Responses to the Referees' comments
"Biotic stress accelerates formation of climate-relevant aerosols in boreal forests" by
Joutsensaari et al.

<mark>Note that after Responses to the referees, there is a revised version of MS where changes in
the text have been marked as yellow background color.</mark>

Anonymous Referee #1

We thank the referee for valuable comments that we have used to improve our manuscript.
We have considered the comments and have modified the manuscript accordingly. Our
detailed responses to the referee's comments are below.

Referee's comment:
1) The authors used seedlings in the laboratory experiments. While this is certainly required
to make the lab experiments tenable, could the authors comment on potential VOCs
emissions difference between adult and juvenile trees? Does the VOC distribution or the total
emission change as maturity is reached?

Authors' response, changes in MS:
This is an important point. Therefore we have added the following sentence to the discussion
(section 3.1).

"We conducted our laboratory experiment with young seedlings due to practical restraints for
a laboratory study, but these results should be representative of emissions of full grown forest
trees because monoterpene composition of needles and wood of Scots pine are under strong
genetic control. A 19-year monitoring study indicated that seedlings of Scots pine
provenances at the age of four and twelve months has similar composition as the fresh cut
stumps 19 years later (Kivimäenpää et al. 2012). "

Referee's comment:
2) The authors randomly selected insect-stressed areas for the model portion of the study (see
Figure 6 figure caption). While the need for random selection is sensible for initial
application, insect outbreaks are not random and are driven by local climate and geography
(see Aukema, Ecography, 2008). Outbreak clustering could lead to concentration of VOCs in
a more limited geographic range, in comparison to random outbreak, and this could lead to a
different AOD distribution, causing local minima. How does the insect outbreak location
impact the results of model?

Authors' response:
We agree, but argue that such clustering would not have an impact on our main conclusion,
i.e. that insect herbivory can affect aerosol forcing on a regional scale. Some indication on the
impact of clustering can be seen in Fig. 6, where two or more model grid cells close to each
other (over Siberia, Eastern Canada and Finland) are randomly selected to experience insect
damage (Fig. 6a). Figure 6b clearly shows that over these areas the strong impact on aerosol
mass is spread more uniformly over a larger region than over areas where only one model
grid is impacted by insect damage. However, over most areas this effect disappears when
looking at CCN concentrations (Fig. 6c). This is because the CCN concentration increase is
strongly impacted by the background aerosol size distribution, which varies between the

51 regions. We also note that given the coarse resolution of the model, each model grid cell is
52 2.8°×2.8° in area, and thus the simulated insect outbreaks are not highly localized.
53
54 Referee's comment:
55 3) The analytical precision of the measured values was likely overestimated in a few places.
56 For example in Table 3, the average limonene emission from Neodiprion sertifer damaged
57 was listed to six significant figures, and this level of precision is not practicable (or needed).
58 In addition, the average alpha-terpineol emission was listed as zero, whereas a true zero
59 cannot be reasonably measured, and instead "below detection limits" (with the detection limit
60 listed) is a more commonly accepted practice.
61
62 Authors' response:
63 We note that analytical precision of VOC emission rates (ng/g(DW)/h) is lower than values
64 presented in tables (e.g., six digits). Due to large variation in concentrations, we have just
65 presented all VOC values with one decimal. However, standard deviations (SD) of values are
66 also presented so reader can estimate accuracy of results. If needed, we can present the values
67 with 2 significant digits in the revised MS.
68
69 Referee's comment:
70 In addition, the average alpha-terpineol emission was listed as zero, whereas a true zero
71 cannot be reasonably measured, and instead "below detection limits" (with the detection limit
72 listed) is a more commonly accepted practice.
73
74 Authors' response, changes in MS:
75 Emission rates are calculated from VOC concentration, sample flow rates and needle dry
76 masses so "detection limit" in VOC emission varies case by case. We estimated the average
77 detection limit was around 0.1 ng/g(DW)/h. In the revised version of manuscript (Tables 3, 4
78 and 5), zero values have been replaced with the term "Not detected" (-) which indicated that
79 values are zero or below detection limit (i.e., very low compared to the values of main
80 compounds).
81
82 Referee's comment:
83 Figure 3 and Figure 4, bottom panels: some of mass concentration and number concentration
84 data points are connected by lines and some are not. What do the lines indicate? And why is
85 this inconsistent–were some of the data points removed or averaged/smoothed?
86
87 Authors' response:
88 The data points are connected with line in each series. However, zeros and not-a-number
89 (NaN) values cannot plot in log scale and thus lines between those and previous/next values
90 are not shown. Anyhow, the values are very low (near to zero) in control experiments so
91 "missing" data points in the figures have not any effect on the results. The results are not
92 averaged or smoothed.
93
94 Referee's comment:
95 Suggested Typographical Corrections…
96
97 Authors' response, changes in MS:
98 Typographical corrections suggested by the referee have been corrected in the revised version
99 of manuscript.
100

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Anonymous Referee #2

We thank the referee for valuable comments. We have considered the comments and have improved accordingly the manuscript (MS). Our detailed responses for the referee's comments are bellow.

Referee's general comment:
None of the elements are flawed and the limitations of the techniques are largely recognized appropriately. However, I find the paper is poorly linked, such that it appears as though it is two separate studies. This must be addressed before it is acceptable for ACP, either by making stronger, clearer linkages or by extending the individual aspects so as to make them suitable for separate publications.

Authors' response:
The main aim of this study is to investigate the climate change feedback between increased herbivore outbreaks, SOA production, and CCN concentrations from a variety of perspectives to provide a broadened perspective of the potential magnitude of the effect. Consequently, this study summarizes the results from field and laboratory experiments, satellite observations and global scale modeling in order to get wider knowledge of the effects of insect herbivory and outbreaks on SOA formation and the Earth's climate. Not just present results from individual studies. We believe that this integrated interdisciplinary approach that evaluates plant biological, ecological and atmospheric processes concomitantly is novel and warrant. We think that one publication connecting individual aspect together is stronger than separate publications with individual aspects. Therefore, we have clarified the linkages between experimental studies, global scale modeling and satellite observations in order to meet the remarks presented by the referee.

Referee's specific comment:
My main concern centres on the lack of linkage between the treatment of SOA formation in the GLOMAP model and the experimental evidence. In only using an enhancement in SOA-precursor emission rates resulting from insect attack, the modelling is isolated from the experiments. It is stated that "for computational affordability, [the authors have] made a simplifying assumption that 13% of [the] oxidation products [of MT] form vapours capable of producing SOA". First, this approach omits any SOA formed from SQT. This may be a reasonable approximation in other GLOMAP applications, but in the context of the current paper where substantial enhancements in SQT are reported from insect attack, this appears over simplistic. The laboratory and field SOA enhancements will undoubtedly include the contributions from such enhancements. The previous demonstration of GLOMAP's ability to respond to increased VOC emissions are based on the MT yield of SOA precursors. Furthermore, scaling the GEIA emissions database of MT emissions to include SQT must assume a constant relationship between SQT emissions and MT and between enhancements of MT and enhancements of SQT. This is clearly not the case from the field measurements reported here, nor from previous studies. Moreover, the omission of stress-responders other than MT or SQT may lead to very significant omission of SOA response. I cannot see a

151 justification for an assumption that a simple scaling of MT emissions will represent a
152 response that can be confidently assumed order of magnitude representative of the
153 measurements.
154
155 Authors' response, changes in MS:
156 We have recognized the lack of linkage between the laboratory and field experiments and the
157 GLOMAP modeling. However, at this point in time we do not believe there is sufficient
158 experimental data on SOA yields from plant stress compounds to incorporate the results into
159 a global model in a meaningful way. However, this is a first attempt at global modelling of
160 the phenomenon that serves as a useful illustration of the possible scale of its global
161 consequences. In all likelihood, the results presented here would actually be a conservative
162 lower limit of the potential impacts of herbivore outbreaks because increasing sesquiterpenes
163 would only increase the observed effect. We do agree with the reviewer, however, that a final
164 word on this matter will need much more detailed investigation in the future – this is not,
165 however, in the scope of this study.
166
167 The technical reason for omitting sesquiterpene from our simulations was that suitable
168 spatially resolved emission datasets at the global scale were not available when the
169 simulations were run. While such datasets have since emerged, we decided not to rerun the
170 model because 1) of its extensive computational expense, and 2) inclusion of sesquiterpenes
171 would not impact our (rather general) conclusion that the insect herbivory can affect aerosol
172 forcing on a regional scale. This decision still seems valid in the light of recent research
173 findings: For example, D'Andrea et al. (2015) estimated that in the boreal forest region
174 monoterpenes are responsible for up to over 80% of SOA formation, while sesquiterpenes
175 play a much less significant role (always below 20%, but in many areas below 10%
176 contribution to SOA).
177
178 However, the reviewer comments make it evident that the original manuscript did a poor job
179 communicating the motivation and aim of the GLOMAP model runs. To remedy this, we
180 have modified the text in the following way:
181
182 Section 2.3, first sentence:
183 "An evaluation of the significance of insect damage on atmospheric boreal aerosol was
184 obtained with a global chemical transport model, GLOMAP, to provide a first estimate of the
185 potential scale of the impact.
186
187 Section 3.3, first paragraph:
188 "We used a simplified SOA formation set-up within the GLOMAP model to assess whether
189 the large-scale insect outbreaks could potentially impact Earth's climate. The model set-up is
190 summarized in Fig. 6a: 10 % of the total boreal conifer forest suffered insect herbivory with a
191 10-fold increase in monoterpene emissions in outbreak areas. Note that the simulations do not
192 include sesquiterpene emissions, as they are not incorporated in the model version used here.
193 Thus the results presented here likely represent a conservative lower-bound of the potential
194 impact as any increases in sesquiterpene emissions would serve to increase SOA yields even
195 more dramatically. Furthermore, D'Andrea et al. (2015) have recently estimated that in the
196 boreal forest region monoterpenes are typically responsible for up to over 80% of SOA
197 formation, while sesquiterpenes play a much less significant role. We do not expect this
198 short-coming to impact our conclusions, which are intended to merely indicate whether insect
199 herbivory could be of regional importance, and thus merit more detailed model studies in the

200 future. A 10-fold increase in monoterpene emissions in 10 % of the total boreal area are
201 conservative estimates --- "

205 Referee's specific comment:
206 There needs to be some clarification of the GLOMAP mechanistic treatment. Is a 13% yield
207 of all oxidation products assumed to be SOA-forming (i.e. from both OH and O3)? If so,
208 what is the justification of the scaling given the enhanced SOA yields were based on O3-
209 initiation only? Unless the yield is from O3-initiation alone, I can only see this as further
210 disconnect between the modelling and measurements.

212 Authors' response:
213 We are not quite certain what the reviewer means here. The fixed 13% yield of SOA forming
214 compounds from monoterpene oxidation is used both for OH and O3 routes in all areas (i.e.
215 both in insect damaged and background areas). We have based our scheme on the observation
216 that insect damage significantly enhances the monoterpene *emissions*, not on the
217 observation that it enhances SOA yields due to O3 pathway (although that of course is true
218 too). Overall, higher emissions lead to higher monoterpene concentrations, which then can
219 react further both via OH and O3 pathways; therefore, the assumption of higher concentration
220 of SOA forming oxidation products also via the OH route is not unrealistic. We further stress
221 that the yield (13%) stays the same for both oxidation pathways, and in all simulated areas.

223 Referee's general comment:
224 In summary, I don't see the clear justification for the assumption that the increase in CCN
225 and SOA mass exhibited in GLOMAP for a given increase in MT bears a close relationship
226 to the phenomenon observed in the measurements. Given the disconnect, I would have
227 probably combined the GLOMAP and satellite components into one phenomenological paper
228 (abstract of which is line 16 onwards of the current abstract) and expand the field and lab
229 experiments into a more quantitative mechanistic paper (abstract lines 10-16 of the current
230 abstract).

232 Authors' response:
233 As mentioned earlier, we believe that one publication including different perspectives to
234 investigate the same question is stronger than separate publications since it evaluates the
235 question across scales - from field and chamber studies to global scale phenomena. We
236 acknowledge that connection between experimental and modeling studies could be stronger.
237 We wish to stress again that the global simulations were not intended as a definitive
238 quantification of the effect of biotic stress on boreal atmospheric aerosol but merely as a first-
239 order approximation to demonstrate that this phenomenon may be of regional importance and
240 thus merits further study.

242 Referee's specific comment:
243 If all elements of the paper are to remain, the following should be considered:
244 i) the coherence between the model and measurements should include results from OH
245 initiated oxidation in the chamber experiments or eliminate the OH-initiated enhancement in
246 condensable vapour concentration in GLOMAP or make a convincing argument for some
247 correspondence between them.

249 Authors' response:

250   In our chamber experiments, ozonolysis of terpenes included also OH induced oxidation
251   because we did not use any OH scavenger which inhibits formation of OH via ozonolysis of
252   VOCs (see Hao et al, 2009). Therefore, we do not believe that chamber experiments with
253   only OH initiated oxidation or the elimination of OH pathways in GLOMAP could change
254   our main conclusions. As stated earlier, GLOMAP model was used to obtain the order-of-
255   magnitude estimate of the potential significance of insect damage on atmospheric boreal
256   aerosol, not to analyze in detail the effect of different SOA formation mechanism.
257
258   Referee's specific comment:
259   ii) the extrapolation of chamber yields to models is fraught with danger and it is
260   understandable that the authors have avoided making a linkage. However, some discussion
261   about the relationship between the 13% yield of condensable vapours in the model and the
262   measured SOA yields should be included. This raises a number of points. The authors
263   recognise the effect that walls can have on leading to underestimates. However, the yields
264   from different chambers under different conditions also give wildly differing values, even for
265   single precursors, which need to be mentioned.
266
267
268   Authors' response:
269   We note that extrapolation of chamber yields to models is not straightforward. "SOA yield"
270   as calculated in a chamber experiment is not necessarily meaningful for global modeling
271   applications that are intended to represent an ambient environment. Yields are affected by a
272   complex suite of variables including, but certainly not limited to, precursor concentration
273   (Kang et al., 2011; Kroll et al., 2008; Pfaffenberger et al., 2013; Presto and Donahue, 2006),
274   seed particle composition/loading (Ehn et al., 2014; Hamilton et al., 2011), and mass of
275   absorbing organic aerosol material present in the chamber (Pankow, 1994; Odum et al.,
276   1996). Thus, while it is potentially useful to compare SOA yield curves (yield vs. organic
277   aerosol loading) between different laboratory experiments to gain insight into differences
278   between the SOA formation behavior of the precursor BVOC profiles, it is not meaningful to
279   arbitrarily select a single SOA yield number from those curves to use in a global modeling
280   application. This is why we used a more simplified approach for the global modeling
281   application where an SOA yield value of 13% was used for biogenic emissions as is common
282   practice in global modeling applications. In this study, average SOA mass yields vary
283   between 0.1–3% in control experiments and 5–40% in insect-damage experiments (overall
284   averages 1% and 18%, respectively). The yield used is line with our insect-damage
285   experiments but higher than obtained from control experiments, which might overestimate
286   SOA formation in low organic mass (control) areas. However, this does not change our main
287   conclusions.
288
289   We also note that differences in chambers, conditions, precursors, etc. have an effect on
290   yields. However, we think that yields determined form the emissions of real boreal forest
291   trees are more representative than from single component (e.g. a-pinene) experiments. We
292   have included discussion on the relationship between model and experimental yields in the
293   revived version of MS (Chapter 3.2).
294
295   We have already discussed (page 10868) the effect of total organic mass loading and wall
296   losses on SOA mass yields as well as compared previous studies on boreal trees. To revised
297   versions of manuscript, we added a general note on the variation of yields depending on
298   chambers, conditions and precursors (Chapter 3.2).
299

Authors' changes in MS:
We have added the following discussion at the end of paragraph on SOA mass yields (Chapter 3.2): "Furthermore, the SOA mass yields determined from different chambers under different conditions can vary widely (Lee et al., 2006; Shilling et al., 2008; Mentel et al., 2013; Hao et al., 2011) and therefore it is not straightforward to assess a suitable yield values for model calculations. In this study, we have used a fixed 13 % yield (all cases) in the GLOMAP modeling as is common established practice for regional to global scale modeling applications. This value is also consistent with our insect-damage experiments (overall averages 18%). This fixed yield value might overestimate SOA formation in control areas with lower VOC and SOA mass concentrations, so the potential effect observed here would be a lower estimate of the potential effect."

Referee's specific comment:
Ozonolysis experiments are very susceptible to the relationship between the position and timing of introduction of ozone into chamber and relationship to the measurement point. A description of the mixing of the plant emissions with the ozone rich air and the methodology for SOA sampling in the chamber should be included.

Authors' response, changes in MS:
The schematic of ozonolysis experiments is shown in Fig. 1 and described on page 10859. At the inlet of the reactor, air flow from the seedling headspace (2 L/min) was mixed (in T-fitting) with an ozone-enriched air flow (total flow 17 l/min). O3 concentrations were measured from main air flow at the inlet and outlet of the reactor. Aerosol samples were collected from the main air flow at the outlet of reactor (see Fig. 1). We have clarified those points in the revised MS (Ch. 2.2.1 and 2.2.3). We have also chanced O3,inlet values in Table 1, now the dilution due to plant chamber air flow was taken into account (values now ca. 10 % lower).

Referee's specific comment:
Chamber experiments using mixtures are more complicated than using single precursors. Since the timescales for oxidation of MT and SQT will be very different, the concept of yield for mixtures is problematic and the way that dilution of a mixture in the real atmosphere occurs will mean that yields do not combine in any way similar to the way they combine in a chamber (and in neither case will they be linear). The method for calculating yield (as plotted in Figure 5) should be described. In reality it will be a combination of sequential yields, the most reactive first. Since ozonolysis of SQT gives significant OH yields, the subsequent SOA formation of less reactive precursors will include some OH-initiation (helping the linkage between the modelling and experiments a little, but not sufficiently, since it will be so different to the atmosphere) and depend on the relative reaction rates of the remaining mixture with different oxidants.

Authors' response:
We note that experiments with VOC mixtures are more complicated (e.g. complicated reaction chemistry) than pure compound experiments. Although, timescales for oxidation of different compound will be very different and subsequent reactions occur, we believe that SOA mass yields determined form real plant emissions are more representative than those derived from single component (e.g. a-pinene) experiments since multi component system in closer atmospheric situations than one component system. The method to calculate yield is described on the page 10861.

Referee's general comment:
I may have missed the point of the paper, but the above queries should be addressed before it is suitable for publication in ACP. Alternatively, the point of linking the experimental and modelling elements of the paper should be much more clearly made.

Authors' response:
Briefly, the main point of the papers is that more frequent insect outbreaks in a warming climate could result in substantial increase in biogenic SOA formation in the boreal zone and, thus, affect aerosol forcing of climate at regional scales. This should be considered in future climate predictions.

Authors' general remarks:
To study comprehensively the effect of insect outbreaks on global scale, very time consuming and intensive studies in different areas are needed, e.g., laboratory and field experiments with different tree species to evaluate effects of biotic and abiotic stress on VOC emissions and SOA formation, updating VOC emission models in global aerosol and climate models (e.g. MEGAN) based on field and laboratory results, aerosol and global scale modeling, etc. We think that this would require a several-year-long project to concern all aspect in detail. Ultimately, this manuscript demonstrates that across a range of scales (laboratory experiments to regional modeling) and across a variety of investigation methods (laboratory and field measurements, GLOMAP modeling, satellite data products) the potential impact of herbivore outbreaks on SOA formation is significant even when the assumptions used would arguably result in a conservative, lower-bound estimate of the effect. This study provides a strong rationale prompting further investigation, and highlights the importance of research on this biosphere-atmosphere climate change feedback.

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Biotic stress accelerates formation of climate-relevant aerosols in boreal forests

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1   **Abstract**

2   Boreal forests are a major source of climate-relevant biogenic secondary organic

3 aerosols (SOA) and will be greatly influenced by increasing temperature. Global warming is

4 predicted to increase emissions of reactive biogenic volatile organic compounds (BVOC)

5 from vegetation directly, but will also induce large-scale insect outbreaks, which significantly

6 increase emissions of reactive BVOC. Thus, climate change factors could substantially

7 accelerate the formation of biogenic SOA in the troposphere. In this study, we have combined

8 results from field and laboratory experiments, satellite observations and global scale

9 modelling in order to evaluate the effects of insect herbivory and large-scale outbreaks on

10 SOA formation and the Earth's climate. Field measurements demonstrated 11-fold and 20-fold

11 increases in monoterpene and sesquiterpene emissions, respectively, from damaged trees

12 during a pine sawfly (*Neodiprion sertifer*) outbreak in eastern Finland. Laboratory chamber

13 experiments showed that feeding by pine weevils (*Hylobius abietis)* increased VOC emissions

14 from Scots pine and Norway spruce seedlings by 10-50 fold resulting in 200-1000 fold

15 increases in SOA masses formed via ozonolysis. The influence of insect damage on aerosol

16 concentrations in boreal forests was studied with a global chemical transport model

17 GLOMAP and MODIS satellite observations. Global scale modelling was performed using a

18 10-fold increase in monoterpene emission rates and assuming 10 % of the boreal forest area

19 was experiencing outbreak. Results showed a clear increase in total particulate mass (local

20 max. 480%) and cloud condensation nuclei concentrations (45 %). Satellite observations

21 indicated a two-fold increase in aerosol optical depth (AOD) over western Canada's pine

22 forests in August during a bark beetle outbreak. These results suggest that more frequent

23 insect outbreaks in a warming climate could result in substantial increase in biogenic SOA

24 formation in the boreal zone and, thus, affect both aerosol direct and indirect forcing of

25 climate at regional scales. The effect of insect outbreaks on VOC emissions and SOA

26 formation should be considered in future climate predictions.

27

1 Introduction

Atmospheric aerosols have a strong but highly uncertain influence on the Earth's radiation balance and climate (IPCC, 2013). Formation of secondary organic aerosols (SOA) in the troposphere, i.e., particle production by oxidation of volatile organic compounds (VOC), is one of the main processes affecting composition and properties of atmospheric aerosols (Hallquist et al., 2009; Jimenez et al., 2009; Kanakidou et al., 2005). VOC emissions from vegetation (i.e., biogenic VOC) are important precursors for SOA (Claeys et al., 2004; Kanakidou et al., 2005; Kavouras et al., 1998; Guenther et al., 1995) as first suggested in 1960 (blue haze) (Went, 1960). On a global scale, biogenic VOC emissions to the atmosphere, mainly monoterpenes and isoprene from terrestrial ecosystems, constitute about 90% of all global VOC emissions (Guenther et al., 1995) and therefore have an important impact on the global climate. Plant-emitted VOC readily react with atmospheric oxidants forming low volatility oxidation products that may have a key role in new particle formation in forested areas (Ehn et al., 2014; Kulmala et al., 2013; Laaksonen et al., 2008). The boreal zone is estimated to be a major source of climate-relevant biogenic aerosol particles (Tunved et al., 2006a) and, in a warmer climate, boreal forests may emit sufficiently large amounts of organic vapours to modify cloud albedo and cool the climate (Spracklen et al., 2008b). However, the contribution of biogenic VOC to the global aerosol burden is still unclear.

Boreal coniferous and mixed deciduous forests cover a land area of about 21.5 million km^2 at northern latitudes (Potapov et al., 2008) and they will be greatly influenced by increasing temperature (IPCC, 2013; Mikkonen et al., 2014). The huge boreal forest biome has the potential to substantially affect global temperatures by controlling the atmospheric CO_2 concentration (Kurz et al., 2008a) and land surface albedo (Bala et al., 2007). However, conifers are known to be sensitive to pest and disease outbreaks (Kurz et al., 2008a; Kurz et al., 2008b). Global warming is predicted to induce large-scale insect outbreaks in the boreal forests (Kurz et al., 2008a; Niemelä et al., 2001; Veteli et al., 2005). Herbivorous insect species could survive better in a warming climate by moving to higher latitudes and escaping from their natural enemies (Berryman, 1987). High mortality of over-wintering herbivorous insect stages due to low winter temperatures is crucial to limiting population growth (Kurz et al., 2008a; Veteli et al., 2005) and therefore climate warming will facilitate large-scale insect outbreaks (Niemelä et al., 2001). In recent years, about 130 000 km^2 of Canada's pine forests

have been affected by large-scale mountain pine beetle outbreaks, and only extremely cold weather is expected to stop the epidemic (Kurz et al., 2008a). The dominating outbreak species in Eurasian forests will be pine sawflies on Scots pine (De Somviele et al., 2007), autumnal moth on mountain birch and winter moth on deciduous tree species (Niemelä et al., 2001).

Feeding by insects induces larger and more diverse biogenic VOC emissions from plants (Blande et al., 2007; Holopainen and Gershenzon, 2010). Herbivore damage to deciduous (Blande et al., 2007) and coniferous (Blande et al., 2009; Amin et al., 2012; Berg et al., 2013; Ghimire et al., 2013) boreal trees results in a substantial increase in highly reactive VOC emissions, e.g., sesquiterpenes (Bonn and Moortgat, 2003). Our first plant chamber experiments (Joutsensaari et al., 2005) demonstrated that simulation of herbivore feeding by a chemical elicitor substantially increased new particle formation by ozonolysis. Furthermore, recent chamber and modelling studies have shown that insect infestation can significantly increase SOA formation (Mentel et al., 2013; Berg et al., 2013; Bergström et al., 2014).

To understand climate change effects on SOA formation in herbivore-stressed forests, there is an urgent need for an integrated interdisciplinary approach that evaluates plant biological, ecological and atmospheric processes concomitantly. In this study, we combined results from field and laboratory experiments, satellite observations and global scale modelling in order to evaluate the effects of insect herbivory and large-scale outbreaks on SOA formation and the Earth's climate. Here we show that insect feeding increases the total VOC emission rates from coniferous trees (i.e. Scots pine and Norway spruce) and significantly enhances formation of climate-relevant aerosols. Firstly, the effects of insect feeding on tree VOC emissions in the boreal forest site and in laboratory experiments were assessed. Secondly, SOA formation by oxidation of plant-emitted VOCs was studied in the laboratory using current ambient (50 ppb) and potential future peak (200 ppb) tropospheric ozone levels. Finally, the influence of large-scale insect outbreaks on local aerosol and cloud condensation nuclei (CCN) concentrations were investigated using satellite observations and global scale modelling.

2   Materials and methods

2.1   Field experiments

To assess the effects of an insect outbreak on VOC emission rates of a forest stand, a field study was conducted at the site of a European pine sawfly, *Neodiprion sertifer* (Geoffroy) (Hymenoptera: Diprionidae) outbreak in Outokumpu, eastern Finland (N 62° 47' 02", E 29° 01' 32") on June 30th 2010. The outbreak covered an area of 50 000 hectares reaching a maximal point in 2009 and showing the first signs of retrogradation in 2010. The mean stand characteristics were the following: age 14.2 y, height 2.23 m, diameter at breast height 1.99 cm, and needle loss rate of 20 % at the end of the growing season. We measured VOC emissions from intact Scots pine trees and trees damaged by the European pine sawfly during the larval feeding period.

We collected VOCs from one branch (third or fourth whorl from the top of the crown) of 10 non-damaged control trees and 10 sawfly-damaged Scots pine trees (for technical reasons 3 samples were lost). Polyethylene terephthalate (PET) bags (size 45 × 55 cm, LOOK, Terinex Ltd, Bedford, England) were heated at +120 °C for 1h before collections to remove any contaminants from the bag, and subsequently cooled. One lateral branch (including the two youngest needle year-classes and feeding larvae on the previous year shoots of damaged seedlings) was enclosed inside the PET bag and fastened securely to the bark taking care not to damage any foliage. The temperature inside the bags was monitored with wireless temperature/humidity loggers (Hygrochron DS1923-F5 iButton, Maxim Integrated Products, Inc., CA). One of the two outermost bag corners was cut and an air inlet was inserted and fastened with a shutter. Clean charcoal-filtered and MnO_2 scrubbed air was pumped through Teflon tubing and into the bag at 600 ml min^{-1} for 15 minutes to flush the system, and then reduced to 300 ml min^{-1} during collections. The volume of the bag was ca. 2 litres during the collection. The remaining bag corner was cut and a stainless steel tube containing approximately 150 mg of Tenax TA-adsorbent (Supelco, mesh 60/80) was inserted and fastened into position. Air was pulled through the Tenax tube by battery-operated sampling pumps (Rietschle Thomas, Puchheim, Germany). For the 15min sampling period the air flow through the Tenax tube was set to 200 ml min^{-1} with an M-5 bubble flowmeter (A.P. Buck, Orlando, FL, USA). A higher flow of the purified replacement air than that into the Tenax tube ensured that no outside VOCs entered the collection bags.

The VOC samples were analyzed with a gas chromatograph-mass spectrometer (Hewlett-Packard GC 6890, MSD 5973, Beaconsfield, UK). Trapped compounds were desorbed with a thermal desorption unit (Perkin-Elmer ATD400 Automatic Thermal Desorption system, Wellesley, MA, USA) at 250 °C for 10 min, cryofocused at -30 °C, and injected onto an HP-5 capillary column (50 m×0.2 mm i.d.×0.5 μm film thickness, Hewlett-Packard) with helium as a carrier gas. The oven temperature program was held at 40 °C for 1 min and then raised to 210 °C at a rate of 5 °C min^{-1}, and to a final temperature of 250 °C at a rate of 20 °C min^{-1}. The compounds (mono-, homo-, and sesquiterpenes and green leaf volatiles, GLVs) were identified by comparing their mass spectra with those in the Wiley library and with pure standards. Monoterpene and sesquiterpene emissions were standardized to 30 °C using previously published algorithms (Guenther et al., 1993; Helmig et al., 2006). Results per unit of needle biomass per hour were calculated as in Faubert *et al.* (2010) with flow rates into the collection bag and the Tenax tubes taken into account.

2.2 Laboratory experiments

2.2.1 Chamber experiments

Figure 1 shows a schematic presentation of the set-up of the plant chamber experiments and Table 1 summarizes the chamber experiments conducted in this study. The SOA formation experiments were carried out in a continuous flow chamber made of Neoflon^{TM} FEP film (type NF-0050, Daikin Industries, Ltd, Japan). The reaction chamber volume was 2 m^3 (1.2 m × 1.2 m × 1.4 m) with an aluminium supporting frame. Air flow from the seedling headspace (2 L min^{-1}) was mixed with an ozone-enriched air flow (target concentrations 45±5 ppb and 190±10 ppb) in a T-fitting at the inlet of the reactor. The total air flow into the reaction chamber was 17 L min^{-1} with an average residence time of 2 h. At the beginning of the trials, VOCs from seedlings were introduced into the chamber 60 minutes (pine) or 90 minutes (spruce) before ozone addition. The duration of the chamber experiment was ca 21 h. The plants diurnal cycle was mimicked by turning off the lights over plant chambers from 24:00 to 03:00. In all experiments, ozone (measured with a DASIBI 1008-RS O$_3$ analyzer), NO$_x$ (Environnement S.A AC 30M NO$_x$ analyzer) and SO$_2$ (Environnement S.A AF21M SO$_2$ analyzer) concentrations were monitored at the inlet and outlet of the chamber. NO$_x$ and SO$_2$

1   values were below detection limits of the analysers (2 ppb) during experiments. Ozone

2   concentrations inside the chamber were stabilised ca. 4-5 h after the start of addition.

3   ### 2.2.2   Plant material and insect treatment

4   Scots pine *Pinus sylvestris* L. seedlings (3-years-old) and Norway spruce *Picea abies* L.

5   Karst. seedlings (3-year old) were used as natural VOC emitters. They were grown in 5 l

6   plastic pots in a mixture of quartz sand and Sphagnum peat. Two intact or insect-damaged

7   seedlings were selected for each SOA-formation experiment. Pot soil was covered with tightly

8   sealed aluminium foil to prevent VOC emission and particle release from the soil entering the

9   plant headspace. Whole plants were enclosed individually in transparent, polyethylene

10   terephthalate PET bags (size 45×55 cm, LOOK, Terinex Ltd, Bedford, England), which were

11   cleaned by pre-heating for 1 h at 120 °C. The opening of the bag was sealed around the outer

12   surface of the polyethylene pot with duct tape. The two outermost corners of the bags were

13   cut, and Teflon tubes were inserted through each. One tube was an air inlet through which

14   clean filtered air was pumped, and the second was an outlet channelling plant headspace air

15   from the bag and into the reaction chamber. Six fluorescent lamps (OSRAM Dulux F

16   24W/41-827, Osram-Melco Ltd., Japan) were positioned around the plants to ensure optimal

17   photosynthesis activity (PAR ca. 350 µmol $m^{-2}s^{-1}$) and VOC emissions at laboratory

18   conditions (24 °C).

19   Each pine and spruce seedling used in chamber experiments had an insect enclosure

20   fitted to the stem. Enclosures were made of polyester mesh and polypropylene foam. Plants

21   damaged by herbivores were infested with four large pine weevil *Hylobius abietis* L.

22   (Coleoptera: Curculionidae) adults that were added to the enclosures. All weevils were kept

23   without food for 24 h prior to experiments to promote feeding, and were left to feed on the

24   stem bark for 48 h before the start of the SOA formation experiment. Insect enclosures

25   attached to control seedlings remained empty. When PET bags were installed for SOA

26   experiments, the weevils and enclosures were removed from plants.

27   ### 2.2.3   VOC and aerosol measurements

28   VOCs were collected in tubes containing about 150 mg of Tenax TA adsorbent

29   (Supelco, mesh 60/80) for 30 minutes with an air flow through the sample tube of 200 ml

30   min^{-1}. GC-MS analysis was the same as in the field experiment but temperature

31   standardization was not done. VOC emissions were quantified as ng g^{-1} (DW) h^{-1} using needle

1 biomass in calculations as weevils only damage conifer bark, but their feeding induces

2 emissions from intact needles in the distal part of the plant (Blande et al., 2009)

3 Particle number concentrations were measured with a condensation particle counter

4 (CPC) (TSI Model 3775, minimum detectable particle diameter 4 nm) and calculated from

5 particle number size distributions. Particle size distributions between 15-740 nm were

6 measured every three minutes at the outlet of the chamber using a scanning mobility particle

7 sizer (SMPS), consisting of a TSI Model 3071A electrostatic classifier and a TSI Model

8 3022A CPC. Particle total mass concentration was calculated from measured number size

9 distribution assuming spherical particle shape and using a density of 1.4 g cm^{-3} for SOA

10 particles (Hao et al., 2009).

11 SOA mass yields were estimated by dividing the formed SOA mass (averaged over

12 several measurements) by the reacted VOC concentrations (i.e., the total terpene

13 concentration at the reactor inlet minus the concentration at the outlet) (Shilling et al., 2008).

14 SOA mass yields were only calculated for steady state situations (i.e. day, night, morning) and

15 thus the first hours of trials with the intensive particle formation were excluded. The

16 experiments were conducted without seed particles, which could lower SOA mass yields by

17 increasing loss of low volatile organics to the chamber walls (Kokkola et al., 2014; Zhang et

18 al., 2014; McVay et al., 2014). However, this would not impact comparisons between the

19 control and herbivore-treated SOA yields because seed particles were not used for either set

20 of plant SOA experiments.

21 **2.3 Global scale modelling**

22 An evaluation of the significance of insect damage on atmospheric boreal aerosol was

23 obtained with a global chemical transport model, GLOMAP (Spracklen et al., 2005), to

24 provide a first estimate of the potential scale of the impact. For GLOMAP modelling, 10%

25 (i.e., ~2.5×10^6 km^2) of the total boreal conifer forest was randomly selected to be suffering

26 insect herbivory and a 10-fold increase in monoterpene emissions was assumed in this area.

27 These values (10 % and 10- fold) were selected as conservative estimates based on our

28 laboratory and field measurements (this study) and recent estimations of biotically stressed

29 tree fractions in Europe (Bergström et al., 2014; Fischer et al., 2012), and are used to present

30 an order-of-magnitude estimate of the effect of insect damage on climate relevant atmospheric

31 particles. It has been estimated that currently 11 % of northern boreal forests and 19% of

1 north–central coniferous/mixed forests are already suffering a significant degree of defoliation

2 (>25 %) (Bergström et al., 2014; Fischer et al., 2012).

3   The GLOMAP aerosol model simulates the emission, transport, microphysical

4 processes and removal of size-resolved aerosol on a global scale with a horizontal resolution

5 of 2.8°×2.8° and 31 vertical levels (Spracklen et al., 2005). The model has been shown to

6 agree well with aerosol observations over the boreal region and to reproduce new particle

7 formation events in Hyytiälä, Finland (Spracklen et al., 2006). It has further been used to

8 demonstrate that emissions of BVOC from boreal forests can double the regional cloud

9 condensation nuclei concentrations (Spracklen et al., 2008a). We simulated monoterpene

10 emissions according to the GEIA inventory (http://www.geiacenter.org/) and, for

11 computational affordability, made a simplifying assumption that 13% of their oxidation

12 products form vapours capable of producing SOA. The constant value used is based on

13 observations in Scandinavian boreal forest (Tunved et al., 2006b). Other aerosol types

14 simulated are sulphate and carbonaceous aerosols from anthropogenic and biomass burning

15 sources (http://aerocom.met.no/Welcome.html) and sea spray. For new particle formation via

16 nucleation, we assumed a linear dependence on the sulphuric acid concentration (so-called

17 activation nucleation, e.g. Sihto et al. (2006)). The cloud condensation nuclei (CCN)

18 concentration was calculated from the simulated aerosol size distribution at 1 km altitude

19 assuming an updraft of 0.3 m s^{-1} and using a physically-based droplet activation scheme

20 (Nenes and Seinfeld, 2003).

21 **2.4 Satellite observations**

22   The influence of large-scale insect outbreak on local aerosol concentrations was

23 investigated using MODIS (Moderate Resolution Imaging Spectroradiometer) satellite

24 observations. MODIS data was used to analyze aerosol optical depth (AOD) over both insect-

25 outbreak (Kurz et al., 2008a) and less infested (control) areas mainly located in British

26 Columbia (BC) and Alberta (AB) provinces in Canada. AOD data for selected areas was

27 analyzed for an eleven-year period (2002-2012). The MODIS instruments are on board the

28 Terra and Aqua satellites and they have made observations since 2000 and 2002, respectively.

29 MODIS AOD data have been widely used and validated against ground-based measurements

30 (Levy et al., 2010).

31   The analysed areas (9-pixel-grid) are described in detail in Table 2 and a map of the

32 areas can be found in Fig. S1 (Supplement) and at *http://goo.gl/maps/m4lO5* (see also a web-

page of Natural Resources Canada (2015): The threat of mountain pine beetle to Canada's boreal forest). The areas are divided into three mountain pine beetle (MPB) outbreak areas (named as MPB-1/2/3) and two control areas (Ctrl-1/2). The areas have been selected based on the MPB migration discovered by Natural Resources Canada (2015). In the first area located in the centre of BC (MPB-1, 330 x 200 km^2 area, west side of city Prince George), MPB outbreak started to expand in 2000 and most of the pine forest was killed by 2006 based on data by the Ministry of Forests, Lands and Natural Resource Operations (2015). In the MPB-2 area (located 130 km east of MPB-1, at the borderline of BC and AB), about half of the area was already suffering a MPB outbreak in 2006 while the MPB outbreak reached the southern part of the MPB-3 area (330 km north of MPB-1, at the borderline of BC and Yukon Territory) from 2010-2011. In contrast, there was not significant MPB displacement before the year 2011 in the control areas of Ctrl-1 (170 km west of MPB-3, at the borderline of BC and Yukon Territory) and Ctrl-2 (370 km east of MPB-3, at the borderline of AB and Saskatchewan) (Natural Resources Canada, 2015).

There are no big cities inside or near the AOD analysis areas; the most populated towns are Prince George (ca. 72 000 inhabitants, MPB-1), Grande Prairie (55 000, MPB-2), Fort McMurray/ Wood Buffalo (66 000, Ctrl-2) (Statistics Canada, 2015). The metropolitan areas in BC and AB are Vancouver (2.5 million, 300 km south of MPB-1), Calgary (1.2 million, 350 km south-east of MPB-2) and Edmonton (1.1 million, 300 km east of MPB-2 and 190 km south-west of Ctrl-2).

We have excluded days with any evidence of forest fire aerosols in our analysis to isolate the effects of herbivore outbreak on AOD from the effects of forest fires (list of excluded days in Table S1, Supplement). Fire days were selected for exclusion by carefully analysing MODIS Terra and Aqua AOD measurements day-by-day, focusing on an area that extended over the entire analysis area to see if there was any indication of confounding smoke aerosol. Figure S2 (Supplement) gives examples of included and excluded days. The region used for this exclusion analysis was larger than that shown in the figure, but for clarity this figure has been reduced to 9x9 pixels. It is evident that smoke does not affect our focus area; however, these days were still excluded due to the AOD levels being clearly elevated in the neighbouring pixels, likely due to smoke from forest fires. As a result of this very strict screening, a substantial amount of measurements were excluded (for instance in August 2010) to form the "smoke free" set of MODIS data.

1   Changes in AOD were evaluated with analysis of covariance (ANCOVA). The analysis

2   was performed with SPSS 21 (SPSS Inc., Chicago, IL). In the first phase, the ANCOVA

3   model consisted of three predictor values: year and study area as categorical variables and

4   daily temperature maximum as a continuous variable. Mean daily temperatures in August

5   were calculated using NCEP Reanalysis data (Kalnay et al., 1996) provided by the

6   NOAA/OAR/ESRL PSD, Boulder, Colorado, USA (NOAA, 2014). Here, the temperature

7   range is narrow and thus the effect of temperature could be approximated as a linear effect in

8   ANCOVA. Temperature is known to affect VOC emission from plants (Guenther et al., 1993;

9   Helmig et al., 2006) and hence affects SOA formation. On the other hand, temperature has

10   been suggested to be a reducing factor for new particle formation and growth (e.g., Hamed et

11   al., 2007 and references therein; Mikkonen et al., 2011). Therefore, the effect of temperature

12   (daily maximum) has been taken into account in AOD analysis results presented here.

13   An alternate approach to AOD data analysis was to hone in on two shorter time periods

14   (period I 2003-2005, period II 2008-2010) in order to highlight the differences between study

15   areas within the worst outbreaks. Pairwise statistical analysis were conducted for those two

16   time periods. In this analysis, the predictor variables were only study area and daily

17   temperature maximum.

18

3   Results and discussion

Our results represent the first synthesis of small-scale field and laboratory measurements with large-scale satellite and regional modelling studies to investigate the impacts of herbivore outbreaks on biogenic SOA formation. In this section, we will first compare VOC emission rates from control and herbivore-infested trees at a field site in eastern Finland and from laboratory experiments. Then, we present results from controlled laboratory experiments where the effects of biotic stress on SOA formation were tested on two different tree species. The remaining sections discuss the larger-scale regional implications of herbivore outbreaks on SOA formation. We present results from a regional model investigating the effect of an herbivore outbreak on particle mass loading and CCN number in boreal forests. Finally, we provide a case study analysis of satellite AOD to investigate the effect of the largest recorded mountain pine beetle outbreak in the Canadian Rockies.

3.1   VOC emissions

In the field experiments, we studied the effect of insect herbivory on VOC emission rates of young Scots pine (*Pinus sylvestris*) saplings in a pine sawfly (*Neodiprion sertifer*) outbreak area of a forest stand (Outokumpu, Finland). The emission rates (Table 3) of total monoterpenes (MT) and sesquiterpenes (SQT) of insect-damaged trees were significantly increased ($p<0.001$) compared to control trees: 11-fold and 20-fold increases were observed, respectively. Limonene was the most abundant MT, but α-pinene had the most distinctive response to insect feeding with a 26-fold increase in emissions. In contrast, emission rates of C6 green leaf volatile (GLV) compounds were not significantly affected.

In the laboratory chamber experiments (Table 1), bark of Scots pine and Norway spruce seedlings was damaged by large pine weevils (*Hylobius abietis*), a major pest of conifer seedlings in Northern Europe. Table 4 and Table 5 show VOC emission rates from the control and insect-damaged Scots pine and Norway spruce seedlings, respectively. In both cases, VOC emissions from the insect-damaged seedlings were significantly higher than from the control seedlings ($p<0.001$). The average MT emission rates of the damaged seedlings was approximately from 12 (spruce) to 18 (pine) and SQT emission rates from 5 (pine) to 85 (spruce) times higher than the controls. The most abundant compounds of Scots pine emissions (control and damaged) were α-pinene, limonene, 3-carene and β-phellandrene and

for Norway spruce α-pinene, limonene, β-phellandrene and β-pinene. The identified SQT fractions represented only 0.2-2 % of all terpenes (both plants and cases).

The current study also showed changes in the relative proportions of measured compounds as shown in Fig. 2. The insect damage changed the profile of Scots pine emissions by promoting MT emissions of the α-pinene, limonene and β-pinene together with SQT emissions of longifolene and (E)-β-farnesene. In contrast, a clear decrease was observed in 3-carene fraction. Increased emissions of the same monoterpenes (α-pinene, limonene and β-pinene) were reported from pine seedling foliage after pine weevil damage and longifolene emission was increased from feeding site on pine stem (Heijari et al., 2011). However, lower emissions of 3-carene from damaged seedlings might also indicate a lower proportion of "3-carene type" Scots pine seedlings (Semiz et al., 2007) in pine weevil treatment.

For Norway spruce, there were increases in relative emissions of the main MT components β-phellandrene, β-pinene and α-pinene and a minor component 1,8-cineole. SQT emissions of longifolene, (E)-β-farnesene and δ-cadinene were clearly increased after insect damage (ca. 85-fold). These levels are similar to emissions reported in a study by Blande et al. (2009) on Norway spruce damaged by pine weevils where large MT emissions were due to resin flow at feeding sites on the branches.

We conducted our laboratory experiment with young seedlings due to practical restraints for a laboratory study, but these results should be representative of emissions of full grown forest trees because monoterpene composition of needles and wood of Scots pine are under strong genetic control. A 19-year monitoring study indicated that seedlings of Scots pine provenances at the age of four and twelve months has similar composition as the fresh cut stumps 19 years later (Kivimäenpää et al., 2012).

The field and laboratory results show that insect damage induced significant changes in the VOC blends emitted by both conifer species. In addition to increasing emissions, there was induction of several highly reactive compounds, including limonene, β-phellandrene, β-myrcene, and (E)-β-farnesene that could have a significant effect on SOA formation processes (Bonn and Moortgat, 2003), e.g., by reducing nucleation threshold and increasing SOA mass.

3.2 SOA formation

SOA formation by oxidation of VOCs emitted from Scots pine and Norway spruce seedlings was studied in a continuous flow reactor system (Fig. 1) in which VOCs emitted from Scots pine or Norway spruce seedlings were channelled into a separate reaction chamber and mixed with ozone enriched air (50 or 200 ppb). Figure 3 shows SOA formation results as a function of the hour of day for the experiments with Scots pine seedlings at the ozone level of 50 ppb. When the air from the headspace of herbivore-damaged seedlings was mixed with ozone-rich air, intensive SOA formation was observed 15-20 minutes after the start of ozone introduction. The SOA mass peaked about 3 hours after the start of the ozone addition; it then decreased during the next 9 hours before stabilizing. It should be noted that the introduction of plant-emitted VOCs to the chamber began 60 minutes before ozone addition and therefore the initial VOC concentrations were higher than later in the trials. During night periods (from midnight to 3 am) the lights over plants were off and SOA formation was lower due to reduced VOC emissions (approx. 50% of day values); however, clear SOA formation was still observed. In contrast, only a very weak SOA formation (roughly 500 fold lower in mass) can be observed in experiments with control plants. Furthermore, particle formation was observed with a longer delay after ozone addition than in herbivore-damage experiments and particle concentrations were very low during night periods.

Experiments at the ozone concentration of 200 ppb showed very similar results for Scots pine and Norway spruce seedlings as shown in Fig. 4. For herbivore-damaged seedlings, clear and intensive new particle formation was observed after ozone introduction whereas only very weak particle formation can be observed in the control experiments. Moreover, lower particle production was observed during the night when lights were off and the VOC emissions were lower.

VOC concentrations were also measured at the outlet of the chamber to evaluate fate of different VOC compounds. The results showed that most of the compounds that were totally consumed in the reaction chamber (e.g. limonene, β-myrcene, terpinolene, β-phellandrene, (*E*)-β-farnesene, δ-cadinene) had two or more carbon double bonds (C=C) making them very reactive with ozone (Kroll and Seinfeld, 2008). Compounds with more than one double bond contribute substantially to SOA growth because of the second-generation products that can be formed by further oxidation (Ng et al., 2006).

Figure 5 shows SOA mass yields (ratio of formed SOA mass and reacted VOC concentrations) as a function of formed organic mass. Average SOA mass yields vary between 0.1-3 % in control experiments and 5-40 % in insect-damage experiments (overall averages 1% and 18%, respectively). A clear reduction of SOA mass yields can be seen with decreasing SOA mass, a similar reduction has typically been observed in SOA formation experiments (Odum et al., 1996; Shilling et al., 2008; Hao et al., 2011). Based on gas/particle partitioning theories and models and smog chamber experiments, the aerosol yield strongly depends on the organic particulate mass (Odum et al., 1996; Pankow, 1994; Song et al., 2005). The organic particulate mass acts as a medium into which oxidation products can be absorbed and hence higher organic particulate mass increases aerosol mass yields. For comparison, Mentel et al. (2013) studied SOA formation from emissions of common temperate and Boreal forest trees (pine, spruce, birch and beech) and they reported yields between 17 and 33 % from experiments with stress-induced emissions, which are significantly higher than obtained experiments containing mainly MTs (4-6 %). It should be noted that recent studies have shown that the depletion of very low volatile VOC to chamber walls could lead to a significant underestimation of SOA formation yields determined from chamber experiments (Kokkola et al., 2014; Zhang et al., 2014). Furthermore, the SOA mass yields determined from different chambers under different conditions can vary widely (Lee et al., 2006; Shilling et al., 2008; Mentel et al., 2013; Hao et al., 2011) and therefore it is not straightforward to assess a suitable yield values for model calculations. In this study, we have used a fixed 13 % yield (all cases) in the GLOMAP modeling as is common established practice for regional to global scale modeling applications. This value is also consistent with our insect-damage experiments (overall averages 18%). This fixed yield value might overestimate SOA formation in control areas with lower VOC and SOA mass concentrations, so the potential effect observed here would be a lower estimate of the potential effect.

The results from 12 different chamber experiments are summarized in Table 6 (average results from the start of the trial at 1-3 pm until the next morning at 9 am). In general, feeding by *H. abietis* weevils increased average VOC emissions from seedlings by 10-50 fold, and ozonolysis of VOCs at 50-200 ppb of O_3 increased total number and mass concentrations of SOA particles by 20-70 fold and 200-1000 fold, respectively. In addition, average SOA mass yields increased from 0.1-3 % to 5-40 % after herbivore feeding. A more pronounced enhancement in SOA formation was observed after herbivore feeding than after increase of ozone concentration from 50 to 200 ppb. This suggests that in the future, insect outbreak-

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1 related changes in VOC emissions might have regionally a more important role in the

2 formation rate of SOA than increases in tropospheric ozone levels (Sitch et al., 2007).

3 **3.3   Global scale modelling**

4 We used a simplified SOA formation set-up within the GLOMAP model to assess

5 whether the large-scale insect outbreaks could potentially impact Earth's climate. The model

6 set-up is summarized in Fig. 6a: 10 % of the total boreal conifer forest suffered insect

7 herbivory with a 10-fold increase in monoterpene emissions in outbreak areas. Note that the

8 simulations do not include sesquiterpene emissions, as they are not incorporated in the model

9 version used here. Thus the results presented here likely represent a conservative lower-bound

10 of the potential impact as any increases in sesquiterpene emissions would serve to increase

11 SOA yields even more dramatically. Furthermore, D'Andrea et al. (2015) have recently

12 estimated that in the boreal forest region monoterpenes are typically responsible for up to over

13 80% of SOA formation, while sesquiterpenes play a much less significant role. We do not

14 expect this short-coming to impact our conclusions, which are intended to merely indicate

15 whether insect herbivory could be of regional importance, and thus merit more detailed model

16 studies in the future. A 10-fold increase in monoterpene emissions in 10 % of the total boreal

17 area are conservative estimates based on field (Table 3) and laboratory (Tables 4 and 5)

18 measurements and an ICP Forests Report (Fischer et al., 2012), respectively. This local

19 increase in monoterpene emissions is much higher than has previously been estimated to

20 result from changes in climate variables from the late 20th century to 2100 (global increase of

21 19-119% (Heald et al., 2008; Tsigaridis and Kanakidou, 2007)). Heald et al. (2008) also

22 predict that changes in SOA formation from climate change alone (temperature, oxidative

23 capacity and removal rates) is very small, and thus the effect of increasing temperature is not

24 simulated here.

25 Relative changes in total particulate mass (Fig. 6b) and cloud condensation nuclei

26 (CCN) concentration (Fig. 6c) were simulated. While the largest simulated relative changes in

27 total particulate mass (up to ~480% increases) were limited to the insect-infested areas (Fig.

28 6b), the particle mass increased more than 50% for an area of 8.7×10^6 km^2, i.e. ~3.5 times that

29 damaged by insects. These large regional increases reflect the dominance of biogenic aerosol

30 precursors and thus the susceptibility of aerosol properties to changes in biogenic VOC in this

31 area. Meanwhile, CCN concentration increased over 20% for an area of 3.8×10^6 km^2 (Fig.

32 6c), i.e. ~1.5 times the insect infested area, while the largest local increases were over 45%.

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The influence of increased VOC emissions were also clearly observed hundreds of kilometres downwind of damaged areas, e.g. over the Arctic Ocean with low background CCN concentrations. Overall, predicted changes in CCN were relatively low because a large fraction of VOC oxidation products condense onto pre-existing aerosols which can already act as CCN in unperturbed conditions. Thus enhanced VOC emissions only affect CCN concentrations if the gas-phase emissions can lead to growth of small nucleation and Aitken mode particles up to CCN size. Taken the increase in aerosol mass and CCN concentration together, global model simulations suggest that large scale insect herbivory in the boreal region can affect both direct and indirect aerosol forcing on a regional scale.

3.4 Satellite observations

Changes in aerosol optical depth (AOD) in western Canada were analyzed from the MODIS instrument satellite data for an eleven-year (2002-2012) period covering three insect outbreak (MPB-1/2/3) and two control (Ctrl-1/2) areas (see Table 2, Fig. S1). The current MPB outbreak in central British Columbia started in the early 1990s and the areas were selected based on the location of the outbreak as it has expanded over the years (Natural Resources Canada, 2015)(ca. in 2000, 2004 and 2010 for MPB-1, MPB-2 and MPB-3 areas, respectively). Days with evidence of forest fire aerosols were excluded in the AOD analysis (see Table S1 in Supplement).

Figure 7 shows the mean AOD values in August over analysed areas in 2002-2012. During years 2002-2004, a clear increase in mean AOD values was observed in MPB-1 and MPB-2 areas (from ca. 0.07 to 0.13). In contrast, no clear increase in AOD was observed in MPB-3 and control areas that are located 200-300 km away from the main infested area. Table 7 shows a pairwise comparison of AOD results (ANCOVA) between different areas for a two-year period of 2003-2004. The statistical analysis confirmed that the mean AOD was significantly higher in areas located near the starting point of the outbreak (MPB-1 and MPB - 2) compared with areas located farther away. During that time period, MPB-1 had a high degree of infestation and MPB-2 was partially infested with MPB whereas no infestation was recorded in other analysis areas (Natural Resources Canada, 2015). After 2004, the mean AOD decreased from ca. 0.13 to 0.07 for subsequent years (2005-2007) in MPB-1 and MPB - 2 areas. The lower AOD values in outbreak areas in later years could be explained by increased tree mortality. Most of the pine trees near the outbreak starting point (MPB-1) were killed by 2006 (Ministry of Forests, 2015) and therefore VOC emissions from trees were

17

likely lower compared with previous years. Typically, the major tree mortality took place approximately one decade after the initial outbreak (Ministry of Forests, 2015).

From 2006-2011, the leading edge of MPB outbreak moved north and east, approaching the MPB-3 area, and the southern part of the MPB-3 area was infested with MPB by 2010. In MPB-3, a mean AOD in August was increased from ca. 0.06 to 0.12 from 2006-2010; however, unlike the results from 2002-2006, a clear increase in AOD was also observed in control areas (Ctrl-1 and Ctrl-2) that are located 100-200 km outside of the infested areas (leading edge of outbreak). In addition, the pairwise comparison for three-year period of 2008-2010 (Table 7) does not show significant increase in AOD values in the infected areas compared with other areas, in fact the results varied area by area.

The difference between two analysed periods (2002-2004 and 2008-2011) could be explained by the change in total outbreak area – the extremely large herbivore-affected area was reached in 2009 (Meddens et al., 2012; Kurz et al., 2008a), indicating that a large amount of reactive VOC was emitted from trees to the atmosphere in that region of Canada. VOC emitted from stressed trees, as well SOA formed can be transported by wind over several hundreds of kilometres as shown by our GLOMAP analysis (see Fig. 6) and, therefore, increases in AOD could be observed in an area wider than the original MPB outbreak area.

An alternate explanation also becomes apparent when honing in on the AOD results from 2009. In MPB-1 and Ctrl-1 areas, the AOD values had a clear peak in 2009 compared with previous and subsequent years, i.e. around 0.15 while the baseline level is below 0.1. However, the ANCOVA results for three year period of 2008-2010 (Table 7) show that at the outbreak starting point (MPB-1), where there was high tree mortality and the main infestation had passed, the mean AOD (3-year average) was significantly lower than in other more active outbreak areas (MPB-2 and MPB-3). This indicates that there might be exceptional reasons for high AOD values in August 2009 when compared with the previous and following years, e.g., weather conditions or forest fires. Based on information from the BC Wildfire Management Branch (2015b), numbers of total fires were significantly higher in 2009 than current 10-year average (3064 vs. 1908). They also stated that "Fire season 2009 will go down in history as one of the busiest due to exceptional weather and fire behaviour conditions." (BC Wildfire Management Branch, 2015a). Despite our best attempts to exclude fire days from the analysis, it is possible that this extreme fire season in 2009 could have some effect on the calculated mean AOD values. For instance, frequent and intense forest fires can raise AOD

base levels even in "smoke-free" cases. Furthermore, we had to exclude totally 15 days of 31 from analysis in August 2009, mainly at the beginning of the month (see Table S1, Supplement), which might affect results.

Clear differences in AOD values between different analysed areas were only detected in August, not in data for the other months or in the data combined for the whole year. This is consistent with the bark beetle attack periods, which typically peak in August (Cudmore et al., 2010; Rankin and Borden, 1991).

Mean temperature in August at analyzed areas is shown in the last panel Fig. 7. Temperature was found to have a statistically significant effect on the AOD and thus the daily maximum temperature was used as a predictor variable in the ANCOVA-model. The model without the temperature effect is not shown in this paper. When the temperature was taken into account in the model, the differences between the outbreak and control areas were enhanced rather than reduced. Maximum temperature was seen to have a reducing effect on AOD within the study period. This is a sign of strong nonlinearity in the effect of temperature to aerosol loading as Goldstein et al. (2009) suggested that the overall effect of temperature is positive in AOD within range from -12 °C to +27 °C. However, within the narrow temperature range of this study, Goldstein et al. (2009) show big variation in the aerosol loading and the sign of the temperature effect cannot be specified.

The satellite observations presented here do not provide direct evidence that bark beetle outbreaks increased AOD in outbreak areas, but they agree well with the results of the GLOMAP model simulations presented previously: increased VOC emission caused by biotic stress increased SOA concentration over MPB outbreak areas. Recent simulations on the impact of MPB infestations on terpene emissions and SOA formation in western North America also showed an enhancement peak on SOA concentrations in central British Columbia in 2004 (Berg et al., 2013), which coincides with one of the major AOD peaks presented in Fig. 7. Other sources of increased AOD, including interacting effects between herbivore outbreaks and forest fires, cannot be completely ruled out with this analysis. For example, increased AOD would be observed with increasing frequency of forest fires in insect affected forests dominated by dead or dying trees. To better isolate the effect of herbivore outbreak on VOC emissions and SOA formation in forest regions, more extensive measurement campaigns need to be conducted directly in the field environment.

4 Conclusions

Our results suggest that more frequent insect outbreaks in a warming climate, in addition to temperature dependent increases of VOC emissions, could result in substantial increases in biogenic SOA formation in the boreal zone. The field and laboratory experiments showed a significant increase in VOC emissions and SOA formation after insect feeding. Furthermore, global scale modelling results and satellite observations indicated a clear increase in CCN concentrations and in AOD values near insect outbreak areas, which affect both aerosol direct and indirect forcing of climate at regional scales. However, the long-term effects of insect outbreaks (e.g., mortality of trees (Långström et al., 2001), VOC emissions from xylem of dead trees (Hyttinen et al., 2010; Kivimäenpää et al., 2012; Haapanala et al., 2012)), and the effects of different tree species (Hyttinen et al., 2010; Eisenbies et al., 2007) needs to be addressed in detail in the future. For instance, conifer trees with a large monoterpene storage capacity in resin ducts can emit reactive VOCs for long periods after intensive herbivore damage whereas the capacity of deciduous trees is very limited.

In the future, anthropogenic emissions (e.g. particulate matter and SO_2) are expected to be reduced through legislation and introduction of new cleaning technologies; therefore formation of biogenic SOA will play an even more important role in global climate change (Andreae et al., 2005; Arneth et al., 2009). Additional SOA formation through oxidation of VOCs released from insect stressed trees may also bolster the important sun-screening biosphere-atmosphere feedback system (Ehn et al., 2014; Lovelock, 2003). SOA could mitigate the impact of global warming on northern terrestrial ecosystems by affecting the Earth's radiation budget but also increase diffuse radiation, which was previously shown to promote plant growth and increase the CO_2 sink in vegetation (Mercado et al., 2009). Furthermore, higher concentrations of biotic SOA particles might have adverse effects on human health (Sunil et al., 2007; Rohr, 2013).

We propose that the effect of insect outbreaks on VOC emissions and SOA formation should be considered in future climate predictions.

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Tables:

Table 1. Summary of conducted chamber experiments. Average ozone concentrations at the inlet ($O3_{inlet}$) and outlet ($O3_{outlet}$) of the reaction chamber, relative humidity (RH) and temperature during experiments.

#	Date	Experiment	$O3_{inlet}$ (ppb)	$O3_{outlet}$ (ppb)	RH (%)	T (°C)
1	9.-10.6.2008	Spruce, control	170	145	5	24
2	12.-13.6.2008	Spruce, control	166	132	9	24
3	10.-11.6.2008	Spruce, damaged	171	140	9	24
4	11.-12.6.2008	Spruce, damaged	164	132	11	24
5	15.-16.6.2008	Pine, control	172	143	9	24
6	18.-19.6.2008	Pine, control	164	129	14	25
7	16.-17.6.2008	Pine, damaged	175	120	12	24
8	17.-18.6.2008	Pine, damaged	164	97	16	25
9	9.-10.7.2008	Pine, control	41	29	13	24
10	10.-11.7.2008	Pine, control	39	28	14	24
11	7.-8.7.2008	Pine, damaged	37	21	13	24
12	8.-9.7.2008	Pine, damaged	41	21	13	24

1 **Table 2.** Summary of AOD analysed areas (3x3-pixel-grid). The MPB outbreak areas (MPB-

2 1/2/3) had clear insect outbreaks during analysis period (2002-2012) whereas controls areas

3 (Ctrl-1/2) did not. The map of areas is shown in Fig S1 (Supplement) and at

4 *http://goo.gl/maps/m4lO5*.

Area name	Covered area (lat., lon.)	Comments
MPB-1	N 52°-55°, W 123°-126°	Very strong MPB outbreak starting 2000, with nearly complete tree mortality by 2006.
MPB-2	N 53°-56°, W 118°-121°	About half of the area suffering MPB outbreak in 2006, located ca. 130 km east of MPB-1.
MPB-3	N 58°-61°, W 124°-127°	MPB migration in the southern part of the area in 2010-2011, ca. 330 km north of MPB-1.
Ctrl-1	N 58°-61°, W 130°-133°	No significant MPB migration before 2011, ca. 150 km west of MPB-3.
Ctrl-2	N 55°-58°, W 109°-112°	No significant MPB migration before 2011, ca. 250 km east of MPB-2

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1 **Table 3**. Temperature standardized (30 °C) emissions of monoterpenes, sesquiterpenes and

2 unstandardized emissions of green leaf volatiles (GLV) and methyl salicylate (ng g^{-1} (DW

3 needles) h^{-1}) from branch shoots of intact (n=8) and *Neodiprion sertifer* -damaged (n=9) of

4 *Pinus sylvestris* trees in a forest site in Outokumpu, Finland. Samples were collected on 30th

5 June 2010, approximately four weeks after the start of larval feeding. *P*-values of the Mann-

6 Whitney test are given.

	Control		*Neodiprion sertifer* -damaged		Significance
	Mean	SD	Mean	SD	
Monoterpenes					
Tricyclene	3.8	3.4	48.5	50.2	0.200
α-pinene	371.7	264.9	9688.7	9815.3	0.001
Camphene	21.2	11.8	289.9	265.0	< 0.001
Sabinene	47.7	38.0	295.2	305.6	0.011
β-pinene	119.2	114.2	2092.5	2900.8	0.036
Myrcene	371.6	462.9	6461.3	8841.9	0.006
Δ3-carene	613.8	715.8	3130.0	4017.0	0.321
Limonene	1703.4	4203.7	13154.5	16704.7	0.004
β-phellandrene[a]	309.7	375.7	3482.6	4934.0	0.036
1,8-cineol	20.8	18.6	81.8	102.0	0.321
γ-terpinene	7.6	6.9	48.3	36.9	0.001
Terpinolene	39.6	53.7	417.5	388.8	0.001
Linalool	13.6	13.3	219.6	247.8	0.011
Camphor	0.3	0.8	0.9	2.8	1.000
Borneol	0.5	0.9	3.3	3.4	0.059
Terpinen-4-ol	0.9	1.4	7.1	14.6	0.815
α-terpineol	1.7	3.2	-	-	0.423
Bornyl acetate	3.4	2.8	63.1	21.0	0.004
Total monoterpenes	3650.7	4625.3	39488.6	34027.9	< 0.001
Sesquiterpenes					
α-copaene	0.3	0.3	10.8	17.1	0.002
Longifolene	1.8	1.9	45.3	66.8	0.006

(E)-β-farnesene	12.2	8.4	181.8	252.0	< 0.001
(E)-β-caryophyllene	1.0	1.3	49.0	58.7	< 0.001
α-humulene	0.2	0.4	8.4	9.5	0.002
δ-cadinene	3.0	1.8	43.6	35.7	< 0.001
α-cubebene[b]	0.2	0.4	4.1	10.3	0.606
α-longipinene[b]	0.6	1.2	56.2	112.0	0.002
β-bourbonene[b]	2.4	5.6	32.5	42.7	0.006
β-cubebene[b]	0.2	0.6	0.3	0.8	1.000
α-amorphene[b]	<0.1	<0.1	11.7	14.8	0.001
(E,E)-α-farnesene[b]	2.7	4.4	30.5	59.8	0.743
α-muurolene[b]	0.6	0.8	19.4	27.4	0.006
Unknown	0.3	0.5	18.4	18.6	0.002
bis-α-bisabolene[b]	0.1	0.4	5.2	9.1	0.200
Total sesquiterpenes	25.7	13.2	517.1	560.3	< 0.001
Total terpenes	3676.3	4625.8	40005.7	34409.0	< 0.001
Aromatics					
Methyl salicylate	0.2	0.6	1.2	2.5	0.481
GLVs					
(E)-2-hexenal	-	-	18.3	31.2	0.277
(Z)-3-hexanol	-	-	3.9	8.3	0.481
1-octen-3-ol	-	-	13.0	38.9	0.743
(Z)-3-hexenyl-acetat	0.7	2.0	19.8	38.8	0.423
Nonanal	11.0	11.5	10.5	18.1	0.481
(Z)-3-hexenyl-butyrate	-	-	2.0	6.0	0.743
(Z)-3-hexenyl-tiglate	-	-	0.1	0.3	0.743
Total GLVs	11.7	11.5	68.7	93.4	0.606

[a] Emission calculated using sabinene as a standard, [b]longifolene as a standard. Dash (-) indicates that the compound was not detected.

34

1 **Table 4.** VOC emission rates per gram of needle dry mass (ng gDW^{-1} h^{-1}) from intact and

2 *Hylobius abietis*-damaged Scots pine seedlings (chamber experiments). Average emission

3 rates with standard deviations (SD) from 4 different experiments are shown. *P*-values of the

4 Mann-Whitney test are given.

	Emission rates (ng gDW^{-1} h^{-1})				
	Intact seedlings		Damaged seedlings		Significance
Compound name	Mean	SD	Mean	SD	
α-pinene	233.0	248.3	6425.6	3256.0	<0.001
Limonene	119.8	151.7	3776.1	2498.8	<0.001
3-carene	337.9	240.9	2676.4	2893.0	0.021
β-phellandrene	116.6	174.3	1915.5	2355.1	<0.001
β-myrcene	44.1	32.9	976.4	851.1	<0.001
β-pinene	25.0	21.6	788.7	446.4	<0.001
Terpinolene	11.2	10.8	214.4	258.5	<0.001
Camphene	26.1	23.4	137.5	108.6	0.001
Sabinene	20.2	18.9	144.2	143.1	0.006
1,8-cineole	16.0	22.0	95.9	58.1	<0.001
γ-terpinene	3.2	3.0	33.0	36.3	<0.001
Bornyl acetate	4.3	4.9	22.6	11.4	<0.001
Linalool	-	-	12.8	19.1	0.006
Camphor	1.1	3.7	5.3	7.7	0.244
Terpinen-4-ol	0.1	0.4	4.7	5.5	<0.001
Borneol	0.2	0.6	4.4	4.5	<0.001
α-terpineol	0.4	1.2	1.7	3.5	0.478
Longifolene[a]	4.8	4.5	33.4	24.9	<0.001
(*E*)-β-farnesene[a]	3.5	5.6	23.8	26.1	<0.001
δ-cadinene[a]	6.3	6.0	27.1	12.2	<0.001
(E)-β-caryophyllene[a]	4.4	5.2	2.7	4.7	0.280
α-humulene[a]	0.1	0.3	0.3	1.1	0.963
Sum of monoterpenes	959.3	758.5	17235.3	9710.2	<0.001
Sum of sesquiterpenes	19.1	12.7	87.3	55.1	<0.001
Sum of terpenes	978.4	771.1	17322.7	9765.3	<0.001

5 [a]sesquiterpenes. Dash (-) indicates that the compound was not detected (i.e., concentration

6 zero or below detection limit ca. 0.1 ng gDW^{-1} h^{-1}).

7

8

1 **Table 5**. VOC emission rates per gram of needle dry mass from intact and *Hylobius abietis*-

2 damaged Norway spruce seedlings (chamber experiments). Average emission rates with

3 standard deviations (SD) from 2 different experiments are shown. *P*-values of the Mann-

4 Whitney test are given.

5

	Emission rates (ng gDW^{-1} h^{-1})				
	Intact seedlings		Damaged seedlings		Significance
Compound name	Mean	SD	Mean	SD	
α-pinene	25.4	15.5	331.7	138.4	<0.001
Limonene	33.6	18.2	154.2	97.4	<0.001
3-carene	13.4	17.7	61.9	27.6	0.003
β-phellandrene	20.0	14.0	446.0	246.3	<0.001
β-myrcene	7.2	4.1	87.1	44.0	<0.001
β-pinene	26.1	19.2	429.6	170.6	<0.001
Terpinolene	-	-	5.0	4.9	0.009
Camphene	6.7	2.8	28.2	7.5	<0.001
Sabinene	-	-	3.9	11.0	0.346
1,8-cineole	0.5	1.1	17.9	6.9	<0.001
γ-terpinene	-	-	1.7	0.6	<0.001
Bornyl acetate	1.9	1.4	6.7	2.8	<0.001
Linalool	-	-	12.2	13.4	0.003
Camphor	-	-	-	-	NaN
Terpinen-4-ol	-	-	0.2	0.6	0.346
Borneol	-	-	0.4	0.7	0.144
α-terpineol	-	-	0.5	1.5	0.346
Longifolene[a]	0.3	0.5	5.0	2.5	0.002
(*E*)-β-farnesene[a]	-	-	15.6	14.9	<0.001
δ-cadinene[a]	-	-	1.3	1.2	0.009
(E)-β-caryophyllene[a]	-	-	0.3	0.9	0.346
α-humulene[a]	-	-	-	-	NaN
Sum monoterpenes	134.7	83.5	1587.1	716.1	<0.001
Sum sesquiterpenes	0.3	0.5	22.2	13.8	<0.001
Sum terpenes	135.0	84.1	1609.3	729.9	<0.001

6 [a]sesquiterpenes. Dash (-) indicates that the compound was not detected (i.e., concentration

7 zero or below detection limit ca. 0.1 ng gDW^{-1} h^{-1}).

8

Table 6. Summary of the main BVOC and SOA parameters from tests with undamaged control and insect-damaged plants (total of 12 chamber experiments, see Table S1). The total terpene, monoterpene, sesquiterpene (SQT) concentrations entering the reaction chamber. SOA number (Ntot) and mass (Mtot) concentrations, average size of particles (GMD, geometric number mean diameter) and SOA mass yields at the reactor outlet.

Parameter	Pine, O_3 50 ppb			Pine, O_3 200 ppb			Spruce, O_3 200 ppb		
	Control	Damaged	Dam./Contr.	Control	Damaged	Dam./Contr.	Control	Damaged	Dam./Contr.
Terpenes (ppb)	5.0±2.6	43±26	8.6	1.3±1.0	64±36	51	0.50±0.34	5.5±2.3	11
Monoterpenes (ppb)	4.9±2.6	43±26	8.7	1.2±1.0	64±36	52	0.50±0.34	5.4±2.3	11
SQT (ppt)	100±40	180±120	1.9	20±20	210±100	11	0.7±1.4	70±50	100
Ntot (cm^{-3})	51±49	1600±1900	32	250±440	4600±5500	18	28±66	2100±1600	73
Mtot ($\mu g\ m^{-3}$)	0.01±0.07	5.9±3.7	490	0.08±0.18	84±40	1000	0.005±0.021	1.2±0.7	230
GMD (nm)	49±21	110±40	2.3	39±17	210±82	5.3	55±53	56±19	1.0
SOA yield (%)	0.08±0.08	9.5±7.7	110	2.7±4.9	39±12	15	0.31±0.38	5.0±2.6	16

Dam./Control, relative difference; SQT, sesquiterpenes; Ntot, total number concentration; Mtot, total mass concentration; GMD, geometric mean diameter (average size of particles). Values are average results (± standard deviation) from two different SOA formation experiments (only one for pine control at 50 ppb O_3) lasting from 1-3 pm until 9 am the next morning.

1 **Table 7**. Pairwise comparisons of AOD values (mean difference, standard error and p-

2 value/significance) between areas in two outbreak periods (2003-2004 and 2008-2010).

3 Significant differences are highlighted in bold text.

4

Pairs in comparison		2003-2004			2008-2010		
		Mean Difference	Std. Error	p-value	Mean Difference	Std. Error	p-value
MPB-1	MPB-2	0.004	0.005	0.389	**-0.036**	0.005	0.000
	MPB-3	**0.039**	0.005	0.000	**-0.022**	0.005	0.000
	Ctrl-1	**0.035**	0.006	0.000	**0.014**	0.006	0.017
	Ctrl-2	**0.030**	0.008	0.000	**-0.043**	0.006	0.000
MPB-2	MPB-1	-0.004	0.005	0.389	**0.036**	0.005	0.000
	MPB-3	**0.034**	0.006	0.000	**0.014**	0.005	0.008
	Ctrl-1	**0.030**	0.007	0.000	**0.050**	0.006	0.000
	Ctrl-2	**0.026**	0.008	0.001	-0.007	0.005	0.182
MPB-3	MPB-1	**-0.039**	0.005	0.000	**0.022**	0.005	0.000
	MPB-2	**-0.034**	0.006	0.000	**-0.014**	0.005	0.008
	Ctrl-1	-0.004	0.006	0.506	**0.036**	0.006	0.000
	Ctrl-2	-0.009	0.008	0.300	**-0.021**	0.006	0.000
Ctrl-1	MPB-1	**-0.035**	0.006	0.000	**-0.014**	0.006	0.017
	MPB-2	**-0.030**	0.007	0.000	**-0.050**	0.006	0.000
	MPB-3	0.004	0.006	0.506	**-0.036**	0.006	0.000
	Ctrl-2	-0.004	0.009	0.634	**-0.057**	0.007	0.000
Ctrl-2	MPB-1	**-0.030**	0.008	0.000	**0.043**	0.006	0.000
	MPB-2	**-0.026**	0.008	0.001	0.007	0.005	0.182
	MPB-3	0.009	0.008	0.300	**0.021**	0.006	0.000
	Ctrl-1	0.004	0.009	0.634	**0.057**	0.007	0.000

5

6

Figures captions:

Figure 1. Schematic presentation of the chamber experiment setup. VOC emissions from tree

seedlings were continuously channelled from a plant chamber (left) to a reaction chamber

(right). At the inlet of the reaction chamber, the air flow from trees was mixed with an ozone-

rich air flow. SMPS denotes a scanning mobility particle sizer and CPC denotes a

condensation particle counter.

Figure 2. Monoterpene (MT, upper panel) and sesquiterpenes (SQT, lower panel) emission

profiles (proportions of total MT/SQT emissions) from control and insect-damaged Scots pine

and Norway spruce seedlings (left axis). The diamonds show total MT and SQT emission

rates per needle dry mass (right axes). The error bars represent the standard deviation of the

averaged value. The results are averages of all one-day experiments.

Figure 3. SOA formation via ozonolysis of VOCs emitted from Scots pine seedlings in

atmospheres enriched with 50 ppb O_3. SOA particle mass size distribution as a function of

time (hour of day) from the control (first panel) and the insect-stressed experiment (second

panel) experiments; total number (third panel) and mass (fourth panel) concentrations. Start

times of the ozone addition are indicated by blue (control) and green (damaged) vertical lines.

Lights were off over the plant chamber from 24:00 to 03:00 (indicated by red vertical lines).

Note that introduction of plant-emitted VOCs to the chamber was started one hour before

ozone addition and therefore more intensive particle formation can be observed at the

beginning of the trials.

Figure 4. SOA formation via ozonolysis of VOCs emitted seedlings in atmospheres enriched

with O_3. SOA particle mass particle size distributions and corresponding total concentrations

as a function of time (hour of day) for **a)** Scots pine and **b)** Norway spruce experiments at 200

ppb of O_3: mass size distributions from control (first panel) and insect-stressed (second panel)

experiments; total number (third panel) and mass (fourth panel) concentrations. Start times of

the ozone addition are indicated by blue and green vertical lines. Lights were off over the plant chamber from 24 to 03 (indicated by red vertical lines). Note that introduction of plant-emitted VOCs to the chamber was started 1-1.5 hour before ozone addition and therefore very intensive particle formation can be observed at the beginning of the trials.

Figure 5. SOA mass yields (i.e. ratio of formed SOA and reacted VOC concentrations) as a function of formed organic mass. Blue marks denotes control and red insect-damage experiments, filled marks average values of one-day experiments

Figure 6. Set-up of global model and simulated changes in aerosol concentrations. **a)** Randomly selected 10 % insect-stressed areas (red, 10-fold increase in monoterpene emissions) of the total boreal conifer forest region (green); **b)** Modelled relative change in total particulate mass concentration at the surface layer and **c)** Modelled relative change in CCN concentration at 0.2% supersaturation at cloud base (1 km altitude).

Figure 7. Mean (±95% confidence interval) and median aerosol optical depth (AOD) in August over different areas in western Canada. AOD was analyzed from MODIS satellite data in three mountain pine beetle (MPB) outbreak areas (named as MPB-1/2/3) and two control (Ctrl-1/2) areas (see Table 2). Effect of daily temperature was taken into account in AOD values. The last panel shows mean temperature in August at analysed areas. Analyzed areas are shown on maps in Fig. S1 (Supplement) and at the web-page *http://goo.gl/maps/m4lO5*.