Emission of volatile organic compounds by plants on the floor of boreal and mid-latitude forests

Valery A. Isidorov1 · Ewa Pirożnikow1 · Viktoria L. Spirina2 · Alexander N. Vasyanin2 · Svetlana A. Kulakova3 · Irina F. Abdulmanova3 · Andrei A. Zaitsev3

Received: 23 August 2021 / Accepted: 3 March 2022 / Published online: 15 March 2022
© The Author(s) 2022

Abstract
The forests of the boreal and mid-latitude zones of the Northern Hemisphere are the largest source of reactive volatile organic compounds (VOCs), which have an important impact on the processes occurring in the atmospheric boundary layer. However, the composition of biogenic emissions from them remains incompletely characterized, as evidenced by the significant excess OH radical concentrations predicted by models in comparison with those observed under the forest canopy. The missing OH sink in the models may be related to the fact that they do not take into account the emission of highly reactive VOCs by vegetation on the forest floor. In this work, we report the results of laboratory determinations of the composition of VOCs emitted by representatives of different groups of plants that form the living soil cover (LSC) in the forests of the boreal and mid-latitude zones: bryophytes, small shrubs, herbaceous plants, and ferns. In the chromatograms of volatile emissions of all 11 studied plant species, 254 compounds with carbon atoms ranging in number from two to 20 were registered. All plants were characterized by the emission of terpenes, accounting for 112 compounds, and the second largest group (35 substances) was formed by carbonyl compounds. Both groups of compounds are characterized by high reactivity and are easily included in the processes of gas-phase oxidation with the participation of radicals HO, NO3 and ozone. These data indicate the importance of a thorough study of the so far disregarded source of VOCs, that is, the LSC in forests.

Keywords Forest floor plants · Volatile organic compounds · Emission · Chemical composition

✉ Valery A. Isidorov
isidorov@uwb.edu.pl

1 Institute of Forest Sciences, Bialystok University of Technology, 15-351, Bialystok, Poland
2 Chemical Department of Perm, State University, 614990 Perm, Russia
3 Faculty of Geography of Perm, State University, 614990 Perm, Russia
1 Introduction

Biogenic volatile organic compounds (VOCs) play an important role in atmospheric processes, participating in the formation of the oxidative potential of the atmosphere, its optical properties and radiation regime. A special role in this is played by terpene compounds, mono- and sesquiterpenes and their oxygen-containing derivatives, which are readily involved in reactions with ozone, OH and NO₃ radicals (Atkinson and Arey 2003), and also undergo photocatalytic oxidation on the surface of atmospheric aerosol particles (Isidorov et al. 1997). Globally, the main source of non-methane biogenic VOCs is continental vegetation (Isidorov 1990; Fehsenfeld et al. 1992; Guenther et al. 1995; Navarro et al. 2014; Sindelarova et al. 2014), with the leading contribution made by forest ecosystems of the boreal and mid-latitude belt (Isidorov 1992; Guenther et al. 1995; van Meening et al. 2017). Their photochemical oxidation in an atmosphere contaminated with nitrogen oxides, NOx, leads to a deterioration in air quality at the earth’s surface due to the formation of excess ozone and other secondary gaseous pollutants. Moreover, terpene compounds have a high potential for the formation of secondary organic aerosols, SOA (Makkonen et al. 2012; Kulmala et al. 2013; Faiola et al. 2014; Kourtchev et al. 2016; Lee et al. 2019). Sesquiterpene hydrocarbons, the products of gas-phase oxidation of which have low volatility, have a particularly high potential for the formation of secondary aerosols. According to quantitative estimates, 150 Tg of biogenic SOA are formed in the atmosphere annually (Hallquist et al. 2009). These aerosols scatter and absorb solar and terrestrial radiation and participate in the formation of clouds, thus exerting a great influence on the climate.

To determine the role of biogenic organic compounds in the formation of secondary atmospheric pollution, various photochemical transport models have been developed with VOC and NOx emissions as input parameters. The results of such modelling largely depend on the completeness of accounting for emissions of key components; any underestimation of VOCs in the emission inventory can lead to underestimation of the estimated ozone levels using photochemical models (Bell and Ellis 2004; Mogensen et al. 2015; Zhou et al. 2017). However, it is well known that biogenic VOC emission data still have significant uncertainties of a factor of 3 to 5 for key compounds such as isoprene (Curci et al. 2009). Recent work on the determination of the total reactivity of hydroxyl radicals (TOHRE) in different types of forests (Di Carlo et al. 2004; Sinha et al. 2010; Nölscher et al. 2013; Yang et al. 2016; Praplan et al. 2020) also indicates the existence of unaccounted for sinks of this radical, that is, the presence of unaccounted sources of reactive biogenic VOCs in the atmosphere. In addition to unidentified and hitherto unaccounted for VOCs released by woody vegetation (or their oxidation products), leaf litter and plants of the living cover of the forest floor may be responsible for the "lost" reactivity.

In recent years, much attention has been paid to decaying deciduous litter as a source of atmospheric VOCs (Isidorov et al. 1999; Isidorov and Janova 2002; Isidorov et al. 2003, 2005, 2010; Hellén et al. 2006; Gray et al. 2010; Aaltonen et al. 2011, 2013; Geenberg et al. 2012; Mäki et al. 2019a, 2019b; Viros et al. 2020, 2021). Quantification of VOC emissions from the forest floor is mainly carried out using flow chambers installed on the soil (Janson 1993; Isidorov et al. 1994; Hayward et al. 2001; Hellén et al. 2006; Asensio et al. 2007; Greenberg et al. 2012; Mäki et al. 2017, 2019a; Kivimäenpää et al. 2018; Wang et al. 2018), but this technique allows the determination of gross fluxes without differentiation into individual elements such as deciduous litter, live plants, soil and root exudates from trees.
Only a few studies have attempted to assess the role of each of these elements. In particular, the authors of a recent publication (Mäki et al. 2017) proceeded from the hypothesis that the vegetation at the bottom of the boreal forest serves not as a source, but as a sink of isoprenoids, since these substances can be adsorbed by plant foliage. Their study supported this hypothesis in that at the experimental sites the fluxes of isoprenoids measured on bare forest soil were higher than fluxes measured on soil with vegetation cover. Somewhat earlier, in chamber experiments with sphagnum moss, the existence of a weak isoprene sink was shown, described by a first-order equation with a rate constant \((3.84–9.35)\times 10^5 \text{ s}^{-1}\), and in the light the sink rate constant was 2.4 times higher than in the dark (Isidorov et al. 1999). As far as we know, no study of the passage of other isoprenoids into the leaf surface of vegetation has been carried out.

To answer the question of whether plants of the living soil cover (LSC) serve as a source or sink of phytogenic VOCs (Isidorov et al. 1999), this study determined the qualitative and semi-quantitative composition of VOC emissions by a number of plants typical of the forest floor of boreal and mid-latitude forests. The study was also motivated by the available information on the significant contribution of LSC plants to the total photosynthetic biomass of many forest types (Zyabchenko 1984) and their excellent adaptation to the light mode prevailing under the forest canopy (Morén and Lindroth 2000; Kolari et al. 2006).

2 Materials and methods

2.1 Plant material

Forest soil cover plants were sampled from different types of forests in different geographic zones. Small shrubs of the Ericaceae family: European blueberry (Vaccinium myrtillus) and pipsissewa (Chimaphilla umbellata), as well as the herbaceous plants catsfoot (Antennaria dioica) and European clefthoof (Asarum europaeum) were collected in the first decade of May 2020 in the forests of the coniferous-deciduous subzone in the east of the European parts of Russia in the Perm Territory (57°28’N, 55°16’E).

One of the "reindeer lichens" (Cladonia arbuscula), wavy-leaved broom moss (Dicranum polysetum), splendid feather moss (Hylocomnium splendens), pin cushion moss (Leucobrium glaucum), Schreber’s big red stem moss (Pleurozium schreberi) and flat-topped bogmoss (Sphagnum fallax) were collected in the first ten days of June of the same year in mixed mid-latitude forests forming the forest complex Pushcha Knysynka in eastern Poland (53°15’N, 23°28’E). The plants were dug out and, after being transported to the laboratory, the soil was washed from the roots of shrubs and flowering plants and the rhizoids of the moss with water and placed for no more than one day in open glass containers containing Knop’s nutrient solution.

2.2 Determination of VOC composition

The composition of organic compounds released into the gas phase by plants was determined in Perm (Russia) and Bialystok (Poland) by solid-phase microextraction in combination with gas chromatography-mass spectrometry (HS-SPME/GC–MS) using the same technique and using the same type of equipment.

The plants were removed from the nutrient solution, placed in a glass container with a volume of 0.75 L, and sealed with a lid with a port for introducing the sorption fiber.
through a silicone membrane. After incubation for 1 h at room temperature and in full daylight, preconditioned fibre with a stationary phase DVB/CAR/PDMS was introduced into the gas phase above the plant. After exposing the fibre for 1 h, it was introduced for 15 min into an injection port of a gas chromatograph HP7890A with the 5975C VL MSD Triple-Axis Detector (Agilent Technologies, USA). The apparatus was fitted with an HP-5 ms capillary column (30 m × 0.25 mm i. d., 0.25 μm film thickness), with electronic pressure control and a split/splitless injector. The latter was operated at 220 °C in splitless mode. The helium flow rate through the column was 1 mL min⁻¹ in constant flow mode. The initial column temperature was 40 °C and rose to 220 °C at a rate of 3 °C min⁻¹. After integration, the fraction of each component in the total ion current (TIC) was calculated.

To calculate linear temperature programmed retention indices (RI) of the analytes, the SPME fibre was inserted for 2−3 s into the head-space of the vial with a mixture of C₆−C₁₈ n-alkanes. Their separation was performed under the above conditions.

2.3 Component identification

To identify the components emitted from plants, two independent analytical parameters were used: mass spectra and calculated linear retention indices. Mass spectrometric identification was carried out with an automatic system for GC–MS data processing supplied by the NIST 14 library (NIST/EPA/NIH Library of Electron Ionization Mass Spectra) as well as by computer search libraries containing the mass spectra and retention indices from Adams’ (2007) and Tkachev’s (2008) collections. The identification was considered reliable if the results of the computer search of the mass spectra library were confirmed by the experimental RI values, i.e. if their deviation from the published database values did not exceed ± 10 u.i. (the average quantity of inter-laboratorial deviation for non-polar stationary phases).

2.4 Component quantification

Quantifying the components would require calibrating the MS detector for each VOC, which is not feasible due to the multicomponent composition of the emissions and the lack of available analytical standards for many of them. Therefore, we performed a semi-quantitative analysis by the method of internal normalization, in which the share of each peak in the TIC of the chromatogram is determined.

The precision of the method was expressed by relative standard deviation (RSD). The peak areas, determined by repeating the analysis of blueberry VOC three times, were used to calculate RDS values that did not exceed 6% for components with a relative content of more than 5% of TIC, but reached 25−30% for components whose content did not reach 1%. A dramatic change in the composition of VOCs is observed at the slightest damage to the plant, which is expressed as a multiple increase in the peak area of "leaf alcohol" (cis-3-hexene-1-ol) and its acetate.

3 Results and discussion

In this work, we studied the composition of volatile emissions of representatives of various groups of plants growing on the forest floor: six species of bryophytes (mosses Dicranum polysetum, Hylocomnium splendens, Leucobrium glaucum, Pleurozium schreberi,
Sphagnum phallax and one of the "deer mosses", lichen Cladonia arbuscula), two representatives of small shrubs from the Ericaceae family (Vaccinium myrtillus and Chimaphilla umbellata), two herbaceous species (Asarum europaeum and Antennaria dioica), and one fern species (Pteridium aquilium). Despite the fact that all these plants were collected in the coniferous-deciduous forests of the sub-boreal (Perm region, Russia) and temperate zones (Poland), they are typical of the more northern boreal forests (Flora 1974).

The chromatograms of all 11 plant species recorded 254 peaks of C2-C20 VOCs, the content of which in the total ion current was no less than 0.1%. Typical VOC chromatograms for some representatives of the studied plant groups are shown in Fig. 1. The number of peaks in the chromatograms of different plants was very different: the maximum number was recorded on the chromatograms of sphagnum moss and dwarf shrub Ch. umbellata (78 and 75 peaks, respectively), and the minimum number (23 peaks of VOC) on the chromatogram of a fern.

The largest number of identified compounds belongs to the group of terpenoids, including 46 C10 monoterpenoids, 69 C15 sesquiterpenoids, and two C20 diterpenoids (the last compounds were registered only in the volatiles of the dwarf shrub Ch. umbellata). It should be noted that some rare sesquiterpenes, such as α-chamipinene, α- and β-isocomenes, and moderphene, were found in the emissions of plants from the living forest cover. As far as we know, these compounds have not been detected previously among plant VOCs, and have not been characterized by the rate constants of the gas-phase reaction with radicals and ozone. The second largest group of 35 compounds was formed by aliphatic saturated and unsaturated carbonyl compounds with carbon atoms numbering from two to eleven. The share of aliphatic C2-C12 alcohols, as well as C6-C21 alkanes and alkenes, accounted for 15 compounds.

The compounds registered in the volatile emissions of all 11 plants on the forest floor were combined according to their chemical nature into 12 groups, the relative content of which (as well as the content of the main representatives of the different groups) is given in Table 1 and Fig. 2. The total composition of the identified components, as well as some analytical parameters used in their identification, is given in the Supplementary Information (Table S1).

As can be seen from the data in Table 1, the volatile emissions of all examined plant species contained monoterpenes in greater or lesser amounts. The most common hydrocarbons in this class were limonene, 3-carene, and α-pinene. In contrast, the release of sesquiterpenes into the gas phase was recorded for only three of the six tested bryophytes. Small shrubs of the Ericaceae family and herbaceous plants turned out to be much richer in these compounds, which are important from the point of view of participation in atmospheric chemical processes, including the formation of secondary aerosols. It was found that the yield of aerosols is positively correlated with the molecular weight of VOCs. Therefore, sesquiterpene C15H24 hydrocarbons with a molecular weight of 204 and high boiling points (240–275 °C) make a greater contribution to the formation of secondary organic aerosols compared to C10H16 monoterpenes (bp 155–175 °C) (Lee et al. 2006; Helmig et al. 2007). The largest amounts of terpene compounds were recorded in the emissions of green moss H. splendens, fern P. aquilium and blueberry V. myrtillus. It is important to emphasize that all three species are among the most common forest floor plants in the boreal and mid-latitude zone.

Unfortunately, in the available literature, one can find only a few data on the rates of VOC emission by living plants of the forest soil cover. A review by Kesselmeier and Staudt (1999) reports that blueberry (Vaccinium uliginosum) are a weak emitter of isoprene (0.09 μg·g−1 h−1), while Labrador tea releases monoterpane hydrocarbons at a
Fig. 1 HS-SPME/GC–MS chromatograms of selected representatives of the forest floor plants. **A**-green moss *Hylocomnium splendens*; **B**-blueberries *Vaccinium myrtillus*; **C**-European clefthoof *Asarum europaeum*
Table 1  Relative group composition (% TIC) of VOCs emitted from selected plants of boreal forests floor. Plants: 1 - lichen Cladonia arbuscula; 2 - Dicranum polysetum; 3 - Hylocomnium splendens; 4 - Leucobrium glaucum; 5 - Pleurozium schreberi; 6 - Sphagnum fallax; 7 - Vaccinium myrtillus; 8 - Chimaphilla umbellata (pipsissewa); 9 - Asarum europaeum (European clefthoof); 10 - Antennaria dioica (catsfoot); 11 - Pteridium aquilium

| Group of compounds | Lichens and mosses | Small shrubs | Herbaceous perennial plants | Fern |
|--------------------|--------------------|--------------|-----------------------------|------|
|                    | 1  2  3  4  5  6  | 7  8         | 9  10 11                   |
| Monoterpenes       |                   |              |                            |      |
| including          |                   |              |                            |      |
| - α-pinene         | -                 | -            | 5.46                        | 17.03|
| - myrcene          | -                 | -            | 2.64                        | 0.92 |
| - 3-carene         | trace             | -            | 2.25                        | 5.65 |
| - limonene         | 0.78              | 2.31         | 20.91                       | 0.25 |
| - γ-terpinene      | -                 | -            | 0.58                        | -    |
| - linalool         | 1.02              | 2.32         | 1.18                        | 3.30 |
| Sesquiterpenes     |                   | -            | 6.26                        | 0.61 |
| including          |                   |              |                            |      |
| - longifolene      | -                 | 2.39         | 0.45                        | -    |
| - α-copaene        | -                 | 1.20         | 0.21                        | -    |
| - α-chamapinene    | -                 | -            | 0.21                        | -    |
| - α-isocomene      | -                 | -            | 0.21                        | -    |
| - β-isocomene      | -                 | -            | 0.21                        | -    |
| - β-caryophyllene  | -                 | 0.43         | 0.16                        | -    |
| - α-humulene       | -                 | 0.32         | 0.32                        | -    |
| - germacrene D     | -                 | -            | 12.18                       | -    |
| - α-farnesene      | -                 | -            | 8.80                        | -    |
| - δ-cadinene       | -                 | 0.33         | 0.15                        | -    |
| Group of compounds           | Lichens and mosses | Small shrubs | Herbaceous perennial plants | Fern |
|-----------------------------|--------------------|--------------|-----------------------------|------|
|                             | 1  | 2  | 3   | 4    | 5  | 6  | 7  | 8    | 9   | 10  | 11  |
| Diterpenes                  | -  | -  | -   | -    | -  | -  | -  | 1.93 | -   | -   | -   |
| Aliphatic alcohols          |    |    |     |      |    |    |    | trace| 0.70|    | 9.24|
| including:                  |    |    |     |      |    |    |    | 7.58 |    |    |      |
| - ethanol                   | 2.98| 4.37| 4.05| 1.04 | 6.67| 1.84| trace| -    |    |    |      |
| - 1-pentanol                | 1.66| -   | -   | 1.24 | -   | 0.91| -   | -    |    |    |      |
| - 1-hexanol                 | 2.13| 1.35| 0.32| 1.55 | 1.43| 5.70| -   | -    |    |    |      |
| - 1-octanol                 | 54.63| 25.36| 5.26| -    | 1.84| 1.99| -   | -    |    |    |      |
| - 3-hexene-1-ol             | -  | -   | -   | -    | -   | 3.73| trace| -    |    |    |      |
| - 1-octen-3-ol              | -  | -   | -   | 6.88 | -   | 4.70| 0.12| -    |    |    | 1.32|
| Aliphatic carbonyls         | 10.04| 24.15| 9.75| 44.00| 49.92| 38.17| 2.20| 0.41 | 1.36|     |      |
| including:                  |    |    |     |      |    |    |    |      |    |    |      |
| - acetone                   | 2.90| 6.20| 1.81| 4.82 | 9.59| 3.91| 2.20| trace | 0.09| -   | -   |
| - hexanal                   | 0.88| 3.01| 2.26| 6.87 | 6.77| 4.88| -   | trace| -   |    | -   |
| - (E)-2-hexenal             | -  | -   | -   | 2.40 | -   | 2.15| -   | -    |    |    | 1.64|
| - octanal                   | 2.81| 4.49| 1.95| trace| 8.39| 1.89| -   | -    |    |    |      |
| - nonanal                   | 2.81| 4.49| 1.95| trace| 12.58| 1.89| - 0.41| 1.28 | trace| -   |      |
| Aliphatic acids             | 10.56| 4.51| 0.71| 14.02| 5.97| 1.55| 0.44| 0.12 | 0.18| 0.46| 0.55|
| including:                  |    |    |     |      |    |    |    |      |    |    |      |
| - acetic acid               | 9.83| 2.86| 0.71| 3.80 | 3.43| 1.55| -   | trace| 0.18| 0.46| 0.55|
| - hexanoic acid             | 0.73| -   | trace| 6.79 | 1.49| trace| -   | 0.12 | -   |    |      |
| - octanoic acid             | -  | 1.65| -   | 0.51 | 1.05| -   | -   | -    |    |    |      |
| Group of compounds       | Lichens and mosses | Small shrubs | Herbaceous perennial plants | Fern |
|--------------------------|-------------------|--------------|-----------------------------|------|
|                          | 1  2  3  4  5  6 | 7  8          | 9  10                       | 11   |
| **Aliphatic esters**     |                  |              |                             |      |
| including:               |                  |              |                             |      |
| - ethyl acetate         | trace            | 1.32         | 0.43                        |      |
| - 3-hexene-1-ol acetate | -                | -            | -                           |      |
| **Aromatic compounds**  | 0.80             | 0.95         | 0.76                        |      |
| including:              |                  |              |                             |      |
| - toluene               | -                | 0.95         | 0.76                        |      |
| - p-cymene              | -                | 2.15         | 0.36                        |      |
| - benzaldehyde          | -                | 1.82         | 2.80                        |      |
| - benzeneacetaldehyde   | -                | 2.15         | 0.36                        |      |
| - thymol                | -                | -            | -                           |      |
| **Furans and lactones** | 1.68             | -            | 6.94                        |      |
| including:              |                  |              |                             |      |
| - 2-ethylfuran          | 0.94             | -            | 1.41                        |      |
| - 2-pentylfuran         | -                | 2.89         | 1.92                        |      |
| γ-valerolactone         | 0.74             | -            | -                           |      |
| **Alkanes & alkenes**   | 5.74             | 6.21         | 2.29                        |      |
| Other compounds         | 0.71             | 1.26         | 0.64                        |      |
| Non identified          | 1.00             | 7.13         | 5.59                        |      |
| Number of peaks         | 31               | 45           | 33                          |      |

*not detected; ** trace-below 0.1% of TIC
fairly high rate (13 μg·g$^{-1}$ h$^{-1}$). Measurements carried out in the pine forests of Karelia (north-west of the Russian Federation) showed that the rate of VOCs emission by flowering heather (*Calluna vulgaris*) and club moss (*Lycopodium clavatum*) at a temperature of 16 °C is 17.1 and 10.1 μg·g$^{-1}$ h$^{-1}$, respectively. At the same time, monoterpenes (α-pinene, camphene, and myrcene) prevailed in heather emissions, while club moss excreted isoprene, C$_2$-C$_5$ hydrocarbons, methyl chloride and ethanol (Isidorov et al. 1994).

It is known that isoprene and terpene compounds are highly reactive and, as a result, have a very short lifetime in the atmosphere (Atkinson and Arey 2003). The same applies to many representatives of other groups of compounds shown in Table 1, primarily to unsaturated lower carbonyl compounds, alcohols and their esters, which are easily included in reactions with radicals and ozone. Consequently, the existence of an "unaccounted sink" of the hydroxyl radical under the forest canopy (Di Carlo et al. 2004; Sinha et al. 2010; Nölscher et al. 2013; Yang et al. 2016; Parlap et al. 2020) can at least partially be attributed to unaccounted emissions of reactive VOCs by plants on the forest floor.

Small shrubs, grasses, mosses and lichens provide a considerable contribution to the overall green biomass of many types of Northern Hemisphere forests and play an important role in the photosynthetic production of boreal forests (Kolari et al. 2006). These plants are adapted to low photosynthetically active radiation (PAR) and begin photosynthesis as early as at a PAR level above 3 μmol·m$^{-2}$·s$^{-1}$ (Morén and Lindroth 2000).

In boreal forests, different feathermoss, peatmoss, and foliose lichen species often form a continuous layer on the forest floor (Hageman and Moroni 2015). According to investigations performed in North European Russia, the biomass of living soil cover in 20-year-old pine forests is (on average) 1,200–2,500 t·km$^{-2}$, increasing to 7,600–8,100 t·km$^{-2}$ in mature forests. In comparison, for the same time interval, pine needle biomass decreased from 5,600–6,700 t·km$^{-2}$ to 3,200–4,700 t·km$^{-2}$ (Zyabchenko 1984). Hence, forest floor plants can make up a principal part of total green biomass and VOC emissions in forests, at least in boreal and temperate regions of the Northern Hemisphere.
In spite of its importance as a component of forest biomass, living soil cover has not been studied sufficiently as a source of atmospheric VOCs. The above results determining the VOC composition by plants of the LSC of forests serve, in our opinion, as the basis for a more thorough study of this source.

4 Conclusion

We found that plants of the living soil cover of forests serve as a source of a large number of VOCs, for many of which a high potential for the formation of ozone and other atmospheric photooxidants and/or secondary aerosols is postulated. This preliminary study was carried out without contact of forest plants with soil and/or deciduous litter, which can absorb some of the released VOCs. Further field and laboratory studies are needed to assess the role of each of these compartments in the total VOC balance under the forest canopy and its dependence on key environmental parameters such as air and soil temperature and humidity. In addition, further studies should pay attention to possible seasonal changes in the emission of VOCs by plants on the forest floor under the influence of changing environmental conditions.

 Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s10874-022-09434-3.

 Author contributions VI and AZ -conceptualization and data curation; EP, SK and IA –plant collection, identification and preparation for HS-SPME analysis; VI, VS and AV – VOCs determination and GC–MS identification; VI – article writing.

 Funding This work was supported by the National Science Centre (Poland) [grant number 2019/35/B/ST10/02252].

 Data availability All data generated or analysed during this study are included in this published article (and its supplementary information file).

 Declarations

 Conflict of interest The authors declare that they have no conflict of interest.

 Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

 References

Aaltonen, H., Pumpainen, J., Pihlatie, M., Hakola, H., Hellén, H., Kulmala, L., Vesala, T., Bäk, J.: Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn. Agricul. Forest Meteorol. 151, 682–691 (2011). https://doi.org/10.1016/j.agrformet.2010.12.010
Isidorov, V., Povarov, V., Stepanov, A.: Forest soil cover: VOC sink or source? In: Proc. EUROTRAC Symp. Borrell, P.M. and Borrel,P. (eds). WIT Press, Southampton, pp. 158–162 (1999).

Isidorov, V.A., Vinogorova, V.T., Rafalowski, K.: HS–SPME analysis of volatile organic compounds of coniferous needle litter. Atmos. Environ. 37, 4645–4650 (2003). https://doi.org/10.1016/j.atmosenv.2003.07.005

Isidorov, V., Vinogorova, V., Rafalowski, K., 2005. Gas chromatographic determination of extractable compounds composition and emission rate of volatile terpenes from larch needle litter. J. Atmos. Chem. 50, 263–278 (2003). https://doi.org/10.1017/s107874-5078-6

Isidorov, V.A., Smolewska, M., Purzyńska-Pugacewicz, A., Tyszkiwicz, Z.: Chemical composition of volatile and extractive compounds of pine and spruce litter in the initial stages of decomposition. Biogeosciences 7, 2785–2794 (2010). https://doi.org/10.5194/bg-7-1-2010

Janson, R.W.: Monoterpene emissions from Scots pine and Norwegian spruce. J. Geophys. Res. 98, 2839–2850 (1993). https://doi.org/10.1029/92JD02394

Kesselmeier, J., Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physi-ology and ecology. J. Atmos. Chem. 33, 23–88 (1999)

Kivimäenpää, M., Markkanen, J.-M., Ghimire, R.P., Holopainen, T., Vuorinen, M., Holopainen, J.K.: Scots pine provenance affects the emission rate and chemical composition of volatile organic compounds of forest floor. Can. J. For. Res. 48, 1373–1381 (2018). https://doi.org/10.1139/cjfr-2018-0049

Kolari, P., Pumpinanen, J., Kulmala, L., Ilvesniemi, H., Nikinmaa, E., Grönholm, T., Hari, P.: Forest floor vegetation plays an important role in photosynthetic production of boreal forests. For. Ecol. Manag. 221, 241–248 (2006). https://doi.org/10.1016/j.foreco.2005.10.021

Kourtchev, I., Giorgio, C., Manninen, A., Wilson, E., Mahon, B., Alto, J., et al.: Enhanced volatile organic compounds emissions and organic aerosol mass increase the oligomer content of atmospheric aerosols. Sci. Rep. 6, 35038 (2016). https://doi.org/10.1038/srep35038

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Mannonen, H., Nieminen, T., et al.: Direct observation of atmospheric aerosol nucleation. Science 339, 943–946 (2013). https://doi.org/10.1126/science.1227385

Lee, A., Goldstein, A.H., Keywood, M.O., et al.: Gas-phase products and secondary aerosol yield from ozonolysis of ten different terpenes. J. Geophys. Res. 111, D07302 (2006). https://doi.org/10.1029/2005JD006437

Lee, S.H., Gordon, H., Yu, H., Lehtipalo, K., Haley, R., Li, Y., Zhang, R.: New particle formation in the atmosphere: From molecular clusters to global climate. J. Geophys. Res.: Atmos. 124, 7098–7146 (2019). https://doi.org/10.1029/2018JD029356

Makkonen, R., Asmi, A., Kerminen, V.M., Boy, M., Arneth, A., Guenther, A., Kulmala, M.: BVOC-aerosol-climate interactions in the global aerosol-climate model ECHAM5.5-HAM2. Atmos. Chem. Phys. 12, 10077–10096 (2012). https://doi.org/10.5194/acp-12-10077-2012

Mäki, M., Heinonsalo, J., Helène, H., Bäck, J.: Contribution of understory vegetation and soil processes to boreal forest isoprenoid exchange. Biogeosciences (5), 1055–1073 (2013). https://doi.org/10.5194/bg-14-1055-2017

Mäki, M., Krasnov, D., Hellen, H., Noe, S.M., Back, J.: Stand type affects fluxes of volatile organic compounds from the forest floor in hemiboreal and boreal climates. Pant and Soil. 441(1–2), 363–381 (2019a). https://doi.org/10.1007/s11104-019-04129-3

Mäki, M., Aalto, J., Helène, H., Pihlatie, M., Bäck, J.: Interannual and seasonal dynamics of volatile organic compounds fluxes from the boreal forest floor. Front. Plant Sci. 10, 191 (2019b). https://doi.org/10.3389/fpls.2019.00191

Morén, A.-S., Lindroth, A.: CO2 exchange at the floor of boreal forests. Agric. for. Meteorol. 101, 1–14 (2000). https://doi.org/10.1016/S0168-1923(99)00160-4

Mogensen, D., Gierens, R., Crowley, J.N., et al.: Simulation of atmospheric OH, O3 and NO3 reactivities within and above the boreal forest. Atmos. Chem. Phys. 15, 3909–3932 (2015). https://doi.org/10.5194/acp-15-3909-2015

Navarro, J.C.A., Smolander, S., Struthers, H., et al.: Global emissions of terpenoid VOCs from terrestrial vegetation in the last millennium. J. Geophys. Res. Atmos. 119, 6867–6885 (2014). https://doi.org/10.1002/2013JD021238

Nölscher, A.C., Bourtsoulidis, E., Bonn, B., Kesselmeier, J., Leliveld, J., Williams, J.: Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011. Biogeosciences 10, 4241–4257 (2013). https://doi.org/10.5194/bg-10-4241-2013
Praplan, A.P., Tykkä, T., Schallhart, S., Tarvainen, V., Bäck, J., Hellén, H.: OH reactivity from the emissions of different tree species: investigating the missing reactivity in a boreal forest. Biogeosciences 17, 4681–4705 (2020). https://doi.org/10.5194/bg-17-4681-2020

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., Müller, J.F., Kuhn U., Stefani, P., Knorr. W.: Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. Atmos. Chem. Phys. 14, 9317–9341 (2014). https://doi.org/10.5194/acp-14-9317-2014

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T., Kajos, M., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., Kulmala, M.: OH reactivity measurements within a boreal forests: Evidence of unknown reactive emissions. Environ. Sci. Technol. 44, 6614–6620 (2010). https://doi.org/10.1021/es101780b.2010

Tkachev, A.V.: Investigation of Plant’s Volatile Compounds. Ofset Publ, Novosibirsk (2008)

van Meening, Y., Karlsson, T., Seifert, A., Schurgers, G., Rinnan, R., Holst, T.: Isoprenoid emission variation of Norway spruce across a European latitudinal transect. Atmos. Environ. 170, 45–57 (2017). https://doi.org/10.1016/j.atmosenv.2017.09.045

Viros, J., Fernandez, C., Wortham, H., Gavinet, J., Lecareux, C., Ormeño, E.: Litter of Mediterranean species as a source of volatile organic compounds. Atmos. Environ. 242, 117815 (2020). https://doi.org/10.1017/1002/eece3.7533

Yang, Y., Shao, M., Wang, X., Nölscher, A., Kessel, S., Guenther, A., Williams, J.: Towards a quantitative understanding of total OH reactivity: A review. Atmos. Environ. 134, 147–161 (2016). https://doi.org/10.1016/j.atmosenv.2016.03.010

Zhou, P., Ganzeveld, L., Rannik, Ü., Zhou, L., Gierens, R., Taipale, D., Mammarella, I., Boy, M.: Simulating ozone dry deposition at a boreal forests with a multi-layer canopy deposition model. Atmos. Chem. Phys. 17, 1361–1379 (2017). https://doi.org/10.5194/acp-17-1361-2017

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.