

## **Anonymous Referee #1**

**NB:** *italic font indicates the referee's comments* and plain text indicates our response. Also, all references to section numbers, tables and figures refer to the revised manuscript. A new section 2.2 will be added, so following 2.x sections are incremented by 1 in our responses. The original Equation 4 was eliminated, so new Equation 4 = old Equation 5, etc. Finally, Table 1 was added, so new Table 2 = old Table 1.

*This is a very interesting and quite comprehensive work. It is also very suitable for publication in Biogeosciences since the topic links vegetation processes to atmospheric and climate change research. The manuscript is generally well written albeit occasionally a bit lengthy. My main concerns are about the methods used for scaling the results. Rather than scaling isoprene emission linearly against light, I would prefer adjusting (decreasing) the alpha-parameter in equation 2 as has been done previously by Harley et al. 1996 (and 1997) and other authors and discussed in Monson et al. 2012. Generally, some references are certainly missing that have to be discussed (see below) but otherwise I have no objections against publication. In the following, I elaborate a bit on questions or remarks related to specific text passages.*

We appreciate all the thoughtful comments and the support for publication of Reviewer #1, and we will make substantial revisions to the manuscript to address these comments. In particular, we will remove Eq. 4 and the linear scaling with light. Instead, we will adjust the parameters in Eq. 2 as suggested by the reviewer. This will require modifications to Fig. 2 and Fig. 5 and numerous modifications to figure captions and the text. We also will add an additional analysis and change Fig. 5 and Fig. 6 to show the model vs. data fit for both years combined, as suggested (see details below). In almost every case below, we will make changes to the text to address the comments raised by the reviewer. We thank the reviewer for the comments, and we have a much improved manuscript because of the input.

### **Abstract**

*L12: Note that it is not the algorithm but the standard parameters that are suitable/ unsuitable for use with the specific vegetation system.*

Will add the text, "with published coefficients" to address this issue.

*L14: The decisive conclusion in the comparison between sites would be if the emission per leaf area *S. pulchra* is approximately equal of if some other factors need to be considered. The absolute emission values are only of secondary importance.*

First, we will change "less" to "little" and then add "suggesting other significant isoprene emitters."

*L18: clarify that the result of the simulations is a decrease of OH radicals when considering isoprene emission (with respective consequences on greenhouse gas concentrations).*

Will change "including the hydroxyl radical (OH)" to "including a reduction of hydroxyl radical (OH) concentrations".

## Introduction

*Please note that there are a couple of newer and more comprehensive reviews about BVOC emission sensitivity (Holopainen and Gershenson 2010) and impacts generally (Sharkey et al. 2008, Harrison et al. 2012) and specifically on the leaf (Vickers et al. 2009, Niinemets 2010) ecosystem (Yuan et al. 2010, Clavijo McCormick et al. 2012) regional (Pinto et al. 2010) and global (Laothavornkitkul et al. 2009, Penuelas and Staudt 2010) scale. Modelling has been described in Grote and Niinemets 2008, Arneth et al. 2011, Monson et al. 2012.*

We will add all the literature citations as suggested, and added to the list of factors which are impacted by climate change in the final sentence of the first paragraph in the introduction. We also will add the following sentence to add more literature citations for modeling: "Isoprene emissions are modelled using algorithms derived from the leaf-level response of emissions to variations in temperature and light which have mechanistic underpinnings (Guenther et al., 1993; Grote and Niinemets, 2008; Monson et al., 2012)."

*Also, the particular focus on isoprene should be more towards the end of this overview or in a separate paragraph.*

We will change the focus of the paragraph to be solely on isoprene, after the transition "This study focuses on isoprene". We will also split this paragraph into two to highlight this shift, and also in response to a comment from Reviewer #2.

*P13356, L10,11: Referring to Guenther et al. 2006 is a very general statement with global focus, while the arctic biosphere systems might require more specific. So, a shift between shrub species abundance might also lead to a decrease of emissions (Faubert et al. 2011) Also, a general statement about BVOC is hardly appropriate since birch for example (which emits no isoprene) has been shown to emit significant amounts of monoterpenes and sesquiterpenes (Tarvainen et al. 2007, Haapanala et al. 2009).*

These are all very good points. Our original intent in citing Guenther et al. 2006 was just for the difference in emission capacities, but we agree this is ambiguous and that we should be more careful with our general statement. We will replace that sentence with the following new paragraph:

"Changing species composition effects on ecosystem BVOC emissions in the Arctic are complex. A study of mountain birch (*B. pubescens*) forests found that ecosystem BVOC emissions (in particular, sesquiterpenes) would decrease because warming would increase nutrient availability that would in turn promote ground-cover species with lower emission capacities (Faubert et al., 2012). But increases in deciduous shrubs could lead to increases in ecosystem BVOC emissions. While *Betula* species are not isoprene emitters, they do emit monoterpenes and sesquiterpenes (Haapanala et al., 2009; Tarvainen et al., 2007), so increases in *Betula* species would lead to increases in ecosystem BVOC emissions, assuming that the replaced grasses and sedges had lower emission capacities."

## Methods

*The description of measurements and modelling should be better separated.*

We will add an additional heading, “Leaf-level modelling” so that both leaf-level and ecosystem modeling have their own headings.

*The measurement description is rather lengthy and should be shortened or put into an appendix.*

Because the analysis of isoprene concentrations for the leaf-level and chamber measurements is routine, we will move the details of the gas chromatography to Supplementary Material. This section is extended because two different but similar gas chromatograph systems were used. The confusion caused by the two systems was also noted by the second reviewer.

We agree that the remaining material in Section 2 is lengthy, but we believe including the material is necessary. First, the second reviewer raises substantial methodological questions, which show there is interest in these details. Second, our reported results include both leaf-level and whole-system measurements, which use different methodologies. Including these results creates a strong paper, but does require a long methods section. Third, while some of the techniques have been applied before, most of these techniques are relatively new in Arctic ecosystems. An example would be using detached leaves for the leaf-level measurements. This is a standard practice at the Toolik Field Station, but this approach was questioned by the second reviewer.

*However, it should be clarified how the sites for chamber measurements are selected and what is in there.*

We will add a table (new Table 1) that describes the species present in the chambers. The following text will also be added to address this issue and also issues raised by Reviewer 2: “The static measurements were made with a rigid transparent plastic chamber that fitted to pre-existing plastic square bases inserted into the soil that were setup for a previous experiment on carbon isotope dynamics. 15 separate measurements across 6 different pre-installed chamber bases were performed over the course of 4 days. The relative abundance of species present in the chambers is given in Table 1 and is representative of moist acidic tundra ecosystems.”

*As pointed out in the general section, I would prefer a change in the alpha parameter to adjust the sensitivity to light rather than assume a simple linear dependency.*

We will make this change—further notes are below in the Results/Discussion section. We will add the following sentence, “To further explore the applicability of the Guenther algorithms to emissions from Arctic plants, an additional fit to the leaf-level data was performed which estimated  $\alpha$  and  $C_{L1}$  with a non-linear, least-squares technique.” We will remove Eq. 4 and the references to it.

*There is also a small conception-error in equation 2 that has been pointed out by Monson et al. 2012 (which will not change the equation anyway).*

We will make note of this new paper in Section 2.3, “These equations are derived from empirical observations but agree well with theoretical considerations, if an adjustment is included to correct a mismatch in the units (Monson et al., 2012).”

*P13363, L20: If you use the canopy model that uses wind speed you should refer to Guenther et al. 1999. However, I doubt that the influence is large.*

We will add this reference.

## **Results/Discussion**

*As indicated above, I would appreciate, if the alpha parameter could be adjusted to the results.*

The will adjust the alpha parameter in Eq. 2. Looking at the data, we also will adjust the CL1 parameter, because this has a larger impact on the more linear shape of the light-response curve. We will change every reference to the old linear analysis to discuss the new technique of optimizing parameters.

*P13367, L12ff: This has actually also been found in other studies (Copeland et al. 2012, Karl et al. 2009) although some studies indicate less emission capacity (Olofsson et al. 2005)*

We will address the first part of this comment by adding the following note to the end of the final paragraph in section 3.1.1, "The agreement in the basal emission rate and response to temperature has been noted previously in high-latitude ecosystems for a range of species (Karl et al., 2009 and references therein) and specifically for *Salix* at lower latitudes (Copeland et al., 2012)."

The reference to Olofsson is more relevant to our simple whole-canopy model, and we will add the following after the first sentence in section 3.2.1, "This maximum value is just over 50 % higher than a previous report ( $0.73 \text{ mg C m}^{-2} \text{ hr}^{-1}$ ) for high-latitude *Salix* plantation ( $58^\circ \text{ N}$ , Olofsson et al., 2005)." Note that we will change the units from the citation. In addition, we will reference Olofsson for the big-leaf model just after introduces Equation 4 in section 2.6, "which has been assumed before in the literature for a high-latitude ecosystem (Olofsson et al., 2005)".

*P13368, L4ff: This reasoning is somewhat strange. If the plots had the same temperature they could hardly be used as warming references.*

We will add the following clarification by modifying the first item in the list, "(1) In the Sweden experiment, warming is accomplished with open-top tents that employ passive warming. By chance, cloudy weather caused the temperatures in the warmed plot to be the same as the control plot at the time of measurement."

*For the seasonality impact, many references can be found but you can refer to the modelling reviews of Grote and Niinemets 2008 and Monson et al. 2012.*

We will add these modeling reviews to Petron et al. reference.

*P13368, L12: add the current replication number*

We will add the following to the end of the paragraph, "Our replication is also low ( $n = 4$ ), but the large difference in means and lower variability results in a significant difference ( $p < 0.01$  as noted above)."

*P13372, L11: this can be discussed a bit further. It seems to corroborate results from Tiiva et al. 2009 but contradicts Haapanala et al. 2009. Perhaps the findings of Ekberg et al. 2011 could serve for explanation?*

We will address these excellent points of Tiiva and Ekberg appending the following text to the last sentence in section 3.2.2, “which is in agreement with a study that found vascular plants contributed over 90 % of the isoprene flux from a boreal peatland (Tiiva et al., 2009). We do note that *Sphagnum* ssp. have complex controls related to photosynthesis and water availability which could affect their contribution to ecosystem isoprene flux under different environmental conditions (Ekberg et al., 2011).”

We do not immediately see the connection to Haapanala et al 2009 (Mountain birch – potentially large source of sesquiterpenes into high latitude atmosphere), but we would be happy to pursue this with further clarification.

*P13373, L2: versus P13375, L10ff: It really seems strange to me that the results in the two years were so different. Seasonality is certainly a factor but then the differences do not disappear in the MEGAN runs although you ran them considering the previous days (you did, didn't you?). To get a more complete picture I suggest adding a third line in Figures 5 and 6 with a pooled data set and an appropriate adjustment of the models (this would demonstrate the best model performance in a global application).*

We did not use the previous day or 10-day temperature algorithm in MEGAN directly, but we do discuss how much of a difference the algorithm would have on the predictions (see the 4<sup>th</sup> and 5<sup>th</sup> paragraphs in section 3.2.1). We note that neither the 1 or 10-day temperature algorithm would change the modeled results to be in better agreement with the observations. An averaging period of 5-days would, but we feel that is too speculative to include based on one pair of observations in two different years. Also, we note that experimental error is at least 20 % with these measurements (3<sup>rd</sup> paragraph in section 3.2.1), which could explain almost ½ of the observed difference. This important issue highlights the necessity of obtaining a record of isoprene fluxes conducted over the entire growing season. See also our responses to Reviewer #2's comment that begins, “*Weather conditions in the Arctic...*” where we make some textual changes that address this issue.

We will add a line with the combined fit to each figure as suggested. To maintain clarity, this will be the 2<sup>nd</sup> dashed line in each of the four panels of both Figures 5 and 6. The dashed line in Figure 5 was just the fit for EC05 shown for EC10, so the combined fit accomplishes the same purpose. The dashed line in Figure 6 was just a one-to-one line, and with the combined fit it would just clutter the graph. We will add the following text in the figure captions to address this: Fig. 5, “The dashed line is the same fit for both years (EC05 and EC10) combined. The statistics for the combined fit with the original big-leaf model (two left-hand panels) are  $r^2 = 0.66$  and slope = 1.31 and with the adjusted big-leaf model (two right-hand panels) are  $r^2 = 0.73$  and slope 1.38.” and Fig. 6, “The dashed line is the same fit for both years (EC05 and EC10) combined. The statistics for the combined fit with MEGAN defaults (two left-hand panels) are  $r^2 = 0.72$  and slope = 0.70 and with MEGAN localized (two right-hand panels) are  $r^2 = 0.70$  and slope 1.57.”

*P13376, L12: What is low? Either this should be given in the figure or indicated somewhere else together with further air chemical boundary conditions. The latter also includes the concentrations of other isoprenoids (probably 0 but should be stated and discussed later).*

This information is available in Table 2 (Table 1 in original manuscript), and we will make a parenthetical note at this point in the manuscript, "(see Table 2 for initialization values for all chemical species)". We will also add this text to the Table 2 caption, "Any chemical species not listed but that is tracked by the model (for example, methyl vinyl ketone and methacrolein) was initialized to zero."

## **Conclusions**

*P13377, L14: simulated instead predicted*

We will make this change as requested.

*P13378, L10ff: No. Due to the general exponential relationship the increase of isoprenoid emission is expected to rise much steeper than predicted for the rest of the earth.*

We will modify the original sentence to, "For the Arctic, the temperature increase is expected to be greater than the global increase (IPCC, 2007), and BVOC emissions would be further amplified because of the exponential relationship between emissions and temperature (Equation 3)."

*However, the big question is how the isoprene emission develop in response to the rising CO<sub>2</sub> concentrations (Arneth et al. 2007, Monson et al. 2012, Harrison et al. 2012).*

Yes, we agree and are working on another manuscript on this topic. We will add the following sentence, "Further, the suppression of isoprene emission by elevated CO<sub>2</sub> concentration can offset the increase predicted from increasing air temperatures (Arneth et al., 2007; Monson et al., 2007)."

*P13378, L16: drought stress instead of water stress.*

We will make this change as suggested.

*P13378, L24ff: Careful. As already mentioned other species might emit less isoprene but eventually other substances such as monoterpenes and sesquiterpenes. The differences and similarities in air chemistry and aerosol impacts could be briefly discussed. It should also be noted that there is difference in abundance and LAI increase that is also a possible effect of climate warming and CO<sub>2</sub> increase. This could mean that besides a loss in abundance, the total emitting foliage amount could still increase (at least theoretically).*

We will split up the original paragraph and add this new text to address this concern:

"If ecosystem changes lead to increases in the abundance of *Salix* or other isoprene-emitting genera, then there will be increases in  $\epsilon$ . But if non-isoprene-emitting genera like *Betula* (birch) increase, then  $\epsilon$  could decrease for isoprene. The impact on monoterpene and sesquiterpene emission capacities would be the opposite, since *Betula* is a significant emitter of these chemical compounds (Haapanala et al.,

2009). This shift in the emissions profile would have impacts on atmospheric chemistry because of the relatively higher reactivity of these compounds compared to isoprene (see Table 2 in Fuentes et al., 2000). Similarly, monoterpenes and sesquiterpenes have higher aerosol yields which could lead to increases in secondary organic aerosol formation and associated impacts on climate (O'Dowd et al., 2002). In addition to changing  $\epsilon$  for isoprene, monoterpenes and sesquiterpenes, climate change could lead to increases in leaf biomass which could offset any reductions in  $\epsilon$ ."

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