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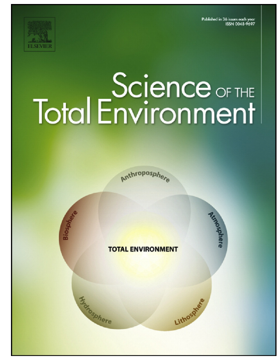

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Impact of primary NO_2 emissions at different urban sites exceeding the European NO_2 standard limit

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Abstract

A large part of the European population is still exposed to ambient nitrogen dioxide (NO_2) levels exceeding the European Union (EU) air quality standards, being a key challenge to reduce NO_2 concentrations across many European urban areas, particularly close to roads. In this work, a trend analysis of pollutants involved in NO_2 processes was done for the period 2003-2014 in traffic sites from three Spanish cities (Barcelona, Madrid and Granada) that still exceed the European NO_2 air quality standard limits. We also estimated the contributions of primary NO_2 emissions and photo-chemically formed NO_2 to the observed ambient NO_2 concentrations in order to explore their possible role in the observed NO_2 concentration trends. The NO_x and NO concentrations at these traffic sites showed significant decreasing trends during the period 2003-2014, especially at Barcelona (BAR_{TR}) and Madrid (MAD_{TR}) traffic stations. The NO_2 concentrations showed statistically significant downward trends at BAR_{TR} and MAD_{TR} and remained unchanged at Granada traffic station (GRA_{TR}) during the study period. Despite the significant decrease in NO_2 concentrations in BCN_{TR} and MAD_{TR} during the analysed period, the NO_2 concentrations observed over these sites still above the annual NO_2 standard limit of 40 µg m^{-3} and, therefore, more efficient measures are still needed. Primary NO_2 emissions significantly influence NO_2 concentrations at the three analysed sites. However, as no drastic changes are expected in the after-exhaust treatment technology that can reduce primary NO_2 emissions to zero in the near future, only a substantial reduction in NO_x emissions will help to comply with the NO_2 European air quality standards. Reduction of 78%, 56% and 16% on NO_x emissions in Barcelona, Madrid and Granada were estimated to be necessary to comply with the NO_2 annual limit of 40 µg m^{-3}.

Keywords:

- Primary NO_2 fraction (f-NO_2)
- NO_x, NO_2, NO and O_3 concentrations
- Air pollution
- EU limit values

1 Introduction

Air pollution is an environmental issue of public health concern (e.g., Pope and Dockery, 2006). Exposure to air pollutants in urban areas, emitted by different sources, can cause severe health problems such as increased morbidity and mortality and alterations in the respiratory, cardiovascular and cerebrovascular systems (WHO, 2013). According to the report of Air quality in Europe (EEA, 2016), $PM_{2.5}$ (particle matter with diameter <2.5 µm), NO_2 and O_3 are responsible for 400,000 premature deaths per year in the European Union (EU). For this reason, the European Commission has established different threshold limits values along the last decades for many ambient air pollutants.

In order to improve air quality in the European continent and meet the air quality standard limits in the European countries, the European Commission (EC) has implemented several stringent emission control measures along the last decades. Various EC control measures focused on vehicle emissions, such as EURO III, IV, V and VI emission standards, entered in force from 2000 to now on for restrictions of road traffic emissions, and 1999/32/EC for shipping emission restrictions. Also, EC has established several control measures for industry emissions, such as the Integrated Pollution Prevention and Control Directives 1996/61/EC and 2008/1/EC, or 1999/13/EC to control the emissions of Volatile Organic Compounds. In addition to these control measures on European scale, regional and local authorities have adopted a number of measures to reduce air pollution. The scope of these control measures and the level of ambition vary significantly among regions and countries. Some of these control measures include the implementation of Low Emission Zones, LEZ (e.g., Holman et al., 2015), public transportation re-organization (e.g., Gramsch et al., 2013; Titos et al., 2015), promotion of public transport or use of bicycles, among others.

As result of the implemented abatement policies, emissions of large number of air pollutants decreased in the last decades across Europe (e.g., Harrison et al., 2008; EEA, 2016), resulting in generally improved air quality across the EU. Nowadays, most European zones meet the air quality limits established for CO, SO_2, and metals (e.g., Querol et al., 2014; Henschel et al., 2013; EEA, 2016). However, emissions of nitrogen oxides (NO_x, NO_x=NO+NO_2) from road transport have not decreased sufficiently, and NO_2 ambient concentration, especially at roadside sites, has not decreased as expected, and even in some cases NO_2 concentration has increased (EEA, 2016). As result, several European cities still exceeding the annual NO_2 air quality limit value of 40 µg m^{-3} for the protection of human health (in force in the European Union since 2010), especially at roadside stations (e.g., Guerreiro et al., 2014; Derwent et al., 2007; Adame and Sole, 2013; Font and Fuller, 2016).

A large part of the population lives in urban areas, therefore, the failure of EU emission control measures to reduce NO_2 ambient concentrations in urban areas has important implications for public health. NO_2 is a toxic gas, mainly formed in the atmosphere by reactions of NO and ozone, although direct NO_2 emissions by traffic, especially diesel fueled vehicles, can also contribute to ambient NO_2 concentration (Carslaw and Beevers, 2004a).

High ambient NO_2 concentrations can cause inflammation of the airways and cardiovascular disease (WHO, 2013; Latza et al., 2009) and even morbidity and mortality (Samoli et al., 2006; Beelen et al., 2008). According to the last European Environment Agency report, NO_2 was responsible for 71,000 premature deaths in EU and for 4,280 premature deaths in Spain in 2013 (EEA, 2016). Also, NO_2 contributes to the formation of secondary aerosols and tropospheric ozone in the atmosphere, which also have adverse impacts on human health (Finlayson-Pitts and Pitts, 2000).

The unexpectedly small decrease of NO_2 ambient concentrations, despite large EU regulatory efforts, together with the strong adverse health effects of long term exposure to this pollutant have led to considerable research in the last few years for understanding NO_2 trends and exploring the potential causes of the observed trends (e.g., Henschel et al., 2015; Escudero et al., 2014). Several studies have shown that NO_2 yearly and hourly exceedances are caused by road traffic emissions (e.g., Degraeuwe et al, 2016; Querol et al., 2014; Wild et al., 2017). Some studies in the UK, Switzerland, Finland and Germany have attributed the weaker downward trends of NO_2 and the non-compliance of NO_2 air quality standards in urban areas to the significant increase of the number of diesel-fueled vehicles together with the increase of primary NO_2 fraction in the NO_x exhaust from diesel vehicles fitted with modern after exhaust treatment technologies (Carslaw, 2005; Anttila et al., 2011; Mavroidis and Chaloulakou, 2011; Kurtenbach et al., 2012). The NO_2 fraction in the total NO_x emitted (f-NO_2) by diesel vehicles not fitted with modern exhaust treatment technologies is about 10-12% and can reach up to 70% for those fitted with particle traps and oxidation catalysts like EURO III, IV, V, VI (Carslaw et al., 2016), being recommended by some authors the control of not only total NO_x emissions but also NO_2 primary emissions (e.g., Carslaw and Beebers, 2004b). However, other studies in Netherlands and Germany showed that reducing primary NO_2 emissions will not have a strong influence on urban NO_2 concentrations and only substantial reduction of local NO_x emissions will help to reduce NO_2 concentration and meet NO_2 European air quality standards (Keuken et al., 2009; Kurtenbach et al., 2012). Also, using an urban NO_2 pollution model with various NO_x emission scenarios, Degraeuwe et al. (2016, 2017) found that the reduction in NO_x emissions of diesel cars is more relevant than the NO_2 fraction in the total NO_x emissions for the reduction of regional and urban NO_2 concentrations. Furthermore, Degraeuwe et al. (2016, 2017) found that f-NO_2 only has a relevant effect in proximity of intense road traffic typically found on artery roads. However, Henschel et al. (2015) could not draw any clear conclusion concerning the role of primary NO_2 emissions or other factors in the observed NO_2 trends at 9 European cities, recommending further research to explore the potential factors affecting the observed trends in ambient NO_2 concentrations in urban areas.

As in other European countries, in Spain, the ambient NO_2 concentrations have not decreased as expected and as a consequence the annual NO_2 limit value of 40 μg m^{-3} established by the EU for the protection of human health has been continuously exceeded at 3 cities with different population and geographical characteristics (Barcelona, Granada and Madrid) (EAA, 2016). Until now the reason for the observed changes in NO_2 concentrations at these urban sites have not been thoroughly investigated. Understanding why concentrations of NO_2 in these Spanish cities have not decreased as anticipated requires a better understanding of NO_2 trend and the exploration of the potential causes of the observed trend. This can provide useful information to plan further actions to effectively mitigate urban NO_2 pollution.

In this study we evaluate the NO_2 concentration and quantify its trend from 2003 to 2014 in three Spanish cities that still exceed the European NO_2 air quality standard limits. In addition, we quantify the contributions of primary NO_2 emissions, photo-chemically formed NO_2 and background concentrations to the observed ambient NO_2 concentrations and investigate their possible role in the observed NO_2 concentration trend. Finally, we provide an estimate of the concentration of NO_x that needs to be reduced to comply NO_2 limits.

2 Methodology

2.1 The study areas and data sets

The measurements presented in this study were registered at Barcelona, Granada and Madrid. Madrid and Barcelona metropolitan areas are the most densely populated regions in Spain, both with more than 3 million inhabitants (www.ine.es). Madrid metropolitan area is located in a continental plateau in the centre of the Iberian Peninsula. Traffic and residential heating are the main sources of pollution in this metropolitan area, since industrial activity consists essentially of light factories (Salvador et al., 2012). Barcelona metropolitan area is located in the North-East of Spain, over the Mediterranean side, being a highly industrialised agglomeration. Anthropogenic emissions from industrial activities and road and shipping traffic are the main sources of NO_x in this metropolitan area (Querol et al., 2017). On the other hand, Granada, situated in the south-eastern of Spain, is a non-industrialised medium-size city with a population of 240 000 inhabitants (350 000 including the metropolitan area; www.ine.es) where road traffic represents the major anthropogenic source of pollution (Titos et al., 2017; Patrón et al., 2017).

NO_x, NO_2, NO and O_3 concentrations, with hourly time resolution, registered at these three cities from 2003 to 2014 are used in this study. Data from two monitoring stations for each metropolitan area are used: one traffic station (TR) and one EMEP (Cooperative Programme for the Monitoring and Evaluation of Long Range Transmission of Air Pollutants in Europe) regional background station (RB). The stations selected for each metropolitan area are described in Table 1. These stations were selected based on the availability of NO, NO_2 and O_3 data at both traffic and EMEP stations. From now on, Barcelona, Granada and Madrid traffic stations will be called BCN_{TR}, GRA_{TR} and MAD_{TR}, respectively, and regional background EMEP stations will be called BCN_{RB}, GRA_{RB} and MAD_{RB}, respectively.

Area	Station			Location		
	Name	Code	Type	Lat.	Long.	Height (m.a.s.l)
Barcelona	Barcelona (Gracia-S.	ES1480A	TR	41.399	2.153	57

	Gervasi)					
	Cabo De Creus	ES0010R	RB	42.319	3.316	23
Granada	Granada Norte	ES1560A	TR	37.196	-3.613	689
	Viznar	ES0007R	RB	37.237	-3.534	1230
Madrid	Escuelas Aguirre	ES0118A	TR	40.422	-3.682	672
	Campisábalos	ES0009R	RB	37.237	-3.534	1360

Table 1. Details of the traffic and regional background stations with availability of NO, NO_2 and O_3 data in the period 2003-2014.

Data from TR stations are available on Generalitat de Catalunya (http://dtes.gencat.cat/icqa), Ayuntamiento de Madrid (http://datos.madrid.es) and Junta de Andalucia (http://www.juntadeandalucia.es/medioambiente) websites. Data from EMEP stations are available on EBAS-NILU database (http://ebas.nilu.no). The measurement protocols followed at the selected stations meet the requirements of the European Air Quality directives and therefore assure the comparability of the data. Finally, fuel consumption data are obtained from the Corporation of strategic Reserves of oil-based products website (www.cores.es).

Due to unavailability of O_3 measurements at Granada Norte station during the period 2012-2014, O_3 data from another urban station in the city of Granada (Palacio de Congresos station) located ~3.5 km from Granada Norte station were used. This is supported by comparable O_3 measurements obtained at both stations during a simultaneous measurement period (Fig. S1 of the Supplementary material). Also, during the second half of 2014, Madrid traffic station was influenced by public construction activities carried out near the station (Madrid City Council, 2014), so we have excluded this period from our analysis.

It's worth noting that there are other three Spanish cities (Córdoba, Murcia and Valencia) that are currently exceeding NO_2 standard limit (MAPAMA, 2015) but were not included in this study due to the unavailability of O_3 measurements at the traffic station or lack of a nearby EMEP station.

2.2 Data analysis

Trends estimation of pollutants concentrations registered at each station were calculated using the Theil-Sen method (Theil, 1950; Sen, 1968) included in the OpenAir data analysis tool (Carslaw and Ropkins, 2012), which was specifically designed for air pollution data treatment. Theil-Sen methodology derives from the nonparametric Mann Kendall test (Kendall, 1976; Hipel and McLeod, 2005), and is more robust and provides more accurate confidence intervals when absurd values occur. The magnitude of this trend analysis is expressed as a slope that represents the rate of increase or decrease per year of each pollutant concentration. The calculated trends were considered statistically significant with significance level of 0.1 (corresponding to 10% chance there is no trend) or lower.

In order to determine f-NO_2 (fraction of NO_2 in the total NO_x emissions) at the studied traffic sites from ambient monitoring data we used the model developed by Abbott (2005). This method has the advantage that it is based on a mathematical representation of the physical and chemical processes involving NO, NO_2 and O_3 in the atmosphere. It requires ambient measurements of NO, NO_2 and O_3 concentrations at traffic and at nearby background site. This method removes the effect of background pollution by considering the difference in the O_x (O_3+NO_2) and NO_x (NO+NO_2) concentrations between an urban traffic station and a nearby background station. A more detailed description of the model is provided in Supplementary Material; although, a brief description is given below.

In Abbott (2005) model, f-NO_2 is obtained from the following regression equation:

$$[\mathrm{O_x}]_{\mathrm{local}} = \mathrm{a}[\mathrm{NO_x}]_{\mathrm{local}} + \mathrm{b} \qquad \text{(Eq. 1)}$$

Where $[\mathrm{O_x}]_{\mathrm{local}}$ and $[\mathrm{NO_x}]_{\mathrm{local}}$ are defined as follow:

$$[\mathrm{O_x}]_{\mathrm{local}} = [\mathrm{NO_2}]_{\mathrm{TR}} + [\mathrm{O_3}]_{\mathrm{TR}} - [\mathrm{NO_2}]_{\mathrm{RB}} - [\mathrm{O_3}]_{\mathrm{RB}} \qquad \text{(Eq. 2)}$$

$$[\mathrm{NO_x}]_{\mathrm{local}} = [\mathrm{NO}]_{\mathrm{TR}} + [\mathrm{NO_2}]_{\mathrm{TR}} - [\mathrm{NO}]_{\mathrm{RB}} - [\mathrm{NO_2}]_{\mathrm{RB}} \qquad \text{(Eq. 3)}$$

Where $[\mathrm{NO}]_{\mathrm{TR}}, [\mathrm{NO_2}]_{\mathrm{TR}}$ and $[\mathrm{O_3}]_{\mathrm{TR}}$ are the concentrations of NO, NO_2 and O_3 (in ppb) at the traffic station and $[\mathrm{NO}]_{\mathrm{RB}}, [\mathrm{NO_2}]_{\mathrm{RB}}$ and $[\mathrm{O_3}]_{\mathrm{RB}}$ are the corresponding concentrations in the nearby background station.

The regression parameter **a** provides the fraction of NO_2 in the total NO_x emissions (f-NO_2), and **b** is the intercept parameter which is expected to be close to zero. The parameter **b** excludes the background oxidant concentrations and represents the net effect of deposition and other chemical and photochemical reactions (different of O_3+NO -> NO_2 and photodissociation of NO_2) that contribute to a lesser extent to ambient NO_x and O_3 concentrations (see Eq. S13 in Supplementary Material). It is worth noting that both parameters **a** and **b** are relatively insensitive to the choice of background monitoring site as was showed by Abbott (2005).

In this study, linear regression analysis on each annual set of hourly $[O_x]_{local}$ and $[NO_x]_{local}$ data was done to retrieve f-NO_2 for each year at BCN_{TR}, GRA_{TR} and MAD_{TR} sites using BCN_{RB}, GRA_{RB} and MAD_{RB} as nearby background sites. The results of this analysis are presented in Table S1 of the Supplementary Material. The results show that for all analyzed sites, despite the scatter, there is a good correlation between $[O_x]_{local}$ and $[NO_x]_{local}$ in each dataset. Also, the values of intercept parameter **b** are, as expected, very small and close to zero, suggesting that BCN_{RB}, GRA_{RB} and MAD_{RB} sites are representative of background conditions for BCN_{TR}, GRA_{TR} and MAD_{TR} sites, respectively.

After the estimation of f-NO_2 we determined the primary and secondary NO_2 concentrations at each traffic station (Anttila et al., 2011). In this calculation we assumed that the total NO_2 concentration observed at each station is composed of primary NO_2 emission ($[NO_2]_{primary}$), secondary NO_2 formed by NO-O_3 reaction ($[NO_2]_{secondary}$) and regional background ($[NO_2]_{RB}$):

$$[NO_2] = [NO_2]_{primary} + [NO_2]_{secondary} + [NO_2]_{RB} \quad \text{(Eq.4)}$$

Where

$$[NO_2]_{primary} = a \cdot [NO_x]_{local} \quad \text{(Eq. 5)}$$

$$[NO_2]_{secondary} = (1\text{-}a) \cdot [NO_x]_{local} + [NO]_{RB} - [NO]_{TR} \quad \text{(Eq. 6)}$$

Finally, to estimate the required NO_x reduction to achieve the NO_2 European standard limits at BCN_{TR}, MAD_{TR} and GRA_{TR} stations we used the roll-back model (De Nevers and Morris, 1975; Lu, 2004; Chaloulakou et al., 2008):

$$R\ (\%) = (C_A - C_R)/(C_A - B) \quad \text{(Eq. 7)}$$

Where R (%) is the necessary NO_x emission reduction, C_A is the actual NO_x mean annual concentration (2014 in this work) and C_R is the NO_x mean concentration corresponding to the necessary reduction level (NO_x objective level). Finally, B is the NO_x background concentration at traffic station. The background concentration in this equation corresponds to the concentration at traffic site when nearby source emissions that influence the NO_x concentration at this site are switched off. The values of B in this case were estimated from the concentrations observed at the three studied traffic stations. For this we calculated the mean hourly annual diurnal NO_x concentrations at each studied traffic station for 2014. The minimum NO_x hourly concentration observed at each studied traffic station was taken as NO_x background concentration at this site. The NO_x background concentrations of 47, 39 and 30 µg/m³ were obtained for BCN_{TR}, MAD_{TR} and GRA_{TR}, respectively.

The roll-back model is widely used due to its simplicity and because it requires very little input data. This model assumes that the spatial distribution of emission sources, meteorological conditions and species are conservative. The NO_x can be considered stable for roll-back modelling, since the transformations are mainly internal to the cycle $NO/NO_2/O_3$. The value of R (%) calculated by this model becomes indeterminate when the actual NO_x annual mean concentration (C_A) is similar to the NO_x background concentration (B). Therefore, this method is limited to those situations where C_A is higher than B. In addition, C_R should be higher than B due to the impossibility to reduce NO_x concentration below the background concentration.

3 Results and discussion

3.1 Levels and trends of atmospheric pollutants

Fig. 1 shows the annual NO, NO_2 and NO_x concentrations and the NO/O_3 annual mixing ratio at TR stations and Table 2 summarizes trend analysis results at TR and RB station.

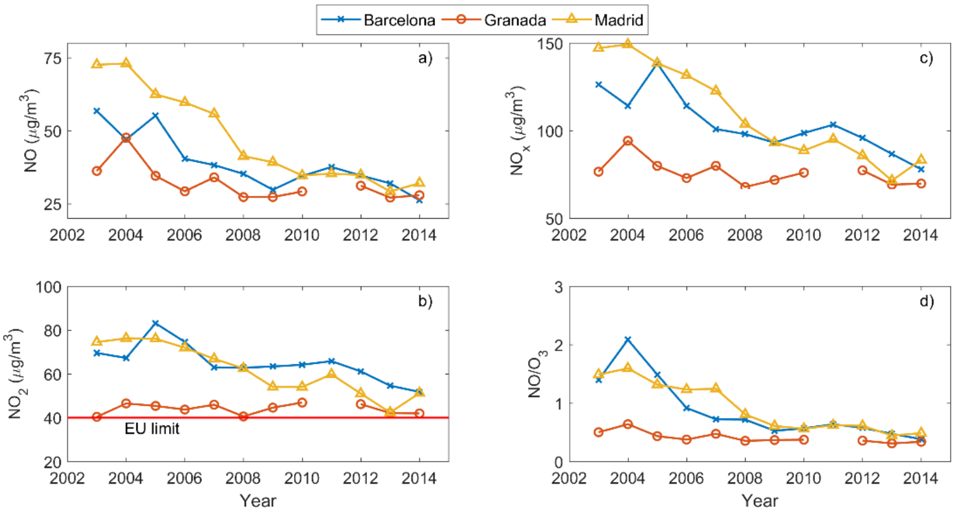

Figure 1. 2003-2014 trends of mean annual (a) NO, (b) NO_2 and (c) NO_x concentrations ($\mu g\ m^{-3}$) and annual (d) NO/O_3 mixing ratio recorded at BCN_{TR}, GRA_{TR} and MAD_{TR}.

	BCN_{TR}	GRA_{TR}	MAD_{TR}	BCN_{RB}	GRA_{RB}	MAD_{RB}
$\boldsymbol{NO}$	-2.15***	-0.52+	-3.39***	-0.01***	-0.02***	-0.01***
$\boldsymbol{NO_2}$	-1.85***	0.02	-2.94***	-0.03*	-0.05*	-0.04***
$\boldsymbol{NO_x}$	-4.16***	-0.65	-6.74***	-0.04***	-0.08*	-0.05***
$\boldsymbol{NO/O_3}$	-0.71***	-0.03+	-0.26***	-----	-----	-----

Table 2. Results of the Theil-Sen trend analysis for the 2003-2014 period. The symbols shown for the *p* values for each trend estimate relate to how statistically significant the trend estimate is: *p*<0.001=* (highest statistical significance), *p*<0.01=**, *p*<0.05=* and *p*<0.1=+; no symbol stands for no significant trend (p>0.1). Units are $\mu g\ m^{-3}\ yr^{-1}$ for NO, NO_2 and NO_x, and yr^{-1} for NO/O_3.**

As expected, NO and NO_x concentrations at MAD_{TR} and BCN_{TR} stations were higher than those registered at GRA_{TR} station during the whole studied period, due to their larger population and vehicles fleet. However, these differences in NO and NO_x concentrations between Madrid/Barcelona and Granada traffic stations decreased significantly along the study period (Fig. 1). For example, the differences in NO and NO_x concentrations between MAD_{TR} and GRA_{TR} stations were 36 (100%) and 70 (92%) $\mu g\ m^{-3}$ on 2003, however, these differences decreased to 4 (14%) and 13 (19%) $\mu g\ m^{-3}$ in 2014. These results show that there was significant reduction in NO and NO_x concentrations at Madrid and Barcelona traffic stations along the studied period in comparison to GRA_{TR} station. This is possibly associated at least partly with the various local/regional emission control measures implemented in Madrid and Barcelona during the analysed period. Local/regional emission control measures to improve air quality started early in Madrid and Barcelona (e.g., ELCACM, 2006; PCACM, 2012; ECACCCM, 2014; PCMCAB, 2013; PDMQLA, 2015; and references therein), however, in Granada these measures started in 2014 (PMCAAGAM, 2014).

High and statistically significant downward trends were observed for NO and NO_x concentrations in Madrid and Barcelona cities, especially at traffic stations (Table 2), probably due to the implemented control measures, both local/regional control measures and EU directives. The NO and NO_x concentrations decreased by approximately 45% and 55%, respectively, between 2003 and 2014 in both MAD_{TR} and BCN_{TR} stations. This high reduction in NO_x ambient concentration is similar to the estimated NO_x emission reduction (of about 40%) for the period 2003-2014 reported by the Spanish national emissions inventory (MAPAMA, 2017). In contrast, the reduction of NO and NO_x concentrations in GRA_{TR} was smaller and not statistically significant (Table 2). The NO and NO_x concentrations in GRA_{TR} decreased by only 25% and 9%, respectively, from 2003 to 2014. The NO_x reduction in GRA_{TR} was much smaller than that expected by the Spanish national inventory emissions (MAPAMA, 2017). This small unexpected reduction in NO_x concentration at GRA_{TR} was probably due to the non-implementation of local/regional emission control measures, especially traffic emission control, in the city of Granada during the analysed period.

It is worth noting that the analysed period includes the global economic recession that took place from 2008 to 2014, which may also have affected the observed NO_x and NO concentrations decreasing trends over the analysed period. As a result of the economic recession, the consumption of fuel oil used in diesel vehicles in Madrid, Barcelona and Granada in 2008-2014 decreased by 19%, 23% and 23%, respectively, with respect to 2003-2007 period. This high decrease in the consumption of fuel oil used by diesel vehicles, which are the main important source of NO_x in urban areas, was associated with a significant decrease in NO and NO_x concentrations in MAD_{TR} and BCN_{TR} stations during the economic recession. The NO concentrations in MAD_{TR} and BCN_{TR} decreased by 45% and 30%, respectively, while the NO_x decreased by 35% and 20%, respectively, in 2008-2014 compared to 2003-2007. However, although the percentage of reduction of the fuel oil consumption in Granada in 2008-2014 was similar to the recorded in BCN_{TR} and MAD_{TR}, reductions of NO and NO_x concentrations in GRA_{TR} were much smaller (22% and 10%, respectively) than those observed at MAD_{TR} and BCN_{TR}. Granada is medium size and non-industrialised city and, thus, the high reduction of the NO and NO_x in MAD_{TR} and BCN_{TR} stations during economic recession in comparison to GRA_{TR} could be attributed to the reduction of NO_x emissions from industrial activities in Madrid and Barcelona cities.

NO_2 concentrations over MAD_{TR} and BCN_{TR} stations showed clear statistically significant downward trends along the analysed period, decreasing by 30% and 25% over MAD_{TR} and BCN_{TR}, respectively, from 2003 to 2014. However, the decrease in NO_2 concentrations observed over MAD_{TR} and BCN_{TR} stations was much less pronounced than the decrease in NO_x (55%) concentrations over both stations. By contrast, the annual NO_2 concentrations at GRA_{TR} station were almost constant during the studied period (ranging from 40-47 µg m^{-3}) and don't show any statistically significant trend. It is worth to note that the annual NO_2 concentrations observed over MAD_{TR} and BCN_{TR} as well as over GRA_{TR} stations is still exceeding the annual NO_2 standard limit of 40 µg m^{-3} established by EU for the human health protection in force since 2010 (Fig. 1). Therefore, the regulatory efforts done were insufficient and thus more stringent emission controls and efficient measures are still needed to improve air quality and to meet the European limit. The possible cause of the unexpectedly stabilization of NO_2 concentrations at GRA_{TR} and of the weaker decreases of NO_2 concentrations at MAD_{TR} and BCN_{TR} stations and non-compliance of NO_2 air quality standards at these stations are investigated in the following sections.

3.2 Primary NO_2 fraction trends

One of the possible reasons of the stabilization of NO_2 concentrations and the weaker decrease of NO_2 concentrations could be attributed to the increase of primary NO_2 fraction in the NO_x exhaust emissions from diesel vehicles fitted with modern after-exhaust treatment technologies (Carslaw, 2005). Primary NO_2 fraction in the total NO_x emissions (f-NO_2) at the studied traffic stations was estimated from ambient monitoring data using the total oxidant method and the results are shown in Fig. 2. Primary NO_2 fraction values ranged from 8%, 11% and 3% in 2003 to 14%, 20% and 12% in 2006/2007 at MAD_{TR}, BCN_{TR} and GRA_{TR}, respectively. Primary NO_2 fraction values obtained in this study are comparable to those found in other European cities. For example, Grice et al. (2009) estimated f-NO_2 values in the range 1.5–24% for various European sites in the period 2000-2005. Anttila et al. (2011) reported f-NO_2 values ranging from 7% to 20% in Helsinki for the period 1994-2008. Also, Keuken et al. (2009) estimated f-NO_2 values in the range 9-13% in Rotterdam in the period 1986-2005. A review of f-NO_2 values obtained by different methodologies between 1986-2012 in Europe can be found in Wild et al. (2017).

The largest f-NO_2 values were obtained at BCN_{TR} station probably due to the influence of ship emissions from the Barcelona port. At GRA_{TR} and MAD_{TR} stations very similar f-NO2 values were observed. As can be seen in Fig. 2, the f-NO_2 clearly increased from 2003 to 2006/2007 in all the studied traffic stations and slightly decreased or remained almost stable from 2007/2008 onwards. This increase in the primary NO_2 fraction was also observed in other urban areas. In fact, this increase started in the early 2000s with the introdution of Euro 3 standards (Carslaw et al., 2016). In London, UK, rapid increase in the f-NO_2 started in 2003 and increased from 5-7% before 2003 to around 25% in 2005 (Carslaw et al., 2007). The increase in f-NO_2 obseved in these European cities was attributed to an increased proportion of diesel-fueled vehicles and an increased penetration of diesel vehicles fitted with particulate filters and oxidation catalysts (Carslaw, 2005; Anttila et al., 2011; Anttila and Tuovinen, 2010; Hueglin et al., 2006). One possible reason expalining the slight decrease or stabilization of f-NO_2 from 2007/2008 to 2014 is the ageing of the diesel vehicle fleet. In fact, Carslaw et al. (2016) reported that the NO_2 fraction decreased from 29% for one-year old vehicles to 22% for four-years old vehicles. The stabilization and slight decline in f-NO_2 observed in MAD_{TR}, BCN_{TR} and GRA_{TR} has been also observed in other European urban sites since 2010 (Grange et al., 2017). The main conclusion drawn from these results is that the increase of the f-NO_2 observed over the studied stations is, at least partly, one of the causes of the observed stabilization and the weaker decrease of NO_2 concentrations during the analised period. Another possible reason, supported by the decrease of the NO/O_3 (Fig. 1), could be the smaller reduction of the concentrations of secondary NO_2 compared to the NO, probably due to the change in the photostationary state (e.g., Henschel et al., 2015).

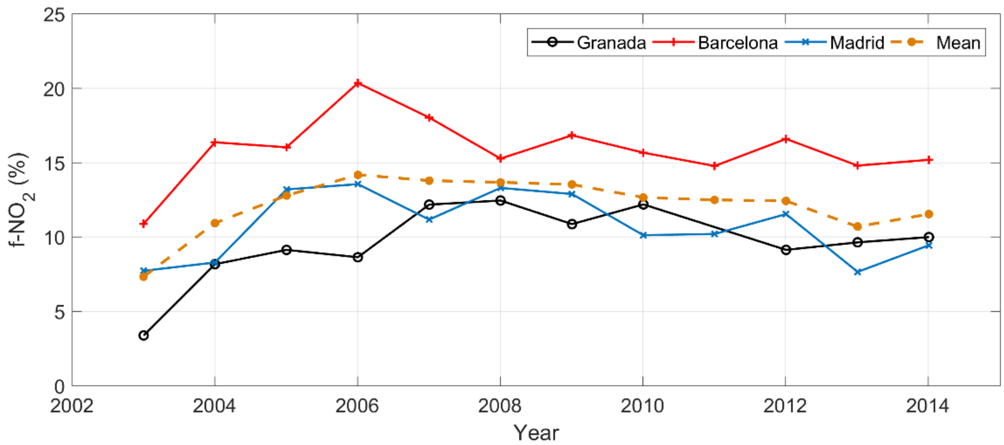

Figure 2. The evolution of the annual f-NO_2 (%) in BCN_{TR}, GRA_{TR} and MAD_{TR} stations during 2003-2014. The mean annual f-NO_2 (%) over the three studied sites is also included in the figure.

3.3 Primary and secondary NO_2 contributions to ambient NO_2 concentrations

The estimated primary, secondary and background NO_2 concentrations at each station are shown in Fig. 3. As can be seen, the primary and secondary NO_2 concentrations at GRA_{TR} remained fairly constant during the analysed period, with mean primary and secondary NO_2 concentrations (± standard diviation) of 8±2 and 33±2 μg m^{-3}, respectively. This result evidences that neither the primary nor the secondary NO_2 concentrations have decreased over the analysed period and points out that, in addition to the European control measures, the implementation of local/regional measures is necessary to improve air quality with respect to NO_2 in this city. As we comented before, the implemetation of local/regional emission controls in Granada began in 2014 and control measures were not implemented before. Since the annual ambient NO_2 concentrations at GRA_{TR} (around 42 μg m^{-3} in 2013 and 2014) are very close to the NO_2 European standard limit, it would be expected that with additional local/regional abatement measures the annual standard limit would be achieved in the near future.

Primary NO_2 concentrations at BCN_{TR} and MAD_{TR} stations increased slightly from about 14 μg m^{-3} in 2003 to 22-26 μg m^{-3} in 2005 and then decreased slightly to about 12 μg m^{-3} in the last years (Fig. 3). In contrast, secondary NO_2 concentrations at BCN_{TR} and MAD_{TR} decreased significantly over the period 2003-2014. At BCN_{TR} station NO_2 concentrations decreased from 54 μg m^{-3} to 38 μg m^{-3} (by 30%) while MAD_{TR} station decreased from 60 to 32 μg m^{-3} (by 45%). The strong NO_2 concentration decrease observed at BCN_{TR} and MAD_{TR} reveals the important role of local/regional control measures in improving air quality with respect to NO_2. However, despite the large decrease observed in the last years in secondary NO_2 concentrations at BCN_{TR} and MAD_{TR} stations, the ambient NO_2 concentrations (around 50 μg m^{-3} at both stations in 2014) still exceding the NO_2 European annual standard limit and therefore more stringent control measures at local/regional level are still needed to comply with the standard limit established by the EU for this pollutant in both cities.

The mean contribution of secondary NO_2 to the measured NO_2 concentrations at BCN_{TR}, MAD_{TR} and GRA_{TR} during the last years (2013-2014) were 73%, 73% and 75%, respectively, while the mean contribution of primary NO_2 to the measured NO_2 concentrations at BCN_{TR}, MAD_{TR} and GRA_{TR} were 24%, 26% and 19%, respectively. These percentages correspond to secondary NO_2 concentrations of 38, 33 and 30 µg m^{-3} and to primary NO_2 concentrations of 13, 12 and 8 µg m^{-3} at BCN_{TR}, MAD_{TR} and GRA_{TR}, respectively. These results highlight the significant impact of primary NO_2 emissions on the measured NO_2 concentrations in BCN_{TR}, MAD_{TR} and GRA_{TR}, especially when compared with the threshold value for compliance with the European NO_2 annual limit of 40 µg m^{-3}. However, even a drastic reduction of primary NO_2 emissions to zero through more effective control measures will not have a strong effect on ambient NO_2 concentrations in BCN_{TR}, MAD_{TR} and GRA_{TR}. For example, a hypothetic drastic reduction of primary NO_2 emissions to zero, without altering the total NO_x-emissions, will decrease the ambient NO_2 concentrations in BCN_{TR}, MAD_{TR} and GRA_{TR} in 2014 to 39, 34 and 34 µg m^{-3}, respectively. Since no drastic changes are expected in the after-exhaust treatment technology that can reduce primary NO_2 emissions to zero in the near future, and given that the secondary NO_2 concentrations constituted the large fraction of total ambient NO_2 measured in BCN_{TR}, MAD_{TR} and GRA_{TR} (> 70%), only a substantial reduction in NO_x emissions (and, therefore, in secondary NO_2 levels) will help to achieve lower NO_2 concentrations and comply with the European air quality standards.

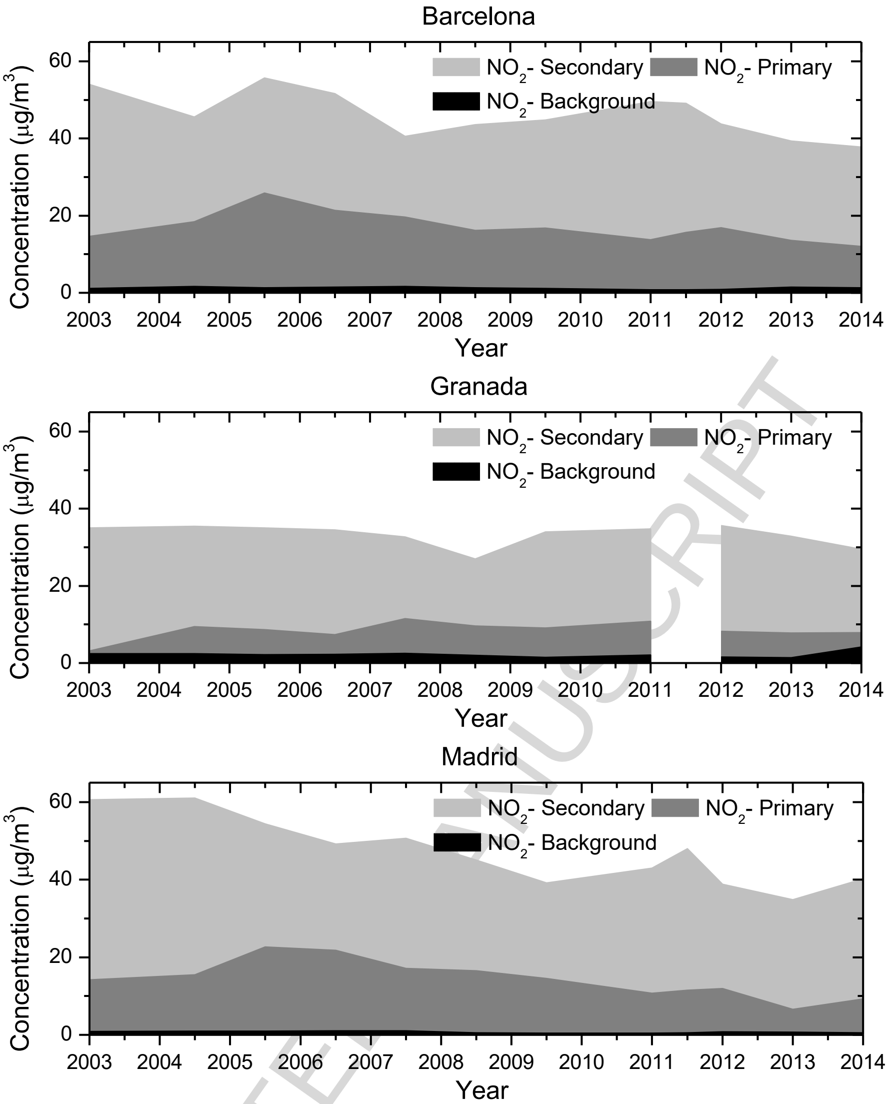

Figure 3. The estimated primary, secondary and background NO_2 concentrations at Barcelona, Granada and Madrid. Note that values are not integrated.

3.4 Estimation of the required NO_x reduction to achieve NO_2 standard limits

An important conclusion of the previous section is that regardless of the NO_2 primary emissions, a more significant reduction in NO_x emissions (due to NO implication on secondary NO_2 formation) is required in order to comply with the NO_2 European standard limit. Thus, in this section we estimate the required NO_x reduction to achieve the NO_2 European standard limits at BCN_{TR}, MAD_{TR} and GRA_{TR} stations.

As in other European urban areas, concentrations of NO_2, NO and NO_x at the studied stations show a significant reduction on weekends compared to working days due to the reduction of anthropogenic activities, especially traffic activities, during the weekend. Therefore, in this study we use the difference in anthropogenic emissions between working days and weekends to estimate the required NO_x reduction to comply with NO_2 European standard limit. To investigate the changes in NO_x and NO_2 concentrations due to changes in anthropogenic activities from working days to weekends, we calculate the relative annual reduction in NO_x concentrations from working days to weekends (1-$\left[\overline{NO_2^{weekends}}\right]/\left[\overline{NO_2^{workdays}}\right]$)*100 and the corresponding reduction in NO_2 concentations (1-$\left[\overline{NO_x^{weekends}}\right]/\left[\overline{NO_x^{workdays}}\right]$)*100 for each year of the dataset. Figure 4 shows the relationship between the relative annual reduction in NO_x concentrations from working days to weekends and the corresponding reduction in NO_2 concentations at the studied traffic stations. As can be seen, both variables show very good linear correlation with determination coefficients (R^2) higher than 0.84. This linear dependency points out that the reduction in the anthropogenic emissions during weekends implies a reduction in NO_x concentrations, and a linear reduction in NO_2 concentration (at least for the range of concentrations observed during the studied period). Thus, in this study we use these linear relationships to estimate the NO_x reductions required to reduce NO_2 concentrations over the three analised stations below the NO_2 annual European standard limit. Considering the annual mean values of the measured NO_2 concentrations in 2014 (51, 50 and 42 µg m^{-3} at BCN_{TR}, MAD_{TR} and GRA_{TR}, respectively), NO_x concentrations in Barcelona, Madrid and Granada in 2014 should be reduced by 31%, 30% and 9% to comply with the NO_2 annual limit of 40 µg m^{-3}. This means that, using Eq. 7, a reduction of NO_x emissions of 78%, 56% and 16% is a prerequisite to meet the annual NO_2 limit of 40 µg m^{-3} at BCN_{TR}, MAD_{TR} and GRA_{TR}.

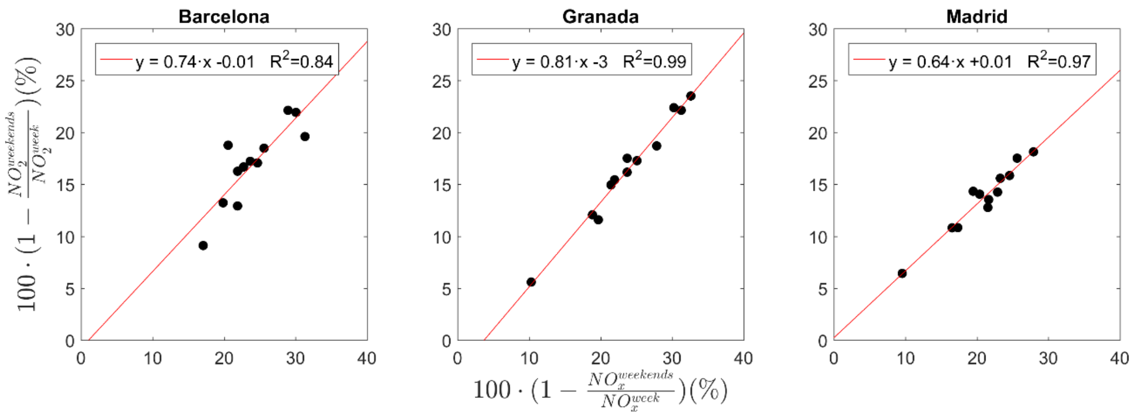

Figure 4. Relative annual reduction in NO_x concentrations from working days to weekends versus the corresponding reduction in NO_2 concentations at each studied traffic station.

4 Conclusions

In this study, air quality data recorded in the 2003-2014 period at 3 Spanish cities that still exceeding the NO_2 European standard limit were analysed. The main conclusions drawn from this study are:

- High and statistically significant downward trends were observed for NO and NO_x concentrations in BCN_{TR} and MAD_{TR}. In contrast, the reduction of these pollutants in GRA_{TR} was smaller and not statistically significant due to the non-implementation of local/regional emission control measures at this city during the analysed period.
- NO_2 concentrations showed clear statistically downward trends in BCN_{TR} and MAD_{TR} during the analysed period with reductions of up to 30%. In contrast, NO_2 concentration at GRA_{TR} showed almost constant values during the studied period. Despite the significant decrease in NO_2 concentration in BCN_{TR} and MAD_{TR}, this decrease was not enough to comply with the EU standard limit, and the NO_2 concentrations observed over BCN_{TR}, MAD_{TR} and as well as over GRA_{TR} still above the annual NO_2 standard limit of 40 µg m^{-3}. Therefore, more stringent emission controls and efficient measures are still needed to improve air quality and to meet the European standard limit at these sites.
- The primary and secondary NO_2 concentrations at GRA_{TR} remained fairly constant during the analysed period. In contrast, the secondary NO_2 concentrations at BCN_{TR} (MAD_{TR}) decreased significantly by 30% (45%) from 2003 to 2014, revealing the important role of the local/regional control measures implemented in Madrid and Barcelona in improving air quality in both cities.
- The mean contribution of primary NO_2 to the measured NO_2 concentrations at BCN_{TR}, MAD_{TR} and GRA_{TR} during the last years (2013-2014) were 24%, 26% and 19%, respectively, which highligh the significant impact of primary NO_2 emissions on the measured NO_2 concentrations. However, as no drastic changes are expected in the after-exhaust treatment technology that can reduce primary NO_2 emissions to zero in the near future, and given that the secondary NO_2 concentrations constituted the large fraction of total ambient NO_2 measured on BCN_{TR}, MAD_{TR} and GRA_{TR} (>70%), only a substantial reduction in NO_x emissions (and, therefore, in secondary

NO_2 levels) will help to achieve lower concentrations of NO_2 and comply with the NO_2 European air quality standards.

- NO_x emissions in Barcelona, Madrid and Granada should be reduced by 78%, 56% and 16% to comply with the NO_2 annual limit of 40 μg m^{-3}. Neverthless, the reduction of NO_2 below the NO_2 European limit, for example up to 35 μg m^{-3}, requires a reduction of NO_x emissions by 110%, 83% and 43% in Barcelona, Madrid and Granada, respectively.

5 Acknowledgments

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6 References

Abbott, J., 2005. Primary nitrogen dioxide emissions from road traffic: analysis of monitoring data. AEA Technology, National Environmental Technology Centre, Report AEAT-1925. http://www.airquality.co.uk/archive/reports/cat05/0703151041_primno2v3.pdf.

Adame, J. A. and Sole, J. G.: Surface ozone variations at a rural area in the northeast of the Iberian Peninsula, Atmos Pollut Res, 4, 130-141, 2013.

Anttila, P. and Tuovinen, J. P.: Trends of primary and secondary pollutant concentrations in Finland in 1994-2007, Atmos Environ, 44, 30-41, 2010.

Anttila, P., Tuovinen, J. P., and Niemi, J. V.: Primary NO_2 emissions and their role in the development of NO_2 concentrations in a traffic environment, Atmos Environ, 45, 986-992, 2011.

Beelen, R., Hoek, G., van den Brandt, P. A., Goldbohm, R. A., Fischer, P., Schouten, L. J., Armstrong, B., and Brunekreef, B.: Long-term exposure to traffic-related air pollution and lung cancer risk, Epidemiology, 19, 702-710, 2008.

Carslaw, D. C. and Beevers, S. D.: Investigating the potential importance of primary NO_2 emissions in a street canyon, Atmos Environ, 38, 3585-3594, 2004a.

Carslaw, D. C. and Beevers, S. D.: New Directions: Should road vehicle emissions legislation consider primary NO_2?, Atmos Environ, 38, 1233-1234, 2004b.

Carslaw, D. C. and Ropkins, K.: openair - An R package for air quality data analysis, Environ Modell Softw, 27-28, 52-61, 2012.

Carslaw, D. C., Beevers, S. D., and Bell, M. C.: Risks of exceeding the hourly EU limit value for nitrogen dioxide resulting from increased road transport emissions of primary nitrogen dioxide, Atmos Environ, 41, 2073-2082, 2007.

Carslaw, D. C., Murrells, T.P., Andersson, J., Keenan, M., 2016. Have vehicle emissions of primary NO2 peaked? Faraday Discuss. 189, 439e454. http://dx.doi.org/ 10.1039/C5FD00162E.

Carslaw, D. C.: Evidence of an increasing NO_2/NO_x emissions ratio from road traffic emissions, Atmos Environ, 39, 4793-4802, 2005.

Chaloulakou, A., Mavroidis, I., and Gavriil, I.: Compliance with the annual NO2 air quality standard in Athens. Required NOx levels and expected health implications, Atmos Environ, 42, 454-465, 2008.

De Nevers, N., Morris, J.R., 1975. Rollback modelling: basic and modified. JAPCA 25, 943–947

Degraeuwe, B., Thunis, P., Clappier, A., Weiss, M., Lefebvre, W., Janssen, S., and Vranckx, S.: Impact of passenger car NO_x emissions and NO_2 fractions on urban NO_2 pollution - Scenario analysis for the city of Antwerp, Belgium, Atmos Environ, 126, 218-224, 2016.

Degraeuwe, B., Thunis, P., Clappier, A., Weiss, M., Lefebvre, W., Janssen, S., and Vranckx, S.: Impact of passenger car NOX emissions on urban NO2 pollution - Scenario analysis for 8 European cities, Atmos Environ, 171, 330-337, 2017.

Derwent, R. G., Simmonds, P. G., Manning, A. J., and Spain, T. G.: Trends over a 20-year period from 1987 to 2007 in surface ozone at the atmospheric research station, Mace Head, Ireland, Atmos Environ, 41, 9091-9098, 2007.

ECACCCM, 2014. Estrategia de Calidad del Aire y Cambio Climático de la Comunidad de Madrid (2013-2020). Plan azul +, http://www.madrid.org/bvirtual/BVCM003469.pdf

EEA, 2016. European Environment Agency. Premature Deaths Attributable to Air Pollution-2016; https://www.eea.europa.eu/media/newsreleases/manyeuropeans-still-exposed-to-air-pollution-2015/premature-deaths-attributableto-air-pollution

ELCACM, 2006. Estrategia Local de Calidad del Aire de la Ciudad de Madrid 2006-2010, http://www.mambiente.munimadrid.es/opencms/export/sites/default/calaire/Anexos/Estrategia_local_calidad_aire.pdf

Escudero, M., Lozano, A., Hierro, J., del Valle, J., Mantilla, E., Urban influence on increasing ozone concentrations in a characteristic Mediterranean agglomeration, Atmospheric Environment, Volume 99, 2014, Pages 322-332, ISSN 1352-2310, https://doi.org/10.1016/j.atmosenv.2014.09.061.

Finlayson-Pitts BJ, Pitts JN. Chemistry of the upper and lower atmosphere: theory, experiments, and applications. San Diego: Academic Press; 2000.

Font, A. and Fuller, G. W.: Did policies to abate atmospheric emissions from traffic have a positive effect in London?, Environ Pollut, 218, 463-474, 2016.

Gramsch, E., Le Nir, G., Araya, M., Rubio, M.A., Moreno, F., Oyola, P., Influence of large changes in public transportation (Transantiago) on the black carbon pollution near streets, Atmospheric Environment, Volume 65, 2013, Pages 153-163, ISSN 1352-2310, https://doi.org/10.1016/j.atmosenv.2012.10.006.

Grange, S. K., Lewis, A. C., Moller, S. J., and Carslaw, D. C.: Lower vehicular primary emissions of NO2 in Europe than assumed in policy projections, Nat Geosci, 10, 914-+, 2017.

Grice, S., Stedman, J., Kent, A., Hobson, M., Norris, J., Abbott, J., and Cooke, S.: Recent trends and projections of primary NO_2 emissions in Europe, Atmos Environ, 43, 2154-2167, 2009.

Guerreiro, C. B. B., Foltescu, V., and de Leeuw, F.: Air quality status and trends in Europe, Atmos Environ, 98, 376-384, 2014.

Harrison, R. M., Stedman, J., and Derwent, D.: New directions: Why are PM_{10} concentrations in Europe not falling?, Atmos Environ, 42, 603-606, 2008.

Henschel, S., Le Tertre, A., Atkinson, R. W., Querol, X., Pandolfi, M., Zeka, A., Haluza, D., Analitis, A., Katsouyanni, K., Bouland, C., Pascal, M., Medina, S., and Goodman, P. G.: Trends of nitrogen oxides in ambient air in nine European cities between 1999 and 2010, Atmos Environ, 117, 234-241, 2015.

Henschel, S., Querol, X., Atkinson, R., Pandolfi, M., Zeka, A., Le Tertre, A., Analitis, A., Katsouyanni, K., Chanel, O., Pascal, M., Bouland, C., Haluzai, D., Medina, S., and Goodman, P. G.: Ambient air SO_2 patterns in 6 European cities, Atmos Environ, 79, 236-247, 2013.

Hipel, K.W., McLeod, A.I., 2005. Time Series Modelling of Water Resources and Environmental Systems. Elsevier, Amsterdam.

Holman, C., Harrison, R., Querol, X., Review of the efficacy of low emission zones to improve urban air quality in European cities, Atmospheric Environment, Volume 111, 2015, Pages 161-169, ISSN 1352-2310, https://doi.org/10.1016/j.atmosenv.2015.04.009.

Hueglin, C., Buchmann, B., and Weber, R. O.: Long-term observation of real-world road traffic emission factors on a motorway in Switzerland, Atmos Environ, 40, 3696-3709, 2006.

Kendall, M.G., 1976. Rank Auto Correlation Methods, fourth ed. Griffin, Oxford.

Keuken, M., Roemer, M., and van den Elshout, S.: Trend analysis of urban NO_2 concentrations and the importance of direct NO_2 emissions versus ozone/NO_x equilibrium, Atmos Environ, 43, 4780-4783, 2009.

Kurtenbach, R., Kleffmann, J., Niedojadlo, A., and Wiesen, P.: Primary NO2 emissions and their impact on air quality in traffic environments in Germany, Environmental Sciences Europe, 24, 21, 2012.

Latza, U., Gerdes, S., and Baur, X.: Effects of nitrogen dioxide on human health: Systematic review of experimental and epidemiological studies conducted between 2002 and 2006, Int J Hyg Envir Heal, 212, 271-287, 2009.

Lu, H.C., 2004. Estimating the emission source reduction of PM10 in central Taiwan. Chemosphere 54, 805–814.

Madrid City Council, 2014: http://www.madrid.es/portales/munimadrid/es/Inicio/Actualidad/Noticias/Renovacion-viaria-en-el-entorno-de-las-Escuelas-Aguirre?vgnextfmt=default&vgnextoid=4039bf9a839b6410VgnVCM1000000b205a0aRCRD&vgnextchannel=a12149fa40ec9410VgnVCM100000171f5a0aRCRD

MAPAMA Spanish Government (in Spanish): Análisis de la Calidad del Aire en España 2015. http://www.mapama.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/libroaire2015_tcm30-187887.pdf

MAPAMA Spanish Government (in Spanish): Inventario de emisiones de España 2017. http://www.mapama.gob.es/es/calidad-y-evaluacion-ambiental/temas/sistema-espanol-de-inventario-sei-/documentoresumeninventariotechosespana-serie1990-2015_tcm7-453240.pdf

Mavroidis, I. and Chaloulakou, A.: Long-term trends of primary and secondary NO_2 production in the Athens area. Variation of the NO_2/NO_x ratio, Atmos Environ, 45, 6872-6879, 2011.

Patron, D., Lyamani, H., Titos, G., Casquero-Vera, J. A., Cardell, C., Mocnik, G., Alados-Arboledas, L., and Olmo, F. J.: Monumental heritage exposure to urban black carbon pollution, Atmos Environ, 170, 22-32, 2017.

PCACM, 2012. Plan de calidad del aire de la ciudad de Madrid 2011–2015, http://www.mambiente.munimadrid.es/opencms/export/sites/default/calaire/Anexos/Plan_2011_15.pdf

PCMCAB, 2013. Plan para Calidad la Mejora de la Calidad del Aire en Barcelona, https://bcnroc.ajuntament.barcelona.cat/jspui/bitstream/11703/85107/1/13667.pdf

PDMQLA, 2015. El Pla d'actuació per a la millora de la qualitat de l'aire, http://mediambient.gencat.cat/web/.content/home/ambits_dactuacio/atmosfera/qualitat_de_laire/oficina_tecnica_de_plans_de_millora/pla_millora_qua_aire_2011_2015/Aire_net_2a_ed.pdf

PMCAAGAM, 2014. Plan de mejora de la calidad del aire de la aglomeración de Granada y área metropolitana. http://www.juntadeandalucia.es/medioambiente/portal_web/web/temas_ambientales/aire/planes_mejora/pca_aglomeracion_granada_area_metrop/PCA_Granada.pdf

Pope, C. A. and Dockery, D. W.: Health effects of fine particulate air pollution: Lines that connect, J Air Waste Manage, 56, 709-742, 2006.

Querol, X., Alastuey, A., Pandolfi, M., Reche, C., Perez, N., Minguillon, M. C., Moreno, T., Viana, M., Escudero, M., Orio, A., Pallares, M., and Reina, F.: 2001-2012 trends on air quality in Spain, Sci Total Environ, 490, 957-969, 2014.

Querol, X., Gangoiti, G., Mantilla, E., Alastuey, A., Minguillón, M. C., Amato, F., Reche, C., Viana, M., Moreno, T., Karanasiou, A., Rivas, I., Pérez, N., Ripoll, A., Brines, M., Ealo, M., Pandolfi, M., Lee, H.-K., Eun, H.-R., Park, Y.-H., Escudero, M., Beddows, D., Harrison, R. M., Bertrand, A., Marchand, N., Lyasota, A., Codina, B., Olid, M., Udina, M., Jiménez-Esteve, B., Soler, M. R., Alonso, L., Millán, M., and Ahn, K.-H.: Phenomenology of high-ozone episodes in NE Spain, Atmos. Chem. Phys., 17, 2817-2838, https://doi.org/10.5194/acp-17-2817-2017, 2017.

Salvador, P., Artinano, B., Viana, M., Alastuey, A., and Querol, X.: Evaluation of the changes in the Madrid metropolitan area influencing air quality: Analysis of 1999-2008 temporal trend of particulate matter, Atmos Environ, 57, 175-185, 2012.

Samoli, E., Aga, E., Touloumi, G., Nislotis, K., Forsberg, B., Lefranc, A., Pekkanen, J., Wojtyniak, B., Schindler, C., Niciu, E., Brunstein, R., Fikfak, M. D., Schwartz, J., and Katsouyanni, K.: Short-term effects of nitrogen dioxide on mortality: an analysis within the APHEA project, Eur Respir J, 27, 1129-1137, 2006.

Sen, P. K.: Estimates of the Regression Coefficient Based on Kendall's Tau, Journal of the American Statistical Association, 63, 1379-1389, 1968.

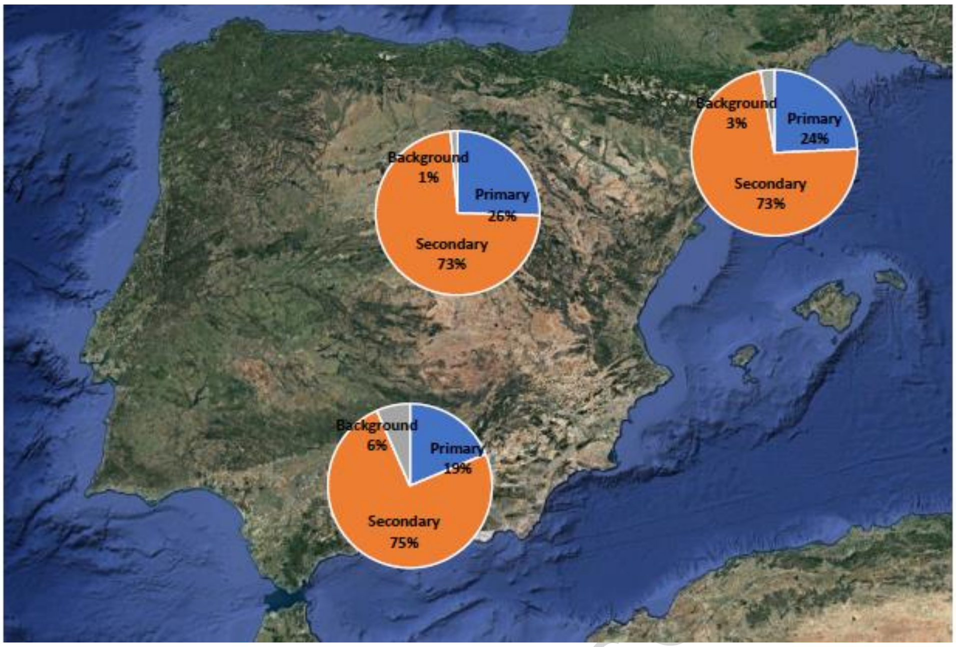
Theil H. A rank invariant method of linear and polynomial regression analysis, I, II, III. Proceedings of the Koninklijke Nederlandse Akademie Wetenschappen, SeriesA — Mathematical Sciences, 386–392, 521–525, 1397–1412; 1950.

Titos, G., del Aguila, A., Cazorla, A., Lyamani, H., Casquero-Vera, J. A., Colombi, C., Cuccia, E., Gianelle, V., Mocnik, G., Alastuey, A., Olmo, F. J., and Alados-Arboledas, L.: Spatial and temporal variability of carbonaceous aerosols: Assessing the impact of biomass burning in the urban environment, Sci Total Environ, 578, 613-625, 2017.

Titos, G., Lyamani, H., Drinovec, L., Olmo, F. J., Mocnik, G., and Alados-Arboledas, L.: Evaluation of the impact of transportation changes on air quality, Atmos Environ, 114, 19-31, 2015.

WHO, 2013. Review of Evidence on Health Aspects on Air Pollution e REVIHAAP Project. Technical Report. WHO Regional Office for Europe, Copenhagen, Denmark. http://www.euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report.pdf.

Wild, R. J., Dube, W. P., Aikin, K. C., Eilerman, S. J., Neuman, J. A., Peischl, J., Ryerson, T. B., and Brown, S. S.: On-road measurements of vehicle NO_2/ NO_x emission ratios in Denver, Colorado, USA, Atmos Environ, 148, 182-189, 2017.



Graphical abstract

Highlights:

- Slight decrease or no change in NO_2 concentrations at the studied sites.
- Primary and secondary NO_2 contributions were estimated using oxidant model.
- Secondary NO_2 is the main contributor to the total NO_2 concentrations.
- Primary NO_2 emissions have a significant influence on NO_2 concentrations.
- Significant reduction in NO_x emissions is required to comply with the NO_2 limit.