ABIOTIC STRESS IMPACT ON AEROSOL MASS SPECTRA OVER A FOREST SITE IN LITHUANIA

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Volatile organic compounds (VOCs) emitted by trees in response to abiotic stress evoke high levels of secondary organic aerosol (SOA) compounds. Few techniques exist to provide chemically-resolved submicron (PM 1) particle mass concentrations and source apportionment of stress-induced emissions from trees and SOA formation. The chemical composition of atmospheric aerosol particles was characterized using an aerosol chemical speciation monitor (ACSM) at a mixed-mature forest site – the Aukštaitija Integrated Monitoring Station in the eastern part of Lithuania. The organic fraction of PM 1 consisted of SOA (76%) and of anthropogenic combustion related primary organic aerosol (POA) (24%). The analysis of tree trunk circumference revealed three shrinkage and three normal increase episodes. During the episodes of tree trunk circumference shrinkage, several m/z signal (m/z 42, 43, 45, 48, 50) intensities were found to be magnified together with the daily SOA concentration. The stress response analysis confirm that tree trunk circumference shrinkage may be observed through the enhancement of selected m/z signals and result in increased SOA levels.

Keywords: aerosol, SOA, ACSM, tree trunk circumference

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1. Introduction

Secondary organic aerosol (SOA) formation from the oxidation of biogenic volatile organic compounds (BVOCs) affects the chemical and physical properties of atmosphere aerosol [1, 2]. Thus, taking into account the importance of SOA formation which significantly contributes to particulate matter in the atmosphere, many laboratory studies on determination of the mass and chemical characteristics of the oxidation of different gas phase precursors are of particular interest [3]. It is known that environmental stress conditions, such as periods of abnormally high temperatures, drought and cold, are the major abiotic stresses that adversely affect tree growth physiology and BVOCs emissions [4–6]. Forest defoliation investigations held by a large European forest survey in 2010 found that abiotic factors were linked to 9% of damaged trees [7].

The sensitivity of Norway spruce annual growth to variations in climate change conditions has also been documented in Lithuania [8, 9]. The intensity of tree damage depends on their ability to respond and adapt to environmental changes, which ensures their sustainable development. Under abiotic stress induced BVOCs emissions and their concentration can vary significantly [10, 11]. While studies have been performed to quantify stress induced VOCs
emissions under high ambient temperatures [12, 13], a quantitative understanding of the temperature-response effects on SOA concentration has not yet been attained. In the last decades extensive investigation has been dedicated to the study of stress induced processes associated with the analysis of the mass spectra and the source apportionment of organic aerosol (OA) [14, 15]. Several mass-to-charge ratios (m/z) were identified as abiotic stress markers in recent studies: m/z 29 (C\textsubscript{2}H\textsubscript{5}+), m/z 31 (CH\textsubscript{3}O+), m/z 57 (C\textsubscript{4}H\textsubscript{5}O+), m/z 58 (C\textsubscript{2}H\textsubscript{2}O\textsubscript{2}+), m/z 71 (C\textsubscript{3}H\textsubscript{5}O\textsubscript{2}+), m/z 82 (C\textsubscript{5}H\textsubscript{6}O+) and m/z 83 (C\textsubscript{5}H\textsubscript{7}O+). Determination of changes in SOA concentration related to abiotic stress provides the means of identification of the specific markers to diagnose the state of forests, assessment of their ability to mitigate climate change and evaluation of the impact on the global SOA concentration.

Therefore, the aim of this study was to gain more insight into the m/z ratios and to investigate the SOA concentration relationship on the abiotic stress related changes in tree trunk circumference.

2. Methods

2.1. Site description

The field experiment was performed at the rural site, the Aukštaitija Integrated Monitoring Station (IMS LT01), located in the eastern part of Lithuania (55.46° N, 26.00° E, 160 m above the sea level) (Fig. 1) in Aukštaitija National Park, distant about 30 km east of the nearest city, Utena. Vegetation in Aukštaitija is characterized by coniferous (Pinus sylvestris L. and Picea abies Karst.) and mixed forests which cover 70% of the national park area [18]. The climate of the region is determined by high precipitation and relative humidity (RH) as well as by low ambient temperature with mean annual values of 664 mm, 81% and 6.4°C, respectively [3, 19–21].

2.2. Sampling

2.2.1. Aerosol chemical composition

The chemical composition of non-refractory submicron particles was measured using an aerosol chemical speciation monitor (ACSM) (Aerodyne Research, Inc., Billerica, MA, USA). In order to get rid of dust and bigger particles in the sampling line, a self-designed PM\textsubscript{10} inlet-impactor and a Nafion dryer were used (MD-110-48S-4, Perma Pure LLC, Toms River, NJ, USA). The aerodynamics lenses placed in the ACSM allowed the further segregation by size, which resulted in only PM\textsubscript{1} particles being investigated. The sampling aerosol flow was 1.6 l/min. During the instrument calibration, the determined calibration parameters were RIE\textsubscript{Org} = 1.4, RIE\textsubscript{NH\textsubscript{4}} = 9.14, RIE\textsubscript{SO\textsubscript{4}} = 4.2, RIE\textsubscript{NO\textsubscript{3}} = 1.1 and RIE\textsubscript{Chl} = 1.3. The response factor was equal to 2.26·10\textsuperscript{-11}. The counting efficiency (CE) was evaluated based on the method suggested by Middlebrook et al. (2012) [22] and was equal to 0.5. The measurements of mass spectra from 21 to 149 m/z were undertaken with a time resolution of 30 min. The ACSM measurements were performed during April–September 2016.

2.2.2. Tree trunk circumference and meteorological parameters

The tree trunk circumference was measured using a logging band dendrometer (DRL26). During the measurement campaign DRL26 was fixed to

Fig. 1. Location of the Aukštaitija Integrated Monitoring Station (IMS LT01).
the trunk of both 4 Scots pines (Pinus sylvestris L.) and 3 Norway spruces (Picea abies Karst.). Changes in stem diameter were registered every 1 hour with a resolution of 0.001 mm. The scale of growing rate indicates the number of millimeters increased after the beginning of the measuring campaign. The DRL26 measurements were performed during the period of May–September 2016. All data in this study are reported in local time (GMT +2:00).

Co-located measurements consisted of meteorological condition monitoring such as air temperature at 2 m height, soil temperature at 0.05 m depth, average wind speed and solar radiation measurements. All mentioned measurements were performed with a time resolution of 1 hour.

3. Results and discussion

3.1. Campaign overview

During the measurement campaign in April–September 2016 the mass concentrations of ammonium, nitrate, sulphate and organic species were evaluated (Fig. 2). Organics contribution to PM$_1$ was dominant and reached 75% (3.87 μg/m$^3$ (SD = 4.31 μg/m$^3$)) of the total loading. The mass concentration of the sulphate compound was significantly lower (0.68 μg/m$^3$ (SD = 0.50 μg/m$^3$)) and during all the period of measurements the contribution to the total loading was 13%. The average mass concentrations of nitrate and ammonium were 0.35 μg/m$^3$ (SD = 0.33 μg/m$^3$) (7% of total loadings) and 0.27 μg/m$^3$ (SD = 0.26 μg/m$^3$) (5% of total loadings), respectively. The positive matrix factorisation (PMF) analysis of the organic mass spectral dataset distinguished OA into four components, including fresh emission-related oxygenated semi-volatile OA (SV-OOA), aged OA-related low-volatile OA (LV-OOA), biomass burning OA (BBOA) and cooking OA (COA). A detailed description of the PMF analysis has been given previously in Pauraitė et al. (2019) [23]. In the current study, the OA factors were divided into SOA and primary OA (POA). POA is characterized by combustion products and summarises the anthropogenic aerosol contribution to the OA concentration. Thus, due to their anthropogenic origin BBOA and COA were combined and analysed as POA. Meantime, SV-OOA and LV-OOA were grouped into SOA and compared to anthropogenic POA due to their secondary formation. As can be seen in Fig. 2, POA showed minor contribution to OA (24%). Two events of high COA and BBOA concentrations (up to 40.4 and 21.8 μg/m$^3$, respectively) were identified during lunch and dinner hours (11 a.m. – 2 p.m. and 6 p.m. – 8 p.m.) (15 July and 13 August). The wind rose analysis showed that barbeque and grill cooking activities in neighbourhood villages located next to Utenas Lake (165 m from the measurement site) caused both events. For the following analysis, days with barbeque activities were excluded as analysis was presented in Pauraitė et al. (2019) [23]. Thus, such chemical

Fig. 2. Contribution of organics (dark green online), sulphate (red), nitrate (blue) and ammonium (yellow) to PM$_1$, contribution of SOA (light green) and POA (purple) to organics and time trends of SOA and POA at IMS LT01 during the measurement campaign.
composition of PM$_1$ and dominance of SOA versus POA demonstrate a low influence of anthropogenic sources at the IMS LT01 station in Aukštaitija.

3.2. Changes in tree trunk circumference and its relation to SOA concentration

In order to understand the relation between the SOA concentration and tree trunk circumference, the tree trunk circumference analysis of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.) was performed. While this study was focused only on the variation of tree trunk circumference, the initial tree trunk circumference of each tree was normalized to the finest tree trunk circumference of each type (Fig. 3). During the measurement campaign the variation of tree trunk circumferences of the selected trees followed a similar pattern: periods of tree trunk circumference increase and shrinkage occurred simultaneously (Fig. 3(a, b)). Moreover, for all selected trees a diurnal variation of the trunk circumference was observed. Herrmann et al. (2016) [24] attribute diurnal variations mainly to transpiration-driven changes in stem water storage.

To investigate the variation of the tree trunk circumference, dendrometer data for each type of trees were averaged and fitted based on the method suggested by Herrmann et al. (2016) [24]. After the fitting, the residuals of the average tree trunk circumference variation were depicted together with the fitted curve normalized to 0 (Fig. 3(c, d)). As can be seen, the variation in the trunk circumference of Scots pines (*Pinus sylvestris* L.) was quite significant, while the variations in the trunk circumference of Norway spruces (*Picea abies* Karst.) were relatively smoother. This could be explained by a different

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Fig. 3. Variations of the tree trunk circumference $c$ and the fitting curve of its average for Scots pines (*Pinus sylvestris* L.) (a) and Norway spruces (*Picea abies* Karst.) (b). Residuals of the tree circumference variation fitting $\Delta c$ and the fitting curve normalized to 0 of Scots pines (*Pinus sylvestris* L.) (c) and Norway spruces (*Picea abies* Karst.) (d). Here $c_p$ is the trunk circumference and $c_{p\text{-average}}$ is the averaged trunk circumference of Scots pine (*Pinus sylvestris* L.); $c_s$ is the trunk circumference and $c_{s\text{-average}}$ is the averaged trunk circumference of Norway spruce (*Picea abies* Karst.).
range of the maximum and minimum adaptation to temperature for each species [25]. For this reason, the variations of Scots pines (*Pinus sylvestris* L.) trunk circumference were used in our study.

On the days with dominant SOA components three events of both increase and shrinkage of the tree trunk circumference were investigated. The duration of each event was from 60 to 90 h. During the events of tree trunk circumference shrinkage, the average air temperature was from 2.7 to 6.5°C higher than that for the events with its increase (Table 1). Also, during all three events the average air temperature was higher than the temperature of soil at a depth of 0.1 m. Additional studies have revealed that temperature is the most important limiting factor for tree trunk circumference growth at the upper tree-line [26]. Furthermore, the previous study [27] reported that a significant negative correlation was observed between the daily increase of the tree trunk circumference and the daily mean temperature. The connection between heat stress and tree limbs and trunks is based on desiccation throughout the canopy. Our study of shrinkage events shows a great agreement with the later observation. Meanwhile, during the increase events of tree trunk circumference the increase in soil temperature was from 0.8 to 1.7°C higher than the average air temperature. This could be explained by normal mechanisms of tree trunk circumference growth during events of suitable circumstances.

Other meteorological parameters such as RH, average wind speed and solar radiation showed a weak correlation with the variation of tree trunk circumference. Even though the influence of individual abiotic stressors was negligible, the sum of several abiotic stressors (solar radiation, RH and temperature) may cause a significant shrinkage in tree trunk circumference. Dong et al. (2012) [28] estimated that when the variability of solar radiation and night-time temperatures were considered together, the correlation with the variation of tree trunk circumference in tropical forests was observed. In our study, during the first and the third events significant shrinkages of tree trunk circumference were observed (2 August 2016 and 9 September 2016) (Fig. 4(a, c)). Moreover, RH and solar radiation changes appeared during both significant shrinkages of tree trunk circumference (Table 1).

![Fig. 4. Variation of the tree trunk circumference c and the signal of m/z 42 during (a–c) shrinkage and (d–f) increase events (here c_p is the circumference of Scots pine (*Pinus sylvestris* L.) trunk).](image)
On 2 August 2016, between 7 and 15 h RH decreased by 44.1% (from 95.1 to 51.0%) and solar radiation increased by 646.7 W/m² and reached the third highest value in August (745.3 W/m²). The air temperature during these hours increased by 7.5°C and reached the daily peak of 22.2°C. As a result, the tree trunk circumference shrank by 0.5 mm (from 22.9 to 22.4 mm). Similar meteorological conditions were observed on 9 September 2016 between 7 and 15 h: the RH dropped from 95 to 42%, the solar radiation reached the second highest daily peak in September (637.4 W/m²) and the air temperature rose from 6.2 to 21.7°C. Consequently, a sum of all these alternations was led by a significant change in shrinkage of the tree trunk circumference from 23.8 to 23.2 mm. Meantime, during the second shrinkage of the tree trunk circumference event (23–27 August 2016) (Fig. 4(b)) no significant changes in RH and solar radiation appeared: the average RH was 81% (SD = 15.9%) and the maximum value of solar radiation reached 706.9 W/m². Only the air temperature showed unusual values and varied from 8 to 27°C indicating one of the hottest days in August 2016. During all three events, significant changes in tree trunk circumference appeared due to changes in various meteorological parameters (RH, solar radiation and temperature), while during the second event only air temperature showed unusual high values and no sudden changes in other meteorological parameters occurred.

During the tree trunk circumference increase events other meteorological parameters, such as RH, average wind speed and solar radiation, showed no significant changes or unusual values (Fig. 4(d–f)). During the days of tree trunk circumference increase events the average of RH varied from 71.3% (SD = 14.2%) (the first event, 5–7 June 2016) to 90.7% (SD = 7.9%) (the second event, 9–11 August 2016). Solar radiation daily peaks varied between 559.7 W/m² (the second event) and 694.1 W/m² (the first event) and were lowest compared with 2 days before and after the events. The maximum values of air temperature were from 17.2°C of the first event to 21.3°C of the second event. The average wind speed varied from 1.0 m/s (SD = 0.5 m/s) during the second event to 1.6 m/s (SD = 0.5 m/s) during the third event. Thus, during the tree trunk circumference increase events the investigated meteorological parameters (RH, air temperature, solar radiation and wind speed)
showed no significant changes and could be described as suitable for normal mechanisms of tree trunk circumference growth.

In addition to the variation of tree trunk circumference dependence on the meteorological parameters, an interaction between these parameters and aerosol mass spectra was determined. After the investigation of all measured m/z signals (from m/z 12 to 149) during the tree trunk circumference shrinkage events, several m/z signals showed a significant response. The intensity of m/z 42 (C₂H₂O⁺), 43 (C₂H₃O⁺), 45 (C₂H₅O⁺), 48 (C₄⁺) and 50 (C₄H₂⁺) signals increased from 5.7 to 8.8 times during the all three events (calculated for daytime and nighttime averaged values). While analysing the selected m/z signals during the tree trunk circumference shrinkage events, all showed the same tendency, therefore only m/z 42 was depicted (Fig. 4). Meanwhile, the intensities of other possible abiotic stress markers (m/z 29, 31, 53, 57, 58, 59, 71, 82 and m/z 83 [16, 17]) increased not significantly (from 2.4 to 4.0 times) following changes of SOA.

The increase in the intensity of the selected m/z signals appeared a few hours later than the shrinkage had started. This could be explained by a complex tree response in order to resist the heat and potentially other abiotic stress factors. Meanwhile, during the events of the tree trunk circumference increase no significant change in the selected m/z signals intensity was observed. Moreover, no clear pattern of changes in the selected m/z signals intensity with time appeared, which indicates normal functions of a tree with no stress induced BVOC emissions.

SOA concentration during all events was analysed. During the shrinkage events, the SOA daily concentration significantly increased. The following day after the first shrinkage event on 2 August, the SOA concentration increased by 1.3 times (from 1.31 to 1.74 μg/m³) and showed a tendency to continue increasing until 5 August when reached 6.16 μg/m³. During the second shrinkage event on 23–27 August, the SOA concentration was constantly increasing from 2.18 to 7.05 μg/m³. The third event, which took place on 9–11 September, resulted in the SOA daily concentration increase from 1.99 to 5.38 μg/m³. Thus, during the first, the second and the third event, the SOA concentration increased by 4.7, 3.2 and 2.7 times, respectively. Meanwhile, during all three events of tree trunk circumference increase no significant change in SOA was observed.

To conclude, the tree response to stress factors by shrinkage of the tree trunk circumference may be followed by increase in the intensity of the m/z 42 (C₂H₂O⁺), 43 (C₂H₃O⁺), 45 (C₂H₅O⁺), 48 (C₄⁺) and 50 (C₄H₂⁺) signals and at least twice increased the SOA concentration. These findings support the hypothesis that the increased intensity of the selected m/z signals is associated with the biogenic stress response and the abiotic stress is an important factor for SOA formation and concentration levels.

4. Conclusions

The results of tree trunk circumference investigation have revealed that both the dominant coniferous species, Scots pines (Pinus sylvestris L.) and Norway spruces (Picea abies Karst.), have a similar growth rate pattern. Nevertheless, the influence of individual abiotic stressors was negligible, however, the sum of several abiotic stressors (solar radiation, RH and temperature) may cause a significant shrinkage in the tree trunk circumference. During the events of tree trunk circumference shrinkage, a great increase of intensities of the selected m/z signals (m/z 42, 43, 45, 48, 50) as well as the increase of the daily concentration of SOA was observed (up to 4.7 times). Meanwhile, the increase in the tree trunk circumference has shown no influence on the intensity of m/z signals and the SOA daily concentration. These findings suggest that the response to abiotic stress related factors may result in changes in aerosol mass spectra and an increased level of aerosol concentration.

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References


ABIOTINIO STRESO ĮTAKA AEROZOLIO DALELIŲ MASĖS SPEKTRUI MIŠKO APLINKOJE LIETUVOJE

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Santrauka

Abiotinio streso veikiami medžiai išskiria laktinius organiniaus junginius (LOJ), kurie yra antrinių aerozolio dalelių (SOA) prekursoriai. Tyrimo tikslas buvo atlikti submikroninių aerozolio dalelių (PM1) masės koncentracijos tyrimus ir šaltinių kilmės atskiriamų medžių abiotinio streso sąlygomis formuojantis SOA. Aerozolio cheminė sudėtis Aukštaitijos integruotojo monitorinio stotyje (IMS LT01) rytinėje Lietuvos dalyje mišroje miško aplinkoje buvo išmatuota aerozolio cheminės sudėties monitoriumi (ACSM). Nustatyta, kad PM1 organikos frakcija sudarytė iš antrinių (76%) ir pirminių (24%) aerozolio dalelių. Medžio kamieno skersmens pokyčių analizė parodė tris medžio kamieno skersmens augimo ir susitraukimo epizodus. Esant abiotinio streso sąlygoms, vyksta medžių kamienų skersmens susitraukimo epizodie, todėl išauga m/z 42, 43, 45, 48 ir 50 signalų intensyvumai nuo 5,7 iki 8,8 kartų, o SOA paros koncentracija padidėja nuo 2,7 iki 4,7 kartų. Iprastai augant medžio kamieno skersmeniui m/z signalų intensyvumai ir SOA koncentracija nekinta. Galima teigti, kad augalų patiriamos abiotinio streso atsakas gali būti identifikuojamas per nustatytų m/z signalų intensyvumų pokyčius ir lemti padidėjusią SOA koncentraciją.