Anonymous Referee #2

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.

The manuscript "Isoprene emissions from a tundra ecosystem" reports results from several short field campaigns conducted in Alaska. We have very limited understanding on VOC emissions from arctic ecosystems, so this manuscript is a welcomed addition to the current body of knowledge. It is also timely and relevant, because climate change in the Arctic areas could have a significant impact on isoprene emissions from these areas.

We appreciate the thoughtful comments of the second reviewer and the endorsement of the intellectual merit and relevance of our work. Many of Reviewer 2's comments focused on methodology, and we worked hard to make our experimental design more clear. We have made textual changes in response to almost every comment from the reviewer, and the manuscript will be stronger with this input.

General comments

I enjoyed reading the Introduction, which very clearly set the work into larger context. However, there is a little problem with the logic in the section 'Previous research on global change factors and deciduous shrub species'. You – correctly – tell about the documented increase in Betula nana, but since B. nana does not emit isoprene, which this manuscript is about, I don't see the point. This section gave me an impression that the measurements here would be on B. nana. Finally, on page 13359 I can find that the leaf-level measurements were made on Salix pulchra. Is it possible to shift the text in the section 'Previous research on global change factors and deciduous shrub species' towards isoprene-emitters and in addition to specifically address Salix? Why did the study focus particularly on this species? Is it an important species in the Arctic global change context? In the Methods, you should again and earlier tell what species is measured.

These are all good points. We address most of these issues later in the manuscript, but we understand that the current order creates confusion. Our intent on discussing *B. nana* is that this is the primary result from a major global change experiment at Toolik for the moist acidic tundra ecosystem. We will add this clarification, "The shrub species in the moist acidic tundra ecosystems near Toolik are dominated by two genera: *Betula* (birch) and *Salix* (willow) (Kade et al., 2012). *Betula spp*. are not isoprene emitters, although they do emit other BVOCs, while *Salix spp*. are strong isoprene emitters (Wiedinmyer, 2004). *Salix spp.* are the focus of this study." And we will also add this note further in the paragraph to highlight results applying generally to deciduous shrubs, "Other studies have focused more generally on the total impact on shrub cover."

In addition, we have added an entire paragraph in this section (final paragraph in Section 1.2) discussing species composition changes in response to Reviewer 1, and this paragraph also clarifies the concerns of Reviewer 2.

In the chamber and EC measurements, you have obviously measured emissions from other species than S. pulchra as well. As I point out later on, you should add vegetation descriptions for both of these measurements. If the percent cover for S. pulchra was 1.6% as you write on page 13371, I assume the 98% was not just bare soil? (By the way, on page 13374, you state that the cover was <1%.) On page 13372, you hint that actually there was no S. pulchra at all in the dynamic chambers, but only Sphagnum mosses. On page 13374, you finally say that 'We ascribe the emissions observed from the static chambers to sedge species'. The reader is quite confused when this information is not presented earlier.

These are important points that we will address, and some of the concerns are shared by Reviewer 1. In response to both reviewers, we will add a new Table 1, which will be a list of species/genera which are present in the static chambers with their corresponding percent cover. Because we will use a different methodology for analyzing the survey data for the static chambers, the new percent cover value for *Salix* is 2.1% and we will use that consistently (particularly in Section 3.3, correcting the mistake pointed out above). In addition, we will emphasize earlier (in Methods Section 2.7) that the smaller dynamic chambers only enclose sphagnum moss, and no *Salix*. Finally, a new reference suggested by Reviewer 1 is consistent with our attribution of only a small amount of the flux to mosses (Tiiva et al., 2009).

For the EC site, we will add a recently published reference with a vegetation survey near the EC tower (Kade et al., 2012) in section 3.2.2: "This moist acidic tundra ecosystem in the footprint of the tower consists of evergreen shrubs, the deciduous shrubs, the sedge *Eriophorum vaginatum* and mosses, and this ecosystem type dominates the ground cover (95 %; for complete details see Section 2.2 in Kade et al., 2012)."

Weather conditions in the Arctic vary a lot and are often shifting from conditions allowing for isoprene synthesis to no isoprene synthesis. Therefore, reliable data collection should take place over long time periods. Here, data were collected in 3 short field campaigns during the peak season. In 2005 there was 2 full days of measurement data, in 2010 one week, and 2011 2-4 days depending on the method. These datasets represent only a snapshot of ecosystem functioning. As the authors state 'Because of the short nature of both datasets, we cannot determine if this difference represents experimental error or a true difference'. The authors also write that 'no conclusions can be drawn from these two short datasets', but still the results are discussed at length. Do you consider that this data is solid enough to allow estimation of ecosystem emission factors and to drive an atmospheric chemistry model to determine their impact on Arctic photochemistry?

We will add clarifications to the text to highlight what we can conclude from the dataset, given the uncertainties. Briefly, we are confident in our emissions estimates and basal emission rates, but we are less confident in longer-term (for example, 1-10 day previous temperature) controls on the basal emission rate. Given that the atmospheric chemistry model is driven by observed emissions, we are confident in those results. The highest observed fluxes in 2005 are reduced by about 1/3 when

compared to similar met conditions in 2010—we are unsure of the mechanism driving this change, but we do explore previous temperature. In the abstract, we highlight what we are confident about, and do not directly mention the potential role of previous temperature. We will rewrite the first sentence to say, "Because of the short nature of both datasets, we cannot assume this observed difference represents a true difference in the underlying capacity of the ecosystem to emit isoprene." The second quoted sentence will be rewritten as follows, "Again, we cannot confirm the role of previous temperature given these two relatively short measurement periods, but variations in tundra ecosystem's capacity to emit isoprene (ε in Eq. 5) warrant further study."

It is not clear whether the leaf-level measurements were made on intact or detached leaves. In general, making isoprene emission measurements on excised leaves does not make sense to me, because isoprene emission is linked to photosynthesis. Could you please explain why this method was chosen? The comparison of measurements on intact and excised leaves mentioned on page 13359 is unclear. On line 15, what does ': : :at times up to 2 h' mean? Line 17, what emission rates? If this is isoprene, it would not take much space to show the mean and standard error for the two groups.

All the leaf-level measurements were performed on excised leaves, and we will emphasize this point in the second paragraph of Section 2.2, "All measurements were made on excised leaves in the laboratory." We apologize for the confusion, since the cartridges were only used for the chamber measurements (except for a cross calibration in the lab), so we will remove those confusing sentences. We will also modify the following sentence to emphasize that gas-exchange parameters were not changed by the excision, "Investigators have done photosynthetic and respiratory experiments (Griffin, data not shown) on excised leaves of *S. pulchra* from this tundra ecosystem, and comparisons have shown no effect of excision on CO_2 gas exchange at times up to 2 hours." We will add the data from the excision experiments, "(n = 3, mean cut/uncut ratio 0.88, standard error = 0.19)". Finally, we will add the following additional information to the end of this paragraph, "We assume the small impact of leaf excision on leaf physiology is due to the relatively low leaf water potentials of tundra plants, since leaf water potential has been observed to become less negative at higher latitudes (Figueroa et al., 2010)."

We are in the process of finding a citation or a personal communication reference for the photosynthesis experiment on excised leaves, and we will add that to the revised manuscript.

To me the temperature of 25C for leaf-level measurements sounds high, and based on the figs 3 and 4, the max. temperature was about 22 degrees during the eddy flux measurements. Same applies for the stepped temperatures; the range 20-32.5C sounds high. Why did you select these temperatures and not ambient temperature?

First, the stepped temperatures are leaf temperatures, which are higher than ambient air temperatures. We will add a citation that notes that leaf temperatures can exceed air temperatures by 7 °C (Wilson, 1957): "Although air temperatures were generally lower than this range, leaf temperatures can be elevated by 7 °C above ambient air temperature in Arctic plants (Wilson, 1957)." Second, we were interested if the same algorithms developed for mid-latitude plants would work for Arctic species, so we tested the leaves in a range when the algorithm predicts large changes in emissions with temperature.

If I understood correctly, leaves taken from greenhouses and control plots were measured under similar conditions, and then the isoprene emission per leaf area from the leaves collected from the greenhouse were 3 times higher than the emissions from the controls. What was the difference per leaf mass? Did the greenhouses affect the leaf structure? What did the greenhouses do to the soil water content? If there was a difference, how would you expect this to affect isoprene emissions? What was the CO2 concentration inside the greenhouses relative ambient and how would you expect this to affect the emissions?

We will add the following text to section 3.1.2:

"This result is not explained by a difference in specific leaf weight, which increased only 3.4 % in greenhouse; this difference is not significant (t-test, p = 0.73). As summarized in Bret-Harte (2001), the main effect of the greenhouse is to increase air temperature, but two side effects are decreased PAR and decreased relative humidity. Decreasing PAR would suppress emissions (Harley et al., 1996), so this does not drive the observed increase in the basal emission rate. In isolation, changes in relative humidity do not impact isoprene emission rates—for example, relative humidity is not included in the Guenther algorithms."

Unfortunately, we do not have any information concerning changes in carbon dioxide concentration or soil moisture. But the reference to Bret-Harte shows that this experimental treatment has been used as an analogue for long-term temperature change in previous publications.

Specific comments:

page 13353 line 5: 'Once BVOCs...' Start a new paragraph here.

In response to the first reviewer, the text now reads "Once isoprene…" but we do start a new paragraph at this point.

line 22: To have a more complete list, you could add a reference to Ekberg et al. 2011 (Boreal Environment Research Ekberg et al. 2011), Holst et al. (Atmospheric Chemistry and Physics 10, 1617-1634, 2010) and Faubert et al. 2012 (Plant and Soil 352: 199-215).

We appreciate these additional references, and we will add them to our list. Faubert did not detect isoprene emissions, so we make a note of that.

page 13355 line 9 onwards: Please specify that the ozone destruction mentioned here is tropospheric/ground-level ozone, not to confuse with ozone depletion in the stratosphere.

We added "tropospheric" to address this.

You should also correct the source of halogens. Helmig et al. (2007) refer to other papers and write ": : :halogens originating from within the sea ice zone."

We changed the sentence to, "Arctic tropospheric O_3 depletion is thought to be linked to emissions of halogens from within the sea ice zone (Helmig et al., 2007 and references therein)."

page 13358 line 3: To my knowledge the hydrocarbon trap does not remove ozone. Was ozone removed from the incoming air?

We believe that some ozone will be removed by the hydrocarbon trap. If this is not the case 3 factors minimize this issue. (1) Ozone levels at Toolik are low (we measured concentrations below 30 ppb, data not shown). (2) Ozone is also removed by the pump within the LI-6400 system (Geron et al., 2006). (3) The reactivity of ozone with isoprene is relatively low. We will add this, "The impact of isoprene reacting with any O_3 not removed by the trap is minimal because the LI-6400 pump also removes most O_3 (Geron et al., 2006) and ambient O_3 concentrations are low."

line 13 onwards: The isoprene analysis part could be easier to understand if you clearly describe the two methods used in separate sections. Now it is a bit confusing and it appears as if some issues are explained twice.

We agree this section is confusing and lengthy. We will move the details of the gas chromatography to the Supplement and also clearly label the two paragraphs. But the sentences referring to excised leaves will say in the main paper and are further discussed in the next comment.

page 13361 line 13: Were the measurements done in situ or using detached leaves, which were measured somewhere else?

All measurements were done with detached leaves—see comments above in response to the comment, "*It is not clear whether the leaf-level measurements…".*

How many plants per experimental plot were measured and how many leaves per plant?

In the first paragraph of section 2.4, we expanded an existing sentence to read, "Each treatment was applied to a 5 by 20 m plot and replicated in 4 blocks with 3 leaves sampled per block."

line 16: The description of statistical analyses is inadequate. You mention a post hoc test you have used, but it must have been preceded by something else.

We will replace the final sentence with the following text to clarify this point, "The data were analysed by first computing a mean from the 3 samples within each block, and then performing an ANOVA on the linear model with the 5 treatments (n = 4). The results were also analysed using Tukey's Honest Significant Difference (HSD) test."

page 13363 line 24: Why canopy type grass if the vegetation was shrubs?

This was the preexisting MEGAN default value used previously.

page 13364 line 7: Was S. pulchra the only plant species present in the footprint area? If not, please add to the manuscript a description of the vegetation.

We will add the text, "This moist acidic tundra ecosystem in the footprint of the tower consists of evergreen shrubs, the deciduous shrubs, the sedge *Eriophorum vaginatum* and mosses, and this

ecosystem type dominates the ground cover (95 %; for complete details see Section 2.2 in Kade et al., 2012)."

line 12 onwards: Please describe the vegetation composition in the chamber bases. Was the same vegetation community measured by dynamic and static chambers?

We will add Table 1 which describes the vegetation community in the static chambers. We will also add the following sentence in the final paragraph of section 2.8, "These smaller dynamic chambers were located to only enclose *Sphagnum ssp*." Also, see our responses to Reviewer 1's comment, "*However, it should be clarified how the sites for chamber measurements*…" which includes textual changes that also address this point.

line 15: What was the chamber made of?

We are conferring with our collaborators that constructed the chambers, and we will include this information in the revised manuscript.

Was it transparent or dark?

We will add the word "transparent" in the sentence.

How many individual chamber bases were measured?

We will also add the sentence, "15 separate measurements across 6 different pre-installed chamber bases were performed over the course of 4 days." These details were previously available in the results section, but we agree they should also be in the methods section.

line 20: Do I understand correctly that one cartridge collection took 4-5 minutes? What did the cartridges contain and how were they analyzed?

We will change this into the following, "Cartridge samples were collected over 15 to 20 min to calculate the change in isoprene concentration with time. Sampling began 2 to 5 minutes after the chamber was in place and each cartridge was filled for 5 minutes. 3 to 4 cartridges were collected for each measurement and then the cartridges were analysed using the procedures outlined in the Supplement."

page 13365 line 1: What do you mean by leak rates and could you please describe the procedure to determine it in more detail? How did you measure isoprene decay in the chamber? Leak and decay are two different things - which is it you think takes place during your measurements?

By decay, we only meant the decrease in isoprene concentration with time, and that we fitted that process with an exponential function. We assumed that the leak rate would be first order with the isoprene concentration. We agree this terminology is confusing and we will change it. In addition, we will add the following brief text, keeping in mind the concerns of the first reviewer on the length of the methods section in the current manuscript, "The leak rate was estimated to be 7% min^{-1} assuming the amount of isoprene lost was proportional to concentration and based on measuring the decrease in isoprene concentration when the chamber was covered with a tarp (performed twice)."

line 12 onwards: The dynamic chamber measurements are not explained in enough detail. Was the chamber flushed first or was the measurement started right away after enclosure? Were ozone and hydrocarbons filtered from these chambers? How was isoprene analyzed?

We will address these concerns by expanding the paragraph as follows:

"Dynamic chamber measurements were also employed with smaller chambers. These smaller dynamic chambers were located to only enclose *Sphagnum ssp*. Similar to the larger static chambers, these chambers had pre-existing bases placed in the ground and the placement of the chamber top did not physically touch any plant matter. The smaller dynamic chambers were circular, with a diameter of 19.2 cm, a height of 5 to 10 cm and an enclosed surface area of 290 cm^2. The flow rate through the chamber was 0.9 L min^{-1}. Fluxes were calculated by measuring the isoprene concentration of air exiting the chamber and subtracting the concentration of isoprene measured in the air entering the chamber, which was not scrubbed for O_3 or hydrocarbons. Because of low ambient O_3 concentrations and the low reactivity of isoprene with O_3, we assume chemical loss of isoprene was small. Two measurements were made of the isoprene concentration exiting the chamber and the results were averaged. Sample collection began at 6 and 30 min after enclosure, and each sample was collected for 20 minutes onto a cartridge and analysed using the procedures described in the Supplement. Temperature and light were measured with the same equipment described for the static chambers."

line 14: Chamber height or volume?

We added the text, "a height of 5 to 10 cm".

page 13367 line 19: Replace 'experiments' with 'treatments'.

We will change this.

line 26: show standard errors for the two groups, please.

We will add these values in parentheses.

line 27: Replace 'p = 0.0000035' with 'p < 0.001'. Show in parentheses where this P-value is derived from. What analysis? Was it a single measurement or repeated measurements? I assume that n=4 – also show that if that is correct. Redo the stats, if you have an incorrect n.

We will add this parenthetical: "($p < 0.01$ from Tukey's Honest Significant Difference, $n = 4$)". We had previously used the P from a linear model, but the p from Tukey is still highly significant.

page 13370 line 28: What model do you refer to?

We will change the sentence to, "Of this set, 4 samples were rejected because our technique of using observed temperature and PAR and a fixed leak rate explained less than 55% of the variation in isoprene concentration (average $r^2 = 0.26$)."

page 13372 line 10: I think you should be careful with conclusions based on measurements done with different techniques.

Yes, this is a good point. That is why we used a range (< 10%) instead of specifying an exact percentage. In addition, we cite additional literature as a response to concerns raised by reviewer 1 that agrees with this 10 % estimate. For addressing reviewer 1, we also raise a cautionary note about variability in moss emissions. We will change "From this," to "Given the uncertainties inherent in using different measurement techniques,".

Fig. 2: You could mention in the figure legend the species measured. Do the 'individual sets of measurements' mean individual leaves?

We will change the caption to, "Normalized isoprene emissions as a function of leaf temperature and light for *S. pulchra* leaves compared to the G93 algorithm (black curves). The individual sets of measurements from the same leaf are denoted by the same colour and type of plotting character."

References cited in replies

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