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Interactive comment

Interactive comment on "Passive adsorption of neighbouring plant volatiles linked to associational susceptibility in a subarctic ecosystem" *by* Adedayo Mofikoya et al.

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Interactive comment on "Passive adsorption of neighbouring plant volatiles linked to associational susceptibility in a subarctic ecosystem" by Adedayo Mofikoya et al. Anonymous Reviewer #2 Received and published: 3 January 2017

The present works presents a dataset of VOC measurements associated with mountain birch and rhododendron in an arctic environment, in order to evaluate potential associate susceptibility for pests. As such the topic is very interesting to the community and appropriate for Biogeosciences. This reviewer acknowledges that such measurements are difficult to obtain and that the research is novel and original. Overall, the dataset appears to be quite limited (at least to the reviewer, who is a working primarily on at-

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Discussion paper

mospheric measurements including VOC). The paper is well written, but the results are mainly presented as tables, which are not very enticing. In the opinion of the reviewer the paper could be considered for publication due to the novelty of the dataset, once questions about the methodology are resolved and the discussion is streamlined to the underlying data.

Author's Response: We thank Reviewer #2 for the succinct review and constructive comments. We have responded to all the comments in the subsequent paragraphs. We will consider incorporating the points raised by the reviewer during subsequent revision of the manuscript and where we cannot do this, we hope that we have been clearly able to express our reasoning.

General comments

Reviewer Comment 1: There may be significant methodological issues: (1) There appears to be only one measurement per plot for MB and less than 1 for Rt. These are not controlled for environmental conditions (T, ozone, humidity...) which surely affect emissions/ reactions as well as desorption. The authors should explain, why this does not affect their results or provide additional/ auxiliary data.

Author's Response: We acknowledge the important points raised here by Reviewer #2, the reviewer is right about the measurement of RT from less than each plot, we had a constrain for time and unfortunately, we ran short of Tenax tubes. We selected 10 RT shoots at random; measured emissions from 6 RT from high density RT plots and 4 from moderate density and found no significant difference in the mean emission rates of compounds between these two groups. Temperature and humidity measurements were taken during sampling and throughout the study period (we will include data in revised version) these were generally uniform during sampling period. Ozone levels and mean daily peak concentrations are generally at lower levels (Komppula et al. 2014) in the subarctic than in boreal and temperate areas. However, O3 concentrations was not measured during our field campaign. An ozone scrubber and charcoal filter was used during collection of volatiles to remove the possible presence of ozone and ambient air volatiles from the replacement air. We will include this information in the methods section of the revised manuscript.

Reviewer Comment 2: There does not seem to be a true control for the VOC measurements, where Tenax is used to measure air rather than a branch. Are the authors certain, that they are indeed measuring desorption from MB rather than ambient concentrations?

Author's Response: We had 4 blank samples; volatile samples were collected from empty bags with no branch and with similar charcoal filters and ozone scrubbers in replacement air as in plant sampling. We did not find any records of volatile compounds in blank air samples after GC-MS analysis. We are absolutely sure on the basis of the blank samples that all detected emissions are from sampled branches. All details for sampling method were given in the cited publications in L162 See (Blande, Turunen & Holopainen 2009). However, we will add more information of replacement air filtering in revised version of the manuscript.

Reviewer Comment 3: In the results section, there seems to be a diverging behavior in the moderate group, which dominates the behavior. This needs to be further investigated, and explained (eg. with temperature data) before the hypothesis given in the introduction of the paper can be accepted.

Author's Response: We explain the temperature dependence of volatile rerelease with data represented in figure 2 as we considered the correlation between temperature and amount of volatiles recovered in the treatment plots. The moderate group generally dominates the behaviour due to the large number in the group – 12, which doubles that in high density group. Moreover, we considered the amount of RT shrubs and not the grouping when we ran the correlation analysis on RT volatile recovery (See Figure 1.)

Reviewer Comment 4: The discussion about associational susceptibility appears to be mainly based on a review of literature, which relies heavily on Holopainen rather than the data presented here. In my opinion this might not be appropriate for a research article, which should focus on the discussion of present results. I suggest to refocus the discussion and to shorten it.

Author's Response: In the revision we will substantially shorten the AR/AS discussion in the herbivory section and focus only on gall mites as an example of arthropods that appeared on most of the plants.

Specific comments

Title: The title might be a bit misleading, given the fact that no associational susceptibility was found/ proven.

Author's Response: Like our response to comment 4, we have statistically significant herbivore results, with gall mites data. We have worded the title of the manuscript carefully to establish only a correlative link, this link doesn't necessarily prove causation.

L120: "focal plant" Âż this might be a good location to clarify, whether MB is the focal plant of this study.

Author's Response: Good point. We will clarify in the revised manuscript.

L166: "The disposable bags had been pre-heated at 120oC for a few hours before use." Âż Please state the reason for this treatment. I assume to remove contaminant semivolatiles (?)

Author's Response: The reviewer's assumption is correct, we will state the reason in the revised manuscript. Heating removed possible semivolatile contaminants, but also more volatile compounds of the bag material.

Section 2.1: In order to help the reader get a better understanding of the site and the plant community, it would be good to add a figure displaying the MB, Rt association in moderate and high density.

Author's Response: We have some plant community photographs from the sampling period, we will include in the revised manuscript.

Section 2.1: Similar to the upper comment, I would appreciate a physical description of the plant heights and other information here (move key information from S1). How far away are MB and Rt branches (on average)?

Author's Response: Like the reviewer noted we have included the average information of vertical distances and other key information in the S1, in the revised version, we will include a more detailed description of quadrant properties including tree height, vertical distances, sampling temperatures among others. We also have a map with scale of each tree location in the sampling site. All of these will be included in the revised manuscript.

L162-164: "One branch from each of the 24 MB trees and 10 Rt branches were selected for volatile sampling: one Rt branches from 6 high Rt density quadrants and a branch each from 4 moderate Rt density quadrants (control had no Rt branches). " Âż I am a bit confused by this description. Does this mean, that the authors did not sample Rt in each of the plots. Could the authors comment on why this decision was made. It appears to me that one would expect a significant variation in VOC emissions between Rt plants.

Author's Response: The reviewer is correct in the fact that RT was not sampled from each plot, there was a constraining time factor, we ran short of sampling tubes and because of the strict natural reserve of the sampling area where very limited damage and collection of plant parts could be done to the vegetation (RT sampling involved cutting sampled ramet as terpene-storing glandular trichomes can be found from bark). However, there was no difference in average RT emission when we compared collection from branches sampled from different RT densities, this is not unexpected as emissions were expressed as measure of plant dry weight.

L168: "A Tenax TA adsorbent tube" Âż Could the authors comment on whether the Tenax was pristine or desorbed before use.

Author's Response: The Tenax tubes were desorbed before use.

L190-191: "Emission rates were expressed as ng g-1 LA m-2 h-1 for birch leaves and ng g-1 leaf DW h-1 for R. tomentosum shoots" Âż could the authors comment on whether storage in bag or adsorption to the bag may be important. Similarly, as the monoterpenes are sticky, to what extent would flow rate, which is approximately given impact the measurements.

Author's Response: Yes there is the possibility that part of the semi-volatile compound emissions may stick to the surface of bags during sample collection. Flow rate of inlet and outlet air were calibrated prior to collection, it is inevitable that some of the compounds might be lost due to sticking on bag surfaces or escaping during collection. However, for every volatile sampling, a new preheated bag was used, the times used for flushing air out of bag, collection of volatiles and bag size was all the same for each sampling procedure.

Section 2.2: Could the authors comment on the recovery. I am a bit concerned that the desorption of VOC from the MB could be flow speed dependent as increasing the flow through the bag may increase desorption from the leaf surface.

Author's Response: The reviewer raises an important point here, we used flow rates that have being used in previous field campaigns in the course of our work. The flow rates (inlet and outlet were calibrated frequently with battery-operated calibrator) are also considered in the emission rate calculations, so any difference in flow rates (either increase or decrease) will most likely be reflected in the value of emission rates.

L219-221: There was no difference in the means of Rt compounds emitted from sampled branches from high and moderate Rt quadrants. Rt branches from high density quadrants had higher emission rates per emitting unit (ng g-1 h-1) Âż These two sentences are confusing. Is there a difference or is there no difference. Or is there a difference for some compounds, but not for others. Please clarify the text.

Author's Response: We are sorry for the mix up. There was no difference between RT emissions. This will be rectified in the revised version.

Results/ Figure 1b-d Âż This may be an optical illusion, but it appears to me that there the linear trend, which is provided by the trend line is mainly dependent on a diverging behavior in the moderate group, where some plots have virtually no recovery, while others have a high recovery (significantly higher than high density plots).

Author's Response: The reviewer is right in noting that some moderate density plots had a higher recovery compared to high density plots, this likely points to the fact that RT density isn't the only factor in adsorption and recovery of RT compounds from MB branches, other factors like temperature and sampling time may also play important roles. Also one high density plot did not have recovery of adhered compounds. Therefore, we expect that temporary sun fleck heating of some branches before VOC collection might have affected our results.

Section: 3.4. "R. TOMENTOSUM ABUNDANCE AND RECOVERY RATE OF ADHERED COMPOUNDS" Âż To what extent can we be sure that the measured recovered compounds are indeed desorbed from MB and do not represent ambient air concentrations. Did the authors do a control in which no branch was sampled?

Author's Response: We are absolutely sure that we have measured desorbed compounds from MB branches, not ambient air concentrations. Prior to VOC collection, the clean bags enclosed on branches were first flushed with filtered air to remove any ambient impurities before volatile collection began (although this might have lead loss of some of the adhered RT compounds). We did take ambient air samples from closed empty bag with our sampling system having charcoal filter and ozone scrubber in replacement air (blank samples) and didn't record any compounds after GC-MS analysis. This information will be added in the revised version of the manuscript. We did not sample unfiltered ambient air samples to see VOC concentrations in the air as we studied only plant surface recovery in this campaign. However, in a field sampling of ambient forest air at noon in a boreal forest site of Finland 1m above RT shoots in forest understorey we found myrcene levels of approximately 5 ngL-1, palustrol levels of approximately 9 ngL-1 and ledol levels of approximately 2 ngL-1 (Mofikoya, unpublished data). Thus, in day time RT compounds can be detected in the ambient air above RT vegetation.

Figure 2a-b Âż Similar to Figure 1, there seems to be an either/or relationship for the presence of compounds. Could the authors comment on this. Since there seems to be a difference between Ledol/Aromadenalene and Paulstrol (which dominates the total), could the authors comment on the reasons such as vapor pressure

Author's Response: The reviewer is right. These compounds behave differently, ledol and aromadendrene were recovered only from few MB trees. As table1 shows, ledol and aromadendrene are emitted at lower amounts from Rt than dominating palustrol. In some plots, these compounds were not emitted. Sesquiterpene aromadendrene was the third most common compound in RT emissions after myrcene and palustrol (Table 1). Aromadendrene has significantly higher vapour pressure (approximately 0.023000 mm/Hg at 25°C) than palustrol (appr. 0.000179 mm/Hg at 25°C), which is a possible cause of lower adherence/recovery rate and more zero observation. Furthermore, aromadendrene emissions might have been photo-oxidized faster on surfaces than sesquiterpene alcohols ledol and palustrol. Ledol, although having low vapor pressure, was emitted in relatively lower amounts from RT plants.

. . . L333-336: "The recovery of other Rt compounds (aromadendrene and ledol) from a small number of MB branches with Rt in the understorey, suggests that Rt presence and density alone may not be enough for adherence of sticky volatile compounds on neighboring plant foliage. Other factors like temperature (Niinemets et al. 2014) and distance (Heil Adame-Alvarez 2010) may play important roles." Âż This is very apparent from Figure 1. I feel that the paper would have been greatly strengthened by additional measurements of these factors.

Author's Response: We agree with reviewer. It is obvious that continuous measurement of leaf and bark temperature of the receiver plant before VOC collection is needed in order to separate how much temperature history and sampling temperature might affect the recovery of adhered compounds. Individual sampling temperatures and vertical distances (means given in Appendix A1) will be included in revised version of the manuscript. We have shown in figure 1 the relationship between RT density and recovery of RT compounds and in figure 2 we show the relationship between recovery of these compounds and sampling temperature.

L 336: "The vertical distances between the base of Rt shoots and the sample MB branches in our study ranged between 100 – 106cm" Âż This would be good information for the methods Section

Author's Response: Thank you for your comments, this information will be moved to the methods section in the revised manuscript.

4.4 Âż The emissions of VOC are very temperature dependent and temperature was measured as part of the sampling. To what extent did the authors look at temperature dependence of emissions and thus also recovery.

Author's Response: Please refer to figure 2 for our analysis of temperature dependence of recovery. All analyses were based on the average temperature inside the VOC sampling bag during the sampling period.

Can the authors also comment on the impacts of chemical reactions with ozone, which will surely affect transport of MT and sequiterpenes and thus the potential of 'communication' between Rt and MT. What are the atmospheric lifetimes of these gases?

Author's Response: Volatiles have been shown to play roles in plant signalling over distances of up to 1.3m (Tscharntke et al. 2001), however these volatiles may be subject to reactions once released into the atmosphere. We mentioned briefly in lines 113-116, the reactive nature of terpene compounds to ozone and OH radicals, and also that sesquiterpene alcohols are less reactive. Atmospheric lifetimes of the compounds depend on the number of C-C double bonds, and the presence of oxidizing pollutants in the atmosphere. Generally, monoterpenes like myrcene and sesquiterpenes like β-caryophyllene are relatively less persistent in the atmosphere when compared to atmospheric lifetimes of sesquiterpene alcohols like ledol and palustrol. The atmospheric lifetimes in minutes with OH radical (OH) and ozone (O3) are for myrcene 39 and 50 min (Atkinson and Arey 2003) and for aromadendrene 490 and 2 min (Bouvier-Brown et al. 2009), respectively. We did not find information of atmospheric lifetimes of ledol and palustrol with OH and O3. However, as saturated compounds their reactivity towards O3 should be very low and their atmospheric lifetimes will be several days rather than hours.

Technical comments (not exhaustive)

L98: It seems inconsistent that mountain birch is abbreviated by its common name (MB), while rhododendron by its taxonomic name (RT).

Author's Response: The reviewer raises a good point, we have used the common MB name for a number of reasons. First the mountain birch is a sub species of B. pubescens, which means the abbreviation of the botanical name would be much longer and cumbersome. Also there isn't a widely accepted general name for RT, Wild Rosemary, Marsh Tea or Labrador tea are other common names that have been used. Also previous scientific name Ledum palustre (e.g. giving the name for ledol and palustrol) is still widely used. So the abbreviation of its current scientific name was better suited in this case.

L168: "sucked air" Âż might be a bit too colloquial L193 and others.

Author's Response: This is noted and will be changed in revised version of manuscript.

Fix references that include the author in the sentence (Guenther et al 2012)

Author's Response: Noted and will be fixed in revised manuscript.

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