Comments are in black and responses in blue.

Response to Reviewer #3

Angot and others measure biogenic volatile organic compound fluxes and atmospheric concentrations in a tundra environment. The measurements were carried out competently and the study is interesting, my comments are only minor.

Line 36: some species have even shorter lifetimes e.g. https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/95JD00368

We have revised this sentence accordingly: "Despite their relatively short atmospheric lifetimes (<u>a few minutes</u> to 1 day for terpenoids) (...)".

Line 177: Was the 30-minute sampling period in order to ensure that enough material was collected? There will be vertical mixing between levels at that time scale, even in the arctic, especially because sensible heat flux and convective energy is higher than many people realize due to the inefficiency of mosses and lichens at moving water vapor to the atmosphere (e.g. https://bg.copernicus.org/articles/8/3375/2011/).

Indeed, the manuscript has been revised accordingly: "Once the balloon reached its apex (~250-300 m a.g.l.), the five pumps were activated simultaneously and samples collected for 30 minutes to ensure that enough material was collected. It should be noted that changes in wind speed and turbulence during the 30-min sampling period often affected the shape of the tethered line and the sampling altitude adding further uncertainty to the vertical profiles presented here".

('Clock' also probably shouldn't be capitalized).

Done.

I'm not really sure what 'Miscellaneous' means in Figure 8. Perhaps it was mentioned in the text but the legend did not define it. I found the used on 216. More explanation of what is included in this grouping (which might accurately be called 'other') because it is not a 'vegetation type' (line 215) would lead to less confusion. Does it combine vascular and non-vascular species for example?

The definition of 'Miscellaneous' (mix of different species, including lichens and moss tundra) has been added to the caption of Figures 6, 7, and 8.

1 Biogenic volatile organic compound ambient mixing ratios and emission rates

2 in the Alaskan Arctic tundra

- 3 Hélène Angot¹, Katelyn McErlean¹, Lu Hu², Dylan B. Millet³, Jacques Hueber¹, Kaixin Cui¹, Jacob Moss¹,
- 4 Catherine Wielgasz², Tyler Milligan¹, Damien Ketcherside², Marion Syndonia Bret-Harte⁴, Detlev Helmig¹
- ⁵ ¹Institute of Arctic and Alpine Research, University of Colorado Boulder, Boulder, CO, USA.
- 6 ²Department of Chemistry and Biochemistry, University of Montana, Missoula, MT, USA.
- ⁷ ³Department of Soil, Water, and Climate, University of Minnesota, Minneapolis-Saint Paul, MN, USA.
- ⁴Institute of Arctic Biology, University of Alaska-Fairbanks, Fairbanks, Alaska, USA.
- 9

10 Abstract

Rapid Arctic warming, a lengthening growing season, and increasing abundance of biogenic volatile 11 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 µgC/m²/h (mean of 85 µgC/m²/h) and monoterpene 23 emission rates remained on average below 1 μ gC/m²/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.

30 1. Introduction

31 As a major source of reactive carbon to the atmosphere, biogenic volatile organic compounds 32 (BVOCs) emitted from vegetation play a significant role in global carbon and oxidation cycles 33 (Fehsenfeld et al., 1992). Global emission estimates of BVOCs are in the range of 700-1100 TgC 34 per year, ~70-80% of which corresponds to terpenoid species: isoprene, monoterpenes (MT), and 35 sesquiterpenes (SQT) (Guenther et al., 1995, 2006; Sindelarova et al., 2014). Despite their 36 relatively short atmospheric lifetimes (a few minutes to 1 day for terpenoids), BVOCs affect 37 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 38 influence radiative scattering) (Arneth et al., 2010; Fuentes et al., 2000; Peñuelas and Staudt, 39 40 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). 41 42 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; 43 44 Unger, 2014). 45 Global models of BVOC emissions assume minimal emissions from the Arctic due to low leaf

46 area index and relatively cold temperatures (Guenther et al., 2006; Sindelarova et al., 2014). 47 However, this assumption relies on few observations and has been increasingly challenged by field 48 data (Tang et al., 2016). Recent measurements have revealed significant BVOC emissions from 49 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 50 et al., 2013; Rinnan et al., 2011; Schollert et al., 2014; Tiiva et al., 2008). These results are of 51 importance because BVOC emissions are expected to increase in the Arctic due to climate 52 53 warming and associated vegetation and land cover change (Faubert et al., 2010; Potosnak et al., 54 2013; Rinnan et al., 2011; Tiiva et al., 2008). Field warming studies have shown strong increases 55 in BVOC emissions from shrub heath (Michelsen et al., 2012; Tiiva et al., 2008). Furthermore, the 56 temperature dependence of Arctic BVOC fluxes appears to be significantly greater than for tropical 57 and subtropical ecosystems (Holst et al., 2010; Rinnan et al., 2014), with up to 2-fold increases in 58 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 59

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response of BVOC emissions to an experimental 3-4°C warming and reported a 260-280%
increase in total emissions. Together, the above results emphasize the strong temperature
sensitivity of BVOC emissions from Arctic ecosystems.

64 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 65 BVOCs might already impact the diurnal cycle of ozone in the Arctic boundary layer (Van Dam 66 67 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 68 processes driving BVOC emissions in the Arctic. While BVOC ambient mixing ratios and 69 70 emission rates have been studied in boreal ecosystems, less attention has been paid to Arctic tundra 71 environments (Lindwall et al., 2015). Here, we report BVOC ambient mixing ratios and emission rates at Toolik Field Station (TFS) in the Alaskan Arctic. This study builds on the previous 72 73 isoprene study at TFS by Potosnak et al. (2013), while also providing a major step forward from 74 that work. In particular, we present the first continuous summertime record of ambient BVOCs 75 (including isoprene and MT) and their first-generation oxidation products in the Arctic tundra 76 environment. The data presented here provide a baseline to investigate future changes in the BVOC 77 emission potential of the under-studied Arctic tundra environment. Due to increasing shrub 78 prevalence across northern Alaska (Berner et al., 2018; Tape et al., 2006), as well as the Eurasian 79 (Macias-Fauria et al., 2012) and Russian Arctic (Forbes et al., 2010), the results of this study have 80 significance to tundra ecosystems across a vast region of the Arctic. We further compare the 81 observed temperature dependence of isoprene emissions with predictions from the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1), a widely used modeling 82 framework for estimating ecosystem-atmosphere BVOC fluxes (Guenther et al., 2012). 83

84 2. Material and Methods

85 **2.1 Study site**

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

greening (Hollesen et al., 2015; Sistla et al., 2013), *Rhododendron tomentosum* (formerly *Ledum palustre*; Labrador tea); *Vaccinium vitis-idaea* (lowbush cranberry), *Eriophorum vaginatum* (cotton grass), *Sphagnum angustifolium* (peat moss), *Alectoria ochroleuca* (witches hair lichen), and many other perennial species of Carex, mosses, and lichens. Vegetation cover at this site is classified as tussock tundra (see Fig.1), which is the most common vegetation type in the northern foothills of the Brooks Range (Elmendorf et al., 2012; Kade et al., 2012; Shaver and Chapin, 1991;

97 Survey, 2012; Walker et al., 1994).

98 Emission measurements and atmospheric sampling were conducted from a weatherproof 99 instrument shelter located ~350 m to the west of TFS (see Fig.S.I.1). Winds at TFS are 100 predominantly from the southerly and northerly sectors (Toolik Field Station Environmental Data 101 Center, 2019), minimizing any influence from camp emissions at the site. Two field campaigns 102 were carried out: the first from mid-July to mid-August 2018, and the second from mid-May to 103 the end of June 2019. These two back-to-back campaigns cover the entire growing season (Sullivan 104 et al., 2007), from the onset of snow melt mid-May to the first snow fall mid-August.

105

2.2 Ambient online measurements of BVOCs and their oxidation products

 106
 2.2.1 Gas chromatography and mass spectrometry with flame ionization detector

 107
 (GC-MS/FID)

108 An automated GC-MS/FID system was deployed for continuous measurements of atmospheric 109 BVOCs at ~2-hour time resolution during the 2018 and 2019 field campaigns. In addition, the 110 system was operated remotely following the 2018 campaign (through September 15th) to collect 111 background values at the beginning of autumn. Air was pulled continuously from an inlet on a 4 112 m meteorological tower located approximately 30 m from the instrument shelter (Van Dam et al., 113 2013). Air passed through a sodium thiosulfate-coated O_3 scrubber for selective O_3 removal – to 114 prevent sampling losses and artifacts for reactive BVOCs (Helmig, 1997; Pollmann et al., 2005) -115 and through a moisture trap to dry the air to a dew point of -45°C. The moisture trap was a Ushaped SilcoSteelTM tube (stainless steel treated) cooled using thermoelectric coolers. Analytes 116 117 were concentrated on a Peltier-cooled (-40°C) multistage micro-adsorbent trap (50 % Tenax-GR 118 and 50 % Carboxen 1016). Analysis was accomplished by thermal desorption and injection for 119 cryogen free GC using a DB-1 column (60 m \times 320 μ m \times 5 μ m) and helium as carrier gas. The 120 oven temperature was set to 40°C for 6 minutes, then increased to 260°C at 20°C/min, and held

121 isothermally at 260°C for 13 minutes. The column flow was split between an FID and a MS for 122 simultaneous quantification and identification. Blanks and calibration standards were regularly 123 injected from a manifold. Isoprene (m/z 67 and 68), methacrolein (MACR) and methylvinylketone 124 (MVK) (*m*/*z* 41, 55, and 70), MT (*m*/*z* 68, 93, 121, and 136), and SQT (*m*/*z* 204, 91, 93, 119, and 125 69) were identified and quantified using the MS in selected ion-monitoring mode (SIM). The 126 response to isoprene was calibrated using a primary gas standard supplied by the National Physical 127 Laboratory (NPL), certified as containing 4.01±0.09 ppb of isoprene in a nitrogen matrix. The 128 analytical uncertainty for isoprene was estimated at 16 % based on the certified uncertainty of the 129 standard and on the repeatability of standard analysis throughout the campaigns. Instrument 130 responses for MACR, MVK, α -pinene, and acetonitrile were calibrated with multi-component 131 standards containing 1007 ppb MACR, 971 ppb MVK, 967 ppb α-pinene, and 1016 ppb 132 acetonitrile (Apel-Riemer Environmental Inc., Miami, FL, USA) dynamically diluted into a stream 133 of ultra-zero grade air to ~3 ppb. Quantification of other terpenoid compounds was based on GC 134 peak area (FID response) plus relative response factors using the effective carbon number concept 135 (Faiola et al., 2012; Scanlon and Willis, 1985). The limit of quantification (LOQ) was ~2 pptv 136 (pmol/mol by volume). In order to monitor and correct for long-term trends in the detection system, 137 including detector drift and decreasing performance of the adsorbent trap, we used peak areas for 138 long-lived chlorofluorocarbons (CFCs) that were monitored in the air samples together with the 139 BVOCs as an internal reference standard. The atmospheric trace gases CCl₃F (CFC-11) and 140 CCl₂FCCl₂F₂(CFC-113) are ideal in this regard because they are ubiquitous in the atmosphere and 141 exhibit little spatial and temporal variability (Karbiwnyk et al., 2003; Wang et al., 2000).

142

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

143 During the summer 2019 campaign, isoprene mixing ratios in ambient air were also measured by 144 PTR-ToF-MS (model 4000, Ionicon Analytik GmbH, Innsbruck, Austria). The sample inlet was 145 located on the 4 m meteorological tower, right next to the GC-MS/FID inlet. In brief, ambient air 146 was continuously pulled through the PTR-ToF-MS drift-tube, where VOCs with proton affinities 147 higher than that of water (>165.2 kcal/mol) were ionized via proton-transfer reaction with primary 148 H_3O^+ ions, then subsequently separated and detected by a time-of-flight mass spectrometer (with 149 a mass resolving power up to 4000). At TFS, the PTR-ToF-MS measured ions from 17-400 m/z150 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 ~55°C, and then subsampled by the instrument through ~100 cm of 151 152 1/16" O.D. PEEK tubing maintained at 60°C. The residence time from the inlet on the 4 m 153 meteorological tower to the drift-tube was less than 5 seconds. Instrument backgrounds were 154 quantified approximately every 5 hours for 20 minutes during the campaign by measuring VOC-155 free air generated by passing ambient air through a heated catalytic converter (375 °C, platinum 156 bead, 1 % wt. Pt, Sigma Aldrich). Calibrations were typically performed every 4 days via dynamic 157 dilution of certified gas standard mixtures containing 25 distinct VOCs including isoprene (Apel-158 Riemer Environmental Inc., Miami, FL, USA). Here, we report isoprene mixing ratios to inter-159 compare with GC-MS measurements; other species will be reported in future work. The 160 measurement uncertainty for isoprene is \sim 25%, which includes uncertainties in the gas standards, 161 calibration method, and data processing.

162

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 intercomparison 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.

170 **2.3 Ambient air vertical profiles**

171 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 172 Alaska Standard Time (AST) on June 15, 2019 and 11:00 am AST on June 16, 2019 in order to 173 174 capture a full diurnal cycle (solar noon around 2 pm AST). Sampling packages were connected to 175 the tether line such that resulting sampling heights were ~30, ~100, ~170, and ~240 m above 176 ground level. One identical sampling package was deployed at the surface. Each sampling package 177 contained an adsorbent cartridge for sample collection (see below) connected to a downstream 178 battery-powered SKC pocket pump controlled using a mechanical relay, a programmable Arduino, 179 and a real-time clock. Once the balloon reached its apex (~ 250-300 m a.g.l.), the five pumps were 180 activated simultaneously and samples collected for 30 minutes to ensure that enough material was

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182 collected. It should be noted that changes in wind speed and turbulence during the 30-min sampling 183 period often affected the shape of the tethered line and the sampling altitude adding further 184 uncertainty to the vertical profiles presented here. At the end of the 30-min sampling period, the 185 balloon was brought back down. The adsorbent cartridges were prepared in house using glass 186 tubing (89 mm long \times 6.4 mm outer diameter, 4.8 mm inner diameter), and loaded with Tenax-187 GR and Carboxen 1016 adsorbents (270 mg of each), following established practice (Ortega and 188 Helmig, 2008 and references therein). An inlet ozone scrubber was installed on each cartridge to 189 prevent BVOC sampling losses. Field blanks were collected by opening a cartridge (with no 190 pumped airflow) during each balloon flight. Following collection, adsorbent cartridges were sealed 191 with Teflon-coated brass caps and stored in the dark at ~4°C until chemical analysis. Samples were 192 analyzed at the University of Colorado Boulder following the method described in S.I. Section 1. 193 Our previous inter-comparison of this cartridge-GC-MS/FID method with independent and 194 concurrent PTR-MS observations showed that the two measurements agree to within their 195 combined uncertainties at ~25% (Hu et al., 2015). Meteorological conditions were monitored and 196 recorded during each balloon flight with a radiosonde (Met1, Grant Pass, OR, USA) attached to 197 the tethered line just below the balloon.

198 2.4 BVOC emission rates

199

2.4.1 Dynamic enclosure measurements

200 We used dynamic enclosure systems operated at low residence time to quantify vegetative BVOC 201 emissions following the procedure described by Ortega et al. (2008) and Ortega and Helmig 202 (2008). Two types of enclosures were used: branch and surface chambers. For branch enclosures, 203 a Tedlar® bag (Jensen Inert Products, Coral Springs, FL) was sealed around the trunk side of a 204 branch. For surface enclosures, the bag was placed around a circular Teflon® base (25 cm wide × 205 16 cm height; see Fig. 2). For both branch and surface enclosures, the bag was connected to a 206 purge-air line and a sampling line, and positioned around the vegetation minimizing contact with 207 foliage. While purging the enclosure (see Section 2.4.3), the vegetation was allowed to acclimate 208 for 24 hours before BVOC sampling began. Samples were collected from the enclosure air, 209 concentrated onto solid-adsorbent cartridges (see Section 2.3) with an automated sampler, and 210 analyzed in-laboratory at the University of Colorado Boulder following the campaign (see S.I. 211 Section 1). Temperature and relative humidity were recorded inside and outside the enclosure (see

Fig. 2; S-THB-M002 sensors, Onset HOBO, Bourne, MA, USA) with a data logger (H21-USB, 212 Onset HOBO, Bourne, MA, USA). Additionally, photosynthetically active radiation (400-700 nm; 213 214 S-LIA-M003, Onset HOBO, Bourne, MA, USA) was measured inside the enclosure. Once 215 installed, enclosures were operated for 2-10 days. The tundra vegetation around TFS is 216 heterogeneous but most dominant species (except Rubus chamaemorus) were sampled. Table 1 217 presents the median relative percent cover of plant species in LTER experimental control plots at 218 TFS (Gough, 2019) and indicates whether plant species were present in surface or bag enclosures. 219 The complete list of species sampled and pictures of the enclosures are available in Figures S.I.3-220 S.I.15; the two sampling sectors are highlighted in Fig.S.I.1. Surface enclosures were divided into

221 three vegetation types: Salix spp. (high isoprene emitter), Betula spp. (e.g., Betula nana

222 dominance), and miscellaneous (mix of different species, including lichens and mosses).

223 2.4.2 Emission rates

224 The emission rate (ER in μ gC/m²/h) for surface enclosures was calculated as follows:

225
$$ER_{surface} = \frac{(C_{out} - C_{in})Q}{S},$$
 (1)

where C_{in} and C_{out} are the inlet and outlet analyte concentrations (in µgC/L), Q is the purge air flow rate (in L/h), and S the surface area of the enclosure (in m²).

228 The ER for branch enclosures (in μ gC/g/h) was calculated as follows:

- 229 $ER_{branch} = \frac{(C_{out} C_{in})Q}{m_{dry}},$ (2)
- 230 where m_{dry} is the dried mass (in g) of leaves enclosed, determined by drying the leaves harvested
- after the experiment at 60-70°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 μ mol/m²/s using the algorithms described in Guenther et al. (1993, 1995).
- 235 2.4.3 Enclosure purge air
- 236 Purge air was provided by an upstream high-capacity oil-free pump providing positive pressure to
- $237 \qquad \text{the enclosure, and equipped with an in-line O_3 scrubber to avoid loss of reactive BVOCs from}$

reaction with O₃ in the enclosure air and during sampling (Helmig, 1997; Pollmann et al., 2005).

239 The purge flow was set to 25 L/min and regularly checked using a volumetric flow meter (Mesa

240 Labs Bios DryCal Defender, Butler, NJ, USA). Excess air escaped from the open end (tied around

241 the Teflon® base) while the sample air flow was pulled into the sampling line (see below).

242 2.4.4 Sample collection

A continuous airflow of 400-500 mL/min was drawn from the enclosure through the sampling line. 243 244 A fraction of this flow was periodically collected at 265-275 mL/min on adsorbent cartridges (see 245 Section 2.3) using a 10-cartridge autosampler (Helmig et al., 2004). During sampling, cartridges 246 were kept at 40°C, *i.e.*, above ambient temperature, to prevent water accumulation on the adsorbent 247 bed (Karbiwnyk et al., 2002). Samples were periodically collected in series to verify lack of analyte 248 breakthrough. Time-integrated samples were collected for 120 min every 2 hours to establish 249 diurnal cycles of BVOC emission. Upon collection, samples were stored in the dark at ~4°C until 250 chemical analysis back at the University of Colorado Boulder.

251 2.4.5 Internal standards

252 In order to identify potential BVOC losses during transport, storage, and chemical analysis, 255 of the employed cartridges were pre-loaded with a four-compound standard mixture prior to the 253 254 field campaigns. These internal standard compounds (toluene, 1, 2, 3-trimethylbenzene, 1, 2, 3, 4-255 tetrahydronaphtalene, and 1, 3, 5-triisopropylbenzene) were carefully chosen to span a wide range 256 of volatility (C_7-C_{15}) and to not interfere (*i.e.*, coelute) with targeted BVOCs. The recovery of these 257 four compounds was assessed at the end of the campaign, following the analytical procedure 258 described in S.I. Section 1. Recovery rates were 101.8 ± 13.5 % (toluene), 95.2 ± 20.1 % (1,2,3-259 trimethylbenzene), $95.6 \pm 26.6 \%$ (1,2,3,4-tetrahydronaphtalene), and $100.9 \pm 18.7 \%$ (1,3,5-260 triisopropylbenzene). These results indicate that, overall, BVOC losses during transport, storage, 261 and chemical analysis were negligible. Ortega et al. (2008) previously evaluated systematic losses 262 of analytes to enclosure systems similar to those used here. The same four-component standard 263 was introduced into the purge air flow of the enclosures to quantify losses as a function of 264 volatility. That work found median losses of MT and SQT on the order of 20-30%. The emission 265 rates presented here are therefore possibly biased low by a similar amount.

266 **2.5 Peak fitting algorithm**

267 The analysis of ambient air and enclosure chromatograms was performed using the TERN

268 (Thermal desorption aerosol GC ExploreR and iNtegration package) peak fitting tool implemented

269 in Igor Pro and available online at <u>https://sites.google.com/site/terninigor/</u> (Isaacman-VanWertz et

270 al., 2017).

271 **2.6 Ancillary parameters**

272 Meteorological parameters. A suite of meteorological instruments was deployed on the 4 m tower. 273 Wind speed and direction were measured at ~4 m above ground level with a Met One 034B-L 274 sensor. As described by Van Dam et al. (2013), temperature was measured at three different heights 275 using RTD temperature probes (model 41342, R.M. Young Company, Traverse City, MI) housed 276 in aspirated radiation shields (model 43502, R.M. Young Company, Traverse City, MI). Regular 277 same-height inter-comparisons were conducted to test for instrumental offsets. Incoming and 278 reflected solar radiation were recorded with LI200X pyranometers (Campbell Scientific 279 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).

286 Nitrogen oxides. Nitrogen oxides (NO_x) were measured with a custom-built, high sensitivity (~5

287 pptv detection limit) single-channel chemiluminescence analyzer (Fontijn et al., 1970). The

288 instrument monitors nitric oxide (NO) and nitrogen dioxide (NO₂) in ambient air using a photolytic

289 converter. Automated switching valves alternated between NO and NO₂ mode every 30 minutes.

290 Calibration was accomplished by dynamic dilution of a 1.5 ppm compressed NO gas standard

291 (Scott-Marrin, Riverside, CA, USA).

292 2.7 Theoretical response of isoprene emissions to temperature in MEGAN2.1

293 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:

 $296 F_T = C_{CE} \gamma_T \sum_j \varkappa_j \varepsilon_j aga{3}$

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 \varkappa_j . We used $\sum_j \varkappa_j \varepsilon_j = 2766 \ \mu g/m^2/h$ 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:

303
$$\gamma_T = E_{opt} \times \frac{200 \, e^{95 \, x}}{200 - 95 \times (1 - e^{200 \, x})}$$
 (4)

304 with

$$305 \qquad x = \frac{\frac{1}{r_{opt}} - \frac{1}{r}}{\frac{1}{0.00831}} \tag{5}$$

$$306 \quad E_{opt} = 2 \times e^{0.08(I_{10} - 297)}$$

$$307 \quad T_{opt} = 313 + 0.6(T_{10} - 297), \tag{7}$$

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

(6)

310 **3. Results and Discussion**

311 **3.1 Ambient air mixing ratios**

312 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

320 Finland. In general, however, BVOC emissions in the Eurasian taiga are relatively low compared

321 to forest ecosystems in warmer climates and are dominated by monoterpenes (Rinne et al., 2009).

322 Isoprene mixing ratios peaked on August 1, 2018 around 4 pm and on June 20, 2019 around 10 323 pm, respectively. These two peaks occurred 3-5 hours after the daily maximum ambient 324 temperature was reached (17.8°C in 2019 and 21.8°C in 2019 – see Fig. 3). The isoprene peak on 325 June 20, 2019 was concomittant with enhanced acetonitrile mixing ratios and particle counts (see 326 Fig. 4), reflecting unusually hazy conditions that day at TFS. We attribute the particle and 327 acetonitrile enhancements to intense wildfires occurring across the Arctic Circle at that time - most 328 of them in southern Alaska and Siberia (Earth Observatory, 2019). Acetonitrile increased by a 329 factor of 4 during this event, compared to a factor of 21 increase for isoprene. The higher emission 330 factor for acetonitrile vs. isoprene from biomass burning in boreal forests (Akagi et al., 2011) and 331 the relatively short lifetime of isoprene (Atkinson, 2000) indicate that the observed isoprene 332 enhancement was due to fresh local biogenic emissions rather than transported wildfire emissions.

333 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 334 335 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 74 336 337 ppty, respectively, during the 2019 campaign (not shown) suggest a low-NOx environment, in line with previous studies at several Arctic locations (Bakwin et al., 1992; Honrath and Jaffe, 1992). 338 339 Under such conditions, MACR and MVK mixing ratios should be used as upper estimates as it has 340 been noted that some low-NOx isoprene oxidation products (isoprene hydroxyhydroperoxides) can 341 undergo rearragement in GC and PTR-MS instruments and be misidentified as MACR and MVK 342 (Rivera-Rios et al., 2014). We found a high correlation between MACR and MVK ($R^2 = 0.95$, p < 343 0.01) and between these two compounds and isoprene ($R^2 \sim 0.80$, p < 0.01). Increases of MACR 344 and MVK mixing ratios above the background were mostly concomitant with isoprene increases, 345 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 346 MACR was 2.7, within the range reported by earlier studies (e.g., Apel et al., 2002; Biesenthal and 347

348 Shepson, 1997; Hakola et al., 2003; Helmig et al., 1998), and no clear diurnal cycle in the ratio 349 was found. This record of ambient air isoprene, MACR, and MVK mixing ratios is, to the best of 350 our knowledge, the first in an Arctic tundra environment. The combined measurement of isoprene 351 and its oxidation products provides a new set of observations to further constrain isoprene 352 chemistry under low-NO_x conditions in atmospheric models (e.g., Bates and Jacob, 2019).

353 3.1.2 Isoprene vertical profiles

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

- 359 Except during the last flight, isoprene mixing ratios were in the range of background levels (~0-360 50 pptv) reported with the GC-MS (see Section 3.1.1). Samples collected from 10-10:30 am on 361 June 16 (see Fig. 5h) showed a pronounced gradient, with 200 pptv at ground level and decreasing 362 mixing ratios with elevation. This maximum at ground-level is expected for a VOC with a surface 363 source (Helmig et al., 1998) while the 200 pptv mixing ratio can likely be attributed to a 364 temperature-driven increase of isoprene emissions by the surrounding vegetation. Indeed, the 365 ambient temperature at ground-level was higher during that flight than during the previous ones 366 (see Fig.S.I.17h). The diurnal cycles of isoprene emissions and temperature are further discussed in Section 3.2.2. Interestingly, the GC-MS and the PTR-ToF-MS did not capture this 200 pptv 367 368 maximum (see Fig. 3 and Fig.S.I.16), which may be because the balloon flights were performed 369 at a different location (near sampling sector B, see Fig.S.I.1) surrounded by a higher fraction of 370 isoprene-emitting shrubs (willow).
- 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
- 374 vegetation under low-PAR conditions. This is further discussed in Section 3.2.2.
- 375 3.1.3 Monoterpenes and Sesquiterpenes

MT mixing ratios ranged from 3 to 537 pptv (14 ± 18 pptv; median \pm standard deviation) during 376 377 the 2019 campaign according to the PTR-ToF-MS measurements. Using the GC-MS/FID, we were 378 able to detect and quantify the following MT in ambient air: α-pinene, camphene, sabinene, p-379 cymene, and limonene. Mean mixing ratios are reported in Table 2 (for values lower than the LOQ, 380 mixing ratios equal to half of the LOQ are used). These compounds have been previously identified 381 as emissions of the widespread circumpolar dwarf birch Betula nana (Li et al., 2019; Vedel-382 Petersen et al., 2015) and other high Arctic vegetation (Schollert et al., 2014). The quantification 383 frequency of camphene, sabinene, p-cymene, and limonene was low (see Table 2) and MT mixing 384 ratios in ambient air were dominated by α -pinene. Several prior studies performed at boreal sites 385 have similarly identified α -pinene as the most abundant monoterpene throughout the growing season (e.g., Hakola et al., 2000; Lindfors et al., 2000; Spirig et al., 2004; Tarvainen et al., 2007). 386 387 We did not detect any sesquiterpene in ambient air above the 2 pptv instrumental LOQ.

388 Overall, isoprene and α -pinene dominated the ambient air BVOC profile at TFS, respectively 389 constituting ~72% and ~24% of total BVOCs quantified in ambient air (on a mixing-ratio basis).

390 3.2 Emission rates

391 3.2.1 Branch enclosures

392 A branch enclosure experiment was performed from July 27 to August 2, 2018 on Salix glauca to 393 investigate BVOC emission rates per dry weight plant biomass (see Fig.S.I.5). Isoprene emission 394 rates ranged from <0.01 to 11 µgC/g/h (with a mean enclosure temperature of 16.5°C and mean 395 PAR of 880 µmol/m²/s), in line with non-normalized emission rates reported at Kobbefjord, 396 Greenland by Kramshøj et al. (2016; Supplementary Table 5) for the same species under slightly 397 different environmental conditions (mean temperature of 24.6°C and mean PAR of 1052 398 µmol/m²/s). Once standardized to 30°C and 1000 µmol/m²/s, our emission rates averaged 5 399 µgC/g/h, in good agreement with standardized emissions reported at Kobbefjord (mean of 7 400 $\mu gC/g/h$) by Vedel-Petersen et al. (2015). The quantified MTs had emissions averaging two orders 401 of magnitude lower than those of isoprene (0.01 vs 1 μ gC/g/h). Emission rates for the sum of α -402 pinene, β -pinene, limonene, camphene, and 1,8-cineole ranged from <0.01 to 0.06 μ gC/g/h. These 403 results are again in good agreement with those reported for the same species at Kobbefjord (~0.01 404 µgC/g/h) by Kramshøj et al. (2016; Supplementary Table 5).

405 3.2.2 Surface emission rates

406 The isoprene surface emission rate, as inferred from surface enclosures, was highly variable and 407 ranged from 0.2 to \sim 2250 µgC/m²/h (see Fig. 6). The 2250 µgC/m²/h maximum, reached on June 408 26, 2019, with an enclosure temperature of 32°C, is higher than maximum values reported at TFS 409 by Potosnak et al. (2013) (1200 μ gC/m²/h at an air temperature of 22°C). It should be noted that 410 these maximum values were observed at different ambient temperatures; we further investigate the 411 temperature dependency of isoprene emissions in Section 3.3. Elevated surface emission rates (*i.e.*, 412 > 500 µgC/m²/h) were all observed while sampling enclosures dominated by Salix spp.. At TFS, the overall 24-hour mean isoprene emission rate amounted to 85 μ gC/m²/h, while the daytime (10 413 414 am-8 pm) and midday (11 am-2 pm) means were 140 and 213 µgC/m²/h, respectively. To put this 415 in perspective, the average isoprene surface emission rate standardized to 30°C and 1000 416 µmol/m²/s (~ 300 µgC/m²/h) was an order of magnitude lower than emission rates reported for 417 warmer mid-latitude or tropical forests. For example, average midday fluxes of 3000 µgC/m²/h 418 were reported in a northern hardwood forest in Michigan (Pressley et al., 2005), while several 419 reports of isoprene emissions from tropical ecosystems give daily estimates of 2500-3000 420 µgC/m²/h (Helmig et al., 1998; Karl et al., 2004; Rinne et al., 2002).

421 Figure 7 shows the measured surface emission rates for α -pinene, β -pinene, limonene, and 1.8-422 cineole. While p-cymene, sabinene, 3-carene, and isocaryophyllene (SQT) were detected in some 423 of the surface enclosure samples, we focus the discussion on the most frequently quantified 424 compounds. It is worth noting that the most frequently observed compounds in enclosure samples 425 are among the most frequently seen MT in ambient air (see Section 3.1.3). Regardless of the 426 species, emission rates remained on average below 1 µgC/m²/h over the course of the study (see 427 Table 3). These results are at the low end of emission rates reported for four vegetation types in 428 high Arctic Greenland (Schollert et al., 2014), but in line with results reported at Kobbefjord, 429 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 436 with an early afternoon maximum, in line with the mean diurnal cycle of enclosure temperature 437 and PAR. These results are in line with the well-established diurnal variation of BVOC emissions 438 in environments ranging from Mediterranean to boreal forests (e.g., Fares et al., 2013; Liu et al., 439 2004; Ruuskanen et al., 2005; Zini et al., 2001) and with the correlation between isoprene ambient 440 air mixing ratios and temperature at TFS (see Section 3.1). Despite the relatively low MT emission 441 rates, a significant diurnal cycle was also observed with peak total MT emissions of $\sim 1 \,\mu gC/m^2/h$ 442 during early afternoon for both Salix spp. and Betula spp. (Fig. 8e-f). A summary of emission rates 443 per vegetation type and time of day is given in Table 3. As can be seen in Table 3 and Fig. 8, PAR 444 and BVOC emissions significantly decreased at night but were still detectable. These sustained 445 BVOC emissions during nighttime confirm observations by Lindwall et al. (2015) during a 24hour experiment with five different Arctic vegetation communities and explain the higher isoprene 446 447 levels observed in the nocturnal boundary layer than above during the diurnal balloon experiment 448 (see Section 3.1.2).

449 The ratio of total MT (given by the sum of α-pinene, β-pinene, limonene, and 1,8-cineole) 450 emissions to isoprene emissions was an order of magnitude higher for *Betula* spp. (0.22) than for 451 *Salix* spp. (0.03). This result, driven by the relatively lower isoprene emissions of *Betula* spp., is 452 in line with earlier studies, suggesting similar emission characteristics for Arctic plants (e.g., 453 Kramshøj et al., 2016; Vedel-Petersen et al., 2015).

454 **4. Insights into future changes**

455 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).

463 Over the course of the two field campaigns at TFS, BVOC surface emission rates were measured
464 over a large span of enclosure temperatures (2-41°C). While isoprene and MT emissions respond
465 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., 466 467 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 468 469 al., 2013). With predicted increase of air temperature in the Arctic, it still remains largely unknown 470 how leaf temperature will change and impact BVOC emissions. As suggested by Tang et al. 471 (2016), long-term parallel observations of both leaf and air temperature are needed. The response 472 of BVOC emissions to temperature discussed here should be interpreted with this potential caveat 473 in mind.

474 While MT emissions remained low and close to the detection limit thus preventing robust 475 quantification of any emission-temperature relationship, isoprene emissions significantly 476 increased with temperature (Fig.9). Figure 9 combines daytime (e.g., with relatively high PAR 477 values) isoprene emission rates from different surface enclosures, with results normalized to 478 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 $20 \pm 1^{\circ}$ C. Emission 479 rates are often standardized to 30°C but we employ 20°C here owing to the colder growth 480 481 environment at TFS (Ekberg et al., 2009). The isoprene emission-temperature relationship 482 observed at TFS (in blue) is very similar to that reported by Tang et al. (2016) at Abisko (Sweden; 483 in pink) for tundra heath (dominated by evergreen and deciduous dwarf shrubs). Results at TFS 484 and Abisko both point to a high isoprene-temperature response for Arctic ecosystems (Tang et al., 485 2016). This is further supported by two warming experiments performed in mesic tundra heath 486 (dominated by Betula nana, Empetrum nigrum, Empetrum hermaphroditum, and Cassiope 487 tetragona) and dry dwarf-shrub tundra (co-dominated by Empetrum hermaphroditum and Salix 488 glauca) in Western Greenland (Kramshøj et al., 2016; Lindwall et al., 2016). Kramshøj et al. 489 (2016) observed a 240% isoprene emission increase with 3°C warming, while Lindwall et al. 490 (2016) reported a 280% increase with 4°C warming. The observationally-derived emission-491 temperature relationship derived here for TFS reveals a 180-215% emission increase with 3-4°C 492 warming.

493 The MEGAN2.1 modeling framework is commonly used to estimate BVOC fluxes between 494 terrestrial ecosystems and the atmosphere (e.g., Millet et al., 2018). Here, we apply the TFS 495 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 496 497 observations below 30°C, with a 170-240% emission increase for a 3-4°C warming. While the 498 model predicts a leveling-off of emissions at approximately 30-35°C, our observations reveal no 499 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 500 statistically ruled out. The key result here is that MEGAN2.1 adequately reproduces the 501 502 temperature dependence response of Arctic ecosystems in the 0-30°C temperature range - ambient 503 temperature > 30°C being unlikely. The highest air temperature on record at TFS (1988-2019) is 504 26.5°C, and the mean summertime (June-August) temperature over that period is 9°C. 505 Additionally, for each year in the 1988-2019 historical dataset, there were only 1 to 23 days (0 to 506 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 507 508 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 509 510 this rate of change, the MEGAN2.1 algorithm adequately represents the temperature dependence 511 response of Arctic ecosystems for the near and intermediate-term future.

512 4.2 Long-term effects of warming

513 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., 514 515 2007). The exponential response of isoprene emissions to temperature observed at TFS adds to a 516 growing body of evidence indicating a high isoprene-temperature response in Arctic ecosystems. 517 However, observations at TFS do not necessarily reflect long-term effects of warming. Schollert 518 et al., (2015) examined how long-term warming affects leaf anatomy of individual arctic plant 519 shoots (Betula nana, Cassiope tetragona, Empetrum hermaphroditum, and Salix arctica). They 520 found that long-term warming results in significantly thicker leaves suggesting anatomical 521 acclimation. While the authors hypothesized that this anatomical acclimation may limit the 522 increase of BVOC emissions at plant shoot-level, Kramshøj et al. (2016) later showed that BVOC 523 emissions from Arctic tundra exposed to six years of experimental warming increase at both the 524 plant shoot and ecosystem levels.

In addition to the direct impact of long-term warming on BVOC emissions, ecosystem-level 525 526 emissions are expected to increase in the Arctic due to climate-driven changes in plant biomass 527 and vegetation composition. For instance, the widespread increase in shrub abundance in the Arctic 528 - 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. 529 530 Additionally, as mentioned above and as discussed extensively by Peñuelas and Staudt (2010) and 531 Loreto and Schnitlzer (2010), emissions of BVOCs might be largely beneficial for plants, 532 conferring them higher protection from abiotic stressors which are predicted to be more severe in 533 the future. Long-term arctic warming may thus favor BVOC-emitting species even further.

534 5. Conclusion

535 While BVOC ambient concentrations and emission rates have been frequently measured in boreal 536 ecosystems, Arctic tundra environments are under studied. We provide here summertime BVOC 537 ambient air mixing ratios and emission rates at Toolik Field Station, on the north flank of the 538 Brooks Range in northern Alaska. We present the first continuous summertime record of ambient 539 air isoprene and its first-generation oxidation products in the Arctic tundra environment. This 540 dataset provides a new set of observations to constrain isoprene chemistry in low-NOx 541 environments. This dataset also provides a baseline to investigate future changes in the BVOC 542 emission potential of the Arctic tundra environment. While the overall mean isoprene emission 543 rate amounted to 85 μ gC/m²/h, elevated (> 500 μ gC/m²/h) isoprene surface emission rates were observed for Salix spp., a known isoprene emitter. We also show that the reponse to temperature 544 545 of isoprene emissions in enclosures dominated by Salix spp. increased exponentially in the 0-40°C 546 range, likely conferring greater thermal protection for these plants. Given the widespread increase 547 in shrub abundance in the Arctic (including Salix spp.), our results support earlier studies (e.g., Valolahti et al., 2015) suggesting that climate-induced changes in the Arctic vegetation 548 549 composition will significantly affect the BVOC emission potential of the Arctic tundra, with 550 implications for atmospheric oxidation processes and climate feedbacks.

551 Data availability

552 Data are available upon request to the corresponding author.

553 Author contribution

554 DH, LH, and DBM designed the experiments and acquired funding. HA led the two field 555 campaigns with significant on-site contribution from KM, JH, LH, DBM, KC, JM, CW, TM, and 556 DH. JH designed and built most of the instruments used in this study. CW acquired the PTR-ToF-557 MS data during the second campaign and DK performed data analysis. MSBH identified the plant 558 species and provided guidance during the field campaigns. KM and HA analyzed the samples in 559 the lab. HA analyzed all the data and prepared the manuscript with contributions from all co-560 authors.

561 Competing interests

562 The authors declare no competing interests.

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916 Table 1: Year 2017 median relative percent cover of plant species in moist acidic tundra long-term

917 ecological research (LTER) experimental control plots at Toolik Field Station. The last column indicates

918 whether plant species were present in surface or bag enclosure experiments in this study.

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

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

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

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942 Table 3: Isoprene and monoterpenes (sum of α -pinene, β -pinene, limonene, and 1,8-cineole) surface

943 emission rates per vegetation type. Miscellaneous refers to a mix of different species, including lichens and

944 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

945 pm-5 am (Alaska Standard Time). The values in brackets represent the average enclosure temperature for

946 each emission rate.

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

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954 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

956 Vegetation Map prepared by Raynolds et al. (2019) and publicly available at <u>www.geobotany.uaf.edu</u>.



Figure 2: Photographs of a surface enclosure experiment setup at Toolik Field Station, Alaska. a) The firststep of the installation consisted in positioning the Teflon® base around the vegetation of interest along

970 with temperature (T), relative humidity (RH), and photosynthetically active radiation (PAR) sensors. b)

971 The second step consisted in positioning the Tedlar® bag around the base. The bag was connected to a

972 purge air and a sampling line. An additional T/RH sensor was also positioned outside the bag.



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





993 Figure 4: Time-series of isoprene (green) and acetonitrile (purple) mixing ratios (in pptv) and of 0.3 µm

- 994 particle counts (yellow) in ambient air at Toolik Field station in June 2019.
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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 µgC/m²/h) for different vegetation types.
 Miscellaneous refers to a mix of different species, including lichens and moss tundra.

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1020Figure 7: Surface emission rates of various monoterpenes (in μ gC/m²/h) for different vegetation types. The1021lower and upper hinges correspond to the first and third quartiles. The upper (lower) whisker extends from1022the hinge to the largest (smallest) value no further than $1.5 \times IQR$ from the hinge, where IQR is the inter-1023quartile range (i.e., the distance between the first and third quartiles). The notches extend $1.58 \times IQR / \sqrt{n}$ 1024and give a ~95% confidence interval for medians. Miscellaneous refers to a mix of different species,1025including lichens and moss tundra.



1029Figure 8: Mean diurnal cycle of isoprene (a-c) and monoterpenes (MT; e-g) surface emission rates (in
 μ gC/m²/h – note the difference scale on the y-axis), d) enclosure temperature (in °C), and h) enclosure

photosynthetically active radiation (PAR in µmol/m²/s). The dots represent the hourly means. The line is

the smoothed conditional mean while the grey shaded region indicates the 95% confidence interval. Hours

are in Alaska Standard Time (UTC-9) and correspond to the end of the 2-hr sampling period for isoprene

and MT emission rates. MT corresponds here to the sum of α-pinene, β-pinene, limonene, and 1,8-cineole.1035Miscellaneous refers to a mix of different species, including lichens and moss tundra.



1038Figure 9: Normalized isoprene surface emission rate (emissions at 20°C set equal to 1.0) as a function of1039enclosure temperature (in °C). This figure shows the response to temperature as observed at Toolik Field1040Station (TFS, in blue) and Abisko, Sweden (in pink; Tang et al., 2016), and as parameterized in MEGAN2.11041(in green). The blue solid line is the exponential fit at TFS. n denotes the number of measurements in each

1042 enclosure temperature bin. It should be noted that the enclosure temperature was on average 5-6°C warmer

1043 than ambient air due to greenhouse heating.

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