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Published in:
Journal of Geophysical Research

DOI:
10.1002/2015JG003295

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Fourfold higher tundra volatile emissions due to arctic summer warming

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Abstract Biogenic volatile organic compounds (BVOCs), which are mainly emitted by vegetation, may create either positive or negative climate forcing feedbacks. In the Subarctic, BVOC emissions are highly responsive to temperature, but the effects of climatic warming on BVOC emissions have not been assessed in more extreme arctic ecosystems. The Arctic undergoes rapid climate change, with air temperatures increasing at twice the rate of the global mean. Also, the amount of winter precipitation is projected to increase in large areas of the Arctic, and it is unknown how winter snow depth affects BVOC emissions during summer. Here we examine the responses of BVOC emissions to experimental summer warming and winter snow addition—each treatment alone and in combination—in an arctic heath during two growing seasons. We observed a 280% increase relative to ambient in BVOC emissions in response to a 4°C summer warming. Snow addition had minor effects on growing season BVOC emissions after one winter but decreased BVOC emissions after the second winter. We also examined differences between canopy and air temperatures and found that the tundra canopy surface was on average 7.7°C and maximum 21.6°C warmer than air. This large difference suggests that the tundra surface temperature is an important driver for emissions of BVOCs, which are temperature dependent. Our results demonstrate a strong response of BVOC emissions to increasing temperatures in the Arctic, suggesting that emission rates will increase with climate warming and thereby feed back to regional climate change.

1. Introduction

Biogenic volatile organic compounds (BVOCs) constitute about 90% of the volatile organic compounds entering the atmosphere [Kesselmeier and Staudt, 1999]. BVOCs play a part in plant development and reproduction, communication within and between trophic levels [Laathawomkikul et al., 2009] and stress tolerance [Peñuelas and Staudt, 2010]. For example, isoprene which is the globally most emitted compound [Guenther et al., 2006] has been suggested to protect plants from heat stress by stabilizing cell membranes and by protecting plant organs from oxidative stress [Sharkey et al., 2008].

The temperature increase in the past three decades has probably increased emission of BVOCs by 10%, and considerable further increases are expected in a future warmer climate [Peñuelas and Staudt, 2010]. These increases are due to enhanced enzymatic activity in BVOC synthesis and higher vapor pressure and diffusion rates in response to warming [Peñuelas and Staudt, 2010]. The increasing emissions create a positive feedback to climate warming by lowering the oxidation capacity of the atmosphere and thereby prolonging the lifetime of the efficient greenhouse gas methane [Peñuelas and Staudt, 2010; Shindell et al., 2009]. However, BVOC emissions can also cause a negative feedback via contribution to formation of aerosols and aerosol growth, which may increase the number of cloud condensation nuclei that scatter sunlight and may thereby cool the climate [Paasonen et al., 2013]. The contribution of BVOCs, particularly terpenes [Carlton et al., 2009; Zhao et al., 2015] (e.g., monoterpenes and sesquiterpenes), to aerosol formation is especially important in northern remote areas [Paasonen et al., 2013]. It has been suggested that the recent warming in the Arctic would have been even greater without the aerosol-induced cooling [Najafi et al., 2015]. This considerable negative feedback of BVOC emissions to high-latitude climate warming is unexpected since the emissions in these cold tundra areas have been expected to be minimal due to sparse vegetation cover, short growing season, and low temperature [Rinnan et al., 2014; Sindelarova et al., 2014].

It has recently been suggested that BVOC emissions from subarctic ecosystems are much more responsive to rising temperatures than elsewhere [Faubert et al., 2010; Peñuelas and Staudt, 2010; Tiiva et al., 2008]. However, response in BVOC emissions to rising temperature in the more extreme Arctic, an area which
undergoes large changes due to climate warming [Elmendorf et al., 2012], has been largely ignored. The Arctic has already warmed significantly during the last three decades, by ~3°C, with temperatures estimated to further increase by 3–11°C by the year 2100 [McBean et al., 2005]. Future snow cover predictions are more uncertain, and model outputs show large variability [Callaghan et al., 2011]. Nevertheless, the model predictions suggest that future winter snow precipitation will increase in large parts of the Arctic [Callaghan et al., 2011; Intergovernmental Panel on Climate Change, 2013]. Snow acts as insulation against low air temperature [Wipf and Rixen, 2010], with deeper snow promoting the activity of soil microorganisms, thereby leading to greater nutrient availability [Semenchuk et al., 2015], and thus potentially increased BVOC emissions [Peñuelas and Staudt, 2010]. On the other hand, snow accumulation may also delay growing season onset and negatively affect plant performance [Cooper et al., 2011], which could reduce the production and emission of BVOCs.

The aim of this study was to elucidate the effect of warming and deeper snow on emission of BVOCs from an arctic ecosystem. We sampled BVOC emissions, using an enclosure technique and absorbent cartridges, in a field experiment situated in the low arctic Western Greenland over two growing seasons. The experiment was a (2 × 2) full factorial design with two treatments: warming by open top chambers and snow addition using snow fences, in six replicates (Figure 1). We measured canopy surface and air temperatures in the same field experiment and calculated the difference (Δ temperature) by subtracting air from surface temperature. This was done in order to investigate the possible difference between these temperatures and to assess if surface heating could be a potential driver of arctic BVOC emission rates.

2. Materials and Methods

2.1. Site Description and Experimental Design

The field experiment was located on a mesic tundra heath on Disko Island, West Greenland (69°14′N/53°32′W), with discontinuous permafrost and a mean annual temperature of ~2.9°C and precipitation of 273 mm (average for 1992–2013). The site was a sparsely vegetated mesic tundra heath dominated by the dwarf shrubs Betula nana L., Empetrum nigrum ssp. hermaphroditum L., Vaccinium uliginosum L., and Cassiope tetragona (L) D. Don, and the lichens Cetraria islandica (L) Ach., Cetraria nivalis (L) Ach. and Stereocaulon spp. (see Table S1 in the supporting information for details on vegetation cover).
We performed our measurements in a (2 × 2) full factorial experiment with two treatments: warming by open top chambers (OTC; levels: control and warming) and passive snow addition (levels: ambient snow and snow addition) using 14.7 m long and 1.5 m high snow fences, replicated in six blocks separated by at least 40 m. In total, 24 plots were included in the study. A more detailed description of the experiment is provided in Blok et al. [2015].

### 2.2. BVOC Measurements

#### 2.2.1. Sampling of BVOCs

An enclosure technique was used for sampling BVOCs from whole ecosystem plots, including vegetation and the underlying soil, 8 and 7 times during the snow-free season in 2013 and 2014, respectively. Transparent polycarbonate measurement chambers (thickness 1.5 mm, 220 × 220 mm, height 200 mm; Vink Finland, Kerava, Finland) were placed on preinstalled aluminum chamber bases (Figure S1 in supporting information). Air, free from ozone (removed using a MnO2 scrubber) and particles (removed by using a charcoal filter), was pumped into the measurement chambers with a flow rate of 200 ml min⁻¹. The chamber headspace was well mixed with a fan. The same flow rate was used for pulling air out from the measurements chamber, through a stainless steel absorbent cartridge filled with 150 mg Tenax TA and 200 mg Carbograph 1TD (Markes International Limited, Llantrisant, UK) adsorbents. The sampling time was 30 min and was performed between 9:30 and 16:00. The cartridges were sealed with Teflon coated brass caps and stored at 4°C before transportation from Greenland to Copenhagen for analysis. Prior to sampling, the measurement chambers were flushed with a flow rate of 1000 ml min⁻¹ for 10 min to replace the headspace with air free from particles and ozone. This flushing was done in order to ensure the sampled BVOCs originated from the system inside the enclosure. Between each measurement, the measurement chambers were cleaned using paper towels to remove water and possible sticky compounds that might have attached on the chamber surface. The system used allowed four-parallel measurements.

#### 2.2.2. Blank Measurements

Blank measurements were performed in situ to determine compounds originating from the used materials or analysis system. The chamber bases were covered with a precleaned polyethylene terephthalate film to exclude vegetation and soil, and the measurements and analyses were conducted as when measuring BVOC emissions from the plots. Compounds found in the blanks were removed from samples.

#### 2.2.3. BVOC Analysis

The BVOCs were analyzed by gas chromatograph-mass spectrometer following thermal desorption at 250°C and cryofocusing at −10°C (for details see Vedel-Petersen et al. [2015]).

Pure standards and the National Institute of Standards and Technology (NIST) library were used for identification of BVOCs, and compounds with an identification quality above 90% (in the NIST library) were included in the data set. The quantification was done using the following standard compounds in 2013: tricyclene, 2-methylfuran, toluene, nonanal, 2-hexenal, 1-octen-3-ol, bornylacetate, α-pinene, camphene, sabinene, β-myrcene, β-pinene, α-phellandrene, 3-carene, d-limonene, 1,8-cineole, α-terpinene, terpinolene, linalool, camphor, borneol, α-copaene, longifolene, β-caryophyllene, α-humulene, cis-3-hexenyl acetate, methyl salicylate, and isoprene. In 2014, the following standards were used: 2-methylfuran, toluene, 2-hexenal, 1-octene-3-ol, cis-3-hexenyl acetate, nonanal, cis-3-hexenyl butyrate, isoprene, α-pinene, camphene, δ-phellandrene, limonene, 1,8-cineole, γ-terpinene, linalool, aromadendrene, and α-humulene. Compounds without a specific pure standard available were quantified using α-pinene for monoterpenes, 1,8-cineole for oxygenated monoterpenes, α-humulene for sesquiterpenes, and toluene for nonterpenoids. BVOCs were grouped into isoprene, monoterpenes, sesquiterpenes, and nonterpenoids. The BVOC emission rates (µg BVOC m⁻² ground area h⁻¹) were calculated using chamber volumes that accounted for differences in surface topography, as in Faubert et al. [2012].

### 2.3. Environmental Variables

During sampling, the photosynthetic photon flux density (PPFD) was recorded every 10 s in ambient conditions as well as inside the OTCs using S-LIA-M003 sensors connected to a HOBO microstation data logger (H21-002 Onset Computers Corporation, Boston, USA). Temperature and relative humidity in the measurement chamber were monitored with a shaded iButton (i-Wire Hygrochron, Maxim Integrated, San Jose, USA) once per minute. Soil temperature (T-Handle Lab Thermometer DTS20HT) at 2 and 5 cm depth was measured close to the chamber base in each plot. The surface temperature inside each chamber
base was recorded before each BVOC measurement, using a portable infrared thermometer (Dual focus infrared thermometer, Micro-Epsilon Group, Ortenburg, Germany).

Soil temperatures (5 cm depth) and canopy air temperatures (2–3 cm above the soil surface) were measured continuously in 2–4 plots per treatment using TinyTag PB-5001 thermistor probes (Gemini Data Loggers, UK) and logged every half hour. Air temperature at 2.2 m height was measured continuously on a weather station at the site and is shown in Figure S2. Soil moisture was measured continuously at 5 cm depth in 2–3 plots per treatment using Decagon EC-5 water content sensors (Decagon Devices, WA, USA) and logged every 10 min and is shown in Figure S3 in the supporting information. Soil moisture data were adjusted for variations in sensor calibration accuracy by aligning recorded winter minimum values to zero for each sensor, with individual soil moisture curves being offset with this correction. Winter snow depth and snowmelt timing was determined from photographs taken by automated cameras (n = 3 snow fence blocks) on a daily basis using identification of snow depth relative to 2 m high marked poles placed near each plot (Figure 1).

2.4. Vegetation Analysis

The vegetation cover within each chamber base was analyzed on 20 July 2013 and 2 August 2014 using the point intercept method. A frame with 49 grid points was placed on top of the aluminum chamber base. A pin was vertically lowered in each grid point, and a hit was recorded every time the pin touched a plant, lichen, litter, or bare soil (covered by cryptogamic crust). This analysis gives a three-dimensional picture of the vegetation cover, and the cover may exceed 100%.

2.5. Measurement of Air and Canopy Surface Temperature

Parallel measurements of canopy surface temperature and air temperature were performed 7 times during the 2014 BVOC measurement campaigns. Canopy surface temperature was measured in a 90 × 90 cm square surrounding the chamber base in each plot using a portable infrared thermometer (Dual focus infrared thermometer, Micro-Epsilon Group, Ortenburg, Germany). The measurements were done by moving the instrument in a zigzag manner over the area while measuring the temperature, and an average temperature for each plot was noted. Air temperature at 1.5 m height was measured simultaneously with four-shaded iButtons (i-Wire Hygrochron, Maxim Integrated, San Jose, USA) attached to the snow fences in each block. A Δ temperature was calculated by subtracting the air from the surface temperature for control plots. In addition, soil moisture, soil temperature at 2 and 5 cm depth, PPFD, and normalized difference vegetation index (NDVI, using SKR 100 sensor, Skye Instruments, Powys, Wales) were measured in each plot.

2.6. Statistical Analyses

All statistical tests were done in SAS Enterprise Guide 7.1 (SAS Institute Inc., Cary, NC, USA) with 0.1 < p < 0.05 reported as tendencies and p < 0.05 reported as significant effects. The data were log transformed if needed to obtain normal distribution and equal variances. A stepwise reduction of the model was used to remove interaction terms with p > 0.2 from the model. The effects of snow addition, warming, and sampling date on BVOC emissions were tested using a three-way repeated mixed model analysis of variance (ANOVA) with a hierarchical design. Snow addition, warming, and date were fixed factors, block was a random factor, and plot was repeated within date. The treatment effects of snow addition and warming on BVOC emissions and the canopy surface temperature averaged over the season were tested with a three-way mixed model ANOVA with snow addition, warming, and year as fixed factors, and block as a random factor. Snow still covered the snow addition side of the snow fences during the first measurement dates each year; and thus, only the ambient snow plots were measured on these dates, which were also excluded from the statistical analysis.

3. Results and Discussion

3.1. Difference Between Canopy Surface Temperature and Air Temperature

The highest canopy surface temperatures measured in the control and warmed plots were 32°C and 42°C, respectively. The canopy surface temperature in ambient conditions during BVOC measurements was 7.7 ± 0.9°C warmer than air temperature at 1.5 m height averaged for the period 14 June to 26 August 2014 (Figure 2, see also Figure S2 in the supporting information for continuous air temperature data). A similar temperature difference has been reported for Alaskan moist acidic tundra [Potosnak et al., 2013] which suggests...
that the canopy heating is a common arctic phenomenon. The maximum \( \Delta \) temperature in ambient conditions, 21.6°C, was measured on a clear-sky day (photosynthetic photon flux density, PPFD, 1590 \( \mu \)mol m\(^{-2}\) s\(^{-1}\)) in the beginning of the season (19 June). Heating of the tundra surface is strongly dependent on the slope inclination and solar radiation, and it vanishes under moderately thick clouds [Körner, 2003]. The warming treatment increased canopy surface temperature on average by 4°C (Figure 2). These results demonstrate the importance of warmer temperatures on the dark surface of the tundra and suggest that high canopy surface temperatures in these sparsely vegetated ecosystems play an important role driving BVOC emissions to higher rates than expected.

3.2. Effect of Warming on BVOC Emissions

Averaged across the two growing seasons, the total BVOC emissions were 280% higher in the warming treatment compared to nonwarmed plots (Figure 3, see Tables S2 and S3 in the supporting information for a list of compounds). This drastic response to a 4°C increase in canopy temperature highlights the sensitivity of BVOC emissions from the Arctic to increasing temperatures. This corresponds with the observed interannual difference in BVOC emissions and the response to warming (Figure 3), which is most likely due to the mean summer temperature being 3.2°C cooler in 2014 than in 2013 (see also Figure S4 in the supporting information for BVOC emissions over the two growing seasons).

The global estimated increase in emissions due to a 2–3°C warming is 30% [Peñuelas and Staudt, 2010], which is considerably less than the increase reported here. The strong emission response in the Arctic corresponds to the findings of Valolahti et al. [2015] who reported a twofold and fivefold increase in the emission of monoterpens and sesquiterpenes, respectively, in response to a 2–4°C warming of a subarctic wet heath. However, the results from the Subarctic [Valolahti et al., 2015] were partly explained by a warming-induced
increase in plants biomass developed over the 12–13 years of warming, a response which had not yet occurred in the present study. On the timescale of our experiment, the vegetation was not affected (Tables S1 in the supporting information for details on vegetation cover), and could not explain the large positive effect of warming on BVOC emissions. This was further supported by that the vegetation greenness (normalized difference vegetation index, NDVI) was unaffected by warming (Figure 4). Instead, both stimulated production and higher volatility and diffusion rates under the warmer temperatures may explain the increased BVOC emission rates. The soil moisture in the warming treatment was continuously lower than in the three other treatments, especially the second year (Figure S3 in the supporting information). The increase in BVOC emission rates caused by warming without snow addition in 2014 could, thus, be partly explained by potential drought stress. Exposure to drought stress has been shown to induce terpene emissions, especially those of isoprene and monoterpenes [Monson et al., 2007; Ormeño et al., 2007].

The effect of warming differed between groups of BVOCs (Figures 5 and S5 and S6 in the supporting information); the emissions of monoterpenes and sesquiterpenes were 5 and 3 times higher in warmed compared to
control plots, respectively, in the first year of measurements. In contrast, the emission of nonterpenoid compounds was not significantly affected by warming (Figure 5). Also, isoprene emission was unaffected by warming, mainly because snow addition counteracted the effect of warming (Figure 5). Isoprene emission was generally low compared to emissions from other high-latitude ecosystems [Lindwall et al., 2015; Schollert et al., 2014], due to the low cover of isoprene-emitting species, such as willow (Salix spp.; Table S1 in the supporting information) [Schollert et al., 2014; Vedel-Petersen et al., 2015].

3.3. Effect of Snow Addition on BVOC Emissions
During both winters, snow depth reached up to 140 cm in snow addition plots and 40 cm in ambient snow plots. The snow addition increased air temperature in the snow-covered plant canopy by 3.8°C in the period December–March and decreased the growing season soil temperature by 1.3°C at 2 cm depth (p < 0.01). The advancement of the growing season was delayed as suggested by the observed reduction in vegetation greenness (NDVI) throughout the season (Figure 4). No differences in the BVOC emissions were detected between snow addition and ambient snow plots after the first winter. However, after two winters, the BVOC emissions were 60% lower in the snow addition plots compared to ambient snow plots (Figure 3, see Figure S4 and Table S3 in the supporting information for statistics). This observed reduction in BVOC emissions may be explained by decreased soil temperature during the snow-free period, with a delayed growing season leading to lowered plant performance [Cooper et al., 2011]. Alternatively, the higher soil moisture in the snow addition treatment compared to ambient snow conditions (Figure S3 in supporting information) may have lessened a potential drought stress and stress-induced emissions.

Although our study showed lower BVOC emissions under increased snow cover, we expect that in the long term, the warmer soils insulated by the deeper snow during winter may increase the summer emissions due to enhanced microbial activity during late winter potentially leading to higher soil nutrient availability and increased plant growth during the growing season [Semenchuk et al., 2015].

4. Conclusions
The investigated ecosystem has sparse vegetation cover, similar to what has been reported for high arctic ecosystems [Arndal et al., 2009; Schollert et al., 2014] but considerably lower than that for subarctic ecosystems [Valolahti et al., 2015]. The cover and biomass of tall shrubs is predicted to increase in tundra areas in a future warmer climate [Elmendorf et al., 2012] which will boost the BVOC production and emissions [Rinnan et al., 2014; Valolahti et al., 2015], amplified by expected increases in air temperatures during the coming decades.

We report strong positive effects of experimental warming on BVOC emissions from whole ecosystem plots in the Arctic. The likely considerable increases in emissions in a warmer arctic climate will lead to a higher contribution by the Arctic to the global BVOC emissions than currently estimated [Sindelarova et al., 2014]. Our results showed a large increase especially in monoterpenes and sesquiterpenes emissions. Earlier studies have shown that both monoterpenes [Zhao et al., 2015] and sesquiterpenes [Griffin et al., 1999] form new particles in the atmosphere, creating a negative feedback to climate warming, due to their contribution to aerosol formation [Najafi et al., 2015; Paasonen et al., 2013]. However, an expected increased cloud cover over the Arctic [Eastman and Warren, 2010] may lessen the tundra surface heating and potentially counteract the effect of warming on BVOC emissions. Both monoterpenes and sesquiterpenes also lower the oxidative capacity of the atmosphere which can prolong the lifetime of methane [Perfuelas and Staudo, 2010; Shindell et al., 2009]. Thus, the increased terpene emissions should be considered when estimating impacts of BVOCs on the oxidative capacity of the troposphere and on aerosol formation, and the following positive or negative feedbacks to the global climate.

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Acknowledgments
We thank Villum Foundation (V/KR022589), the Danish Council for Independent Research | Natural Sciences (DFF-4002-00495 and DFF-0602-010718), and the Carlsberg Foundation for funding the project. The Danish National Research Foundation supported the activities within the Center for Permafrost (CENPERM DNRF100). We are grateful to the board and staff of the Arctic Station, University of Copenhagen for providing facilities, and we acknowledge DiskoBasis/Arctic Station for providing ecosystem data. We thank Esben V. Nielsen, Gosha Sylvestr, and Magnus Kramshøj for laboratory assistance. Guy Schurgers, Magnus Kramshøj, Ida Vedel-Petersen, Jing Tang, and Ylva Persson offered valuable comments on the manuscript. Data are provided in the supporting information.


