Herbivore-shrub interactions influence ecosystem respiration and BVOC composition in the subarctic

Cole G. Brachmann[1,2], Tage Vowles[2,3], Riikka Rinnan[4,5], Mats P. Björkman[1,2], Anna Ekberg[6], and Robert G. Björk[1,2]

5 1Department of Earth Sciences, University of Gothenburg, Gothenburg, Sweden

2Gothenburg Global Biodiversity Centre, Gothenburg, Sweden

3IVL Swedish Environmental Research Institute, Gothenburg, Sweden

4Terrestrial Ecology Section, Department of Biology, University of Copenhagen, Copenhagen, Denmark

5Center for Permafrost (CENPERM), Department of Geosciences and Natural Resource Management, University of Copenhagen, Copenhagen, Denmark

10 6Centre for Environmental and Climate Research, Lund University, Lund, Sweden

Correspondence to: Cole G. Brachmann (cole.brachmann@gu.se)

Abstract. Arctic ecosystems are warming nearly four times faster than the global average which is resulting in plant community shifts and subsequent changes in biogeochemical processes such as gaseous fluxes. Additionally, herbivores shape plant communities and thereby alter the magnitude and composition of ecosystem respiration

15 and BVOC emissions. Here we determine the effect of large mammalian herbivores on ecosystem respiration and BVOC emissions in two southern and two northern sites in Sweden, encompassing mountain birch (LOMB) and shrub heath (LORI) communities in the south and low-herb meadow (RIGA) and shrub heath (RIRI) communities in the north. Herbivory significantly decreased ecosystem respiration at RIGA and altered the BVOC composition between sites. However, plant community composition had a larger effect on ecosystem respiration as RIGA had

20 35% higher emissions than the next highest emitting site (LOMB). Additionally, LOMB had the highest emissions of terpenes with the northern sites having significantly lower emissions. Differences between sites were primarily due to differences in exclosure effects, soil temperature and prevalence of different shrub growth forms. Our results suggest that herbivory has a significant effect on trace gas fluxes in a productive meadow community and differences between communities may be driven by differences in shrub composition.

25 **1 Introduction**

Arctic ecosystems are particularly susceptible to climate change effects as the rate of warming is nearly four times that of temperate regions (Rantanen et al., 2022). This leads to climate driven vegetation shifts in tundra

environments that will have associated repercussions on soil greenhouse gas (GHG), and other trace gas, fluxes (Virkkala et al., 2018), which are important environmental properties as they feedback directly to the climate.

30   Plant communities largely determine the production and consumption of trace gases through photosynthesis and respiration, production of secondary compounds (such as biogenic volatile organic compounds: BVOCs), and regulation of the microbial community (Ward et al., 2013). The plant species composition of a community then influences the magnitude of the trace gas fluxes (such as CO_2) and the composition and quantity of the BVOC species released. CO_2 is the primary GHG responsible for climate warming and its release (ecosystem respiration;

35   ER) and uptake (gross primary production; GPP) from plants and soils in the Arctic is crucial, as Arctic soils store approximately 50% of the global terrestrial belowground carbon (Mishra et al., 2021; Hugelius et al., 2014, 2013; Sistla et al., 2013). ER is one of the largest contributors to CO_2 emissions globally (Liu et al., 2022; Sharkhuu et al., 2016) and is predicted to be increasingly vital to the CO_2 balance of northern regions as it is driven by vegetation change, productivity and microbial activity (Liu et al., 2022; Parker et al., 2015). BVOC emissions,

40   which are chemicals produced by plants for a variety of purposes including reproductive signalling, communication, and herbivore deterrence (Peñuelas and Staudt, 2010), although predicted to be driven directly by temperature change in high latitude communities (Rinnan et al., 2020), are also determined by plant community structure in terms of the magnitude and composition of these emissions. BVOCs play a role in climate warming primarily through their interaction with ozone, effects on the lifetime of methane in the atmosphere, and the

45   formation of secondary organic aerosols (Boy et al., 2022; Calfapietra et al., 2013; Peñuelas and Staudt, 2010). Thus, influences of vegetation changes on ER and BVOC emissions can impact the feedback effects on climate change potentially exacerbating or mediating its effects, with implications regionally and globally (Peñuelas and Staudt, 2010; Heimann and Reichstein, 2008).

The magnitude of ER differs between plant communities within the forest-tundra ecotone (Treat et al., 2018).

50   Subarctic birch forest, composed of mountain birch trees and deciduous shrubs primarily, have larger ER compared to tundra heath and meadow communities due to the high contribution from woody deciduous vegetation and stimulation of microbial communities through litter and mycorrhizal inputs to the soil (Virkkala et al., 2021; Strimbeck et al., 2019; Parker et al., 2015). Heath communities have been found to have the lowest ER from these community types attributed to the relatively slow decomposition of organic matter in the soil (Sørensen

55   et al., 2018; Parker et al., 2015). Concomitantly, the shift to ectomycorrhizae-dominated communities coincides with increased ER as they more effectively scavenge organic carbon and contribute to higher productivity (Parker et al., 2015). Shifts in plant community composition due to climate change have been well documented in tundra ecosystems (Bjorkman et al., 2020; Elmendorf et al., 2012), and have subsequent effects on ER (Virkkala et al.,

2018). Increases in vegetation biomass in tundra could increase the magnitude of BVOC fluxes (Rinnan et al.,

60   2011), however, vegetation composition changes will likely have a stronger effect on the composition of BVOCs emitted as the composition of VOCs emitted are plant species-specific (Peñuelas and Staudt, 2010). Therefore, changes in plant communities most likely will have a large effect on ER and BVOC emissions.

Herbivores can act to either enhance or mediate changes in vegetation communities through selective foraging and nutrient input (Ylänne et al., 2020; Barthelemy et al., 2018; Vowles et al., 2017b; Olofsson et al., 2009). Both

65   selective foraging and nutrient addition can have large impacts on the plant community by shifting the competitive advantage of certain species and stimulating microbial activity (Bardgett and Wardle, 2003; Olofsson et al., 2002). Herbivory likely influences soil gaseous fluxes indirectly through altering the trajectory of vegetation community changes (Metcalfe and Olofsson, 2015; Cahoon et al., 2012). Therefore, by changing the plant community in an area, herbivores can influence the magnitude and direction of both ER and BVOC fluxes (Vowles and Björk,

70   2019). However, studies assessing the consequences of large herbivore grazing on ER and BVOC fluxes are lacking in tundra ecosystems and are important for a broader understanding of feedback mechanisms in the Arctic (Vowles and Björk, 2019; Köster et al., 2018; Ylänne et al., 2015; Metcalfe and Olofsson, 2015; Cahoon et al., 2012).

Thus, here we investigate the role of herbivory in regulating ER and BVOC fluxes through interactions with

75   vegetation communities in Swedish montane and tundra habitats. If herbivory is a driver of these fluxes, we predicted that excluding herbivores would increase ER and alter BVOC composition by shifting the plant community to one more dominated by deciduous shrubs. Therefore, we hypothesize that differences between plant communities, in terms of dominance of functional types, soil characteristics and climate properties, would be the strongest predictor of trace gas fluxes, regardless of the presence of herbivory. This paper aims to address two

80   main questions: (1) How do vegetation shifts indirectly caused by large herbivore exclusion affect the magnitude of ER and composition of BVOC fluxes? (2) Are these effects consistent among different vegetation communities?

2 Methods

2.1 Study sites

85   The study was conducted at four sites within the Swedish Scandes, two in the south and two in the north of the mountain range, from June 2013 to June 2014 (Fig. 1). These sites encompassed three distinct community types: birch forest, shrub heath, and low-herb meadow. The southern sites included the birch forest and a shrub heath

community, and the northern sites contained the low herb meadow and a second shrub heath community. The southern sites are referred to as: Långfjället mountain birch forest (LOMB hereafter; 62°03'59"N, 12°14'56"E;

90 809 m a.s.l.) and Långfjället shrub heath (LORI hereafter; 62°06'53"N, 12°16'30"E; 853 m a.s.l.), located approximately 5 km apart near Grövelsjön in the county of Dalarna. The Northern sites are referred to as: Ritsem shrub heath (RIRI hereafter; 67°46'33"N, 17°32'22"E; 847 m a.s.l.) and Ritsem low herb meadow (RIGA hereafter; 67°49'35"N, 17°43'02"E; 719 m a.s.l.), located approximately 10 km apart near Ritsem, Norrbotten County. The primary large mammalian herbivore in our sites is reindeer (Rangifer tarandus tarandus) which had

95 tentative density estimates of 2.8 reindeer per km2 near Långfjället and 2.2 reindeer per km2 near RIGA and 1.4 reindeer per km2 near RIRI previously reported for the three Sami herding villages nearest our sites (Vowles et al., 2017b, a). Långfjället is in an area with slightly higher reindeer density than RIGA or RIRI although the exact difference shifts slightly over time, and RIGA and RIRI are located in adjacent Sami villages. Moose (Alces alces) are another large herbivore that could be present at all of the study sites, with potential instances of roe deer

100 (Capreolus capreolus) at LOMB. The moose populations are similar for the management areas in which our sites are located, and both have a density of approximately 1-2 moose per 1000 ha over the study period according to county board hunting statistics (SCAB Statistik Älgdata accessed 2022).
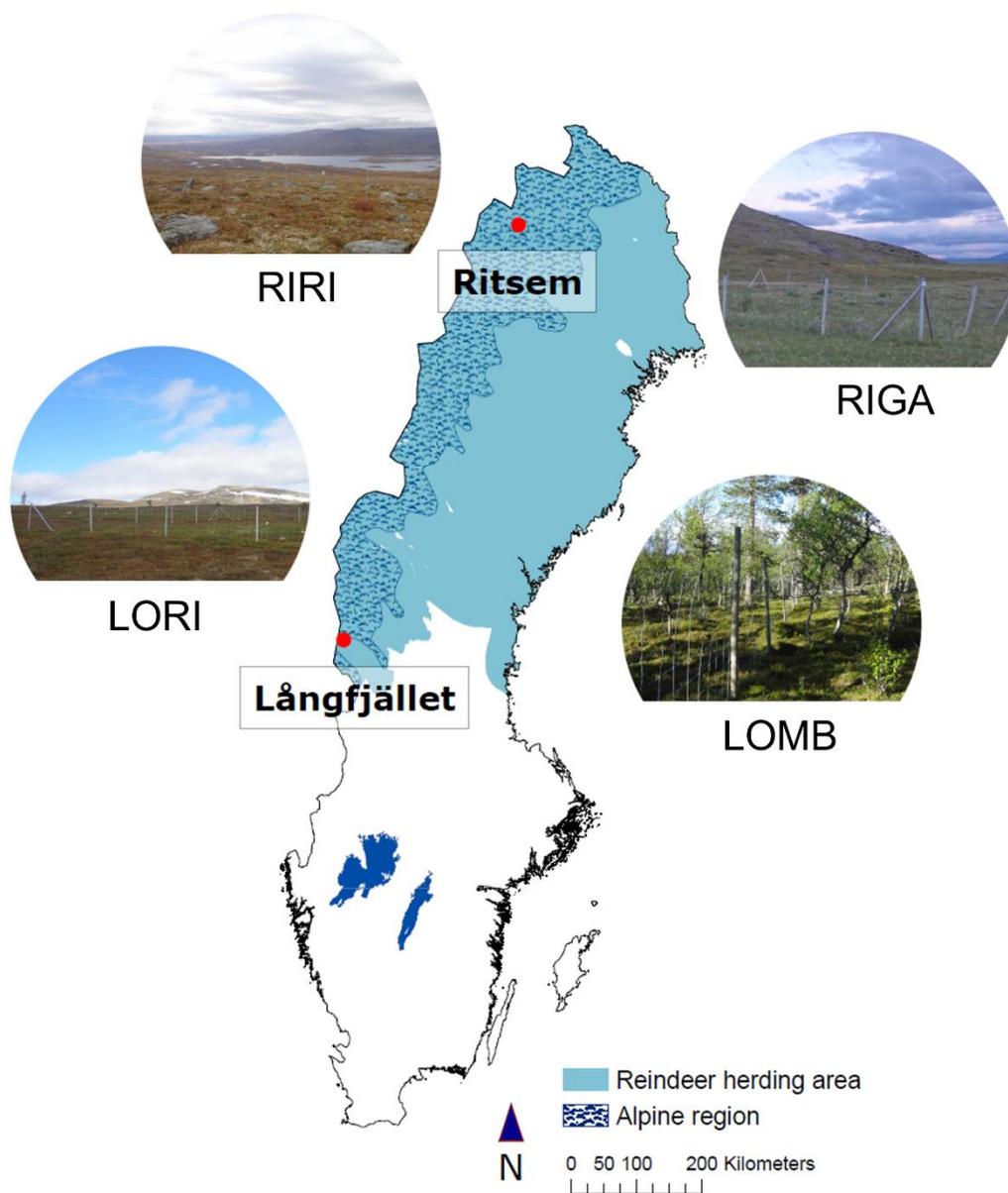
Fig. 1. Map of study sites and communities with overlay of reindeer herding area and alpine regions in Sweden. Photo credits: Tage Vowles.

The climate conditions at each site have been previously described (Vowles et al., 2017b, a). LOMB had an average temperature of 2.8 °C during the study period measured by temperatures loggers installed at each site.

Biogeosciences
Discussions

LORI mean temperature was 2.8 °C during the study period. The average annual precipitation from 1961-1990 was 697 mm according to the nearest SMHI weather station at Grövelsjön (Vowles et al., 2017b). RIGA mean

110 temperature was 0.9 °C and RIRI was -0.3 °C. The Ritsem sites had an average annual precipitation of 510 mm between 1961 and 1990 according to the nearest SMHI weather station (Vowles et al., 2017b). The vegetation communities at each of the four sites has been previously described in detail (Vowles et al., 2017b, a). LOMB contains a tree layer almost entirely of *Betula pubescens ssp. tortuosa*, with a field layer containing dwarf shrubs: *Empetrum nigrum*, *Vaccinium myrtillus* and Vaccinium vitis-idaea, graminoids: *Deschampsia flexuosa* and

115 *Nardus stricta*, and forbs: *Melanpyrum pratense* and *Solidago virgaurea*. LORI is composed mostly of dwarf shrubs, mainly*: E. nigrum*, *V. myrtillus*, *V. vitis-idaea*, *Calluna vulgaris* and *Betula nana*. This site also contains some limited graminoids, primarily *D. flexuosa*. RIRI contains the same species as previously mentioned plus additional graminoid and forb species as the bedrock is calcareous providing more nutrients into the soil. The predominant additional graminoids are *Calamagrostis lapponica* and *Carex bigelowii*, and the additional forbs

120 are *Bistorta vivipara* and *Hieracium sect. Alpina*. Finally, RIGA is primarily composed of shrubs: *B. nana*, and Salix sp., graminoids: *Deschampsia cespitosa*, *D. flexuosa*, and *Carex aquatilis*, and forbs: *Viola biflora*, *Thalictrum alpinum* and *Saussurea alpina*.

Table 1. Site characteristics for each location used in the study. Mean air temperature, soil temperature, soil moisture, NH$_4^+$ and NO$_3^-$ are reported for the duration of the study period; June 2013 - June 2014. Mean precipitation is reported
125 **from 1961-1990 according to the nearest SMHI weather station to each of the sites, which is Grövelsjön for LOMB and LORI, and Ritsem for RIGA and RIRI.**

Site	Mean Air Temperature (°C)	Mean Precipitation (mm)	Soil Temperature (°C)	Soil Moisture (%)	NH$_4^+$ (µg 10 cm^{-2} burial length^{-1})	NO$_3^-$ (µg 10 cm^{-2} burial length^{-1})
LOMB	2.8	697	11.5	19.9	14.62	3.45
LORI	2.8	697	11.6	28.9	34.52	1.75
RIGA	0.9	510	11.3	78.7	4.02	3.25
RIRI	-0.3	510	10.8	38.6	7.30	1.95

The effect of herbivory on ER and BVOC fluxes was determined using herbivore exclosure fences. The fences (25 x 25 m) were installed at each site in 1995 and are composed of wire mesh 1.7 m high that functions to exclude

130 reindeer and other large mammalian herbivores from accessing the sites (Vowles et al., 2017b, a). By preventing access to a site, exclosure fences allow for an estimation of the effect of large mammal herbivory by comparing to ambient conditions in pairwise 25 x 25 m plots without fences. In RIGA only two of the three originally

established ambient plots could be located and so a new ambient plot was established in 2012 (Vowles et al., 2017a).

135 **2.2 Ecosystem respiration**

ER during the growing season was measured using a closed-chamber technique (Björkman et al., 2010a). Three permanent PVC soil collars (10 cm diameter) were inserted at random locations within the central area of each plot, at least 1 m from the edge. An opaque chamber was sealed onto the collar during measurements where air from the headspace was circulated into 20 ml sample vials over 30 s using an electric pump (flow rate 0.5L/min).

140 Samples were obtained at 3, 6, 10, 30, and 50 minutes after the chamber was sealed onto the collar. The samples were analyzed for CO_2 concentration using gas chromatography (Agilent 7890A GC coupled to an Isoprime GC 5 interface and an Isoprime 100 IRMS, Aglient Technologies, Santa Clara, U.S.) and fluxes estimated as a linear change in CO_2 concentration over time.

Winter ER was estimated during the snow-covered period at the LORI and LOMB sites based on Fick´s first law

145 on diffusion (Pirk et al., 2016; Björkman et al., 2010b; Sommerfeld et al., 1993). Air samples were withdrawn from the snowpack (at every 10 cm) using a gas-tight syringe fitted to 1/6" stainless steel tubings attached to an avalanche probe inserted into the snow above each flux collar. The air samples were then transferred to headspace vials for storage until analysed by gas chromatography. After air sampling, snow density, snow temperature and snow profile characteristics were collected from adjacent snowpack (to avoid disruption of the snowpack at the

150 sampling location) to be used in the flux calculations (see Björkman et al., 2010b for further details).

Q10-values for each of the collars for the growing season (RIRI and RIGA) and for the full year (LORI and LOMB) were estimated based on the Arrhenius equation, by plotting the natural logarithm of the CO_2 emissions against the measured soil temperature (in 1000/K) as outlined in Davidson and Janssens (2006). Furthermore, to enable a direct comparison between the sites, an interpolation approach (Björkman et al., 2010a) was used for the

155 growing season data where data was first interpolated between two conjuncting measurements to generate a flux per day and summed up as cumulative count of emissions during July 02 - September 02 (2013).

2.3 BVOC emissions

BVOC fluxes were measured twice for each site during the growing season (sampling dates can be found in Table S1) using transparent teflon chambers fitted to the soil collars. The chamber was placed onto the soil collar at the

160 time of measurement with a temperature logger connected to the chamber to record temperature throughout the measurement. A pump was used to circulate air from the chamber through stainless steel adsorbent cartridges

containing 150 mg Tenax TA and 200 mg Carbograph 1TD (Markes International Limited) at 200 ml min-1 and then back into the chamber for a through-flow measurement of BVOCs over 20 minutes. At the end of the measurement, the collected air sample volume was recorded to calculate the BVOC flux. The adsorbent cartridges

165   were analyzed using gas chromatography-mass spectrometry following thermal desorption (Clarus 500, PerkinElmer, Waltham, MA, USA; Ekberg et al., 2009). The obtained chromatograms were analyzed using PARADISe software (Johnsen et al., 2017) and the compounds identified by matching with the NIST mass spectral library. Terpene compounds were quantified by comparing to standards where pure standards were used for identification and quantification of α-pinene, β-pinene, 3-carene, limonene, eucalyptol and caryophyllene,

170   while for all other monoterpenes and sesquiterpenes, α -pinene and caryophyllene were used for quantification, respectively. Mean terpene emissions are detailed for each site and treatment in Table S2. BVOC emission rates were calculated for monoterpenes (MT) and sesquiterpenes (SQT), while the NIST-identified dataset with peak areas of all other compounds was used to describe the chemical composition of the emitted BVOC blend.

2.4 Vegetation assessments

175   The vegetation was measured in each plot using twenty 1 m2 subplots within which cover of each species was visually estimated (Vowles et al., 2017b). All subplots were located within a 22 x 22 m area to reduce edge effects from influencing the estimations. The total cover estimates were allowed to go beyond 100% as individuals may go beyond the range of the subplot and to account for overlapping layers of vegetation. All identified species were grouped into growth form categories to use in an ordination analysis. The growth forms are deciduous prostrate

180   dwarf shrub, deciduous semi-prostrate dwarf shrub, deciduous tall shrub, evergreen prostrate dwarf shrub, evergreen semi-prostrate dwarf shrub, evergreen tall shrub, forb, graminoid, non-vascular species, and other which encompasses the percent ground cover attributable to abiotic and bare ground components. The vegetation within the chamber is not necessarily 1:1 with the surrounding vegetation surveyed, but we proceed on the assumption that the chamber takes a representative subsample of the vegetation or that the measured fluxes can be tied to the

185   prevalence of vegetation types in the fence/ambient plot.

2.5 Abiotic conditions

Temperature loggers (Tinytag plus 2 TGP-4020; Gemini Data Loggers, Chichester, UK) were placed in the centre of each plot which measured hourly soil temperatures at 2 cm depth for the duration of the experiment. From the temperature data, thawing degree-days (TDD), which is the sum of all mean daily temperatures above 0°C, were

190 calculated from the soil temperature data according to Molau and Mølgaard (1996) for the period that the chambers were in the ground.

Air temperature was also recorded hourly by one logger (Tinytag plus 2 TGP-4500; Gemini Data Loggers, Chichester, UK) at each site, at a height of approximately 2 m (Table S3). Mean temperatures were calculated from the loggers at each site for the experimental period. In order to obtain a mean temperature for a whole year,

195 site means were calculated from June 12, 2013 – June 11, 2014 at the Långfjället sites and from June 27, 2013 – June 26, 2014 at the Ritsem sites. Minor gaps (no more than seven days) in the temperature series caused by malfunctioning loggers were filled in using linear regression against the logger which gave the highest R2-value. Soil moisture was measured from the top 6 cm on the same sampling dates as ER using a Delta ML2x Theta probe (Delta-T Devices Ltd, Cambridge, U.K.). Moisture was measured as % water content in the soil (Figure S2).

200 Plant Root Simulator (PRS®) Probes (Western Ag Innovations, Inc., Saskatoon, Canada), which contain ion exchange resin membranes, were used to measure soil NO_3^- and NH_4^+ availability in situ at each plot. Four cation and four anion probes were installed to 10 cm depth, close to the centre of each plot, at the beginning of the experimental period. Before the winter season, the original probes were removed and replaced with a new set of probes, which were then removed at the end of the experiment. After removal, the probes were cleaned and sent

205 to Western Ag Innovations in Saskatoon, Canada, for ion extraction and analysis.

2.6 Statistical analyses

All statistical analyses were carried out with R statistical software version 4.2.1 (Team, 2022). A mixed effects model was used to explore differences in CO_2 flux between exclosures and ambient plots, with treatment, date, site and soil temperature as fixed factors and plot as random factor using the nlme package (Pinheiro et al., 2015).

210 Soil moisture was also tested but left out of the final model after stepwise reduction. Additionally, a rational quadratic correlation structure was included in the model to account for temporal correlation between measurements (Kravchenko and Robertson, 2015). Several correlation structures were tested (including autoregressive, linear, exponential, Gaussian and spherical) and the Akaike information criterion was used to select the best fitting structure. The lsmeans package (Lenth, 2016) was used to test for treatment effects at

215 individual sites, using pairwise t-tests with Bonferroni P-value adjustments. Model parameters were evaluated with a mixed model analysis of variance (ANOVA) for significance.

The differences in MT and SQT emissions from each site and treatment were evaluated using linear mixed effects models using the lme4 package (Bates et al., 2015) on log transformed data, where the best performing model for MT data included site and treatment as fixed effects with plot and date as random effects, and the best performing

220   model for SQT data included site, treatment and soil temperature as fixed effects with plot and date included as random effects. The use of these models for categorical data as opposed to an ANOVA is the specification of plot and date as random effects allowing them to be explicitly accounted for in the model. A linear mixed model was used to follow up on β-pinene differences using site and treatment as fixed effects, and plot and date as random effects. The differences in BVOC composition from each measurement was evaluated using a redundancy analysis

225   (RDA) ordination using the vegan package (Oksanen et al., 2019) on Hellinger transformed total BVOC compound data. As a constrained ordination RDA also allows for determination of the relationships between the measurements and environmental variables (treatment, soil temperature, percent cover of vegetation growth forms in the surrounding area, NH_4^+ and NO_3^-) which were confirmed through an accompanying ANOVA on the RDA output. The interaction between herbivory and the shrub types was also evaluated through RDA and subsequent

230   ANOVA. 85% Confidence ellipses were drawn for each group within the RDA as they have been shown to have a good fit with data without being too conservative as estimates (Payton et al., 2003, 2000). All analyses utilized an alpha of 0.05 for significance where appropriate.

3 Results

3.1 Ecosystem respiration

235   Growing season respiration varied between sites with RIGA having the highest average ER (215 ± 19 mg CO_2 m-2 h-1), which was 35% higher than LOMB (159 ± 17 mg CO_2 m-2 h-1), and about three times higher than both shrub heath sites (83 ± 7 and 58 ± 8 mg CO_2 m-2 h-1; at Ritsem and Långfjället respectively). Significant growing-season Arrhenius relationships were only found at the RIGA ($Q10 = 3.0\pm0.2$ and 2.8 ± 1.0, fences and ambient respectively) and RIRI ($Q10 = 4.4\pm2.7$ and 11.3 ± 4.2, fences and ambient respectively) sites (Fig. 2). Annual

240   Arrhenius relationships (but not with growing season data alone) was found significant for most LOMB plots ($Q10 = 33.1\pm17.5$ and 18.0 ± 9.4, fences and ambient respectively) and LORI ($Q10 = 8.0\pm3.6$ and 5.5 ± 1.1, fences and ambient respectively), although the predictiveness for the growing season was not sufficient for the LOMB site (Fig. 2). Timepoint interpolated data over the growing season was instead used for site comparisons (Fig. 3).

10
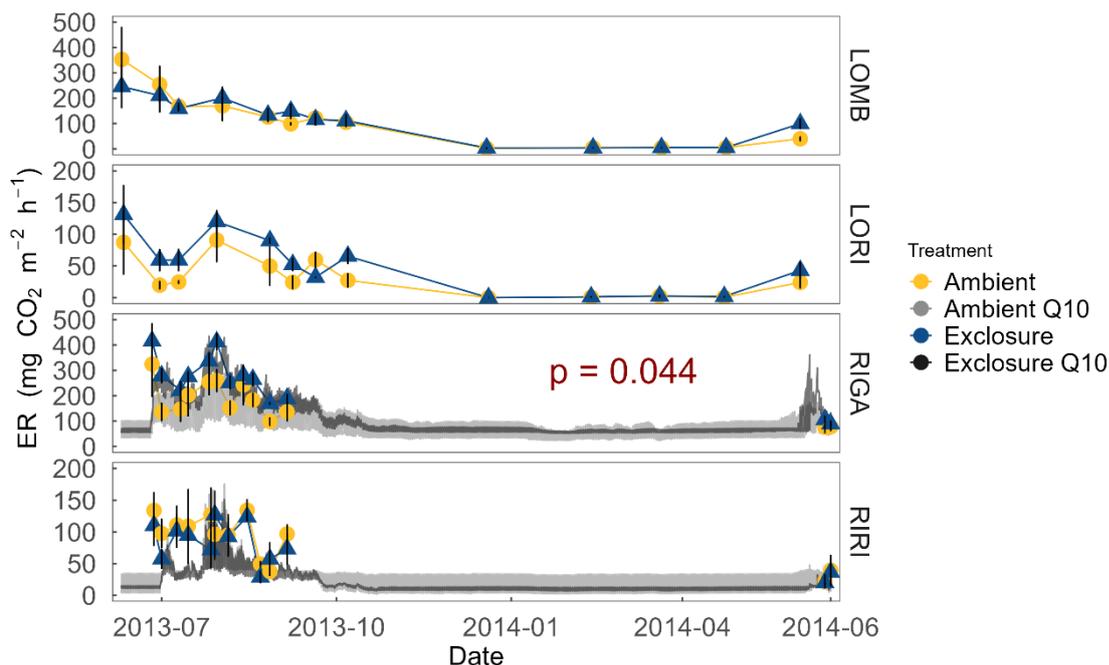
Fig. 2. ER at each site measured year-round from July 2013 to July 2014. ER was not measured over-winter in the Ritsem sites. Interpolated ER using associated Q_{10}-values is also plotted for sites with a significant Arrhenius relationship ($\alpha = 0.05$) as an estimate of ER on a shorter temporal scale. Exclosure and ambient treatments were not significantly different, except in RIGA where exclosures consistently had higher ER during the growing season. Error bars denote standard error of the mean.
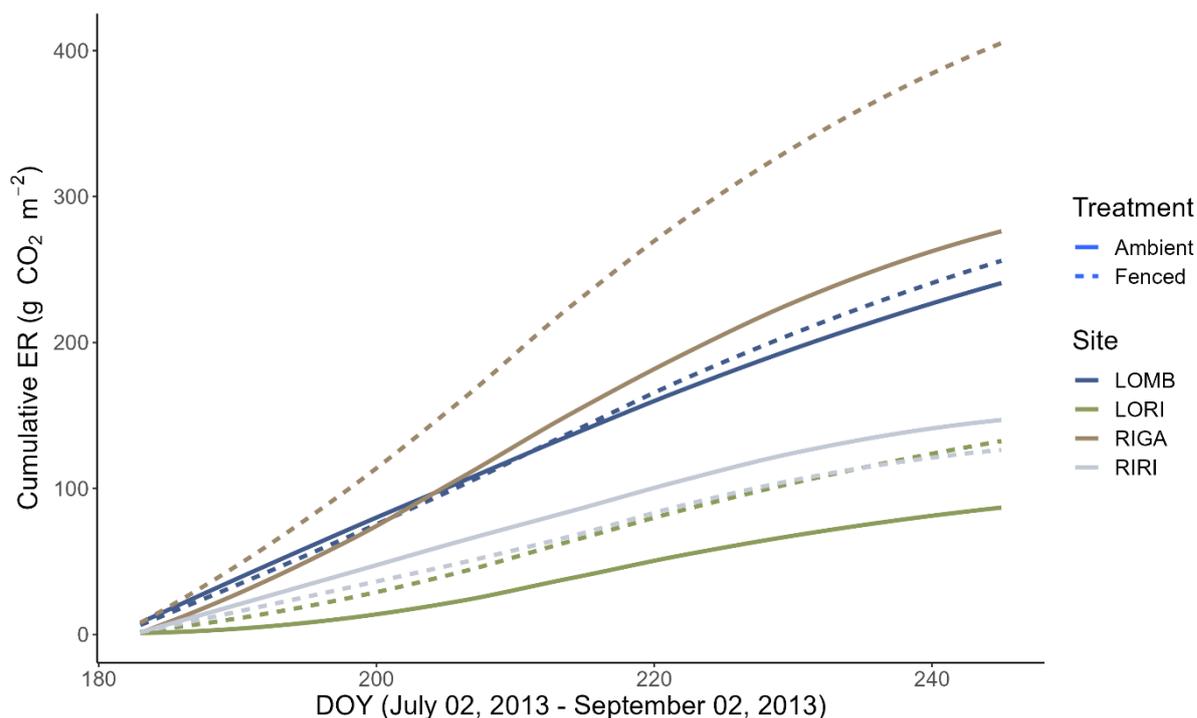
250

Fig. 3. Cumulative ER between July 02 - September 02, 2013, in all four sites separated by treatment. The cumulative fluxes were calculated from interpolated fluxes that estimate the daily ER between measurement days using the slope and intercept values of the measured fluxes. Three of the sites had higher cumulative ER in the fenced plots compared to control, with RIGA having the largest difference between the treatments.

255 The linear mixed effects model indicated that ER was higher in the exclosures in RIGA over the growing season, whereas herbivory did not have a significant effect in the other sites (Fig. 2). Treatment ($F_{2,16}$ = 124.1, p < 0.001), site ($F_{3,16}$ = 18.7, p < 0.001), date ($F_{1,234}$ = 56.6, p < 0.001) and soil temperature ($F_{1,234}$ = 5.3, p = 0.022) were all significant predictors for the overall model.

3.2 BVOC emissions

260 Herbivory did not have significant effects on MT or SQT emission rates in any of the plant communities (Figure 4). However, for MT emissions RIRI ($T_{4.09}$ = -3.48, p = 0.024) was significantly different from LOMB ambient (as reference level); subsequently the intercept (reference level in this context) is also significant ($T_{3.96}$ = 17.57, p < 0.001). SQT emissions were not different between any of the sites, however the intercept (ambient LOMB with

a temperature of 0 °C) was significant ($T_{11.17} = 3.02$, $p = 0.012$) indicating that soil temperature may have an effect

265   on SQT emissions but over a larger range than we had sampled.
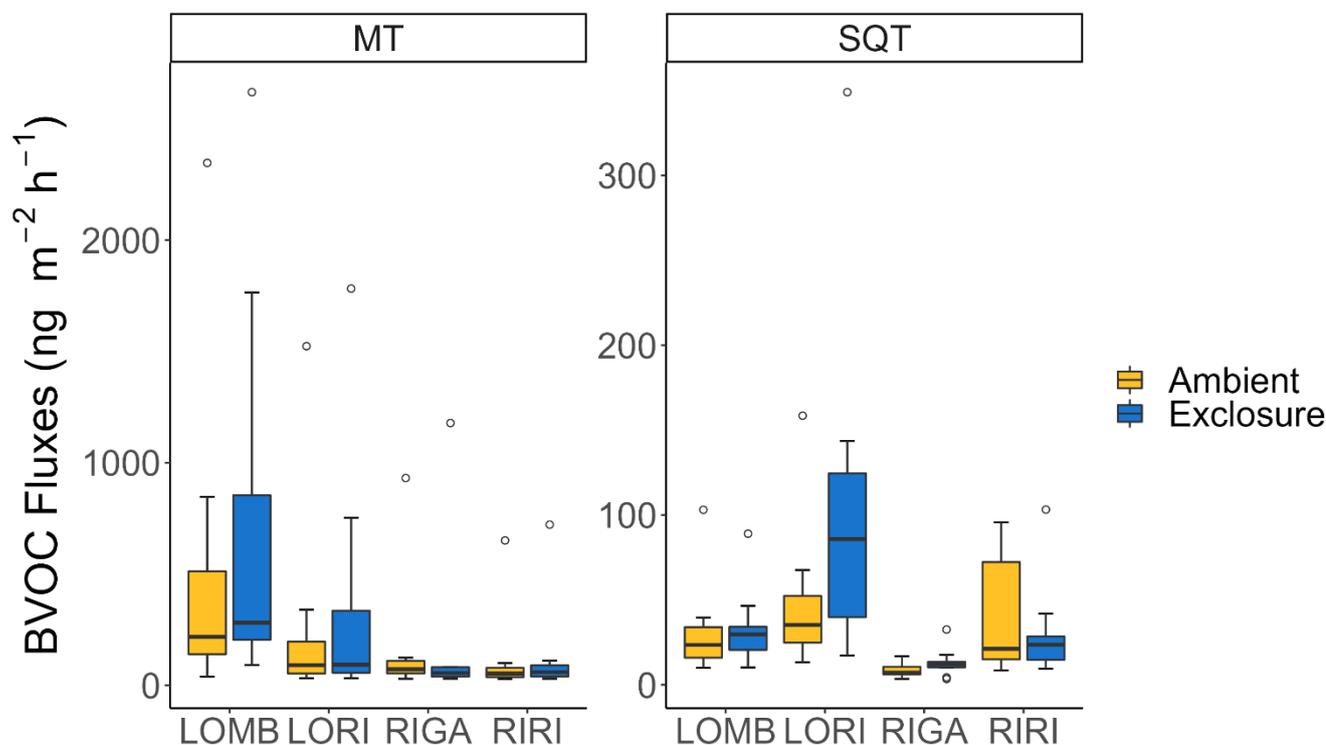
Fig. 4. Log of average monoterpene (MT) and sesquiterpene (SQT) emissions from each site in each treatment condition. Herbivory did not affect the magnitude of either MT or SQT emission at any site. Letters denote significant differences between sites and treatment according to linear mixed models on log transformed data and are assigned
270   **independently for each panel.**

The redundancy analysis showed clear distinctions between the four sites in their emitted BVOC composition (Figure 5), although the 85% confidence ellipses overlapped between all sites. The analysis determined that treatment ($F_{1,79} = 3.427$, $p = 0.005$), soil temperature ($F_{1,79} = 13.822$, $p < 0.001$), percent cover of abiotic components ($F_{1,79} = 2.292$, $p = 0.042$) and all shrub categories (deciduous prostrate dwarf shrub: $F_{1,79} = 9.162$, p

275   < 0.001, deciduous semi-prostrate dwarf shrub: $F_{1,79} = 4.973$, $p < 0.001$, deciduous tall shrub: $F_{1,79} = 6.841$, p < 0.001, evergreen prostrate dwarf shrub: $F_{1,79} = 5.211$, $p < 0.001$, evergreen semi-prostrate dwarf shrub: $F_{1,79} = 6.663$, $p < 0.001$, evergreen tall shrub: $F_{1,79} = 2.548$, $p = 0.015$) had significant effects on the differences between

measurements in terms of their BVOC compositions. Additionally, of the interactions between treatment and shrub types that were investigated, only deciduous prostrate shrubs were significant drivers of BVOC composition

280   ($F_{1,79}$ = 4.149, p < 0.001). Two BVOCs had correlations greater than 0.7 and are important for distinguishing between sites (2-Ethylfuran: r = 0.71, p = 0.01; and β-pinene: r = 0.75, p = 0.01); although, 2-Ethylfuran is a tentative NIST identification, whereas β-pinene was identified by comparing to a standard and so the confidence of its assignment is high. β-pinene emissions were marginally lower in RIRI ($T_{3.96}$ = -2.67, p = 0.055) as compared to LOMB (as the reference level in the model) but the intercept itself was significant ($T_{4.12}$ = 21.09, p < 0.001),

285   however treatment did not have an effect on β-pinene emissions.
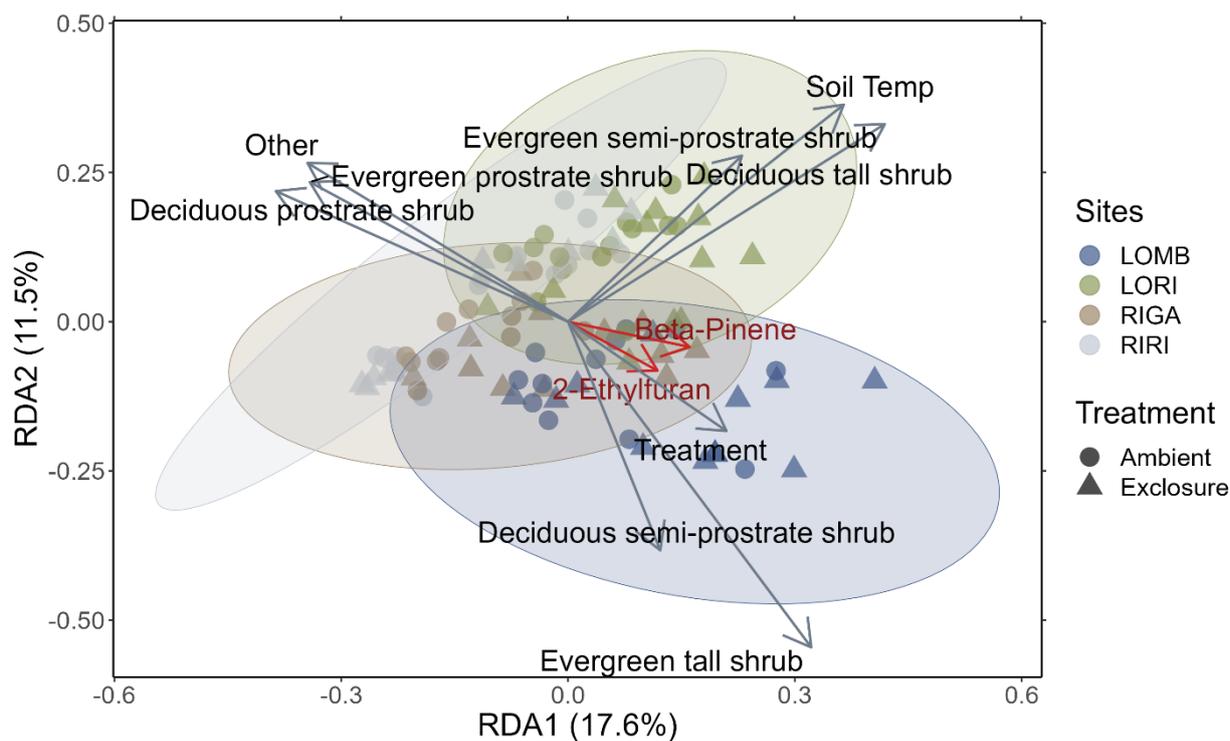
Fig. 5. Redundancy analysis of BVOC compounds emitted from each site constrained by environmental properties. Circles represent ambient and triangles exclosure plots. Vectors correspond to significant environmental variables with the length of the vector representing the strength of the relationship. Ellipses are 85% confidence ellipses that

290   **correspond to the standard deviation of the plotted points for each site separately. The red vectors correspond to the BVOC compounds with correlation values greater than 0.7. Treatment, soil temperature, percent cover of abiotic components and all shrub categories were significantly related to the composition of BVOCs emitted from each measurement (sites scores).**

3.3 Soil conditions

295   LOMB had the highest mean air temperature (2.6°C), followed by LORI (2.5°C), RIGA (0.5°C) and RIRI (-0.3°C), as measured by the site loggers (Fig. S1). TDD were significantly different between exclosures and ambient plots at three of the four sites (LOMB: t_{16} = 2.36, p = 0.031, LORI: t_{16} = 2.54, p = 0.022, RIGA: t_{16} = -3.16, p = 0.006; Fig. S3); however, the direction of the treatment effect varied between sites. At the Långfjället sites, ambient plots were warmer than exclosures, while RIGA ambient were significantly cooler. No statistically

300   significant differences in soil moisture were found between exclosures and ambient plots (Fig. S2). There were also no differences in the supply rate of NO_3^- or NH_4^+ between any of the sites or the treatment conditions (Fig. S4). However, there was 3.5 times the amount of NH_4^+ in the southern sites (LOMB and LORI) compared to the northern sites (RIGA and RIRI) in winter; a pattern which was not discernable in the growing season.

4 Discussion

305   Herbivory by large mammals significantly decreased ER in the low-herb meadow community, but no effect in the other three communities was found. The meadow community also has the highest plant productivity (Vowles et al., 2017b), which results in this community having larger ER in general (Treat et al., 2018). ER is driven by cellular respiration from both plants, including roots, and the microbial community; therefore, productive habitats, those with higher plant and microbial biomass, generally emit more CO_2 (Liu et al., 2018). By influencing

310   vegetation composition herbivores alter ER; specifically in RIGA exclosures resulted in a large increase in tall deciduous shrubs compared to semi-prostrate evergreen shrubs in ambient plots (Vowles et al., 2017a). By limiting deciduous shrub expansion and simultaneously promoting less productive evergreen shrubs through selective foraging (Ravolainen et al., 2011; Zamin and Grogan, 2013), large herbivores reduced the ER of the meadow as deciduous shrubs can have a disproportionate effect on soil respiration (Cahoon et al., 2012). The direction of the

315   herbivory effect agrees with changes observed in a wet tundra site, where long-term removal of lemming herbivory increased the net production of CO_2 by reducing productivity (Lara et al., 2017). In this case, when lemmings were excluded the habitat shifted from one dominated by graminoids to a less productive community with higher proportions of mosses and lichen. However, the increase in CO_2 emission was only observed in net ecosystem exchange (NEE). In fact, few studies have found a significant effect of herbivory on ER specifically, even if those

320   studies did find links between herbivory and NEE (Du et al., 2022; Hu et al., 2017; Lara et al., 2017). In our study, herbivory failed to have an effect on the ER of the mountain birch and heath sites. Since the mountain birch site did not have any significant changes in deciduous shrub or tree cover between exclosure and ambient conditions

15

(Vowles et al., 2017b) it follows that there would not be a strong change in ER. Both heath sites in our study did have changes in deciduous shrub cover due to herbivore exclusion (Vowles et al., 2017b) and heath habitats have

325 previously been found to have low ER that can be even further dampened by removal of large herbivores (Min et al., 2021; Treat et al., 2018). However, the herbivory effect on ER in our low productivity heath communities may have remained consistent due to opposing influences of the soil communities or other plant types, or the effect size may be too low in low productive sites to be discerned statistically. Nevertheless, the findings in our study are unique as it suggests that the herbivores affect ER in high productive meadow habitat, but not in low productive

330 heaths. Thus, herbivory can act to modify the magnitude of fluxes in tundra communities with the root determinant of these fluxes being the characteristics of the community itself (e.g. moisture, dominant vegetation, etc).

BVOC composition was affected by large mammal herbivory, but to a lesser extent than by site, soil temperature and shrub dynamics. BVOC composition in LOMB, LORI and RIRI were predominantly related to increases in different shrub types with RIGA not strongly tied to any specific shrub type. The interaction between herbivory

335 and deciduous prostrate shrubs found in our study is likely a driver of the change in BVOC composition as long-term herbivore exclosure alters the vegetation at each site (Vowles et al., 2017b, a). Two BVOC compounds were observed to have strong influence on distinguishing between individual BVOC measurements in terms of chemical composition. These compounds were β-pinene and 2-ethylfuran (the latter tentatively identified). Their emission rates generally increased toward LOMB and had a close trajectory to the treatment effect, indicating that they may

340 be more common when herbivores are excluded. β-pinene is a monoterpene commonly produced by many species and is generally associated with defensive and antimicrobial properties, in particular it has been shown to affect bacteria, fungi and insect larvae (Silva et al., 2012; Mercier et al., 2009). The mixed-model indicated that β-pinene emissions had a tendency to be lower in RIRI and compared to LOMB, and therefore may be tied to the vegetation differences in the two sites. Since 2-ethylfuran was not quantifiable it is not possible to disentangle the strength

345 of its vector from site or treatment effects. 2-ethylfuran is predominantly a plant defensive chemical with antimicrobial properties shown to be effective against fungi, nematodes and can also inhibit seed germination in some species (Lazazzara et al., 2018; Aissani et al., 2015; Bradow and Connick, 1990). It has also been found to be emitted in BVOC samples from mountain birch and tundra ecosystems (Ryde et al., 2021; Wester-Larsen et al., 2020), although in low amounts. These compounds may be emitted more by vegetation characteristic of

350 LOMB, namely mountain birch, tall evergreen shrubs and deciduous semi-prostrate shrubs. Since they also follow a similar trajectory as the treatment effect, it is possible that herbivory reduces the amount of these anti-microbial compounds emitted. This could be due to herbivory inadvertently selecting for vegetation that emit these compounds, or vegetation producing more anti-microbial compounds when released from herbivory pressure.

Alternatively, these compounds may serve a dual role as olfactory cues that function to improve foraging success

355   in large mammals as the role of many volatiles in mammalian herbivory is not well known (Kimball et al., 2012; Moore et al., 2004; Palo, 1984). Previous research has evaluated the effect of herbivory on BVOC emissions, but primarily from the perspective of insect herbivory or herbivory in general (Rieksta et al., 2021, 2020; Ghimire et al., 2021; Li et al., 2019; Faiola et al., 2015; Rinnan, 2013); explicit consideration of large mammal herbivory on BVOC dynamics is not well established (Vowles and Björk, 2019; Bartolome et al., 2007). Further research into

360   interactions between plants and large mammalian herbivore through BVOCs, especially regarding anti-browsing vs olfactory cues, may increase understanding of herbivores' role in structuring plant communities, as our data suggest that large mammalian herbivores and specific BVOC compounds may influence each other.

Large mammal herbivory did not affect the magnitude of BVOC emissions, although there was a non-significant indication of reducing emissions. Contrastingly, insect herbivory has been shown repeatedly to increase BVOC

365   emissions (Rieksta et al., 2021; Ghimire et al., 2021; Rieksta et al., 2020; Li et al., 2019; Faiola et al., 2015). However, studies on direct insect herbivory usually evaluate the instantaneous impact on individual plants as opposed to the indirect effects of long-term vegetation shifts caused by large mammal herbivory. Direct herbivory effects are derived from the consumption of plant biomass typically without removing the entire individual but damaging the leaf tissue and result in a pulse of volatiles as the leaves or stems are broken and stimulates the

370   production of herbivore deterrence linked compounds (Rinnan, 2013; Dicke, 2009). Large mammals may have similar effects on smaller spatiotemporal scales, e.g., when consuming a single individual, but the effect of these herbivores on the composition of the vegetation community, especially shrubs, likely has a stronger indirect effect on the BVOC fluxes after 18 years of herbivore exclusion. The amount of monoterpenes emitted differed between sites with the southern sites generally having slightly higher emissions than the northern sites. The higher

375   proportion of tall shrubs from the southern sites compared to prostrate shrubs in the north may drive these differences in MT emission (Ghirardo et al., 2020). Contrastingly, the amount of sesquiterpenes did not change across any of the sites and was much lower than the MT emissions in the southern sites. The change in MT and SQT emissions between sites is related to the dominant vegetation at each location where shrub species in simulated tundra ecosystems have been shown to contribute to terpene formation to different degrees (Ghirardo

380   et al., 2020). BVOC emissions vary substantially between individual plant species and so direct patterns can be difficult to detect in a community (Rinnan et al., 2011). Emissions also vary seasonally and with temperature (Rinnan et al., 2011; Faubert et al., 2010), and environments can take up a portion of VOCs from the atmosphere (Baggesen et al., 2021), which was not evaluated in this study. Herbivory effects did not provide a strong enough

385 signal in the magnitude of BVOCs emitted to determine a change compared to the high amount of variation in these compounds naturally.

5 Conclusions

Our data suggest that herbivory alters the strength of ER in a productive meadow community but is not strong enough to have an impact in heath and mountain birch ecosystems. Large mammal herbivory also alters BVOC emission composition through its effects on the proportion of shrub species, however there is no effect on the

390 magnitude of these emissions. The influence of large mammals on shrub dynamics likely drives the effects observed as shrubs have a disproportionate effect on the ecosystem's productivity and carbon fluxes. Predicted changes in plant communities, especially shrub encroachment, will feedback onto climate change through their effect on carbon fluxes and these effects may be situationally mediated by herbivory. Overall, the productivity of plant communities and the capacity for soils to support plant growth are likely most important for climate change

395 feedbacks in tundra ecosystems.

Appendix A

Table A1. Terpene emissions from each site averaged for each sampling date. Sites were measured twice in summer of 2013, once near the start of the growing season and once near the end. Compounds were identified through the NIST database and quantified by comparing to pure standards. All units are ng m^{-2} h^{-1}, standard error is displayed in

400 **brackets.**

| Site	Sampling date	Total terpene emissions	Monoterpene emissions	Sesquiterpene emissions
LOMB	2013-07-05	418.3 (98.4)	880.0 (207.9)	49.0 (10.8)
	2013-08-01	193.5 (46.4)	416.6 (101.7)	15.1 (2.2)
LORI	2013-07-06	248.3 (54.9)	423.4 (74.5)	108.1 (39.2)
	2013-08-02	129.1 (23.1)	242.6 (30.1)	38.3 (17.4)
RIGA	2013-07-11	64.8 (7.7)	137.6 (16.2)	6.5 (0.8)
	2013-07-26	113.3 (14.4)	236.1 (26.6)	15.1 (4.6)
RIRI	2013-07-10	41.9 (3.6)	84.3 (6.5)	8.0 (1.3)
	2013-07-27	117.6 (23.3)	186.2 (20.1)	62.8 (25.8)

Table A2. Mean terpene emissions from each site and treatment condition. Standard error is reported in brackets. Compounds were identified through the NIST database and quantified by comparing to pure standards. All units are ng m^{-2} h^{-1}.

Site	Treatment	Unidentified MT1	Unidentified MT2	α-pinene	β-pinene
LOMB	Exclosure	91.5 (45.8)	209.8 (75.9)	1764.7 (689.2)	2664.3 (356.7)
	Ambient	39.2 (5.3)	117.0 (35.4)	846.6 (441.9)	2346.4 (352.8)
LORI	Exclosure	32.2 (1.3)	48.3 (3.8)	196.2 (48.9)	1782.0 (213.4)
	Ambient	32.1 (0.7)	46.1 (2.4)	148.4 (22.4)	1523.4 (128.6)
RIGA	Exclosure	29.8 (0.9)	41.8 (3.7)	81.2 (8.4)	1178.2 (143.0)
	Ambient	29.5 (1.1)	39.7 (3.3)	124.5 (28.3)	931.2 (119.0)
RIRI	Exclosure	29.5 (1.3)	40.5 (2.6)	83.0 (11.2)	722.0 (152.8)
	Ambient	29.7 (0.8)	38.5 (2.0)	71.0 (5.7)	651.0 (92.0)

Site	Treatment	3-Carene	Cymene	D-Limonene	Linalool
LOMB	Exclosure	353.7 (120.9)	550.2 (270.8)	200.1 (74.4)	206.2 (39.1)
	Ambient	401.0 (157.8)	269.5 (86.8)	147.2 (48.7)	166.1 (28.6)
LORI	Exclosure	59.4 (5.9)	121.9 (21.6)	64.4 (6.8)	753.1 (391.9)
	Ambient	84.8 (10.8)	96.3 (9.5)	55.4 (3.9)	340.2 (78.9)
RIGA	Exclosure	32.7 (3.2)	61.2 (4.9)	49.9 (6.3)	82.1 (14.0)
	Ambient	68.4 (18.0)	105.0 (29.5)	58.2 (10.9)	76.8 (5.6)
RIRI	Exclosure	37.8 (4.7)	77.8 (11.6)	40.8 (3.9)	110.9 (23.3)
	Ambient	34.8 (2.0)	67.5 (4.0)	37.8 (2.2)	100.5 (17.6)

Site	Treatment	α-Cubebene	Unidentified SQT1	Unidentified SQT2	Unidentified SQT3
LOMB	Exclosure	18.3 (7.0)	31.3 (15.1)	28.0 (8.2)	27.3 (10.1)
	Ambient	18.9 (5.9)	14.9 (2.1)	19.0 (2.1)	27.9 (8.6)
LORI	Exclosure	98.3 (47.6)	17.2 (3.4)	22.5 (4.4)	112.3 (56.8)
	Ambient	37.7 (13.5)	13.2 (1.2)	24.6 (8.2)	39.1 (14.2)
RIGA	Exclosure	3.4 (0.5)	13.5 (1.9)	13.3 (3.0)	17.6 (11.0)
	Ambient	3.4 (0.4)	10.9 (1.7)	16.8 (8.4)	7.8 (3.7)
RIRI	Exclosure	13.8 (7.2)	23.9 (8.1)	29.7 (14.4)	23.2 (9.8)
	Ambient	14.5 (6.3)	82.3 (64.8)	42.0 (22.0)	17.8 (6.1)

Site	Treatment	Germacrene D	α-Bourbonene	Copaene	Caryophyllene
LOMB	Exclosure	34.2 (13.9)	33.8 (10.6)	89.0 (27.5)	46.4 (8.0)
	Ambient	35.6 (11.8)	28.9 (9.2)	103.1 (28.5)	39.5 (7.3)
LORI	Exclosure	143.6 (69.0)	59.9 (21.7)	349.1 (138.3)	128.5 (53.2)
	Ambient	56.8 (19.9)	32.8 (9.9)	158.5 (52.4)	67.5 (19.4)
RIGA	Exclosure	4.3 (0.9)	10.1 (1.8)	10.7 (3.0)	32.5 (10.0)
	Ambient	3.8 (0.5)	6.1 (1.2)	6.3 (0.7)	14.4 (2.6)
RIRI	Exclosure	24.7 (12.0)	41.9 (23.9)	103.2 (51.1)	17.1 (6.9)
	Ambient	24.5 (10.0)	90.5 (54.7)	95.7 (46.6)	16.3 (4.8)

Site	Treatment	α-Farnesene	cis-Calamenene
LOMB	Exclosure	10.2 (1.1)	12.1 (2.3)
	Ambient	9.9 (1.0)	12.0 (2.1)
LORI	Exclosure	73.3 (30.8)	33.1 (15.1)
	Ambient	25.4 (8.0)	14.8 (4.1)
RIGA	Exclosure	12.1 (3.5)	12.3 (5.9)
	Ambient	9.5 (2.4)	6.2 (1.4)
RIRI	Exclosure	11.5 (4.6)	9.4 (3.2)
	Ambient	8.5 (1.5)	9.2 (2.2)

405   **Table A3. Air temperature recorded for each sampling date at each site.**

Site	Sampling date	Air Temperature (°C)
LOMB	2013-07-05	18.8
	2013-08-01	15.9
LORI	2013-07-06	19.1
	2013-08-02	20.5
RIGA	2013-07-11	8.3
	2013-07-26	22.4
RIRI	2013-07-10	6.2
	2013-07-27	22.4
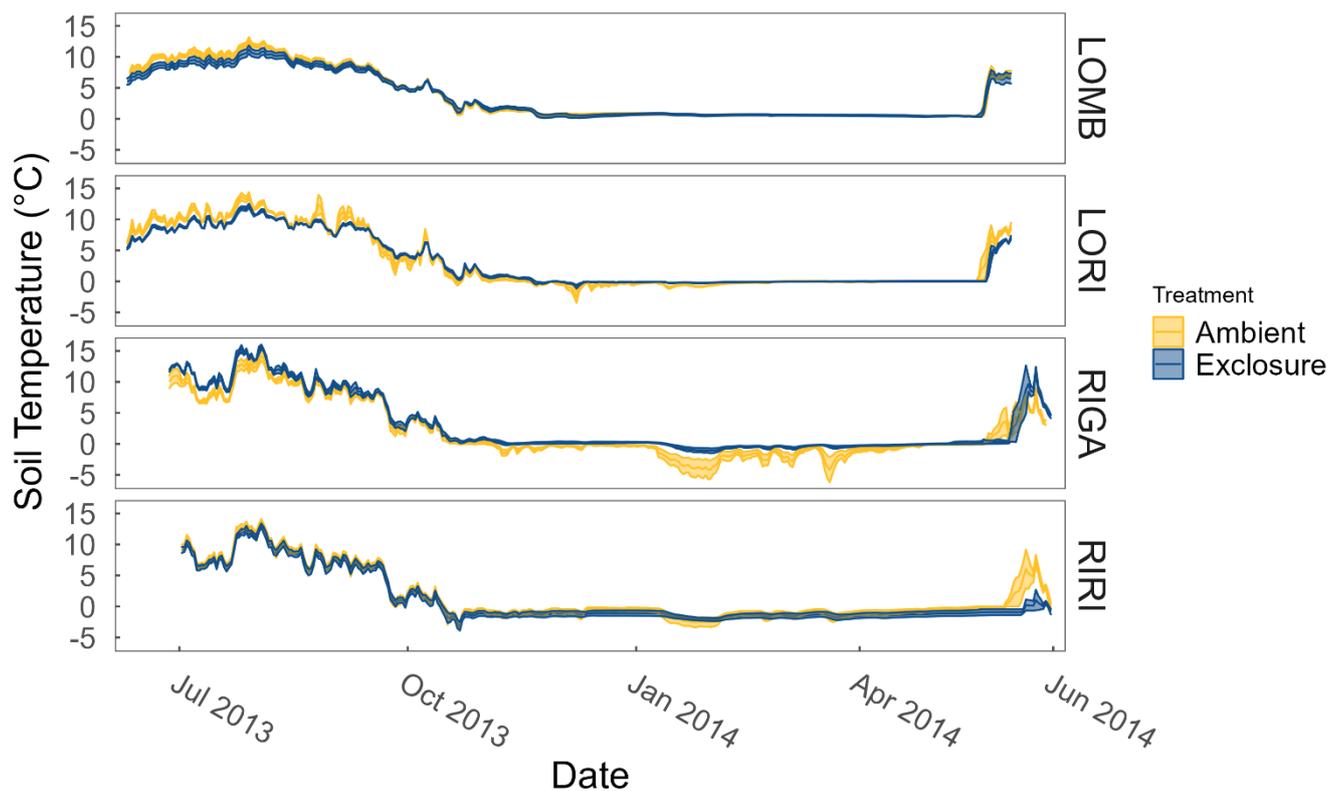
Fig. A1. Soil temperatures at each site and treatment measured year-round by temperature loggers (Tinytag plus 2 TGP-4020;
410   **Gemini Data Loggers, Chichester, UK) at 2 cm depth. Ribbons correspond to the standard error around the mean.**

20
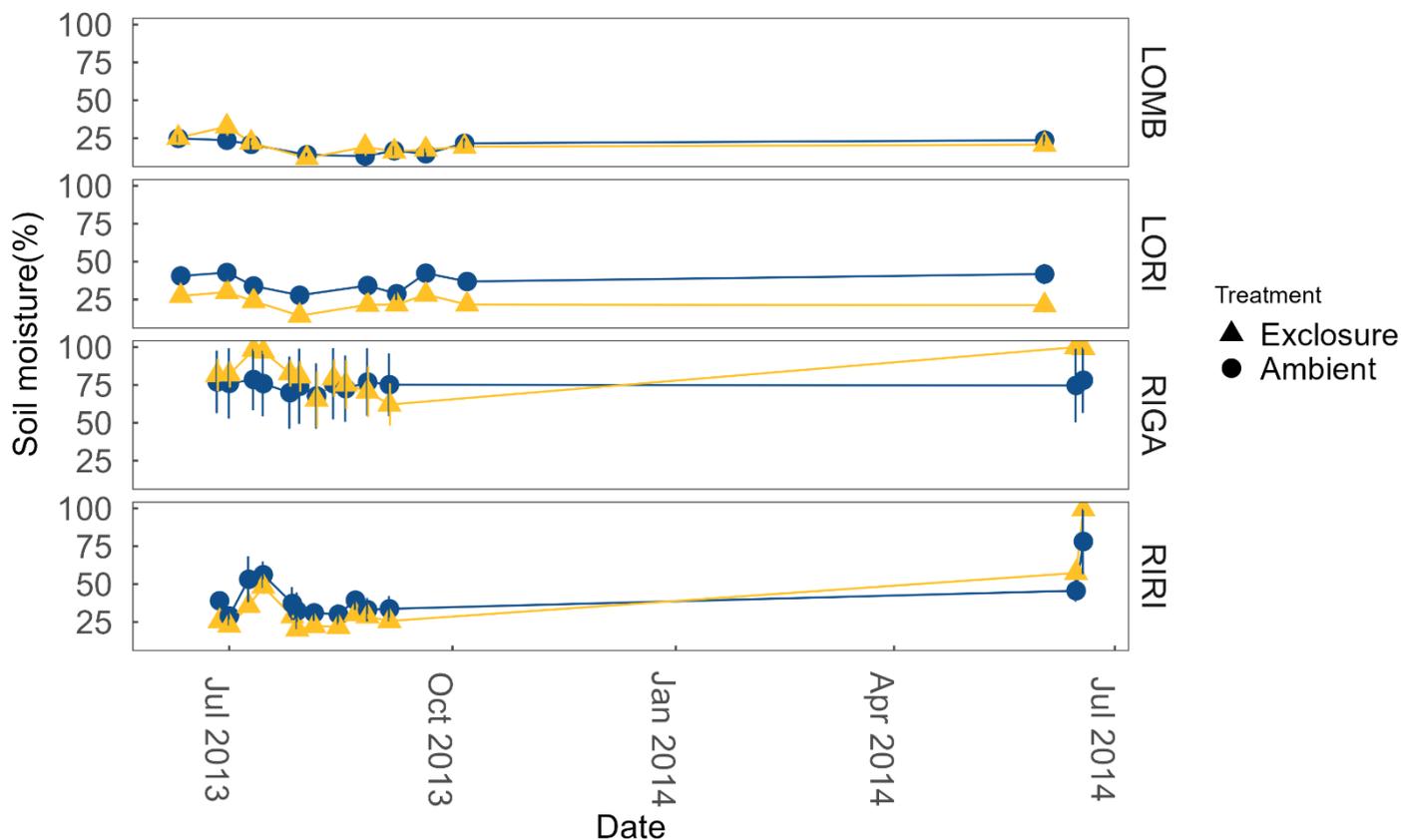
Fig. A2. Soil moisture at each site and treatment condition over the full year.
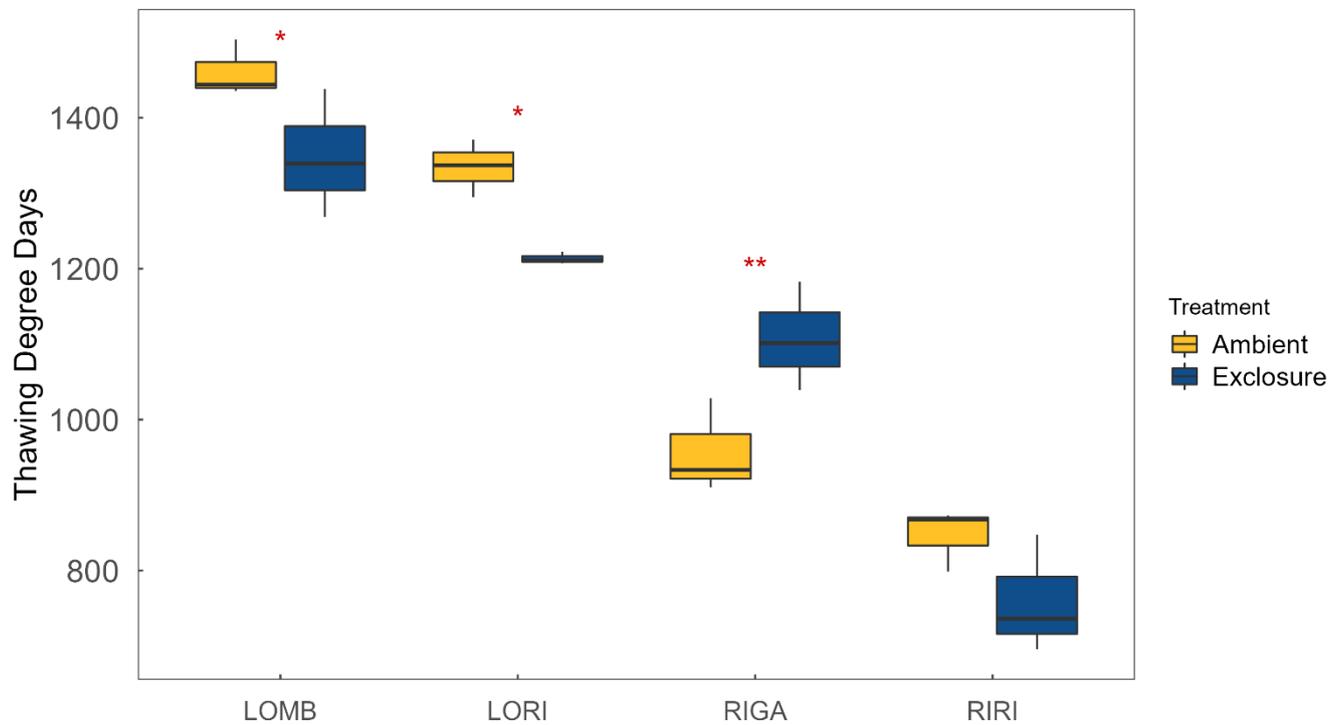
415

Fig. A3. Thawing degree days, measured as the sum of all mean daily temperatures above 0°C calculated from the soil temperature data, for each site and treatment. Significant differences between ambient and exclosure conditions were found for LOMB, LORI and RIGA, with ambient having more TDD in the southern sites (LOMB and LORI) and fewer in RIGA.
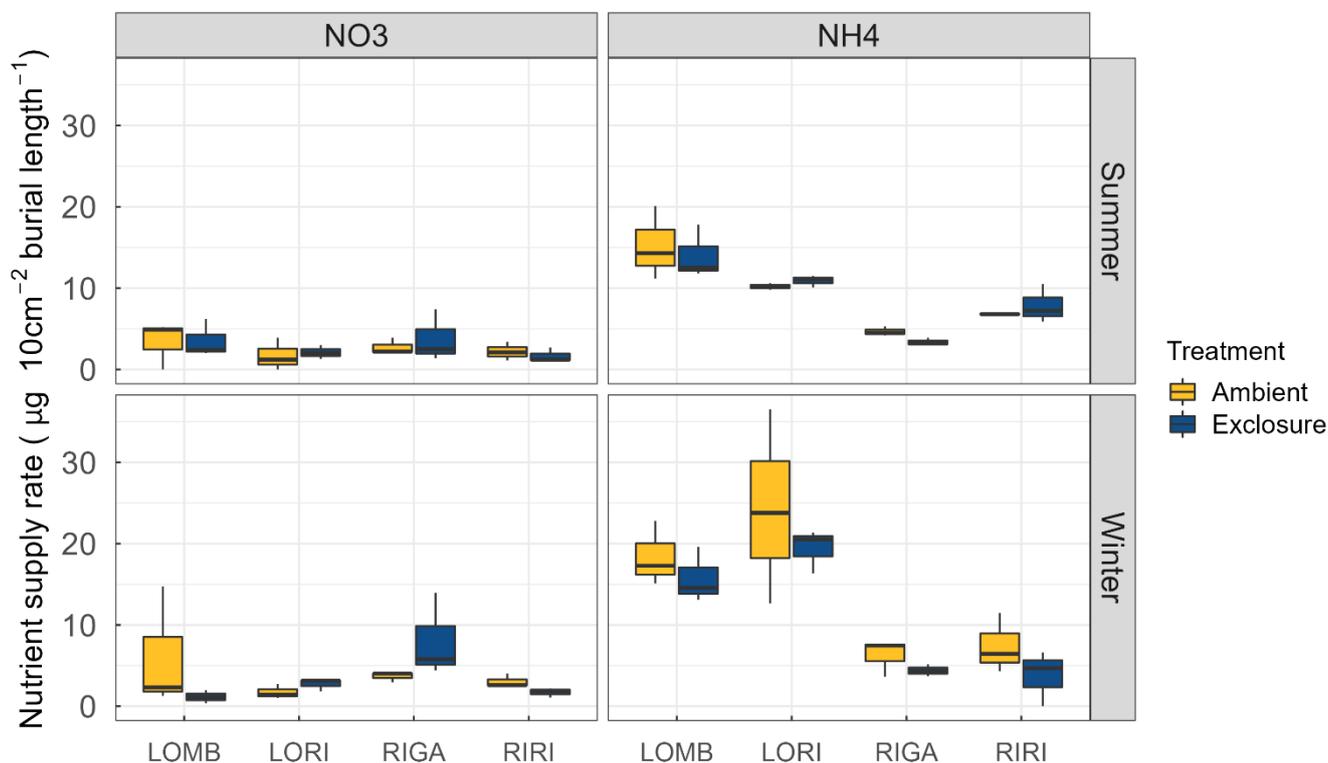
420

Fig. A4. Supply rate of NO$_3^-$ and NH$_4^+$ in each site and treatment condition. The supply rate is calculated for the surface area of the probe (10 cm^2) and the burial length. The burial length was different for southern and northern sites and varied between seasons. LOMB and LORI probes were buried for 121 days in summer and 235/236 in winter; respectively. RIRI and RIGA probes were buried 71 days in summer and 283 in winter. Nitrogen was measured through PRS probes and transformed to supply rate following
425 **manufacturers protocol. No significant differences were found between exclosure and ambient conditions for any site or nutrient. There was, however, a significant decrease in the amount of NH$_4^+$ in the northern sites compared to the southern sites in winter.**

Author contributions

RGB and TV designed the experiments. RGB, TV and MPB led the field campaigns. RR and TV processed the raw data. CGB

analyzed the data and wrote the original manuscript. All coauthors provided edits and reviewed the manuscript.

430 **Competing interests**

The authors declare that none of the authors has any competing interests.

Biogeosciences

Discussions

Open Access

EGU

440 **References**

Aissani, N., Urgeghe, P. P., Oplos, C., Saba, M., Tocco, G., Petretto, G. L., Eloh, K., Menkissoglu-Spiroudi, U., Ntalli, N., and Caboni, P.: Nematicidal Activity of the Volatilome of Eruca sativa on Meloidogyne incognita, J. Agric. Food Chem., 63, 6120–6125, https://doi.org/10.1021/acs.jafc.5b02425, 2015.

Baggesen, N., Li, T., Seco, R., Holst, T., Michelsen, A., and Rinnan, R.: Phenological stage of tundra vegetation controls

445 bidirectional exchange of BVOCs in a climate change experiment on a subarctic heath, Glob. Chang. Biol., 27, 2928–2944, https://doi.org/10.1111/gcb.15596, 2021.

Bardgett, R. D. and Wardle, D. A.: Herbivore-mediated linkages between aboveground and belowground communities, Ecology, 84, 2258–2268, https://doi.org/10.1890/02-0274, 2003.

Barthelemy, H., Stark, S., Michelsen, A., and Olofsson, J.: Urine is an important nitrogen source for plants irrespective of

450 vegetation composition in an Arctic tundra: Insights from a 15N-enriched urea tracer experiment, J. Ecol., 106, 367–378, https://doi.org/10.1111/1365-2745.12820, 2018.

Bartolome, J., Penuelas, J., Filella, I., Llusia, J., Broncano, M. J., and Plaixats, J.: Mass scans from a proton transfer mass spectrometry analysis of air over Mediterranean shrubland browsed by horses, J. Environ. Biol., 28, 697–700, 2007.

Bates, D., Mächler, M., Bolker, B., and Walker, S.: Fitting linear mixed-effects models using lme4, J. Stat. Softw., 67, 1–48,

455 https://doi.org/doi:10.18637/jss.v067.i01, 2015.

Bjorkman, A. D., García Criado, M., Myers-Smith, I. H., Ravolainen, V., Jónsdóttir, I. S., Westergaard, K. B., Lawler, J. P., Aronsson, M., Bennett, B., Gardfjell, H., Heiðmarsson, S., Stewart, L., and Normand, S.: Status and trends in Arctic vegetation: Evidence from experimental warming and long-term monitoring, Ambio, 49, 678–692, https://doi.org/10.1007/s13280-019-01161-6, 2020.

460 Björkman, M. P., Morgner, E., Björk, R. G., Cooper, E. J., Elberling, B., and Klemedtsson, L.: A comparison of annual and seasonal carbon dioxide effluxes between sub-Arctic Sweden and High-Arctic Svalbard, Polar Res., 29, 75–84, https://doi.org/10.1111/j.1751-8369.2010.00150.x, 2010a.

Björkman, M. P., Morgner, E., Cooper, E. J., Elberling, B., Klemedtsson, L., and Björk, R. G.: Winter carbon dioxide effluxes from arctic ecosystems: An overview and comparison of methodologies, Global Biogeochem. Cycles, 24, 1–10, https://doi.org/10.1029/2009GB003667, 2010b.

Boy, M., Zhou, P., Kurtén, T., Chen, D., Xavier, C., Clusius, P., Roldin, P., Baykara, M., Pichelstorfer, L., Foreback, B., Bäck, J., Petäjä, T., Makkonen, R., Kerminen, V. M., Pihlatie, M., Aalto, J., and Kulmala, M.: Positive feedback mechanism between biogenic volatile organic compounds and the methane lifetime in future climates, npj Clim. Atmos. Sci., 5, https://doi.org/10.1038/s41612-022-00292-0, 2022.

Bradow, J. M. and Connick, W. J.: Volatile seed germination inhibitors from plant residues, J. Chem. Ecol., 16, 645–666, https://doi.org/10.1007/BF01016477, 1990.

Cahoon, S. M. P., Sullivan, P. F., Post, E., and Welker, J. M.: Large herbivores limit CO 2 uptake and suppress carbon cycle responses to warming in West Greenland, Glob. Chang. Biol., 18, 469–479, https://doi.org/10.1111/j.1365-2486.2011.02528.x, 2012.

Calfapietra, C., Fares, S., Manes, F., Morani, A., Sgrigna, G., and Loreto, F.: Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review, Environ. Pollut., 183, 71–80, https://doi.org/10.1016/j.envpol.2013.03.012, 2013.

Davidson, E. A. and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165–173, https://doi.org/10.1038/nature04514, 2006.

Dicke, M.: Behavioural and community ecology of plants that cry for help, Plant, Cell Environ., 32, 654–665, https://doi.org/10.1111/j.1365-3040.2008.01913.x, 2009.

Du, C., Zhou, G., and Gao, Y.: Grazing exclusion alters carbon flux of alpine meadow in the Tibetan Plateau, Agric. For. Meteorol., 314, 108774, https://doi.org/10.1016/j.agrformet.2021.108774, 2022.

Ekberg, A., Arneth, A., Hakola, H., Hayward, S., and Holst, T.: Isoprene emission from wetland sedges, Biogeosciences, 6, 601–613, https://doi.org/10.5194/bg-6-601-2009, 2009.

Elmendorf, S. C., Henry, G. H. R., Hollister, R. D., Björk, R. G., Bjorkman, A. D., Callaghan, T. V., Collier, L. S., Cooper, E. J., Cornelissen, J. H. C., Day, T. A., Fosaa, A. M., Gould, W. A., Grétarsdóttir, J., Harte, J., Hermanutz, L., Hik, D. S., Hofgaard, A., Jarrad, F., Jónsdóttir, I. S., Keuper, F., Klanderud, K., Klein, J. A., Koh, S., Kudo, G., Lang, S. I., Loewen, V., May, J. L., Mercado, J., Michelsen, A., Molau, U., Myers-Smith, I. H., Oberbauer, S. F., Pieper, S., Post, E., Rixen, C., Robinson, C. H., Schmidt, N. M., Shaver, G. R., Stenström, A., Tolvanen, A., Totland, Ø., Troxler, T., Wahren, C. H., Webber, P. J., Welker, J. M., and Wookey, P. A.: Global assessment of experimental climate warming on tundra vegetation: Heterogeneity over space and time, Ecol. Lett., 15, 164–175, https://doi.org/10.1111/j.1461-0248.2011.01716.x, 2012.

Faiola, C. L., Jobson, B. T., and VanReken, T. M.: Impacts of simulated herbivory on volatile organic compound emission profiles from coniferous plants, Biogeosciences, 12, 527–547, https://doi.org/10.5194/bg-12-527-2015, 2015.

495   Faubert, P., Tiiva, P., Rinnan, Å., Michelsen, A., Holopainen, J. K., and Rinnan, R.: Doubled volatile organic compound
      emissions from subarctic tundra under simulated climate warming, New Phytol., 187, 199–208, https://doi.org/10.1111/j.1469-
      8137.2010.03270.x, 2010.

      Ghimire, R. P., Silfver, T., Myller, K., Oksanen, E., Holopainen, J. K., and Mikola, J.: BVOC Emissions From a Subarctic
      Ecosystem, as Controlled by Insect Herbivore Pressure and Temperature, Ecosystems, https://doi.org/10.1007/s10021-021-
500   00690-0, 2021.

      Ghirardo, A., Lindstein, F., Koch, K., Buegger, F., Schloter, M., Albert, A., Michelsen, A., Winkler, J. B., Schnitzler, J. P.,
      and Rinnan, R.: Origin of volatile organic compound emissions from subarctic tundra under global warming, Glob. Chang.
      Biol., 26, 1908–1925, https://doi.org/10.1111/gcb.14935, 2020.

      Heimann, M. and Reichstein, M.: Terrestrial ecosystem carbon dynamics and climate feedbacks, Nature, 451, 289–292,
505   https://doi.org/10.1038/nature06591, 2008.

      Hu, Y. G., Zhang, Z. H., Wang, S. P., Zhang, Z. S., Zhao, Y., and Wang, Z. R.: The weak effects of fencing on ecosystem
      respiration, CH4, and N2O fluxes in a Tibetan alpine meadow during the growing season, Sci. Cold Arid Reg., 9, 554–567,
      https://doi.org/10.3724/SP.J.1226.2017.00554.The, 2017.

      Hugelius, G., Tarnocai, C., Broll, G., Canadell, J. G., Kuhry, P., and Swanson, D. K.: The northern circumpolar soil carbon
510   database: Spatially distributed datasets of soil coverage and soil carbon storage in the northern permafrost regions, Earth Syst.
      Sci. Data, 5, 3–13, https://doi.org/10.5194/essd-5-3-2013, 2013.

      Hugelius, G., Strauss, J., Zubrzycki, S., Harden, J. W., Schuur, E. A. G., Ping, C. L., Schirrmeister, L., Grosse, G., Michaelson,
      G. J., Koven, C. D., O'Donnell, J. A., Elberling, B., Mishra, U., Camill, P., Yu, Z., Palmtag, J., and Kuhry, P.: Estimated stocks
      of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps, Biogeosciences, 11, 6573–6593,
515   https://doi.org/10.5194/bg-11-6573-2014, 2014.

      Johnsen, L. G., Skou, P. B., Khakimov, B., and Bro, R.: Gas chromatography – mass spectrometry data processing made easy,
      J. Chromatogr. A, 1503, 57–64, https://doi.org/10.1016/j.chroma.2017.04.052, 2017.

      Kimball, B. A., Russell, J. H., and Ott, P. K.: Phytochemical variation within a single plant species influences foraging behavior
      of deer, Oikos, 121, 743–751, https://doi.org/10.1111/j.1600-0706.2011.19515.x, 2012.

520   Köster, K., Köster, E., Berninger, F., Heinonsalo, J., and Pumpanen, J.: Contrasting effects of reindeer grazing on CO2, CH4,
      and N2O fluxes originating from the northern boreal forest floor, L. Degrad. Dev., 29, 374–381,
      https://doi.org/10.1002/ldr.2868, 2018.

      Kravchenko, A. N. and Robertson, G. P.: Statistical Challenges in Analyses of Chamber-Based Soil CO 2 and N 2 O Emissions
      Data , Soil Sci. Soc. Am. J., 79, 200–211, https://doi.org/10.2136/sssaj2014.08.0325, 2015.

525   Lara, M. J., Johnson, D. R., Andresen, C., Hollister, R. D., and Tweedie, C. E.: Peak season carbon exchange shifts from a
      sink to a source following 50+ years of herbivore exclusion in an Arctic tundra ecosystem, J. Ecol., 105, 122–131,
      https://doi.org/10.1111/1365-2745.12654, 2017.

Lazazzara, V., Bueschl, C., Parich, A., Pertot, I., Schuhmacher, R., and Perazzolli, M.: Downy mildew symptoms on grapevines can be reduced by volatile organic compounds of resistant genotypes, Sci. Rep., 8, 1–14, https://doi.org/10.1038/s41598-018-19776-2, 2018.

530 Lenth, R.: Least squares means. R Package "lsmeans," 2016.

Li, T., Holst, T., Michelsen, A., and Rinnan, R.: Amplification of plant volatile defence against insect herbivory in a warming Arctic tundra, Nat. Plants, 5, 568–574, https://doi.org/10.1038/s41477-019-0439-3, 2019.

Liu, W., Lü, X., Xu, W., Shi, H., Hou, L., Li, L., and Yuan, W.: Effects of water and nitrogen addition on ecosystem respiration

535 across three types of steppe: The role of plant and microbial biomass, Sci. Total Environ., 619–620, 103–111, https://doi.org/10.1016/j.scitotenv.2017.11.119, 2018.

Liu, Z., Kimball, J. S., Ballantyne, A. P., Parazoo, N. C., Wang, W. J., Bastos, A., Madani, N., Natali, S. M., Watts, J. D., Rogers, B. M., Ciais, P., Yu, K., Virkkala, A., Chevallier, F., Peters, W., Prabir, K. P., and Chandra, N.: Respiratory loss during late-growing season determines the net carbon dioxide sink in northern permafrost regions, Nat. Commun., 13,

540 https://doi.org/10.1038/s41467-022-33293-x, 2022.

Mercier, B., Prost, J., and Prost, M.: The essential oil of turpentine and its major volatile fraction (α- and β-pinenes): A review, Int. J. Occup. Med. Environ. Health, 22, 331–342, https://doi.org/10.2478/v10001-009-0032-5, 2009.

Metcalfe, D. B. and Olofsson, J.: Distinct impacts of different mammalian herbivore assemblages on arctic tundra CO2 exchange during the peak of the growing season, Oikos, 124, 1632–1638, https://doi.org/10.1111/oik.02085, 2015.

545 Min, E., Wilcots, M. E., Naeem, S., Gough, L., McLaren, J. R., Rowe, R. J., Rastetter, E. B., Boelman, N. T., and Griffin, K. L.: Herbivore absence can shift dry heath tundra from carbon source to sink during peak growing season, Environ. Res. Lett., 16, https://doi.org/10.1088/1748-9326/abd3d0, 2021.

Mishra, U., Hugelius, G., Shelef, E., Yang, Y., Strauss, J., Lupachev, A., Harden, J. W., Jastrow, J. D., Ping, C. L., Riley, W. J., Schuur, E. A. G., Matamala, R., Siewert, M., Nave, L. E., Koven, C. D., Fuchs, M., Palmtag, J., Kuhry, P., Treat, C. C.,

550 Zubrzycki, S., Hoffman, F. M., Elberling, B., Camill, P., Veremeeva, A., and Orr, A.: Spatial heterogeneity and environmental predictors of permafrost region soil organic carbon stocks, Sci. Adv., 7, 1–13, https://doi.org/10.1126/sciadv.aaz5236, 2021.

Molau, U. and Mølgaard, P.: ITEX Manual, Second Edi., https://doi.org/10.1016/j.admp.2012.03.463, 1996.

Moore, B. D., Wallis, I. R., Palá-Paúl, J., Brophy, J. J., Willis, R. H., and Foley, W. J.: Antiherbivore chemistry of Eucalyptus - Cues and deterrents for marsupial folivores, J. Chem. Ecol., 30, 1743–1769,

555 https://doi.org/10.1023/B:JOEC.0000042399.06553.c6, 2004.

Oksanen, J., Blanchet, G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P., O'Hara, R., Simpson, G., Solymos, P., Stevens, M., Szoecs, E., and Wagner, H.: Vegan: Community Ecology Package, https://github.com/vegandevs/vegan, 2019.

Olofsson, J., Moen, J., and Oksanen, L.: Effects of herbivory on competition intensity in two arctic-alpine tundra communities with different productivity, Oikos, 96, 265–272, https://doi.org/10.1034/j.1600-0706.2002.960208.x, 2002.

560 Olofsson, J., Oksanen, L., Callaghan, T., Hulme, P. E., Oksanen, T., and Suominen, O.: Herbivores inhibit climate-driven shrub expansion on the tundra, Glob. Chang. Biol., 15, 2681–2693, https://doi.org/10.1111/j.1365-2486.2009.01935.x, 2009.

Palo, R. T.: Distribution of birch (Betula SPP.), willow (Salix SPP.), and poplar (Populus SPP.) secondary metabolites and their potential role as chemical defense against herbivores, J. Chem. Ecol., 10, 499–520, https://doi.org/10.1007/BF00988096, 1984.

565   Parker, T. C., Subke, J. A., and Wookey, P. A.: Rapid carbon turnover beneath shrub and tree vegetation is associated with low soil carbon stocks at a subarctic treeline, Glob. Chang. Biol., 21, 2070–2081, https://doi.org/10.1111/gcb.12793, 2015.

Payton, M. E., Miller, A. E., and Raun, W. R.: Testing statistical hypotheses using standard error bars and confidence intervals, Commun. Soil Sci. Plant Anal., 31, 547–551, https://doi.org/10.1080/00103620009370458, 2000.

Payton, M. E., Greenstone, M. H., and Schenker, N.: Overlapping confidence intervals or standard error intervals: What do
570   they mean in terms of statistical significance?, J. Insect Sci., 3, https://doi.org/10.1093/jis/3.1.34, 2003.

Peñuelas, J. and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15, 133–144, https://doi.org/10.1016/j.tplants.2009.12.005, 2010.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., and Team, R. C.: nlme: linear and nonlinear mixed effects models, 2015.

Pirk, N., Tamstorf, M. P., Lund, M., Mastepanov, M., Pedersen, S. H., Mylius, M. R., Parmentier, F. J. W., Christiansen, H.
575   H., and Christensen, T. R.: Snowpack fluxes of methane and carbon dioxide from high Arctic tundra, J. Geophys. Res. Biogeosciences, 121, 2886–2900, https://doi.org/10.1002/2016JG003486, 2016.

Rantanen, M., Karpechko, A. Y., Lipponen, A., Nordling, K., Hyvärinen, O., Ruosteenoja, K., Vihma, T., and Laaksonen, A.: The Arctic has warmed nearly four times faster than the globe since 1979, Commun. Earth Environ., 3, 1–10, https://doi.org/10.1038/s43247-022-00498-3, 2022.

580   Ravolainen, V. T., Bråthen, K. A., Ims, R. A., Yoccoz, N. G., Henden, J. A., and Killengreen, S. T.: Rapid, landscape scale responses in riparian tundra vegetation to exclusion of small and large mammalian herbivores, Basic Appl. Ecol., 12, 643–653, https://doi.org/10.1016/j.baae.2011.09.009, 2011.

Rieksta, J., Li, T., Junker, R. R., Jepsen, J. U., Ryde, I., and Rinnan, R.: Insect Herbivory Strongly Modifies Mountain Birch Volatile Emissions, Front. Plant Sci., 11, 1–12, https://doi.org/10.3389/fpls.2020.558979, 2020.

585   Rieksta, J., Li, T., Michelsen, A., and Rinnan, R.: Synergistic effects of insect herbivory and changing climate on plant volatile emissions in the subarctic tundra, Glob. Chang. Biol., 27, 5030–5042, https://doi.org/10.1111/gcb.15773, 2021.

Rinnan, R.: Off-season biogenic volatile organic compound emissions from heath mesocosms: responses to vegetation cutting, Front. Microbiol., 4, https://doi.org/10.3389/fmicb.2013.00224, 2013.

Rinnan, R., Rinnan, Å., Faubert, P., Tiiva, P., Holopainen, J. K., and Michelsen, A.: Few long-term effects of simulated climate
590   change on volatile organic compound emissions and leaf chemistry of three subarctic dwarf shrubs, Environ. Exp. Bot., 72, 377–386, https://doi.org/10.1016/j.envexpbot.2010.11.006, 2011.

Rinnan, R., Iversen, L. L., Tang, J., Vedel-Petersen, I., Schollert, M., and Schurgers, G.: Separating direct and indirect effects of rising temperatures on biogenic volatile emissions in the Arctic, Proc. Natl. Acad. Sci. U. S. A., 117, 32476–32483, https://doi.org/10.1073/pnas.2008901117, 2020.

595 Ryde, I., Li, T., Rieksta, J., Dos Santos, B. M., Neilson, E. H. J., Gericke, O., Jepsen, J. U., Bork, L. R. H., Holm, H. S., and Rinnan, R.: Seasonal and elevational variability in the induction of specialized compounds from mountain birch (Betula pubescens var. pumila) by winter moth larvae (Operophtera brumata), Tree Physiol., 41, 1019–1033, https://doi.org/10.1093/treephys/tpab023, 2021.

Sharkhuu, A., Plante, A. F., Enkhmandal, O., Gonneau, C., Casper, B. B., Boldgiv, B., and Petraitis, P. S.: Soil and ecosystem
600 respiration responses to grazing, watering and experimental warming chamber treatments across topographical gradients in northern Mongolia, Geoderma, 269, 91–98, https://doi.org/10.1016/j.geoderma.2016.01.041, 2016.

Silva, A. C. R. da, Lopes, P. M., Azevedo, M. M. B. de, Costa, D. C. M., Alviano, C. S., and Alviano, D. S.: Biological activities of α-pinene and β-pinene enantiomers, Molecules, 17, 6305–6316, 2012.

Sistla, S. A., Moore, J. C., Simpson, R. T., Gough, L., Shaver, G. R., and Schimel, J. P.: Long-term warming restructures
605 Arctic tundra without changing net soil carbon storage, Nature, 497, 615–617, https://doi.org/10.1038/nature12129, 2013.

Sommerfeld, R. A., Mosier, A. R., and Musselman, R. C.: CO2, CH4 and N2O flux through a Wyoming snowpack and implications for global budgets, Nature, 361, 140–142, 1993.

Sørensen, M. V., Strimbeck, R., Nystuen, K. O., Kapas, R. E., Enquist, B. J., and Graae, B. J.: Draining the pool? Carbon storage and fluxes in three alpine plant communities, Ecosystems, 21, 316–330, 2018.

610 Strimbeck, R., Graae, B. J., Lang, S., and Sørensen, M. V.: Functional group contributions to carbon fluxes in arctic-alpine ecosystems, Arctic, Antarct. Alp. Res., 51, 58–68, 2019.

Team, R. C.: R: A Language for Statistical Computing, https://www.r-project.org/, 2022.

Treat, C. C., Marushchak, M. E., Voigt, C., Zhang, Y., Tan, Z., Zhuang, Q., Virtanen, T. A., Räsänen, A., Biasi, C., Hugelius, G., Kaverin, D., Miller, P. A., Stendel, M., Romanovsky, V., Rivkin, F., Martikainen, P. J., and Shurpali, N. J.: Tundra
615 landscape heterogeneity, not interannual variability, controls the decadal regional carbon balance in the Western Russian Arctic, Glob. Chang. Biol., 24, 5188–5204, https://doi.org/10.1111/gcb.14421, 2018.

Virkkala, A. M., Virtanen, T., Lehtonen, A., Rinne, J., and Luoto, M.: The current state of CO2 flux chamber studies in the Arctic tundra: A review, Prog. Phys. Geogr., 42, 162–184, https://doi.org/10.1177/0309133317745784, 2018.

Virkkala, A. M., Aalto, J., Rogers, B. M., Tagesson, T., Treat, C. C., Natali, S. M., Watts, J. D., Potter, S., Lehtonen, A.,
620 Mauritz, M., Schuur, E. A. G., Kochendorfer, J., Zona, D., Oechel, W., Kobayashi, H., Humphreys, E., Goeckede, M., Iwata, H., Lafleur, P. M., Euskirchen, E. S., Bokhorst, S., Marushchak, M., Martikainen, P. J., Elberling, B., Voigt, C., Biasi, C., Sonnentag, O., Parmentier, F.-J. W., Ueyama, M., Celis, G., St. Louis, V. L., Emmerton, C. A., Peichl, M., Chi, J., Järveoja, J., Nilsson, M. B., Oberbauer, S. F., Torn, M. S., Park, S.-J., Dolman, H., Mammarella, I., Chae, N., Poyatos, R., López-Blanco, E., Christensen, T. R., Kwon, M. J., Sachs, T., Holl, D., and Luoto, M.: Statistical upscaling of ecosystem CO2 fluxes
625 across the terrestrial tundra and boreal domain: Regional patterns and uncertainties, Glob. Chang. Biol., 00, 1–20, 2021.

Vowles, T. and Björk, R. G.: Implications of evergreen shrub expansion in the Arctic, J. Ecol., 107, 650–655, https://doi.org/10.1111/1365-2745.13081, 2019.

Vowles, T., Lovehav, C., Molau, U., and Björk, R. G.: Contrasting impacts of reindeer grazing in two tundra grasslands, Environ. Res. Lett., 12, https://doi.org/10.1088/1748-9326/aa62af, 2017a.

630 Vowles, T., Gunnarsson, B., Molau, U., Hickler, T., Klemedtsson, L., and Björk, R. G.: Expansion of deciduous tall shrubs but not evergreen dwarf shrubs inhibited by reindeer in Scandes mountain range, J. Ecol., 105, 1547–1561, https://doi.org/10.1111/1365-2745.12753, 2017b.

Ward, S. E., Ostle, N. J., Oakley, S., Quirk, H., Henrys, P. A., and Bardgett, R. D.: Warming effects on greenhouse gas fluxes in peatlands are modulated by vegetation composition, Ecol. Lett., 16, 1285–1293, https://doi.org/10.1111/ele.12167, 2013.

635 Wester-Larsen, L., Kramshøj, M., Albers, C. N., and Rinnan, R.: Biogenic Volatile Organic Compounds in Arctic Soil: A Field Study of Concentrations and Variability With Vegetation Cover, J. Geophys. Res. Biogeosciences, 125, 1–15, https://doi.org/10.1029/2019JG005551, 2020.

Ylänne, H., Stark, S., and Tolvanen, A.: Vegetation shift from deciduous to evergreen dwarf shrubs in response to selective herbivory offsets carbon losses: Evidence from 19 years of warming and simulated herbivory in the subarctic tundra, Glob.

640 Chang. Biol., 21, 3696–3711, https://doi.org/10.1111/gcb.12964, 2015.

Ylänne, H., Kaarlejärvi, E., Väisänen, M., Männistö, M. K., Ahonen, S. H. K., Olofsson, J., and Stark, S.: Removal of grazers alters the response of tundra soil carbon to warming and enhanced nitrogen availability, Ecol. Monogr., 90, 1–13, https://doi.org/10.1002/ecm.1396, 2020.

Zamin, T. J. and Grogan, P.: Caribou exclusion during a population low increases deciduous and evergreen shrub species

645 biomass and nitrogen pools in low Arctic tundra, J. Ecol., 101, 671–683, https://doi.org/10.1111/1365-2745.12082, 2013.