Production of highly oxidized organic compounds from ozonolysis of \( \beta \)-caryophyllene: laboratory and field measurements

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We conducted a laboratory investigation to identify highly-oxidized organic compounds formed in sesquiterpene (C\(_{15}\)H\(_{24}\), SQT) ozonolysis. The dominant sesquiterpene previously identified from branch emissions of Scots pine, \( \beta \)-caryophyllene, was used for this study. Using the latest mass spectrometric methods, we identified several highly oxidized organic compounds corresponding to RO\(_2\) radical, closed-shell monomer and dimer species. The most abundant compounds detected were monomers C\(_{15}\)H\(_{24}\)O\(_7\),9,11 and C\(_{15}\)H\(_{22}\)O\(_9\),11, and dimers C\(_{29}\)H\(_{46}\)O\(_{12}\),14,16 and C\(_{30}\)H\(_{46}\)O\(_{12}\),14,16. These oxidized organic compounds have very low saturation vapour pressures, an O-to-C ratio of about 0.3–0.9, and they are all classified as extremely low-volatility products (ELVOC). The molar yield of ELVOC was determined to be 1.7% ± 1.28%. Highly-oxidized organic compounds were also measured at a boreal forest site, and few possible \( \beta \)-caryophyllene oxidation products were identified, but the concentrations were extremely low, reaching a maximum of a few hundred thousand molecules cm\(^{-3}\) in spring.

Introduction

New nanoparticles formed from atmospheric vapours require very low-volatility compounds that are able to condense onto them and make them grow larger (Metzger et al. 2010, Riipinen et al. 2012). These compounds are very likely highly-oxidized reaction products of biogenic origin, such as processed monoterpene emissions from terrestrial vegetation. The recent discovery of extremely low-volatility organic compounds (ELVOC) from monoterpene ozonolysis suggests that these low-volatility products play a crucial role in the formation of secondary organic aerosol (SOA) (Ehn et al. 2014). In atmospheric conditions, the formation of these compounds could be explained by the gas-phase autoxidation process, which explains the formation of extremely low-volatility products via consecutive RO\(_2\) radical isomerization and O\(_2\) addition reactions (Crounse et al. 2013, Rissanen et al. 2014, Jokinen et al. 2014). The importance of ELVOC and other low-volatility products originating from monoterpenes and isoprene to cloud con-
densation nuclei (CCN) production has recently been studied (Jokinen et al. 2015), indicating that these compounds may affect cloud formation properties and thereby the radiative balance of the planet. Detailed knowledge is required about other ELVOC production pathways and yields to explain the discrepancies between the modelled and measured SOAs (Heald et al. 2011).

To date the role of terpenes other than monoterpenes and isoprene in the formation of extremely low-volatile products has not been studied, but the formation of secondary organic aerosol from sesquiterpene ozonolysis has been reported with SOA yields from 6% up to almost 100%, depending on the relative humidity (Hoffmann et al. 1997, Winterhalter et al. 2009). Sesquiterpenes (C_{15}H_{24}, SQT) are highly reactive with NO$_3$ and OH radicals. Reactions of volatile organic compounds (VOC) with ozone (O$_3$) are generally slow, but in the atmosphere O$_3$ is the main oxidant removing SQT (Hoffmann et al. 1997). Studies have shown that the endocyclic double bond reacts with ozone more likely (> 95%) than the exocyclic double bond (Winterhalter et al. 2009). However, the information on reaction rates ($k$) of SQT with oxidants in the literature is limited, and some very contradictory $k$-values have been determined and published because of the difficulties with the high SQT reactivity (Bonn and Moortgat 2003). For example, $k$ reported by Ghalaieny et al. (2012) is 320 times smaller than that given by Shu and Atkinson (1995). It has been suggested that pure SQTs are virtually impossible to detect in the ambient air because they immediately react with oxidants. In the USA, SQTs are estimated to account for about 9% of the non-methane hydrocarbon emissions (Helmig et al. 2006), and even values as high as 40% SQT’s of the total BVOC emission rates have been recorded in northern Finland during spring (Tarvainen et al. 2004). If SQT had similar molar yields of ELVOC as monoterpenes (~1–7%), they might be as important to particle growth as monoterpane emissions are. In this study, we were focused on detecting the reaction products of SQT ozonolysis and determining their yields using both laboratory experiments and ambient air samples.

Here, we present the results of a laboratory study of β-caryophyllene (BCP) ozonolysis, where we measured the end products with the same mass spectrometric method that has been used previously for the direct ELVOC detection from the gas-phase (e.g. Ehn et al. 2014, Jokinen et al. 2014). We show that β-caryophyllene produces highly-oxidized reaction products in a similar autoxidation scheme to that of the monoterpenes. We report the yield of highly-oxidized species using the latest knowledge of the reaction rates, $k$(SQT + O$_3$) (Richters et al. 2015). We also report the first ambient measurements of selected highly-oxidized sesquiterpene species at the SMEAR II station in Hyttilä, Finland, during spring, when terpene emissions are usually at their highest level.

Methods

Laboratory set-up and field site

All laboratory experiments were performed in a borosilicate flow reactor (approx. 205 cm long, inner diameter of 4.7 cm) with a residence time ($\tau$) of about 18 s. All measurements were conducted at the room temperature (~293–296 K) and at the ambient pressure. Liquid β-caryophyllene (≥ 98%) was purchased from Sigma-Aldrich. The gas sample was made by bubbling nitrogen gas through the liquid BCP precursor which was then directed to the flow tube using variable flow rates of the carrier gas. Ozone was produced with an ozone generator (Dasibi 1008-PC) and the ozone concentration was monitored with a Thermo Fisher 49-ozone analyser. Ozone concentration was kept constant throughout the experiments (at about 20 ppbv after dilution in the flow tube). Mixing of the sample gas with the oxidant was done in the front of the flow tube. BCP concentrations varying between 17–335 ppbv were used in these experiments (at about 20 ppbv after dilution in the flow tube). BCP concentrations were kept constant throughout the experiments (at about 20 ppbv after dilution in the flow tube). Mixing of the sample gas with the oxidant was done in the front of the flow tube. BCP concentrations varying between 17–335 ppbv were used in these experiments (concentration after dilution in the flow tube). An OH scavenger was not used during these experiments.

To calculate the concentration of BCP in the sample flow, we used a saturation vapour pressure of 4.16 Pa which was obtained using the EPI programme suite (United States Environmental Protection Agency 2015). Dilution in the flow tube was taken into account using the sample flow
of the mass spectrometer, 10–12 l min$^{-1}$, which was also the total flow of the flow reactor. The reaction rate coefficient $[k(BCP + O_3) = 1.1 \times 10^{14}$ cm$^3$ molecules$^{-1}$ s$^{-1}$] was taken from the literature (Shu and Atkinson 1995, Richters et al. 2015). The reacted BCP concentration was calculated according to: $[\text{reacted BCP}] = k \times \{O_3\} \times \{BCP\} \times \tau$ ($\tau = 18$ s).

Ambient measurements were made during the HydeSpring 2011 campaign at the SMEAR II station in Hyytiälä (Hari and Kulmala 2005), southern Finland, during which both ambient ion and neutral compounds were detected simultaneously using the latest mass spectrometric methods (see section ‘Instrumentation’ below). The campaign lasted from early March to the second week of April. The last two weeks of the data from the campaign were used for this study. This was because the emission rates of sesquiterpenes have been reported to be at their highest level during early spring, when temperatures rise with increasing radiation and trees start emitting more VOCs (Tarvainen et al. 2004, Aalto et al. 2015).

**Instrumentation**

The chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-API-TOF) was used to detect the formed sesquiterpene ozonolysis products in the experiments. The CI-API-TOF was run in the negative ion mode and concentrated nitric acid (HNO$_3$) was ionized to reagent ions, nitrate and its oligomers (NO$_3^-$, HNO$_3$NO$_3^-$ and (HNO$_3$)$_2$NO$_3^-$) with a soft X-ray ionizer (Hamamatsu L9490) in the laboratory experiments. The chemical ionization inlet is a design adopted from Eisele and Tanner (1993) and modified to be used without the radioactive source and to fit the API-TOF. In the field measurements, an Am-241 $\alpha$-radiation was used for ionization (for details see Jokinen et al. 2012). Using different ionization methods in the field and laboratory experiments for creating the reagent ions did not affect the end product detection. The only difference between the methods was the higher absolute count rate due to more efficient ion production in the Americium source.

After ionization, the nitrate ions are guided to surround the sample air that travels in the centre of the inlet gas-stream with a flow rate of 10 l min$^{-1}$, without any wall contact. Reagent ions in the sheath air are guided to meet the sample flow using electric fields. The sample is ionized either via a proton transfer, e.g. HA + NO$_3^-$ → A$^- +$ HNO$_3$, or via clustering with the reagent ion, e.g. HA + NO$_3^-$ → HA • NO$_3^-$. In this study, the highly-oxidized sesquiterpene products were all detected as nitrate clusters. Concentrations of the highly-oxidized organics, $[\text{ELVOC}_{\text{SQRT}}]$, in the laboratory experiments were calculated using signal normalization with the sum of reagent ions $[\text{NO}_3^-, \text{HNO}_3\text{NO}_3^-, \text{(HNO}_3\text{)}_2\text{NO}_3^-]$ and the calibration factor for sulphuric acid, $C = 5 \times 10^9$ molecules cm$^{-3}$ (Jokinen et al. 2012):

$$[\text{ELVOC}_{\text{SQRT}}] = \Sigma \text{SQTpa}/\Sigma \text{Rpa} \times C,$$

where SQTpa are the SQT peak areas, and Rpa are the reagent peak areas ($\text{NO}_3^- + \text{HNO}_3\text{NO}_3^- + \text{(HNO}_3\text{)}_2\text{NO}_3^-$).

Ambient concentrations were calculated using $C = 1.89 \times 10^{10}$ molecules cm$^{-3}$, which includes the losses to the inlet tubing (length 60 cm).

The uncertainty related to ELVOC measurements is based on the work of Ehn et al. (2014) who demonstrated that the collision frequency of an ELVOC with the charger ion is almost equal to that of SA and the charger ions. Thus, we assumed the collision-limited charging of ELVOC in our experiments to have an uncertainty of $\pm50\%$. Other sources of uncertainty include the mass flow controller flow errors (according to the manufacturer $\pm1\%$), ozone monitor error (according to the manufacturer $\pm1\%$), flow controller errors (according to the manufacturer $\pm2\%$), uncertainty in the BCP vapour pressure of $\pm50\%$ (Helmig et al. 2003, United States Environmental Protection Agency 2015), error due to the residence time in the flow tube (error in the flow rate and volume of the flow tube) of $\pm3\%$ and uncertainty in the reaction rate coefficient of $\pm10\%$ (Shu and Atkinson 1995). By including a simple first-order diffusion limited wall loss correction, the obtained yields would be roughly 30% higher (i.e. with a diffusion coefficient the diffusion-limited wall loss, $k = 3.65D/r^2 = 0.033$ s$^{-1}$, obtained using $D = 0.05$ cm$^2$ s$^{-1}$ and $r = 2.35$ cm; Ehn et al. 2014). The total uncertainty was calculated using the
propagation of uncertainties. The total uncertainty of the concentrations reported was estimated to be ±75% when including all the above errors. During the HydeSpring2011 campaign, the CI-API-TOF was used without an ion filter, so the reported concentrations included a small fraction of naturally-charged ions (usually < 5%) that contributed to the total signal.

During the field campaign, the naturally-charged ion composition was also measured during the spring months, using an API-TOF without any ionization prior to the mass spectrometer. We used a wide (40 mm inner diameter) steel sample tube to suck in ambient air at a large flow rate to reduce wall losses. Out of the total flow, 6 l min⁻¹ were drawn toward the API-TOF orifice via a 30-cm-long tube (8 mm inner diameter) located inside of and at the centre of the larger tube. The orifice itself drew a flow of 0.8 l min⁻¹ into the instrument. The larger total flow sampled through the wider tube was adjusted to optimize transmission of ions from the ambient air into the orifice. The API-TOF was run in the negative ion mode, so that we were able to compare the composition of charged and neutral species during the campaign.

Theory behind BCP ozonolysis

In the atmosphere, ozonolysis is estimated to remove > 98% of the BCP (Hoffmann et al. 1997). In the case of BCP, ozone will attack the endocyclic double bond about 100 times faster than the exocyclic double bond (Nguyen et al. 2009), forming a primary ozonide (POZ, see scheme for ozonolysis in Fig. 1). Reaction with the exocyclic double bond also leads to POZ formation, but since its significance has been found negligible, we only considered the reaction of ozone and endocyclic double bond in detail.

Two possible conformers, POZ₁ and POZ₂, exist from the initial reaction with ozone and their isomerization into each other is relatively easy because of the small energy barrier separating the two structures. Chemically active POZs can be stabilized in collisions with the carrier gas, or they can break the ring structure leading to the formation of two different Criegee intermediates (CI), CI₁ and CI₂ (Fig. 1).

In the atmosphere, the ring structure of a stabilized primary ozonide is broken within seconds, leading to the formation of a thermalized CI. These do not usually react in unimolecular but in bimolecular reactions with e.g. SO₂, water and organic acids. A fast decomposition of the POZ leads to the formation of an excited CI, the behaviour of which we now examine closer. The formed CIs also have possible anti- and syn-conformers, but they do not isomerize as easily as the initial POZs. In this case the syn-conformer structure is meant when the oxygen in the radical centre points towards the alkylic group of the compound (also in Fig. 1).

In the case of excited CIs, two fast unimolecular reactions are possible before the stabilization with the surrounding carrier gas occurs. One of them is the formation of a dioxirane-type intermediate product and the other one is a 1,4-hydrogen shift creating a vinylic hydroperoxy radical. The latter channel is possible for CI₁₄A, CI₁₈B and CI₂₆A intermediates of Scheme 1 (Nguyen et al. 2009). After a loss of OH radical from the hydroperoxy radical, the molecule is left with an alkyl radical centre that can accommodate an oxygen molecule, forming a RO₂ radical. After the formation of RO₂, an intramolecular hydrogen shift can take place, starting autoxidation of the molecule (Crounce et al. 2013). This is a viable reaction path to extremely low-volatile organic compounds (ELVOC). Nguyen et al. (2009) calculated the relative distribution of intermediate products (RAD1 and RAD2) for the ozonolysis of the endocyclic double bond of BCP. The results for RAD1A, RAD1B and RAD2A in ozonolysis scheme (Fig. 1) were 0.1%, 6.7% and 1.4%, respectively, and thus the maximum yield of the formed alkyl radicals is estimated to be 8.2% and corresponds to the maximum theoretical yield of ELVOC obtained from the ozonolysis. However, the radicals can be lost in multiple different reaction pathways that do not form ELVOC (e.g. Rissanen et al. 2014), which can result in much lower yields for ELVOC.

Estimating vapour pressures of the BCP oxidation products

We estimated the volatility of the highly-oxi-
dized compounds according to their carbon oxidation state oSc (Droll et al. 2011),

\[ \text{oSc} = 2 \frac{n_0 - n_\text{H}}{n_c - n_c} \]  

(2)

where \( n_c \) is the number of carbon atoms, \( n_\text{H} \) is the number of hydrogen atoms and \( n_0 \) is the number of oxygen atoms in the molecule; the O-to-C ratio; and saturation concentration, \( C^0 \) (Donahue et al. 2011)

\[ \log_{10} C^0 = \left( n_0 - n_c \right) b_C - n_0 b_O - 2 \frac{n_c n_0}{n_c + n_0} b_{CO}, \]  

(3)

where \( b_C \) is the carbon–carbon interaction term (about 0.475), \( b_O \) is the oxygen-oxygen interaction term (about 2.3), \( b_{CO} \) is the carbon-oxygen nonideality (about –0.3) and \( n_0^0 \) is the carbon number at \( C^0 = 1 \mu g \text{ m}^{-3} \) for alkane. These terms were adopted from Donahue et al. (2011).

After calculating these three parameters we found that all the detected SQT oxidation prod-
Highly oxidized organic compounds from ozonolysis of β-caryophyllene

Products can be classified as extremely low-volatile organic compounds if they have an oxygen number of five or more (C_{15}H_{22}O_5 upwards), meaning that these compounds have a saturation concentration of log_{10} (C_{15}H_{22}O_5 / µg m^{-3}) < -3.5 (Donahue et al. 2011).

Results and discussion

Laboratory experiments

We started the laboratory experiments with β-caryophyllene injection into the flow tube, followed by addition of ozone, to see whether the reaction product spectrum would reveal similar highly oxidized compounds to those measured with several different monoterpenes (Ehn et al. 2014, Jokinen et al. 2015). In the mass spectrum, the formed monomers with a C_{15} carbon skeleton and dimers with a C_{29}–C_{30} carbon skeleton with high oxygen content were detected in the mass-to-charge ratio (m/z) ranges 340–520 Th and 350–800 Th, respectively (Fig. 2).

The most intense signals were observed in the monomer range at m/z of 378.14 Th and 408.11 Th corresponding to C_{15}H_{24}O_7 and C_{15}H_{22}O_9, respectively. The highly-oxidized ELVOC RO_2 radicals produced in the ozonolysis initiated autoxidation, as suggested by Jokinen et al. (2014), were detected and identified as C_{15}H_{23}O_8,10,12 (with 2–4 possible –OOH groups). The corresponding closed-shell monomers were also detected and they had a composition of C_{15}H_{22}O_7,9,11,13 (loss of –OH from the corresponding RO_2). We found several peaks that could be explained by the autoxidation from ozonolysis, and also by OH-initiated reactions, in the monomer range (Table 1). However, the peaks with an elemental composition of C_{15}H_{24}O_7,9,11 cannot be explained by pseudo-unimolecular autoxidation steps only. Since the flow tube experiments were done in a relatively high concentration of BCP, the fate of the formed RO_2 radicals will also be

![Fig. 2](image-url)
the reaction with other RO₂ radicals. This way an ELVOC RO₂ radical (e.g., C₁₅H₂₃O₈⁻) could undergo a reaction with RO₂ radical to form a RO radical (C₁₅H₂₃O₇⁻). After an intramolecular H-transfer (formation of the next RO₂ radical) and a further reaction with HO₂ can explained the peak identified as C₁₅H₂₄O₇⁻. Further autoxidation steps before the RO₂ + RO₂ reaction will lead to the production of the detected C₁₅H₂₄O₉⁻ and C₁₅H₂₄O₁₁⁻. The strongest dimer signals were identified as C₂₉H₄₆O₁₂⁻,₁₄⁻,₁₆⁻ and C₃₀H₄₆O₁₂⁻,₁₄⁻,₁₆⁻ (Fig. 2).

From these experiments, we can conclude that β-caryophyllene, and thus probably also other endocyclic SQTs, are able to produce highly-oxidized reaction products under atmospheric conditions. The detected compounds, from C₁₅H₂₃O₅⁻ to C₁₅H₂₃O₁₃⁻, have an O-to-C ratio from 0.33 to 0.87, carbon oxidation state (oSC) from −0.8 to 0.27 and log₁₀(C/µg⁻¹ m⁻³) from −4.5 to −21.0.

We calculated the total yield for highly-oxidized organic compounds from β-caryophyllene ozonolysis (without OH-scavenger) using a reaction rate of 1.1 × 10⁻¹⁴ cm³ molecules⁻¹ s⁻¹ [k(BCP + O₃)] that is obtained from both theoretical calculations (Nguyen et al. 2009) and experimental works (Shu and Atkinson 1995, Winterhalter et al. 2009, Richters et al. 2015). However, it should be noted that the values reported in the literature for the same reaction rate vary up to three orders of magnitude, depending on the method used (Ghalaieny et al. 2012). Ozonolysis of BCP produces OH radicals (~6%–10% from endocyclic and 16.4% from exocyclic double bond reactions; Winterhalter et al. 2009, Shu and Atkinson 1995), and since no OH-scavenger was used in this experiment, the oxidation of BCP with OH is competing with ozonolysis. We calculated the total yield of highly-oxidized organic compounds (ELVOC) to be 1.7% ± 1.28%. This result was obtained when only the data points closest to the linear fit (magenta squares in Fig. 3) and the reaction rate (k) from Richters et al. (2015) were used. When the entire data range was included, the ELVOC yield dropped to 1.1% ± 0.83%, which is still within the measurement uncertainty.

**Field measurements**

The field measurement campaign was carried out during the spring months in 2011 at the SMEAR II station. In Finland, spring is the season when emission rates of terpenes from the forest are increasing rapidly with the increasing temperature, sometimes even creating bursts of emissions (Tarvainen et al. 2004, Aalto et al. 2015). We followed the most abundant compositions observed in the β-caryophyllene ozonolysis system during the last two weeks of the campaign (between 28 March and 12 April 2011), as before this period no signals of SQT oxidation products were observed. Since the spectra in ambient air are more diverse than the ones in laboratory conditions and concentrations are generally lower, we used the knowledge from the laboratory experiments with the exact mass, mass defect and isotopic patterns of each compound to identify them from other possible elemental compositions. The peak intensities of the possible BCP products detected in the mass spectrum in Hyytiälä were very low (Fig. 4). There were many other possibilities for the same integer mass-to-charge ratios, but we were able to fit the peaks according to the exact mass of a few highly-oxidized BCP products, and thus quantify concentrations of these species. However, it has to be noted that oxidation of other SQTs than BCP will likely lead to products with

<table>
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<tr>
<th>m/z</th>
<th>RO₂ (O₃)</th>
<th>m/z</th>
<th>Monomer (O₃)</th>
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<tbody>
<tr>
<td>361</td>
<td>C₁₅H₂₃O₅⁻</td>
<td>344</td>
<td>C₁₅H₂₃O₅⁻</td>
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<td>408</td>
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<tr>
<td>457</td>
<td>C₁₅H₂₃O₈⁻</td>
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<tr>
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<td>458</td>
<td>C₁₅H₂₃O₁₃⁻</td>
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similar elemental compositions, and thus these identified peaks could have additional contribution from other SQTs. Ambient measurement results were thus presented as they were oxidation products of any ambient SQT.

**Observation of electrically neutral SQT oxidation products**

Concentrations of the three detected, highly-oxidized organic neutral molecules from SQT oxidation followed each other during our measurements (Fig. 5A). Their diurnal patterns were quite similar to the corresponding naturally-charged ions (Fig. 6), with the exception of the neutral BCP oxidation products which reached their maximum concentrations during midday. Both neutral molecules and ions had another peak in the late evening. The higher neutral SQT oxidation product concentrations during
daytime were possibly due to the emission rate of SQT from vegetation being the highest during that period, when temperatures are much higher than at nighttime. The nighttime increase in SQT signals was possibly due to the change in the oxidation chemistry, the ozonolysis being the prominent oxidation channel after sunset. The maximum concentrations of highly-oxidized BCP ozonolysis products were just above the detection limit (LOD) for sulphuric acid (3.6 × 10^4 molecules cm^{-3}) (Jokinen et al. 2012), reaching a maximum of a few 10^5 molecules cm^{-3}. The LOD was in this case used as a guideline for the extremely low-volatile molecules assuming they would have similar volatilities as sulphuric acid. The highest concentration during the field measurements was observed from C_{15}H_{24}O_{9}.

Observations of SQT oxidation products in naturally-charged ions

During the first week (Fig. 5B), the signals of all of the detected highly-oxidized naturally-charged ions were weak and their identification was difficult to some extent due to several different compounds present within the same mass spectral peaks. Those days had high concentrations of bisulphate (sulphuric acid) and its oligomer ions, the signals of which contributed to the measured ion distribution. As a strong acid with very low proton affinity, sulphuric acid was the dominant ion and thus only a few other signals were detected during daytime. During the last week of the measurements, we saw an indication of the effect of the rising temperature on the BCP ozonolysis product signals (Fig. 5C). The most intense signal observed was from C_{15}H_{24}O_{9}NO_{3}^−, with an O-to-C ratio of 0.6. The maximum signals of the BCP ozonolysis products were seen around midday or late in the evening when sulphuric acid signals decreased. Altogether, even when the SQT oxidation products were at their highest level (in the evening), their maximum contribution to the total ion counts detected was ~0.02%, however a slight positive trend of signals increasing towards the end of spring was present. A longer period should be recorded for more detailed analysis of BCP oxidation product evolution in the ambient air.
Conclusions

This study reports important information on the ozonolysis reaction products of one of the most emitted sesquiterpene, β-caryophyllene. This extremely reactive compound with atmospheric ozone was shown to produce low-volatile organic compounds that were detected in laboratory and ambient-air measurements. The spectrum obtained from β-caryophyllene ozonolysis showed similar patterns as that of ELVOC [part deleted] (Ehn et al. 2014, Jokinen et al. 2015, Schobesberger et al. 2013). Formations of oxidized monomers with a C15 carbon skeleton and dimers with a C30 carbon skeleton were detected immediately when ozone was introduced into the BCP system. In the laboratory experiments, we positively identified several highly-oxidized organic compounds in the mass spectra corresponding to the RO2 radical, monomer and dimer species. The most abundant monomer species in this study were C15H24O7-9-11 and C15H22O9-11, and the most intense dimer signals were identified as C29H46O12,14,16 and C30H46O12,14,16. These oxidized organic compounds have the O-to-C ratio of ~0.3–0.9 in the monomer and ~0.3–0.6 in the dimer range. The volatility of these reaction products was evaluated using several quantities, including their O-to-C ratio, and all of the detected compounds were classified as extremely low-volatile organic compounds due to their saturation concentration (log10(C0/µg m–3) < 3.5; Donahue et al. 2011).

The yield of ELVOC from BCP ozonolysis without using an OH scavenger was determined to be 1.7% ± 1.28%, which seems reasonable as the maximum theoretical yield is ~8%. The lower yield may be explained by other reactions occurring before the autoxidation sequence takes place, determining the fate of the initially-formed primary ozonide. If the breaking of the POZ needed for radical formation is hindered, it can lead to a dramatic transformation in the dominant oxidation pathway from a radical-forming process at a low carbon number (isoprene and maybe monoterpenes) to a secondary ozonide-forming process at a high carbon number like in the case of sesquiterpenes (Chuong et al. 2004), thereby also decreasing the possible low-volatile product formation.

Highly-oxidized organic compounds were also measured at the SMEAR II station. Three sesquiterpene oxidation products, originating from BCP or other SQTs, were identified in both naturally-charged ions and in neutral form in the ambient air in the spring of 2011. The observed concentrations of the neutral species were extremely small, reaching a maximum of a few hundred thousand molecules cm–3 during the two weeks of measurements. In naturally-charged ions, the SQT ELVOC contributed a minimal signal that was up to 0.02% of the total ion signal detected at this site.

The contribution of low-volatile products from the SQT ozonolysis (BCP and others) may affect the SOA burden and contribute to aerosol growth in places where high emission rates of SQT are observed, e.g. in the USA or northern Finland (Tarvainen et al. 2004). BCP ozonolys-
sis products are classified as ELVOC when the number of oxygen atoms in the product molecule reaches five or more, after which they are able to affect nanoparticle growth by condensing onto them. However, the impact might be important only locally or regionally if the emissions are high compared with emissions other important VOCs such as monoterpenes and certain anthropogenic hydrocarbons. Further and more exact information is needed on the reactivity of different SQTs emitted by terrestrial vegetation before we can evaluate the effect of SQT ELVOC on atmospheric new particle formation and growth.

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References


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