Ozone and nitrogen dioxide concentrations in a Holm oak urban park and an adjacent open area in Siena

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Abstract

Urban parks play important role in providing social and ecosystem services; the improvement of air quality through the absorption of gaseous pollutants and the interception of airborne particles is one the most important services of urban trees within those parks. Surveys performed in Italian urban environments show that leaves of Holm oak (*Quercus ilex* L.) are efficient accumulators of airborne trace elements and polycyclic aromatic hydrocarbons, but few data are available on the uptake of gaseous pollutants such as O_3, NO_2. This study aimed at determining, with passive samplers, seasonal variations in O_3 and NO_2 air concentrations under the canopy of *Q. ilex* and in an adjacent open area at increasing distances (1, 5, 10 m) from a busy road in Siena. The survey was performed in July, November 2011, January, April 2012; the results showed a similar seasonal distribution of average O_3 concentrations along the two transects, with much higher values (up to 69 μg m^{-3}) in July. On the contrary, the highest NO_2 concentrations were recorded in January and in all seasons their distribution pattern was characterized by a decrease of average values at increasing distances from the road, especially under the *Q. ilex* canopy. Although preliminary, results indicate that in Siena *Q. ilex* trees attenuate NO_2 concentrations but not O_3.
Keywords: urban ecosystems, Quercus ilex, air pollutants, O_3, NO_2.

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1 Introduction

More than half of the world's population live in cities and among increasing urbanization effects there is the degradation of the water, soil and air quality. The atmospheric pollution is a major environmental concern in most urban environments because an increasing number of epidemiological studies links the exposure to fine particulate matters, O_3 and other pollutants with increasing cardiovascular mortality and morbidity [1]. Urban vegetation captures airborne gases, particulates and aerosols more effectively than other exposed surfaces and trees with the large surface of leaves and turbulences created by their structure are more effective than shorter vegetation in the pollutant removal [2]. In many Italian cities the evergreen Holm oak (*Quercus ilex* L.) is one of the most widespread trees and its leaves have a dense hair cover and thick waxy cuticles which enhance the scavenging and retention of airborne particulates, the incorporation of polycyclic aromatic hydrocarbons and other lipophilic organic pollutants. Thus, the determination of total concentrations of persistent atmospheric pollutants in Holm oak leaves allowed us to trace spatial and temporal trends of metals and persistent organic pollutants deposition in Rome [3], Naples [4], Siena [5] and other Italian urban environments.

In contrast to persistent pollutants which are mainly deposited on tree leaves by interception, impaction or sedimentation of airborne particles, the gaseous pollutants such as O_3, NO_2 and SO_2 are primarily absorbed through leaf stomata [2]. Accurate measurements of their uptake is difficult because it depends on meteorological conditions and the tree transpiration rates. Different empirical models have been developed to estimate the removal of air gaseous pollutants by urban trees [6, 7] and most estimates indicate a significant mitigation of O_3, NO_2, SO_2 and CO concentrations. Paoletti [8] for instance, estimated that in Florence urban environment a *Q. ilex* tree removes 112 g of O_3 in a year. However, there are not direct measurements of the ability of urban Holm oaks to reduce atmospheric levels of O_3. By using passive samplers to determine air concentrations of O_3 and NO_2 inside and outside the tree canopy Harris and Manning [9] concluded that current models are inadequate for estimating the pollutant uptake by urban trees. Furthermore, Setälä *et al.* [10] found that in northern climate the role of tree foliage in removing air pollutants is insignificant.

In the framework of studies aimed at evaluating the role of urban Holm oak in the mitigation of air pollution in Siena urban environment [5, 11] in this work we determined through passive samplers, seasonal variations of NO_2 and O_3 atmospheric concentrations along two transects facing a busy urban road: one transect was located in a *Q. ilex* stand, the other in an adjacent open area.

2 Materials and methods

2.1 Study area and sampling

Siena is a small medieval town in central Italy (about 55000 inhabitants) and the vehicular traffic, especially in roads around the city centre, is the main source of atmospheric pollutants. The climate is temperate and mild (average precipitation about 750 mm yr^{-1}) and climatic and topographic characteristics favour the dispersal of atmospheric pollutants, which as a rule, have concentrations in the low or moderate range [12]. Seasonal changes of O_3 and NO_2 concentrations were determined at a distance of 1, 5 and 10 m from Via Fiorentina along two transects perpendicular to the direction of the vehicular traffic (Fig. 1). One transect was located in a Holm oak stand (a private park: Villa Patrizia), the other in a nearby open field area. The traffic intensity in Via Fiorentina ranges

Figure 1: The two transects with samplers at 1, 5, and 10 m from Via Fiorentina (Siena), inside and outside the Holm oak park at Villa Patrizia.

from 200 to 1500 vehicles h^{-1}. The passive samplers were located at a height of 2 m above the ground (behind the tree crown in the park) for 28 days in July 2011, November 2011, January 2012 and April 2012.

2.2 Analytical determinations

Passive samplers are based on molecular diffusion and despite some limitations they have been successfully applied in several studies, showing strong agreement with data from continuous monitoring devices [13]. In each month the samplers were replaced weekly with a total of 48 samples for each transect. The concentrations of NO_2 and O_3 were determined by using standard colorimetric methods and an UV/VIS spectrometer (Lambda 25, Perkin Elmer). The O_3 was determined by measuring at 430 nm the azide produced through the addition of 3-methyl-2-benzothiazolinone hydrazone (MBTH) to the exposed cartridge. The NO_2^- was determined at 537 nm after extraction with 5 ml of Milli-Q water. Calibration curves were obtained with solution (from 5 to 50 mg l^{-1}) of 4-pyridylaldehyde and sodium nitrite. Procedural blanks were below the detection limit; the precision and accuracy of sampling and analytical procedures were checked by replicate determinations and the use of standard solutions.

The analysis of variance (ANOVA) was made to assess the effect of different distances from the road and between the Holm oak grove and open field transect on measured parameters. The variance levels were checked for homogeneity and concentrations were reported as mean ± SD. Multiple comparisons were performed by one-way ANOVA and individual differences were tested by a Fischer test after the demonstration of significant intergroup differences. Differences with $p<0.05$ were considered significant.

3 Results

In all sampling sites the average NO_2 concentrations were higher in the cooler months (up to 84 μg m^{-3} in January and November) than in April and July (max= 45 μg $/m^3$). During all sampling periods the highest NO_2 levels were measured at the edge of Via Fiorentina and values progressively decreased at the distance of 5 and 10 m. However, as shown in Figure 2 the decrease under the Holm oak canopy was greater than in the adjacent open area. Especially in winter, when the highest NO_2 concentrations were recorded (Fig. 3).

During the four sampling periods the distribution of average O_3 levels along the two transects was similar (Fig. 4) and concentrations of O_3 were much higher in July (from 65 to 72 μg $/m^{-3}$) than in November, January and April (Fig. 5).

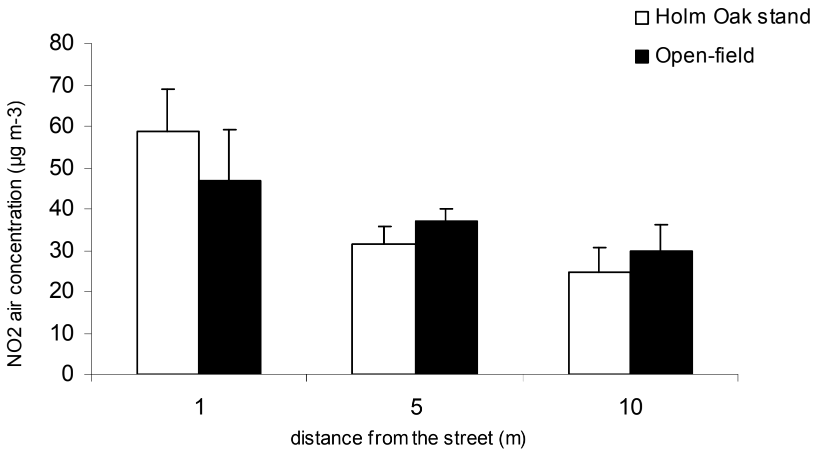

Figure 2: Average NO_2 concentrations (± SD) along the two transects during the four sampling periods. Each bar represents a mean of 16 replicates.

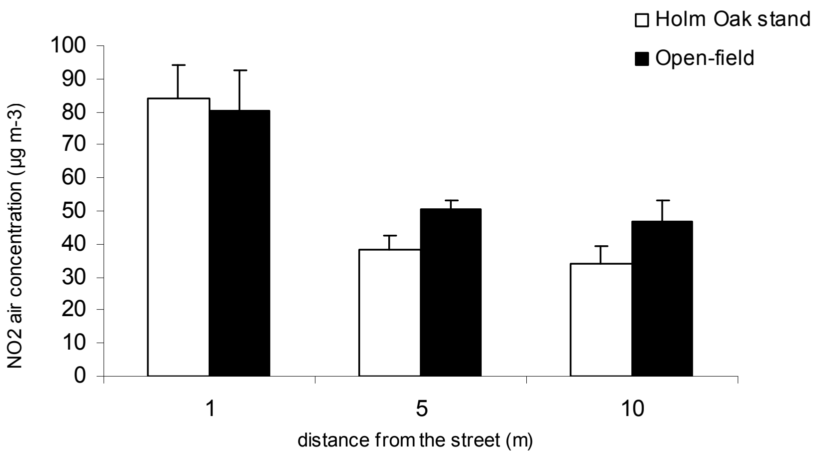

Figure 3: Average NO_2 concentrations (± SD) along the two transects in January. Each bar represents a mean of 4 replicates.

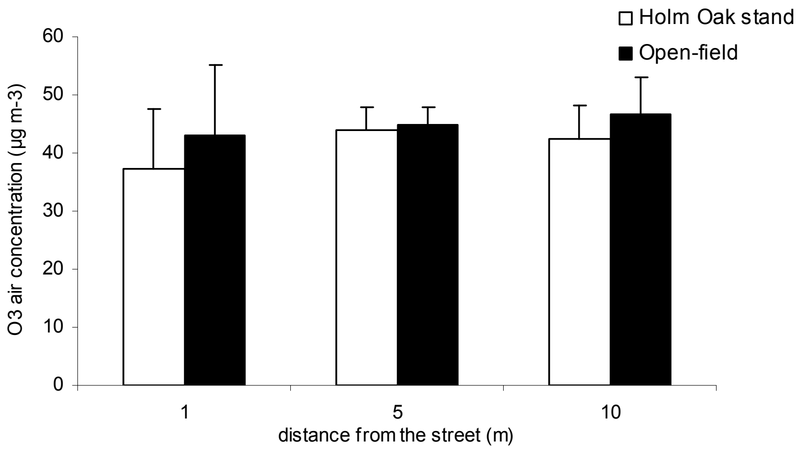

Figure 4: Average O_3 concentrations (± SD) along the two transects during the four sampling periods. Each bar represents a mean of 16 replicates.

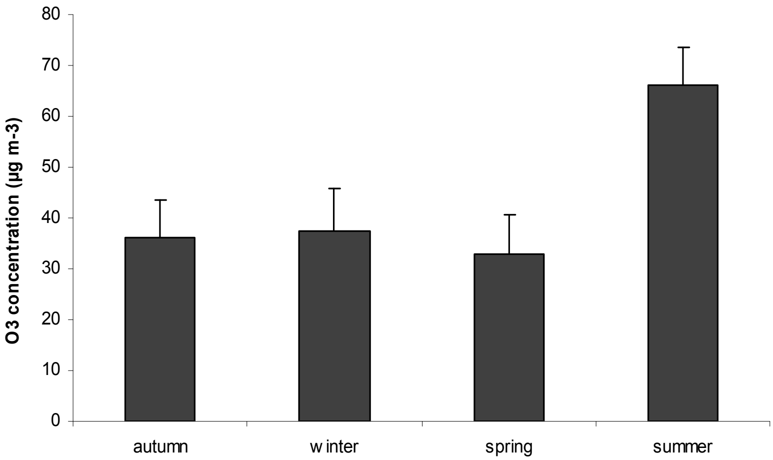

Figure 5: Average O_3 concentrations (± SD) during the four sampling periods along the two transects. Each bar represents a mean of 48 replicates.

4 Discussion

Our results show that O_3 and NO_2 monitoring with passive samplers gave results in the same range of those recorded during the 2011 near a busy road, by the local agency for the control of air pollution in Siena (O_3 = 51.4 ± 3.1 and NO_2 =

46.3±3.3) [12]. In general, these values are lower than those reported for other Italian and European cities [14]. Average NO_2 concentrations were significantly higher in the colder months (January and November) and along the two transects the values decreased at increasing distances from Via Fiorentina. At 5 m and 10 m from the road the NO_2 concentrations under *Q. ilex* canopy were lower than those measured at the same distance in the open area, likely indicating the capability of Holm oak trees to remove NO_2 from the urban atmosphere. On the contrary, measurements with passive samplers showed much higher O_3 concentrations in July and no statistically significant differences were found among average values measured at increasing distance from the road or between O_3 concentrations measured under the tree canopy and in those in the open area transect. Although model-based studies in Italian urban and extraurban Holm-oak forests [8, 15] suggested an O_3 mitigation by *Q. ilex*, our direct measurements with passive samplers under the tree canopy seem to exclude a significant O_3 uptake. However, as the potential stomatal uptake of O_3 by Holm oaks increases under conditions of high physiological activity and moderate to high irradiance such as in September–October (after the typical Mediterranean post-summer rainfalls) [15] a further O_3 monitoring under *Q. ilex* canopy during this period will be performed to validate the results of our measurements.

5 Conclusions

This research provided additional information on O_3 and NO_2 concentrations in Siena urban area and on their uptake by Holm oak trees. Average concentrations of the two pollutants measured with passive samplers in Via Fiorentina resulted in the same range of those recorded during the 2011 in another busy road in Siena urban environment through a continuous monitoring device [12]. In general, NO_2 and O_3 levels were lower than limits established for the protection of human health. Although in Italian urban areas the *Q. ilex* trees are deemed efficient removers of particulate and gaseous atmospheric pollutants, our survey on spatial and temporal variations of O_3 and NO_2 concentrations under the canopy of Holm oak trees and in a adjacent open area indicated that in Siena urban environment the oaks play a significant role in the uptake of NO_2, but it does not seem to mitigate O_3 concentrations.

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