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Titanium dioxide (TiO_2) fine particle capture and BVOC emissions of *Betula pendula* and *Betula pubescens* at different wind speeds

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HIGHLIGHTS

- Surface structure of trees is less important for capturing fine fraction of fine particles.
- Airborne fine particles penetrates into the intercellular space of the leaf via stomata.
- Wind have effect on BVOC emissions of silver birch and pubescent birch.

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ABSTRACT

Trees are known to affect air quality by capturing a remarkable amount of particles from the atmosphere. However, the significance of trees in removing very fine particles (diameter less than 0.5 μm) is not well understood. We determined particle capture efficiency (C_p) of two birch species: *Betula pendula* and *Betula pubescens* by using inert titanium dioxide fine particles (TiO_2, geometric mean diameter 0.270 μm) at three wind speeds (1, 3 and 6 ms^{-1}) in a wind tunnel. Capture efficiencies were determined by measuring densities of TiO_2 particles on leaf surfaces by scanning electron microscopy. In addition, the particle intake into an inner structure of leaves was studied by transmission electron microscopy. The effects of fine particle exposure and wind speed on emission rates of biogenic volatile organic compounds (BVOCs) were measured. Particles were captured (C_p) equally efficiently on foliage of *B. pendula* (0.0026 ± 0.0005) % and *B. pubescens* (0.0025 ± 0.0006) %. Increasing wind speed significantly decreased C_p. Increasing wind speed increased deposition velocity (V_g) on *B. pendula* but not on *B. pubescens*. Particles were deposited more efficiently on the underside of *B. pendula* leaves, whereas deposition was similar on the upper and under sides of *B. pubescens* leaves. TiO_2 particles were found inside three of five *B. pendula* leaves exposed to particles at a wind speed of 1 ms^{-1} indicating that particles can penetrate into the plant structure. Emission rates of several mono-, homo- and sesquiterpenes were highest at a wind speed of 3 ms^{-1} in *B. pendula*. In *B. pubescens*, emission rates of a few monoterpenes and nonanal decreased linearly with wind speed, but emission rates of sesquiterpenes were lowest at 3 ms^{-1} and increased at 6 ms^{-1}. Emission rates of a few green leaf volatile compounds increased with increasing wind speed in both species. The results of this study suggest that the surface structure of trees is less important for capturing particles with a diameter of ca 0.3 μm than for larger particles. Airborne fine particles penetrated into the intercellular space of the leaf via stomata, and this mechanism should be studied further for a better understanding of nanomaterial accumulation in nature. Wind can affect BVOC emissions and composition.

1. Introduction

Trees remove a considerable amount of particulate matter from the atmosphere by capturing it on foliage (Beckett et al., 2000). This

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particle removal capacity of trees is one of the ecosystem services that have been estimated to be worth millions of dollars (e.g. 60.1 million $ y^{-1} in New York City, U.S.) in health care savings through improved air quality (Nowak et al., 2013). This estimation was made for particles in the size range of $PM_{2.5}$ (Nowak et al., 2013), which has been shown to be the most harmful to human health (Schwartz et al., 1996). More adverse health effects are usually related to particles in the lower range of the $PM_{2.5}$ (i.e. below 1 μm) (Oberdörster et al., 2005), but the removal capacity of these particles by trees or other vegetation is rarely studied (Lin and Khlystov, 2012).

Particle capture on trees is a complicated process. When impaction is the main deposition method, physical characteristics of particles, such as a larger size and faster velocity, increase the deposition rate, but key parameters of foliage, such as a smaller leaf size, complex structure and reduced transpiration, also increase capture of particles with a size over 0.5 μm (Beckett et al., 2000; Räsänen et al., 2012, 2013). Thermal movement known as Brownian diffusion is the main deposition method for particles smaller than 0.5 μm (Hinds, 1999). In fact, deposition of ultrafine particles ($PM_{0.1}$, diameter below 0.1 μm) can increase with decreasing particle size (Grantz et al., 2003; Lin and Khlystov, 2012). Leaf structural characteristics have an influence on particle deposition on surfaces. For example, the presence of abundant structural waxes has been shown to increase the particle load on leaf surfaces (Wedding et al., 1975; Burkhardt et al., 1995). Foliar particle capture efficiency (C_p) of particles with an average size of 0.7 μm was observed to be twice as high for hairy pubescent birch (*Betula pubescens*) than for less hairy silver birch (*Betula pendula*) (Räsänen et al., 2013). Very little is known about the penetration of solid particulates into plant leaves, but earlier studies have shown that hydrophilic nanoparticles (fluorescent polystyrene particles with carboxylate-modified surfaces: FluoSpheres, *Trans*-FluoSpheres) in water suspension can penetrate through the stomata of leek (*Allium porrum*) and broad bean (*Vicia faba*) (Eichert et al., 2008).

Trees also affect air quality by emitting biogenic volatile organic compounds (BVOCs) which plants need e.g. for reproduction and defense against abiotic and biotic stress factors (Holopainen, 2011). Calfapietra et al. (2013) suggested that low BVOC-emitting tree species should be favored in the VOC-limited urban areas to reduce formation of ozone, an air pollutant with harmful effects on humans and vegetation. However, BVOCs break down ozone which can lead to new particle formation and cloud formation that could locally cool the climate (Kavouras et al., 1998; Holopainen, 2011). Terpenoids, such as monoterpenes and sesquiterpenes, are particularly reactive BVOCs in the atmosphere (Atkinson and Arey, 2003). Of the European tree species, *B. pendula* and *B. pubescens* have high emission potentials for sesquiterpenes and moderate emission potentials for monoterpenes (Steinbrecher, 2009). Holopainen and Gershenzon (2010) summarized a number of external factors (e.g. elevated temperature, high light intensity, water and salt stress, herbivore damage and pathogen infection) that lead to higher BVOC emissions from vegetation. Effects of subtler external factors, such as wind speed or particle pollution, on BVOC emissions are not well understood. Juuti et al. (1990) showed that pronounced needle movement caused by air movement had no detectable effect on monoterpene emissions of Monterey pine (*Pinus radiata*). The results of a more recent study suggested that wind induced abrasion of branches increased monoterpene emissions from *Chamaecyparis obtusa* (Japanese cypress) (Mochizuki et al., 2011). Birch leaves contain glandular trichomes that are storage structures for volatile terpenoids (Biswas et al., 2009). Glandular trichomes are a likely source of sesquiterpenes in *Betula* species, since their density was shown to correlate positively with sesquiterpene emission in *B. nana* leaves (Schollert et al. in press). Wind can also cause membrane damage and induce emissions of lipoxygenase products, such as many green leaf volatiles (GLVs) (Creelman and Mullet, 1997; Vuorinen et al., 2004; Scala et al., 2013). Thus, in birches, the subtle mechanical damage by wind or particles on leaf surfaces might increase BVOC emissions. In nature, wind can modulate plant and leaf properties that affect particle capture by foliage. Wind influences tree growth and function by regulating factors such as plant structure and posture, gas exchange, heat transfer, water use efficiency, abrasion and visible damage (Grace, 1988; Knight et al., 1992; de Langre, 2008). A higher wind speed can lower stomatal conductance (Räsänen et al., 2012), which can control emissions of water-soluble BVOCs (Niinemets et al., 2004; Harley et al., 2014) and potentially affect the intake of particles.

The aim of this study was to determine how efficient silver birch (*Betula pendula*) and pubescent birch (*Betula pubescens*) are at capturing dry and inert titanium dioxide (TiO_2) fine particles. We also wanted to find out if particles can penetrate through the stomata into the intercellular space of birch leaves. Other aims were to reveal if increasing wind speed and inert fine particle deposition can change the BVOC emissions of birches.

2. Material and methods

2.1. Wind tunnel and particle exposure devices

The wind tunnel system (described in detail by Räsänen et al., 2012) consisted of a six meter long air duct with a diameter of 50 cm. Saplings were placed one at a time into a transparent section of the tunnel that was illuminated with a greenhouse lamp at a photosynthetically active radiation (PAR) level of 450 μmol m^{-2} s^{-1} during a two-hour run (Räsänen et al., 2013). Artificial fine particles with a geometric mean diameter (GMD) of 270 nm and a geometric standard deviation (GSD) of 1.6 were produced from TiO_2 powder (Inframat®, Manchester, CT, USA) with a powder disperser (Palas RGB 1000, Palas, Germany). TiO_2 fine particles have two main different forms referred to as 'anatase' and 'rutile'. Anatase TiO_2 particles are reactive and have an effect on cellular function of Arabidopsis (*Arabidopsis thaliana*) (Wang et al., 2011). In this study, we selected the more inert 'rutile' form of TiO_2 fine particles for particle exposure to minimize chemical reactions on leaf surfaces and inside the leaves. Particles were propelled towards the sapling in a wind flow generated by an axial fan. The axial fan was controlled by a frequency converter to generate the required wind speed (1, 3 or 6 m s^{-1}). Particle mass concentration (μg m^{-3}) in the tunnel was determined from filter collections done in each run. The particle size distribution (15–750 nm) was measured with a scanning mobility particle sizer (SMPS) equipped with a condensation particle counter (CPC 3025A, TSI, USA) and a differential mobility analyzer (DMA 3081, TSI, USA).

2.2. Plant material

One-year-old silver birch (*Betula pendula*) saplings were provided by the Natural Resources Institute Finland, Suonenjoki research unit, and one-year-old pubescent birch (*Betula pubescens*) saplings were obtained from Taimityllilä Ltd., Mäntyharju, Finland. In May 2010, saplings were repotted into two liter pots filled with a 2:1 (v:v) peat:sand mixture and 1 g of N:P:K (9:3.5:5) slow release fertilizer and maintained in a greenhouse at the Kuopio campus of the University of Eastern Finland. Saplings were watered according to their needs, and fertilized weekly with 0.1% N:P:K (19:4:20). After two weeks in the greenhouse saplings were transported to growth chambers where light and temperature conditions were adjusted to represent a typical light:dark rhythm and temperature of June in central Finland (Skarp et al., 1983). Lights went on at