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Linking the contents of hydrophobic PAHs with the canopy water storage capacity of coniferous trees☆

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ABSTRACT

The canopy water storage capacity (S) is an important parameter for the hydrological cycle in forests. One factor which influences the S is leaf texture, which in turn is thought to be affected by the contents of polycyclic aromatic hydrocarbons (PAHs). In order to improve our understanding of S we simulated rainfall and measured the S of coniferous species growing under various conditions. The contents of 18 PAHs were measured in the needles. The species chosen were: Scots pine (*Pinus sylvestris* L), Norway spruce (*Picea abies* (L.) H. Karst) and silver fir (*Abies Alba* Mill.). Sample branches were collected in 3 locations: A - forest; B - housing estate; C - city center. We found that PAHs have a significant impact on the S of tree crowns. The increase in the total content of all of polycyclic aromatic hydrocarbons (SUM.PAH) translates into an increase of S for all species. The S is the highest for the *P. abies* species, followed by *P. sylvestris* and *A. alba* at all locations. Within the same species, an increase in the value of S is associated with an increase in the PAH content in needles measured by gas chromatography. For *A.alba*, the average S increased from 11.54% of the total amount of simulated rain (ml g^{-1}) at location A, to 17.10% at location B, and 21.02% at location C. Similarly for *P. abies* the S was 21.78%, 29.06% and 34.36% at locations A, B and C respectively.

The study extends the knowledge of the mechanisms of plant surface adhesion and the anthropogenic factors that may modify this process as well as foliage properties.

1. Introduction

The amount of rainwater retained by tree crowns, estimated as the difference between total precipitation and throughfall, usually comprises between 10 and 50% of the total precipitation amount (Li et al., 2016; Sadeghi et al., 2016). It is thus an important parameter of ecohydrological processes (Crockford and Richardson, 2000; Chang, 2006; Van Stan et al., 2015). Nevertheless, it is one of the least known components of the soil water balance equations (Pypker et al., 2005) and its parameterization is not well recognized. This is understandable because many factors affect the process of canopy water storage and interception. The factors include some characteristics of rainfall (intensity, duration, rain drop size), forest stands, the nature of the species, atmospheric conditions as well as pollution (Wang et al., 2012; Zhang et al., 2016).

The S is conditioned by the physical feature (texture) of the plant material, which determines the angle between the surface of leaves and the tangent to the shape of water droplets. Surface tension as well as the associated hydrophobicity and hydrophilicity are determined primarily by the amount of wax in the leaf (Sase et al., 1998) and by the presence of hairs (Hamlett et al., 2011; Fernandez et al., 2011). The leaf surface properties are affected by the changing environment, mainly the amount of pollution (Kosiba, 2008; Popek et al., 2013; Mori et al., 2015). The size of the contact angle of the raindrop to the leaf surface has indeed been used as a bioindicator of air pollution (Tranquada and Erb, 2014). The size of this internal

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contact angle of droplets is referred to as the wettability of plant material and strongly affects the S (Klamerus-Iwan et al., 2018).

Tree species differ in the amount of pollution accumulated on their surface (Dzierżanowski et al., 2011; Sæbø et al., 2012). Pollution in the form different sizes of particulate matter (PM10 and PM2.5), tar substances rich in polycyclic aromatic hydrocarbons (PAHs) and metals which settle on leaves may cause changes in plant material hydrophilicity (Klamerus-Iwan et al., 2018; Klamerus-Iwan and Witek, 2018). Contamination with polycyclic aromatic hydrocarbons may also change the hydrological characteristics of soils (Klamerus-Iwan et al., 2015; Błońska et al., 2016). Therefore it is of interest how PAHs modify the condition of leaf surfaces and thereby influence S.

Because of the long life cycle, heavily PAHs penetrate into the wax of tree needles in a perennial setting (Popek et al., 2013). Evergreen plants are able to accumulate high quantities of air pollutants during the winter season (Freer-Smith et al., 2005), when concentration of pollutants in the air is the highest (Pikridas et al., 2013). For that reason, we examined the contents of PAHs at the end of winter, before young shoots appeared. It is surprising that there has been little focus on evergreen shrub species, since evergreen plants have been shown to be very efficient in capturing ultra-fine particles (Freer-Smith et al., 2005). The need to examine the effect of pollution on the ecohydrological properties of coniferous species appears to be particularly important in the face of frequent, more intensive rainfall in autumn and spring in continental Europe (Matuszko and Węglarczyk, 2014) and the effects on stream water management (Berland et al., 2017).

The issue of an increasing amount of air pollution in cities has been raised many times (Matyssek et al., 2012; EEA, 2016; COST Action FP1204) and is the subject of several projects within the framework of European programs (COST Action FP1204). However, not much is known about the nature and magnitude of the effect of pollution on the S and interception. Here we report experiments which aim to determine how PAHs contained in pollution affect S.

We hypothesize that air pollution composed of selected PAHs considerably affects the amount of rainwater that is retained by plants. In particular, we address the question whether hydrophobic PAHs reduce S or whether their presence on needles, steadily eroding over time, changes the structure of the needle surface so that the amount of water retained increases.

In our study, leaf samples were collected in the city of Kraków, with high levels of pollution (Muskała et al., 2015; Błońska et al., 2016). We implemented a series of studies under laboratory conditions which included spraying of tree twigs, collected at two locations in the city center and at one outside the city. The background for the S values was constituted by the results obtained from the content of selected PAHs determined in leaves in studies using gas chromatography – mass spectrometry (GC-MS). The present study fills a gap in the knowledge of hydrological properties of foliage resulting from various degrees of PAHs contamination.

2. Methodology

2.1. Selection of area and sample collection

Three tree species were selected for this study: Scots pine (*Pinus sylvestris* L), Norway spruce (*Picea abies* L), and silver fir (*Abies Alba* Mill). Three geographic sampling sites were selected. The control site was set up in the forest area of the Czarna Rózga Forest Reserve belonging to the ecological class "0", i.e., an area with a minimal pollution impact (GPS 50.983333, 20.016666), designated by the letter A. The other two areas are both in the city of Kraków (Poland); one in a residential area with air pollution mainly from coal burning (GPS 50.080865, 19.963346), designated by B, and the other near a main road with strong pollution caused by car fuel fumes (50.080865, 19.963346) designated by C.

Five trees of each species were selected at each location, and 2 branches of 1.5 m in length were collected from each tree. One of the two branches represented the previous year's needles and the other older needles. The branches were collected from the north and south crown sides across the middle line of the crown. These branches were then transported to a laboratory separately, in plastic containers. The collected sample branches were used to determine the content of 18 PAHs in leaves and to measure the canopy water storage capacity.

We measured 10 samples per species per location, which is a compromise between statistical accuracy, variability in the examined parameters, and the costs of pollutant concentration measurements on leaf surfaces. The tree material for the study was collected at the end of February 2017.

2.2. Measurement of the canopy water storage capacity in the laboratory

All measurements were performed immediately upon arrival at the laboratory from the 3 sampling locations. From each of the 1.5 m branches, a 0.5 m fragment was extracted. Longer branches had been collected to prevent withering. In the laboratory, rainfall was artificially simulated over the branches. They were arranged in a way that resembled their natural configuration in the tree, and water spraying was made from a constant distance of 0.4 m. Next we determined the fresh total biomass (FTB) of woody material and needles. FTB was used because biomass is a better predictor of water retention in shrub and tree crowns compared to plant area and plant density (Garcia-Estringana et al., 2010; Klamerus-Iwan and Błońska, 2018). The tests were performed indoors in the absence of wind, under the conditions of controlled humidity (48%) and at the temperature of 21 °C. This is because the temperature is important for the density of water and the droplet adhesion to the plant material. It is possible to convert S for any given temperature by means of an adjusted calculator (Klamerus-Iwan and Błońska, 2018).

Simulated rainfall (P) with a fixed water dose of 150.0 g was conducted on 10 selected branches of each of the 3 tree species. The branches were weighed before and after rainfall stimulation. The amount of water that increased on the branch during the rain was marked as W.

Because we know the amount of water used for each simulation (P), the total branch biomass (FTB) and the amount of water retained on the branch (W), we can calculate the S of a particular branch per unit of biomass. For this S calculation, we used the following formula (Garcia-Estringana et al., 2010): S = W/FTB, which was expressed in g g^{-1}.

However, assuming the full 150.0 ml dose of rainfall to equate the full precipitation on the branches, we can calculate what percentage of the water was stored by a branch. The expression of S in percentage gives a knowledge of the amount of water that is collected on the branches from the whole rain.

$$\frac{P\,[g]}{S\,[g]} = \frac{100\%}{S\,[\%]}$$

The proportion can easily work in two directions. In the experiment, we obtained S in g^{-1}, which we converted to S in %. However, when having S in %, it is possible to calculate S in g.

We did not focus on the issue of seasonal changes due to the fact that the needle life cycle lasts 3 years for pine trees, 5–7 years for spruce and even 8–11-year for fir (Kozlowski and Pallardy, 1979).