

Dear Associate Editor,

Please find attached a point-by-point response to the reviewers and a marked-up manuscript version. We have made the following relevant changes in the manuscript:

- We have tried to better link the mixing ratio measurements to the emission rate measurements to present a whole story.
- We have used standardized emission rates when possible/appropriate.
- We have modified Figure 5 (isoprene vertical profiles with the tethered balloon) to make it easier to distinguish measurement points at different heights.
- We have made it clearer that we used air temperature instead of leaf temperature and included a brief discussion on the topic.
- We have included a discussion on long-term effects of warming. Section 4 of the manuscript has been reorganized and now includes parts of the text that used to be in the “Implications and conclusions” section.

Sincerely yours,

Hélène Angot on behalf on the authors.

Comments are in black and responses in blue.

Response to Reviewer #1

This paper aims at quantifying terpenoid mixing ratios and emission rates of dominant vegetation in northern Alaska. The authors have intensively compared their data with the published data from northern Sweden and Greenland and derived site-specific temperature response curve. This paper is well written and the data from this paper can provide base quantification of BVOC emissions from this less-studied area.

Thank you for the positive feedback. Our responses to the specific comments are provided below.

A variety of measurements have been used in this paper and I, as a modeler, will leave the measurement part to other reviewer(s). My main concern of this paper is that the mixing ratio measurements are not much linked to the emission rate measurements. It is a lot of data presented (which was good), but I think the authors should bring these data together to present a whole story.

We agree with the reviewer and have tried to better link the mixing ratio measurements to the emission rate measurements in the revised manuscript. We have, for instance, made the following additions:

“It is worth noting that the most frequently observed compounds in enclosure samples are among the most frequently seen MT in ambient air (see Section 3.1.3)”.

“Regardless of the vegetation type, isoprene emission rates exhibited a significant diurnal cycle with an early afternoon maximum, in line with the mean diurnal cycle of enclosure temperature and PAR. These results are in line with the well-established diurnal variation of BVOC emissions in environments ranging from Mediterranean to boreal forests (e.g., Fares et al., 2013; Liu et al., 2004; Ruuskanen et al., 2005; Zini et al., 2001) and with the correlation between isoprene ambient air mixing ratios and temperature at TFS (see Section 3.1). (...) As can be seen in Table 3 and Fig. 8, PAR and BVOC emissions significantly decreased at night but were still detectable. These sustained BVOC emissions during nighttime confirm observations by Lindwall et al. (2015) during a 24-hour experiment with five different Arctic vegetation communities and explain the higher isoprene levels observed in the nocturnal boundary layer than above during the diurnal balloon experiment (see Section 3.1.2).”

Then, another part is about comparing emission ranges with literature values. The measurement conditions could vary largely and also in different periods of growing season. It is difficult to directly conclude that the measurement values are in the range of published values. I think standardized emission rates (using commonly-used Guenther algorithm) are needed in this case.

We totally agree and have used standardized emission rates (when possible/appropriate) in the revised manuscript (see below). We have also added the average enclosure temperature for each emission rate reported in Table 3.

“A branch enclosure experiment was performed from July 27 to August 2, 2018 on *Salix glauca* to investigate BVOC emission rates per dry weight plant biomass (see Fig.S.I.5). Isoprene emission rates ranged from <0.01 to 11 $\mu\text{gC/g/h}$ (with a mean enclosure temperature of 16.5°C and mean PAR of 880 $\mu\text{mol/m}^2/\text{s}$), in line with non-normalized emission rates reported at Kobbefjord, Greenland by Kramshøj et al. (2016; Supplementary Table 5) for the same species under slightly different environmental conditions (mean temperature of 24.6°C and mean PAR of 1052 $\mu\text{mol/m}^2/\text{s}$). Once standardized to 30°C and 1000 $\mu\text{mol/m}^2/\text{s}$, our emission rates averaged 5 $\mu\text{gC/g/h}$, in good agreement with standardized emissions reported at Kobbefjord (mean of 7 $\mu\text{gC/g/h}$) by Vedel-Petersen et al. (2015).”

“The isoprene surface emission rate, as inferred from surface enclosures, was highly variable and ranged from 0.2 to ~2250 $\mu\text{gC/m}^2/\text{h}$ (see Fig. 6). The 2250 $\mu\text{gC/m}^2/\text{h}$ maximum, reached on June 26, 2019, with an enclosure temperature of 32°C, is higher than maximum values reported at TFS by Potosnak et al. (2013) (1200 $\mu\text{gC/m}^2/\text{h}$ at an air temperature of 22°C). It should be noted that these maximum values were observed at different ambient temperatures; we further investigate the temperature dependency of isoprene emissions in Section 3.3. Elevated surface emission rates (*i.e.*, > 500 $\mu\text{gC/m}^2/\text{h}$) were all observed while the vegetation in sampling enclosures was dominated by *Salix* spp.. At TFS, the overall 24-hour mean isoprene emission rate amounted to 85 $\mu\text{gC/m}^2/\text{h}$, while the daytime (10 am-8 pm) and midday (11 am-2 pm) means were 140 and 213 $\mu\text{gC/m}^2/\text{h}$, respectively. To put this in perspective, the average isoprene surface emission rate standardized to 30°C and 1000 $\mu\text{mol/m}^2/\text{s}$ (~ 300 $\mu\text{gC/m}^2/\text{h}$) was an order of magnitude lower than emission rates reported for warmer mid-latitude or tropical forests.”

Here are some detailed comments:

Introduction: I would think one to two sentences could be needed to justify the importance of studying BVOC emissions on impacting atmospheric chemistry from

this less-polluted arctic region. Then I think the aim of this study should be elevated, so what are the main aim of this study apart from quantifying emissions and mixing ratios.

We thank the reviewer for these suggestions. We have made the following changes in the revised manuscript:

“Changing BVOC emissions in the Arctic due to climate and land cover shifts can thus be expected to perturb the overall oxidative chemistry of the region. Previous studies have hypothesized that BVOC might already impact the diurnal cycle of ozone in the Arctic boundary layer (Van Dam et al., 2016). Changing BVOC emissions can also further affect climate through various feedback mechanisms; Quantifying these changes requires an accurate understanding of the underlying processes driving BVOC emissions in the Arctic” (...). “The data presented here provide a baseline to investigate future changes in the BVOC emission potential of the under-studied Arctic tundra environment. Due to increasing shrub prevalence across northern Alaska, as well as the Eurasian and Russian Arctic, the results of this study have significance to tundra ecosystems across a vast region of the Arctic”.

L52-53, the field warming increases of BVOC emission is not only seen with long-term warming but also found with a short-term field warming like 3 years in the same area.

We have replaced “Long-term field warming studies” by “Field warming studies” in the revised manuscript. Thank you for pointing that out.

L97, please describe the start and end of a normal growing season for this site.

We have clarified this in the revised manuscript: “These two back-to-back campaigns cover the entire growing season, from the onset of snow melt mid-May to the first snow fall mid-August”.

Table1 *Rhododendron tomentosum* seems the 2nd highest covered in this area and why not present emission from this species separately?

Rhododendron tomentosum was indeed present in most of the surface enclosures but was difficult to study separately due to low individual plant biomass.

Fig. 3, I have a bit difficulty to find all measurements points at different heights. Suggest to use more distinguishing colors combining with different symbols.

We assume the reviewer actually refers to Figure 5 (vertical profiles with the tethered balloon). We have updated this Figure in the revised manuscript (see below; one panel per balloon flight) to make it easier to distinguish measurement points at different heights.

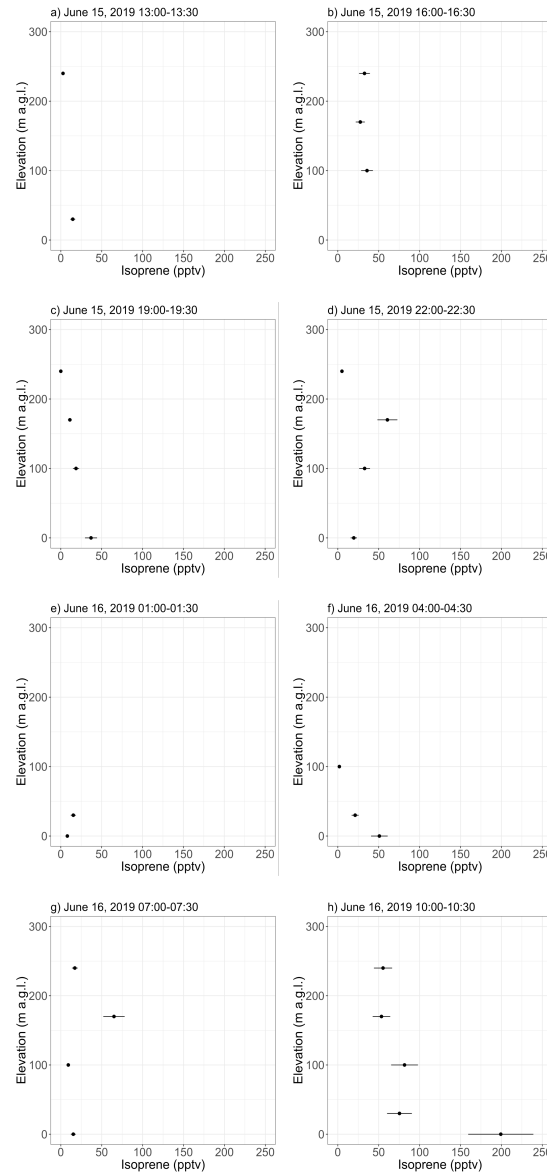


Figure 5: Vertical profiles of isoprene mixing ratios as inferred from 30-min samples collected with a tethered balloon. The error bars show the analytical uncertainty for isoprene (20 %). Samples with an isoprene mixing ratio lower than blanks were discarded. Hours are in Alaska Standard Time (UTC-9).

L362, as far as I know, *Cassiope tetragona* is also a MT emitter.

Thank you for this suggestion; *Cassiope tetragona* is included in “other high Arctic vegetation”.

L372-L380, how valid it is to state that the values are in the range of published values if focusing on the emission rates potentially measured at very different temperature and light conditions. I would suggest comparing the standardized emission rates with other studies if possible.

See response to main comment #2.

L435, What does this mean “account for differing leaf area. . .”? This is the emission rate of the per ground area, right? Please clarify.

We have replaced “leaf area” by “total biomass” in the revised manuscript.

L436, If dividing all fluxes with the standard emission rates at 20 degree, then it gives a multiplication of environmental responses (unit-less). As PAR is measured in the chamber, why not take away the light variation part before only looking at temperature response curve? Then about Fig. 9, how did you deal with the MEGAN temperature response curve, as I did not see the normalized emission rate to 1 around 30 degree?

We followed the same methodology as in Tang et al. (2016) and only used daytime observations with relatively high PAR values. Figure 9 thus only represents the isoprene emission-temperature relationship. This has been clarified in the revised manuscript: “Figure 9 combines daytime (e.g., with relatively high PAR values) isoprene emission rates from different surface enclosures”.

Please note that the MEGAN temperature response curve was also normalized by dividing all fluxes by the mean emission rate at 20°C.

L464-L468, MEGAN uses leaf temperature, not ambient air temperature for emission estimations. With predicted strong increase of air temperature in the Arctic, it still remains largely unknown (interesting to know) how plant leaf temperature can change and thus impact on BVOC emissions. I think it is important to have this in the discussion context.

Thank you for raising this important point. We agree that it is important to have this in the discussion and have added the following paragraph in Section 4.2 of the revised manuscript:

“Over the course of the two field campaigns at TFS, BVOC surface emission rates were measured over a large span of enclosure temperatures (2-41°C). While isoprene and MT emissions respond to leaf temperature (Guenther et al., 1993), air temperature was used here in place of leaf temperature – which has been assumed before in the literature for high-latitude ecosystems (e.g., Olofsson et al., 2005; Potosnak et al., 2013). Several studies have, however, suggested a decoupling of leaf and air temperature in tundra environments (Lindwall et al., 2016; Potosnak et al., 2013). With predicted increase of air temperature in the Arctic, it still remains largely unknown how leaf temperature will change and impact BVOC emissions. As suggested by Tang et al. (2016), long-term parallel observations of both leaf and air temperature are needed. The response of BVOC emissions to temperature discussed here should be interpreted with this potential caveat in mind.”

Comments are in black and responses in blue.

Response to Reviewer #2

The manuscript presents results from a series of well-designed experiments that explore emissions of isoprene and monoterpenes from Arctic plants to the atmosphere. The experimental design is sound and well-described, except for a few minor points noted below. The main conclusion is that the rapidly warming Arctic will cause sharply increased emissions of isoprene, which previous studies have shown to have a significant impact on atmospheric chemistry. Overall, this paper supports previous research findings, but the detail and atmospheric chemistry perspective make it a valuable contribution to the literature.

Thank you for the positive feedback. Our responses to the specific comments are provided below.

While the focus of the paper is from the atmosphere-exchange perspective, several eco-physiological concepts which have been discussed previously for Arctic BVOC emissions should be addressed. First, given the emphasis placed in the paper on the response of emissions to warming, the acclimation process should be addressed (see one reference below).

That is a very good point; thank you for raising it. We have added a new subsection in the revised manuscript (Section 4.2) to discuss long-term effects of warming, including the acclimation process:

“BVOC produced by plants are involved in plant growth, reproduction, and defense, and plants use isoprene emissions as a thermotolerance mechanism (Peñuelas and Staudt, 2010; Sasaki et al., 2007). The exponential response of isoprene emissions to temperature observed at TFS adds to a growing body of evidence indicating a high isoprene-temperature response in Arctic ecosystems. However, observations at TFS do not necessarily reflect long-term effects of warming. Schollert et al., (2015) examined how long-term warming affects leaf anatomy of individual arctic plant shoots (*Betula nana*, *Cassiope tetragona*, *Empetrum hermaphroditum*, and *Salix arctica*). They found that long-term warming results in significantly thicker leaves suggesting anatomical acclimation. While the authors hypothesized that this anatomical acclimation may limit the increase of BVOC emissions at plant shoot-level, Kramshøj et al. (2016) later showed that BVOC emissions from Arctic tundra exposed to six years of experimental warming increase at both the plant shoot and ecosystem levels.

In addition to the direct impact of long-term warming on BVOC emissions, ecosystem-level emissions are expected to increase in the Arctic due to climate-driven changes in plant biomass and vegetation composition. For instance, the widespread increase in shrub abundance in the Arctic – due to a longer growing season and enhanced nutrient availability (Berner et al., 2018; Sturm et al., 2001) – will likely significantly affect the BVOC emission potential of the Arctic tundra. Additionally, as mentioned above and as discussed extensively by Peñuelas and Staudt (2010) and Loreto and Schnitzler (2010), emissions of BVOCs might be largely beneficial for plants, conferring them higher protection from abiotic stressors which are predicted to be more severe in the future. Long-term arctic warming may thus favor BVOC-emitting species even further.”

Second, temperature in the current study refers to air temperature, but isoprene and other MT emissions respond to leaf temperature. And leaf temperature in turn depends on plant water relations in addition to air temperature. Given the unique eco-hydrology of tundra plants, some attention should be paid to this driver. In particular, was soil moisture monitored for any of the chamber experiments? Was SM measured at the tower?

We unfortunately did not monitor soil moisture but have made it clearer that the current study refers to air temperature:

“Over the course of the two field campaigns at TFS, BVOC surface emission rates were measured over a large span of enclosure temperatures (2-41°C). While isoprene and MT emissions respond to leaf temperature (Guenther et al., 1993), air temperature was used here in place of leaf temperature – which has been assumed before in the literature for high-latitude ecosystems (e.g., Olofsson et al., 2005; Potosnak et al., 2013). Several studies have, however, suggested a decoupling of leaf and air temperature in tundra environments (Lindwall et al., 2016; Potosnak et al., 2013). With predicted increase of air temperature in the Arctic, it still remains largely unknown how leaf temperature will change and impact BVOC emissions. As suggested by Tang et al. (2016), long-term parallel observations of both leaf and air temperature are needed. The response of BVOC emissions to temperature discussed here should be interpreted with this potential caveat in mind.”

Line 62: Delete second “to.”

Done, thanks for noticing this typo.

Line 81: The term “flanks” is a bit odd. At least it should be singular.

Done.

Line 86: Italicize “*Vaccinium vitis-idaea*.”

Done.

Line 109: very briefly give the details on the “moisture trap.” Were cooled glass beads used?

We have added a short description of the moisture trap in the revised manuscript: “The moisture trap was a U-shaped SilcoSteel™ tube (stainless steel treated) cooled using thermoelectric coolers”. Note that the tube was empty (no glass beads).

Line 110: What absorbents were used?

This has been added to the revised manuscript: “Analytes were concentrated on a Peltier-cooled multistage micro-adsorbent trap (50 % Tenax-GR and 50 % Carboxen 1016)”.

Line 129: How large was this combined effect, in percent terms?

We observed a progressive 80 % decline in CFC-113 peak area.

Line 154: What uncertainty is introduced by data processing? Do you mean something related to statistics?

The error introduced by data processing relates to the error in averaging the data from 2 minutes to 10 minutes, as well as error induced from peak fitting in the data processing software.

Line 166: Please note when solar noon occurs at the site in AST.

This has been added to the revised manuscript: “A total of eight vertical profiles were performed at ~3-hour intervals between 12:30 pm AST on June 15, 2019 and 11:00 am AST on June 16, 2019 in order to capture a full diurnal cycle (solar noon around 2 pm AST)”.

Line 179: Add a brief mention of how the tubes were capped.

This has been added to the revised manuscript: “Following collection, adsorbent cartridges were sealed with Teflon-coated brass caps and stored in the dark at ~4°C until chemical analysis”.

Lines 315-318: I concur with this conclusion. You could make this more clear and impactful by stating that both the intense wildfires regionally and the isoprene emissions locally were driven by high air temperature. But further, could there have been an influence on the photochemical lifetime of isoprene due to the products of the wildfire? Could the main isoprene oxidants, OH & ozone, be suppressed?

The occurrence of wildfires depends on meteorology (e.g., temperature and soil moisture) but also vegetation type and coverage, and lightning frequency. Fire emissions are a complicated mixture of trace gases and aerosols, many of which are short-lived and chemically reactive. This mixture affects the atmospheric composition in complex ways that are not completely understood. Recent measurements during the NASA/NOAA ATOM and FIREX-AQ campaigns have shown that wildfires might actually be responsible for increased ozone mixing ratios in aged plumes (Bourgeois et al., in prep). Our surface ozone measurements at Toolik Field Station suggest that mean ozone mixing ratios increased from ~27 ppb during June 1-19, 2019 to ~34 ppb during the June 20, 2019 fire event.

Lines 319-335: Since you are integrating results and discussion, what’s the implication of these results?

We have added the following sentence in the revised version of the manuscript: “This record of ambient air isoprene, MACR, and MVK mixing ratios is, to the best of our knowledge, the first in an Arctic tundra environment. The combined measurement of isoprene and its oxidation products provides a new set of observations to further constrain isoprene chemistry under low-NO_x conditions in atmospheric models (Bates and Jacob, 2019).”

Lines 338: There is no need to refer explicitly back to the Materials and Methods section, so “(see Section 2.3)” can be removed.

Done.

Lines 343-345: What’s the implication? Is the isoprene ‘sticking around’ from the more productive part of the day or is production continuing throughout the ‘night’ (low-PAR conditions).

We now refer to Section 3.2.2: “Samples collected on June 16, 2019 from 4 to 4:30 am (see Fig. 5f) show decreasing isoprene mixing ratios with increasing elevation, suggesting higher levels (25-50 pptv) in the nocturnal boundary layer than above. This result suggests continuing isoprene emissions by the surrounding vegetation under low-PAR conditions. This is further discussed in Section 3.2.2”.

Lines 347-350: This is more than ‘consistent.’ I would change the wording to something along the lines of ‘expected.’

This has been modified in the revised manuscript: “This maximum at ground-level is expected for a VOC with a surface source (Helmig et al., 1998) while the 200 pptv mixing ratio can likely be attributed to a temperature-driven increase of isoprene emissions by the surrounding vegetation.”

Line 383: this is a really high number and should be highlighted in the abstract. Unadjusted for temperature, biomass and light, it’s similar to results from many midland low-latitude forests. Later in the paragraph, you give the comparison, which is good. But, I think the key is that the extreme values are so high.

We agree and have highlighted this result in the abstract of the revised manuscript.

Line 406-409: Should explicitly state that even with nearly 24 hours of light, still get the typical diurnal pattern. The key is that low sun angles translate to very low PAR (non-linearly), and therefore you still see the typical diurnal pattern. Later in the paragraph, you get to this explicitly, but the discussion should be combined for clarity. Also, this should be related to the diurnal balloon experiment results.

We have clarified this in the revised manuscript: “Figures 8a-c show the mean diurnal cycle (over the two campaigns) of isoprene surface emission rates for different vegetation types. The two field campaigns were carried out during the midnight sun period, which could possibly sustain BVOC emissions during nighttime. It should, however, be noted that low sun angles translate to very low PAR and a typical diurnal pattern is observed in summer at TFS despite 24 hours of light (see Fig.8h).”

We have also related these results to the balloon vertical profiles: “These sustained BVOC emissions during nighttime confirm observations by Lindwall et al. (2015) during a 24-hour experiment with five different Arctic vegetation communities and explain the higher isoprene levels observed in the nocturnal boundary layer than above during the diurnal balloon experiment (see Section 3.1.2).”

Lines 455-459: This needs to be tempered a bit. There are issues of timescales and acclimation. Also, I assume there are relatively few chamber measurements between 35 and 40 deg C, hence a leveling off is within statistical probabilities. Also, you will argue against this point in the following paragraph, so this could be presented more clearly to readers.

We have added the number of chamber measurements in each temperature bin in the revised Figure 9. We do agree that, given the relatively few chamber measurements at $T > 30^{\circ}\text{C}$, a leveling-off is within statistical probabilities. We have therefore tempered this paragraph accordingly in the revised manuscript (and in the abstract):

“While the model predicts a leveling-off of emissions at approximately 30-35°C, our observations reveal no such phenomenon within the 0-40°C enclosure temperature range (Fig. 9). However, given the limited number of enclosure measurements above 30°C, a leveling-off of emissions cannot be statistically ruled out. The key result here is that MEGAN2.1 adequately reproduces the temperature dependence response of Arctic ecosystems in the 0-30°C temperature range – ambient temperature $> 30^{\circ}\text{C}$ being unlikely.”

Lines 461-462: I think I understand what this sentence is trying to convey, but it is confusing and the statement could be clearer. You that for every year in the dataset, there were 1-23 days with a temp above 20 deg C?

We have clarified this sentence in the revised manuscript: “Additionally, for each year in the 1988-2019 historical dataset, there were only 1 to 23 days (0 to 4 days) per year with a maximum temperature above 20°C (above 25°C)”.

Line 471: “Under” might be a better word choice than “scarcely.”

The wording has been changed accordingly in the revised manuscript.

Line 472: Same comment as Line 81 about “flanks.”

Done.

Line 474: “Elevated” compared to what? Expectations or previous measurements?

This has been clarified in the revised manuscript: “While the overall mean isoprene emission rate amounted to 85 $\mu\text{gC}/\text{m}^2/\text{h}$ at TFS, elevated ($> 500 \mu\text{gC}/\text{m}^2/\text{h}$) isoprene surface emission rates were observed for *Salix* spp., a known isoprene emitter.”

Line 477: Thermotolerance hasn't been addressed previously in the manuscript. At the minimum, a citation is necessary, but it might be best to remove this if it's not explored more thoroughly with regards to Arctic plants.

Thermotolerance is now addressed in Section 4.2 of the revised manuscript (see above).

Line 485: Can remove "likely" since "suggesting" is already in the sentence and provides sufficient caution.

Done.

Line 486-490: Here thermotolerance is addressed a bit further, with references. But it would be better to have a short paragraph or group of sentences that speculates specifically about the role thermotolerance could play in promoting isoprene-emitting species in the Arctic. The current allusions here and at Line 477 makes the topic appear as tacked on.

This is now addressed in Section 4.2 of the revised manuscript (see above).

Line 839, Table 1: some mention of the lack of measurements for *R. chamaemorus* would be useful, since it is the dominant species.

Indeed. This has been added in the revised manuscript: "The tundra vegetation around TFS is heterogeneous but most dominant species (except *Rubus chamaemorus*) were sampled."

Line 992, Figure 5: Solid, colored lines connecting the points would help visually highlight vertical trends.

We have updated this Figure in the revised manuscript (see below; one panel per balloon flight) to make it easier to distinguish measurement points at different heights.

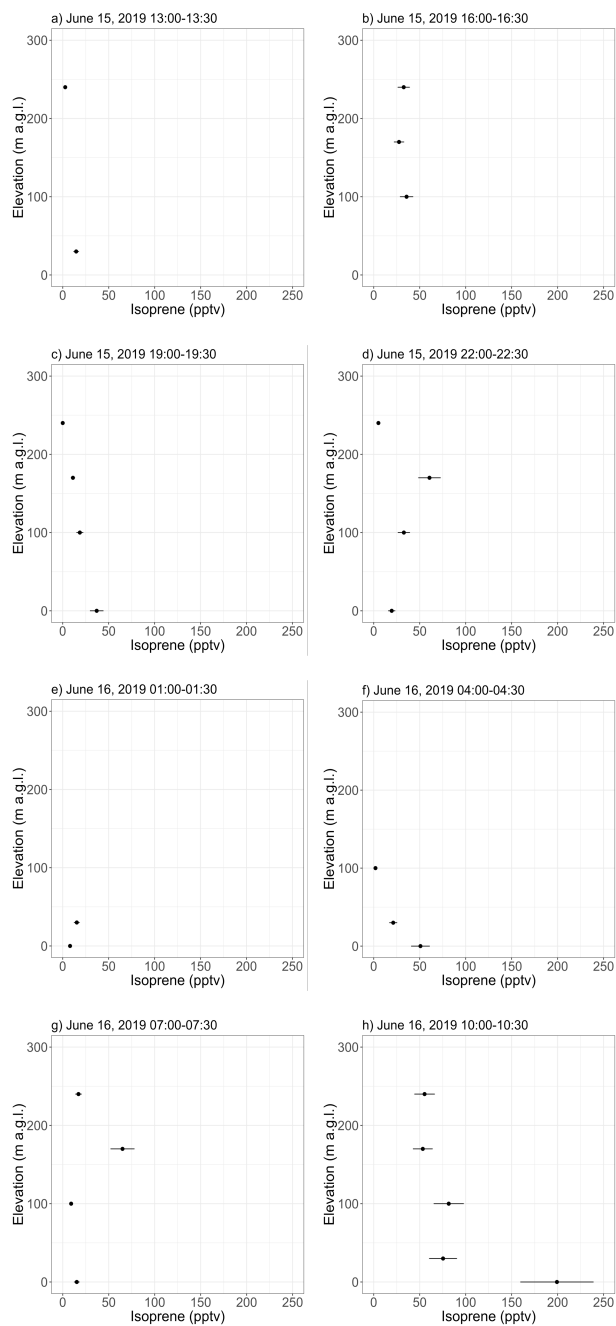


Figure 5: Vertical profiles of isoprene mixing ratios as inferred from 30-min samples collected with a tethered balloon. The error bars show the analytical uncertainty for isoprene (20 %). Samples with an isoprene mixing ratio lower than blanks were discarded. Hours are in Alaska Standard Time (UTC-9).

1 Biogenic volatile organic compound ambient mixing ratios and emission rates 2 in the Alaskan Arctic tundra

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9

10 Abstract

11 Rapid Arctic warming, a lengthening growing season, and increasing abundance of biogenic volatile
12 organic compounds (BVOC)-emitting shrubs are all anticipated to increase atmospheric BVOCs in the
13 Arctic atmosphere, with implications for atmospheric oxidation processes and climate feedbacks.
14 Quantifying these changes requires an accurate understanding of the underlying processes driving BVOC
15 emissions in the Arctic. While boreal ecosystems have been widely studied, little attention has been paid to
16 Arctic tundra environments. Here, we report terpenoid (isoprene, monoterpenes, and sesquiterpenes)
17 ambient mixing ratios and emission rates from key dominant vegetation species at Toolik Field Station
18 (TFS; 68°38'N, 149°36'W) in northern Alaska during two back-to-back field campaigns (summers 2018
19 and 2019) covering the entire growing season. Isoprene ambient mixing ratios observed at TFS fell within
20 the range of values reported in the Eurasian taiga (0-500 pptv), while monoterpene and sesquiterpene
21 ambient mixing ratios were respectively close to and below the instrumental quantification limit (~2 pptv).
22 Isoprene surface emission rates ranged from 0.2 to 2250 $\mu\text{gC}/\text{m}^2/\text{h}$ (mean of 85 $\mu\text{gC}/\text{m}^2/\text{h}$) and monoterpene
23 emission rates remained on average below 1 $\mu\text{gC}/\text{m}^2/\text{h}$ over the course of the study. We further quantified
24 the temperature dependence of isoprene emissions from local vegetation including *Salix* spp. (a known
25 isoprene emitter), and compared the results to predictions from the Model of Emissions of Gases and
26 Aerosols from Nature version 2.1 (MEGAN2.1). Our observations suggest a 180-215% emission increase
27 in response to a 3-4°C warming and, the MEGAN2.1 temperature algorithm exhibits a close fit with
28 observations for enclosure temperatures in the 0-30°C range. The data presented here provide a baseline to
29 investigate future changes in the BVOC emission potential of the under-studied Arctic tundra environment.

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1. Introduction

As a major source of reactive carbon to the atmosphere, biogenic volatile organic compounds (BVOCs) emitted from vegetation play a significant role in global carbon and oxidation cycles (Fehsenfeld et al., 1992). Global emission estimates of BVOCs are in the range of 700-1100 TgC per year, ~70-80% of which corresponds to terpenoid species: isoprene, monoterpenes (MT), and sesquiterpenes (SQT) (Guenther et al., 1995, 2006; Sindelarova et al., 2014). Despite their relatively short atmospheric lifetimes (1 hour to 1 day for terpenoids), BVOCs affect climate through their effects on the hydroxyl radical (OH, which dictates the lifetime of atmospheric methane), tropospheric ozone (O₃, a key greenhouse gas), and aerosols (which influence radiative scattering) (Arneth et al., 2010; Fuentes et al., 2000; Peñuelas and Staudt, 2010). The oxidation of those BVOCs also drives the formation of secondary organic aerosols (SOA) through both gas- and aqueous-phase mechanisms (Carlton et al., 2009; Lim et al., 2005). The potential for increased SOA formation, expected to result in climate cooling (Kulmala et al., 2004), complicates the climate feedbacks of BVOC emissions (Tsigaridis and Kanakidou, 2007; Unger, 2014).

Global models of BVOC emissions assume minimal emissions from the Arctic due to low leaf area index and relatively cold temperatures (Guenther et al., 2006; Sindelarova et al., 2014). However, this assumption relies on few observations and has been increasingly challenged by field data (Tang et al., 2016). Recent measurements have revealed significant BVOC emissions from Arctic tundra and vegetation, including *Sphagnum* mosses, wetland sedges, and dwarf shrubs (Ekberg et al., 2009, 2011; Faubert et al., 2010; Holst et al., 2010; Lindfors et al., 2000; Potosnak et al., 2013; Rinnan et al., 2011; Schollert et al., 2014; Tiiva et al., 2008). These results are of importance because BVOC emissions are expected to increase in the Arctic due to climate warming and associated vegetation and land cover change (Faubert et al., 2010; Potosnak et al., 2013; Rinnan et al., 2011; Tiiva et al., 2008). Field warming studies have shown strong increases in BVOC emissions from shrub heath (Michelsen et al., 2012; Tiiva et al., 2008). Furthermore, the temperature dependence of Arctic BVOC fluxes appears to be significantly greater than for tropical and subtropical ecosystems (Holst et al., 2010; Rinnan et al., 2014), with up to 2-fold increases in MT emissions and 5-fold increases in SQT emissions by subarctic heath for a 2°C warming (Valolahti et al., 2015). Similarly, Kramshøj et al. (2016) and Lindwall et al. (2016) examined the response of BVOC emissions to an experimental 3-4°C warming and reported a 260-280%

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70 increase in total emissions. Together, the above results emphasize the strong temperature
71 sensitivity of BVOC emissions from Arctic ecosystems.

72 Changing BVOC emissions in the Arctic due to climate and land cover shifts can thus be expected
73 to perturb the overall oxidative chemistry of the region. Previous studies have hypothesized that
74 BVOCs might already impact the diurnal cycle of ozone in the Arctic boundary layer (Van Dam
75 et al., 2016). Changing BVOC emissions can also further affect climate through various feedback
76 mechanisms. Quantifying these changes requires an accurate understanding of the underlying
77 processes driving BVOC emissions in the Arctic. While BVOC ambient mixing ratios and
78 emission rates have been studied in boreal ecosystems, less attention has been paid to Arctic tundra
79 environments (Lindwall et al., 2015). Here, we report BVOC ambient mixing ratios and emission
80 rates at Toolik Field Station (TFS) in the Alaskan Arctic. This study builds on the previous
81 isoprene study at TFS by Potosnak et al. (2013), while also providing a major step forward from
82 that work. In particular, we present the first continuous summertime record of ambient BVOCs
83 (including isoprene and MT) and their first-generation oxidation products in the Arctic tundra
84 environment. The data presented here provide a baseline to investigate future changes in the BVOC
85 emission potential of the under-studied Arctic tundra environment. Due to increasing shrub
86 prevalence across northern Alaska (Berner et al., 2018; Tape et al., 2006), as well as the Eurasian
87 (Macias-Fauria et al., 2012) and Russian Arctic (Forbes et al., 2010), the results of this study have
88 significance to tundra ecosystems across a vast region of the Arctic. We further compare the
89 observed temperature dependence of isoprene emissions with predictions from the Model of
90 Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1), a widely used modeling
91 framework for estimating ecosystem-atmosphere BVOC fluxes (Guenther et al., 2012).

92 2. Material and Methods

93 2.1 Study site

94 This study was carried out at TFS, a Long-Term Ecological Research (LTER) site located in the
95 tundra on the north flank of the Brooks Range in northern Alaska (68°38'N, 149°36'W; see Fig.1).
96 Vegetation speciation and dynamics, and their changes over time, have been well documented at
97 the site. *Betula* (birch) and *Salix* (willow) are the most common deciduous shrubs (Kade et al.,
98 2012). Common plant species include *Betula nana* (dwarf birch), a major player in ongoing Arctic
99 greening (Hollesen et al., 2015; Sistla et al., 2013), *Rhododendron tomentosum* (formerly *Ledum*

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110 *palustre*; Labrador tea); *Vaccinium vitis-idaea* (lowbush cranberry), *Eriophorum vaginatum*
111 (cotton grass), *Sphagnum angustifolium* (peat moss), *Alectoria ochroleuca* (witches hair lichen),
112 and many other perennial species of *Carex*, mosses, and lichens. Vegetation cover at this site is
113 classified as tussock tundra (see Fig.1), which is the most common vegetation type in the northern
114 foothills of the Brooks Range (Elmendorf et al., 2012; Kade et al., 2012; Shaver and Chapin, 1991;
115 Survey, 2012; Walker et al., 1994).

116 Emission measurements and atmospheric sampling were conducted from a weatherproof
117 instrument shelter located ~350 m to the west of TFS (see Fig.S.I.1). Winds at TFS are
118 predominantly from the southerly and northerly sectors (Toolik Field Station Environmental Data
119 Center, 2019), minimizing any influence from camp emissions at the site. Two field campaigns
120 were carried out: the first from mid-July to mid-August 2018, and the second from mid-May to
121 the end of June 2019. These two back-to-back campaigns cover the entire growing season (Sullivan
122 et al., 2007), from the onset of snow melt mid-May to the first snow fall mid-August.

123 2.2 Ambient online measurements of BVOCs and their oxidation products

124 2.2.1 Gas chromatography and mass spectrometry with flame ionization detector 125 (GC-MS/FID)

126 An automated GC-MS/FID system was deployed for continuous measurements of atmospheric
127 BVOCs at ~2-hour time resolution during the 2018 and 2019 field campaigns. In addition, the
128 system was operated remotely following the 2018 campaign (through September 15th) to collect
129 background values at the beginning of autumn. Air was pulled continuously from an inlet on a 4
130 m meteorological tower located approximately 30 m from the instrument shelter (Van Dam et al.,
131 2013). Air passed through a sodium thiosulfate-coated O₃ scrubber for selective O₃ removal – to
132 prevent sampling losses and artifacts for reactive BVOCs (Helmig, 1997; Pollmann et al., 2005) –
133 and through a moisture trap to dry the air to a dew point of -45°C. The moisture trap was a U-
134 shaped SilcoSteel™ tube (stainless steel treated) cooled using thermoelectric coolers. Analytes
135 were concentrated on a Peltier-cooled (-40°C) multistage micro-adsorbent trap (50 % Tenax-GR
136 and 50 % Carboxen 1016). Analysis was accomplished by thermal desorption and injection for
137 cryogen free GC using a DB-1 column (60 m × 320 µm × 5 µm) and helium as carrier gas. The
138 oven temperature was set to 40°C for 6 minutes, then increased to 260°C at 20°C/min, and held
139 isothermally at 260°C for 13 minutes. The column flow was split between an FID and a MS for

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simultaneous quantification and identification. Blanks and calibration standards were regularly injected from a manifold. Isoprene (m/z 67 and 68), methacrolein (MACR) and methylvinylketone (MVK) (m/z 41, 55, and 70), MT (m/z 68, 93, 121, and 136), and SQT (m/z 204, 91, 93, 119, and 69) were identified and quantified using the MS in selected ion-monitoring mode (SIM). The response to isoprene was calibrated using a primary gas standard supplied by the National Physical Laboratory (NPL), certified as containing 4.01 ± 0.09 ppb of isoprene in a nitrogen matrix. The analytical uncertainty for isoprene was estimated at 16 % based on the certified uncertainty of the standard and on the repeatability of standard analysis throughout the campaigns. Instrument responses for MACR, MVK, α -pinene, and acetonitrile were calibrated with multi-component standards containing 1007 ppb MACR, 971 ppb MVK, 967 ppb α -pinene, and 1016 ppb acetonitrile (Apel-Riemer Environmental Inc., Miami, FL, USA) dynamically diluted into a stream of ultra-zero grade air to ~ 3 ppb. Quantification of other terpenoid compounds was based on GC peak area (FID response) plus relative response factors using the effective carbon number concept (Faiola et al., 2012; Scanlon and Willis, 1985). The limit of quantification (LOQ) was ~ 2 pptv (pmol/mol by volume). In order to monitor and correct for long-term trends in the detection system, including detector drift and decreasing performance of the adsorbent trap, we used peak areas for long-lived chlorofluorocarbons (CFCs) that were monitored in the air samples together with the BVOCs as an internal reference standard. The atmospheric trace gases CCl_3F (CFC-11) and $\text{CCl}_2\text{FCCl}_2\text{F}_2$ (CFC-113) are ideal in this regard because they are ubiquitous in the atmosphere and exhibit little spatial and temporal variability (Karbiwnyk et al., 2003; Wang et al., 2000).

2.2.2 Proton-Transfer-Reaction Time-of-Flight Mass-Spectrometry (PTR-ToF-MS)

During the summer 2019 campaign, isoprene mixing ratios in ambient air were also measured by PTR-ToF-MS (model 4000, Ionicon Analytik GmbH, Innsbruck, Austria). The sample inlet was located on the 4 m meteorological tower, right next to the GC-MS/FID inlet. In brief, ambient air was continuously pulled through the PTR-ToF-MS drift-tube, where VOCs with proton affinities higher than that of water (>165.2 kcal/mol) were ionized via proton-transfer reaction with primary H_3O^+ ions, then subsequently separated and detected by a time-of-flight mass spectrometer (with a mass resolving power up to 4000). At TFS, the PTR-ToF-MS measured ions from 17–400 m/z every 2 minutes. Ambient air was drawn to the instrument at 10–15 L/min via ~ 30 m of 1/4" O.D. PFA tubing maintained at $\sim 55^\circ\text{C}$, and then subsampled by the instrument through ~ 100 cm of

1/16" O.D. PEEK tubing maintained at 60°C. The residence time from the inlet on the 4 m meteorological tower to the drift-tube was less than 5 seconds. Instrument backgrounds were quantified approximately every 5 hours for 20 minutes during the campaign by measuring VOC-free air generated by passing ambient air through a heated catalytic converter (375 °C, platinum bead, 1 % wt. Pt, Sigma Aldrich). Calibrations were typically performed every 4 days via dynamic dilution of certified gas standard mixtures containing 25 distinct VOCs including isoprene (Apel-Riemer Environmental Inc., Miami, FL, USA). Here, we report isoprene mixing ratios to intercompare with GC-MS measurements; other species will be reported in future work. The measurement uncertainty for isoprene is ~25%, which includes uncertainties in the gas standards, calibration method, and data processing.

2.2.3 Instrument inter-comparison

Figure S.I.2 shows a comparison of the GC-MS and PTR-ToF-MS isoprene mixing ratios in ambient air. With a correlation coefficient of 0.93 and a linear regression slope of 0.7-1.0, the two measurements agreed within their combined measurement uncertainties, in line with earlier inter-comparison studies (e.g., Dunne et al., 2018; de Gouw et al., 2003). Similarly, we found a correlation coefficient of 0.96 between GC-MS and PTR-ToF-MS MVK+MACR mixing ratios (not shown). The good agreement between these two independent techniques gives us confidence that the ambient air results presented here are robust.

2.3 Ambient air vertical profiles

Vertical isoprene mixing ratio profiles were obtained using a 12-foot diameter SkyDoc tethered balloon. A total of eight vertical profiles were performed at ~3-hour intervals between 12:30 pm Alaska Standard Time (AST) on June 15, 2019 and 11:00 am AST on June 16, 2019 [in order to capture a full diurnal cycle \(solar noon around 2 pm AST\)](#). Sampling packages were connected to the tether line such that resulting sampling heights were ~30, ~100, ~170, and ~240 m above ground level. One identical sampling package was deployed at the surface. Each sampling package contained an adsorbent cartridge for sample collection (see below) connected to a downstream battery-powered SKC pocket pump controlled using a mechanical relay, a programmable Arduino, and a real-time Clock. Once the balloon reached its apex (~250-300 m a.g.l.), the five pumps were activated simultaneously and samples collected for 30 minutes. At the end of the 30-min sampling period, the balloon was brought back down. The adsorbent cartridges were prepared in house using

201 glass tubing (89 mm long \times 6.4 mm outer diameter, 4.8 mm inner diameter), and loaded with
202 Tenax-GR and Carboxen 1016 adsorbents (270 mg of each), following established practice (Ortega
203 and Helmig, 2008 and references therein). An inlet ozone scrubber was installed on each cartridge
204 to prevent BVOC sampling losses. Field blanks were collected by opening a cartridge (with no
205 pumped airflow) during each balloon flight. Following collection, adsorbent cartridges were sealed
206 with Teflon-coated brass caps and stored in the dark at $\sim 4^{\circ}\text{C}$ until chemical analysis. Samples were
207 analyzed at the University of Colorado Boulder following the method described in S.I. Section 1.
208 Our previous inter-comparison of this cartridge-GC-MS/FID method with independent and
209 concurrent PTR-MS observations showed that the two measurements agree to within their
210 combined uncertainties at $\sim 25\%$ (Hu et al., 2015). Meteorological conditions were monitored and
211 recorded during each balloon flight with a radiosonde (Met1, Grant Pass, OR, USA) attached to
212 the tethered line just below the balloon.

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213 **2.4 BVOC emission rates**

214 **2.4.1 Dynamic enclosure measurements**

215 We used dynamic enclosure systems operated at low residence time to quantify vegetative BVOC
216 emissions following the procedure described by Ortega et al. (2008) and Ortega and Helmig
217 (2008). Two types of enclosures were used: branch and surface chambers. For branch enclosures,
218 a Tedlar® bag (Jensen Inert Products, Coral Springs, FL) was sealed around the trunk side of a
219 branch. For surface enclosures, the bag was placed around a circular Teflon® base (25 cm wide \times
220 16 cm height; see Fig. 2). For both branch and surface enclosures, the bag was connected to a
221 purge-air line and a sampling line, and positioned around the vegetation minimizing contact with
222 foliage. While purging the enclosure (see Section 2.4.3), the vegetation was allowed to acclimate
223 for 24 hours before BVOC sampling began. Samples were collected from the enclosure air,
224 concentrated onto solid-adsorbent cartridges (see Section 2.3) with an automated sampler, and
225 analyzed in-laboratory at the University of Colorado Boulder following the campaign (see S.I.
226 Section 1). Temperature and relative humidity were recorded inside and outside the enclosure (see
227 Fig. 2; S-THB-M002 sensors, Onset HOBO, Bourne, MA, USA) with a data logger (H21-USB,
228 Onset HOBO, Bourne, MA, USA). Additionally, photosynthetically active radiation (400-700 nm;
229 S-LIA-M003, Onset HOBO, Bourne, MA, USA) was measured inside the enclosure. Once
230 installed, enclosures were operated for 2-10 days. The tundra vegetation around TFS is

heterogeneous but most dominant species (*except Rubus chamaemorus*) were sampled. Table 1 presents the median relative percent cover of plant species in LTER experimental control plots at TFS (Gough, 2019) and indicates whether plant species were present in surface or bag enclosures. The complete list of species sampled and pictures of the enclosures are available in Figures S.I.3-S.I.15; the two sampling sectors are highlighted in Fig.S.I.1. Surface enclosures were divided into three vegetation types: *Salix* spp. (high isoprene emitter), *Betula* spp. (e.g., *Betula nana* dominance), and miscellaneous (mix of different species, including lichens and mosses).

2.4.2 Emission rates

The emission rate (ER in $\mu\text{gC}/\text{m}^2/\text{h}$) for surface enclosures was calculated as follows:

$$ER_{\text{surface}} = \frac{(C_{\text{out}} - C_{\text{in}})Q}{S}, \quad (1)$$

where C_{in} and C_{out} are the inlet and outlet analyte concentrations (in $\mu\text{gC}/\text{L}$), Q is the purge air flow rate (in L/h), and S the surface area of the enclosure (in m^2).

The ER for branch enclosures (in $\mu\text{gC}/\text{g}/\text{h}$) was calculated as follows:

$$ER_{\text{branch}} = \frac{(C_{\text{out}} - C_{\text{in}})Q}{m_{\text{dry}}}, \quad (2)$$

where m_{dry} is the dried mass (in g) of leaves enclosed, determined by drying the leaves – harvested after the experiment – at $60\text{--}70^\circ\text{C}$ until a consistent weight was achieved (Ortega and Helmig, 2008).

Emission rates were standardized to 30°C and to a PAR level of $1000 \mu\text{mol}/\text{m}^2/\text{s}$ using the algorithms described in Guenther et al. (1993, 1995).

2.4.3 Enclosure purge air

Purge air was provided by an upstream high-capacity oil-free pump providing positive pressure to the enclosure, and equipped with an in-line O_3 scrubber to avoid loss of reactive BVOCs from reaction with O_3 in the enclosure air and during sampling (Helmig, 1997; Pollmann et al., 2005). The purge flow was set to $25 \text{ L}/\text{min}$ and regularly checked using a volumetric flow meter (Mesa Labs Bios DryCal Defender, Butler, NJ, USA). Excess air escaped from the open end (tied around the Teflon® base) while the sample air flow was pulled into the sampling line (see below).

2.4.4 Sample collection

A continuous airflow of 400-500 mL/min was drawn from the enclosure through the sampling line. A fraction of this flow was periodically collected at 265-275 mL/min on adsorbent cartridges (see Section 2.3) using a 10-cartridge autosampler (Helmig et al., 2004). During sampling, cartridges were kept at 40°C, *i.e.*, above ambient temperature, to prevent water accumulation on the adsorbent bed (Karbiwnyk et al., 2002). Samples were periodically collected in series to verify lack of analyte breakthrough. Time-integrated samples were collected for 120 min every 2 hours to establish diurnal cycles of BVOC emission. Upon collection, samples were stored in the dark at ~4°C until chemical analysis back at the University of Colorado Boulder.

2.4.5 Internal standards

In order to identify potential BVOC losses during transport, storage, and chemical analysis, of the employed cartridges were pre-loaded with a four-compound standard mixture prior to the field campaigns. These internal standard compounds (toluene, 1, 2, 3-trimethylbenzene, 1, 2, 3, 4-tetrahydronaphthalene, and 1, 3, 5-triisopropylbenzene) were carefully chosen to span a wide range of volatility (C₇-C₁₅) and to not interfere (*i.e.*, coelute) with targeted BVOCs. The recovery of these four compounds was assessed at the end of the campaign, following the analytical procedure described in S.I. Section 1. Recovery rates were 101.8 ± 13.5 % (toluene), 95.2 ± 20.1 % (1,2,3-trimethylbenzene), 95.6 ± 26.6 % (1,2,3,4-tetrahydronaphthalene), and 100.9 ± 18.7 % (1,3,5-triisopropylbenzene). These results indicate that, overall, BVOC losses during transport, storage, and chemical analysis were negligible. Ortega et al. (2008) previously evaluated systematic losses of analytes to enclosure systems similar to those used here. The same four-component standard was introduced into the purge air flow of the enclosures to quantify losses as a function of volatility. That work found median losses of MT and SQT on the order of 20-30%. The emission rates presented here are therefore possibly biased low by a similar amount.

2.5 Peak fitting algorithm

The analysis of ambient air and enclosure chromatograms was performed using the TERN (Thermal desorption aerosol GC ExploreR and iNtegration package) peak fitting tool implemented in Igor Pro and available online at <https://sites.google.com/site/ternigor/> (Isaacman-VanWertz et al., 2017).

2.6 Ancillary parameters

Meteorological parameters. A suite of meteorological instruments was deployed on the 4 m tower. Wind speed and direction were measured at ~4 m above ground level with a Met One 034B-L sensor. As described by Van Dam et al. (2013), temperature was measured at three different heights using RTD temperature probes (model 41342, R.M. Young Company, Traverse City, MI) housed in aspirated radiation shields (model 43502, R.M. Young Company, Traverse City, MI). Regular same-height inter-comparisons were conducted to test for instrumental offsets. Incoming and reflected solar radiation were recorded with LI200X pyranometers (Campbell Scientific Instruments).

In addition, historical (1988-2019) meteorological data recorded by TFS Environmental Data Center are available at: https://toolik.alaska.edu/edc/abiotic_monitoring/data_query.php

Particle measurements. A Met One Instruments Model 212-2 8-channel (0.3 to 10 μm) particle profiler was operated continuously on the roof of the weatherproof instrument shelter. This instrument uses a laser-diode based optical sensor and light scatter technology to detect, size, and count particles (<http://mail.metone.com/particulate-Aero212.htm>).

Nitrogen oxides. Nitrogen oxides (NO_x) were measured with a custom-built, high sensitivity (~5 pptv detection limit) single-channel chemiluminescence analyzer (Fontijn et al., 1970). The instrument monitors nitric oxide (NO) and nitrogen dioxide (NO_2) in ambient air using a photolytic converter. Automated switching valves alternated between NO and NO_2 mode every 30 minutes. Calibration was accomplished by dynamic dilution of a 1.5 ppm compressed NO gas standard (Scott-Marrin, Riverside, CA, USA).

2.7 Theoretical response of isoprene emissions to temperature in MEGAN2.1

We applied our isoprene emission measurements to evaluate the temperature response algorithms embedded in MEGAN2.1 (Guenther et al., 2012). Theoretical isoprene emission rates (F_T) were calculated for TFS as:

$$F_T = C_{CE} \gamma_T \sum_j \kappa_j \varepsilon_j \quad (3)$$

where C_{CE} is the canopy environment coefficient (assigned a value that results in $\gamma_T = 1$ under standard conditions), and ε_j is the emission factor under standard conditions for vegetation type j

with fractional grid box areal coverage κ_j . We used $\sum_j \kappa_j \varepsilon_j = 2766 \mu\text{g}/\text{m}^2/\text{h}$ at TFS based on the high resolution (1 km) global emission factor input file available at <https://bai.ess.uci.edu/megan/data-and-code/megan21>. The temperature activity factor (γ_T) was calculated as:

$$\gamma_T = E_{opt} \times \frac{200 e^{95x}}{200 - 95 \times (1 - e^{200x})} \quad (4)$$

with

$$x = \frac{\frac{1}{T_{opt}} - \frac{1}{T}}{0.00831} \quad (5)$$

$$E_{opt} = 2 \times e^{0.08(T_{10} - 297)} \quad (6)$$

$$T_{opt} = 313 + 0.6(T_{10} - 297), \quad (7)$$

where T is the enclosure ambient air temperature and T_{10} the average enclosure air temperature over the past 10 days.

3. Results and Discussion

3.1 Ambient air mixing ratios

3.1.1 Isoprene and oxidation products

Figure 3 (top panels) shows the time-series of isoprene mixing ratios in ambient air recorded over the course of this study at TFS with the GC system. Mixing ratios were highly variable and ranged from below the quantification limit to 505 pptv (mean of 36.1 pptv). The PTR-ToF-MS gave similar results (see Fig.S.I.16a). These mixing ratios fall within the range of values reported in the Eurasian taiga (e.g., Hakola et al., 2000, 2003; Lappalainen et al., 2009). For example, Hakola et al. (2003) reported a maximum monthly mean mixing ratio of 98 pptv (in July) in Central Finland while Hakola et al. (2000) observed mixing ratios ranging from a few pptv to ~600 pptv in Eastern Finland. In general, however, BVOC emissions in the Eurasian taiga are relatively low compared to forest ecosystems in warmer climates and are dominated by monoterpenes (Rinne et al., 2009).

Isoprene mixing ratios peaked on August 1, 2018 around 4 pm and on June 20, 2019 around 10 pm, respectively. These two peaks occurred 3-5 hours after the daily maximum ambient temperature was reached (17.8°C in 2018 and 21.8°C in 2019 – see Fig. 3). The isoprene peak on

June 20, 2019 was concomitant with enhanced acetonitrile mixing ratios and particle counts (see Fig. 4), reflecting unusually hazy conditions that day at TFS. We attribute the particle and acetonitrile enhancements to intense wildfires occurring across the Arctic Circle at that time – most of them in southern Alaska and Siberia (Earth Observatory, 2019). Acetonitrile increased by a factor of 4 during this event, compared to a factor of 21 increase for isoprene. The higher emission factor for acetonitrile vs. isoprene from biomass burning in boreal forests (Akagi et al., 2011) and the relatively short lifetime of isoprene (Atkinson, 2000) indicate that the observed isoprene enhancement was due to fresh local biogenic emissions rather than transported wildfire emissions.

Over the course of this study, we recorded MACR and MVK mixing ratios respectively ranging from below the quantification limit to 95 pptv (12.4 ± 16.1 pptv; mean \pm standard deviation) and from below the quantification limit to 450 pptv (43.1 ± 66.7 pptv; see Fig. 3, top panels). The PTR-ToF-MS gave similar results (see Fig.S.I.16b). Median NO and NO₂ mixing ratios of 21 and 74 pptv, respectively, during the 2019 campaign (not shown) suggest a low-NO_x environment, in line with previous studies at several Arctic locations (Bakwin et al., 1992; Honrath and Jaffe, 1992). Under such conditions, MACR and MVK mixing ratios should be used as upper estimates as it has been noted that some low-NO_x isoprene oxidation products (isoprene hydroxyhydroperoxides) can undergo rearrangement in GC and PTR-MS instruments and be misidentified as MACR and MVK (Rivera-Rios et al., 2014). We found a high correlation between MACR and MVK ($R^2 = 0.95$, $p < 0.01$) and between these two compounds and isoprene ($R^2 \sim 0.80$, $p < 0.01$). Increases of MACR and MVK mixing ratios above the background were mostly concomitant with isoprene increases, suggesting that atmospheric or within-plant oxidation of isoprene was their main source (Biesenthal et al., 1997; Hakola et al., 2003; Jardine et al., 2012). The mean ratio of MVK to MACR was 2.7, within the range reported by earlier studies (e.g., Apel et al., 2002; Biesenthal and Shepson, 1997; Hakola et al., 2003; Helmig et al., 1998), and no clear diurnal cycle in the ratio was found. This record of ambient air isoprene, MACR, and MVK mixing ratios is, to the best of our knowledge, the first in an Arctic tundra environment. The combined measurement of isoprene and its oxidation products provides a new set of observations to further constrain isoprene chemistry under low-NO_x conditions in atmospheric models (e.g., Bates and Jacob, 2019).

3.1.2 Isoprene vertical profiles

370 Figure 5 shows vertical profiles (0 to ~250 m a.g.l.) of isoprene mixing ratios derived from the 30-
371 min tethered balloon samples collected on June 15 and 16, 2019. Temperature profiles (see
372 Fig.S.I.17) indicate that most of the flights were performed in a convective boundary layer (Holton
373 and Hakim, 2013). A nocturnal boundary layer was, however, observed in the first ~50 m from ~2
374 am to ~4:30 am (see Fig.S.I.17e-f) – with temperature increasing with elevation.

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375 Except during the last flight, isoprene mixing ratios were in the range of background levels (~0-
376 50 pptv) reported with the GC-MS (see Section 3.1.1). Samples collected from 10-10:30 am on
377 June 16 (see Fig. 5h) showed a pronounced gradient, with 200 pptv at ground level and decreasing
378 mixing ratios with elevation. This maximum at ground-level is expected for a VOC with a surface
379 source (Helmig et al., 1998) while the 200 pptv mixing ratio can likely be attributed to a
380 temperature-driven increase of isoprene emissions by the surrounding vegetation. Indeed, the
381 ambient temperature at ground-level was higher during that flight than during the previous ones
382 (see Fig.S.I.17h). The diurnal cycles of isoprene emissions and temperature are further discussed
383 in Section 3.2.2. Interestingly, the GC-MS and the PTR-ToF-MS did not capture this 200 pptv
384 maximum (see Fig. 3 and Fig.S.I.16), which may be because the balloon flights were performed
385 at a different location (near sampling sector B, see Fig.S.I.1) surrounded by a higher fraction of
386 isoprene-emitting shrubs (willow).

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387 Samples collected on June 16, 2019 from 4 to 4:30 am (see Fig. 5f) show decreasing isoprene
388 mixing ratios with increasing elevation, suggesting higher levels (25-50 pptv) in the nocturnal
389 boundary layer than above. This result suggests continuing isoprene emissions by the surrounding
390 vegetation under low-PAR conditions. This is further discussed in Section 3.2.2.

391 3.1.3 Monoterpenes and Sesquiterpenes

392 MT mixing ratios ranged from 3 to 537 pptv (14 ± 18 pptv; median \pm standard deviation) during
393 the 2019 campaign according to the PTR-ToF-MS measurements. Using the GC-MS/FID, we were
394 able to detect and quantify the following MT in ambient air: α -pinene, camphene, sabinene, p-
395 cymene, and limonene. Mean mixing ratios are reported in Table 2 (for values lower than the LOQ,
396 mixing ratios equal to half of the LOQ are used). These compounds have been previously identified
397 as emissions of the widespread circumpolar dwarf birch *Betula nana* (Li et al., 2019; Vedel-
398 Petersen et al., 2015) and other high Arctic vegetation (Schollert et al., 2014). The quantification
399 frequency of camphene, sabinene, p-cymene, and limonene was low (see Table 2) and MT mixing

404 ratios in ambient air were dominated by α -pinene. Several prior studies performed at boreal sites
405 have similarly identified α -pinene as the most abundant monoterpene throughout the growing
406 season (e.g., Hakola et al., 2000; Lindfors et al., 2000; Spirig et al., 2004; Tarvainen et al., 2007).
407 We did not detect any sesquiterpene in ambient air above the 2 pptv instrumental LOQ.

408 Overall, isoprene and α -pinene dominated the ambient air BVOC profile at TFS, respectively
409 constituting ~72% and ~24% of total BVOCs quantified in ambient air (on a mixing-ratio basis).

410 3.2 Emission rates

411 3.2.1 Branch enclosures

412 A branch enclosure experiment was performed from July 27 to August 2, 2018 on *Salix glauca* to
413 investigate BVOC emission rates per dry weight plant biomass (see Fig.S.I.5). Isoprene emission
414 rates ranged from <0.01 to 11 $\mu\text{gC/g/h}$ (with a mean enclosure temperature of 16.5°C and mean
415 PAR of 880 $\mu\text{mol/m}^2/\text{s}$), in line with non-normalized emission rates reported at Kobbefjord,
416 Greenland by Kramshøj et al. (2016; Supplementary Table 5) for the same species under slightly
417 different environmental conditions (mean temperature of 24.6°C and mean PAR of 1052
418 $\mu\text{mol/m}^2/\text{s}$). Once standardized to 30°C and 1000 $\mu\text{mol/m}^2/\text{s}$, our emission rates averaged 5
419 $\mu\text{gC/g/h}$, in good agreement with standardized emissions reported at Kobbefjord (mean of 7
420 $\mu\text{gC/g/h}$) by Vedel-Petersen et al. (2015). The quantified MTs had emissions averaging two orders
421 of magnitude lower than those of isoprene (0.01 vs 1 $\mu\text{gC/g/h}$). Emission rates for the sum of α -
422 pinene, β -pinene, limonene, camphene, and 1,8-cineole ranged from <0.01 to 0.06 $\mu\text{gC/g/h}$. These
423 results are again in good agreement with those reported for the same species at Kobbefjord (~0.01
424 $\mu\text{gC/g/h}$) by Kramshøj et al. (2016; Supplementary Table 5).

425 3.2.2 Surface emission rates

426 The isoprene surface emission rate, as inferred from surface enclosures, was highly variable and
427 ranged from 0.2 to ~2250 $\mu\text{gC/m}^2/\text{h}$ (see Fig. 6). The 2250 $\mu\text{gC/m}^2/\text{h}$ maximum, reached on June
428 26, 2019, with an enclosure temperature of 32°C, is higher than maximum values reported at TFS
429 by Potosnak et al. (2013) (1200 $\mu\text{gC/m}^2/\text{h}$ at an air temperature of 22°C). It should be noted that
430 these maximum values were observed at different ambient temperatures; we further investigate the
431 temperature dependency of isoprene emissions in Section 3.3. Elevated surface emission rates (*i.e.*,
432 > 500 $\mu\text{gC/m}^2/\text{h}$) were all observed while sampling enclosures dominated by *Salix* spp.. At TFS,

Deleted: and in a high-latitude (58°N) *Salix* plantation by Olofsson et al. (2005) (730 $\mu\text{gC/m}^2/\text{h}$)

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the overall 24-hour mean isoprene emission rate amounted to 85 $\mu\text{gC}/\text{m}^2/\text{h}$, while the daytime (10 am-8 pm) and midday (11 am-2 pm) means were 140 and 213 $\mu\text{gC}/\text{m}^2/\text{h}$, respectively. To put this in perspective, the average isoprene surface emission rate standardized to 30°C and 1000 $\mu\text{mol}/\text{m}^2/\text{s}$ ($\sim 300 \mu\text{gC}/\text{m}^2/\text{h}$) was an order of magnitude lower than emission rates reported for warmer mid-latitude or tropical forests. For example, average midday fluxes of 3000 $\mu\text{gC}/\text{m}^2/\text{h}$ were reported in a northern hardwood forest in Michigan (Pressley et al., 2005), while several reports of isoprene emissions from tropical ecosystems give daily estimates of 2500-3000 $\mu\text{gC}/\text{m}^2/\text{h}$ (Helmig et al., 1998; Karl et al., 2004; Rinne et al., 2002).

Figure 7 shows the measured surface emission rates for α -pinene, β -pinene, limonene, and 1,8-cineole. While p-cymene, sabinene, 3-carene, and isocaryophyllene (SQT) were detected in some of the surface enclosure samples, we focus the discussion on the most frequently quantified compounds. It is worth noting that the most frequently observed compounds in enclosure samples are among the most frequently seen MT in ambient air (see Section 3.1.3). Regardless of the species, emission rates remained on average below 1 $\mu\text{gC}/\text{m}^2/\text{h}$ over the course of the study (see Table 3). These results are at the low end of emission rates reported for four vegetation types in high Arctic Greenland (Schollert et al., 2014), but in line with results reported at Kobbefjord, Greenland by Kramshøj et al. (2016; Supplementary Table 4).

Figures 8a-c show the mean diurnal cycle (over the two campaigns) of isoprene surface emission rates for different vegetation types (see Fig.S.I.3-15 for nomenclature). The two field campaigns were carried out during the midnight sun period, which could possibly sustain BVOC emissions during nighttime. It should, however, be noted that low sun angles translate to very low PAR and a typical diurnal pattern is observed in summer at TFS despite 24 hours of light (see Fig. 8h). Regardless of the vegetation type, isoprene emission rates exhibited a significant diurnal cycle with an early afternoon maximum, in line with the mean diurnal cycle of enclosure temperature and PAR. These results are in line with the well-established diurnal variation of BVOC emissions in environments ranging from Mediterranean to boreal forests (e.g., Fares et al., 2013; Liu et al., 2004; Ruuskanen et al., 2005; Zini et al., 2001) and with the correlation between isoprene ambient air mixing ratios and temperature at TFS (see Section 3.1). Despite the relatively low MT emission rates, a significant diurnal cycle was also observed with peak total MT emissions of $\sim 1 \mu\text{gC}/\text{m}^2/\text{h}$ during early afternoon for both *Salix* spp. and *Betula* spp. (Fig. 8e-f). A summary of emission rates

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per vegetation type and time of day is given in Table 3. As can be seen in Table 3 and Fig. 8, PAR and BVOC emissions significantly decreased at night but were still detectable. These sustained BVOC emissions during nighttime confirm observations by Lindwall et al. (2015) during a 24-hour experiment with five different Arctic vegetation communities, and explain the higher isoprene levels observed in the nocturnal boundary layer than above during the diurnal balloon experiment (see Section 3.1.2).

The ratio of total MT (given by the sum of α -pinene, β -pinene, limonene, and 1,8-cineole) emissions to isoprene emissions was an order of magnitude higher for *Betula* spp. (0.22) than for *Salix* spp. (0.03). This result, driven by the relatively lower isoprene emissions of *Betula* spp., is in line with earlier studies, suggesting similar emission characteristics for Arctic plants (e.g., Kramshøj et al., 2016; Vedel-Petersen et al., 2015).

4. Insights into future changes

4.1 Response of isoprene emissions to temperature

The Arctic has warmed significantly during the last three decades and temperatures are projected to increase an additional 5-13°C by the end of the century (Overland et al., 2014). Heat wave frequency is also increasing in the terrestrial Arctic (Dobricic et al., 2020). For example, western Siberia experienced an unusually warm May in 2020, with temperatures of 20-25°C (Freedman and Cappucci, 2020). In that context, numerous studies have pointed out the likelihood of increased BVOC emissions due to Arctic warming and associated vegetation and land cover change (Faubert et al., 2010; Potosnak et al., 2013; Rinnan et al., 2011; Tiiva et al., 2008).

Over the course of the two field campaigns at TFS, BVOC surface emission rates were measured over a large span of enclosure temperatures (2-41°C). While isoprene and MT emissions respond to leaf temperature (Guenther et al., 1993), air temperature was used here in place of leaf temperature – which has been assumed before in the literature for high-latitude ecosystems (e.g., Olofsson et al., 2005; Potosnak et al., 2013). Several studies have, however, suggested a decoupling of leaf and air temperature in tundra environments (Lindwall et al., 2016; Potosnak et al., 2013). With predicted increase of air temperature in the Arctic, it still remains largely unknown how leaf temperature will change and impact BVOC emissions. As suggested by Tang et al. (2016), long-term parallel observations of both leaf and air temperature are needed. The response

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of BVOC emissions to temperature discussed here should be interpreted with this potential caveat in mind.

While MT emissions remained low and close to the detection limit thus preventing robust quantification of any emission-temperature relationship, isoprene emissions significantly increased with temperature (Fig.9). Figure 9 combines daytime (e.g., with relatively high PAR values) isoprene emission rates from different surface enclosures, with results normalized to account for differing total biomass and species distributions (with *Salix* spp. the dominant emitter). Specifically, we divided all fluxes by the enclosure-specific mean emission at $20 \pm 1^\circ\text{C}$. Emission rates are often standardized to 30°C but we employ 20°C here owing to the colder growth environment at TFS (Ekberg et al., 2009). The isoprene emission-temperature relationship observed at TFS (in blue) is very similar to that reported by Tang et al. (2016) at Abisko (Sweden; in pink) for tundra heath (dominated by evergreen and deciduous dwarf shrubs). Results at TFS and Abisko both point to a high isoprene-temperature response for Arctic ecosystems (Tang et al., 2016). This is further supported by two warming experiments performed in mesic tundra heath (dominated by *Betula nana*, *Empetrum nigrum*, *Empetrum hermaphroditum*, and *Cassiope tetragona*) and dry dwarf-shrub tundra (co-dominated by *Empetrum hermaphroditum* and *Salix glauca*) in Western Greenland (Kramshøj et al., 2016; Lindwall et al., 2016). Kramshøj et al. (2016) observed a 240% isoprene emission increase with 3°C warming, while Lindwall et al. (2016) reported a 280% increase with 4°C warming. The observationally-derived emission-temperature relationship derived here for TFS reveals a 180-215% emission increase with $3\text{-}4^\circ\text{C}$ warming.

The MEGAN2.1 modeling framework is commonly used to estimate BVOC fluxes between terrestrial ecosystems and the atmosphere (e.g., Millet et al., 2018). Here, we apply the TFS observations to evaluate the MEGAN2.1 emission-temperature relationship for this Arctic environment. Figure 9 shows that the model temperature algorithm provides a close fit with observations below 30°C , with a 170-240% emission increase for a $3\text{-}4^\circ\text{C}$ warming. While the model predicts a leveling-off of emissions at approximately $30\text{-}35^\circ\text{C}$, our observations reveal no such phenomenon within the $0\text{-}40^\circ\text{C}$ enclosure temperature range (Fig. 9). However, given the limited number of enclosure measurements above 30°C , a leveling-off of emissions cannot be statistically ruled out. The key result here is that MEGAN2.1 adequately reproduces the

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temperature dependence response of Arctic ecosystems in the 0-30°C temperature range – ambient temperature > 30°C being unlikely. The highest air temperature on record at TFS (1988-2019) is 26.5°C, and the mean summertime (June-August) temperature over that period is 9°C. Additionally, for each year in the 1988-2019 historical dataset, there were only 1 to 23 days (0 to 4 days) per year with a maximum temperature above 20°C (above 25°C). If global greenhouse gas emissions continue to increase, temperatures are expected to rise 6-7°C in northern Alaska by the end of the century (annual average; Markon et al., 2012) while the number of days with temperatures above 25°C could triple (Lader et al., 2017). Based on current climate conditions and this rate of change, the MEGAN2.1 algorithm adequately represents the temperature dependence response of Arctic ecosystems for the near and intermediate-term future.

4.2 Long-term effects of warming

BVOC produced by plants are involved in plant growth, reproduction, and defense, and plants use isoprene emissions as a thermotolerance mechanism (Peñuelas and Staudt, 2010; Sasaki et al., 2007). The exponential response of isoprene emissions to temperature observed at TFS adds to a growing body of evidence indicating a high isoprene-temperature response in Arctic ecosystems. However, observations at TFS do not necessarily reflect long-term effects of warming. Schollert et al., (2015) examined how long-term warming affects leaf anatomy of individual arctic plant shoots (*Betula nana*, *Cassiope tetragona*, *Empetrum hermaphroditum*, and *Salix arctica*). They found that long-term warming results in significantly thicker leaves suggesting anatomical acclimation. While the authors hypothesized that this anatomical acclimation may limit the increase of BVOC emissions at plant shoot-level, Kramshøj et al. (2016) later showed that BVOC emissions from Arctic tundra exposed to six years of experimental warming increase at both the plant shoot and ecosystem levels.

In addition to the direct impact of long-term warming on BVOC emissions, ecosystem-level emissions are expected to increase in the Arctic due to climate-driven changes in plant biomass and vegetation composition. For instance, the widespread increase in shrub abundance in the Arctic – due to a longer growing season and enhanced nutrient availability (Berner et al., 2018; Sturm et al., 2001) – will likely significantly affect the BVOC emission potential of the Arctic tundra. Additionally, as mentioned above and as discussed extensively by Peñuelas and Staudt (2010) and Loreto and Schnitzler (2010), emissions of BVOCs might be largely beneficial for plants.

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To put the above finding in perspective,

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591 conferring them higher protection from abiotic stressors which are predicted to be more severe in
592 the future. Long-term arctic warming may thus favor BVOC-emitting species even further.

593 5. Conclusion

594 While BVOC ambient concentrations and emission rates have been frequently measured in boreal
595 ecosystems, Arctic tundra environments are under studied. We provide here summertime BVOC
596 ambient air mixing ratios and emission rates at Toolik Field Station, on the north flank of the
597 Brooks Range in northern Alaska. We present the first continuous summertime record of ambient
598 air isoprene and its first-generation oxidation products in the Arctic tundra environment. This
599 dataset provides a new set of observations to constrain isoprene chemistry in low-NO_x
600 environments. This dataset also provides a baseline to investigate future changes in the BVOC
601 emission potential of the Arctic tundra environment. While the overall mean isoprene emission
602 rate amounted to 85 µgC/m²/h, elevated (> 500 µgC/m²/h) isoprene surface emission rates were
603 observed for *Salix* spp., a known isoprene emitter. We also show that the response to temperature
604 of isoprene emissions in enclosures dominated by *Salix* spp. increased exponentially in the 0–40°C
605 range, likely conferring greater thermal protection for these plants. Given the widespread increase
606 in shrub abundance in the Arctic (including *Salix* spp.), our results support earlier studies (e.g.,
607 Valolahti et al., 2015) suggesting that climate-induced changes in the Arctic vegetation
608 composition will significantly affect the BVOC emission potential of the Arctic tundra, with
609 implications for atmospheric oxidation processes and climate feedbacks.

610 Data availability

611 Data are available upon request to the corresponding author.

612 Author contribution

613 DH, LH, and DBM designed the experiments and acquired funding. HA led the two field
614 campaigns with significant on-site contribution from KM, JH, LH, DBM, KC, JM, CW, TM, and
615 DH. JH designed and built most of the instruments used in this study. CW acquired the PTR-ToF-
616 MS data during the second campaign and DK performed data analysis. MSBH identified the plant
617 species and provided guidance during the field campaigns. KM and HA analyzed the samples in
618 the lab. HA analyzed all the data and prepared the manuscript with contributions from all co-
619 authors.

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629 **Competing interests**

630 The authors declare no competing interests.

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983

984 Table 1: Year 2017 median relative percent cover of plant species in moist acidic tundra long-term
 985 ecological research (LTER) experimental control plots at Toolik Field Station. The last column indicates
 986 whether plant species were present in surface or bag enclosure experiments in this study.

Plant name	Relative land surface cover in moist acidic tundra (%) (Gough, 2019)	Present in surface or bag enclosures
<i>Andromeda polifolia</i>	0.6	yes
<i>Betula nana</i>	14.4	yes
<i>Carex bigelowii</i>	1.0	yes
<i>Cassiope tetragona</i>	2.0	yes
<i>Empetrum nigrum</i>	3.8	yes
<i>Eriophorum vaginatum</i>	8.6	yes
<i>Ledum palustre</i>	10.5	yes
<i>Mixed Lichens</i>	2.1	yes
<i>Mixed moss</i>	6.0	yes
<i>Pedicularis lapponica</i>	0.6	no
<i>Polygonum bistorta</i>	0.6	no
<i>Rubus chamaemorus</i>	20.2	no
<i>Salix pulchra</i>	4.9	yes
<i>Vaccinium uliginosum</i>	1.9	yes
<i>Vaccinium vitis-idaea</i>	6.6	yes

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Table 2: Average mixings ratios with standard deviation, along with minimum (min) and maximum (max) values and quantification frequency (QF) of the measured monoterpenes in ambient air. LOQ stands for limit of quantification. For values lower than the LOQ, mixing ratios equal to half of the LOQ were used to calculate the mean.

	mean \pm standard deviation (pptv)	Min (pptv)	Max (pptv)	QF (%)
α -pinene	11.7 \pm 8.1	< LOQ	61.6	88
camphene	< LOQ	< LOQ	21.9	11
sabinene	< LOQ	< LOQ	34.2	11
p-cymene	2.0 \pm 1.9	< LOQ	12.3	32
limonene	< LOQ	< LOQ	2.9	< 1

1010 Table 3: Isoprene and monoterpenes (sum of α -pinene, β -pinene, limonene, and 1,8-cineole) surface
 1011 emission rates per vegetation type. Miscellaneous refers to a mix of different species, including lichens and
 1012 moss tundra (see Fig.S.I.3-15). Daytime refers to 10 am-8 pm, midday to 11 am-2 pm, and nighttime to 11
 1013 pm-5 am (Alaska Standard Time). The values in brackets represent the average enclosure temperature for
 1014 each emission rate.

	mean \pm standard deviation ($\mu\text{gC}/\text{m}^2/\text{h}$)	daytime mean \pm standard deviation ($\mu\text{gC}/\text{m}^2/\text{h}$)	midday mean \pm standard deviation ($\mu\text{gC}/\text{m}^2/\text{h}$)	nighttime mean \pm standard deviation ($\mu\text{gC}/\text{m}^2/\text{h}$)
isoprene				
<i>Salix</i> spp.	149 \pm 327 [17.6°C]	232 \pm 400 [23.9°C]	334 \pm 473 [27.0°C]	7 \pm 10 [8.0°C]
<i>Betula</i> spp.	12 \pm 30 [13.7°C]	19 \pm 38 [17.4°C]	28 \pm 37 [20.1°C]	5 \pm 14 [5.8°C]
Miscellaneous	38 \pm 81 [11.8°C]	57 \pm 100 [14.8°C]	104 \pm 135 [16.2°C]	21 \pm 64 [8.2°C]
monoterpenes				
<i>Salix</i> spp.	0.8 \pm 1.3 [17.6°C]	1.1 \pm 1.5 [23.9°C]	1.4 \pm 1.7 [27.0°C]	0.4 \pm 1.0 [8.0°C]
<i>Betula</i> spp.	0.5 \pm 0.6 [13.7°C]	0.7 \pm 0.7 [17.4°C]	1.0 \pm 0.8 [20.1°C]	0.2 \pm 0.2 [5.8°C]
Miscellaneous	1.1 \pm 1.4 [11.8°C]	1.3 \pm 1.6 [14.8°C]	1.7 \pm 2.0 [16.2°C]	1.0 \pm 1.4 [8.2°C]

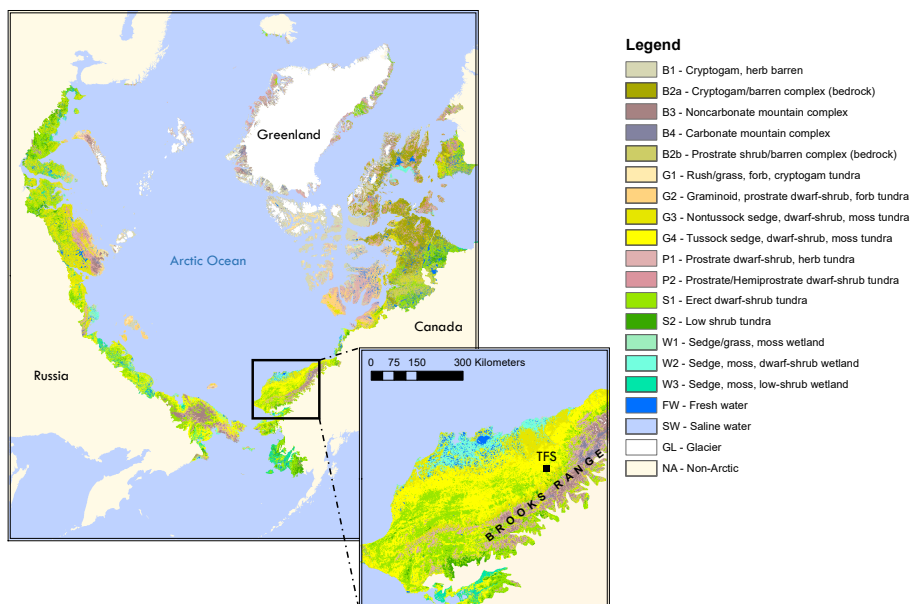


Figure 1: Location of Toolik Field Station (TFS) on the north flanks of the Brooks Range in northern Alaska along with arctic vegetation type. This Figure was made using the raster version of the Circumpolar Arctic Vegetation Map prepared by Raynolds et al. (2019) and publicly available at www.geobotany.uaf.edu.

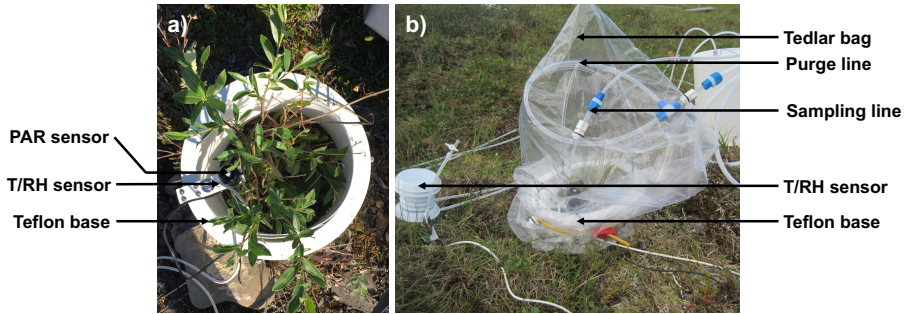
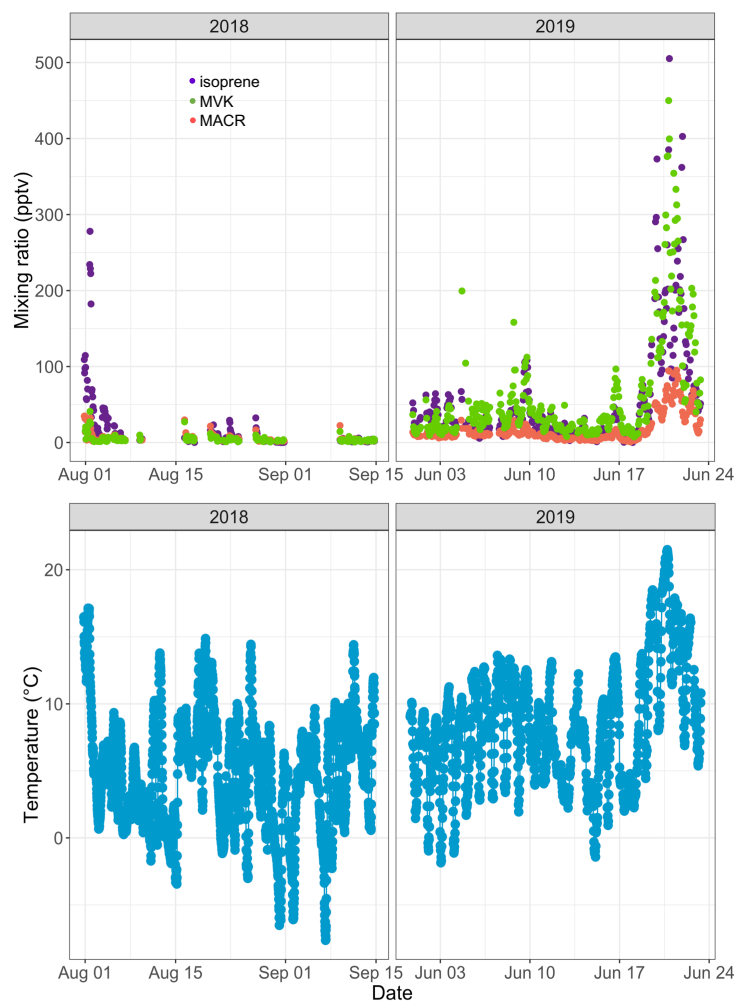


Figure 2: Photographs of a surface enclosure experiment setup at Toolik Field Station, Alaska. a) The first step of the installation consisted in positioning the Teflon® base around the vegetation of interest along with temperature (T), relative humidity (RH), and photosynthetically active radiation (PAR) sensors. b) The second step consisted in positioning the Tedlar® bag around the base. The bag was connected to a purge air and a sampling line. An additional T/RH sensor was also positioned outside the bag.

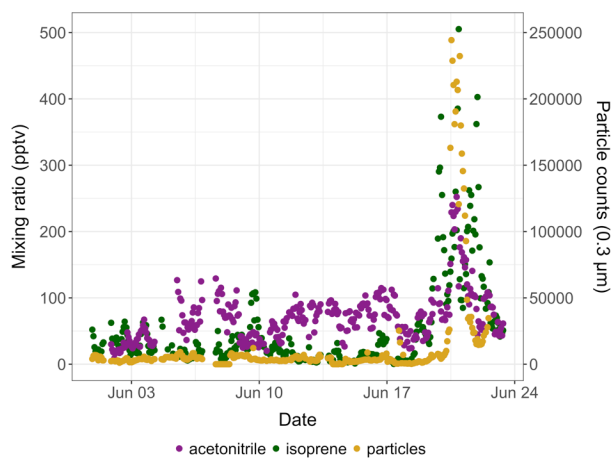


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1055 Figure 3: Time-series of isoprene (purple), methylvinylketone (MVK, green), and methacrolein (MACR,
 1056 salmon) mixing ratios (in pptv) in ambient air at Toolik Field station (top panels) and of 30-min-averaged
 1057 ambient temperature (in °C) at 4 meters above ground level (bottom panels).

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1061 Figure 4: Time-series of isoprene (green) and acetonitrile (purple) mixing ratios (in pptv) and of 0.3 μm
 1062 particle counts (yellow) in ambient air at Toolik Field station in June 2019.

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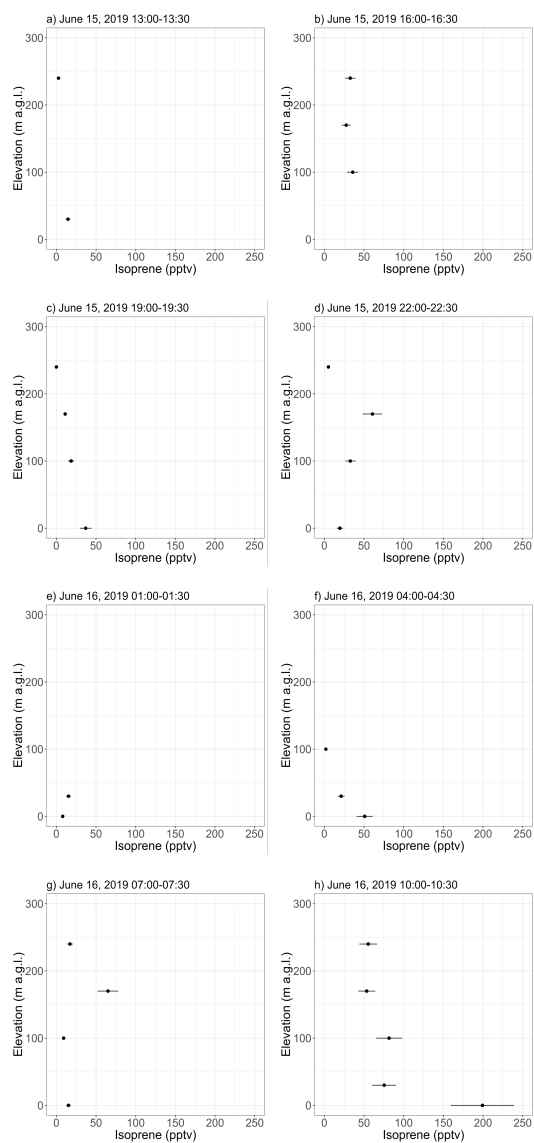
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Figure 5: Vertical profiles of isoprene mixing ratios as inferred from 30-min samples collected with a tethered balloon. The error bars show the analytical uncertainty for isoprene (20 %). Samples with an isoprene mixing ratio lower than blanks were discarded. Hours are in Alaska Standard Time (UTC-9).

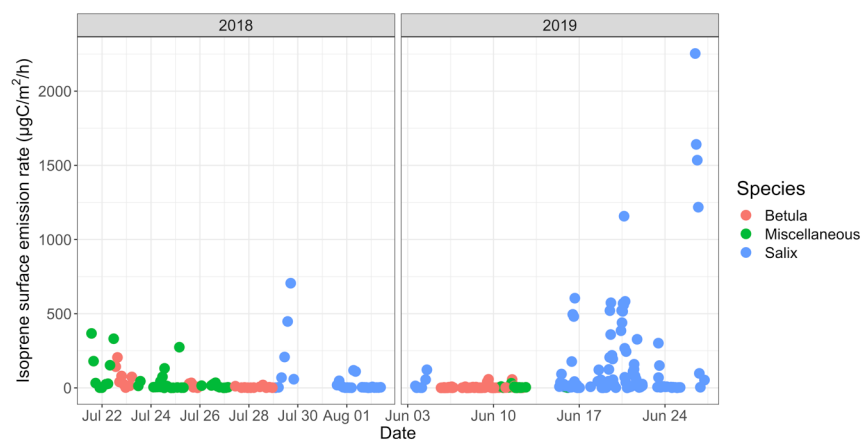
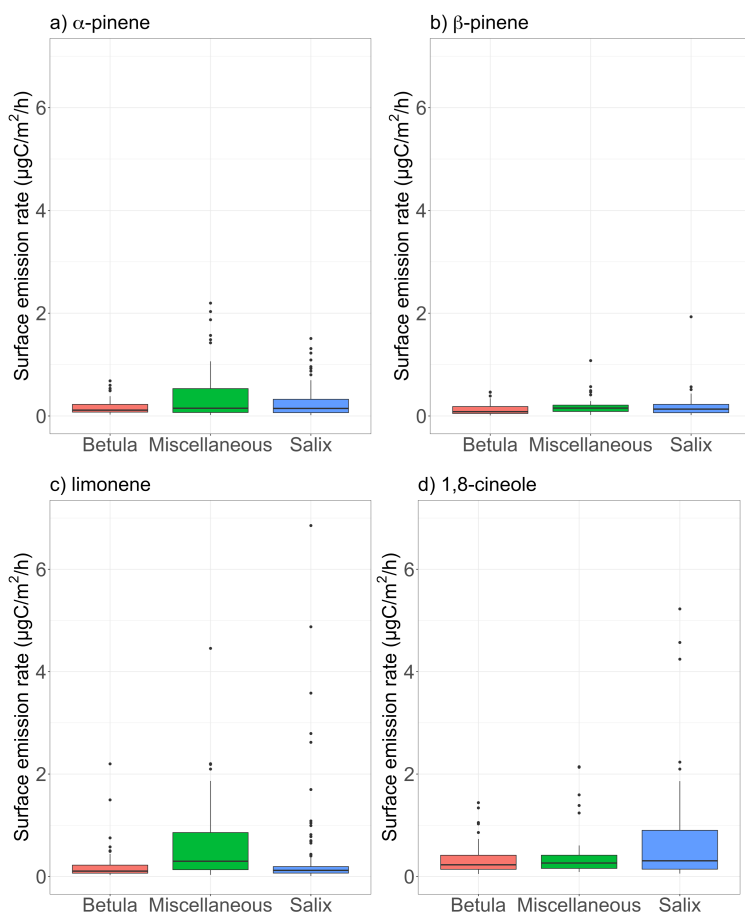


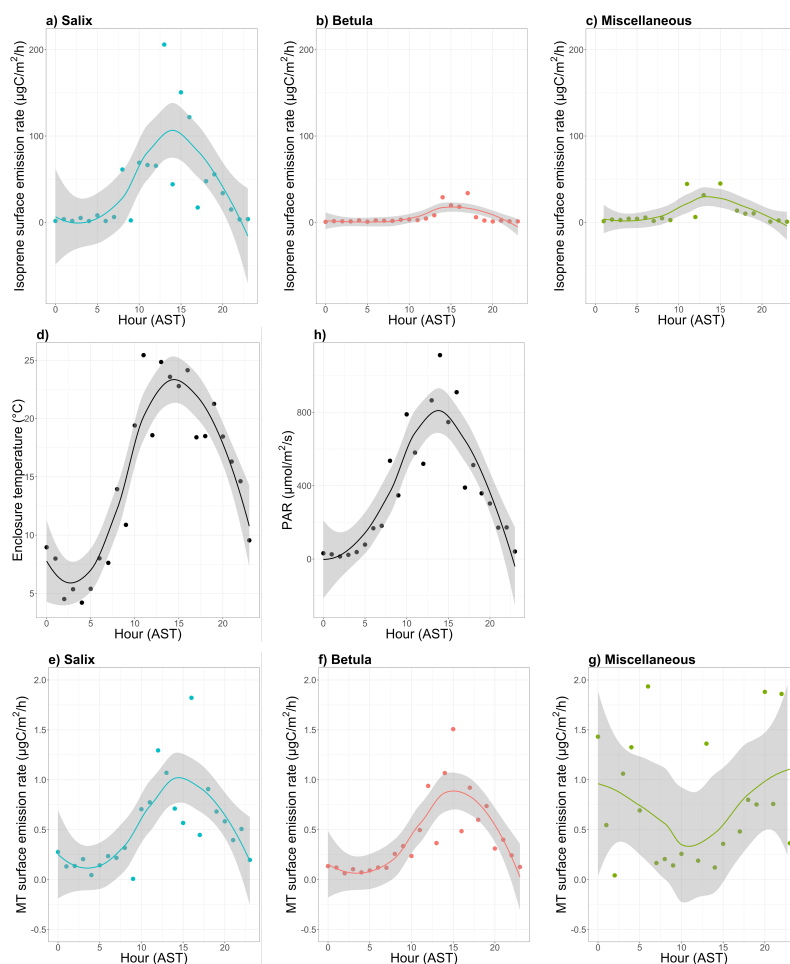
Figure 6: Time-series of isoprene surface emission rates (in $\mu\text{gC}/\text{m}^2/\text{h}$) for different vegetation types.



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1087 Figure 7: Surface emission rates of various monoterpenes (in $\mu\text{gC}/\text{m}^2/\text{h}$) for different vegetation types. The
 1088 lower and upper hinges correspond to the first and third quartiles. The upper (lower) whisker extends from
 1089 the hinge to the largest (smallest) value no further than $1.5 \times IQR$ from the hinge, where IQR is the inter-
 1090 quartile range (i.e., the distance between the first and third quartiles). The notches extend $1.58 \times IQR/\sqrt{n}$
 1091 and give a ~95% confidence interval for medians.

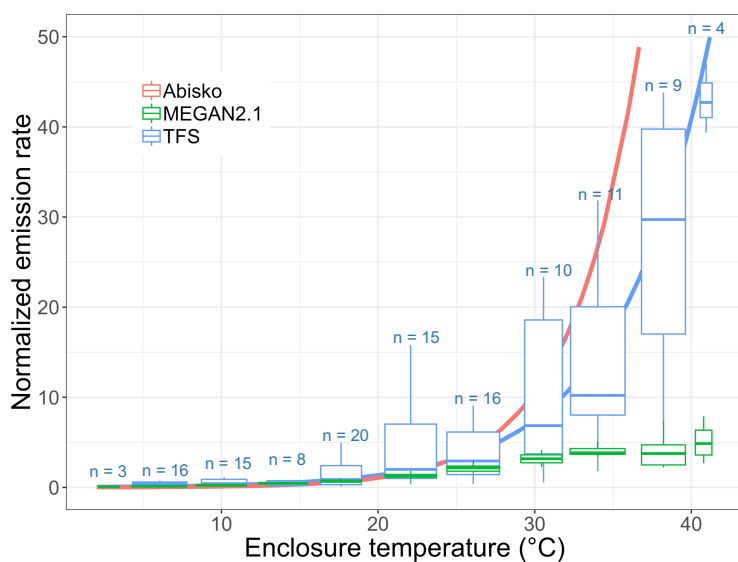
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1094 Figure 8: Mean diurnal cycle of isoprene (a-c) and monoterpenes (MT; e-g) surface emission rates (in
 1095 $\mu\text{gC}/\text{m}^2/\text{h}$ – note the difference scale on the y-axis), d) enclosure temperature (in $^{\circ}\text{C}$), and h) enclosure
 1096 photosynthetically active radiation (PAR in $\mu\text{mol}/\text{m}^2/\text{s}$). The dots represent the hourly means. The line is
 1097 the smoothed conditional mean while the grey shaded region indicates the 95% confidence interval. Hours
 1098 are in Alaska Standard Time (UTC-9) and correspond to the end of the 2-hr sampling period for isoprene
 1099 and MT emission rates. MT corresponds here to the sum of α -pinene, β -pinene, limonene, and 1,8-cineole.

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1101

1102 Figure 9: Normalized isoprene surface emission rate (emissions at 20°C set equal to 1.0) as a function of
 1103 enclosure temperature (in °C). This figure shows the response to temperature as observed at Toolik Field
 1104 Station (TFS, in blue) and Abisko, Sweden (in pink; Tang et al., 2016), and as parameterized in MEGAN2.1
 1105 (in green). The blue solid line is the exponential fit at TFS. n denotes the number of measurements in each
 1106 enclosure temperature bin. It should be noted that the enclosure temperature was on average 5-6°C warmer
 1107 than ambient air due to greenhouse heating.