Our Response to the comments of Referee #1 from May 29.

We thank the referee for his/her comments, but before answering these in detail we would like to stress again that this paper is intended to highlight a previously neglected source of organic aerosol. We cannot say exactly how important it is, but this paper makes it clear that the issue needs serious attention. The question mark at the end of our paper's title is important and should be noted: Biotic stress: a significant contributor to organic aerosol in Europe? The intention is not to provide an answer, but to stimulate debate and further research.

We would like to mention that the manuscript is the result of intensive interaction of modelers and experimentalists and was developed in close cooperation, which was considered fruitful from both sides. Indeed, the work done for this paper readily generates ideas for new laboratory experiments, and for the type of field data which will be needed before our question can be answered in a reasonable manner.

Referee #1:

The manuscript by Bergstroem et al. uses previously published yields obtained from BVOC oxidation experiments in response to stress and attempts to upscale these emission enhancements and their impact on OA loadings to the regional scale based on EMEP model simulation. While the influence of BVOCs on atmospheric composition is of great interest and importance, I see several major shortcomings of the presented assessment.

Major comments: It is claimed that up to 50-70% of the BSOA could originate from stress induced biotic emissions; yet the only evidence presented, are previously published results based on laboratory investigations showing emission enhancements of MeSA, MT and a speculative C17 compound along with potential aerosol yields under laboratory conditions.
The authors then compare modeled OA concentrations with observed OA concentrations at one field site. OA is likely comprised of thousands of different chemical species originating from multiple primary and secondary sources (e.g. Jimenez et al., Science, 2009; Aumont et al., ACP, 2012). It is the most complicated (and thus least suitable) quantity to test a model output in order to support the current hypothesis. As the authors have previously published (Bergstroem et al.,2012), there is a wide model range of OA, some underpredicting, some even overpredicting OA concentrations without the need to introduce additional OA sources. It is not demonstrated convincingly that biotic stress

significantly alters the measured OA loading at this site or in general under realistic atmospheric conditions. Without comparing to specific aerosol tracers or ecosystem scale VOC measurements, it is, in my opinion, not possible to quantitatively attribute biotic stress induced emission enhancements to the OA aerosol budget.

Response: Referee #1 is correct; we claim that up to 50 – 70 % of the BSOA could originate from stress induced biotic emissions. It is important to note the word "could", and it is also important for other scientists to know that such a source of BSOA is possible.
We do not agree with the line of argument that it is unnecessary to consider a new class of volatiles as possible contributors to SOA formation. It is a normal and accepted procedure, if a potential new source has been discovered, and their strength has been characterized in the laboratory, to test if this source is of potential importance in the real atmosphere. One way to test this is to implement the source in a model, and compare with SOA from 'traditional' sources, which for forests almost universally comprise isoprene and terpenes. Another line of work could be to go out and try to measure the tracers; this is something that we strongly encourage, and we believe our work provides a good incentive for such studies.

In this paper we publish new emission ratios, which were not so explicitly given before, and resume yields from a previous publication, which can be applied very simply by other models, too. We also suggest a method to assess current stress in forest using forest reports. To our knowledge that has not been tried before.

Indeed, when only looking at the balance between modeling and observation there may be no need to introduce another source for OA. Our argumentation is NOT to propose a "necessary, missing SOA source". Emissions induced by biotic stress are real and their existence has been well known since many years, but the possible link to SOA has not been explored. Neglecting the impacts of biotic stress on BVOC emissions and therewith on SOA formation just because a balance between modeling and observations seems to be closed would be scientifically inadequate. As we know that such emissions efficiently form SOA (see Mentel et al., 2013): we thought it important to quantify this class of emissions and its SOA potential. This class of SOA has (except for Berg et al., 2013) been ignored in all SOA studies that we are aware of, partly through lack of recognition of such potential SOA, partly because of the difficulty of assessing biotic SIE.
It is of special importance because biotic SIE are likely changing in a changing climate giving rise to couplings and feedbacks between climate change and atmospheric chemistry.

Moreover, we clearly state the limits of our approach and do NOT pretend to have solved the problem, because present modeling can result in both, over- and underpredicted SOA loadings. The purpose of the paper is to stimulate more work on the role of SIE for SOA formation, including detailed field measurements. However the latter will be difficult. We agree that it would be good if it were possible to use specific aerosol tracers to demonstrate stress induced emissions substantially contribute to OA formation especially to BSOA. However, so far there is no usable aerosol tracer that allows distinguishing whether fragments originate from hydrocarbons that have been emitted constitutively or as a consequence of stress to plants. Once the hydrocarbon is oxidized, this information is lost.

Referee #1: As such the comparison between model and measurements is perhaps a necessary but certainly not a sufficient criterion.

Our response: We agree. The comparison between measured and calculated SOA loadings as shown in Fig. 2 was made to show that the assumptions on the degree of infestation do not lead to unrealistic results. This is clearly accentuated by the corresponding text where it is written: "Since the model SIE are treated as a simple fraction of the "unstressed" MT emissions an improvement in model results when adding SIE is not a proof that the stress induced emissions are correctly modelled; the model improvement could also be due compensation of underestimated regular BVOC emissions…" (P. 13622 lines 4 ff).

Referee #1: It is not clear at all why the authors do not choose to compare with the most obvious dataset to test their hypothesis: ambient VOC observations of the suspected compounds, which should be available for one of the reported sites. Without demonstrating that stress induced VOC concentrations play a significant role under real world conditions, the presented results are inconclusive. Without field verification there is no hard scientific evidence that biotic stress plays a significant role on atmospheric composition and the aerosol formation potential.

Our response: Again, we agree in principle, but suitable VOC observations are not available to our knowledge. There is an intrinsic problem especially for sesquiterpenes and the C_{17} BVOC.

Sesquiterpenes are highly reactive towards ozone. Their lifetimes therefore are in the range of minutes and ambient concentrations may be unmeasurably low. As the contribution of a certain compound to SOA formation is not determined by its concentration but by its oxidative consumption, low ambient concentrations do not at all hint to a low contribution to particle formation of sesquiterpenes. Low concentrations may be caused by a high oxidative consumption and therefore may be combined with high contribution to SOA formation. Similarly, from the laboratory measurements described in Mentel et al. (2013) we know that the C_{17} compounds are too reactive towards ozone to allow finding them at high ambient concentrations.

There is only one stress induced emission of an unreactive compound that would allow finding it at higher concentrations, methyl salicylate (MeSA). MeSA does not react with ozone and it is not very reactive towards OH. Correspondingly, there is a report on ambient MeSA concentrations in the literature (Karl et al., 2008) and we used the data for comparison (Page 13624, lines 4 – 6): "Our estimated MeSA concentrations are of the same order of magnitude as observed by Karl et al. (2008). They found MeSA mixing ratios of ~100 ppt(v) within and above the canopy of a walnut agroforest."

We note that a limited evaluation of our estimate on the fraction of infested trees by comparison with ambient data – as requested by referee #1 - was made. It was made using the so far only applicable BVOC for this validation that we are aware of. (If the referee has any suggestion for suitable data-sets that are available in the open literature we will make a comparison.)

Referee #1: Based on current ambient concentration and emission measurements available in the literature, one could actually argue, that abiotic stresses could be similarly (or perhaps far more) important drivers of biogenic OA formation (e.g. Schade and Goldstein, GRL, 2003; Haase et al., ACP, 2011; Kim et al., JAC, 2011; Kaser et al., ACP, 2013.). The authors do not discuss abiotic stresses, which for the purpose of realistic model scenarios is another major short coming. It is not clear why only biotic stresses should be important with respect to climate change.

Our response: We agree, every kind of stress to plants is important for BVOC emissions and for SOA formation. Exactly this is the reason why we propose to consider stress in our modelling. The references point out a very important phenomenon, increased monoterpene (MT) emissions after mechanical woundings, e.g. clear outs, storms, or hail storms. Actually those should be

covered by our findings that MT have a SOA yield 5%-8% independent of the detailed composition (Mentel et al. 2009, Lang-Yona et al. 2010, Mentel et al. 2013). To a first approximation, SOA should scale in this case with the amount of MT. We are well aware of the importance of abiotic stresses e.g. BVOC emissions under heat stress (Kleist et al., BG, 2012). The role of abiotic stress is also mentioned in Mentel et al. (2013).
However, in this manuscript we focused on impacts of biotic stresses and not on impacts of abiotic stresses. Biotic stress is well worth considering in its own right - as explained in the manuscript, forest reports show that infestation by insects is ubiquitous in European forests.

Referee #1: Upscaling laboratory emissions is subject to great uncertainty, which is evident by the presented speculation on page 6 (line 170); it is not clear whether the C17 compound is produced by insects or the plants themselves. It would seem that only if the vegetation persistently emitted the compound in response to the elicitor, it could perhaps play a role in enhancing atmospheric concentrations. However, without data on ambient concentrations this again is pure speculation.

Our response: As written clearly in the text, for our considerations it is not important if the class C_{17} BVOC is produced by the insects or by the plants themselves. We use the ratio of constitutive emissions to C_{17} emissions as measured in the laboratory in context of the study by Mentel et al. (2013) to estimate the source strengths in case of severe infestation. As written above, the C_{17} compounds are highly reactive towards ozone and accumulation will only be possible at near to zero ozone concentrations as in our chambers. We would like to turn the argument around, we think it is interesting information for future assessments that bee keepers keep track and records of bark lice, sometimes in quasi-quantitative way (stock balances): a new way of assessing (one type of) biotic stress by infestation.

Referee #1: In summary the manuscript can not convincingly (i.e. quantitatively) demonstrate whether biotic stress induced emissions play a significant or negligible role for OA aerosol formation in the atmosphere. Without ambient VOC measurements of the suspected compounds I do not see how the current manuscript can be improved. As a consequence the modeling activity can not realistically constrain lower or upper limits of the effect of stress induced emissions on organic aerosol formation in the real world and the added scientific value to what is already known and has been published (e.g. Mentel et al., current special issue) is limited.

Our response: We clearly see an added scientific value to what is known and has been published. Indeed we used the laboratory data published by Mentel et al. as the base. But, as noted before, we used data from forest research to scale up the findings given by Mentel et al. and we calculated SOA formation in consideration of all other known SOA precursors. As a result of our modeling we estimate the possible contribution of biogenic emissions induced by biotic stress to SOA formation to 50% to 70%. This was not known before, such data can only be obtained by modeling where atmospheric processes are treated at realistic ambient levels e.g. gas to particle partitioning; and, together with the studies of Berg et al. (2013), this is one of the first attempts to model stress induced emissions from biotic stress.

We are aware that the uncertainty of the results is high, but we make this clear (and again, our title ends with a question mark). The potential importance of the source is shown to be high also. We believe our approach is the best way to highlight both the potential and the uncertainties of this source, and preferable to simply ignoring a source altogether because of lacks in suitable data and information about the distribution of stress and its specific effects (P. 13608 lines 6ff).

Minor comments of Referee #1:

Page 3, line 84: it is not explained or referenced what causes a stronger response for spruce trees

Response: Thanks for pointing out this unclear referencing. Engelmann spruce attacked by bark beetles respond with higher BVOC-emissions and SOA-formation than lodgpole pine according to Berg et al. (2013). We will adjust the text so that it is clear that the information is from Berg et al.

Page 4: line 96: delete "the"

Thanks for spotting this typo, the extra "the" will be removed.

Figure 2, OA: concentrations – the plot compares observed OA <1 um with modeled OA<2.5 um. What is the difference in mass loadings (1um vs 2.5 um) based on size distribution measurements at this site? If negligible it should be explained.

All BSOA in this work is assumed to be formed through gas-particle partitioning to the accumulation mode, which in the EMEP model has a mass-median diameter of 330 nm. This assumption is consistent with many studies over Europe and at Hyytiala (e.g. Allan et al., 2006, McDonald et al., 2007, Beddows et al., 2014). The difference between OA in PM1 and PM2.5 is thus negligible, especially in the context of the much larger uncertainties discussed here. We will add text on this to the paper.

C17 compound: even though an exact identification might not be possible, it would at the minimum be important to indicate the molecular composition of the compound is (e.g. C17HxOxN?....) –. As presented now, it is hard to justify the discussion on the atmospheric fate solely based on a qualitative lifetime, such as the combined lifetime of OH and O3 (or other losses in the cuvette such as surface losses)

Our response: The C_{17} compounds are identified and this identification is described in Mentel et al. (2013). We here only used the nomenclature but as requested we will add the names of the compounds.
The discussion on possible atmospheric fates was mainly performed for MeSA. The low reactivity of MeSA to OH might cause that dry deposition or reactions with NO_3 become an important pathway of MeSA removal from the atmosphere. As SOA formation from NO_3 oxidation of MeSA is unknown so far and dry deposition does not lead to SOA formation this had to be discussed. For the C_{17} BVOC this was not made in that detail because these compounds are highly reactive towards ozone and thus, their atmospheric fate is obvious.

Page 6/7: it is rather odd arguing that defoliation is an early warning sign – defoliation, as it can occur under severe drought stress (e.g. crown changing events), is typically considered a very severe sign of ecosystem stress.

The phrasing "early warning sign" was cited from a forest report by Fischer et al. We also used tree infestation by insects also reported in the forest reports for our assessment in addition to defoliation. We do not qualify defoliation but only use it as stress indicator in a very general way.

Finally, we hope that we have made the intention of this paper clearer with this reply. The paper

is intended to highlight a potentially important source of SOA, and to encourage the new scientific studies that will be required before we can truly quantify and understand biotic stress. The uncertainties are large, but this paper shows that there is a strong need for better information on this previously neglected source of SOA.

References:

Allan, J., Alfarra, M., Bower, K. et al., Size and composition measurements of background aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer Atmos. Chem. Physics, 2006, 6, 315-327

Beddows, D. C. S.; Dall'Osto, M.; Harrison, R. M. et al., Variations in tropospheric submicron particle size distributions across the European continent 2008-2009 Atmospheric Chemistry and Physics, 2014, 14, 4327-4348

Berg, A. R., Heald, C. L., Huff Hartz, et al., The impact of bark beetle infestations on monoterpene emissions and secondary organic aerosol formation in western North America, Atmos. Chem. Phys., 13, 3149-3161, doi:10.5194/acp-13-3149-2013, 2013.

Karl, T., Guenther, A., Turnipseed, A., Patton, E. G., and Jardine, K.: Chemical sensing of plant stress at the ecosystem scale, Biogeosciences, 5, 1287–1294, doi:10.5194/bg-5-1287-2008, 2008.

Kleist, E., Mentel, T. F., Andres, S. et al., Irreversible impacts of heat on the emissions of 10 monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species, Biogeosciences, 9, 5111–5123, doi:10.5194/bg-9-5111-2012, 2012.

Lang-Yona, N., Rudich, Y., Mentel, Th. F. et al., , The chemical and microphysical properties of secondary organic aerosols from Holm Oak emissions, Atmos. Chem. Phys., 10, 7253-7265, doi:10.5194/acp-10-7253-2010, 2010.

McDonald, A. G.; Bealey, W. J.; Fowler, D.; et al., Quantifying the effect of urban tree planting on concentrations and depositions of PM10 in two UK conurbations Atmos. Environ., 2007, 41, 8455-8467

Mentel, Th. F., Wildt, J., Kiendler-Scharr, A., et al., Photochemical production of aerosols from real plant emissions, Atmos. Chem. Phys., 9, 4387-4406, doi:10.5194/acp-9-4387-2009, 2009.

Mentel, Th. F., Kleist, E., Andres, S., et al., D Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks, Atmos. Chem. Phys., 13, 8755-8770, doi:10.5194/acp-13-8755-2013, 2013.