Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks

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Abstract. Atmospheric aerosols impact climate by scattering and absorbing solar radiation and by acting as ice and cloud condensation nuclei. Biogenic secondary organic aerosols (BSOAs) comprise an important component of atmospheric aerosols. Biogenic volatile organic compounds (BVOCs) emitted by vegetation are the source of BSOAs. Pathogens and insect attacks, heat waves and droughts can induce stress to plants that may impact their BVOC emissions, and hence the yield and type of formed BSOAs, and possibly their climatic effects. This raises questions of whether stress-induced changes in BSOA formation may attenuate or amplify effects of climate change. In this study we assess the potential impact of stress-induced BVOC emissions on BSOA formation for tree species typical for mixed deciduous and Boreal Eurasian forests. We studied the photochemical BSOA formation for plants infested by aphids in a laboratory setup under well-controlled conditions and applied in addition heat and drought stress. The results indicate that stress conditions substantially modify BSOA formation and yield. Stress-induced emissions of sesquiterpenes, methyl salicylate, and C₁₇-BVOCs increase BSOA yields. Mixtures including these compounds exhibit BSOA yields between 17 and 33 %, significantly higher than mixtures containing mainly monoterpenes (4–6 % yield). Green leaf volatiles suppress SOA formation, presumably by scavenging OH, similar to isoprene. By classifying emission types, stressors and BSOA formation potential, we discuss possible climatic feedbacks regarding aerosol effects. We conclude that stress situations for plants due to climate change should be considered in climate–vegetation feedback mechanisms.

1 Introduction

Terrestrial vegetation is a key player in the biogeochemical cycles of carbon and water and thus a key player for Earth’s climate (Carslaw et al., 2010). In addition vegetation constantly emits reactive biogenic volatile organic compounds (BVOCs) to the atmosphere, where they participate in atmospheric gas-phase chemistry and particle formation. At the global scale, BVOC emissions exceed anthropogenic VOC emissions by an order of magnitude (Guenther et al., 1995, 2012). BVOCs play an important role in atmospheric oxidation cycles; they affect ozone formation, the oxidation capacity of the atmosphere, and they are important players in new particle formation (Riipinen et al., 2011). BVOC (monoterpenene) oxidation products generate biogenic secondary organic aerosols (BSOAs) and increase the number and size of aerosol particles (Tunved et al., 2006). Both attributes are significant with respect to the direct and the indirect effects of aerosols on the radiation budget of the Earth via scattering, absorption of sunlight and through modification of cloud properties (Tunved et al., 2008; Kerminen et al., 2005; Spracklen et al., 2008; Heald et al., 2008). Kulmala et al. (2004) and Goldstein et al. (2009) proposed that the increase in BSOA burden would cause a negative climate...
feedback through scattering of incoming solar radiation between the terrestrial ecosystem and the atmosphere, attenuating the temperature increase expected due to climate warming.

Climatic changes will alter the environmental conditions for vegetation (Sitch et al., 2007). Vegetation models predict that under future global climatic changes, forests in temperate and Boreal regions will flourish and spread, suggesting that this expansion will increase the annual global production of BVOCs and BSOAs (Lathière et al., 2005; Tsigaridis and Kanakidou, 2007). Climate models also predict frequent heat waves as well as changes in precipitation (Trenberth et al., 2007). It is noted that predictions of future BVOC emissions assume equilibrium between vegetation and climate (Lathière et al., 2005). However, noticeable climate change will appear already within the next decades, whereas vegetation propagates by only several tens of kilometers in 100 yr (Chen et al., 2011). Thus the timescale of substantial climatic changes may be short compared to typical adaptation times of vegetation.

We thus hypothesize that vegetation in many regions will be forced out of the optimal living conditions as the plants will be exposed to more heat waves, dryness, pollution, insect outbreaks or various diseases due to climate change (Arnth et al., 2010). It is projected that such deviations will disturb the functioning of plants, denominated as stress to the plants. Our recent experiments suggest that it may not be sufficient to consider only isoprene and monoterpenes (MT) and BSOAs originating from those compounds in future (and current) climate scenarios. In addition stress-induced BVOC emissions as well as climate-change-induced impacts on BVOC emissions (Kleist et al., 2012) should be considered.

Phenomenological algorithms of BVOC emissions consider temperature and light intensity as the driving factors for the emission strengths of monoterpenes and isoprene (e.g. Guenther et al., 1993; Schuh et al., 1997; Kesselmeier and Staudt, 1999), but omit BVOC emissions in response to other stresses on plants (Heiden et al., 1999, 2003; Arneth et al., 2007). It is noted that predictions of future BVOC emissions assume equilibrium between vegetation and climate (Lathière et al., 2005). However, noticeable climate change will appear already within the next decades, whereas vegetation propagates by only several tens of kilometers in 100 yr (Chen et al., 2011). Thus the timescale of substantial climatic changes may be short compared to typical adaptation times of vegetation.

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Recently, we studied the effect of heat stress on constitutive emissions and SIEs in terms of de novo emissions and emissions from storage pools (Kleist et al., 2012). Here we survey which SIEs contribute to BSOA formation and to what extent they contribute to BSOA formation when included in a natural BVOC mix. To assess BSOA formation from SIEs we performed experiments with real plants in the Jülich Plant Atmosphere Chamber (JPAC). The plants were exposed to biotic stressors (aphid attack) and, in addition, to heat and drought stress in order to characterize the impact of abiotic stressors on BSOA formation.

2 Experimental section

Experiments were conducted in the JPAC facility. A detailed description of the chamber setup and its performance is given in Mentel et al. (2009). In short, the facility consists of three borosilicate glass chambers (0.164 m$^3$, 1.150 m$^3$, and 1.450 m$^3$) with Teflon floors. Each chamber is mounted in separate climate-controlled housing (adjustable between 10 and 50°C). Either one of the two smaller chambers was used as the plant chamber. The large chamber was used as the reaction chamber for studying BSOA formation. Discharge lamps (HQI 400 W/D; Osram, Munich, Germany) simulated the solar light spectrum. At full illumination the photosynthetic photon flux density (PPFD) was 480 µmol m$^{-2}$ s$^{-1}$ in the 1.150 m$^3$ chamber and 800 µmol m$^{-2}$ s$^{-1}$ in the 0.164 m$^3$ chamber.

Clean air was pumped through the plant chamber to take up BVOCs emitted by the plants. A fraction of the air leaving the plant chamber (≈ 16 L min$^{-1}$) was fed into the reaction chamber. The reaction chamber had a separate inflow of ≈ 16 L min$^{-1}$ to add ozone and humidified air. The residence time in the reaction chamber was about 45 min.

The conditions in the reaction chamber were held constant for all experiments (T = 17 ± 0.5°C, RH = 63 ± 2 %, [O$_3$] = 85–90 ppb without UV light, [NO$_x$] < 300 ppt). OH radicals were generated by ozone photolysis (internal UV lamp, Philips, TUV 40 W, max$_{\lambda}$ = 254 nm, J(O$^1$D) ≈ 2.9 × 10$^{-3}$ s$^{-1}$) and subsequent reaction of O$^1$D with water. OH radicals were generated when the BVOC concentrations in the reaction chamber had reached a steady state. OH radical concentrations ranged from 10$^7$ to 10$^9$ cm$^{-3}$. The presence of OH radicals induced new particle formation. Particle concentration (particle diameter $d_p > 7$ nm) and size distribution (10 nm < $d_p < 700$ nm) were measured by a condensation particle counter (CPC TSI3022A) and a scanning mobility particle sizer (SMPS TSI3071+TSI3025A), respectively.

BVOC concentrations were measured at the outlet air of the plant chamber and the reaction chamber using GC-MS (Heiden et al., 1999). OH concentrations were determined by the decrease of deuterated cyclohexane (C$_6$D$_{12}$) added to

the reaction chamber (Kiendler-Scharr et al., 2009). Calibration of the GC-MS was conducted as described in Heiden et al. (2003). To calibrate the C_{17}-BVOCs emitted from insect-infested spruce we used 8-heptadecene (Fluka, GC purity) as a surrogate for emitted C_{17}-compounds.

After changing the conditions in the plant chamber we allocated 8 h for establishing new steady state conditions in the reaction chamber before the next experiment. Particle formation was studied once a day with time intervals longer than 12 h with UV off between two particle events. In these periods the reaction chamber was flushed and conditioned by the reaction chamber before the next experiment. Particle formation and BVOC consumption in the applied concentration range (see later Figs. 2, 3, 5, and 7). Under these conditions the diurnal light cycle was the same with PPFD = 480 \mu mol m^{-2} s^{-1} during the periods of illumination. To vary the emission strength, the plant chamber temperature was set to either 15 or 20°C on several occasions.

In Experiment #1 we used seedlings of one Silver birch (Betula pendula L.), one Scots pine (Pinus sylvestris L.), and one Norway spruce (Picea abies L.) together as the BVOC source. The spruce showed a high degree of aphid infestation. No infestation was visible for the other trees, but they also may have been infested. The plants were introduced into the 1.150 m^3 plant chamber, acclimated for one day and investigated over 18 days. A diurnal cycle of light was applied: 13 h illumination, 9 h darkness and simulations of twilight at different days. PPFD was varied from day to day in steps of 120 \mu mol m^{-2} s^{-1} at T = 15°C on several occasions.

We performed five experiments – three with plants and two control experiments. These experiments are summarized in Table 1. For Experiments #1, #2, and #3 with plants we used three- to four-year-old seedlings of spruce (Picea abies L.), pine (Pinus sylvestris L.), beech (Fagus sylvatica L.), and birch (Betula pendula L.). The plants were stored near a natural forest before the measurements to obtain realistic conditions with all the impacts that plants experience in their natural environment. The plants suffered from typical diseases as insect or pathogen attacks and featured SIEs when they were introduced into the plant chamber. Up to four plants were introduced together into the plant chamber (see Table 1).

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In Experiment #2 we investigated an individual Norway spruce severely infested by aphids. This plant was investigated for 11 days in total. During the first five days, moderate temperatures were applied to the plant (days 5 to 1, T = 15 or 20°C, Table 2). Higher temperatures of 35°C and 30°C were applied on day 0 and day 1, respectively. During the remaining 4 days, moderate temperatures of 20°C were applied (days 2 to 5). During the entire measurement period the diurnal light cycle was the same with PPFD =

<table>
<thead>
<tr>
<th>No</th>
<th>Purpose of experiment</th>
<th>Plants used</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Impact of biotic SIEs on BSOA formation</td>
<td>Silver birch, Scots pine, Norway spruce</td>
<td>High degree of aphid infestation of spruce</td>
</tr>
<tr>
<td>1c</td>
<td>Contribution of MeSa to BSOA formation</td>
<td>Control experiment with BVOCs from diffusion source</td>
<td>MeSa addition to α-pinene</td>
</tr>
<tr>
<td>2</td>
<td>Impact of heat stress on BSOA formation from biotic SIEs</td>
<td>Norway spruce</td>
<td>High degree of aphid infestation</td>
</tr>
<tr>
<td>3</td>
<td>Impact of drought stress on BSOA formation (interaction of GLV emissions and emissions of C_{17}-BVOCs)</td>
<td>Silver birch, European beech, Norway spruce</td>
<td>Spruce infested by Cinara pilicornis</td>
</tr>
<tr>
<td>3c</td>
<td>Impact of green leaf volatiles on BSOA formation</td>
<td>Control experiment with BVOCs from diffusion source</td>
<td>(Z)-3-hexenol addition to α-pinene</td>
</tr>
</tbody>
</table>
480/0 µmol m\(^{-2}\) s\(^{-1}\) during periods of illumination/darkness. Table 2 lists the temperatures together with the measured MT/SQT ratios ([µg m\(^{-3}\)]/[µg m\(^{-3}\)]).

<table>
<thead>
<tr>
<th>Day</th>
<th>T [°C]</th>
<th>MT/SQT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>0.49</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>1.7</td>
</tr>
<tr>
<td>5</td>
<td>&gt;100</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>66</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>81</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>&gt;100</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 2. Plant chamber temperatures and MT/SQT concentration ratios ([µg m\(^{-3}\)]/[µg m\(^{-3}\)]) during Experiment #2 with Norway spruce. Days relative to the day of heat stress application at day 0. Note that the needle temperature was about 4°C higher than the listed plant chamber temperature during periods of illumination (compare Kleist et al., 2012).

In Experiment #3 we used a set of four trees typical for the central European mixed forest (one spruce, one birch and two beech seedlings). The spruce was infested by the aphid Cinara pilicornis and emitted long-chained C\(_{17}\)-alkenes. The birch did not show visible symptoms of injury, but both beech seedlings showed symptoms of drought stress visible by leaf curling. We did not irrigate the soil for 5 days in order to apply drought stress in addition to the infestation. The diurnal light cycle was PPFD = 480/0 µmol m\(^{-2}\) s\(^{-1}\) during periods of illumination/darkness. Plant chamber temperature was held constant at 20°C except for the last day, when it was increased to 25°C.

For the control Experiments #1c and #3c the substances were evaporated from diffusion sources, diluted by synthetic air and continuously flushed into the reaction chamber. As for plant emissions BSOA formation was induced by ozone photolysis in the presence of water and subsequent OH formation. UV light was switched on and particle formation was induced when steady state concentrations were reached after three hours. Conditions in the reaction chamber were kept identical to those of the experiments with the plants.

In control Experiment #1c we determined the impact of methyl salicylate (MeSa) on BSOA formation. We added MeSa, deuterated cyclohexane-d12 and α-pinene to the reaction chamber. Concentrations of α-pinene and cyclohexane-d12 were held constant, and the steady state concentration of α-pinene would have been 27 ± 3 µg m\(^{-3}\) (4.8 ± 0.6 ppb) if ozone reactions had been absent; cyclohexane-d12 concentrations were 1.5 µg m\(^{-3}\) (∼0.4 ppb). MeSa concentrations were varied between 0 and 55 µg m\(^{-3}\) (0 to 8.8 ppb). BSOA formation was induced by oxidation of the reaction mix by OH radicals ([OH] ~ 6 × 10\(^7\) cm\(^{-3}\) (see Fig. 3), [O\(_3\)] 40–50 ppb with UV light switched on and [O\(_3\)] = 85–90 ppb with UV light switched off, reaction chamber temperature 17 ± 0.5°C, RH = 63 ± 2 %), OH concentrations were determined from the difference of cyclohexane-d12 concentrations at chamber outlet with and without the UV light. Less than 60% of the added MeSa reacted with OH radicals due to the low reactivity of MeSa.

In control Experiment #3c we investigated the drastic effect of GLV observed in Experiment #3 induced by drought stress. Again we added α-pinene (43 ± 4 µg m\(^{-3}\)) and cyclohexane-d12 to trace OH concentrations to the reaction chamber. As a typical GLV we added (Z)-3-hexenol to the chamber in varying concentrations at otherwise unchanged conditions. Experiments were conducted from day to day with (Z)-3-hexenol concentrations varying from 0 to 48 µg m\(^{-3}\). BSOA formation was induced by oxidation of α-pinene by OH ([OH] ~ 6 × 10\(^7\)–1.6 × 10\(^7\) cm\(^{-3}\), [O\(_3\)] = 85–90 ppb in the absence and 40–50 ppb in the presence of UV light, respectively, T = 17 ± 0.5°C, RH = 63 ± 2 %).

For the determination of incremental mass yields one needs to know the amount of chemically consumed BVOCs. This quantity was directly obtained by comparing the concentrations of the reactants entering and leaving the reaction chamber. Generally, more than 98% of the MT and SQT entering the reaction chamber were oxidized at the typical OH and O\(_3\) concentrations in the reaction chamber. In these cases the chemical consumption was set equal to the input amount. For MeSa, which reacted to less than 60%, the chemical consumption was calculated from the difference of MeSa concentrations with and without UV light switched on.

Maximum BSOA mass was reached after 1–2 h, depending on the concentrations of BVOCs and oxidants. The observed maximal particle mass was corrected for the loss by outflow and plotted versus the BVOC consumption in the reaction chamber as described in Mentel et al. (2009). As the basis for BVOC consumption we used the mass (in µg m\(^{-3}\)) summed up over all detected BVOCs, independent of their biosynthetic origin.

It has to be noted that uncertainties for the yields given here were determined from statistical errors only. Possible systematic errors such as erroneous calibration (GC-MS data: ±15% for MT and ±20% for SQT) were not included. All measurements were performed under low-NO\(_x\) conditions (NO\(_x\) < 300 ppt).

3 Results

3.1 Experiment #1: BSOA formation from sesquiterpenes and methyl salicylate

Under the conditions of Experiment #1, the plants emitted mainly SQT and phenolic BVOCs, indicating that the main portion of the emissions was induced by biotic stress, most probably due to the insect infestation. Considering that there was no active control on the stress impacts imposed
Fig. 1. BVOC concentrations at the inlet of the reaction chamber determined in Experiment #1. Concentrations were averaged for 4 h before particle formation was induced in the reaction chamber. GLV = green leaf volatiles, mainly C6-alcohols and -aldehydes with significant emissions only at day 5, MT = monoterpenes, phenolic = phenolic BVOCs originating downstream of the shikimate pathway, SQT = sesquiterpenes. (A) At constant PPFD = 480 µmol m$^{-2}$ s$^{-1}$ and constant plant chamber temperature = 15 °C, during a measurement period of five consecutive days. (B) At different PPFD and constant plant chamber temperature = 15 ± 0.5 °C. Note that the pattern depicted for PPFD = 480 µmol m$^{-2}$ s$^{-1}$ is not included in (A).

by the insect infestation, both emission strengths as well as the emission patterns were fairly stable for constant temperature and constant PPFD (Fig. 1a). The ratios SQT/MT and phenolic/MT covered ranges of 4.1–5.8 (average = 4.8 ± 0.8) and 3.2–5.6 (average = 3.8 ± 1.0), respectively. Variation of temperature changed essentially only the emission strengths. SQT and phenolic BVOCs are de novo emissions and the emission strengths also depend on PPFD (Fig. 1b, Kleist et al., 2012). This observation is in agreement with the results of Gouinguene and Turlings (2002).

For 120 ≤ PPFD ≤ 480 µmol m$^{-2}$ s$^{-1}$ SQT/MT and phenolic/MT varied from 9 to 21 and from 6 to 9, respectively.

In Experiment #1 with the infested spruce, SQT contributed up to 56 % to the total emissions and phenolic BVOCs up to 44 %. MT (≤ 10 %) and GLV (≤ 1 %) were only minor fractions of the mix of reactive BVOCs. The dominating SQT were α-farnesene (~27 %) and β-farnesene (~66 %). About 95 % of the phenolic BVOCs were methyl salicylate (MeSa). Other phenolic BVOCs that were emitted in minor amounts were compounds such as methyl benzilate (~1 %) and benzyl benzoate (~0.7 %). Table 3 lists the BVOCs found in the emission mix, their concentrations and their contribution to the total VOC emissions from this set of plants.

SOA formation was observed only in the presence of OH as for unstressed plants (Mentel et al., 2009). Ozonolysis alone did not lead to SOA formation. A 22 ± 2 % incremental SOA mass yield was determined for this mixture from the slope of linear fit in Fig 2. This incremental yield is significantly higher than the 4–6 % value measured for a mixture consisting of MT only (Mentel et al., 2009; Lang-Yona et al., 2010), but is similar to that obtained for stressed transgenic poplar plants (Kiendler-Scharr et al., 2012) that exhibited a similar emission pattern as the plants used here. The positive x-intercept in Fig. 2 and in similar plots in the following indicates the nucleation threshold in JPAC (Mentel et al., 2009) and is not further considered here.

It was impossible to identify the contribution of the different BVOCs on SOA formation because the plants coemitted SQT and MeSa. Therefore we determined independently the SOA yield for MeSa in control Experiment #1c using α-pinene and MeSa from artificial sources. The α-pinene
was used as a representative for constitutive SOA precursors to induce SOA formation. Its concentration was held constant at 27 µg m$^{-3}$ (4.5 ppb), while MeSa concentrations were varied between 0 and 55 µg m$^{-3}$ (0 to 8.8 ppb). The incremental mass yield of the α-pinene/MeSa mixture was determined to 20 ± 3% (slope in Fig. 3). Since only MeSa concentrations were varied, the incremental yield is due to MeSa. The OH concentrations were not affected much by the increasing MeSa concentrations due to the low reactivity of MeSa (Fig. 3). The incremental yield for MeSa has the same magnitude as that obtained with the mix of MeSa and SQT emitted from the set of plants in Experiment #1, suggesting that both MeSa and SQT have similar BSOA yields of about 20%.

### 3.2 Experiment #2: impacts of heat stress on BSOA formation

Figure 4 shows the concentrations of different BVOC classes at the inlet of the reaction chamber during Experiment #2 with the infested spruce over 11 days. The emission strengths of SQT and MT decreased over the first 4 days (days −5 to −2 in Table 2 and Fig. 4) and also the emission pattern was not strictly constant. During the first 4 days, SQT emissions were higher than MT emissions. Only on day −1, when the temperature of the plant chamber increased to 25°C, were the MT emissions somewhat higher than SQT emissions.

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**Table 3.** Major BVOCs emitted from the set of plants used in Experiment #1 (data is for day 5 in Fig. 1). BVOCs with concentrations above 0.1 µg m$^{-3}$ are listed explicitly. Concentrations listed for the sum of BVOC classes (bold) include also BVOCs with concentrations below 0.1 µg m$^{-3}$.

<table>
<thead>
<tr>
<th>BVOC Class</th>
<th>Conc. [µg m$^{-3}$]</th>
<th>Contribution [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>0.71</td>
<td>0.4</td>
</tr>
<tr>
<td>(Z)-3-hexenol</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>(Z)-3-hexenylacetate</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Sum green leaf volatiles</strong> (GLV)</td>
<td>2.01</td>
<td>1.1</td>
</tr>
<tr>
<td>α-pinene</td>
<td>1.05</td>
<td>0.57</td>
</tr>
<tr>
<td>Camphene</td>
<td>0.21</td>
<td>0.11</td>
</tr>
<tr>
<td>Sabinene</td>
<td>0.14</td>
<td>0.08</td>
</tr>
<tr>
<td>Myrcene</td>
<td>0.77</td>
<td>0.42</td>
</tr>
<tr>
<td>β-pinene</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>Δ3-carene</td>
<td>0.68</td>
<td>0.37</td>
</tr>
<tr>
<td>Limonene</td>
<td>0.53</td>
<td>0.29</td>
</tr>
<tr>
<td>β-phellandrene + cis-ocimene$^a$</td>
<td>0.28</td>
<td>0.15</td>
</tr>
<tr>
<td>(E)-β-ocimene</td>
<td>4.57</td>
<td>2.5</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>3.22</td>
<td>1.7</td>
</tr>
<tr>
<td>Alloocimene</td>
<td>2.15</td>
<td>1.2</td>
</tr>
<tr>
<td>1,8-cineole</td>
<td>0.77</td>
<td>0.4</td>
</tr>
<tr>
<td>DMNT$^b$</td>
<td>2.07</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>Sum monoterpenes</strong> (MT)</td>
<td>17.9</td>
<td>9.7</td>
</tr>
<tr>
<td>(E)-β-caryophyllene$^c$</td>
<td>0.11</td>
<td>0.06</td>
</tr>
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<td>(E)-α-bergamotene</td>
<td>0.13</td>
<td>0.07</td>
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<tr>
<td>(E)-β-farnesene</td>
<td>65.5</td>
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<tr>
<td>α-curcumene$^c$</td>
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<td>0.08</td>
</tr>
<tr>
<td>(E)-farnesene$^c$</td>
<td>0.26</td>
<td>0.14</td>
</tr>
<tr>
<td>β-bisabolene</td>
<td>0.18</td>
<td>0.1</td>
</tr>
<tr>
<td>(E, E)-α-farnesene</td>
<td>30.1</td>
<td>16.3</td>
</tr>
<tr>
<td>Δ-cadinene</td>
<td>0.17</td>
<td>0.09</td>
</tr>
<tr>
<td>(Z)-α-bisabolene</td>
<td>4.37</td>
<td>2.4</td>
</tr>
<tr>
<td><strong>Sum sesquiterpenes</strong> (SQT)</td>
<td>104</td>
<td>56.3</td>
</tr>
<tr>
<td>MeSa</td>
<td>48</td>
<td>26</td>
</tr>
<tr>
<td>Benzoic acid methyl ester</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Benzyl benzoate</td>
<td>0.5</td>
<td>0.27</td>
</tr>
<tr>
<td><strong>Sum phenolic BVOCs</strong></td>
<td>59.9</td>
<td>32.4</td>
</tr>
<tr>
<td>Other BVOCs$^d$</td>
<td>0.22</td>
<td>0.1</td>
</tr>
</tbody>
</table>

$^a$ Treated together because of a strong overlap in chromatographic peaks.

$^b$ DMNT = (Z)-4,8-dimethyl-1,3,7-nonatriene = homoterpene (C$_{11}$) but for simplification added to monoterpenes.

$^c$ Only tentative identification with match quality below 95% or overlap with other chromatographic peaks.

$^d$ Includes compounds with so far unknown biosynthesis as nonanal, decanal, etc.
When the spruce was exposed to heat stress of \( T = 35^\circ C \) for 9 h on day 0 and \( T = 30^\circ C \) for 10 h on day 1, we observed a strong increase of MT emissions due to a damage of the resin ducts where MT are stored. SQT emissions changed significantly less during the heat stress (compare Kleist et al., 2012).

Following the heat stress, the plant was held at 20 \(^\circ\) C for another 4 days (day 2–day 5), during which SQT emissions decreased each day until they reached the instrumental detection limit on day 3. The heat stress had caused a decline of SQT. The MT emissions also decreased from day 2 to day 5, possible due to plant internal repair of pool damage.

BSOA formation was measured during the whole period of 11 days. For the days −5 to day −2 with MT/SQT ratios of 0.27–0.49 the incremental yield for this BVOC mix containing significant portions of SQT was 17 ± 1 %. With the onset of the heat stress on day 0 the MT emissions increased more than 20 fold, while the SQT emissions decreased. As can be seen in Fig. 5 (large red triangle), the increased total emissions at day 0 led to more BSOA mass during the heat stress than during the days before. This is only a single observation; however, the data point for day 0 is significantly off the line of the SQT-dominated yield curve. Moreover, the monoterpane-dominated mix at day 0–day 2 (Table 2, red triangles in Fig. 5) gave 8.8 ± 0.2 %, \( R^2 = 0.96 \) for the incremental yield. This is lower than that before the heat stress and closer to the expected MT-PM yields of 4–6 % (Mentel et al., 2009; Lang-Yona et al., 2010).

During the period day 2 to day 5 after applying the heat stress, the plant was held at moderate \( T = 20^\circ C \) and the MT emissions dropped back to lower amounts, but SQT emissions did not recover. The total BVOC emissions were lower than before the heat stress, and from day 3 on the MT emis-
sions were so low that formation of particles with $d_p>7\text{ nm}$ was not observed at all.

3.3 Experiment #3: interaction of C$_{17}$-BVOC emissions and GLV emissions during drought stress

In experiment #3 with birch, beech, and a spruce infested by Cinara pilicornis, C$_{17}$-BVOCs dominated the BVOC mix exiting the plant chamber contributing to about 60 % to the emission of carbon (MT $\sim$ 30 %, SQT $\sim$ 5 %, GLV $\sim$ 2 %). The most abundant C$_{17}$-compounds were 8-heptadecene, 6,9-heptadecadiene, and 3,6,9-heptadecatriene. On day 0, when the leaves of the beeches showed strong curling due to the continuing drought, a strong emission pulse of GLV appeared. As shown in Fig. 6, on day 0 the GLV contributed nearly 40 % to the emitted carbon, whereas the contribution of MT dropped from 25 to 4 % (11 to 3 ppbC). After the strong GLV pulse, the MT remained at a low level ($\sim$ 4 %). The contribution of GLV was about 10 % for the next days and decreased to roughly 3 % about a week after the strong pulse. Both the contribution of the C$_{17}$-BVOCs to the emission pattern as well as the absolute emissions of these compounds increased during the period day 1 to day 8 (Fig. 6).

Figure 7 shows the data obtained for maximum BSOA mass during that experiment. With the exception of the strong GLV pulse, we observed a good linear relationship between maximum BSOA volume and BVOC concentrations with an incremental yield of $33 \pm 6$ % (black circles in Fig. 7). This yield is even higher than that obtained for the mixtures consisting mainly of SQT ($17 \pm 1$ %), MeSa ($20 \pm 3$ %) and SQT & MeSa ($22 \pm 2$ %). In contrast, the data point obtained at the high GLV contribution to the mixture (green square in Fig. 7) showed a significant deviation from the linear relationship obtained for BVOCs dominated by C$_{17}$-BVOC emissions. The mix containing the GLV had obviously a much lower potential for BSOA formation than the mix without GLV.

The less efficient particle formation during the GLV emission pulse suggests a counteracting effect of GLV on BSOA yield. Therefore we investigated the impact of GLV emissions on BSOA formation in reference Experiment #3c with $\alpha$-pinene as constitutive BSOA precursor and (Z)-3-hexenol as surrogate for a GLV. The $\alpha$-pinene concentration was held constant at $43 \pm 4 \mu g\text{ m}^{-3}$, while (Z)-3-hexenol was added to the chamber in concentrations varying from 0 to 48 $\mu g\text{ m}^{-3}$. The amount of BSOA formed from the mixtures of $\alpha$-pinene and (Z)-3-hexenol as well as the OH concentrations in the reaction chamber decreased with increasing (Z)-3-hexenol addition (Fig. 8). It is clearly seen that with increasing (Z)-3-hexenol addition and consumption the formation of BSOA mass and the OH radical concentrations are suppressed (note the logarithmic scale for OH in Fig. 8). The suppressing impact of (Z)-3-hexenol on particle formation may possibly be similar to that of isoprene (Kiendler-Scharr et al., 2009). The data obtained with (Z)-3-hexenol confirmed that the deviation of the data point at high GLV in Experiment #3 (green square in Fig. 7) was due to the suppressing effect of GLV.

In all three experiments with plants, the BVOCs were introduced into the reaction chamber together with up to 90 ppb ozone (see the Experimental section). Particle formation ($d_p>7\text{ nm}$) from ozonolysis alone was negligible when BVOC concentrations were below 50 $\mu g\text{ m}^{-3}$ ($\sim$ 100 ppbC), even in the presence of up to 36 % SQT ($17 \mu g\text{ m}^{-3}$). In these experiments BVOC concentrations were more than an order of magnitude higher than those typically observed in the planetary boundary layer. Our observation supports the role of OH for the particle formation process in the atmosphere.
In order to assess the impact of SIEs we will refer to previous experiments in the JPAC chamber with unstressed spruce and pine, and α-pinene (Mentel et al., 2009). In these cases, MT emissions constituted more than 85 % of the BVOC emissions, and OH-initiated BSOA formation resulted in linear relationships between consumed BVOC mass and observed BSOA mass giving the incremental yields for BSOA formation as listed in Table 4 (Mentel et al., 2009). Because of their low contribution to emissions from the unstressed plants, neither SQT, phenolic BVOCs, nor isoprene had significant impact on the incremental yields in these experiments. The incremental yields for MT-dominated BVOC mixes, including holm oak, were 4 to 6 %, independent of the plant species and independent of the detailed MT emission pattern (Mentel et al., 2009; Lang-Yona et al., 2010). Hao et al. (2011) found BSOA mass yields of 3–11 % in experiments with pine and spruce emissions with variable MT pattern, commensurable to our findings, if their higher loads are considered. We derive incremental mass yields of 20 ± 3 % for MeSa and of 17 ± 1 % for SQT from Experiments #1c and #2, respectively (Table 4). The SQT and MeSa incremental yields are about the same within the errors and we conclude that SQT and MeSa must have contributed according to their turnover to the BSOA yields of ≈20 % in Experiment #1 (Table 4 and Kiendler-Scharr et al., 2012). Compared to the incremental yields of MT-SOAs, the yields of SQT-SOAs and MeSa-SOAs are about a factor of 4 larger. Therefore we conclude that in biotic stress situations, when plants emit SQT or MeSa, more BSOA mass (and more BSOA particles) can be formed from the same amount of C emitted as BVOCs.

Under infestation by aphid Cinara pilicornis causing emissions of C_{17}-BVOC, (Experiment #3) the enhancement of the incremental BSOA yield (33 %) is even larger, about a factor of 6 compared to MT. This is attributed to the C_{17}-BVOCs. Not much is known with respect to the emissions of the C_{17}-compounds; however, one of the major components, 8-heptadecene, was found by Nazzi et al. (2002) during interactions of the parasitic mite Varroa destructor and plant cells, indicating that the C_{17}-compounds were indeed of biogenic origin. Measurements with the isolated spruce after Experiment #3 showed that the C_{17}-BVOCs originated indeed from the plant that was infested by the aphid Cinara pilicornis. We did not separate out whether these compounds originated from the plant itself or from the insects or the insects’ excrements that were visible as small droplets on needles and branches of the plant. However, independent of the detailed emission mechanism, these compounds originate from the coupled plant–insect system and were therefore treated as a stress-induced BVOC class.

Emissions of MeSa and SQT are not specific for the plant species and stress conditions investigated here. Phenolic BVOCs (with MeSa being predominant) originate from the phenylpropanoid pathway (Colquhoun et al., 2010), and the activity of this pathway is induced in particular by pathogen attack (e.g. Jansen et al., 2011, and references cited therein). Emissions of MeSa and SQT during insect infestation were also reported for Eurasian (Kleist et al., 2012) and for a North American conifer species (Joó et al., 2011). Therefore the importance of our SIE-SOA yields may apply to a wider range of situations and regions despite the limited number of experiments presented here.

### 4.2 Impacts of SIEs on BSOA formation and climate

Since MeSa, SQT, and C_{17}-BVOCs provide a larger incremental yield per emitted carbon than constitutive MT emissions, particles grow to larger sizes. (In addition more aerosol particles were formed in our experiments.) If the biotic stress to plants occurs as a regional phenomenon, the enhanced aerosol size (and number) will contribute on a regional scale to the direct (Pilinis et al., 1995; Chen et al., 2009; Kaufman et al., 2002) and indirect aerosol effects (Albrecht, 1989; Twomey, 1977; Kaufman et al., 2002; Lohmann and Feichter, 2005; Quaas et al., 2009) on climate.

SIE-SOAs will provide extra growth and thus potentially stronger scattering compared to the same turnover of constitutive MT amount. A similar argument holds for the first indirect effect (Twomey effect): to become cloud condensation nuclei, i.e. CCN-active, particles must grow to several tens of nm or even more. Provided that SIE-SOAs are as good CCN as MT-SOAs, they will add extra growth and formation of more CCN, which could lead to more and smaller cloud droplets (for a given amount of available water) and thus to
more reflective clouds. Both direct and first indirect effect eventually exert a cooling effect which counteracts warming, thus constituting an overall negative feedback if the plant stress was favored or caused by heat.

The increase of the cloud droplet number which increases the cloud albedo also prolongates the cloud lifetime by suppression of rain (second indirect effects). If the plant stress that induced GL V emissions is caused or favored by drought periods, suppression of BSOA formation by GL V emissions can decrease the cloud droplet number and increase rain probability. This behavior could also provide a negative feedback.

The discussion above considered only the higher incremental mass yields, thus the potential of SQT and MeSa to form more SOA. The eventual effect does not only depend on the incremental yield but also on the emitted amounts of BVOCs and their turnover in the atmosphere. In a situation of long periods with increased SIEs as depicted in Figs. 1 and 6, the situation is straightforward and will lead to aerosol effects as sketched above. However, if stress causes plant damage as shown in Experiment #2 (Fig. 4), the BSOA production may die out to zero after a short pulse.

The situation becomes more complex if one considers the GL V that were triggered by drought stress. Although GL V themselves have some limited mass yield of 3 % (for (Z)-3-hexenol, Hamilton et al., 2009), they can hinder BSOA formation from constitutive emissions such as α-pinene (Experiment #3c) or diminish the BSOA potential even of the very effective SIEs of C_{17}-BVOCs (green data point in Fig. 7). This effect of GL V goes along with a drop in OH radical concentration (Fig. 8), in contrast to the effect of MeSa (Fig. 3). The GL V effect shows similarity to the suppressing effect of isoprene (Kiendler-Scharr et al., 2009, 2012), where the reactive isoprene with a limited BSOA mass yield of a few percent prevents nucleation and BSOA formation from constitutive MT emission and SIEs, respectively. While climate warming could enhance the isoprene-to-MT ratio steadily, the GL V effect would become active episodically whenever plants are damaged in cases such as drought stress. This may lead to a positive feedback, namely, drought → GL V → less OH → less BSOA → increasing heat → extended drought.

4.3 Examples for possible feedback effects via SIE-SOAs

Although we quantified BSOA formation potentials for various SIEs, the difficulty to quantify stressors and their impacts impedes quantitative upscaling of our results, as the amounts of current and future SIEs remain unknown. A major uncertainty herein is the future evolution of biotic stressors like pathogen and insect attacks. The effect of climate change on pathogens and herbivorous insects depends on the detailed conditions of the ecosystems. However, there is evidence that biotic stress will increase together with heat waves and droughts (e.g. Ayres and Lombardero, 2000; Arneth and Niinemets, 2010; Bentz et al., 2010; Hicke et al., 2012; Sturrock et al., 2011). Indeed, plant responses to biotic stresses are highly complex, and the biotic stressors applied in this study may represent only a limited set of biotic stress in general, presumably even for insect attacks. Nevertheless we intend to initialize a discussion about SIEs and SIE-SOAs in current and future climate. Important aspects herein are feedbacks and couplings between vegetation, atmosphere, and climate.

Previous studies provided some basic knowledge about impacts of stress on BVOC emissions. The number of biosynthetic pathways wherein SIEs are synthesized is limited, and SIE production proceeds via the induction of activities within these biosynthetic pathways. Therefore classes of SIEs as GL V, phenolic BVOCs, mono- or sesquiterpenes

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Table 4. Overview over incremental BSOA mass yields.

<table>
<thead>
<tr>
<th>Name</th>
<th>BVOC source</th>
<th>Action</th>
<th>Major BVOCs</th>
<th>Incremental Mass yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp1</td>
<td>Stand</td>
<td>Aphid infestation</td>
<td>SQT/MeSa</td>
<td>22 ± 2 %</td>
</tr>
<tr>
<td>Exp1c</td>
<td>Diff. source</td>
<td>None</td>
<td>MeSa</td>
<td>20 ± 3 %</td>
</tr>
<tr>
<td>Exp2</td>
<td>Spruce</td>
<td>Aphid infestation &amp; heat</td>
<td>SQT</td>
<td>17 ± 1 %</td>
</tr>
<tr>
<td>Exp3</td>
<td>Stand</td>
<td>Cinara pilicornis infestation &amp; drought</td>
<td>C_{17}-BVOCs</td>
<td>33 ± 6 %</td>
</tr>
<tr>
<td>Exp3c</td>
<td>Diff. source</td>
<td>None</td>
<td>α-pinene + Z-3-hexenol</td>
<td>20 ± 6 %</td>
</tr>
<tr>
<td>a</td>
<td>Grey poplar</td>
<td>Ozone pulse</td>
<td>SQT/MeSa</td>
<td>20 ± 6 %</td>
</tr>
<tr>
<td>b</td>
<td>Pine</td>
<td>None</td>
<td>MT 80 %</td>
<td>5.3 ± 0.5 %</td>
</tr>
<tr>
<td>c</td>
<td>Spruce</td>
<td>None</td>
<td>MT 90 %</td>
<td>4.2 ± 0.7 %</td>
</tr>
<tr>
<td>b</td>
<td>Diff. source</td>
<td>None</td>
<td>α-pinene</td>
<td>5.2 ± 0.5 %</td>
</tr>
<tr>
<td>c</td>
<td>Holm Oak</td>
<td>Heat 25–35 °C</td>
<td>MT</td>
<td>6.0 ± 0.6 %</td>
</tr>
<tr>
<td>d</td>
<td>Pine /Spruce</td>
<td>None</td>
<td>MT</td>
<td>3–11 %</td>
</tr>
</tbody>
</table>

a Kiendler-Scharr et al. (2012), b Mentel et al. (2009), c Lang-Yona et al. (2010), and d Hao et al. (2011).
Table 5. BVOC emissions used for estimating impacts of stress-induced emissions on BSOA formation. Type: Const = constitutive emissions, SIEs = stress-induced emissions. The BSOA column gives the effect of emissions on BSOA assuming increase in emission strengths of the respective BVOC group. The arrows in columns biotic, heat, and drought indicate expected trends for the emissions of the respective BVOC group in case of biotic, heat, and drought stress, respectively.

<table>
<thead>
<tr>
<th>BVOC group</th>
<th>Type</th>
<th>BSOA</th>
<th>Aphid infestation</th>
<th>Heat</th>
<th>Drought</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT emissions from pools</td>
<td>Const.</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>*↓</td>
</tr>
<tr>
<td>MT de novo emissions</td>
<td>Const.</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓↓</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Const.</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↓↓</td>
</tr>
<tr>
<td>SQT/de novo</td>
<td>SIEs</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓–</td>
</tr>
<tr>
<td>phenolic BVOCs</td>
<td>SIEs</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓–</td>
</tr>
<tr>
<td>GLV</td>
<td>SIEs</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑–</td>
</tr>
<tr>
<td>C_{17}-BVOCs</td>
<td>SIEs</td>
<td>↑</td>
<td>↑</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

~ not described in literature, *: low direct stress impacts,

in different proportions are emitted in response to the biotic stress. As we found that classes of BVOCs have similar BSOA yields (Table 4), the variability of BSOA formation potential compared to the variability of emissions is strongly diminished.

Based on this knowledge we will discuss a case scenario (Table 5) wherein we only consider the aerosol effects of constitutive MT-SOAs and SIE-SOAs based on the formation potentials in Table 4. In Table 5 we sketch expected effects of BVOC emissions on BSOA formation based on the results presented here. Furthermore possible responses of constitutive emissions and SIEs to aphid infestation and to heat and drought are outlined. In Table 5 we took also into account the basic emission mechanisms as BVOC emissions may either be produced de novo or arise from storage in plant organs and impacts of stress vary with the emission mechanisms. For example, heat or drought can strongly suppress overall biosynthetic activity. Coherently, de novo MT emissions will tend to decrease. However, under heat stress MT emissions from plant internal pools can still increase on timescales of days to weeks (e.g. Kleist et al., 2012).

The base cases are constitutive MT emissions. Incremental yields of MT are independent of the detailed MT mix, and the amount of produced particle mass predominantly depends on the amount of emitted MT (Mentel et al., 2009; Lang-Yona et al., 2010; Hao et al., 2011). The increased BSOA mass due to increasing MT emissions is indicated by the upward-pointing arrow in the “BSOA” column in Table 5. The prediction of future BVOC emissions is uncertain; however, according to e.g. Lathière et al. (2005) higher mean temperatures as well as expansion of vegetation zones will cause higher overall MT emissions, resulting in higher BSOA mass (Tsagaridis and Kanakidou, 2007). Hence, under negligible stress, the consequence of increased MT emissions will be a negative climatic feedback, as already suggested by Kulmala et al. (2004) and corroborated by Spracklen et al. (2008). However, already the presence of more than 10% of isoprene in a given constitutive mix will suppress particle formation (Kiendler-Scharr et al., 2009). As indicated by downward-pointing arrow in the “BSOA” column in Table 5, increasing isoprene emissions will thus weaken the negative feedback of MT-SOAs.

SIEs are not abundant when the plants do not suffer from that stress. Therefore biotic stresses increase the emission of BVOCs, which in the case of MeSa, SQT, and C_{17}-BVOCs have in addition a higher SOA formation potential than constitutive emissions (Table 4). Emissions of SQT, phenolic BVOCs, or C_{17}-BVOCs may appear only episodically and not permanently. Nevertheless, these emissions can last for weeks, and with high BSOA formation potentials of 20% or 30% they may have a substantial impact. Thus, biotic stress – more precisely, aphid infestation – will likely enhance SIEs and, as was shown in this study, will lead to increased BSOA formation (upward arrows Table 5) unless the stressor induces strong GLV emissions. In cases of strong GLV emissions the yields of BSOA formation will be suppressed as indicated by the downward arrow in Table 5. It is therefore likely that biotic stress will always lead to a negative feedback as long as the stress is not killing the host and GLV emissions remain low.

In an example we will now apply the scenario in Table 5 in order to depict that possible couplings between stress to plants, BSOA formation, and changing climate are very complicated. For simplicity the impacts of future stress on particle formation are assessed for the isolated ecosystem and impacts on net photosynthesis and transpiration are not considered. We also neglect complications by possible anthropogenic enhancement of biogenic SOA production (Kanakidou et al., 2000; de Gouw et al., 2005; Tsagaridis and Kanakidou, 2007; Weber et al., 2007; de Gouw and Jiminez, 2009; Clarton et al., 2010; Spracklen et al., 2011). We further do not take into account that future climate conditions will likely alter the physico-chemical processes leading to

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particle formation in the atmosphere as well as atmospheric boundary layer conditions such as OH levels and NOx concentrations. Each of those omissions will modify the simplified scenario in Table 5 in one way or the other when taken into account, but will probably not reverse the qualitative trends.

For estimation of the sign of possible feedbacks we refer to the relation of increasing BSOA production, particle size, and cooling aerosol effects as described in Sect. 4.2. Therefore, if less particulate mass is produced from the BVOC mix either by reduced amounts of emissions or by suppression by isoprene and GLV, we expect a positive feedback. If more BSOA mass is produced from increased emissions of MT, we expect a negative feedback.

Based on these considerations we show two possible feedback schemes for the example of a temperate forest suffering either from heat/drought or from an aphid infestation (Fig. 9). Under heat and drought stress the BVOC emissions from the forest will decrease. BSOA formation will be also decrease if de novo emissions of MT dominate. Reduced BSOA formation will result in a positive climatic feedback. In contrast, aphid infestation has only negligible impacts on constitutive MT emissions but can induce strong emissions of phenolic BVOCs, SQT or C_{17}-BVOCs. As long as aphid infestations do not induce strong GLV emissions, higher BSOA yields are expected due to higher total emission strength and the higher incremental yield of the SIEs that make the new BVOC mix.

Such a scenario would lead to a negative climate feedback (Topping et al., 2013; Paasonen et al., 2013).

Compensating effects may operate in the same forest type with a certain mixture of BVOC emitters (trees). The situation will become more complex when more stresses act together. If future climate favors aphid infestation, this will cause a negative feedback as sketched in Fig. 9. Severe heat stress can change this scenario. Upon heat stress, constitutive de novo MT emissions and SIEs will be suppressed (Kleist et al., 2012) and, depending on the degree of this effect, the negative feedback may switch to a positive feedback.

In an environment with diverse ecosystems and a variety of biotic and abiotic stresses, scenarios are even more complex, making even qualitative extrapolations of our findings difficult. However, if the class composition is known, it would be possible to calculate the effect of BSOA based on our findings. Note that other factors, such as stress impacts on net photosynthesis and transpiration as well as changing physico-chemical processes in the atmosphere, should be considered in addition.

Despite the complexity, impacts of biotic stresses on ecosystems and impacts of climate change on top are obviously important and should be considered. As an example, the expansion of tree damage by bark beetles in the Rocky Mountains and its front range has been linked to climatic change and the associated temperature changes (Bentz et al., 2010; Berg et al., 2013). Such extreme events should have impacts on the pattern and amount of the BVOCs emitted.
from the ecosystem, causing alterations of BSOA formation on a regional scale. Ongoing climate change with probably extreme events may exert significant stresses onto the ecosystem. We therefore conclude that also with respect to BVOC emissions the ecosystem response to different stress must be considered when developing scenarios for future climate change. Taking into account only the negative feedback by higher BVOC emissions and BSOA formation due to mean temperature increase may fall too short considering the complexity of the system.

5 Conclusions

We determined the BSOA formation potential of stress-induced emissions (SIEs) from common trees of temperate and Boreal forests (pine, spruce, birch, and beech). BSOA mass yields were larger than those due to constitutive monoterpene (MT) emissions: 17 ± 1 % for sesquiterpenes (SQT), 20 ± 3 % for methyl salicylate (MeSa), and 33 ± 6 % for C_{17}-BVOCs. In contrast to these SIE classes, green leaf volatiles (GLV) emitted due to stress have the potential to decrease BSOA mass and number. Increased GLV emissions support positive feedback in case GLV emissions are related to heat but exert a potential negative feedback when related to drought. Our results clearly indicate that different stress conditions can affect biogenic BSOA production: stress-induced changes of BVOC emission patterns and strength strongly impact BSOA formation, causing increased (SQT, MeSa, C_{17}-BVOCs) or decreased (GLV) BSOA formation.

Our study and consequent considerations strongly suggest the importance of SIEs for possible feedbacks between climate and vegetation via BSOA formation. Biotic stress such as aphid infestation supports negative feedback, and this may be effective already today. But heat and drought can turn the negative feedback proposed by Kulmala et al. (2004) and Goldstein et al. (2009) into a positive feedback, e.g. in forests dominated by de novo emitters. Since it is likely that climate change will affect SIEs from vegetation, SIEs and their BSOA formation potential have to be considered in future climate scenarios.

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