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Spatio-temporal variations of ozone and nitrogen dioxide concentrations under urban trees and in a nearby open area

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ABSTRACT

The evergreen *Quercus ilex* L. is one of the most common trees in Italian urban environments and is considered effective in the uptake of particulate and gaseous atmospheric pollutants. However, the few available estimates on O_3 and NO_2 removal by urban *Q. ilex* originate from model-based studies (which indicate NO_2/O_3 removal capacity of *Q. ilex*) and not from direct measurements of air pollutant concentrations. Thus, in the urban area of Siena (central Italy) we began long-term monitoring of O_3/NO_2 concentrations using passive samplers at a distance of 1, 5, 10 m from a busy road, under the canopies of *Q. ilex* and in a nearby open-field. Measurements performed in the period June 2011–October 2013 showed always a greater decrease of NO_2 concentrations under the *Q. ilex* canopy than in the open-field transect. Conversely, a decrease of average O_3 concentrations under the tree canopy was found only in autumn after the typical Mediterranean post-summer rainfalls. Our results indicate that interactions between O_3/NO_2 concentrations and trees in Mediterranean urban ecosystems are affected by temporal variations in climatic conditions. We argue therefore that the direct measurement of atmospheric pollutant concentrations should be chosen to describe local changes of aerial pollution.

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1. Introduction

In urban environments the green spaces and trees provide numerous ecological, social and psychological services (e.g. Pataki et al., 2011; Perino et al., 2014). The abatement of atmospheric pollution is one of the key benefits of urban vegetation (e.g. Nowak et al., 2006; Tallis et al., 2011). Tree leaves absorb CO_2 and gaseous pollutants such as O_3, NO_2, SO_2 primarily by uptake via leaf stomata (though some gases are removed by the plant surface) and accumulate airborne particulates (by interception, impaction or sedimentation) more effectively than other exposed surfaces (Escobedo and Nowak, 2009). The extent of removal is dependent on plant species traits (such as canopy structure, leaf area, morphology and biomass), planting density, pollutant concentrations, atmospheric precipitation and other meteorological factors affecting tree transpiration and the deposition velocity of air pollutants (e.g. Fowler, 2002; Matyssek et al., 2004; Manes et al., 2012).

Tropospheric O_3 is a major air pollutant and urban populations in Europe, particularly in southern countries, are often exposed to O_3 concentrations exceeding the European target value set for the protection of human health as well as vegetation (EEA, 2012). Nitrogen dioxide (NO_2) is another major pollutant whose atmospheric levels in urban areas are largely due to the transport sector, a prevalent source of NO_x (NO_2, NO) emissions. In the lower atmosphere, photolysis of NO_2 in presence of volatile organic compounds (VOCs), leads to the net formation of O_3. (Atkinson, 2000; Duan et al., 2008). Thus, although trees absorb gaseous pollutants, they also contribute to the tropospheric O_3 formation by producing VOCs such as isoprenoids (which are estimated to be 2–3 times more reactive than weighted average emissions from petrol combustion; Carter, 1994; Calfapietra et al., 2013).

In Italy, the evergreen *Quercus ilex* L. has a wide natural distribution and has been used since the sixteenth century in the landscaping of urban and rural parks. Its leaves have dense hair cover and thick waxy cuticles which enhance the scavenging and retention of airborne particulates and the incorporation of polycyclic aromatic hydrocarbons and other lipophilic organic pollutants (Orecchio, 2007; Fantozzi et al., 2012). Therefore, *Q. ilex* leaves are one the most used environmental matrices for the biomonitoring of pollutant deposition in Italian urban environments (Monaci et al., 2000; Gratani et al., 2008; De Nicola et al., 2008).

Mediterranean evergreen and sclerophyllous species tolerate potentially harmful O_3 and NO_2 concentrations through a strong emission of monoterpenes which enable them to counteract the oxidative stress (Kesselmeier et al., 1996; Nali et al., 2004). Plants of the genus *Quercus* are among the strongest VOCs emitters and emissions by *Q. ilex* have been associated with the O_3 production in urban environments during summer (Loreto et al., 2009). However, it is generally deemed that the O_3 uptake by urban trees is usually greater than the O_3 formation (e.g. Nowak et al., 2000) and reduction in atmospheric concentrations of NO_x and other gaseous pollutants due to the presence of vegetation have been observed and suggested for a number of urban and peri-urban environments (e.g. Manes et al., 2012; Alonso et al., 2011; Leung et al., 2011; Calfapietra et al., 2013; Salmond et al., 2013). By applying the Urban Forest Effects (UFORE) model, designed to statistically estimate urban forest characteristics and functions (including O_3 removal and VOC emission), Paoletti (2009) estimated for *Q. ilex* in Florence urban environment an annual O_3 removal of 70 g/tree and a VOC emission of 341 g/tree. However, '*in situ*' measurements of the pollutant uptake are lacking and various shortcomings have recently been recognized in the ability of some models to quantify pollutant removal by urban trees (e.g. Pataki et al., 2011).

By using passive samplers, Harris and Manning (2010) measured the concentrations of O_3 and NO_2 inside and directly adjacent to individual tree canopies and found that the average NO_2 concentrations were significantly higher inside the canopies than outside; conversely, O_3 concentrations were higher outside the canopy. Based on these findings Harris and Manning (2010) concluded that current models may be insufficient for describing exposure to and uptake of NO_2 and O_3 by urban trees, particularly for those not forming a closed canopy with neighboring trees. Setälä et al. (2013) by measuring air pollutant concentrations with passive samplers under tree canopies in urban park/forest vegetation and adjacent treeless open areas in two Finnish cities found that concentrations of NO_2 and anthropogenic VOCs did not differ significantly between summer (tree leaf-period) and winter (leaf-free periods). Furthermore, vegetation-related environmental variables such as number and size of trees and canopy