



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

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## Abstract

Rapid Arctic warming, a lengthening growing season, and increasing abundance of biogenic volatile organic compounds (BVOC)-emitting shrubs are all anticipated to increase atmospheric BVOCs in the Arctic atmosphere, with implications for atmospheric oxidation processes and climate feedbacks. Quantifying these changes requires an accurate understanding of the underlying processes driving BVOC emissions in the Arctic. While boreal ecosystems have been widely studied, little attention has been paid to Arctic tundra environments. Here, we report terpenoid (isoprene, monoterpenes, and sesquiterpenes) ambient mixing ratios and emission rates from key dominant vegetation species at Toolik Field Station (TFS; 68°38'N, 149°36'W) in northern Alaska during two back-to-back field campaigns (summers 2018 and 2019) covering the entire growing season. Isoprene ambient mixing ratios observed at TFS fell within the range of values reported in the Eurasian taiga (0-500 pptv), while monoterpene and sesquiterpene ambient mixing ratios were respectively close to and below the instrumental quantification limit (~2 pptv). We further quantified the temperature dependence of isoprene emissions from local vegetation including *Salix* spp. (a known isoprene emitter), and compared the results to predictions from the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1). Our observations suggest a 180-215% emission increase in response to a 3-4°C warming. The MEGAN2.1 temperature algorithm exhibits a close fit with observations for enclosure temperatures below 30°C. Above 30°C, MEGAN2.1 predicts an isoprene emission plateau that is not observed in the enclosure flux measurements at TFS. More studies are needed to better constrain the warming response of isoprene and other BVOCs for a wide range of Arctic species.



## 29      1. Introduction

30      As a major source of reactive carbon to the atmosphere, biogenic volatile organic compounds  
31      (BVOCs) emitted from vegetation play a significant role in global carbon and oxidation cycles  
32      (Fehsenfeld et al., 1992). Global emission estimates of BVOCs are in the range of 700-1100 TgC  
33      per year, ~70-80% of which corresponds to terpenoid species: isoprene, monoterpenes (MT), and  
34      sesquiterpenes (SQT) (Guenther et al., 1995, 2006; Sindelarova et al., 2014). Despite their  
35      relatively short atmospheric lifetimes (1 hour to 1 day for terpenoids), BVOCs affect climate  
36      through their effects on the hydroxyl radical (OH, which dictates the lifetime of atmospheric  
37      methane), tropospheric ozone (O<sub>3</sub>, a key greenhouse gas), and aerosols (which influence radiative  
38      scattering) (Arneth et al., 2010; Fuentes et al., 2000; Peñuelas and Staudt, 2010). The oxidation of  
39      those BVOCs also drives the formation of secondary organic aerosols (SOA) through both gas-  
40      and aqueous-phase mechanisms (Carlton et al., 2009; Lim et al., 2005). The potential for increased  
41      SOA formation, expected to result in climate cooling (Kulmala et al., 2004), complicates the  
42      climate feedbacks of BVOC emissions (Tsigaridis and Kanakidou, 2007; Unger, 2014).

43      Global models of BVOC emissions assume minimal emissions from the Arctic due to low leaf  
44      area index and relatively cold temperatures (Guenther et al., 2006; Sindelarova et al., 2014).  
45      However, this assumption relies on few observations and has been increasingly challenged by field  
46      data (Tang et al., 2016). Recent measurements have revealed significant BVOC emissions from  
47      Arctic tundra and vegetation, including *Sphagnum* mosses, wetland sedges, and dwarf shrubs  
48      (Ekberg et al., 2009, 2011; Faubert et al., 2010; Holst et al., 2010; Lindfors et al., 2000; Potosnak  
49      et al., 2013; Rinnan et al., 2011; Schollert et al., 2014; Tiiva et al., 2008). These results are of  
50      importance because BVOC emissions are expected to increase in the Arctic due to climate  
51      warming and associated vegetation and land cover change (Faubert et al., 2010; Potosnak et al.,  
52      2013; Rinnan et al., 2011; Tiiva et al., 2008). Long-term field warming studies have shown strong  
53      increases in BVOC emissions from shrub heath (Michelsen et al., 2012; Tiiva et al., 2008).  
54      Furthermore, the temperature dependence of Arctic BVOC fluxes appears to be significantly  
55      greater than for tropical and subtropical ecosystems (Holst et al., 2010; Rinnan et al., 2014), with  
56      up to 2-fold increases in MT emissions and 5-fold increases in SQT emissions by subarctic heath  
57      for a 2°C warming (Valolahti et al., 2015). Similarly, Kramshøj et al. (2016) and Lindwall et al.  
58      (2016) examined the response of BVOC emissions to an experimental 3-4°C warming and reported



59 a 260-280% increase in total emissions. Together, the above results emphasize the strong  
 60 temperature sensitivity of BVOC emissions from Arctic ecosystems.

61 Changing BVOC emissions in the Arctic due to climate and land cover shifts can thus be expected  
 62 to perturb to the overall oxidative chemistry of the region, and to further affect climate through  
 63 various feedback mechanisms. Quantifying these changes requires an accurate understanding of  
 64 the underlying processes driving BVOC emissions in the Arctic. While BVOC ambient mixing  
 65 ratios and emission rates have been studied in boreal ecosystems, less attention has been paid to  
 66 Arctic tundra environments (Lindwall et al., 2015). Here, we report BVOC ambient mixing ratios  
 67 and emission rates at Toolik Field Station (TFS) in the Alaskan Arctic. This study builds on the  
 68 previous isoprene study at TFS by Potosnak et al. (2013), while also providing a major step forward  
 69 from that work. In particular, we present the first continuous summertime record of ambient  
 70 BVOCs (including isoprene and MT) and their first-generation oxidation products in the Arctic  
 71 tundra environment. We further compare the observed temperature dependence of isoprene  
 72 emissions with predictions from the Model of Emissions of Gases and Aerosols from Nature  
 73 version 2.1 (MEGAN2.1), a widely used modeling framework for estimating ecosystem-  
 74 atmosphere BVOC fluxes (Guenther et al., 2012). Due to increasing shrub prevalence across  
 75 northern Alaska (Berner et al., 2018; Tape et al., 2006), as well as the Eurasian (Macias-Fauria et  
 76 al., 2012) and Russian Arctic (Forbes et al., 2010), the results of this study have significance to  
 77 tundra ecosystems across a vast region of the Arctic.

## 78 **2. Material and Methods**

### 79 **2.1 Study site**

80 This study was carried out at TFS, a Long-Term Ecological Research (LTER) site located in the  
 81 tundra on the north flanks of the Brooks Range in northern Alaska (68°38'N, 149°36'W; see  
 82 Fig.1). Vegetation speciation and dynamics, and their changes over time, have been well  
 83 documented at the site. *Betula* (birch) and *Salix* (willow) are the most common deciduous shrubs  
 84 (Kade et al., 2012). Common plant species include *Betula nana* (dwarf birch), a major player in  
 85 ongoing Arctic greening (Holleisen et al., 2015; Sistla et al., 2013), *Rhododendron tomentosum*  
 86 (formerly *Ledum palustre*; Labrador tea); *Vaccinium vitis-idaea* (lowbush cranberry), *Eriophorum*  
 87 *vaginatum* (cotton grass), *Sphagnum angustifolium* (peat moss), *Alectoria ochroleuca* (witches  
 88 hair lichen), and many other perennial species of *Carex*, mosses, and lichens. Vegetation cover at



89 this site is classified as tussock tundra (see Fig.1), which is the most common vegetation type in  
90 the northern foothills of the Brooks Range (Elmendorf et al., 2012; Kade et al., 2012; Shaver and  
91 Chapin, 1991; Survey, 2012; Walker et al., 1994).

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

## 99 **2.2 Ambient online measurements of BVOCs and their oxidation products**

### 100 **2.2.1 Gas chromatography and mass spectrometry with flame ionization detector** 101 **(GC-MS/FID)**

102 An automated GC-MS/FID system was deployed for continuous measurements of atmospheric  
103 BVOCs at ~2-hour time resolution during the 2018 and 2019 field campaigns. In addition, the  
104 system was operated remotely following the 2018 campaign (through September 15<sup>th</sup>) to collect  
105 background values at the beginning of autumn. Air was pulled continuously from an inlet on a 4  
106 m meteorological tower located approximately 30 m from the instrument shelter (Van Dam et al.,  
107 2013). Air passed through a sodium thiosulfate-coated O<sub>3</sub> scrubber for selective O<sub>3</sub> removal – to  
108 prevent sampling losses and artifacts for reactive BVOCs (Helmig, 1997; Pollmann et al., 2005) –  
109 and through a moisture trap to dry the air to a dew point of -30°C. Analytes were concentrated on  
110 a Peltier-cooled (-40°C) multistage adsorbent trap. Analysis was accomplished by thermal  
111 desorption and injection for cryogen free GC using a DB-1 column (60 m × 320 µm × 5 µm) and  
112 helium as carrier gas. The oven temperature was set to 40°C for 6 minutes, then increased to 260°C  
113 at 20°C/min, and held isothermally at 260°C for 13 minutes. The column flow was split between  
114 an FID and a MS for simultaneous quantification and identification. Blanks and calibration  
115 standards were regularly injected from a manifold. Isoprene (*m/z* 67 and 68), methacrolein  
116 (MACR) and methylvinylketone (MVK) (*m/z* 41, 55, and 70), MT (*m/z* 68, 93, 121, and 136), and  
117 SQT (*m/z* 204, 91, 93, 119, and 69) were identified and quantified using the MS in selected ion-  
118 monitoring mode (SIM). The response to isoprene was calibrated using a primary gas standard





119 supplied by the National Physical Laboratory (NPL), certified as containing  $4.01 \pm 0.09$  ppb of  
120 isoprene in a nitrogen matrix. The analytical uncertainty for isoprene was estimated at 16 % based  
121 on the certified uncertainty of the standard and on the repeatability of standard analysis throughout  
122 the campaigns. Instrument responses for MACR, MVK,  $\alpha$ -pinene, and acetonitrile were calibrated  
123 with multi-component standards containing 1007 ppb MACR, 971 ppb MVK, 967 ppb  $\alpha$ -pinene,  
124 and 1016 ppb acetonitrile (Apel-Riemer Environmental Inc., Miami, FL, USA) dynamically  
125 diluted into a stream of ultra-zero grade air to  $\sim 3$  ppb. Quantification of other terpenoid compounds  
126 was based on GC peak area (FID response) plus relative response factors using the effective carbon  
127 number concept (Faiola et al., 2012; Scanlon and Willis, 1985). The limit of quantification (LOQ)  
128 was  $\sim 2$  pptv (pmol/mol by volume). In order to monitor and correct for long-term trends in the  
129 detection system, including detector drift and decreasing performance of the adsorbent trap, we  
130 used peak areas for long-lived chlorofluorocarbons (CFCs) that were monitored in the air samples  
131 together with the BVOCs as an internal reference standard. The atmospheric trace gases  $\text{CCl}_3\text{F}$   
132 (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  
133 atmosphere and exhibit little spatial and temporal variability (Karbiwnyk et al., 2003; Wang et al.,  
134 2000).

#### 135 2.2.2 Proton-Transfer-Reaction Time-of-Flight Mass-Spectrometry (PTR-ToF-MS)

136 During the summer 2019 campaign, isoprene mixing ratios in ambient air were also measured by  
137 PTR-ToF-MS (model 4000, Ionicon Analytik GmbH, Innsbruck, Austria). The sample inlet was  
138 located on the 4 m meteorological tower, right next to the GC-MS/FID inlet. In brief, ambient air  
139 was continuously pulled through the PTR-ToF-MS drift-tube, where VOCs with proton affinities  
140 higher than that of water ( $> 165.2$  kcal/mol) were ionized via proton-transfer reaction with primary  
141  $\text{H}_3\text{O}^+$  ions, then subsequently separated and detected by a time-of-flight mass spectrometer (with  
142 a mass resolving power up to 4000). At TFS, the PTR-ToF-MS measured ions from 17–400  $m/z$   
143 every 2 minutes. Ambient air was drawn to the instrument at 10–15 L/min via  $\sim 30$  m of 1/4" O.D.  
144 PFA tubing maintained at  $\sim 55^\circ\text{C}$ , and then subsampled by the instrument through  $\sim 100$  cm of  
145 1/16" O.D. PEEK tubing maintained at  $60^\circ\text{C}$ . The residence time from the inlet on the 4 m  
146 meteorological tower to the drift-tube was less than 5 seconds. Instrument backgrounds were  
147 quantified approximately every 5 hours for 20 minutes during the campaign by measuring VOC-  
148 free air generated by passing ambient air through a heated catalytic converter ( $375^\circ\text{C}$ , platinum



149 bead, 1 % wt. Pt, Sigma Aldrich). Calibrations were typically performed every 4 days via dynamic  
 150 dilution of certified gas standard mixtures containing 25 distinct VOCs including isoprene (Apel-  
 151 Riemer Environmental Inc., Miami, FL, USA). Here, we report isoprene mixing ratios to inter-  
 152 compare with GC-MS measurements; other species will be reported in future work. The  
 153 measurement uncertainty for isoprene is ~25%, which includes uncertainties in the gas standards,  
 154 calibration method, and data processing.

### 155 2.2.3 Instrument inter-comparison

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

## 163 2.3 Ambient air vertical profiles

164 Vertical isoprene mixing ratio profiles were obtained using a 12-foot diameter SkyDoc tethered  
 165 balloon. A total of eight vertical profiles were performed at ~3-hour intervals between 12:30 pm  
 166 Alaska Standard Time (AST) on June 15, 2019 and 11:00 am AST on June 16, 2019. Sampling  
 167 packages were connected to the tether line such that resulting sampling heights were ~30, ~100,  
 168 ~170, and ~240 m above ground level. One identical sampling package was deployed at the  
 169 surface. Each sampling package contained an adsorbent cartridge for sample collection (see below)  
 170 connected to a downstream battery-powered SKC pocket pump controlled using a mechanical  
 171 relay, a programmable Arduino, and a real-time Clock. Once the balloon reached its apex (~ 250-  
 172 300 m a.g.l.), the five pumps were activated simultaneously and samples collected for 30 minutes.  
 173 At the end of the 30-min sampling period, the balloon was brought back down. The adsorbent  
 174 cartridges were prepared in house using glass tubing (89 mm long × 6.4 mm outer diameter, 4.8  
 175 mm inner diameter), and loaded with Tenax-GR and Carboxen 1016 adsorbents (270 mg of each),  
 176 following established practice (Ortega and Helmig, 2008 and references therein). An inlet ozone  
 177 scrubber was installed on each cartridge to prevent BVOC sampling losses. Field blanks were  
 178 collected by opening a cartridge (with no pumped airflow) during each balloon flight. Following



179 collection, samples were stored in the dark at  $\sim 4^{\circ}\text{C}$  until chemical analysis. Samples were analyzed  
 180 at the University of Colorado Boulder following the method described in S.I. Section 1. Our  
 181 previous inter-comparison of this cartridge-GC-MS/FID method with independent and concurrent  
 182 PTR-MS observations showed that the two measurements agree to within their combined  
 183 uncertainties at  $\sim 25\%$  (Hu et al., 2015). Meteorological conditions were monitored and recorded  
 184 during each balloon flight with a radiosonde (Met1, Grant Pass, OR, USA) attached to the tethered  
 185 line just below the balloon.

## 186 **2.4 BVOC emission rates**

### 187 **2.4.1 Dynamic enclosure measurements**

188 We used dynamic enclosure systems operated at low residence time to quantify vegetative BVOC  
 189 emissions following the procedure described by Ortega et al. (2008) and Ortega and Helmig  
 190 (2008). Two types of enclosures were used: branch and surface chambers. For branch enclosures,  
 191 a Tedlar® bag (Jensen Inert Products, Coral Springs, FL) was sealed around the trunk side of a  
 192 branch. For surface enclosures, the bag was placed around a circular Teflon® base (25 cm wide  $\times$   
 193 16 cm height; see Fig. 2). For both branch and surface enclosures, the bag was connected to a  
 194 purge-air line and a sampling line, and positioned around the vegetation minimizing contact with  
 195 foliage. While purging the enclosure (see Section 2.4.3), the vegetation was allowed to acclimate  
 196 for 24 hours before BVOC sampling began. Samples were collected from the enclosure air,  
 197 concentrated onto solid-adsorbent cartridges (see Section 2.3) with an automated sampler, and  
 198 analyzed in-laboratory at the University of Colorado Boulder following the campaign (see S.I.  
 199 Section 1). Temperature and relative humidity were recorded inside and outside the enclosure (see  
 200 Fig. 2; S-THB-M002 sensors, Onset HOBO, Bourne, MA, USA) with a data logger (H21-USB,  
 201 Onset HOBO, Bourne, MA, USA). Additionally, photosynthetically active radiation (400-700 nm;  
 202 S-LIA-M003, Onset HOBO, Bourne, MA, USA) was measured inside the enclosure. Once  
 203 installed, enclosures were operated for 2-10 days. The tundra vegetation around TFS is  
 204 heterogeneous but most dominant species were sampled. Table 1 presents the median relative  
 205 percent cover of plant species in LTER experimental control plots at TFS (Gough, 2019) and  
 206 indicates whether plant species were present in surface or bag enclosures. The complete list of  
 207 species sampled and pictures of the enclosures are available in Figures S.I.3-S.I.15; the two  
 208 sampling sectors are highlighted in Fig.S.I.1. Surface enclosures were divided into three vegetation



209 types: *Salix* spp. (high isoprene emitter), *Betula* spp. (e.g., *Betula nana* dominance), and  
 210 miscellaneous (mix of different species, including lichens and mosses).

#### 211 2.4.2 Emission rates

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

$$213 \quad ER_{\text{surface}} = \frac{(C_{\text{out}} - C_{\text{in}})Q}{S}, \quad (1)$$

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

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

$$217 \quad ER_{\text{branch}} = \frac{(C_{\text{out}} - C_{\text{in}})Q}{m_{\text{dry}}}, \quad (2)$$

218 where  $m_{\text{dry}}$  is the dried mass (in g) of leaves enclosed, determined by drying the leaves – harvested  
 219 after the experiment – at  $60\text{--}70^\circ\text{C}$  until a consistent weight was achieved (Ortega and Helmig,  
 220 2008).

#### 221 2.4.3 Enclosure purge air

222 Purge air was provided by an upstream high-capacity oil-free pump providing positive pressure to  
 223 the enclosure, and equipped with an in-line  $\text{O}_3$  scrubber to avoid loss of reactive BVOCs from  
 224 reaction with  $\text{O}_3$  in the enclosure air and during sampling (Helmig, 1997; Pollmann et al., 2005).  
 225 The purge flow was set to  $25 \text{ L}/\text{min}$  and regularly checked using a volumetric flow meter (Mesa  
 226 Labs Bios DryCal Defender, Butler, NJ, USA). Excess air escaped from the open end (tied around  
 227 the Teflon® base) while the sample air flow was pulled into the sampling line (see below).

#### 228 2.4.4 Sample collection

229 A continuous airflow of  $400\text{--}500 \text{ mL}/\text{min}$  was drawn from the enclosure through the sampling line.  
 230 A fraction of this flow was periodically collected at  $265\text{--}275 \text{ mL}/\text{min}$  on adsorbent cartridges (see  
 231 Section 2.3) using a 10-cartridge autosampler (Helmig et al., 2004). During sampling, cartridges  
 232 were kept at  $40^\circ\text{C}$ , i.e., above ambient temperature, to prevent water accumulation on the adsorbent  
 233 bed (Karbiwnyk et al., 2002). Samples were periodically collected in series to verify lack of analyte  
 234 breakthrough. Time-integrated samples were collected for 120 min every 2 hours to establish



235 diurnal cycles of BVOC emission. Upon collection, samples were stored in the dark at  $\sim 4^{\circ}\text{C}$  until  
 236 chemical analysis back at the University of Colorado Boulder.

#### 237 2.4.5 Internal standards

238 In order to identify potential BVOC losses during transport, storage, and chemical analysis, 255  
 239 of the employed cartridges were pre-loaded with a four-compound standard mixture prior to the  
 240 field campaigns. These internal standard compounds (toluene, 1, 2, 3-trimethylbenzene, 1, 2, 3, 4-  
 241 tetrahydronaphtalene, and 1, 3, 5-triisopropylbenzene) were carefully chosen to span a wide range  
 242 of volatility ( $\text{C}_7\text{-C}_{15}$ ) and to not interfere (*i.e.*, coelute) with targeted BVOCs. The recovery of these  
 243 four compounds was assessed at the end of the campaign, following the analytical procedure  
 244 described in S.I. Section 1. Recovery rates were  $101.8 \pm 13.5\%$  (toluene),  $95.2 \pm 20.1\%$  (1,2,3-  
 245 trimethylbenzene),  $95.6 \pm 26.6\%$  (1,2,3,4-tetrahydronaphtalene), and  $100.9 \pm 18.7\%$  (1,3,5-  
 246 triisopropylbenzene). These results indicate that, overall, BVOC losses during transport, storage,  
 247 and chemical analysis were negligible. Ortega et al. (2008) previously evaluated systematic losses  
 248 of analytes to enclosure systems similar to those used here. The same four-component standard  
 249 was introduced into the purge air flow of the enclosures to quantify losses as a function of  
 250 volatility. That work found median losses of MT and SQT on the order of 20-30%. The emission  
 251 rates presented here are therefore possibly biased low by a similar amount.

#### 252 2.5 Peak fitting algorithm

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

#### 257 2.6 Ancillary parameters

258 *Meteorological parameters.* A suite of meteorological instruments was deployed on the 4 m tower.  
 259 Wind speed and direction were measured at  $\sim 4$  m above ground level with a Met One 034B-L  
 260 sensor. As described by Van Dam et al. (2013), temperature was measured at three different heights  
 261 using RTD temperature probes (model 41342, R.M. Young Company, Traverse City, MI) housed  
 262 in aspirated radiation shields (model 43502, R.M. Young Company, Traverse City, MI). Regular  
 263 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](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  $\mu\text{m}$ ) 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 ( $\text{NO}_x$ ) were measured with a custom-built, high sensitivity ( $\sim 5$  pptv detection limit) single-channel chemiluminescence analyzer (Fontijn et al., 1970). The instrument monitors nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) in ambient air using a photolytic converter. Automated switching valves alternated between NO and  $\text{NO}_2$  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  $\varepsilon_j$  is the emission factor under standard conditions for vegetation type  $j$  with fractional grid box areal coverage  $\kappa_j$ . 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 ( $\gamma_T$ ) 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 ( $12.4 \pm 16.1$  pptv; mean  $\pm$  standard deviation) and from below the quantification limit to 450 pptv ( $43.1 \pm 66.7$  pptv; see Fig. 3, top panels). The PTR-ToF-MS gave similar results (see Fig.S.I.16b). Median NO and NO<sub>2</sub> mixing ratios of 21 and 74 pptv, respectively, during the 2019 campaign (not shown) suggest a low-NO<sub>x</sub> 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<sub>x</sub> 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.

### 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 30-min tethered balloon samples collected on June 15 and 16, 2019 (see Section 2.3). 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.

Except during the last flight, isoprene mixing ratios were in the range of background levels (~0–50 pptv) reported with the GC-MS (see Section 3.1.1). Samples collected on June 16, 2019 from 4 to 4:30 am show decreasing isoprene mixing ratios with increasing elevation, suggesting higher levels (25–50 pptv) in the nocturnal boundary layer than above. Samples collected from 10–10:30 am on June 16 (*i.e.*, during the last flight) showed a pronounced gradient, with 200 pptv at ground level and decreasing mixing ratios with elevation. This maximum at ground-level is consistent with a surface source (Helmig et al., 1998) and can likely be attributed to a temperature-driven



increase of isoprene emissions by the surrounding vegetation. Indeed, the ambient temperature at ground-level was higher during that flight than during the previous ones (see Fig.S.I.17h). Interestingly, the GC-MS and the PTR-ToF-MS did not capture this 200 pptv maximum (see Fig. 3 and Fig.S.I.16), which may be because the balloon flights were performed at a different location (near sampling sector B, see Fig.S.I.1) surrounded by a higher fraction of isoprene-emitting shrubs (willow).

### 3.1.3 Monoterpenes and Sesquiterpenes

MT mixing ratios ranged from 3 to 537 pptv ( $14 \pm 18$  pptv; median  $\pm$  standard deviation) during the 2019 campaign according to the PTR-ToF-MS measurements. Using the GC-MS/FID, we were able to detect and quantify the following MT in ambient air:  $\alpha$ -pinene, camphene, sabinene, p-cymene, and limonene. Mean mixing ratios are reported in Table 2 (for values lower than the LOQ, mixing ratios equal to half of the LOQ are used). These compounds have been previously identified as emissions of the widespread circumpolar dwarf birch *Betula nana* (Li et al., 2019; Vedel-Petersen et al., 2015) and other high Arctic vegetation (Schollert et al., 2014). The quantification frequency of camphene, sabinene, p-cymene, and limonene was low (see Table 2) and MT mixing ratios in ambient air were dominated by  $\alpha$ -pinene. Several prior studies performed at boreal sites have similarly identified  $\alpha$ -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). We did not detect any sesquiterpene in ambient air above the 2 pptv instrumental LOQ.

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

## 3.2 Emission rates

### 3.2.1 Branch enclosures

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  $\mu\text{gC/g/h}$ , in line with results reported for the same species at Kobbefjord, Greenland (0.8 to 12.1  $\mu\text{gC/g/h}$ ) by Vedel-Petersen et al. (2015) and Kramshøj et al. (2016; Supplementary Table 5). The quantified MTs had emissions averaging two orders of magnitude lower than those of isoprene (0.01 vs 1  $\mu\text{gC/g/h}$ ). Emission rates for the sum of  $\alpha$ -



pinene,  $\beta$ -pinene, limonene, camphene, and 1,8-cineole ranged from  $<0.01$  to  $0.06 \mu\text{gC/g/h}$ . These results are again in good agreement with those reported for the same species at Kobbefjord ( $\sim 0.01 \mu\text{gC/g/h}$ ) by Kramshøj et al. (2016; Supplementary Table 5).

### 3.2.2 Surface emission rates

The isoprene surface emission rate, as inferred from surface enclosures, was highly variable and ranged from  $0.2$  to  $\sim 2250 \mu\text{gC/m}^2/\text{h}$  (see Fig. 6). The  $2250 \mu\text{gC/m}^2/\text{h}$  maximum, reached on June 26, 2019, is higher than maximum values reported at TFS by Potosnak et al. (2013) ( $1200 \mu\text{gC/m}^2/\text{h}$ ) and in a high-latitude ( $58^\circ\text{N}$ ) *Salix* plantation by Olofsson et al. (2005) ( $730 \mu\text{gC/m}^2/\text{h}$ ). It should be noted that these experiments were likely performed 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 sampling enclosures dominated by *Salix* spp.. At TFS, the overall 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, isoprene surface emission rates were much lower than for mid-latitude or tropical forests. For example, average midday fluxes of  $3000 \mu\text{gC/m}^2/\text{h}$  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  $2500$ – $3000 \mu\text{gC/m}^2/\text{h}$  (Helmig et al., 1998; Karl et al., 2004; Rinne et al., 2002).

Figure 7 shows the measured surface emission rates for  $\alpha$ -pinene,  $\beta$ -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. Regardless of the species, emission rates remained on average below  $1 \mu\text{gC/m}^2/\text{h}$  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). 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



407 results are in line with the well-established diurnal variation of BVOC emissions in environments  
 408 ranging from Mediterranean to boreal forests (e.g., Fares et al., 2013; Liu et al., 2004; Ruuskanen  
 409 et al., 2005; Zini et al., 2001). Despite the relatively low MT emission rates, a significant diurnal  
 410 cycle was also observed with peak total MT emissions of  $\sim 1 \mu\text{gC}/\text{m}^2/\text{h}$  during early afternoon for  
 411 both *Salix* spp. and *Betula* spp. (Fig. 8e-f). A summary of emission rates per vegetation type and  
 412 time of day is given in Table 3. It should be noted that the two field campaigns were carried out  
 413 during the midnight sun period, which could possibly sustain BVOC emissions during nighttime.  
 414 As can be seen in Table 3 and Fig. 8, PAR and BVOC emissions significantly decreased at night  
 415 but were still detectable. These results confirm those obtained by Lindwall et al. (2015) during a  
 416 24-hour experiment with five different Arctic vegetation communities.

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

### 422 3.3 Response of isoprene emissions to temperature

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

430 Over the course of the two field campaigns at TFS, BVOC surface emission rates were measured  
 431 over a large span of enclosure temperatures (2-41°C). While MT emissions remained low and close  
 432 to the detection limit thus preventing robust quantification of any emission-temperature  
 433 relationship, isoprene emissions significantly increased with temperature (Fig.9). Figure 9  
 434 combines isoprene emission rates from different surface enclosures, with results normalized to  
 435 account for differing leaf area and species distributions (with *Salix* spp. the dominant emitter).  
 436 Specifically, we divided all fluxes by the enclosure-specific mean emission at  $20 \pm 1^\circ\text{C}$ . Emission



437 rates are often standardized to 30°C but we employ 20°C here owing to the colder growth  
 438 environment at TFS (Ekberg et al., 2009). The isoprene emission-temperature relationship  
 439 observed at TFS (in blue) is very similar to that reported by Tang et al. (2016) at Abisko (Sweden;  
 440 in pink) for tundra heath (dominated by evergreen and deciduous dwarf shrubs). Results at TFS  
 441 and Abisko both point to a high isoprene-temperature response for Arctic ecosystems (Tang et al.,  
 442 2016). This is further supported by two warming experiments performed in mesic tundra heath  
 443 (dominated by *Betula nana*, *Empetrum nigrum*, *Empetrum hermaphroditum*, and *Cassiope*  
 444 *tetragona*) and dry dwarf-shrub tundra (co-dominated by *Empetrum hermaphroditum* and *Salix*  
 445 *glauca*) in Western Greenland (Kramshøj et al., 2016; Lindwall et al., 2016). Kramshøj et al.  
 446 (2016) observed a 240% isoprene emission increase with 3°C warming, while Lindwall et al.  
 447 (2016) reported a 280% increase with 4°C warming. The observationally-derived emission-  
 448 temperature relationship derived here for TFS reveals a 180-215% emission increase with 3-4°C  
 449 warming, adding to a growing body of evidence indicating a high isoprene-temperature response  
 450 in Arctic ecosystems.

451 The MEGAN2.1 modeling framework is commonly used to estimate BVOC fluxes between  
 452 terrestrial ecosystems and the atmosphere (e.g., Millet et al., 2018). Here, we apply the TFS  
 453 observations to evaluate the MEGAN2.1 emission-temperature relationship for this Arctic  
 454 environment. Figure 9 shows that the model temperature algorithm provides a close fit with  
 455 observations below 30°C, with a 170-240% emission increase for a 3-4°C warming. However, the  
 456 model predicts a leveling-off of emissions at approximately 30-35°C, whereas our observations  
 457 reveal no such leveling-off within the 0-40°C enclosure temperature range (Fig. 9). Current models  
 458 can therefore be expected to strongly underpredict isoprene emissions in this region for  
 459 temperatures above 30°C.

460 To put the above finding in perspective, the highest air temperature on record at TFS (1988-2019)  
 461 is 26.5°C, and the mean summertime (June-August) temperature over that period is 9°C. Only 1-  
 462 23 and 0-4 days per year over that timespan recorded daily maximum temperatures above 20°C  
 463 and 25°C, respectively. If global greenhouse gas emissions continue to increase, temperatures are  
 464 expected to rise 6-7°C in northern Alaska by the end of the century (annual average; Markon et  
 465 al., 2012) while the number of days with temperatures above 25°C could triple (Lader et al., 2017).  
 466 Based on current climate conditions and this rate of change, the MEGAN2.1 algorithm can still be



467 expected to adequately represent the temperature dependence response of Arctic ecosystems for  
 468 the near and intermediate-term future.

#### 469 **4. Implications and conclusions**

470 While BVOC ambient concentrations and emission rates have been frequently measured in boreal  
 471 ecosystems, Arctic tundra environments are scarcely studied. We provide here summertime BVOC  
 472 ambient air mixing ratios and emission rates at Toolik Field Station, on the north flanks of the  
 473 Brooks Range in northern Alaska. These data provide a baseline to investigate future changes in  
 474 the BVOC emission potential of the Arctic tundra environment. Elevated isoprene surface  
 475 emission rates ( $> 500 \mu\text{gC}/\text{m}^2/\text{h}$ ) were observed for *Salix* spp., a known isoprene emitter. The  
 476 response to temperature of isoprene emissions in enclosures dominated by *Salix* spp. increased  
 477 exponentially in the 0–40°C range, likely conferring greater thermal protection for these plants.  
 478 Our study indicates that the temperature algorithm in MEGAN2.1, a widely used modelling  
 479 framework for BVOC emissions, provides a good fit with observations in the Arctic tundra for  
 480 temperatures below 30°C. However, more studies are needed to better constrain the warming  
 481 response of isoprene and other BVOCs for a wider range of Arctic species.

482 In the context of a widespread increase in shrub abundance (including *Salix* spp.) in the Arctic  
 483 (Berner et al., 2018; Sturm et al., 2001) due to a longer growing season and enhanced nutrient  
 484 availability, our results support earlier studies (e.g., Valolahti et al., 2015) suggesting that climate-  
 485 induced changes in the Arctic vegetation composition will likely significantly affect the BVOC  
 486 emission potential of the Arctic tundra. As discussed extensively by Peñuelas and Staudt (2010)  
 487 and Loreto and Schnitzler (2010), emissions of BVOCs might be largely beneficial for plants,  
 488 conferring them higher protection from abiotic stressors (e.g., heat, air pollution, high irradiance)  
 489 which are predicted to be more severe in the future. Arctic warming may thus favor BVOC-  
 490 emitting species even further.

#### 491 **Data availability**

492 Data are available upon request to the corresponding author.

#### 493 **Author contribution**



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

#### 501 **Competing interests**

502 The authors declare no competing interests.

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Table 1: Year 2017 median relative percent cover of plant species in moist acidic tundra long-term ecological research (LTER) experimental control plots at Toolik Field Station. The last column indicates 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



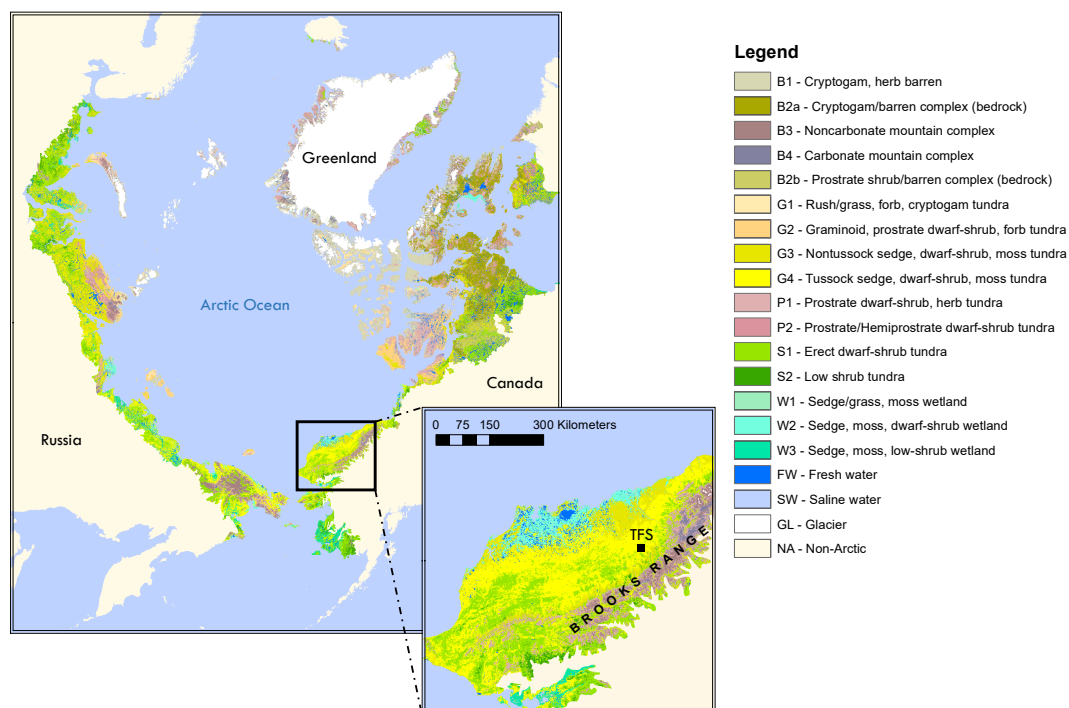
Table 2: Average mixings ratios with standard deviation, along with minimum (min) and maximum (max) values and quantification frequency (QF) of the measured monoterpenes in ambient air. LOQ stands for limit of quantification. For values lower than the LOQ, mixing ratios equal to half of the LOQ were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

	mean $\pm$ standard deviation (pptv)	Min (pptv)	Max (pptv)	QF (%)
$\alpha$ -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



Table 3: Isoprene and monoterpenes (sum of  $\alpha$ -pinene,  $\beta$ -pinene, limonene, and 1,8-cineole) surface emission rates per vegetation type. Miscellaneous refers to a mix of different species, including lichens and 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 pm-5 am (Alaska Standard Time).

	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.	$149 \pm 327$	$232 \pm 400$	$334 \pm 473$	$7 \pm 10$
<i>Betula</i> spp.	$12 \pm 30$	$19 \pm 38$	$28 \pm 37$	$5 \pm 14$
Miscellaneous	$38 \pm 81$	$57 \pm 100$	$104 \pm 135$	$21 \pm 64$
monoterpenes				
<i>Salix</i> spp.	$0.8 \pm 1.3$	$1.1 \pm 1.5$	$1.4 \pm 1.7$	$0.4 \pm 1.0$
<i>Betula</i> spp.	$0.5 \pm 0.6$	$0.7 \pm 0.7$	$1.0 \pm 0.8$	$0.2 \pm 0.2$
Miscellaneous	$1.1 \pm 1.4$	$1.3 \pm 1.6$	$1.7 \pm 2.0$	$1.0 \pm 1.4$



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

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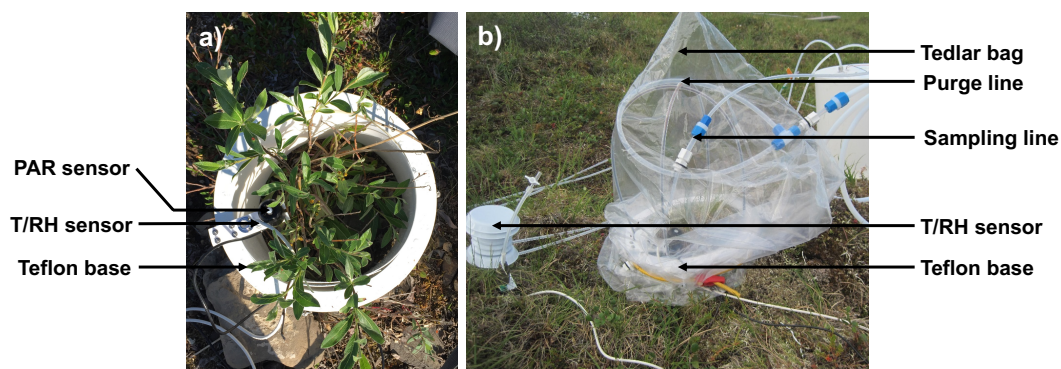
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891 Figure 2: Photographs of a surface enclosure experiment setup at Toolik Field Station, Alaska. a) The first  
 892 step of the installation consisted in positioning the Teflon® base around the vegetation of interest along  
 893 with temperature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

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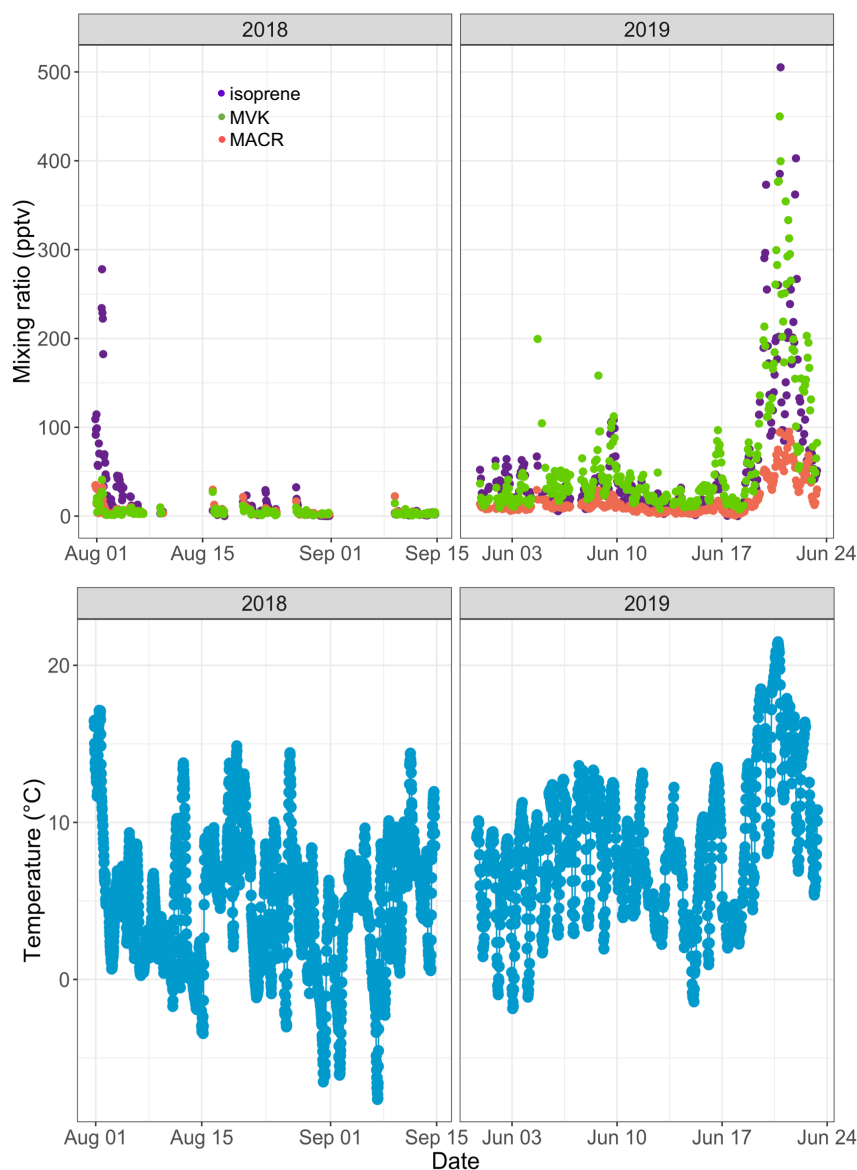
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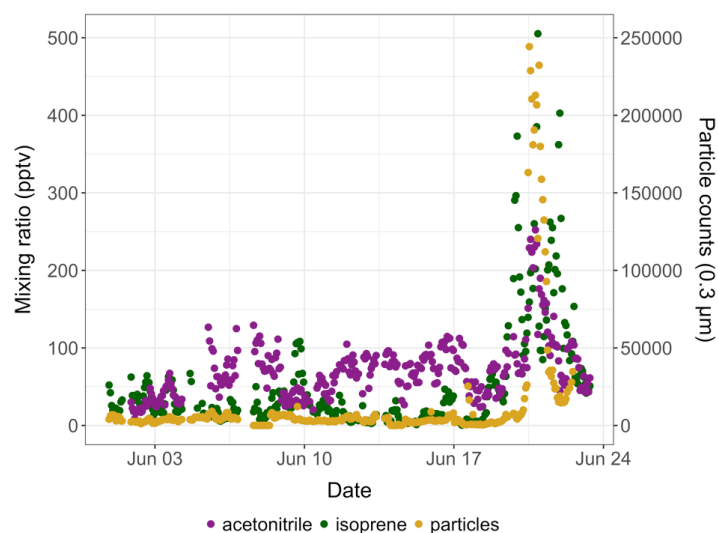


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910 Figure 3: Time-series of isoprene (purple), methylvinylketone (MVK, green), and methacrolein (MACR,  
 911 salmon) mixing ratios (in pptv) in ambient air at Toolik Field station (top panels) and of 30-min-averaged  
 912 ambient temperature (in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

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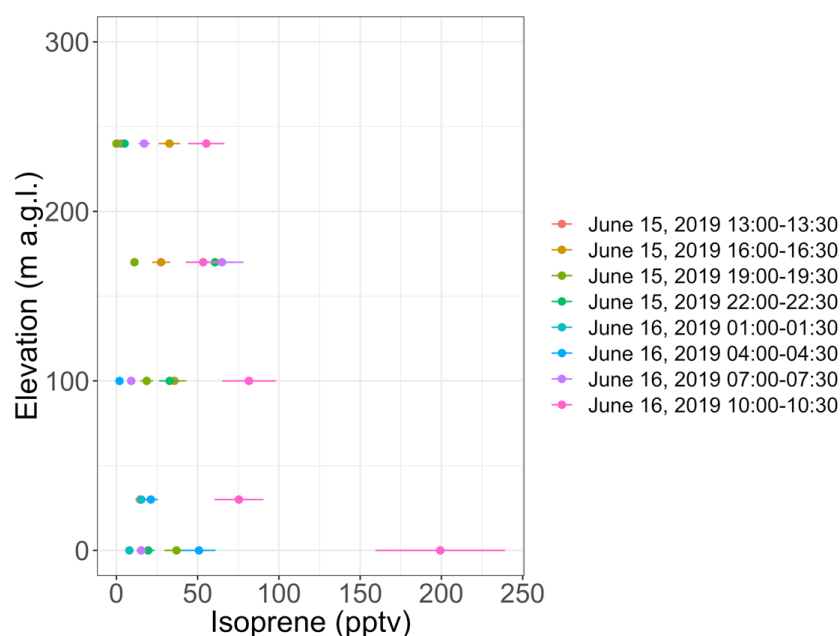
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916 Figure 4: Time-series of isoprene (green) and acetonitrile (purple) mixing ratios (in pptv) and of 0.3 μm  
 917 particle counts (yellow) in ambient air at Toolik Field station in June 2019.

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

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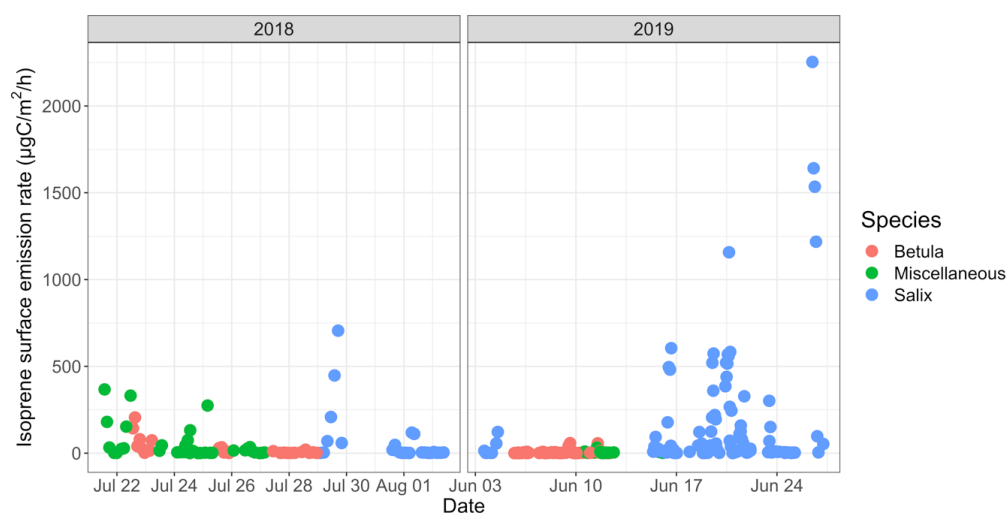
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 936 Figure 6: Time-series of isoprene surface emission rates (in  $\mu\text{gC}/\text{m}^2/\text{h}$ ) for different vegetation types.

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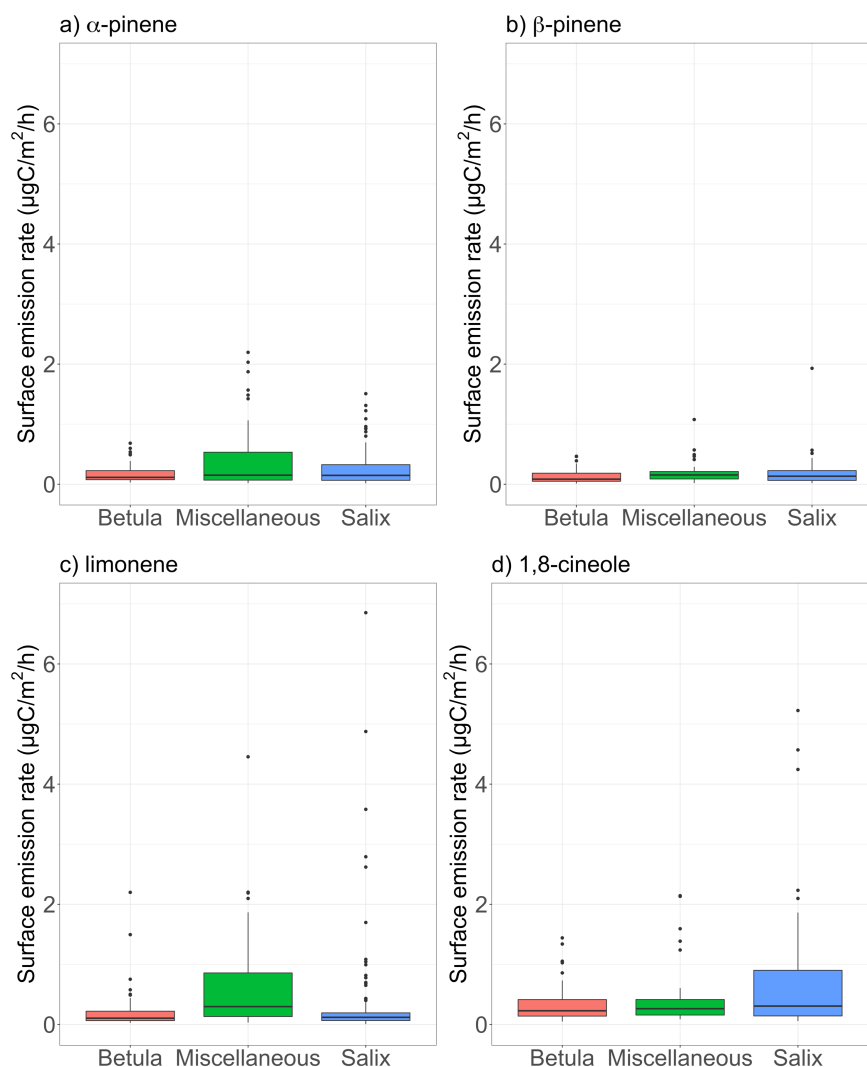
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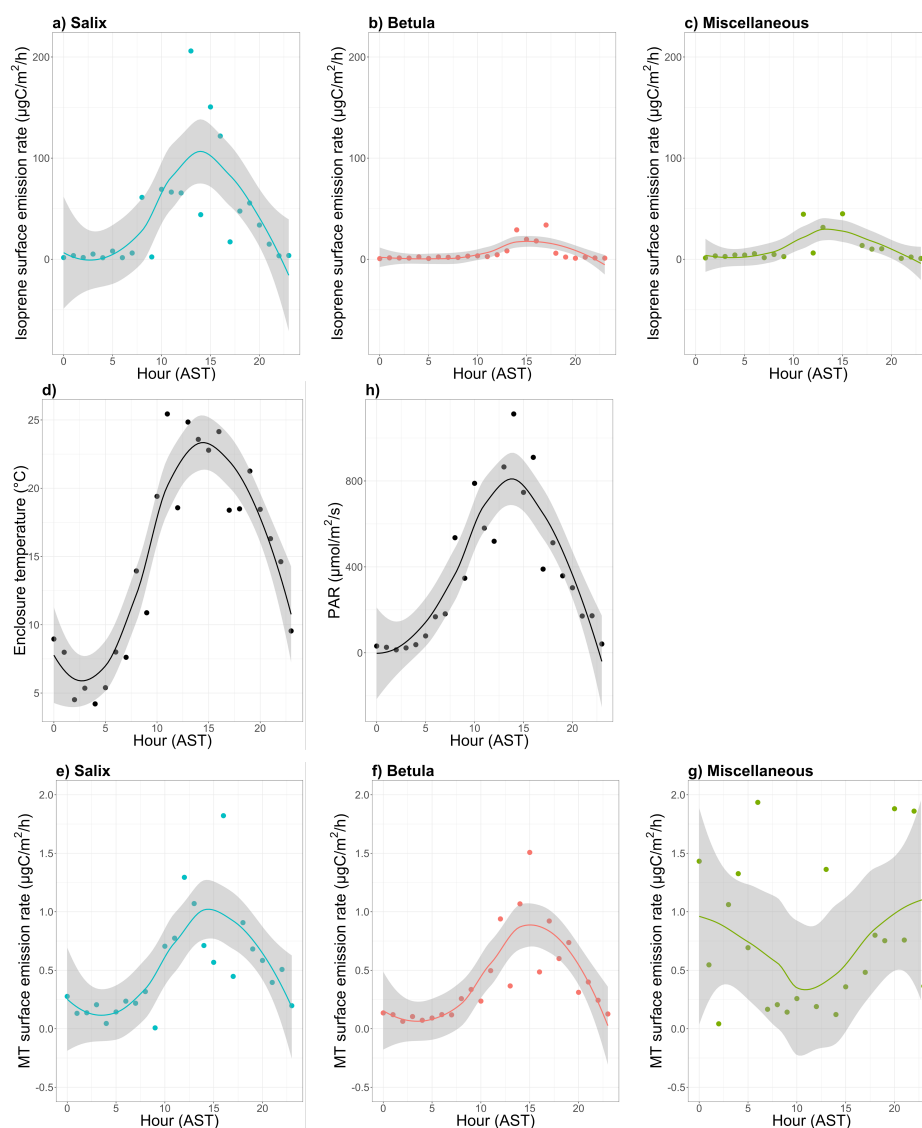
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948 Figure 7: Surface emission rates of various monoterpenes (in  $\mu\text{gC}/\text{m}^2/\text{h}$ ) for different vegetation types. The  
 949 lower and upper hinges correspond to the first and third quartiles. The upper (lower) whisker extends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

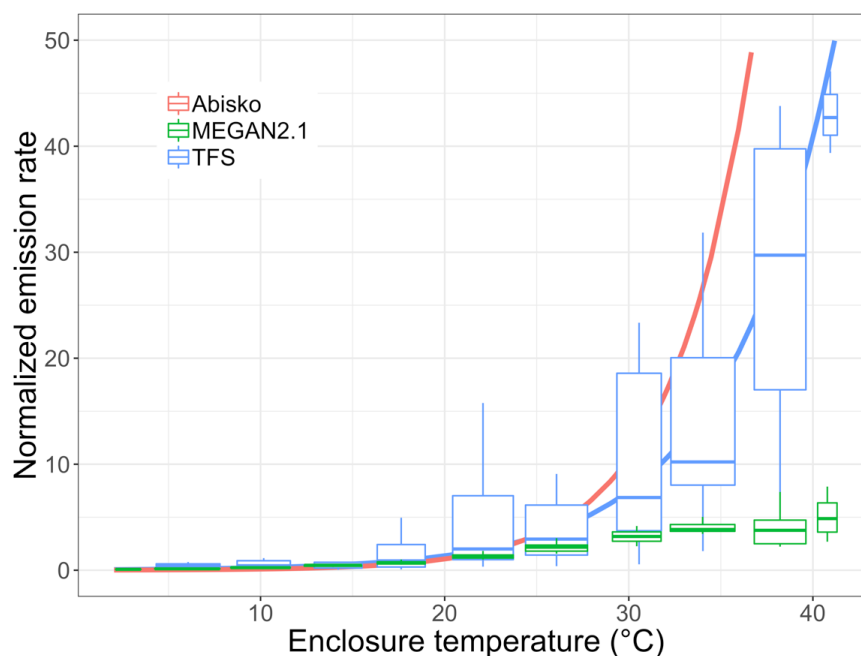
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955 Figure 8: Mean diurnal cycle of isoprene (a-c) and monoterpenes (MT; e-g) surface emission rates (in  
 956  $\mu\text{gC}/\text{m}^2/\text{h}$  – note the difference scale on the y-axis), d) enclosure temperature (in  $^{\circ}\text{C}$ ), and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

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