



Large increases in Arctic biogenic volatile emissions are a direct effect of warming

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1 **Large increases in arctic biogenic volatile organic compound**
2 **emissions are a direct effect of warming**

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14 **Biogenic volatile organic compounds are reactive gases that can contribute to atmospheric**
15 **aerosol formation¹. Their emission from vegetation is dependent on temperature and light**
16 **availability². Increasing temperature, changing cloud cover, and shifting composition of**
17 **vegetation communities can be expected to affect emissions in the Arctic, where the ongoing**
18 **climate changes are particularly severe³. Here we present biogenic volatile organic compound**
19 **emission data from arctic tundra exposed to six years of experimental warming or reduced**
20 **sunlight treatment in a randomized block design. By separately assessing the emission**
21 **response of the whole ecosystem, plant shoots and soil in four measurements covering the**
22 **growing season, we have identified that warming increased the emissions directly rather than**
23 **via a change in the plant biomass and species composition. Warming caused a 260% increase**
24 **in total emission rate for the ecosystem and a 90% increase in emission rates for plants, while**
25 **having no effect on soil emissions. Compared to the control, reduced sunlight decreased**
26 **emissions by 69% for the ecosystem, 61-65% for plants and 78% for soil. The detected strong**
27 **emission response is considerably higher than observed at more southern latitudes,**
28 **emphasizing the high temperature sensitivity of ecosystem processes in the changing Arctic.**

29 All organisms release VOCs for a range of physiological and ecological reasons, but
30 the majority of emissions is derived from vegetation². When low-volatile BVOC oxidation products
31 condensate onto aerosol surfaces, it enhances the formation and growth of secondary organic
32 aerosols⁴. The emission of BVOCs therefore indirectly affects the Earth's radiation balance, as
33 secondary organic aerosols scatter solar radiation and act as cloud condensation nuclei, leading to
34 enhanced albedo⁵.

35 BVOC emission rates in general peak in the tropics and then decrease towards the
36 poles⁶. In the Arctic, models have assumed minimal emissions due to low temperatures, short
37 growing seasons and sparse vegetation cover^{6,7}. However, recent field studies indicate that

38 emissions from arctic tundra greatly exceed estimates based upon models relying on ambient air
39 temperatures rather than canopy temperatures^{8,9}, which are strongly decoupled from air temperature
40 due to the low-stature canopy and adaptations of arctic plants ensuring maximal trapping of heat to
41 warm the canopy^{10,11}.

42 Light is needed for photosynthesis, and BVOCs like isoprene that are directly released
43 upon biosynthesis are emitted light-dependently¹². The production and diffusion rates of BVOCs
44 correlate with temperature, with typical exponential response curves¹². Direct solar radiation has
45 especially large influence on leaf temperatures in low canopy vegetation¹¹, such as tundra, and
46 changes in cloud cover could thus indirectly have a large impact on emission rates.

47 While the effect of changes in light availability has hardly been considered, long term
48 field studies suggest that BVOC emission response to experimental warming is much larger in high
49 latitude compared to other ecosystems¹³⁻¹⁶, indicating that the effect of climate changes on BVOC
50 emission is dependent on the type and state of the ecosystem¹⁶. A potential reason for the large
51 temperature response in high latitude systems is that the increased BVOC emission is an indirect
52 result of temperature-driven plant biomass increase in these temperature-limited ecosystems¹³. The
53 ongoing warming of the Arctic has led to increased plant biomass and altered species composition
54 in the tundra¹⁷, and experimental warming studies indicate that the biomass increase is linear over
55 time¹⁸.

56 In order to identify the mechanisms behind the large emission responses observed in
57 the Arctic, we assessed the effects of warming (W) and reduced sunlight (RS) on BVOC emissions
58 from arctic tundra separately for the whole ecosystem, dominant plants and soil. We examined the
59 responses to elevated temperature using Plexiglas open top chambers, which increase air
60 temperature by 2-3 °C, and to RS using dome-shaped hessian tents, which decrease
61 photosynthetically active radiation (PAR) by 65%, in dry dwarf-shrub tundra in Western Greenland

62 (64°07'N, 51°21'W). The experiment had six replicate plots for each treatment. The vegetation was
63 homogeneous and co-dominated by the crowberry *Empetrum hermaphroditum* and grey willow
64 *Salix glauca* (Supplementary Table S1) with occasional spots of bare soil. Both plant species are
65 common dwarf shrubs with a circumboreal-polar distribution.

66 The BVOC emissions were estimated using enclosure technique and collection of the
67 emitted volatiles in adsorbent cartridges, which were analyzed by gas chromatography-mass
68 spectrometry (see Methods). The ecosystem emissions were measured by enclosing whole
69 ecosystem plots (33 × 33 cm) including intact vegetation and the underlain soil. The plant
70 measurements were made on enclosed shoots of *E. hermaphroditum* and *S. glauca*, and the soil
71 measurements were made on enclosed bare soil spots.

72 The unmanipulated heath proved to be a significant source of BVOCs having a
73 daytime emission rate of 338 $\mu\text{g m}^{-2}$ ground area h^{-1} averaged across the season (Fig. 1a). Isoprene,
74 which was primarily emitted by *S. glauca*, dominated the emission profile constituting 87% of the
75 total emission (Supplementary Tables S1 and S2). Non-terpenoid compounds accounted for 7% of
76 the total emission, while sesquiterpenes and monoterpenes, primarily emitted by *E.*
77 *hermaphroditum* (Supplementary Table S1 and S3), accounted for 5% and 1%, respectively. Across
78 the season, the ecosystem BVOC emission was consistently higher from W and lower from the RS
79 treatment compared to the control (Fig. 1a).

80 W increased the enclosure temperature by 3.1 °C averaged over all measurements
81 (Supplementary Table S2), but it also decreased soil moisture from 22.0% in control to 17.8% in W
82 (Supplementary Table S3). This decrease in soil moisture in response to warming is well in
83 agreement with the projected changes in soil moisture under climate change¹⁹. The aboveground
84 plant biomass was lower in both RS and W compared to the control (Supplementary Table 3S), and
85 in order to not let this difference interact with the assessment of treatment effects on the emissions,

86 we proportioned the ecosystem emission to the estimated aboveground plant biomass in each plot
87 (see Methods). The decrease in aboveground plant biomass in W was in line with earlier findings
88 from water limited arctic ecosystems^{17,18}, and was likely due to amplified drought stress in the W
89 plots¹¹.

90 Proportioned to aboveground plant biomass, average ecosystem emissions increased
91 260% in W compared to the control (Fig. 2a). This temperature relationship corresponds to a Q10 of
92 22, in which Q10 describes the factor by which the emission rate increases with a 10 °C rise in
93 temperature. The high Q10 highlights the extreme temperature sensitivity of BVOC emissions from
94 arctic tundra relative to other processes affected by warming; for example, the Q10 for BVOC
95 emissions is typically between 3-6 (ref. 16), and that for biological processes in general is around
96 2.5 (ref. 20).

97 The ecosystem BVOC emission increase was primarily driven by isoprene and non-
98 terpenoid compounds, increasing 240% and 590% compared to the control, respectively (Fig. 2a).
99 The monoterpene and sesquiterpene emission response to warming was substantial but less
100 profound, with 140% and 60% increases in emissions, respectively. The effect of warming was
101 much greater than expected based on the parameterizations used in models applying exponential
102 relationships between emission rate and temperature²¹ and more drastic than the increase
103 documented for a subarctic heath^{14,22}. Furthermore, the effect was a consequence of direct
104 stimulation of biosynthesis, rather than a result of higher plant biomass due to warming¹³. The large
105 response to warming may be linked to the effects of decreased soil moisture, which is a key driver
106 of vegetation properties in arctic-alpine ecosystems²³. Moderate drought stress has in some cases
107 increased isoprene emissions^{15,16}, possibly by limiting the naturally cooling evapotranspiration
108 process, resulting in higher leaf temperatures¹¹.

109 On average RS decreased PAR by 65%, air temperature in the enclosures by 5.7 °C
110 (Supplementary Table S2) and soil temperature by 0.5 °C (Supplementary Table S3). Corrected for
111 plant biomass, the total BVOC emission from RS was 69% lower than the control, mainly due to
112 lower isoprene emissions (Fig. 2a). The decrease may be explained by the reduced temperature and
113 probably to a higher extent by the light dependency of the emission of isoprene that is released upon
114 synthesis, and thus coupled to photosynthesis^{21,25}.

115 The treatment responses in the plant shoot BVOC emissions were in agreement with
116 the responses at the ecosystem level. Compared to the control, the total BVOC emissions from *S.*
117 *glauca* and *E. hermaphroditum* increased with 90% in W, and decreased with 61-65% in RS (Fig.
118 2b and 2c). *S. glauca* had an average emission rate of 7.8 µg g⁻¹ dw leaf biomass h⁻¹ with isoprene
119 accounting for 85% of the total emission (Fig. 2b). The average emission rate of *E. hermaphroditum*
120 was 2.6 µg g⁻¹ dw leaf biomass h⁻¹, mainly consisting of sesquiterpenes and non-terpenoid
121 compounds (Fig. 2c).

122 In general, the emissions from bare soil proved to be substantial, constituting 20% of
123 the total BVOCs released from the whole ecosystem measurements. Total soil BVOC emission rate
124 was 59.1 µg m⁻² h⁻¹, with non-terpenoid compounds accounting for 95%. The seasonal variation in
125 soil and plant emissions is shown in Supplementary Figure S1, and complete lists of compounds
126 emitted are shown in Supplementary Tables S4-S7.

127 The emission in RS was 78% lower than in the control (Fig. 2d), and thus it followed
128 the negative response observed also in the plant and ecosystem measurements. However, in contrast
129 to the stimulation of plant and ecosystem emissions, W had no effects on the soil emissions (Fig.
130 2d). The decrease in soil emissions by RS cannot be fully explained by abiotic factors since soil
131 temperature at 3-5 cm depth only decreased by 0.5 °C (Supplementary Table S3), and solar
132 radiation only directly affects the soil surface. Instead, we suggest that root biomass played a role.

133 The majority of BVOCs released from soil derive from the rhizosphere including emissions from
134 roots, rhizospheric bacteria and fungi²⁶. Reduced light availability increases allocation of resources
135 to stem and leaves at the expense of roots²⁷ suggesting reduced biomass and thereby lower root-
136 derived emissions in the RS treatment. Also the decrease in aboveground plant biomass in RS
137 (Supplementary Table S3) has probably been accompanied by a decrease in root biomass. Results
138 from an earlier long term warming experiment in arctic tundra indicate that belowground plant
139 biomass is unaffected by open top chamber warming, which could explain the lacking soil emission
140 response to warming in our study²⁸.

141 To assess which biological or environmental factors affect the ecosystem-level BVOC
142 emissions, we conducted a partial least squares (PLS) regression²⁹ analysis on the ecosystem
143 emission of the dominant BVOC, isoprene. Isoprene emission correlated positively with net
144 ecosystem exchange, the biomass of *S. glauca*, a strong isoprene emitter², and PAR (Fig. 3) which
145 is in agreement with the well-established light dependence of isoprene emission¹². In contrast,
146 several soil-related, inter-correlated, variables had a negative relationship with ecosystem isoprene
147 emission (Fig. 3). The most influential of these variables were ecosystem respiration, soil microbial
148 biomass carbon and bacterial abundance (number of 16S rDNA copies). We hypothesize that the
149 negative relationship demonstrates active soil bacterial uptake of isoprene in the ecosystem³⁰. The
150 responses of this process to climate change and the importance to the ecosystem net emissions
151 remain to be untangled.

152 Our results demonstrate several-fold increased BVOC emission from a dry arctic
153 tundra heath in response to a realistic temperature increase mimicking projected warming in the
154 Arctic³. The drastic increase is in agreement, but cannot be fully explained by increases in
155 emissions per gram leaf biomass of the dominant plant species. The unexplained emission increase
156 may be due to strong temperature dependency in BVOC emission from mosses, lichens,

157 decomposing litter and subdominant vascular plants in the whole ecosystem plots (Supplementary
158 Table S1). Reduced sunlight decreased emission rates both from plants, soil, and the whole
159 ecosystem, probably due to both reduced light availability *per se* and surface cooling.

160 Our results emphasize the increasing importance of BVOC emissions from the Arctic
161 under climate change. Since 1979, arctic land surface has warmed at a rate of 0.5 °C per decade and
162 in 2100 temperatures in the Arctic are projected to have increased by 2-8 °C (ref. 3). In remote
163 areas, such as the Arctic, where the air is clean, the growth of particles large enough to act as cloud
164 condensation nuclei, is tightly coupled to the emission of BVOCs¹, and warming-induced emissions
165 in the Arctic may therefore lead to increased cloud formation. As BVOC emissions are highly
166 regulated by sunlight availability, the warming-induced emissions might in fact initiate a negative
167 feedback mechanism between the biosphere, aerosols and climate.

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170 **Additional Information**

171 The processed data for this manuscript can be found in the Figshare database

172 (http://figshare.com/authors/Magnus_Kramsh_j/830572).

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227 [arctic-swipa-climate-change-and-the-cryosphere/743](http://www.amap.no/documents/doc/snow-water-ice-and-permafrost-in-the-arctic-swipa-climate-change-and-the-cryosphere/743)>
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274

275 **Author Contributions**

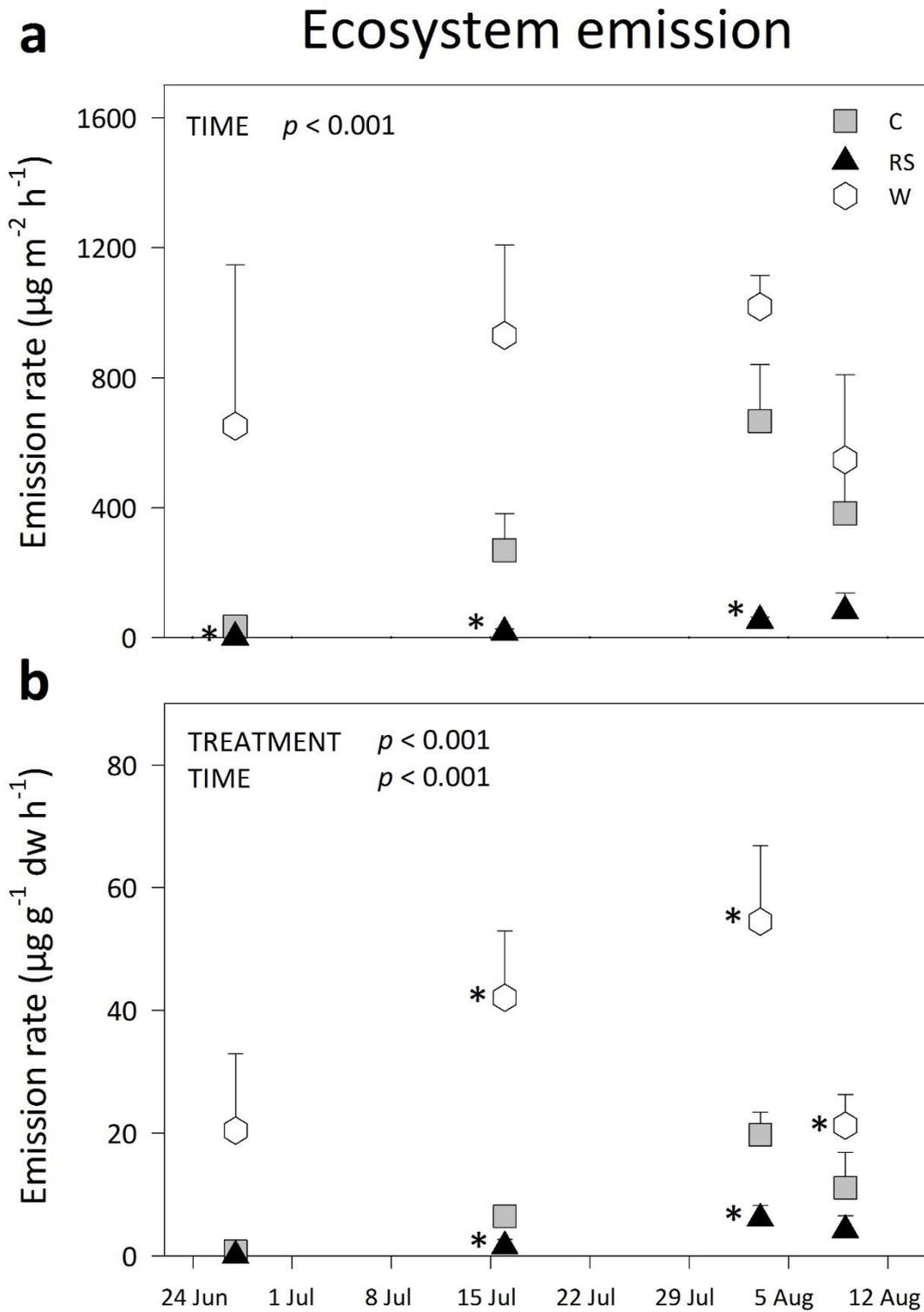
276 MK and IVP collected the data. MK, IVP, MS and RR analyzed and interpreted the dataset. ÅR
277 performed the PLS analysis. JN and HRP established the experimental site. MK wrote the
278 manuscript with contributions from all authors.

279

280 **Author Information**

281 The authors declare no competing financial interests.

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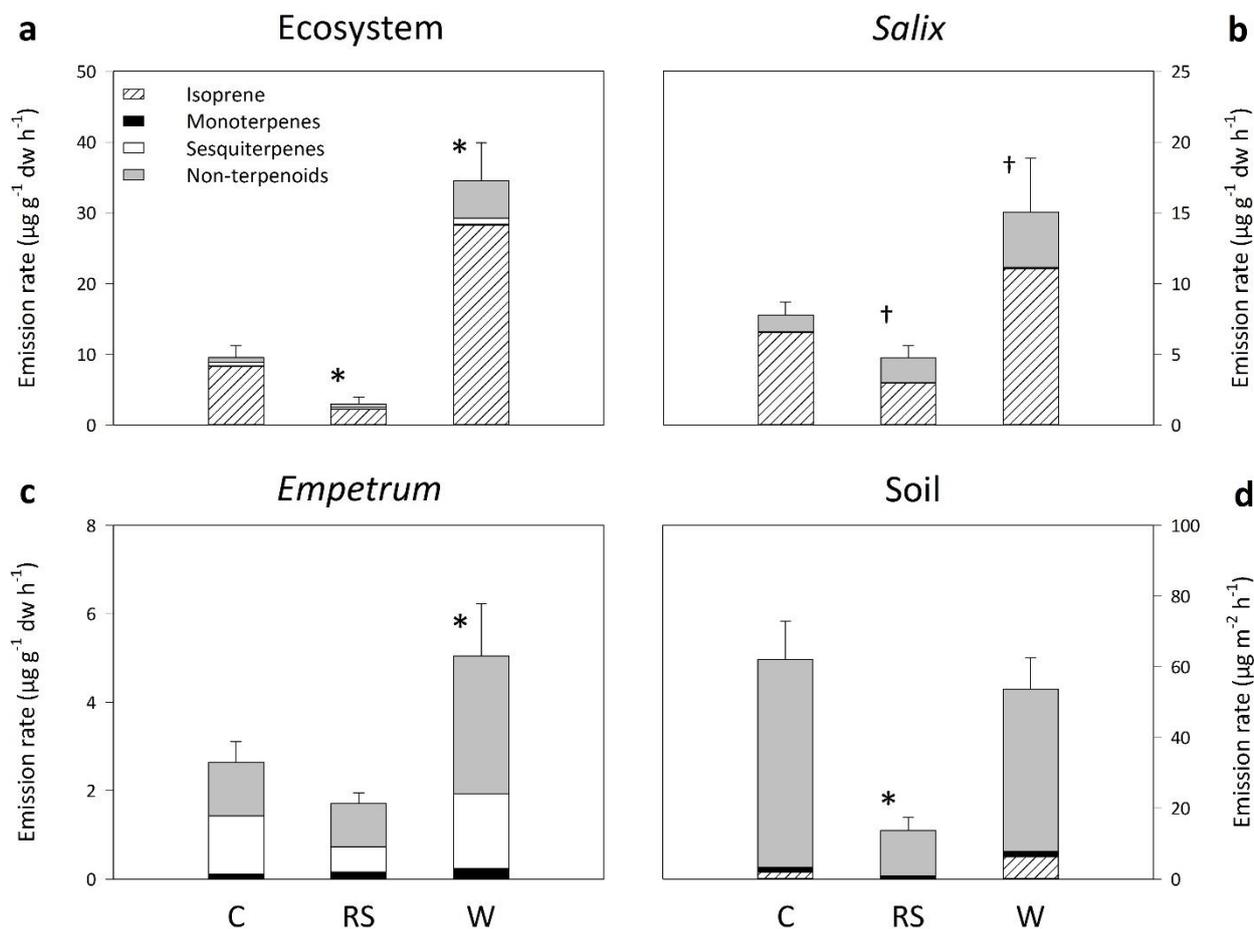
283

284 **Figure 1: Biogenic volatile organic compound emission across the season. a**, Mean emission

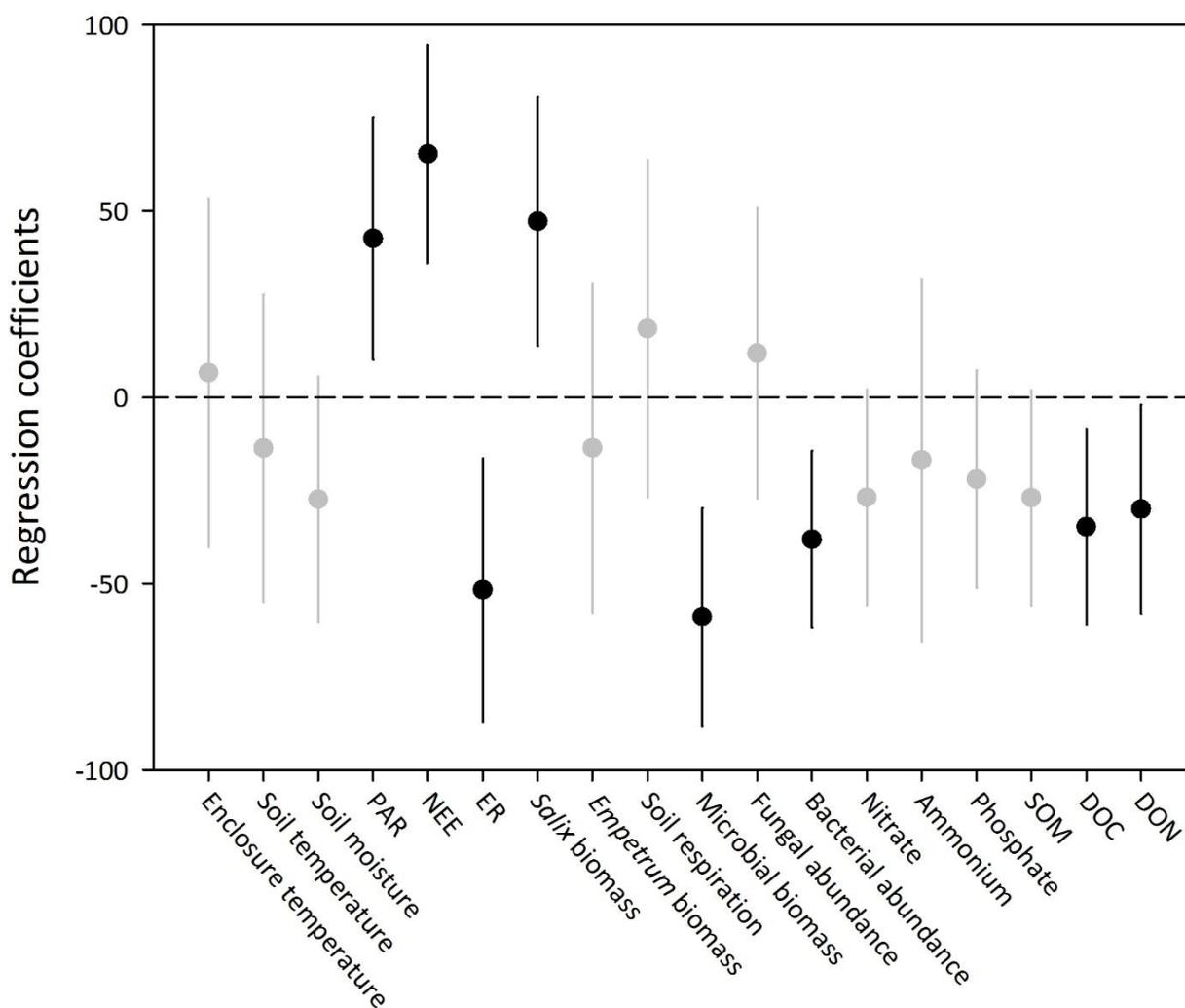
285 rate ($n = 5$) per ground area and **b**, mean emission rate ($n = 5$) per dry weight plant biomass.

286 Statistically significant p -values for the repeated measures ANOVA are shown. Asterisks signify

287 statistically significant difference from the control within the measurement dates (Dunnett's test, * p
 288 < 0.05). C, control; RS, reduced sunlight; W, warming. Error bars show standard error of the mean.
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290
 291 **Figure 2: Growing season average of biogenic volatile organic compound emission. a,**
 292 **Emission from whole ecosystem corrected for plant biomass ($n = 5$) b, Emission from *Salix glauca***
 293 **($n = 6$) c, Emission from *Empetrum hermaphroditum* ($n = 6$) and d, Emission from soil ($n = 6$). The**
 294 **division of the total emissions to isoprene, monoterpenes, sesquiterpenes and non-terpenoids is**
 295 **shown. Symbols signify statistically significant difference compared to control (Mixed model,**
 296 **Dunnett's test, * $p < 0.05$; † $p < 0.1$). Error bars represent standard error of the mean.**
 297



298

299 **Figure 3: Correlation between measured background variables and isoprene emission for the**

300 **tundra ecosystem.** Average regression coefficients for the partial least squares regression on

301 isoprene emission. The error bars show $1.96 \times$ standard error calculated from 1000 bootstrap

302 samples. Significant factors are shown in black. PAR, photosynthetically active radiation; NEE, net

303 ecosystem exchange; ER, ecosystem respiration; SOM, soil organic matter; DOC, dissolved organic

304 carbon; DON, dissolved organic nitrogen.

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308 **Methods**

309 **Study site and experimental setup**

310 The data were collected during the growing season of 2013 in Kobbefjord, 20 km southeast of
311 Nuuk, Greenland (64°07'N, 51°21'W). The experiment that was initiated in 2007 (ref. 31) spanned
312 approx. 50 x 100 m and consisted of 18 hexagon-shaped plots (diameter 1.2 m). Control plots and
313 the treatments W and RS were distributed to the experiment in randomized complete block design
314 ($n = 6$). One block was excluded from the “whole ecosystem” measurements, because the
315 vegetation composition in this block differed from the other blocks. It did not have any *Salix*
316 *glauca*, which was one of the two dominant species in the studied tundra ($n = 5$).

317

318 **Sampling of BVOCs**

319 Plant and soil BVOC emission was measured using a dynamic headspace sampling technique, while
320 ecosystem emission was measured using a push-pull enclosure technique^{13,32}. Air was circulated
321 through the systems by battery-operated pumps connected via Teflon tubes. The incoming air was
322 purified by an activated charcoal filter to remove particles and VOCs, and by a MnO₂ scrubber to
323 remove ozone³³. Air was pumped out of the enclosures through stainless steel adsorbent cartridges
324 containing 150 mg Tenax TA and 200 mg Carbograph 1TD (Markes International Limited,
325 Llantrisant, UK) at 200 ml min⁻¹. Following the 30 minute long sampling, the adsorbent cartridges
326 were sealed with Teflon-coated brass caps, and stored refrigerated until analysis. The used
327 adsorbent cartridges capture compounds in the range C5-C30. Using this method a number of
328 oxygenated BVOCs might not be captured quantitatively.

329 We used precleaned (120 °C for 1 hr.) disposable polyethylene terephthalate (PET)
330 bags that were attached to a polyvinyl chloride (PVC) cylinder (diameter 10 cm) installed in bare

331 soil or around a shoot of *S. glauca* or *E. hermaphroditum*, for soil and plant enclosures,
332 respectively. The adsorbent cartridge was inserted into the PET bag through a hole cut in the corner,
333 which was afterwards tightly closed with plastic-coated wire. Prior to each measurement, the bags
334 were ventilated for five minutes with an inflow rate of 1000 ml min⁻¹, and during measurements the
335 inflow was set to 500 ml min⁻¹. For ecosystem enclosures, a transparent polycarbonate chamber (25
336 L; Vink Finland, Kerava, Finland), equipped with a fan to ensure well-mixed headspace, was placed
337 on the permanent chamber base in each plot. The cartridge was mounted directly on the chamber
338 and the inflow rate was set to 215 ml min⁻¹.

339 Blank samples were collected to account for VOCs released from sampling materials
340 or analysis system. During all measurements, shaded iButtons (Hygrochron, Maxim Integrated, San
341 Jose, USA) placed inside the enclosure logged temperature and relative humidity once per minute.
342 PAR was monitored in each treatment using S-LIA-M003 sensors connected to a HOBO micro
343 station data logger (H21-002, Onset computers corporation, Boston, USA).

344

345 **Analysis of BVOCs**

346 The BVOC samples were analyzed by a gas chromatograph-mass spectrometer (7890A Series GC
347 coupled with a 5975C inert MSD/DS Performance Turbo EI System, Agilent, Santa Clara, CA,
348 USA) after thermal desorption (UNITY2 coupled with an ULTRA autosampler, Markes,
349 Llantrisant, UK). The carrier gas was helium and oven temperature was held at 40 °C for 1 min,
350 then raised to 210 °C at a rate of 5 °C min⁻¹, and finally further to 250 °C at a rate of 20 °C min⁻¹.
351 BVOCs were separated using an HP-5 capillary column (50 m, diameter 0.2 mm, film thickness
352 0.33 µm).

353 BVOCs were identified using pure standards and according to their mass spectra in
354 the NIST 8.0 mass spectral data library, and quantified with pure standards (see Supplementary

355 Table S8 for a list of compounds). Standard solutions were injected into adsorbent cartridges in a
356 stream of Helium and analyzed as samples. When quantifying compounds for which no pure
357 standard was available, α -pinene was used for monoterpenes, humulene was used for sesquiterpenes
358 and toluene was used for non-terpenoids. Compounds were classified into one of following four
359 groups: isoprene, monoterpenes, sesquiterpenes and non-terpenoids.

360 The plant emissions were calculated on leaf dry weight basis, soil emissions on
361 ground area basis, and ecosystem emissions both on ground area basis and per dry weight estimated
362 aboveground plant biomass in each plot. All emission rates are reported as actual, not normalized,
363 emissions.

364

365 **Vegetation analysis and estimation of plant biomass**

366 The vegetation cover of vascular plants, mosses, lichens and litter was estimated in the plots
367 subjected to ecosystem-level BVOC emission measurements and in 21 additional plots adjacent to
368 the field experiment. The analysis was conducted in mid-July by the point intercept method using a
369 35 x 35 cm frame with 25 fixed points³⁴. In the additional plots, the vegetation was harvested, oven
370 dried (60 °C for 72 hrs.) and weighed. For each species, linear regression was used to model the
371 biomass in the experimental plots, based on the point intercept data.

372

373 **Ecosystem emission per gram plant biomass**

374 Isoprene emission was calculated per gram *S. glauca* present in each plot, monoterpene and
375 sesquiterpene emission was calculated per gram biomass of all vascular plants except *S. glauca* and
376 the emission of non-terpenoid compounds was calculated per gram total plant biomass.

377

378 **Q10-value for ecosystem emission**

379 Q10 was calculated using the following formula:

$$380 \quad Q10 = \frac{E_W^{10/(T_W - T_C)}}{E_C}$$

381 where E_W is the average ecosystem BVOC emission rate in the warmed plots and E_C is the average
382 ecosystem BVOC emission rate in the controls. T_W is the average temperature inside the enclosures
383 in the warmed plots and T_C is the average temperature inside the enclosures in the controls.

384

385 **Background data**

386 In each plot, soil temperature at 3-5 cm depth was monitored every hour using M-Log 5W Wireless
387 Temperature Data Loggers (Geoprecision, Ettlingen, Germany). Soil moisture was measured once a
388 week during the entire growing season.

389 Net ecosystem exchange, ecosystem respiration and soil respiration were measured weekly with a
390 LI-6400XT portable gas-analyzer (LI-COR, Biosciences, Lincoln, USA; see Haugwitz et al. paper
391 in preparation). The concentrations of dissolved organic nitrogen, ammonium, nitrate and phosphate
392 in the soil were determined in ddH₂O-extracts of fresh soil using spectrophotometry (see Haugwitz
393 et al. paper in preparation). Dissolved organic carbon (DOC) was analyzed with a Shimadzu TOC-L
394 CSH/CSNTM total organic carbon analyzer (Shimadzu, Kyoto, Japan), and microbial biomass was
395 estimated from the difference in the DOC concentration in the chloroform-fumigated and non-
396 fumigated samples³⁵. DNA was extracted from freeze-dried soil using FastDNATM Spin Kit for Soil,
397 and subsequently quantitative polymerase chain reaction was performed targeting ITS2 region and
398 16S rDNA to estimate the fungal and bacterial abundance in the soil (see Haugwitz et al. paper in
399 preparation).

400

401 **Statistical tests**

402 The treatment effects on BVOC emissions in repeated measurements were tested by a linear mixed
403 model in SAS 9.2. including Treatment (three levels: Control, W and RS) and Time as fixed factors
404 and Block as a random factor. Interactions with p -values > 0.2 were stepwise removed from the
405 model. One-way ANOVA was used to test for treatment effects within each measurement and for
406 growing season averages. A Dunnett's test was used as a post hoc test to compare each treatment to
407 the control. The effects of biological and environmental factors on the ecosystem-level isoprene
408 emission were assessed by the PLS analysis. The tested variables, measured in the same plot,
409 included enclosure temperature, soil temperature, soil moisture, PAR, *S. glauca* biomass and *E.*
410 *hermaphroditum* biomass described in the present study and net ecosystem exchange, ecosystem
411 respiration, soil respiration, microbial biomass, fungal and bacterial abundance, nitrate, ammonium,
412 phosphate, soil organic matter, dissolved organic carbon and dissolved organic nitrogen (see
413 Haugwitz et al. paper in preparation). The PLS was performed with a cross-validation with six
414 segments in a Venetian blinds according to isoprene emission. In order to estimate the uncertainty
415 in the regression coefficients of each of the factors a resampling scheme – bootstrapping³⁶ – was
416 performed 1000 times. One component PLS models were used throughout the analysis, and the
417 standard error was calculated as given in Wehrens et al. (ref. 36).

418

419 **Method references**

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