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Chemical reaction rates of ozone in water infusions of wheat, beech, oak and pine leaves of different ages

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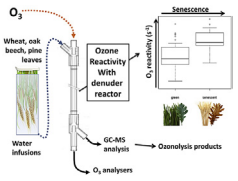
HIGHLIGHTS

- Leaves infusion solutions were prepared to mimic rain or dew water on leaves.
- Ozone reaction rates of these solutions were measured with a denuder reactor.
- Wheat infusions showed higher reaction rates than beech, oak and pine infusions.
- Ascorbate, VOC and ozonolysis products were measured in senescing wheat infusions.
- Senescing leaves showed large reaction rates likely due to out-leaching compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we present results from a laboratory experiment designed to evaluate the first-order chemical reaction rate (k) of ozone in water films on plant leaves occurring during dew or rain events. Ozone deposition to wet cuticles is indeed known to be a significant pathway of ozone deposition, but the underlying processes are not yet well understood. Leaf infusions obtained by infusing plant leaves with water at room temperature were introduced into a wet effluent denuder fed with a flux of ozone-rich air. Ozone, water vapour concentrations and temperature were measured in both inlet and outlet airflows in order to compute ozone reaction rates k_r using an ozone reaction-diffusion model in the water film. Ascorbate solutions were used to validate the set up and led to $k_r = 3.6\ 10^7\ M^{-1}\ s^{-1}$ consistent with the literature. Ozone reaction rates were determined for wheat, beech, oak and pine leaves infusions at several developmental stages, as well as for rain samples. Leaf infusions reaction rates were between 240 s^{-1} and 3.4 10^5 s^{-1} depending on species and developmental stage, while k for rain water ranged from 130 to 830 s^{-1}. Wheat leaves solutions showed significantly ($P < 0.001$) higher k_r (median 73800 s^{-1}) compared to the other tree species (median 4560 s^{-1}). Senescing or dead leaves also showed significantly ($P < 0.001$) larger k (median 21100 s^{-1}) compared to non-senescent leaves (median 3200 s^{-1}). In wheat, k also increased with increasing yellow leaf fraction. Our results are in the range of previously reported ozone deposition on wet leaves in field or chamber studies. Composition of leaves infusions and previous studies on throughfall and dew composition shows that reaction of ozone with inorganic compounds may only explain the smallest measured k. The largest k observed during senescent

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are most likely due to reaction with organic material. This is confirmed by LC-MS measurements which showed detection of ascorbate and VOCs as well as the reaction products of ozone with these compounds.

1. Introduction

Tropospheric ozone (O_3) is a major atmospheric pollutant that affects the global greenhouse gas budget of the Earth's atmosphere and disrupts plant and animal physiology (Karnosky et al., 2007; Ren et al., 2007). The concentration of tropospheric O_3 has increased over the last century and is forecast to rise two to four fold within the next decades (Anfossi and Sandroni, 1997; Vingarzan, 2004). A fundamental challenge of evaluating the impact of ozone on crop or forest productivity is to distinguish stomatal deposition that penetrates into the leaf from deposition on other surfaces (soil, leaf cuticles) or chemical destruction in the canopy air.

At the canopy scale, the net total ozone deposition is typically measured by the eddy-covariance technique (Lamaud et al., 2009). Soil deposition on bare soils can also be easily measured using the same methodology (Stella et al., 2011a). In the presence of vegetation, stomatal deposition of ozone is generally calculated from canopy-scale stomatal conductance for water vapour, derived from latent heat flux measurements, assuming that plant transpiration is the main component of total ecosystem evapotranspiration and that ozone is fully destroyed at the evaporative sites inside the leaf stomatal cavity (Altimir et al., 2006; Fares et al., 2012; Hogg et al., 2007; Lamaud et al., 2009; Launiainen et al., 2013). With the extra assumption that ozone destruction in canopy air is negligible, ozone deposition on leaf cuticles is estimated as the residual of total ozone deposition *minus* stomatal and soil deposition. To estimate stomatal or cuticular ozone deposition, modelling approaches can also be used where the canopy is represented either as a single big leaf (Emberson et al., 2000; Stella et al., 2011b; Tuzet et al., 2011) or decomposed into several vegetation layers (Launiainen et al., 2013; Rannik et al., 2012; Wolfe et al., 2011). Leaf chambers are powerful tools, especially newly designed (Altimir et al., 2006; Plake et al., 2015). They allow distinguishing between cuticular and stomatal ozone exchange in a similar manner as eddy covariance but with the advantages of being more sensitive, of having a better estimation of the stomatal flux, while avoiding the complication of including the soil pathway. The chambers and modelling approaches are however exposed to the same caveats: stomata do not completely close in the dark (Caird et al., 2007; Musselman and Minnick, 2000; Ogee et al., 2003). Although it was shown that ozone deposition increased when leaves were artificially wetted in controlled chambers (Fuentes et al., 1994), the exact process behind ozone deposition on wet cuticles is still unclear.

In a previous study (Potier et al., 2015) we used the multilayer, multi-leaf soil-vegetation-atmosphere model MuSICA with process-based formulations to represent stomatal and cuticular ozone deposition rates, including deposition on wet cuticles, i.e. cuticles with liquid water films from dew or rain. These water films on leaf surfaces, thereafter termed “water film”, were modelled from the balance between incoming water (rain or condensation), drainage and evaporation and a wettability parameter. The wetness due to water adsorption as modelled in Grontoft et al. (2004) or in Altimir et al. (2006) is not considered here. Moreover, in determining the water film thickness, no distinction was made between wetness due to dew or rain, although we know rain will wash the leaves while dew will not, leading to a different leaf composition. Ozone deposition on wet cuticles was then accounted for by solving a steady-state, diffusion-reaction equation in the water film, assuming a first-order chemical reaction rate (k). By testing this model against ozone deposition measurements performed over a winter wheat field for three years we found that large k values were needed, between 10^3 s^{-1} during full development and up to 10^5 s^{-1} during senescence (Potier et al., 2015). The presence of organic compounds in the water film may explain such high reaction rates (Fuentes et al., 1994), but the nature of these compounds and their seasonal and inter-specific variations is still unknown.

In this study, we experimentally determined the first-order chemical reaction rate of ozone in water solutions obtained from infusion of leaves, hereafter called leaf infusions, and would be comparable to water films formed during intense wetness events or rain. Ozone reaction rates in these leaf infusions were estimated for different plant species and at different leaf development stages and also compared to those found in the model simulations of Potier et al. (2015).

2. Material and methods

2.1. Leaf sampling and infusion preparation

All plant samplings took place in fields and arboretums around our institution (Grignon, 20 km West of Paris). Between the 26th of June and the 17th of July 2014, wheat (*Triticum aestivum*) leaves ($n = 30$) were sampled. Beech (*Fagus sylvatica*) and oak (*Quercus robur*) leaves and pine (*Pinus strobus*) needles were also sampled on the 11th of July and the 29th of August. For each species and sampling date, leaf blades or needles were pulled together into a glass cylinder filled with 20 mL of ultrapure water (milliQ filtration unit, Millipore), and left to infuse for 1 h. Special care was taken to maintain the petioles outside the solution during the entire infusion time. The sampled leaves were then scanned on a blue surface and analysed with ScanArea (Dornbusch et al., 2010) to determine their total surface area and the percentage of non-green (yellow) area. Leaves were taken directly from the field in order to get all surface contaminants in the solution. The leaves were in the dark prior and during the infusion to minimise stomatal aperture. The petioles were sealed with wax films and kept out of the water infusion. The number of replicates was between 4 and 9 depending on the species. No stirring was applied to avoid any damages to the leaves. Infusing both sides of the leaves were thought to be representative of dew with cooling of the leaves. Evaporation from the water sample during infusion was not an issue as we measured the weight of liquid after infusion. Within a given species all leaves were selected of the same age except for pine for which the same cohort of needles was not always selected. For wheat, leaves were sampled at the same position for a given date.

For wheat the total leaf area used in the solution was around 382 ± 90 cm^2 and the yellow fraction varied from 0.09% to 90.4%, depending on the sampling date. If such surface area intercepted 20 mL of rain this would correspond to a water holding capacity of about 0.26 kg m^{-2}, i.e., a typical value for vegetation canopies (Rutter et al., 1971), although maybe an upper limit on wheat canopies (Kang et al., 2005). For beech, the total leaf area was 357 and