation factor (VIF)	$\mathrm{VIF_k} = \frac{1}{1-R_k^2}$
	Condition index (CI)	$\mathrm{CI_k} = \sqrt{\frac{\lambda_{max}}{\lambda_k}}$
Generalized linear model	–	$g(\mu_i) = \beta_0 + \beta_1 X_{i,1} + \cdots + \beta_k X_{i,k}$
Linear-circular correlation	Mardia linear-circular correlation coefficient	$r_c^2 = \frac{r_{xc}^2 + r_{xs}^2 - 2r_{xc}r_{xs}r_{cs}}{1-r_{cs}^2}$

[a] R_k^2 is the unadjusted R-squared when X_k is regressed against all the other variables in the model

[b] λ_k and λ_{max} are the correlation matrix eigenvalue of the X_k independent variable and the maximum eigenvalue of the set of independent variables, respectively

[c] $g(\mu_i)$ is a smooth and invertible linearizing link function. β_k is the regression coefficient of the variable X_k

[d] r_c is the correlation coefficient between the linear (x) and circular (θ) variables, where $r_{xc} = corr(x, cos\theta)$, $r_{xs} = corr(x, sin\theta)$ and $r_{cs} = corr(cos\theta, sin\theta)$

high NO concentrations in this season. It should also be noted that NO levels registered in the monitoring stations in the Lisbon region are higher than those registered in the Porto region, especially in winter. According to the Portuguese Automobile Association, in 2010, the number of passenger cars in the Lisbon region was approximately 1,020,000 and that in the Porto region around 740,000. This may explain why the NO levels registered in Lisbon were higher, particularly in the traffic influenced monitoring stations of that region.

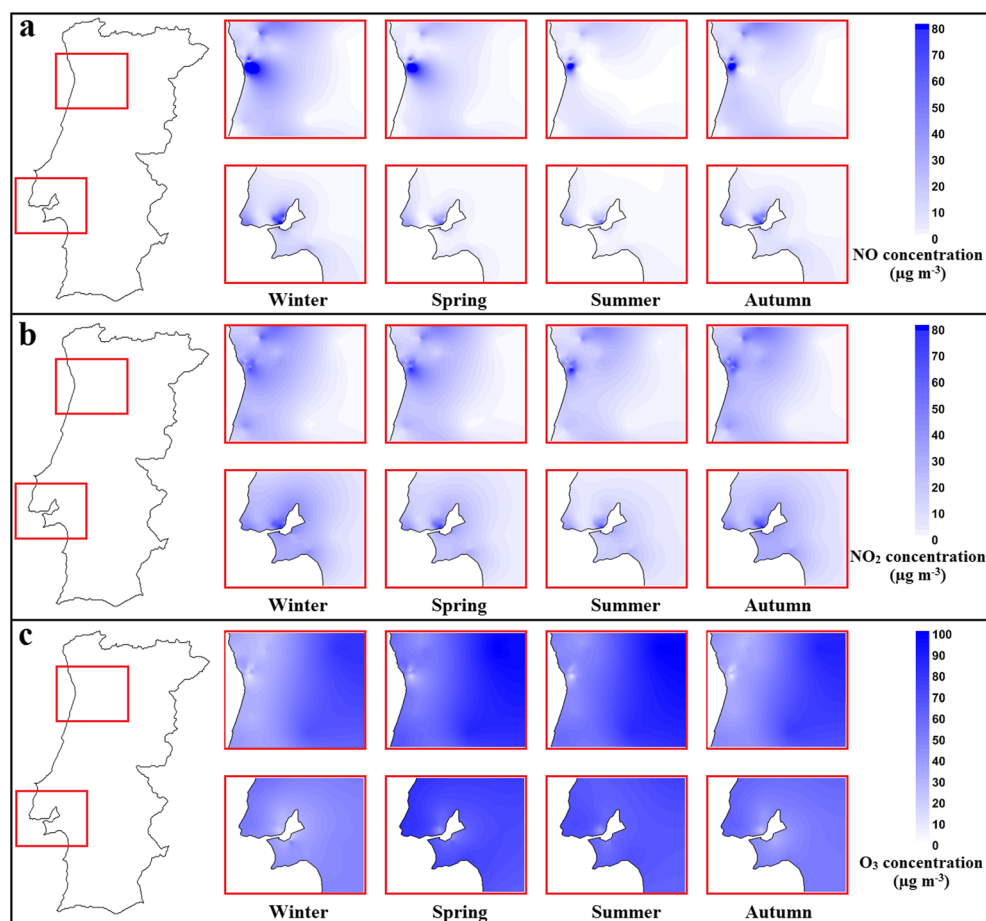The NO_2 concentration pattern (Fig. 2b) does not show a marked seasonality, as in the case of NO, although the NO_2 levels registered in summer are slightly lower than those found in the rest of the seasons (Table 3(B)). The decrease in NO_2 concentration in summer is not as pronounced as in NO due to the fact that NO_2 is mainly a secondary pollutant and the increased photochemical activity of daytime NO_X-VOC-CO chemistry in this season accelerates its production (see reactions (4) and (5) in Appendix A in the Online Resource).

An increase in ozone levels may lead to an increase in the percentage of NO, which is oxidized to NO_2 (reaction (3) in Appendix A in the Online Resource) (Mavroidis and Chaloulakou 2011). The spatial pattern of NO_2 concentrations

Table 3 Global average concentration for all the monitoring stations considered and maximum average concentration registered in a single monitoring station of NO (A), NO_2 (B) and O_3 (C) for both Porto and Lisbon

			Winter	Spring	Summer	Autumn
A	NO concentration in microgram per cubic metre (Porto area)		Winter	Spring	Summer	Autumn
		Global average	24.7	13.4	11.0	22.1
		Standard deviation	18.0	14.5	10.6	17.5
		Single station maximum average	89.9	78.7	56.8	88.9
		Standard deviation	34.4	18.3	3.9	3.5
	NO concentration in microgram per cubic metre (Lisbon area)		Winter	Spring	Summer	Autumn
		Global average	31.2	15.9	12.7	22.8
		Standard deviation	28.2	18.6	16.2	22.5
		Single station maximum average	99.6	70.0	57.2	79.7
		Standard deviation	34.1	12.2	8.4	20.7
B	NO_2 concentration in microgram per cubic metre (Porto area)		Winter	Spring	Summer	Autumn
		Global average	31.6	27.3	24.8	32.3
		Standard deviation	11.8	12.1	11.5	13.6
		Single station maximum average	53.5	55.0	47.9	58.1
		Standard deviation	3.9	7.7	0.6	6.2
	NO_2 concentration in microgram per cubic metre (Lisbon area)		Winter	Spring	Summer	Autumn
		Global average	36.5	29.1	23.6	33.6
		Standard deviation	14.5	14.5	12.7	13.7
		Single station maximum average	67.1	66.2	61.8	70.1
		Standard deviation	27.5	14.7	22.0	19.7
C	O_3 concentration in microgram per cubic metre (Porto area)		Winter	Spring	Summer	Autumn
		Global average	31.4	51.5	46.8	34.4
		Standard deviation	9.9	10.5	9.8	10.8
		Single station maximum average	69.1	86.7	84.6	77.4
		Standard deviation	3.4	5.1	9.0	9.0
	O_3 concentration in microgram per cubic metre (Lisbon area)		Winter	Spring	Summer	Autumn
		Global average	37.2	64.1	61.0	45.0
		Standard deviation	9.0	10.6	8.1	8.8
		Single station maximum average	54.7	80.9	72.4	62.0
		Standard deviation	4.8	5.0	5.6	6.7

Fig. 2 Seasonally averaged (1995–2010) concentration maps of NO (**a**), NO$_2$ (**b**) and O$_3$ (**c**) for the most industrialized and urbanized regions of Portugal
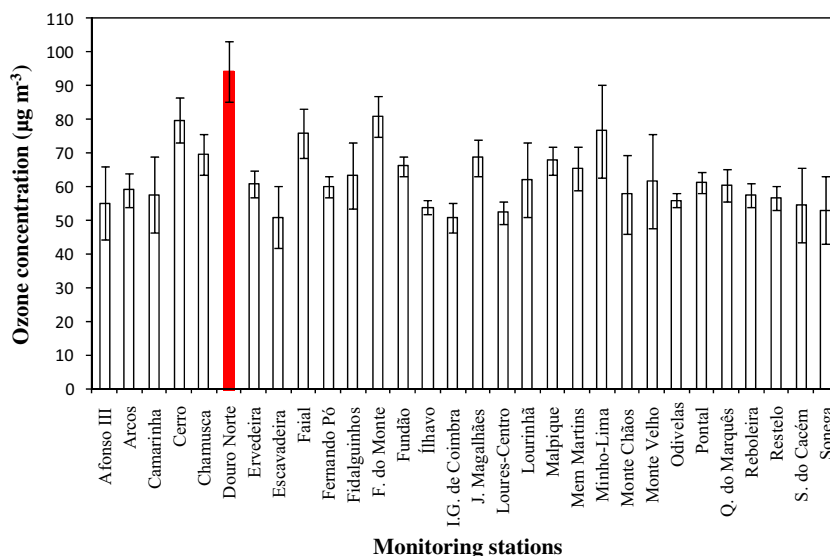

is the same as the NO spatial pattern, reaching the highest concentrations near the most densely populated areas of Lisbon and Porto.

The highest O$_3$ concentrations are reached in spring and summer (Table 3(C)), thus following a seasonal pattern opposite to the one of NO. The photochemical activity in spring and summer is higher because incident solar radiation and temperature reach their annual maximum values. Furthermore, the reduced emission of primary pollutants (particularly NO) in these months prevents the formation of NO$_2$ (see reaction (3) in Appendix A in the Online Resource) and results in an increased accumulation of ozone. The spatial

Fig. 3 Mean and standard deviation of hourly ozone concentrations registered at the air quality monitoring stations that measured an ozone concentration equal to or greater than 50 μg m^{-3} for the period 1995–2010

pattern of O_3 concentrations in all seasons (Fig. 2c) showed that the highest levels are registered outside the most densely populated metropolitan areas, probably due to the VOC-sensitive nature of these regions, where ozone production decreases with higher nitrogen oxide levels.

Moreover, the high ozone concentration stands out throughout the entire year in Douro Norte rural station, located in a mountainous area of NE Portugal. This station showed the highest average ($94.4\ \mu g\ m^{-3}$) of hourly ozone concentration recorded in the study period (Fig. 3). The Kruskal-Wallis non-parametric test (Kruskal and Wallis 1952) and the Dunn's test (Dunn 1964) were conducted to assess the statistically significant differences between ozone concentrations registered in Douro Norte and the other stations. Statistically significant differences were observed in every pairwise test ($p < 0.001$) at 0.05 level of significance. Carvalho et al. (2010) highlighted the importance of the long-range transport of atmospheric pollutants or its precursors due to atmospheric flow patterns, mainly from NW of Spain, in the high ozone levels registered in these areas (Fig. 4).

Annual trend of NO, NO$_2$ and O$_3$ concentrations

The results obtained by the SQMK test at 95 % level of significance for 29 monitoring stations having a minimum of 10 years of continuous data in the data series of the study period 1995–2010 are shown in Table 4.

The NO concentration presents a significant decreasing trend ($U < -1.96$) in most of urban and suburban stations, with an average decrease value of -1.54 and $-0.60\ \mu g\ m^{-3}\ year^{-1}$, respectively. The high decreasing rates of NO concentration in Avenida da Liberdade ($U = -3.33$, $-2.33\ \mu g\ m^{-3}\ year^{-1}$), Entrecampos ($U = -3.60$, $-2.47\ \mu g\ m^{-3}\ year^{-1}$) and Mouzinho ($U = -3.31$, $-3.40\ \mu g\ m^{-3}\ year^{-1}$) urban traffic stations are remarkable. The three monitoring stations mentioned above are under a strong influence of complex road systems. These very steep declines of NO concentration in urban traffic stations may be attributed to restrictions on the transport sector fuel requirements (Directive 98/70/EC) and the implementation of catalytic converters in gasoline and diesel vehicles. This has led to a decrease in the NO/NO$_2$ ratio in all the urban traffic monitoring stations considered. 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 might be due to the increased primary NO$_2$ emissions of modern diesel cars with after-treatment technologies (Keuken et al. 2012). Only the Lavradio ($U = -3.96$, $-2.01\ \mu g\ m^{-3}\ year^{-1}$) and Chelas ($U = -2.52$, $-1.40\ \mu g\ m^{-3}\ year^{-1}$) monitoring stations show a decreasing trend in NO$_2$ concentration. The starting year of this trend in these stations (2001 for Lavradio and 1999 for Chelas) is about the same as the one pointed out for NO. The NO/NO$_2$ ratio for both stations remained constant.

Fig. 4 Four general air mass pathways to the Douro Norte monitoring station in terms of direction of flow, wind speed and frequency, obtained with HYSPLIT transport and dispersion model. The atmospheric transport regime described by air mass 2 is associated with the highest O$_3$ levels for the period 2004–2007 (from Carvalho et al. 2010)
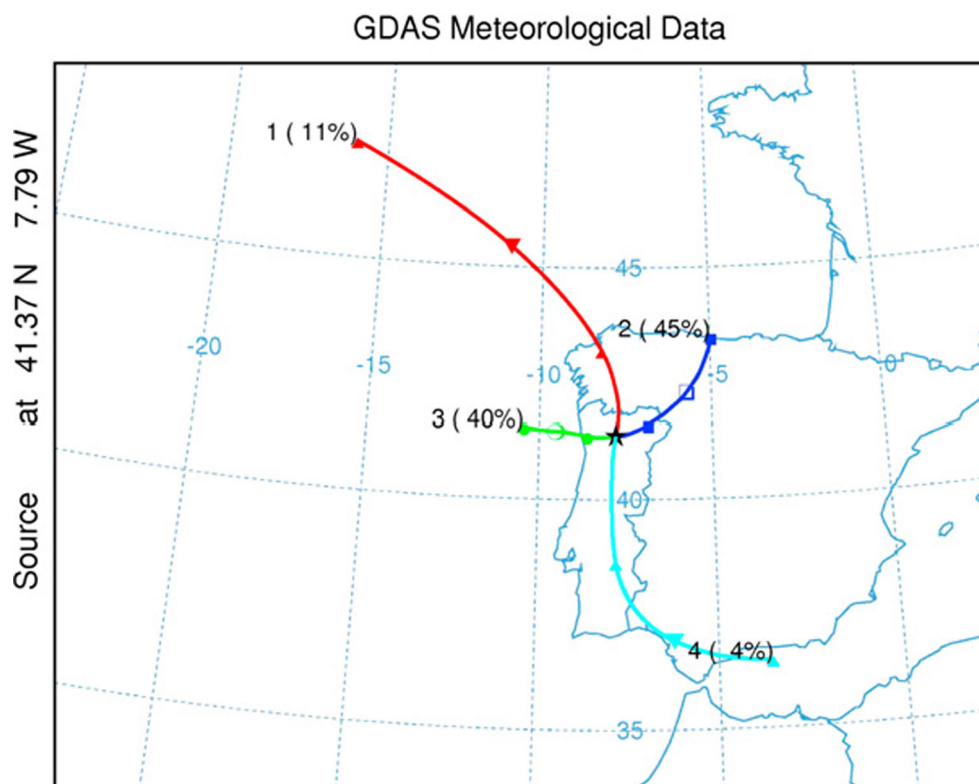
Table 4 Statistically significant sequential Mann-Kendall trend test results (*U* statistics and trend start year) for NO, NO$_2$ and O$_3$ concentrations throughout the study period 1995–2010 and slope estimation of the linear trend

Monitoring station	Type	NO			NO$_2$			O$_3$		
		U	Trend start	µg m^{-3} year^{-1}	*U*	Trend start	µg m^{-3} year^{-1}	*U*	Trend start	µg m^{-3} year^{-1}
Laranjeiro	Urban background	−1.70		−0.5861	0.45		0.2523	3.85	2005	1.7382
Alfragide	Urban background				0.14		−0.0759	−2.06	2005	−1.7451
Reboleira	Urban background	−1.16		−0.1374						
Alto Seixalinho	Urban traffic	1.44		0.3152	2.70	2006	0.8228	2.44	2009	1.8129
Escavadeira	Urban industrial	0.63		0.1457	0.09		0.0755			
Lavradio	Urban industrial	−3.33	2002	−1.5486	−3.96	2001	−2.0111			
Coimbra	Urban traffic				−1.32		−0.8186	0.86		0.6083
Av. 24-Espinho	Urban traffic	−2.77	2007	−0.8606	0.98		0.2905			
E. Avanca	Rural background				0.08		−0.1498			
E. Teixugueira	Suburban industrial	−2.52	2008	−0.6187	−0.86		0.1557	1.92		1.1197
Pe Joaquim Neves	Urban traffic							2.06	2009	0.9628
Av. da Liberdade	Urban traffic	−3.33	2005	−2.3316	1.08		−0.2622			
Beato	Urban background	−3.42	2004	−0.3846	1.71		0.3067	3.45	2001	1.6611
Chelas	Urban background	−4.14	2000	−1.0820	−2.52	1999	−1.4009			
Entrecampos	Urban traffic	−3.60	2001	−2.4701	0.63		0.4180	4.86	2000	2.5546
Olivais	Urban background	−0.63		−0.1148	1.35		0.4096			
St. Cruz Benfica	Urban traffic	−2.43	2009	−1.6517	−0.99		−0.0646			
Loures Centro	Urban background	−0.63		−0.3557						
Don Manuel II	Urban traffic	−3.66	2004	−1.3649	−0.08		0.0254	1.95		1.2682
VN Telha-Maia	Suburb. background	−2.74	2007	−0.3446	−1.37		−0.1883	0.14		0.1467
Custóias	Suburb. background	−2.74	2008	−1.3432	0.06		−0.3799	1.65		0.6820
Leça do Balio	Suburb. background	−1.70		−0.8023	1.52		0.9135	0.45		0.0609
Mouzinho	Urban traffic	−3.31	2003	−3.3975	−1.88		−1.5542			
Fco. Sá Carneiro	Urban traffic							1.52		1.3793
Monte Velho	Rural background	−1.34		−0.0790	−0.45		0.0047	0.54		0.0295
Sonega	Rural industrial	−1.44		−0.1389	−0.99		−0.0921	−0.86		0.1038
Paio Pires	Suburb. background	0.23		0.0330	1.32		1.0614	1.95		2.9147
Monte Chaos	Suburban industrial	−2.34	2008	−0.1037	−1.44		−0.2676	2.34	2009	1.4904
Ermesinde	Urban background	−2.41	2008	−0.3487	0.86		0.2787	2.47	2005	0.8332

The decreasing trend of the NO$_2$ levels registered in Lavradio, an urban industrial station located in the Setúbal Peninsula on the south bank of the Tagus, may have resulted from the combination of several reasons, such as the closure in the early 2000 of manufacturing units dedicated to the production of ammonia and urea, the relocation of shipyards and the construction of the regional circular motorway, which has cut the local traffic. On the other hand, Chelas is an urban background station located in the eastern part of Lisbon that has undergone several interventions to avoid congestions and to contribute to a more fluid traffic towards the city centre. It has also benefited from the construction of the metro red line.

The 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 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 located near complex road systems. Road traffic is the only large emission source of nitrogen oxides in this area, leading to a decrease in the NO/NO$_2$ ratio. Figure 5 presents the temporal evolution of NO and NO$_2$ concentrations registered at the stations highlighted above throughout the study period, where the statistically significant trends can be observed.
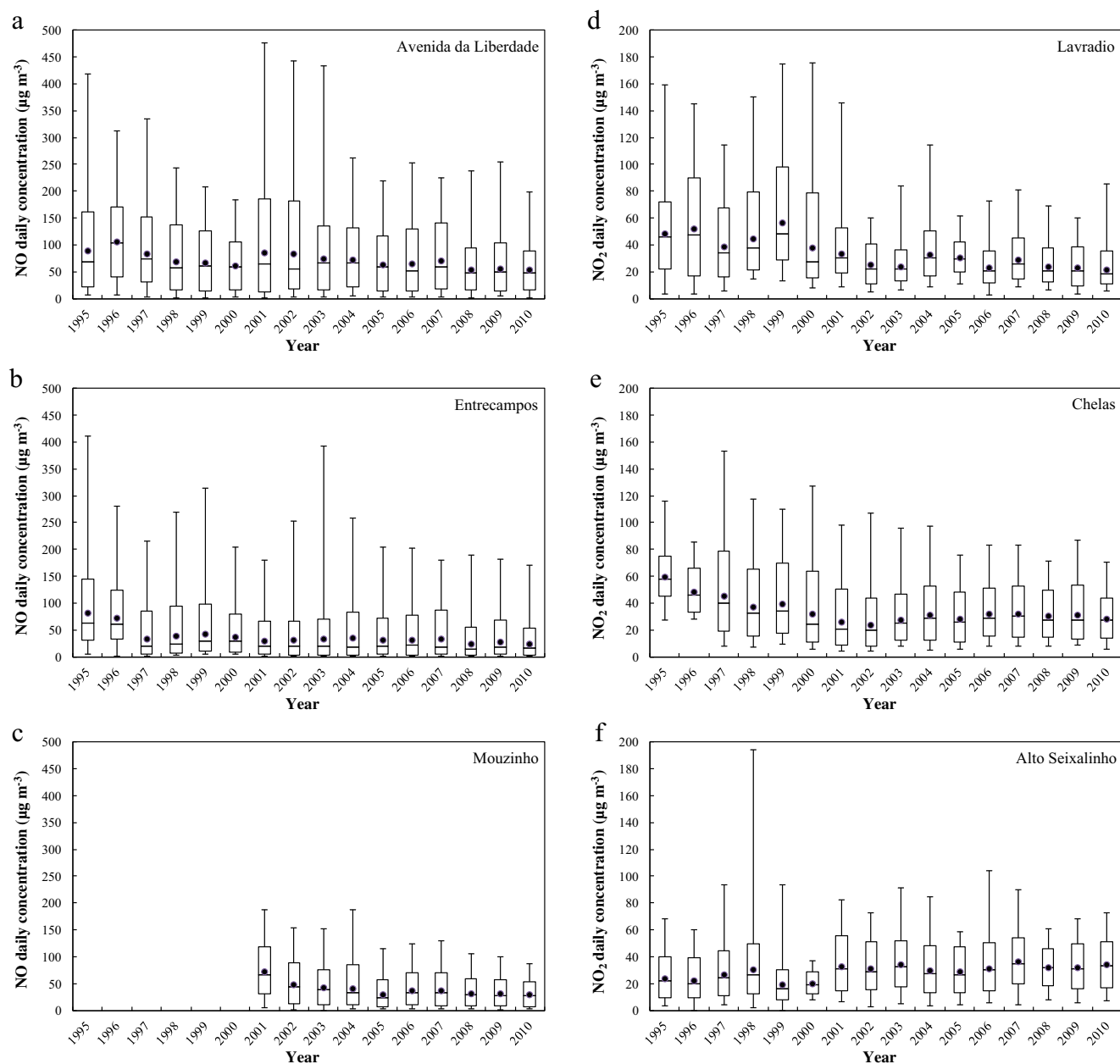
Fig. 5 NO annual concentration throughout the study period monitored at Avenida da Liberdade (**a**), Entrecampos (**b**) and Mouzinho (**c**) and NO$_2$ annual concentration registered at Lavradio (**d**), Chelas (**e**) and Alto Seixalinho (**f**), in terms of mean (*dot*), median (*horizontal line*), 10th and 90th percentile (*box*) and minimum and maximum values (*whiskers*)
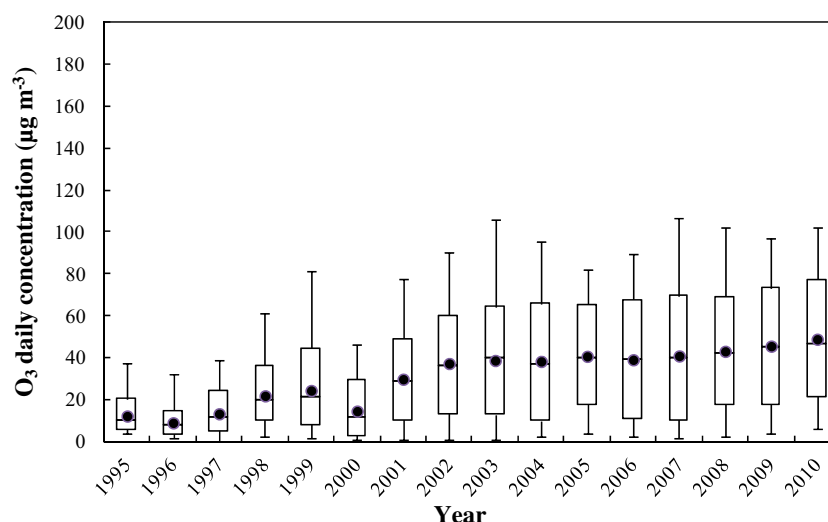
Several stations showed a significant upward trend in O$_3$ concentration, for example the Entrecampos station ($U = 4.86$, $+2.55\ \mu g\ m^{-3}\ year^{-1}$), as illustrated in Fig. 6. This urban traffic station presented a strong downward trend in NO concentration, while NO$_2$ concentration did not exhibit any significant trend. This results in a decrease of the NO/NO$_2$ ratio and, therefore, an increase in the availability of ozone (see reactions (1), (2) and (3) in Appendix A in the Online Resource). A similar behavior can be observed in other stations. The increase rate in O$_3$ concentration is higher in traffic stations than in industrial or background stations because the decrease rate in NO concentration is higher at traffic-impacted sites.

Ozone estimation model: urban and rural case studies

The independent variables used to study the contribution to ozone levels recorded in the period 2004–2010 in the Entrecampos urban traffic station and the Douro Norte rural background station were NO, NO$_2$, NO$_X$, NO/NO$_2$ and NO$_2$/NO$_X$ ratios, SO$_2$, PM$_{10}$, temperature range (T_{range}), pressure (P), relative humidity (RH), wind speed (WS), wind direction (*sin* WD and *cos* WD), solar radiation (SR), dew point temperature (Dew) and precipitation (Precip).

An estimation model was developed from several of the variables listed above. The step-by-step process used to build

Fig. 6 Annual mean (*dot*) and median (*horizontal line*), 10th and 90th percentile (*box*) and minimum and maximum values (*whiskers*) of O$_3$ daily concentration registered at the Entrecampos urban station

the model, as well as its most relevant results, is detailed in the Online Resource (Appendix E).

From the results of the stepwise regression analysis shown in Table 5, the set of independent variables NO$_2$/NO$_X$ ratio, solar radiation, wind speed, relative humidity, sine and cosine of wind direction, precipitation, PM$_{10}$ and temperature range was selected to calculate the equation for predicting ozone concentration using a generalized linear model (GLM) at the Entrecampos urban station. On the other hand, the independent variables selected at the Douro Norte rural station for this purpose were relative humidity, sine and cosine of wind direction, PM$_{10}$, NO$_2$/NO$_X$ ratio, solar radiation, temperature range and precipitation. The prediction equation obtained by the GLM using data from the period 2004–2010 is shown in Fig. 7a, b for Entrecampos and Douro Norte, respectively.

The ozone concentration values obtained by the prediction equation at the Entrecampos urban station (Fig. 7a) fit satisfactorily the concentrations measured in the year 2013 (the latest year for which validated data of pollutants concentration is available in the air quality monitoring network of Portugal). Despite the difficulty in predicting extreme values of regression models (Hubbard and Cobourn 1998), the proposed

model appears to be able to predict the most extreme ozone events in this monitoring station, as well as the minimum ozone values. The average absolute error of the prediction for the year 2013 was 9.0 μg m^{-3}, and 84 % of the absolute errors were less than 10 μg m^{-3}.

As shown in Fig. 7b, the fit of the predicted ozone concentrations registered in the year 2013 in the Douro Norte rural station is not as high as in the case of the Entrecampos urban station, due to the smaller variance in ozone concentration explained by the independent variables included in the SMRA model for Douro Norte ($adjR^2 = 0.492$). 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 (Gordon et al. 2014) and consequently contribute to the local photochemical ozone production from transported precursors, which can explain the low variance provided by predictor variables introduced in the model due to the lack of data of VOC concentrations. In addition, their local geography also plays a key role in ozone concentrations recorded at this site. Even so, the seasonal variation of ozone concentration was captured successfully by the model and the predicted extreme ozone events are

Table 5 Stepwise regression model for O$_3$ concentration at the Entrecampos urban station and the Douro Norte rural station

Entrecampos	NO$_2$/NO$_X$	SR	WS	RH	*sin* WD	*cos* WD	Precip	PM$_{10}$	T_{range}
Adjusted R^2	0.595	0.649	0.679	0.689	0.694	0.701	0.704	0.706	0.707
F change	3150.2	327.7	202.2	69.3	38.0	51.4	22.6	16.4	5.3
Sig. F change	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.022
Douro Norte	RH	*sin* WD	*cos* WD	PM$_{10}$	NO$_2$/NO$_X$	SR	T_{range}	Precip	
Adjusted R^2	0.342	0.383	0.417	0.441	0.460	0.482	0.489	0.492	
F change	924.2	116.1	106.7	74.7	66.1	76.2	24.7	10.6	
Sig. F change	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	

a

$$[O_3] = EXP[2.509 + 2.079(NO_2/NO_X) + 6.348 \cdot 10^{-5}SR + 0.068WS - 0.013RH - 0.205WD_{sin} - 0.119WD_{cos} + 0.008Precip - 0.002PM_{10} + 0.002T_{range}]$$

b

$$[O_3] = EXP[4.597 - 0.01RH - 0.034WD_{sin} - 0.062WD_{cos} + 0.002PM_{10} + 0.219(NO_2/NO_X) + 6.228 \cdot 10^{-5}SR + 0.001T_{range} + 0.003Precip]$$
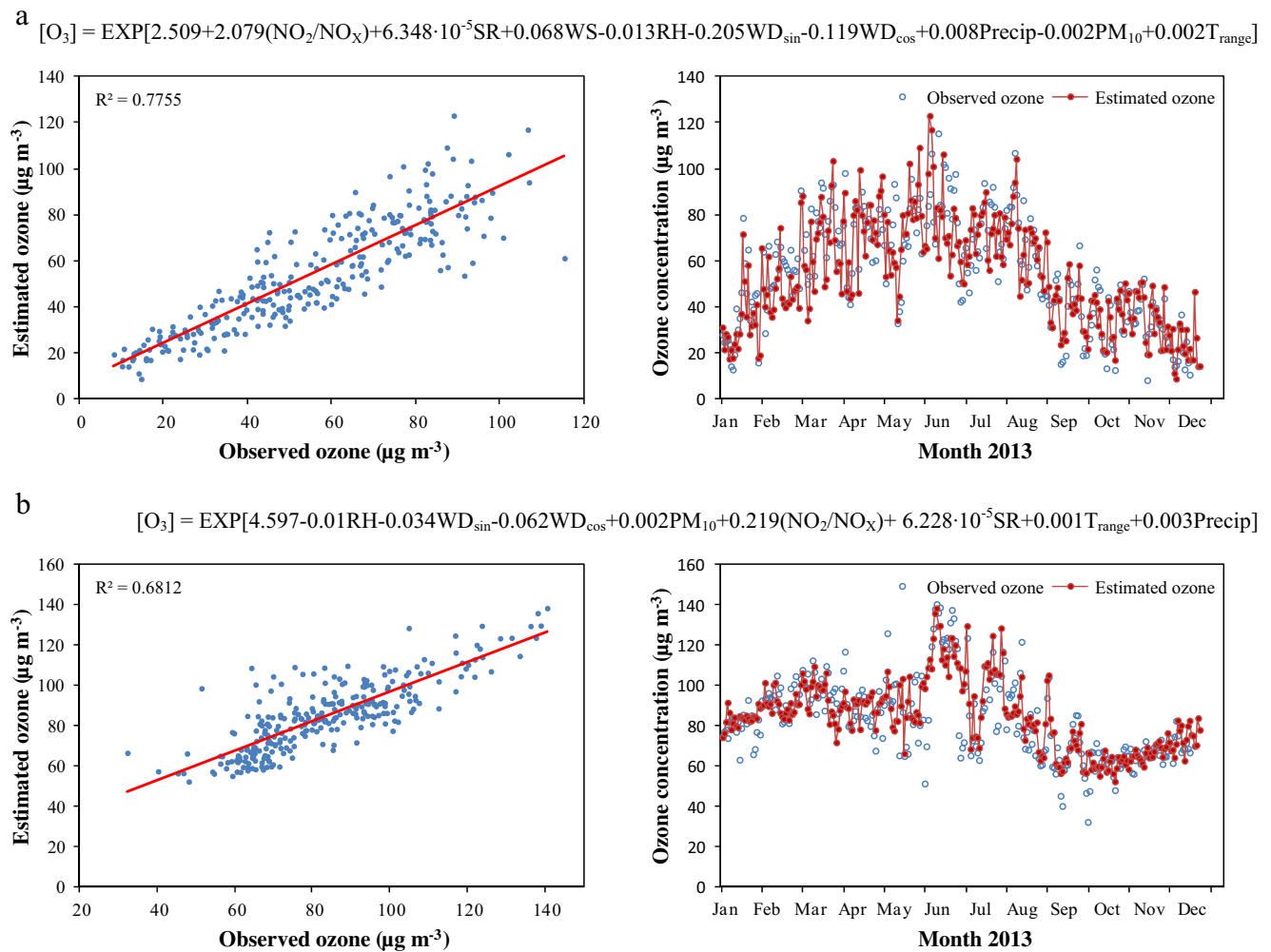

Fig. 7 Observed and estimated values of ozone concentration provided by the GLM estimation equation for the year 2013 at the Entrecampos urban station (**a**) and the Douro Norte rural station (**b**). The estimation equation is shown on the *upper part* of both charts

seen to agree closely with the observed concentrations, but minimum ozone values seem to be a little overpredicted. The average absolute error of the prediction for this station was 10.2 µg m^{-3} for the year 2013, whereas 78 % of the absolute errors were less than 10 µg m^{-3}.

Conclusions

Together with meteorological variables, 16 years of NO, NO$_2$ and O$_3$ concentrations collected over the period 1995–2010 at several air quality monitoring stations in mainland Portugal were analyzed. The variation in NO concentration showed a marked seasonal pattern, with the highest levels occurring in the colder months, especially near the most densely populated metropolitan areas. The seasonal fluctuations of NO$_2$ concentrations are not so marked. Despite an overall downward trend in the NO concentration, no statistically significant trend towards a decrease of NO$_2$ levels was observed in most of the monitoring stations. Ozone showed an opposite seasonal

pattern to the pattern of NO. Several stations showed a significant upward trend in O$_3$ levels as a result of the decrease in the NO/NO$_2$ ratio.

The ozone trends observed in this study in the northern region could be extrapolated to other rural areas in the NW of the 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. Moreover, O$_3$ trends are strongly affected by changes in emissions of photochemical precursors, so the analysis of future concentration patterns will be very useful to confirm the influence of these factors. Despite the general drop in 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.

A strong correlation between ozone and wind direction was obtained at a representative site in that region, emphasizing the importance of long-range ozone transport. For this rural site, the percentage of variance in O$_3$ concentrations explained

by other pollutants is relatively low. Meteorological variables such as wind direction explained most of the variance. At the urban traffic site, most of the variance is explained by the NO_2/NO_X ratio.

The concentration values obtained by the daily ozone estimation model in an urban traffic station fit those registered on the last validated data available. In a northern rural area, minimum ozone values seem to be a little overestimated, but the estimated ozone concentrations in extreme events agree with the concentrations observed. This ozone estimation model could be useful when applied to different urban areas in the Iberian Peninsula under severely polluted conditions.

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