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Biogenic volatile organic compound emissions along a high arctic soil moisture gradient

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HIGHLIGHTS

- Biogenic volatile organic compound (BVOC) emissions from the Arctic are poorly understood
- We assessed BVOC emissions over a soil moisture gradient in the High Arctic
- BVOC measurements were coupled with CO2 exchange, vegetation and soil analyses
- BVOC emissions were dependent on the vegetation composition controlled by soil moisture

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ABSTRACT

Emissions of biogenic volatile organic compounds (BVOCs) from terrestrial ecosystems are important for the atmospheric chemistry and the formation of secondary organic aerosols, and may therefore influence the climate. Global warming is predicted to change patterns in precipitation and plant species compositions, especially in arctic regions where the temperature increase will be most pronounced. These changes are potentially highly important for the BVOC emissions but studies investigating the effects are lacking. The aim of this study was to investigate the quality and quantity of BVOC emissions from a high arctic soil moisture gradient extending from dry tundra to a wet fen. Ecosystem BVOC emissions were sampled five times in the July-August period using a push-pull enclosure technique, and BVOCs trapped in absorbent cartridges were analyzed using gas chromatography–mass spectrometry. Plant species compositions were estimated using the point intercept method. In order to take into account important underlying ecosystem processes, gross ecosystem production, ecosystem respiration and net ecosystem production were measured in connection with chamber-based BVOC measurements. Highest emissions of BVOCs were found from vegetation communities dominated by *Salix arctica* and *Cassiope tetragona*, which had emission profiles dominated by isoprene and monoterpenes, respectively. These results show that emissions of BVOCs are highly dependent on the plant cover supported by the varying soil moisture, suggesting that high arctic BVOC emissions may affect the climate differently if soil water content and plant cover change.

1. Introduction

Emissions of climate-relevant trace gases, biogenic volatile organic compounds (BVOCs), from high latitude ecosystems are more temperature sensitive than emissions from ecosystems at lower latitudes (See Faubert et al., 2010a for details). Global models of BVOC emissions estimate the emissions from the Arctic to be low (Guenther et al., 2006; Sindelarova et al., 2014). However, to date, only two studies have reported field measured BVOC emissions from the High Arctic (Schollert et al., 2014; Lindwall et al., 2015). These two studies focus on dry ecosystems, and both report significant BVOC emissions, with rates comparable to the Subarctic. Even though valuable data were reported, we still have limited understanding about BVOC emissions from different vegetation types in the High Arctic. The BVOC emission rates and blends from an ecosystem are strongly linked to plant species composition (Kesselmeier and Staudt, 1999), phenology (Peñuelas et al., 2009) and climate (Peñuelas and Staudt, 2010). Climate models predict that the global warming will be most pronounced in the arctic regions with a mean annual warming between 2.2 and 2.4 times the global average by the year 2100 (IPCC, 2013). This might be important for ecosystem BVOC emissions, which are exponentially increased by increasing temperature (Kesselmeier and Staudt, 1999; Peñuelas and Llusia, 2001). Furthermore, a warmer climate will increase arctic plant biomass, the length of the growing season and cause changes in plant

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species composition (Walker et al., 2006; Peñuelas and Staudt, 2010; Elmendorf et al., 2014). For instance, temperature driven expansions of shrubs in arctic areas have already occurred (Sturm et al., 2001; Jia et al., 2003), and further environmental and biotic changes will affect the BVOC emissions (Rinnan et al., 2014; Valolahti et al., 2015).

Moreover, climate warming is likely to cause changes in soil moisture which, in turn, might influence both plant species cover and biomass, and the distribution of high arctic vegetation types (Walker, 2000; Virtanen et al., 2006; le Roux et al., 2013). Since BVOC emissions are strongly influenced both by the effect of available soil water and the plant species composition (Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009; Insam and Seewald, 2010; Peñuelas and Staudt, 2010) it is very likely that changes in soil moisture will affect the BVOC emissions. The soil moisture is affected by the amount of precipitation, which is expected to increase in the future. On the other hand, warming would also increase evapotranspiration. Furthermore, snow melt water supplies moisture to the arctic soil in the spring, and the amount is dependent on winter precipitation. Thus, future soil moisture content is hard to predict (IPCC, 2013).

A wide range of BVOCs are released from plants and soil to the atmosphere. Global BVOC emissions from terrestrial ecosystems are estimated to be 700 - 1500 Tg C per year (Peñuelas and Llusia, 2001; Laothawornkitkul et al., 2009; Guenther et al., 2012; Sindelarova et al., 2014). Terpenoids, including for example isoprene (C_5), monoterpenes (C_{10}) and sesquiterpenes (C_{15}) is an important group of BVOCs released from plants. In fact, isoprene is by far the single most abundant BVOC with estimated global emissions of 412 – 601 Tg C (Guenther et al., 1995; Laothawornkitkul et al., 2009). Non-terpenoid BVOCs emitted from terrestrial ecosystems include a range of alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids (Kesselmeier and Staudt, 1999; Peñuelas and Llusia, 2001).

Emissions of BVOCs serve many functions. For instance, BVOCs are involved in plant defense, reproduction, growth and protection against stresses (Kesselmeier and Staudt, 1999; Pichersky and Gershenzon, 2002; Laothawornkitkul et al., 2009). When emitted, BVOCs affect the chemistry in the atmosphere and therefore also the climate. For instance, BVOCs can prolong the lifetime of methane by reacting with OH radicals that could otherwise have oxidized methane (Laothawornkitkul et al., 2009). Depending on the atmospheric concentration of nitrogen oxides, BVOCs can also either increase or decrease the concentration of ozone in the troposphere (Chameides et al., 1988; Kesselmeier and Staudt, 1999; Laothawornkitkul et al., 2009; Peñuelas and Staudt, 2010).

In addition to their impact on the gas phase chemistry in the atmospheric, oxidized BVOCs have rather low vapor pressure compared to the primary compounds and may condensate to form secondary organic aerosols (SOA). Aerosols can impact the climate and plant life directly by scattering solar radiation (Fehsenfeld et al., 1992; Fuentes et al., 2000; Peñuelas and Staudt, 2010) or indirectly by acting as cloud condensation nuclei which also affects the Earth's radiative balance (Laothawornkitkul et al., 2009).

Therefore, even though it is clear that BVOCs have an impact on the climate, little is known about the emission rates and blends in the Arctic, an area which undergoes rapid climate changes. Never before have BVOC emission rates been measured from high arctic ecosystems, except for in dry heaths (Schollert et al., 2014; Lindwall et al., 2015). Hence, the aim of this study was to investigate the quality and quantity of BVOC emissions from a high arctic soil moisture gradient extending from dry tundra to a wet fen, and to investigate what factors were driving BVOC emissions. The variation in soil moisture supported a number of different dominant plant species from cushion-forming *Dryas octopetala* inhabiting well-drained areas, dwarf shrub heaths with *Cassiope tetragona*, *Salix arctica*, to grasses and sedges typical for arctic wetlands. *In situ* BVOC measurements were coupled with measurements of CO_2 exchange and environmental variables such as soil moisture and temperature, air temperature and light intensity.

2. Materials and methods

2.1. Site description and experimental set-up

The study was conducted in the high arctic Zackenberg valley, NE Greenland (74°30′N, 20°30′W) over the summer and early autumn 2013. Mean annual temperature 2 m above terrain is -9.1 °C (2003 – 2013) and annual accumulated precipitation is approximately 205 mm (Mylius et al., 2014). Mean temperatures 2 m above terrain and total precipitation were 7.2 °C and 7 mm for July and 5.4 °C and 76mm for August. The duration of the growing season is 64 – 113 days depending on the vegetation type (Ellebjerg et al., 2008).

In the late growing season 2012 aluminum chamber bases (22 cm x 22 cm) were installed into the soil, to a depth of approximately 10 cm, as a transect on a north facing slope. The chamber bases were installed in seven different positions covering different vegetation types down the 40 m long slope (see Supplementary Fig. S1), with increasing soil moisture content from the top (position 1) towards the bottom (position 7). Each position had three replicate chamber bases with a distance of approximately 1-5 m.

The percentage cover of vascular plant species, mosses, lichens, litter, organic crust and bare soil within each plot was estimated on 17 August using the non-destructive point intercept method (Jonasson, 1988).

2.2. Sampling of BVOCs

BVOC emissions were measured five times during July and August, by placing a transparent polycarbonate chamber with a thickness of 1.5 mm and a height of 20 cm on top of the chamber base. In order to ensure an airtight chamber headspace, a groove of the chamber base was filled with water. Prior to the BVOC measurements the chamber was flushed with air free from particles, BVOCs and ozone for a period of 10 min at a rate of 1000 ml min^{-1}. A charcoal filter removed particles and BVOCs and a MnO_2 scrubber removed ozone (Ortega and Helmig, 2008). During BVOC measurements the inlet air flow was set to 200 ml min^{-1}. The outflow air was drawn through a stainless steel tube filled with 150 mg Tenax TA and 200 mg Carbograph 1 TD (Markes International Limited, Llantrisant, UK) at a rate of 200 ml min^{-1} for 30 min, representing a sampled air volume of 6 L. During the flushing and measurement, a fan circulated the air inside the chamber. After the BVOC sampling the adsorbent tube was sealed with a Teflon coated brass cap and brought to the University of Copenhagen for analysis. Between samplings the chamber was wiped with paper towels to remove condensed water and possible BVOCs sticking to the chamber surface. Blank samples were collected by conducting BVOC measurements on chamber bases covered with a pre-cleaned polyethylene terephthalate (PET) film. Several factors bring uncertainty to BVOC measurements using an enclosure technique. These include changes in environmental conditions (e.g., temperature, relative humidity and light), lack of turbulent mixing by wind and potential decrease in CO_2 and buildup of BVOC concentrations (Ortega and Helmig, 2008).

2.3. Measurements of environmental variables

During BVOC measurements chamber air temperatures and relative humidity were measured every minute using shaded Ibuttons (i-Wire Hygrochron, Maxim Intergrated, San Jose, USA) and ambient photosynthetic photon flux density (PPFD) was monitored using S-LIA-M003 PAR sensors coupled to a HOBO micro station data logger (H21-002 Onset computers corporation, Boston). Soil moisture was measured using Theta probe (Delta-T Devices, United Kingdom) and soil temperature was measured with a hand held digital thermometer at a depth of 2 cm in four places adjacent to the chamber bases.