Postprint of: García-Gómez. H. et al. "Atmospheric pollutants in peri-urban forests of Quercus ilex : evidence of pollution abatement and threats for vegetation" in Environmental science and pollution research (Ed. Springer), published online 01 dec. 2015. The final version is available at DOI 10.1007/11356-015-5862-z

Atmospheric pollutants in peri-urban forests of *Quercus ilex*: evidence of pollution abatement and threats for vegetation.

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Keywords

Atmospheric pollution;nitrogen; ozone; aerosols; ecosystem services; Mediterranean vegetation.

Abstract

Peri-urban vegetation is generally accepted as a significant remover of atmospheric pollutants, but it could also be threatened by these compounds, with origin in both urban and non-urban areas. To characterize the seasonal and geographical variation of pollutant concentrations and to improve the empirical understanding of the influence of Mediterranean broadleaf evergreen forests on air quality, four forests of *Quercus ilex* (three peri-urban and one remote) were monitored in different areas in Spain. Concentrations of nitrogen dioxide (NO_2), ammonia (NH_3), nitric acid (HNO_3) and ozone (O_3) were measured during two years in open areas and inside the forests and aerosols (PM_{10}) were monitored in open areas during one year. Ozone was the only air pollutant expected to have direct phytotoxic effects on vegetation according to current thresholds for the protection of vegetation. The concentrations of N compounds were not high enough to directly affect vegetation but could be contributing through atmospheric N deposition to the eutrophization of these ecosystems. Peri-urban forests of *Quercus ilex* showed a significant below-canopy reduction of gaseous concentrations (particularly NH_3, with a mean reduction of 29–38%), which indicated the feasibility of these forests to provide an ecosystem service of air quality improvement. Well-designed monitoring programs are needed to further investigate air quality improvement by peri-urban ecosystems while assessing the threat that air pollution can pose to vegetation.

Acknowledgements

This research was funded by the Spanish project EDEN (CGL2009-13188-C03-02), by the project from Autonomous Government of Madrid AGRISOST-CM (P2013/ABI-2717), and by the European Projects ECLAIRE (FP7-ENV-2011/282910) and Life RESPIRA (LIFE13 ENV/ES/000417). This study was also supported by the Ministry of Agriculture, Food and Environment (Resolución 15398, BOE n° 230). The authors would like to acknowledge the Department of Environment (DGQA) of the Autonomous Government of Catalonia for performing the active monitoring of air pollutants at LC ("MSY" station from GAW/ACTRIS monitoring networks).

1. Introduction

The continuous growth of urban population has turned air quality into one of the main environmental concerns worldwide. Current urban development needs to consider designs and strategies that minimize atmospheric pollution to improve well-being and human health. In the last years, particular attention has been paid to investigate the role of urban and peri-urban vegetation in improving air quality. Vegetation can remove air pollutants via dry deposition, through interception in the canopy surfaces, and via absorption of gases through the stomata. In particular, urban and peri-urban vegetation has been proposed as a method to reduce air pollutants such as ozone, nitrogen oxides and particulate matter (Alonso et al. 2011; Kroeger et al. 2014; Nowak et al. 2014; Sgrigna et al. 2015). On the other hand, air pollution can affect these forests, impairing their capacity to provide ecosystem services.

Peri-urban areas are transition zones between the denser urban core and the rural hinterland, where natural habitats can be exposed to intermediate concentrations of pollutants linked to both urban and rural activities. Among the most common gaseous pollutants, nitrogen oxides (NO_2, NO) reach peri-urban areas transported from human agglomerations and highways where they are produced as a result of combustion processes. Nitrogen oxides are in turn precursors for the formation of photochemical oxidants such as ozone (O_3) and nitric acid (HNO_3). Ozone is one of the most important and pervasive air pollutants currently affecting vegetation (Kroeger et al. 2014). This pollutant is particularly important in the Mediterranean region, where the highest concentrations in Europe are registered (EEA 2013). Ozone levels are usually greater in peri-urban and rural areas than in busy urban centres, due to its rapid destruction by reacting with the NO emitted in the cities (The Royal Society 2008). Nitric acid is one of the main components of photochemical smog, together with ozone, and with a similar spatial distribution (Bytnerowicz et al. 1999). In contrast, ammonia (NH_3) is mainly emitted from agricultural and livestock activities in rural areas. Ammonia and nitric acid can quickly react with each other, or with other atmospheric gases, to formsecondary inorganic aerosols (SIA), that can represent an important fraction of the particulate matter (PM) concentration measured at regional background stations (EEA 2013). Although atmospheric N pollutant levels are usually not high enough to directly damage vegetation, atmospheric N deposition can contribute to both eutrophication and acidification of ecosystems, which is a bigger problem than the direct exposure to these compounds (Dise et al. 2011; EEA 2013). Atmospheric N deposition can be particularly important in peri-urban areas that are receiving contributions of N compounds from both urban and agricultural activities. In fact, Mediterranean forests and mountain scrublands close to Barcelona and Madrid cities have been reported to be threatened by N deposition (García-Gómez et al. 2014).

Air pollutant gases and particles are removed from the atmosphere through both wet and dry deposition. In Mediterranean environments, atmospheric deposition can be dominated by dry deposition, which can represent up to 50–95% of the total deposition in Mediterranean forests (Bytnerowicz and Fenn 1996). In this sense, urban and peri-urban vegetation, through increasing dry deposition, can represent a good strategy to improve air quality, particularly in this region. Dry deposition to vegetation is a function of multiple factors, such as air concentration, chemical properties of the depositing species, atmospheric turbulence, moisture and reactivity of receptor surfaces, and vegetation structure and activity (Fowler et al. 2009).

Measuring pollutant concentrations outside and within peri-urban forests can provide an insight into the role of vegetation in removing air pollutants (Cavanagh et al. 2009; Setälä et al. 2013; Grundström and Pleijel 2014). Although urban vegetation is accepted as an efficient remover of air pollutants, most of the studies are based on large-scale modelling (e.g. Nowak et al. 2014) or laboratory studies (e.g. Chaparro-Suárez et al. 2011), but there are few empirical evidences of the reduction in pollutant concentrations inside urban forested areas (Cavanagh et al. 2009; Grundström and Pleijel 2014). Besides, atmospheric pollution represents a risk for the urban and peri-urban vegetation and should be monitored, particularly in forest potentially withstanding other stressful conditions. Interestingly, NH_3 and HNO_3 concentrations are scarcely measured in the main air-quality networks, despite being major drivers of atmospheric N dry deposition to vegetation (Bytnerowicz et al. 2010).

In order to study tropospheric O_3, gaseous N compounds, and suspended PM in peri-urban forests in Spain, three peri-urban forests of holm oak (*Quercus ilex* L.) were selected near to three cities in Spain with increasing population and with different influences of traffic and agricultural pollution sources (based on their distances to highways, percentage of agricultural land use and presence of livestock). Another holm oak forest site, far from anthropogenic emissions of air pollutants, was established for comparison. Holm oak is an evergreen broadleaf tree species representative of the Mediterranean Basin and it is present over a wide range of environments in the region, from cold semi-arid to temperate humid bioclimates. This study was enclosed in the EDEN project (*Effects of nitrogen deposition in Mediterranean evergreen holm oak forests*), whose main goal was to determine and characterize the nitrogen inputs to holm oak forests in the Iberian Peninsula and the effects in the nitrogen biogeochemical cycle. In the present study, air quality measurements from EDEN project are presented and discussed, with the following objectives: 1) to analyse the main air pollutants that could be affecting holm oak forests close to cities, 2) to characterize air pollutant temporal and geographical variation, and 3) to compare air pollutant concentrations outside and inside the forest to improve the empirical understanding of the influence of vegetation on air quality.

2. Material and methods

2.1. Study sites

Three holm-oak (*Quercus ilex*) forests were selected in the vicinity of three cities in Spain with increasing population (Fig. 1, Table 1). The Can Balasc (CB) site is placed in a forest located in a natural protected area 4 km away from Barcelona with acidic soils and Mediterranean sub-humid climate. The Tres Cantos site (TC) is a forest located in a natural protected area at 9 km from Madrid, growing on acidic sandy soil with Mediterranean semi-arid climate. The Carrascal site (CA) is located in an agricultural area close to Pamplona (15 km), with calcareous soil and Mediterranean humid climate, and it is the most agricultural-influenced among the three peri-urban forests. The canopy in all the sites is dominated by *Quercus ilex*,mixed with *Q. humilis*in CB. In the case of TC, vegetation was historically managed as a traditional *dehesa* (a savannah-like agrosilvopastoral system) of *Q. ilex*, but the low management intensity during the last decades has allowed vegetation to grow as a moderately open forest. An additional holm oak forest was selected as a non-urban reference in La Castanya (LC), a long-term biogeochemical study site in a protected mountainous area (Parc Natural del Montseny), situated 40 km away from Barcelona (Fig. 1) and is included in the GAW/ACTRIS monitoring networks ("MSY" station). This site presents moderately acidic soils and montane Mediterranean climate and it is relatively sheltered from the surrounding lowland sources of atmospheric pollutants (Hereter and Sánchez 1999). The description of the sites was complemented with land use cover and livestock density data obtained from the Corine Land Cover 2006 of the European Environment Agency (http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster-3) and from the Spanish National Statistic Institute (http://www.ine.es) respectively (Table 1). ArcGIS software (version 9.2; Environmental Systems Research Institute Inc., Redlands, CA, USA) was employed to summarize these data using a buffer of 25 km radius around the sampling sites. Meteorological variables were monitored in CB, TC and LC sites, and data from the closest meteorological station were collected for the CA site.

2.2. Air pollution monitoring

Atmospheric concentrations of ozone (O_3), ammonia (NH_3), nitrogen dioxide (NO_2) and nitric acid vapour (HNO_3) were monitored during two years using passive samplers. In every location, two plots were installed: an open-field plot (O) and a below-canopy plot (F –forest plot). Open and below-canopy plots were selected in order to maintain the same orientation, exposure and elevation.Two replicate samplers per gaseous species were exposed at 2 m height in each plot. Gases were measured during two-week-long periods between February 2011 and February 2013; except O_3 in CA, where the sampling survey was only extended until April 2012. Exceptionally, some sampling periods (3% of the total monitoring time) lasted approximately four weeks. In

these cases, the same result has been used for the two corresponding regular sampling periods.. During every exposure period, unexposed samplers were used as blanks for each site and type of passive sampler. After collection, all samples were kept refrigerated (4º C) in darkness until they were analysed in the laboratory.

Tube-type samplers (Radiello®) were used to measure atmospheric concentrations of NH_3, NO_2 and O_3. Laboratory analyses were performed according to Radiello's specifications (Fondazione Salvatore Maugeri, 2006). Atmospheric concentrations of HNO_3 were measured by means of badge-type samplers manufactured following Bytnerowicz et al. (2005). In CA, Passam® passive samplers and methods were employed during the second year for monitoring NO_2 after checking their comparability with Radiello®. For these sampling periods, correction proposed by Plaisance (2011) was applied to avoid biases caused by high wind speeds. The variability of the duplicate passive samplers for each air pollutant averaged from 7% for O_3 to 28% for HNO_3.

Additionally, concentration of O_3 and nitrogen oxides (NO and NO_2) were continuously monitored in open-field locations in LC and TC sites with active monitors (in LC: MCV® 48AV and Thermo Scientific® 42i-TL, respectively; in TC:ML® 9810B and ML® 9841, respectively). Simultaneous measurements with passive samplers and active monitors were used to estimate mean experimental sampling rates, which were applied to calculate atmospheric concentrations. The experimental sampling rates obtained in LC were employed in CB and CA calculations as well, after checking the similarity with concentrations registered at the closest air quality monitoring stations.

Using the data from the active monitors, accumulated O_3 exposure was calculated as AOT40, which is the accumulated amount of hourly O_3 concentrations over the threshold value of 40 nl l^{-1}. Following the Ambient Air Quality Directive 2008/50/EC, AOT40 was calculated for the period May–July with the hourly mean values from 8 to 20 hours. Additionally, following the recommendations from the Convention on Long-range Transboundary Air Pollution (CLRTAP 2011), AOT40 was calculated for the entire year (the growing season for *Q. ilex*) during daylight hours.

2.3. Particulate matter sampling

Particulate matter with diameter up to 10 µm (PM_{10}) was collected with 150 mm quartz micro-fibre filters (2500 QAO-UP, Pall Life Sciences) using high volume samplers installed in open-field plots of TC, CA and LC sites (Digitel® DH80 in LC -MSY monitoring station; MCV® CAV-A/mb in TC and CA). Samples were collected from February 2012 to February 2013 once a week,using a flow of 30 m^3 h^{-1} during 24-h periods. The day of the week for PM_{10} collection changed weekly. The concentration was gravimetrically determined and main secondary inorganic aerosols (SO_4^{2-}, NO_3^- and NH_4^+) were water-extracted and analysed by ion

chromatography. For statistical comparison purposes with gaseous pollutant concentrations, PM_{10} data were grouped and averaged in accordance to passive sampling periods (except for the comparison of the natural dust events with the rest of the samples).

2.4. Statistical analysis

Non-parametric statistics was selected for this study because most of the variables did not show a normal distribution according to Shapiro-Wilk test and normal probability plots. Differences among seasons or sites were analysed using the Kruskal-Wallis test; when significant differences were found, differences between pairs of sites were assessed with the Mann-Whitney U test. Correlation between variables was tested with the Spearman rank order correlation coefficient. Differences in pollutant concentration between O and F plots were analysed by applying the Wilcoxon matched pair test to the entire sampling period. The temporal variability is described in this study by the coefficient of variation (CV = standard deviation / mean) of the two-week concentrations for the entire study period. The variability of the duplicate passive samplers for each air pollutant is also described by their respective CV. In this work, seasons were considered as periods of three consecutive months, beginning on 1st January. Statistica software (version 12; StatSoft, Tulsa, OK) was used for statistical analysis. Alfa level was set at 0.05.

3. Results

3.1. Temporal and spatial patterns of gaseous pollutants

Seasonal and annual pollutant concentrations and differences among sites are described below based on concentrations in the O plots (Fig. 2; Table 2).

The annual mean of atmospheric NO_2 concentration ranged from 4.3 µg m^{-3} in LC to 16.2 µg m^{-3} in CB (Table 2). The highest two-week concentration reached 39.3 and 37.1 µg m^{-3} registered in CB and TC respectively during the winter 2012 (Supplement, S1). On average for the four sites, temporal variability of NO_2 concentration was 53%. Levels of NO_2 tended to peak during the coldest seasons (autumn and winter). Significant seasonal differences were detected in the sites closest to the big cities of Barcelona and Madrid (CB and TC). LC experienced the lowest concentrations and the lowest inter-seasonal variability (Fig. 2).

Atmospheric NH_3 concentration (Table 2) was the highest in CA (2.5 µg m^{-3}) and the lowest in TC and LC (0.7 µg m^{-3}). The maximum two-week value (5.3 µg m^{-3})was recorded in CA during late winter (Supplement, S2). The temporal variability showed a mean of 55% across sites. A consistent seasonal pattern was found in TC, where NH_3 concentration increased during spring and summer and decreased during autumn and winter (Fig. 2; Supplement, S2). LC showed a similar seasonal pattern but differences were not statistically significant ($p = 0.06$). On the contrary, in CB and CA, the highest seasonal concentrations occurred in winter.

The concentration of HNO_3 tended to be higher in the sites closest to the Mediterranean coast (CB and LC), but differences among sites were not statistically significant (Table 2). The maximum two-week concentrations found in CB and LC (14.5 and 13.9 μg m^{-3} in summer of 2012, respectively) were twice the maximum values found in TC and CA (Supplement, S3). The temporal variability in HNO_3 concentration was higher than the variability found for the other air pollutants, with an average value of 110%. A general seasonal pattern was detected in HNO_3 concentrations, with higher values during spring and summer and lower values in autumn and winter (Fig. 2).

The annual mean of atmospheric O_3 concentrations (Table 2) were significantly lower in the sites closest to the big cities of Barcelona and Madrid (57.0 μg m^{-3} in CB and 69.1 μg m^{-3} in TC) than in the more rural ones (77.4 μg m^{-3} and 78.2 μg m^{-3} in CA and LC, respectively). Ozone was the air pollutant showing the smallest temporal variability with a mean value of 32%. All sites showed similar seasonal patterns with higher O_3 concentration during spring and summer than in autumn and winter (Fig. 2). Ozone exposure accumulated during May-July expressed as AOT40 ranged from 3.9 ppm h in CA in 2011 to 28.3 ppm h in TC in 2012 (Table 3). When accumulating O_3 exposure throughout the growing season, AOT40 values ranged from 8.2 ppm h in CA in 2011 to 49.6 ppm h in TC in 2012 (Table 3).

3.2. Temporal and spatial patterns of particulate matter

The concentration of PM_{10} was higher in CA and TC than in LC (Table 2), although differences were only significant between CA and LC, which showed the lowest annual concentration (18.0 μg m^{-3}). Temporal variability in PM_{10} concentrations was 50% on average for the three sites. Significant seasonal variations were found in TC and LC, with the highest PM_{10} concentrations registered in summer and the lowest in autumn (Fig. 3A). Saharan dust events represented 10% of the total amount of samples, and occurred more frequently during the summer season. In the three sites, the highest 24h-concentrations of PM_{10} (up to 126.4 μg m^{-3}) were collected during these natural dust events, generally doubling the levels found in the rest of the samples (Fig. 3B).

Regarding SIA composition, no differences among sites were found in particulate ammonium (NH_4^+), while particulate nitrate (NO_3^-) was significantly the highest in CA (Table 2). Apparently, Saharan dust intrusions did not affect the NH_4^+ and NO_3^- concentration in PM_{10} (data not shown). The atmospheric concentration of both water-soluble nitrogen aerosols showed a marked seasonality, with higher values detected in winter than in the rest of seasons (Figs. 3C and 3D). However, only for NO_3^- in CA and LC, these differences were statistically significant. Gaseous nitrogen forms generally predominated over the particulate forms, particularly in spring and summer (Figs. 3E and 3F). However, NO_3^- clearly predominated over HNO_3 during winter in TC and CA and during autumn in LC, and NH_4^+ predominated over NH_3 during winter in TC.

Additionally, no seasonal variations were recorded in ammonium gas/particle ratio in CA (Fig. 3F).

3.3. Differences in gaseous pollutant concentrations between open-field and below-canopy plots

Below-canopy concentrations of gaseous pollutants were, in general, smaller than levels found in the open-field plots (Fig. 4). These differences were more remarkable for NH_3, which showed an annual mean concentration in F plots 40% lower than in the O plots in average for the four sites (56% in LC, and 29–38% in the peri-urban forests). In the case of NO_2, differences were not significant in CB, while the concentrations were significantly lower in the F plots in the rest of sites (41% in CA, 13% in TC and 6% in LC). For HNO_3, the reduction detected inside the forest was significant in TC and CA, showing average concentrations 11–13% lower in the F plot compared to the O plot. Ozone concentrations were significantly lower inside the forests in TC and LC (annual mean difference of 7% and 5%, respectively).

The reduction of air pollutant concentrations inside the forest showed few evident seasonal patterns. Nitrogen dioxide experienced the highest decrease in concentrations below-canopy (Supplement, S1) during autumn and winter in TC and CA (none and 34% on average for both seasons, respectively), while in LC this difference was larger in spring (18%). The differences in NH_3 levels were consistent most of the time (31% on average; Supplement, S2), although smaller during the summer in the three peri-urban forests. Regarding HNO_3 (Supplement, S3), differences between forest and open plots were slightly higher during spring and autumn in TC and CA (24% in both sites, averaged for both seasons). The reduction of O_3 concentrations inside the forest resulted slightly larger during summer and autumn (8% in TC and 7% in LC, averaged for both seasons; Supplement, S4).

3.4. Correlation analysis of pollutant concentrations and meteorology

Atmospheric concentrations of NO_2 were poorly correlated with meteorological variables, with the exception of TC site, where NO_2 levels were negatively correlated to temperature, daily solar radiation and wind speed, and positively correlated to relative humidity. In the rest of sites, NO_2 concentrations were negatively correlated with precipitation in CB and LC, and with wind speed in CA (Table 4). In the case of NH_3 concentrations, no correlation was found in CA. In the other sites, relative humidity was negatively correlated to NH_3 concentration, while temperature and daily solar radiation were positively correlated in TC and LC, and negatively in CB. Concentrations of HNO_3 and O_3 were positively correlated with temperature and daily solar radiation, and negatively with relative humidity in all sites. Besides, HNO_3 and O_3 concentrations

showed a positive correlation with wind speed in TC and CA, and a negative correlation with precipitation in TC (Table 4).

The concentrations of PM_{10} were negatively correlated with precipitation in TC and CA and positively with solar radiation and temperature in TC and LC. In TC, PM_{10} was also negatively correlated with humidity. Besides, PM_{10} was negatively correlated with wind speed in LC. Particulate nitrate was negatively related to temperature and solar radiation only in CA. NH_4^+ concentrations did not show important correlations with meteorological variables. Particulate SO_4^{2-} was positively correlated to temperature and solar radiation and negatively with wind speed only in LC (Table 4).

No significant correlations among gaseous pollutant were found in CA. In the other sites, O_3 and HNO_3 concentrations were positively correlated (Table 4). In TC, O_3 was also negatively correlated to NO_2 and NH_3 was positively correlated to O_3 and HNO_3. Particulate NH_4^+ concentration was correlated with particulate NO_3^- in the three sites, and with SO_4^{2-} in CA and LC. However, NH_4^+ was not correlated with NH_3 in any of the sites. Particulate nitrate was positively related to NO_2 in TC and CA, and negatively correlated with HNO_3 only in CA (Table 4). Ammonia and HNO_3 concentrations were positively correlated to PM_{10} in TC and LC. Finally, scarce significant correlations with meteorological variables were found for the below-canopy reductions of atmospheric pollutant concentrations (data not shown).

4. Discussion

4.1. Air pollution affecting peri-urban forests

The annual mean of atmospheric NO_2 concentrations decreased from CB to LC (from 16.2 to 4.3 $\mu g\ m^{-3}$), indicating an order of influence of urban and traffic emissions (CB > TC ≥ CA > LC). The levels of NO_2 in the three peri-urban forests (CB, TC and CA) were in the range of values recorded in suburban background monitoring stations in 2012 (AirBase v8 dataset; EEA 2014). Therefore, suburban stations might be considered representative of NO_2 concentration registered in peri-urban forests. Concentrations of NO_2 in the three peri-urban forests followed the expected seasonal pattern of monitoring stations influenced by urban emissions, with highest values recorded during autumn and winter. This seasonal pattern is associated with increasing emissions due to urban combustion for heating purposes and with the lower photochemical intensity during the cold season (Karanasiou et al. 2014). The decrease of NO_2 with wind speed in TC and CA pointed to a higher influence of local sources rather than regional contribution. Similar results have been reported in other Mediterranean urban sites (Karanasiou et al. 2014). An analogous response would be expected at CB, but the higher urban density around the site and the lower wind speed (annual mean of 0.8 $m\ s^{-1}$) could be impairing pollutant dispersion. The forest site in

LC was more representative of background NO_2 concentrations, since the annual mean was close to the average value of 3.7–3.5 μg m^{-3} recorded in background stations in Spain in 2011 and 2012 respectively (MAGRAMA 2014). Moreover, NO_2 concentrations in LC did not show clear seasonal variations, demonstrating the lack of influence of urban emissions. After adding the estimated NO concentration (from the active monitors), none of the sites are expected to reach the critical level for the protection of vegetation (30 μg m^{-3}, as annual mean) established in the European Air Quality Directive.

The annual mean of NH_3 concentrations in CB, TC and LC were low and similar to the levels recorded in Spanish background stations (0.9 μg m^{-3} in 2012; Hjellbrekke 2014). These values were lower than concentrations measured in urban backgrounds of their respective closest cities (1.7 μg m^{-3} in Madrid and 7.3 μg m^{-3} in Barcelona; Reche et al. 2014), and far from levels registered in regions with intensive farming or livestock (up to 60 μg m^{-3}; Fowler et al. 1998; Pinho et al. 2012). The higher concentrations found in CA (annual mean of 2.5 μg m^{-3}) probably is related to the presence of livestock in the nearby area. The seasonal pattern of NH_3 concentrations in TC and LC, with higher values during spring and summer, could be explained by an increasing volatilisation and emission of NH_3 from biological sources under warm conditions. In the case of CB, the highest values recorded in autumn and winter might be related to the emissions of NH_3 from an industrial area 6.5 km west of CB. Concentrations of NH_3 at this site were significantly correlated with west winds ($p < 0.01$; data not shown), the most frequent wind in autumn and winter. The winter maxima NH_3 levels in CA were in agreement with the fertilization practices of cereal crops in the region during this season. Since the annual mean of NH_3 concentrations did not exceed the 3 μg m^{-3} critical level proposed for the protection of higher plants in any of the sites, these forests are not expected to experience relevant ammonia pollution effects (CLRTAP 2011). Moreover, the critical level of 1 μg m^{-3} for the protection of lichens and bryophytes (Cape et al. 2009; CLRTAP 2011) was only exceeded in CA.

No significant differences in HNO_3 annual concentration were detected among the sites included in this study. The concentrations of HNO_3 in the three peri-urban forests were in the range of values found in other peri-urban areas in the Mediterranean region (summer values of 2.8–4.2 μg m^{-3}; Danalatos and Glavas 1999) and higher than in urban sites (yearly averaged values of 0.8–1.5 μg m^{-3}; Anatolaki and Tsitouridou 2007; Tzanis et al. 2009). However, even the highest concentrations were below the values reported in forested areas of San Bernardino Mountains in Southern California, where topography, climate and emissions linked tohigh population favour HNO_3 formation (Bytnerowicz and Fenn 1996; Jovan et al. 2012). The typical higher HNO_3 values recorded during spring and summer in the study sites can be explained by the photochemical origin of this pollutant (Bytnerowicz et al. 2010; Tzanis et al. 2009). In this sense, positive correlations between solar radiation and HNO_3 concentration were found for all the sites.

The highest levels were found in LC, which must respond to pollutant-transport mechanisms rather than to an in-situ formation of HNO_3, since this is a rural site with low concentration of NO_2 (chemical precursor of HNO_3). In fact, ageing of air masses over the Iberian Peninsula and recirculation along the Mediterranean coast have been reported as processes increasing levels of oxidants, acidic compounds, aerosols and ozone (Escudero et al. 2014; Millán et al. 2002). Although very little information is available on direct effects of HNO_3 on vegetation, the concentrations found in this study are much lower than the levels reported for epicuticular damage (Padgett et al. 2009).

The annual mean concentration of O_3increased from CB to LC, following an opposite order of urban influence to the one found for NO_2 concentration. A similar behaviour has been described in other studies around cities in the Mediterranean area (Domínguez-López et al. 2014; Escudero et al. 2014*)*. CB showed an annual mean similar to values found in 2012 in Spanish suburban areas, while the other sites showed values clearly typical of rural areas (means of 59.0and 67.8µg m^{-3}, respectively; EEA 2014). Ozone concentrations in the peri-urban forests showed the typical seasonal variations with higher levels during spring and summer, responding to the sum of the hemispheric-scale spring maximum, the increased photochemical production and transport processes, as well as the above mentioned ageing of air masses and recirculation (Cristofanelli and Bonasoni 2009; Millán et al. 2002). In fact, ozone concentrations were significantly correlated with temperature and solar radiation. Besides, the emission of biogenic volatile organic compounds (BVOCs) by vegetation is known to be correlated with temperature, and can exacerbate photochemical reactivity, and thus O_3 formation (Calfapietra et al. 2013). All the calculated AOT40 values were above the concentration-based O_3 critical level proposed by the CLRTAP for protecting forest trees (5 ppm h for the growing season; CLRTAP 2011). The threshold levels for the protection of vegetation established in the European Directive 2008/50/EC (9 ppm h for the period May–July) were also overreached, with the exception of CB site in 2011. Moreover, experimental values of AOT40 similar to those found in this study have been proved to cause a decrease of growth in seedlings of *Q. ilex* (Alonso et al. 2014; Gerosa et al. 2015).

In the two peri-urban forests with aerosol measurements (TC and CA), the annual mean concentrations of PM_{10} were close to the urban background levels measured in Spanish big cities in 2012 (mean of 26 µg m^{-3}; MAGRAMA, 2014), and well above the values measured in Spanish background stations (12.9 µg m^{-3}; Hjellbrekke 2014). On the other hand, concentrations of particulate NO_3^- and NH_4^+ were similar to the national background levels in TC (1.2 µg NO_3^- m^{-3}, and 0.4 µg NH_4^+ m^{-3}; Hjellbrekke 2014), but almost double in CA. The increased concentration of NO_3^- and NH_4^+ in CA could respond to the elevated NH_3 concentration caused by agricultural activities, which, combined with the low temperatures, facilitates the formation and stability of ammonium nitrate (NH_4NO_3). Moreover, at this site, NO_3^- and HNO_3showed a negative

correlation, suggesting the existence of conversion of one into the other. The seasonality in PM_{10} is in agreement with previous studies that attributed the higher summer concentrations to low precipitation, high resuspension, photochemical oxidation and higher frequency of Saharan dust outbreaks (Escudero et al. 2005; Querol et al. 2008; Rodríguez et al. 2002). Interestingly, the natural events of Saharan dust did not modify NO_3^- and NH_4^+ concentrations. The seasonality observed on particulate N compounds was more related with the thermal instability of NH_4NO_3, pointing out the importance of temperature-dependent processes within the SIA in the Mediterranean region (Querol et al. 2008; Pey et al. 2009). Gaseous HNO_3 and NH_3 predominated over particulate forms most of the year but aerosol fraction was important mainly during winter. This seasonal variation in gas/aerosol ratios may have implications for N dry deposition estimations and, therefore, should be further investigated. Little information is available on direct effects of particles on vegetation and no threshold of aerosol concentration has been defined yet for the protection of vegetation.

According to the established thresholds and the available scientific evidences, the results indicate that O_3 is the only air pollutant considered in this work which is expected to have direct phytotoxic effects on vegetation. The concentrations of N compounds seemed to be not high enough to directly affect vegetation but could be contributing through atmospheric N deposition to the eutrophization of these ecosystems. Moreover, although evergreen broadleaf Mediterranean woody species are assumed to be tolerant to air pollution due to their sclerophyllic adaptations, recent publications suggest that the addition and interaction of different stress factors (O_3, N deposition, drought) can be affecting the growth of the trees (Alonso et al. 2014; Gerosa et al. 2015) and accompanying pastures (Calvete-Sogo et al. 2014). Thus, monitoring of nitrogen compounds such as NH_3 and HNO_3 should be incorporated into air quality monitoring networks.

4.2. Below-canopy reduction of atmospheric pollutant concentrations

Air pollutant concentrations measured outside and inside the forest (O and F plots) were compared to analyse the influence of vegetation in air quality. In general, the pollutants considered showed lower concentrations inside the forests. Below-canopy reduction of NO_2 concentration in our study sites ranged from none in CB, to 41% in CA.This high reduction detected in CA could be enhanced by the location of the sampling plots, which were at the same distance, but on the opposite sides of a highway. As a result, the O and F plots were located downwind and upwind from the highway, respectively, in relation to predominant winds (Supplement, Figure S5). Statistically significant reductions of NO_2 concentrations inside holm oak forests were found in TC and LC, with averaged values of 13% and 6%, respectively. These reductions are comparable to (Grundström and Pleijel 2014) or higher than (Harris and Manning 2010; Setälä et al. 2013) values reported in similar empirical studies with deciduous forest

species. The larger differences in NO_2 levels in LC were detected during spring, the time when holm oak forests usually show higher stomatal conductance (Alonso et al. 2008). Other authors have reported that NO_2 deposition onto forest canopy is governed by plant stomatal aperture (Chaparro-Suárez et al. 2011; Sparks 2009). This behaviour was not observed in TC and CA, where the highest reductions were found during autumn and winter, suggesting that other atmospheric and biogeochemical interactions could be implicated and need further research. In this sense, the lack of below-canopy reduction in CB could not be explained by meteorological variables or different pollutant exposure. Other authors have suggested that NO emissions from forest soil in areas with high O_3 levels, could result in the formation of NO_2 below the canopy (Harris and Manning, 2010; Fowler, 2002), diminishing the difference of NO_2 concentrations between outside and inside the canopy. Since dry deposition of atmospheric pollutants depends on multiple factors such as micrometeorology, spatial heterogeneity, plant structure and physiology, and biochemical interaction, further research is needed to clarify the influence of vegetation on air quality.

Below-canopy concentrations of NH_3 were on average 40% lower than in the open field, suggesting that holm oak forests act as sinks of ammonia. This difference was relatively higher in the most natural forest (56% in LC) than in the peri-urban ones (29–38%). Since NH_3 stomatal fluxes are bi-directional, emission or deposition of NH_3 will occur depending on ecosystem N-status, stomatal conductance, and the ratio between atmospheric and canopy NH_3 concentration (Behera et al. 2013; Fowler et al. 2009). The below-canopy reductions of NH_3 were consistent throughout most of the year, but smaller during the summer, a period of low plant physiological activity in this type of forest. These results indicate a certain regulation of NH_3 fluxes by stomatal uptake. However, NH_3 canopy retention was not the highest in spring, when plants usually experience maximum stomatal conductance, thus other mechanisms must affect the overall ammonia retention by the canopy in autumn and winter. Among other major drivers of atmospheric NH_3 deposition into the canopy, leaf area density, and leaf surface wetness and acidity can enhance the deposition onto the cuticles and epiphytic communities (Geiser et al. 2010; Massad et al. 2010).

The differences in HNO_3 concentration between O and F plots were only significantly detected in TC and CA, with reductions of 11–13% on annual average. Among the N gaseous pollutants, $HNO_3$is supposed to have the highest surface deposition velocity due to its highly reactive and soluble nature,which should lead to large rates of deposition onto leaf surfaces (Fowler et al. 2009). However, the rates of bellow-canopy HNO_3 reduction are similar to those ofNO_2 in TC and LC, and lower than those ofNH_3. No clear seasonal patterns were found in the below-canopy reduction of HNO_3 concentrations that could indicate the main processes involved in HNO_3 dry deposition in these forests.

In regards to O_3 concentrations, urban and peri-urban vegetation has been proposed as a strategy to absorb O_3 and diminish atmospheric concentrations (Alonso et al. 2011; Kroeger et al. 2014). In our study, O_3 levels were significantly reduced inside the forests in TC and LC with an average decrease of 5–7%. The largest below-canopy reduction of O_3 concentration occurred in summer and autumn, suggesting that stomatal uptake was not the only process involved in this decline, since stomatal conductance in usually low during the summer in these forests due to drought stress. Actually, non-stomatal O_3 deposition in holm oak forests has been reported to account up to ca. 60 % of the total ozone flux (Fares et al. 2014). Surface wetness of the canopy and other forest surfaces can enhance non-stomatal deposition of O_3 (Altimir et al. 2006). This process could explain the higher reductions of O_3 detected during autumn, the wettest season in all the sites. Besides, increased BVOCs emissions linked to high temperatures during the summer could be favouring the photochemical production of O_3 (Calfapietra et al. 2013). This formation of O_3 should be more apparent in the open-field plots due to their higher insolation,increasing the difference in O_3 concentrations between O and F plots during this season.

5. Conclusions

Peri-urban forests are exposed to air pollutants coming from both urban and rural activities. Ozone concentrations around Spanish cities are high enough to directly impact peri-urban vegetation. The concentrations of N compounds would no directly threat vegetation, but could be contributing, through atmospheric N deposition, to the eutrophization of these ecosystems. Besides, the interaction of different stress factors (O_3, N deposition, drought) could be affecting plant growth and ecosystem functioning. On the other hand, peri-urban forests of *Quercus ilex* have proved to experience a significant below-canopy reduction of pollutant concentrations, particularly of NH_3, but also of NO_2, HNO_3 and O_3. These results provide scientific evidence of the ability of these ecosystems to improve air quality in urban agglomerations, but further research is still needed to quantify the relevance of this ecosystem service. The high variability found in this study across sites and seasons points that processes and environmental factors involved in air pollution removal must be characterized in order to manage these forest for improving air quality. Well-designed monitoring programs of urban and peri-urban forests could accomplish both objectives of further investigate air quality improvement while assessing the threat that air pollution can pose to vegetation.

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Table 1. Characterization of the study sites.

Site code	**CB**	**TC**	**CA**	**LC**
Site name	**Can Balasc**	**Tres Cantos**	**Carrascal**	**La Castanya**
Province (administrative unit)	Barcelona	Madrid	Navarra	Barcelona
Type of site	Peri-urban	Peri-urban	Peri-urban	Rural
Altitude (m)	255	705	592	696
Longitude	2º 04' 54" E	3º 43' 59" O	1º 38' 40" O	2º 21' 29" E
Latitude	41º 25' 47" N	40º 35' 17" N	42º 39' 13" N	41º 46' 47" N
Mean annual temperature (ºC) [1]	15.2	14.6	12.3	13.7
Mean annual rainfall (mm y^{-1}) [1]	652	348	645	812
Distance to the nearest big city (km)	4	9	15	40
Population of the nearest big city (million inhabitants)	1.6	3.2	0.20	1.6
Distance to the nearest highway (km)	0.15	1.5	0.05	16
Average daily flow in the nearest road (thousand vehicles day^{-1}) [2]	40-50	50-60	20-30	20-30
Agricultural land-use cover [3]	23%	21%	62%	23%
Artificial land-use cover [3]	35%	28%	3.1%	7.6%
Livestock density (LU km^{-2}) [4]	14.5	13.7	26.9	88.8

[1] : Mean values calculated for the study period.
[2]: Values for 2012 from the Spanish Ministry of Development (http://www.fomento.gob.es/).
[3, 4] :From the Corine Land Cover 2006 (http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster-3) and the Spanish National Statistic Institute (http://www.ine.es), respectively, using a buffer of 25 km radius around the sampling sites.

Table 2.Basic statistics of the monitored pollutant concentrations in open-field plots for the entire monitoring periods.

	SITE	MEAN	MIN. – MAX.	CV
NO_2 ($\mu g\ m^{-3}$)	**CB**	16.2 ± 1.0 a	5.7 – 39.3	42%
	TC	11.1 ± 1.1 b	3.8 – 37.1	71%
	CA	10.6 ± 0.7 b	4.4 – 26.0	45%
	LC	4.3 ± 0.3 c	0.8 – 9.4	52%
NH_3 ($\mu g\ m^{-3}$)	**CB**	1.0 ± 1.0 b	0.3 – 2.6	53%
	TC	0.7 ± 0.1 c	0.1 – 1.7	60%
	CA	2.5 ± 0.2 a	0.6 – 5.3	47%
	LC	0.7 ± 0.1 c	0.1 – 1.7	59%
HNO_3 ($\mu g\ m^{-3}$)	**CB**	2.7 ± 0.6	0.0 – 14.5	134%
	TC	1.5 ± 0.2	0.0 – 6.4	73%
	CA	2.3 ± 0.3	0.3 – 9.7	98%
	LC	3.3 ± 0.7	0.0 – 13.9	134%
O_3 ($\mu g\ m^{-3}$)	**CB**	57.0 ± 2.4 c	10.8 – 86.1	30%
	TC	69.1 ± 2.9 b	28.7 – 101.4	30%
	CA	77.4 ± 4.7 a	25.3 – 122.3	32%
	LC	78.2 ± 3.2 a	34.9 – 117.3	29%
PM_{10} ($\mu g\ m^{-3}$)	**TC**	23.0 ± 3.2 ab	5.2 – 61.0	67%
	CA	26.9 ± 2.6 a	6.8 – 49.2	41%
	LC	18.0 ± 1.5 b	4.8 – 32.8	41%
NO_3^- ($\mu g\ m^{-3}$)	**TC**	1.3 ± 0.4 b	0.1 – 8.1	129%
	CA	2.2 ± 1.5 a	0.5 – 8.8	99%
	LC	1.1 ± 0.2 b	0.2 – 4.2	80%
NH_4^+ ($\mu g\ m^{-3}$)	**TC**	0.6 ± 0.1	0.2 – 2.7	54%
	CA	0.9 ± 0.2	0.3 – 3.7	97%
	LC	0.5 ± 0.1	0.0 – 1.6	71%
SO_4^{2-} ($\mu g\ m^{-3}$)	**TC**	1.2 ± 0.2 b	0.1 – 4.2	70%
	CA	1.9 ± 0.2 a	0.8 – 3.7	48%
	LC	1.7 ± 0.2 a	0.4 – 3.3	52%

Mean: arithmetic mean ± standard error. Min. – Max.: Minimum and maximum two-week values. CV: coefficient of variation, representing the temporal variability. Different letters indicate significant differences ($p < 0.05$) between sites. The absence of letters indicates no significant differences.

Table 3. Ozone exposure expressed as AOT40 for years 2011 and 2012, following criteria from the Convention on Long-range Transboundary Air Pollution (CLRTAP) and the Ambient Air Quality Directive 2008/50/EC.

AOT40 (ppm h)				
SITE	**CLRTAP (Jan–Dec)**		**Directive 2008/50/EC (May–July)**	
	2011	**2012**	**2011**	**2012**
CB	8.2	18.8	3.7	9.4
TC	31.8	49.6	17.4	28.3
CA	32.6	32.3	15.5	16.5
LC	27.3	34.9	12.5	18.3

FIGURE CAPTIONS

Fig. 1 Distribution of *Quercus ilex* habitats in Spain, and location of the study sites. LC: La Castanya (Barcelona); CB: Can Balasc (Barcelona); CA: Carrascal (Navarra); TC: Tres Cantos (Madrid).

Fig. 2 Seasonal mean concentration of atmospheric pollutants in the open-field (O) plots of the four study sites and standard error of the mean. Different letters indicate significant differences amongseasons.

Fig. 3 Seasonal mean concentrations of aerosols and standard errors, and ratios of particulate to gaseous pollutants in the three aerosol monitoring sites. A) PM_{10} concentration; B) PM_{10} concentration for measurements during Saharan dust events compared with the rest of the samples; C) particulate nitrate concentrations; D) particulate ammonium concentrations; E) concentrations ratios of nitric acid and particulate nitrate, expressed as percentage of the sum of both compounds; F) concentrations ratios of ammonia and particulate ammonium, expressed as percentage of the sum of both compounds. Different letters indicate significant differences between seasons. One outlier value (CA, spring) was removed from the graphs C–F.

Fig. 4 Mean concentration of pollutants in O plots (open field) and F plots (below canopy), and standard error of the mean. Significance of the Wilcoxon matched pairs test: *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$.

Fig. 1

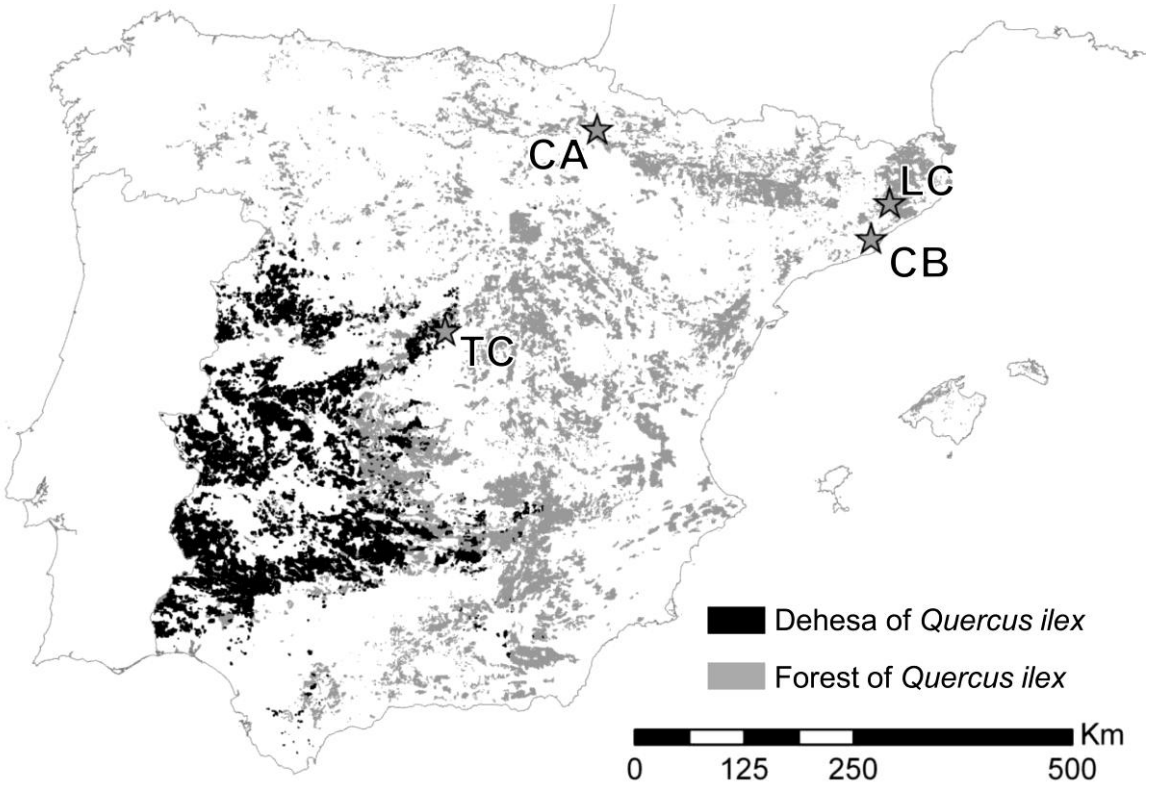

CA
LC
CB
TC
Dehesa of *Quercus ilex*
Forest of *Quercus ilex*
Km
0
125
250
500

Fig. 2

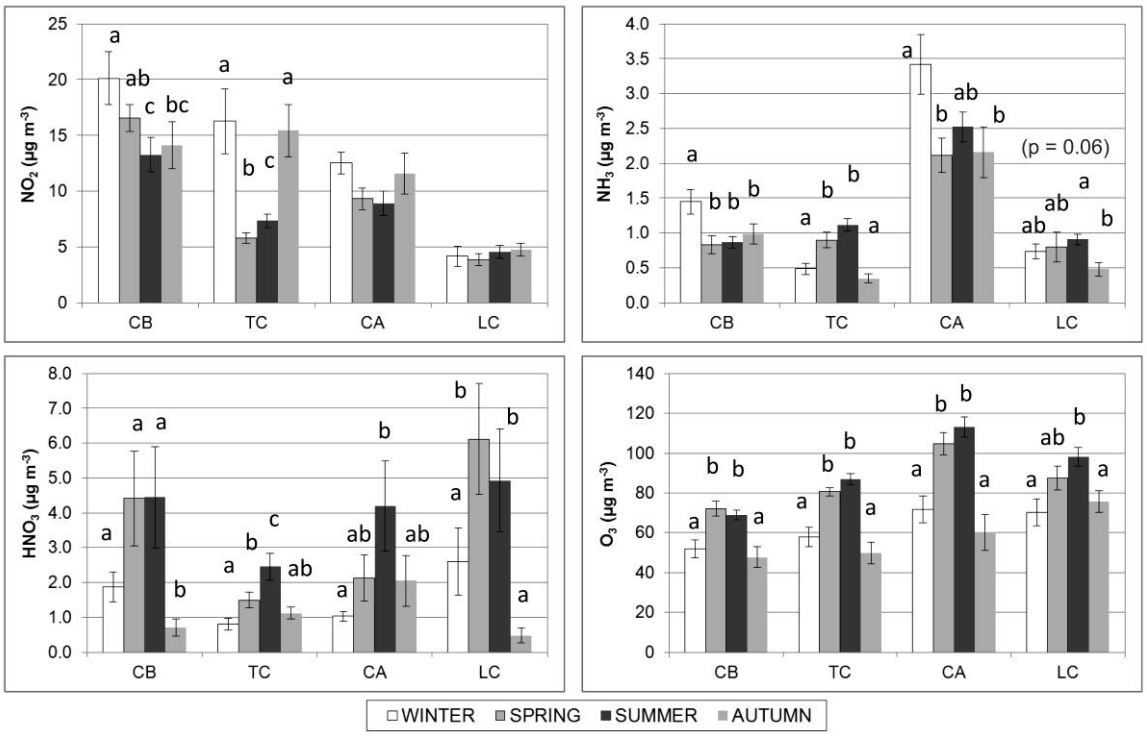

NO2 (µg m-3)
NH3 (µg m-3)
HNO3 (µg m-3)
O3 (µg m-3)
(p = 0.06)
CB
TC
CA
LC
WINTER
SPRING
SUMMER
AUTUMN

Fig. 3

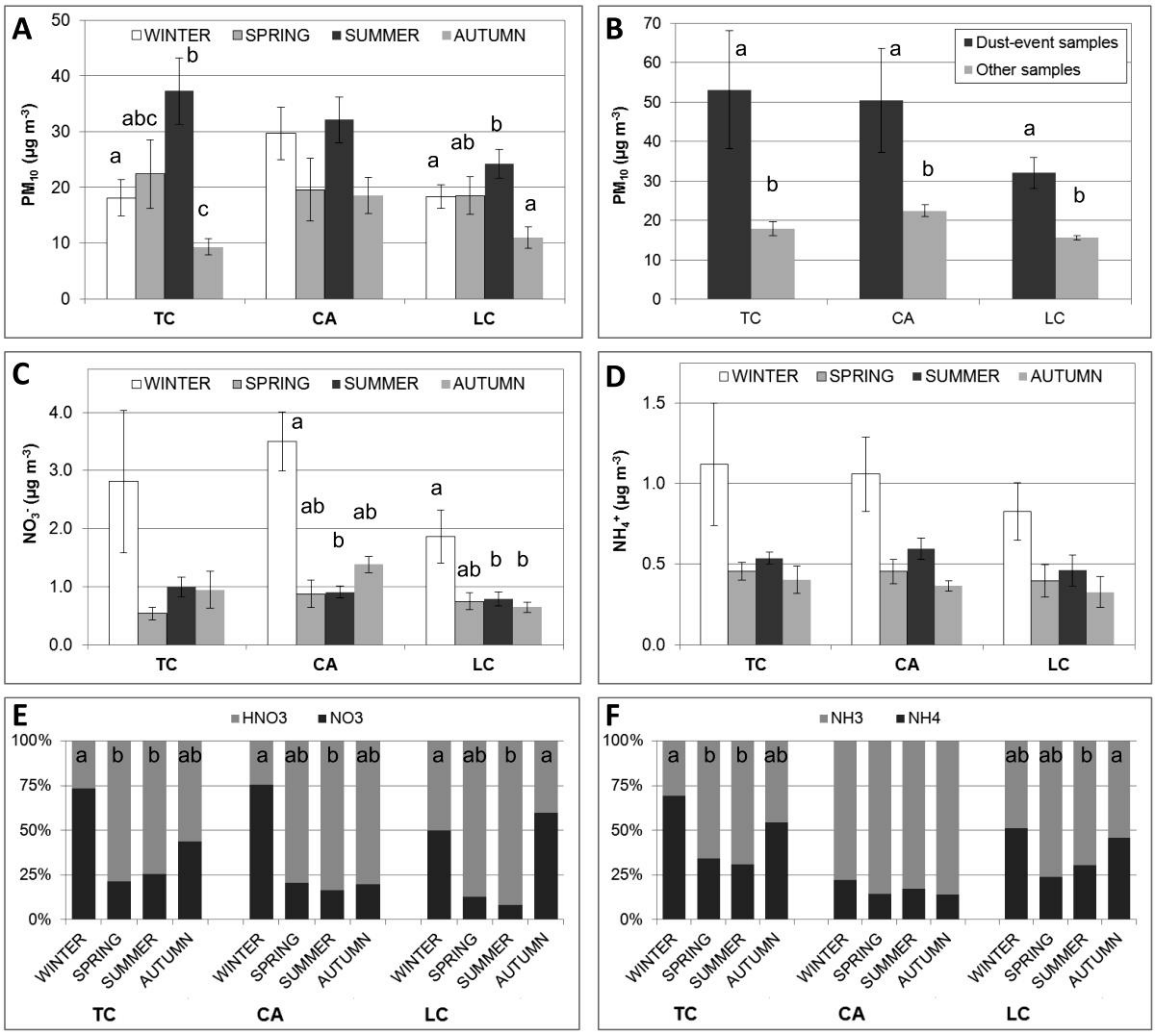
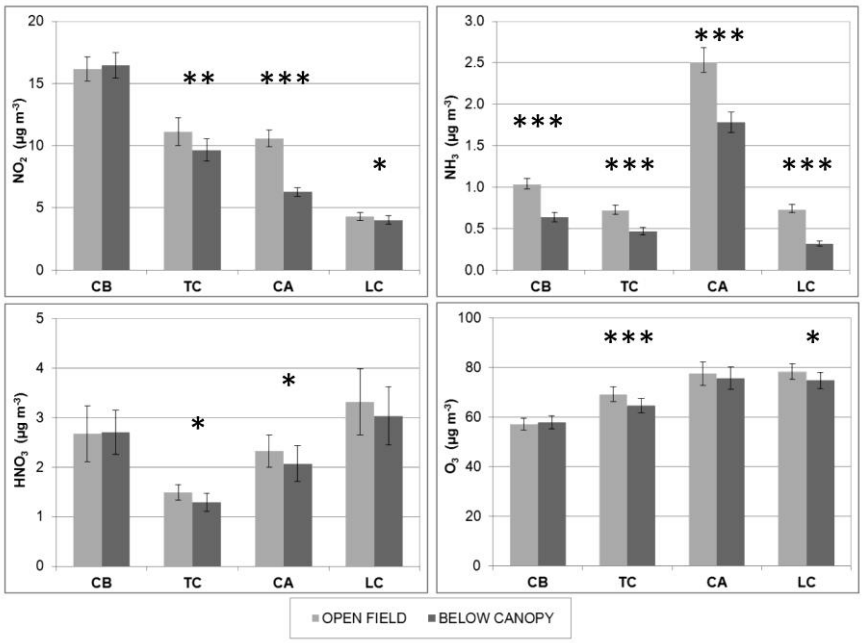

A
WINTER
SPRING
SUMMER
AUTUMN
PM10 (µg m-3)
TC
CA
LC
B
Dust-event samples
Other samples
C
NO3- (µg m-3)
D
NH4+ (µg m-3)
E
HNO3
NO3
F
NH3
NH4

Fig. 4


NO2 (µg m-3)
NH3 (µg m-3)
HNO3 (µg m-3)
O3 (µg m-3)
CB
TC
CA
LC
OPEN FIELD
BELOW CANOPY