Normalizing time in terms of space: What drives the fate of spring thaw-released nitrogen in a sloping Arctic landscape?

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ABSTRACT

In the Arctic tundra, snowmelt is followed by soil thaw allowing water and dissolved nutrients to move downslope. However, the fate of the released nitrogen (N) remains unclear, which includes the fraction of N that is lost to downslope transport or converted to N gases.

We have quantified the release of N2O into the soil solution and the loss of gaseous N upon thaw and up to a month after first thaw in an Arctic hillslope in W Greenland. We further investigated which factors of the slope ecosystem that influence the N2O concentrations and N2O fluxes throughout two snowmelt and growing seasons using a Structural Equation Model (SEM) linking physical, biological and biogeochemical characteristics across the slope.

Snowmelt controls growing season onset, but varies in the landscape. To account for this, we normalized the spatiotemporal variation in snowmelt and soil thaw by measuring N2O release and N2O loss in a controlled laboratory thaw experiment with topsoil cores from along the slope. We furthermore normalized seasonal progression of ecosystem variables in space based on the first day of soil thaw in the field. We tested the variable Day After Soil Thaw (DAST) as the temporal driver in our SEM, and found that season progression is the most important factor to describe patterns in N2O concentrations and N2O fluxes. We conclude that DAST is a useful tool for analysing seasonal patterns in a spatially heterogeneous snowmelt landscape and between different snowmelt years.

When normalizing based on first day of soil thaw, we saw that the decreasing N2O content over the season did not control the increasing N2O emissions. Rather, nitrification replaced denitrification as the main N2O-source during the growing season, where soil temperatures increased and soil moisture decreased. The gaseous N loss from the slope during the first month of thaw was minor and amounted to 1% of the annual N deposition. A N2O pulse released into solution after 24 h of thaw, when meltwater moves along the slope and connects upslope with downslope ecosystems, thus constituted a “hot moment” for interaction between landscape N pools, but the N2O was immobilized by microorganisms or taken up by plants rather than denitrified and did thus not constitute a hot moment for N2O emissions. Thus, our results regarding what drives the fate of spring-thaw released N in the sloping Arctic landscape highlight the importance of snowmelt timing and the following number of Day After Soil Thaw as a normalizing factor for biogeochemical processes. This provides an analytical concept for reducing spatial and inter-annual variability to understand general seasonal patterns otherwise hidden.

1. Introduction

In a nitrogen (N) limited Arctic ecosystem, physical and biological conditions that affect N inputs, outputs and turnover are important controls on ecosystem productivity, carbon (C) and N pool sizes and the net balance of greenhouse gas fluxes (Sistla et al., 2012; Voigt et al., 2020).

The topography of an area influences soil temperature, soil moisture
and soil nutrient status across arctic hillslopes not the least due to different conditions of wind exposure, drainage and snow melt timing (Miller, 1982). Soil temperature, soil moisture and nutrient status impact decomposition rates (Hicks Pries et al., 2013), vegetation community composition (Mekonnen et al., 2021), nitrogen fixation rates (Stewart et al., 2011) and gaseous N exchange with the atmosphere (Voigt et al., 2020). Especially soil moisture is an important link between topography and redox conditions, which drives very different N processes including nitrification under arid conditions and denitrification under wet conditions (Stewart et al., 2014).

Soil moisture and -temperature varies spatially along the slope, but also temporally, especially from snowmelt to freeze-up. At soil thaw, temperatures are low and moisture is high due to snowmelt. Pulses of inorganic and organic N have been observed immediately after soil thaw, likely due to mobilization of N from winter mineralization and release of organic N from microbes upon wetting (Bilbrough et al., 2000; Buckeridge and Grogan, 2008; Buckeridge & Grogan, 2010; Sistla and Schimel, 2013). As the season progresses and thaw depth increases, soil temperatures increase and soil moisture content, depending on precipitation patterns, typically decreases (e.g. Rasmussen et al., 2020), Plants emerge, photosynthesize, grow and acquire N, which is therefore found in low concentrations in the mid-growing season tundra soil (Rasmussen et al., 2020). In late August, a peak in inorganic N (Christiansen et al., 2012) may be explained by decreasing plant N demand due to senescence, which additionally mobilizes nutrients from the leaves of deciduous plants to the stem and roots (e.g. Estiarte and Peñuelas, 2015). Ultimately, soil freezing causes lysis of microbes, releasing organic N into solution (Buckeridge & Grogan, 2010; Semenchuk et al., 2015).

Because spatial variations in snowmelt and soil thaw can be more pronounced than temporal trends, studies in areas with marked topography may struggle to find significant effects of time or position on slope on any given Day of Year (DOY) (e.g., Kolstad et al., 2021). Arguably, a common variable in the two directions of variation (position in the landscape and season progression, respectively), is the disappearance of snow, followed by soil thaw (Niitynen et al., 2020).

The biologically available N-form nitrate (NO$_3^-$) is water-soluble and a sought-after N-source for tundra plant communities (Liu et al., 2018) and soil microbes (e.g. Sistla et al., 2012) alike. Because of its solubility and the fact that soil thaw may release mineralized N into solution (Buckeridge and Grogan, 2008; Sistla and Schimel, 2013), the early spring can be a period of nitrate transport and redistribution in the landscape. At this point in time, a thin layer of topsoil has thawed and snowmelt water moves downslope through the thawed layer, possibly picking up NO$_3^-$ released into solution upon thaw. The importance of this phenomenon is poorly quantified. If much NO$_3^-$ is released in the spring topsoil, lateral N movement in the early spring may result in an additional N-input to downslope soil and vegetation pools (e.g., Pedersen et al., 2020; Rasmussen et al., 2021). However, the N released by thawing could result in a “hot moment” (e.g. Kuzyakov and Blagodatskaya 2015) where N can be nitrified, denitrified and lost as gaseous N (N$_2$, N$_2$O) immediately (Buckeridge et al., 2010) or directly reincorporated (immobilized by microbes, ammonified or assimilated by plants) and thereby limit further N movement down the slope (e.g. Rastetter et al., 2004).

NO$_3^-$ availability is directly linked to emissions of the potent greenhouse gas nitrous oxide (N$_2$O) under anaerobic conditions (Bowman and Focht, 1974). N turnover within a sloping ecosystem can, both via nitrification of NH$_4^+$ to NO$_3^-$ and the denitrification of NO$_3^-$ to N$_2$, cause production of N$_2$O as an intermediary or a by-product, which, if not reduced in the soil, can be emitted to the atmosphere. Identifying the dominating response factors for NO$_3^-$ production and consumption may thus lead us closer to the causes and sensitivities of N$_2$O emissions and N$_2$ loss from the ecosystem over the season.

In this study, we quantify the release of NO$_3^-$ along the slope with a focus on the first thaw and the following fate of nitrogen, including the gaseous loss of N to the atmosphere.

We propose a normalization method based on the first day of soil thaw (Day After Soil Thaw, DAST) as a temporal variable. This variable is intimately linked to the first day of snow-free conditions and can be relevant instead of the often used date-time or Day of Year (DOY). Relating measurements of biogeochemical markers relative to the day when soil temperature first passed 0.2 °C instead of the DOY of the measurement allow us to compare sites along a slope as the snow pack melts back throughout the growing season.

We normalize to DAST by, firstly, in a controlled laboratory incubation experiment, measuring the actual release of NO$_3^-$ into solution upon the first month of thaw in top soil cores sampled across an Arctic tundra heath slope in Western Greenland. The cores were sampled all over the slope, but earlier downslope than upslope, following the snowmelt up the slope, and sampling on the first day of snow-free conditions, where soil was still frozen to the top. We compare the amount of NO$_3^-$ released to the total N and the N lost as N$_2$O and N$_2$ upon thaw. By doing so, we follow the consequences of snow melt and soil thaw for N cycling in direct relation to thaw along the slope, thus isolating temporal variation from spatial variation. With this laboratory approach, we aim to answer the question: how much NO$_3^-$ is released into solution upon thaw, and how much of this is lost as gaseous N or available for transport?

Secondly, we test the use of a temporal variable, Day After Soil Thaw (DAST), in a Structural Equation Model (SEM), which analyses links between spatially-specific biological, physical and chemical conditions measured in situ along the slope over two years with different snowmelt timing. With the SEM built on the field data, but with the process understanding backed by the lab experiment, we test whether the effects of topography on snowmelt and soil thaw confounds the temporal patterns of N in solution, making DAST a useful tool for studying temporal patterns. Furthermore, we apply the method in order to address the question: controlling for the effect of topography, which environmental conditions have most power in explaining NO$_3^-$ availability along the slope throughout the thaw and growing season?

We hypothesize that 1) DAST is an important explanatory factor of soil N status and that 2) DAST is relevant to describe N$_2$O fluxes linked to NO$_3^-$ availability along a slope.

2. Methods

2.1. Study area

The Blæsedalen study site is situated on Disko Island, Western Greenland (69°16’N; 53°27’W). The basaltic bedrock has been shaped by past glaciations to form a north-south directed U-valley between table mountains rising to approximately 900 m to the east, west and north. The area is affected by permafrost with active layers of up to 1 m in wet areas and >3 m in well-drained areas (D’Imperio et al., 2017).

The area has an arctic maritime climate, with mean annual air temperature of −3.0 ± 1.8 °C (Hollesen et al., 2015; Westergaard-Nielsen et al., 2018) and annual mean precipitation of about 436 mm y$^{-1}$, with 42% falling as snow (Hansen et al., 2006). N deposition amounts to 1 kg N ha$^{-1}$ y$^{-1}$, and N$_2$ fixation supplies the ecosystem with comparable amounts of N (Anderson et al., 2018; Hobara et al., 2006; Rousk et al., 2017).

2.2. Field site

A study site was set up in 2014, covering 35 × 50 m of a west-facing slope with an inclination of 10–20°. The slope has a soil depth of 40–90 cm on top of colluvial material weathered from the slope bedrock of the size stones to boulders. At the foot of the slope, a small wetland has formed with peat formation in the top 20–40 cm. The slope leads up to a snow accumulation area with a semi-permanent snow fan, from which meltwater moves downslope throughout most of the growing season. The grain size classification of the soil is sand (USDA, 1996), dominated
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The slope represents a vegetation gradient. Upslope, the snow persists longer on average, and the growing season is shortest; which means that vegetation is dominated by the prostrate dwarf shrub Salix herbaacea. In the early season, soil tends to be cooler and wetter upslope than downslope, because active layer development happens later. In the later growing season, however, the active layer is more developed, and water drains deeper through the soil and downslope, causing generally warmer and drier conditions upslope than downslope. Moving downslope, the vegetation contains gradually less Salix herbaacea, but is dominated by low shrubs such as Salix arctica, Betula nana, Cassiope tetragona and Empetrum nigrum, interlain with mesic tundra mosses such as Tomen-

Typnum nitens, Racemitrium lanuginosum and Sphagnum sp.

The slope was divided into five zones perpendicularr to the direction of inclination, based on the vegetation composition. For each zone, five replicate plots were established (see overview in Fig. S1). The zones, were, from the top: Near Snow, Top, Mid, End and Reception area. The exact positions of all four corners of all plots were measured with DGPS (GNSS, Trimble, US) with an accuracy of 2 cm in the summer 2018.

On the slope, topsoil cores were sampled and used in an incubation experiment designed to determine the amount of NO3 released and the flux of N2O upon soil thaw (section 2.4). Further, the across- and along slope physical, chemical and biological characteristics were monitored in situ to test the DAST variable and understand the drivers behind the fate of NO3 released upon soil thaw and its link to N2O fluxes over the whole thaw and growing season (section 2.3). Finally, samples were obtained in the early and the late growing season for laboratory analysis of N2O/N2 ratios (section 2.5). An overview figure of the data collection and which data was used for which results can be found in Fig. S2.

2.3. Physical, chemical and biological characteristics along the slope

All plots were analysed for vegetation composition using the pinpoint method and normalized difference vegetation index (NDVI) over the growing seasons 2017 and 2018. In all plots, soil temperatures at 2 cm depth were measured year-round 2018–2019 (Tinytag, Gemini Data logger, UK) and in three to five replicates for each zone, soil moisture (vol. %) and temperatures in 10 and 20 cm were measured from July 2018 to late August 2019 (Decagon Devices, METER Group, USA). In July 2018, soil water suction cups were installed in 10–20 cm and 20–30 cm in all plots (Prenart Equipment Aps, DK). Soil water was subsequently extracted from the soil approximately every 5 days until late August in 2018 and from the first appearance of liquid water at those depths in 2019 until mid-August. Soil water was analysed for concentration of total organic carbon (TOC) (Shimadzu TOC analyser; Kyoto, Japan), NH4-N, NO3-N and Total Dissolved Nitrogen (TDN) (FlAstar 5000; Höganäs, Sweden). N2O surface fluxes were measured every week using the static chamber method (such as in Kolstad et al., 2021) during the growing seasons of 2018 and 2019, starting right after snowmelt in 2019. A transparent polycarbonate chamber (21 × 21 × 19.5 cm) was placed air-tight on pre-installed metal frames inside the plots, and 12 ml chamber air was extracted five times during a period of 3 h and kept in evacuated vials (Labco Scientific, High Wycombe, UK) until N2O analysis by gas chromatography (Agilent 7890A GC, Agilent Technologies, Santa Clara, USA). Chamber temperature was measured during the measurement period and air was mixed inside chamber before each 12 ml air extraction.

The two studied growing seasons 2018 and 2019 had very different onsets. Where snowmelt was unusually late in 2018, with 50% snow-free conditions around 13th of June, the 2019 snowmelt was unusually early, with 50% snow-free conditions the 15th of May (Rasmussen et al., 2021).

2.4. Controlled soil thaw experiment

On the first day of snow-free conditions along the slope, at the edge of the snowpack when soil was still frozen, the top 15 cm of soil (in 3 replicates) was sampled using a hammer and a soil corer with an inner diameter of 5 cm. At the footslope, the first samples were taken on 10th of June, and the last set of samples at the shoulder slope was taken 15th of July. In total, 40 topsoil cores (two-three replicates on 14 different spots along and across the slope) were kept frozen during storage and transport, and used in a controlled thaw experiment (see below) before being analysed for soil moisture content, total N and total C (Flash, 2000; Thermo Scientific, Bremen, Germany).

In order to assess the N release into solution and the release of N gases from the system upon thaw, we divided the frozen top soil cores into three replicates per sampling location. One replicate was kept frozen and stored as backup. The second was used for monitoring of N2O fluxes over the first month of thaw (LGR N2OIA2-915 gas analyser, Los Gatos Research, CA, USA), and the third was used for soil water extraction over the first month. The experiment was initiated (time zero) by transferring the cores from −6 °C to +5 °C (samples were stored at −18 °C, but moved to −6 °C for the last week before experiment start). Sampling of soil water and measurement of N2O fluxes were subsequently done on all samples at time 0h, 24h, 48h, 72h, 144h, 240h (10d), 504h (21d) and 744h (31d).

For the extraction of soil water, we used microirrhizons (Rhizosphere Research Products B. V., Wageningen, Netherlands), which were inserted in holes pre-drilled horizontally into the frozen cores about 5 cm from the top. Upon thaw, the soil enclosed the suction cup, and 1–2 ml of water was extracted with a syringe during each sampling. Just after removal of the samples from the freezer (Hour 0), however, no liquid water could be extracted from the cores. The amount of extracted water was in total maximum 14 ml, which, with the size of the cores in mind, was not considered enough to require introduction of replacement water into the cores. The soil water was frozen until analysis of NO3-N content using Ion Chromatography (ThermoFisher Scientific, MA, USA).

When measuring N2O fluxes over the first month of thaw, one core at a time per sampling point was moved into a cooling box and connected to a LGR N2OIA2-915 gas analyser (Los Gatos Research, CA, USA) via a closed loop system, where headspace air trace gas concentrations were measured over at least 20 min until a visible (or no visible) flux was observed.

Raw data from the LGR was pre-processed and flux rates calculated using the HMR package (Pedersen et al., 2010) in R 4.0.

Trend analysis (student’s t-test) was conducted on the NO3-N concentrations and N2O flux rates over the first month of thaw.

2.5. N2/N2O ratios and total gaseous N loss

Six top soil samples of 4 cm depth with a diameter of 5.5 cm were obtained from the Reception area and the Top zones (foot slope and shoulder slope, respectively) twice over the 2018 growing season, and once from the End zone. The sampling points represented early growing season and late growing season, thus varying points after soil thaw, and they had different soil moisture contents (vol. %) at the point of sampling. Table S1 lists the date, the day after soil thaw and the ambient soil moisture contents of the samples. Samples were wrapped in plastic, frozen and kept frozen during transport to the lab, where N2 and N2O fluxes were measured at ambient soil moisture conditions using the helium (He) substitution method, where soil-gas exchange is recorded in a controlled headspace atmosphere with He replacing N2. For details, see Butterbach-Bahl et al. (2002).

In order to estimate the net gaseous N loss from the system, the time- and spatially most relevant measured N2/N2O ratios from within the first 31 days after soil thaw were applied to the soil thaw experiment, giving an estimate of the total gaseous N loss over the first 31 days of soil thaw.
The time-integrated gaseous N flux was calculated by linear interpolation of flux rates between measurement points and summing up to net fluxes.

The N₂ and N₂O fluxes were finally scaled to the entire slope area (1000 m²), which was calculated using the distance between DGPS recorded outer limits of the plots furthest upslope and downslope, and the full horizontal span of the slope.

### 2.6. Structural Equation Modelling

Structural Equation Modelling (SEM) is a method with a wide range of applications and has been used for many types of complex systems, including in ecology (Grace, 2010). The method tests a postulated hypothesis of the internal relationships between empirically measured or constructed variables and is thus able to analyse networks of hypothesised causal relationships, where variables can act as predictors and responses simultaneously. Competing models are compared and the most relevant model selected (Marsh et al., 2004).

We constructed an a priori model of how the measured physical, biological and chemical variables across the slope related to each other, with NO₃ concentration as the central dependent variable, and we tested the hypothesized model against the in situ field measurements from the slope obtained during 2018 and 2019. The included variables are shown in Table 1 and an illustration of the construct model is depicted in Fig. S3.

The Day After Soil Thaw (DAST) variable was constructed by calculating the number of days that had passed since the day the soil temperature at 20 cm depth had passed 0.2 °C in spring 2018 and 2019, respectively. At this point, the ice in the soil had melted and temperatures started increasing fast, so as to signify a beginning of the growing season. In order to test how useful the DAST variable is across different snowmelt seasons, data from both 2018 and 2019 was used as one dataset normalized based on their respective DAST value.

NDVI (Normalized Difference Vegetation Index) was used as a proxy for aboveground vegetation biomass, and a variable representing the relative amount of N fixers (moss, lichen) in the vegetation cover was deduced from the vegetation composition analysis.

The a priori model of the ecosystem causal links was tested using the SEM software package lavaan 0.6–7 (Yves Rosseel, 2012) in R 4.0. If links between variables were not significant, we excluded them from the model one by one, starting from the most insignificant (with a new iteration after each exclusion). The overall model performance was evaluated using χ² statistical test of model significance and Root Mean Square Error of Approximation (RMSEA) (Marsh et al., 2004). The lavaan package is best suited with a full datasets with no missing data, and as such, in the cases where data for different variables (e.g., N₂O flux and soil water chemistry, which are both labour intensive when covering the whole slope) were not collected at the exact same date, gap filling had to be done. In this process, we gave priority to geographic position (sampling point) over exact date of data collection. Thus, if the choice fell between extrapolating e.g. soil net N₂O flux to the next or previous day, or to extrapolate soil water chemical composition from a neighbouring plot, because the two were not measured on the same date, we chose the first, as we believe spatial heterogeneity in e.g., soil moisture to be higher than the difference from one day to the next.

### 3. Results

#### 3.1. Thaw release of NO₃ and N₂O

Upon the very first exposure to positive spring temperatures (5 °C) in the incubation experiment, a pulse of NO₃-N was observed in the soil solution reaching a mean of 2.3 mg/L, but with several samples with > 4 mg/L (Fig. 1, A). The median concentration of NO₃-N in the days thereafter decreased only slightly (overall linear trend coefficient -0.002 mg/L h⁻¹, intercept 1.8, R² = 0.079, p < 0.05), but with less variation. On day 6 (hour 144), day 10 (hour 240) and day 31 (hour 744) after exposure to thaw, the smallest variance across the slope was measured, whereas day 21 (hour 504) showed a larger spread with some samples containing as much NO₃-N as 4 mg/L.

Scaled to the entire slope area of 1000 m², the top 15 cm soil contained in total 244 g NO₃-N in solution (at an average of 60% Gravimetric Water Content, GWC) 24 h after exposure to thaw temperatures. After 31 days, the number had dropped to 64.5 g NO₃-N (with an average of 45% GWC).

In the incubation experiment, net N₂O fluxes were 0.25–2 μg/m²/h.

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Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Period of measurement used</th>
<th>Intervals of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil temperature 20 cm depth</td>
<td>July-August 2018–2019</td>
<td>30 min intervals</td>
</tr>
<tr>
<td>Soil moisture 20 cm depth</td>
<td>July-August 2018–2019</td>
<td>30 min intervals</td>
</tr>
<tr>
<td>#Day After Soil Thaw (DAST)</td>
<td>June–August 2018,</td>
<td>N/A</td>
</tr>
<tr>
<td>Soil water chemical composition</td>
<td>June–August 2019</td>
<td>5 d intervals</td>
</tr>
<tr>
<td>(NO₃, NH₄, TDN, TOC)</td>
<td>June–August 2019</td>
<td>Monthly</td>
</tr>
<tr>
<td>NDVI (Normalized Difference Vegetation Index)</td>
<td>June–July 2018,</td>
<td></td>
</tr>
<tr>
<td>N₂O surface flux</td>
<td>June–August 2018,</td>
<td>Weekly</td>
</tr>
<tr>
<td>% of N fixers (mosses, lichen) of vegetation cover</td>
<td>July 2018</td>
<td>Vegetation analysis once</td>
</tr>
</tbody>
</table>

Fig. 1. A) NO₃-N concentrations (mg/L), and B) N₂ flux rates (solid line with std. err. denoted as dashed line) and N₂O net flux rates (boxplots) (μg m⁻² h⁻¹) across the slope in the first 31 days after exposure to thaw temperatures (5 °C). Boxplots display means (solid line) with quartiles, while the error bars show the 95% CI. n = 14 for each point in time.
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Table 2

<table>
<thead>
<tr>
<th>Position on slope</th>
<th>Sampling #Day after soil thaw</th>
<th>Ambient soil moisture (vol. %)</th>
<th>N2/N2O flux ratio ±SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>0</td>
<td>71.1 ± 0.8</td>
<td>1.1 ± 0.8</td>
</tr>
<tr>
<td>Top</td>
<td>18</td>
<td>61.0 ± 2.1</td>
<td>5.4 ± 2.5</td>
</tr>
<tr>
<td>End</td>
<td>11</td>
<td>68.4 ± 3.5</td>
<td>4.4 ± 3.2</td>
</tr>
<tr>
<td>Reception area</td>
<td>17</td>
<td>58.8 ± 4.8</td>
<td>16.8 ± 7.4</td>
</tr>
<tr>
<td>Reception area</td>
<td>52</td>
<td>55.4 ± 6.8</td>
<td>5.7 ± 3.1</td>
</tr>
</tbody>
</table>

Field measurements of soil physical conditions, soil water chemistry, and N2O fluxes along the slope, which were the input to the SEM, are presented for each measurement date in 2018 and 2019 in Figs S5.1-5.6 and S6.1-6.6.

The decoupling between NO3-N fluxes, although with very small explanatory power (coefficient = −0.068). However, the vegetation NDVI (p < 0.01) showed a direct link to N2O fluxes, and so did season progression (DAST).

4. Discussion

4.1. Early season N loss

Only a small proportion (<1%) of the total N in the soil was in the incubation experiment released into solution as NO3-N upon soil thaw. However, the 244 g N released as mineral N makes up 100–200% of the annual average N deposition in the area, which is estimated to be about 0.1–0.2 kg N/y in an area of 1000 m2 (Andersson et al. 2018). Similarly, the 244 g N released as mineral N makes up 100–200% of estimated annual N fixation (Hobara et al., 2006; Roßk et al., 2017). The release of this mineral N into solution within a short time span of days therefore constitutes a hot moment for N turnover in the thawing soil (e.g., Kurzyakov and Blagodatskaya 2015). The release of N-gasses, however, amounted to only 1–2% of that of NO3-N during the same period in the incubations, and about 80% of the gaseous N loss was in the form of N2. Scaling this gaseous N loss measured in the first month after snowmelt (9.3 g N) to the 1000 m2 of the slope, the loss during the first month makes up 0.5–1% of the average N deposition and 0.5–1% of the average estimated N fixation. Although the sample size of 14 cores covering the slope is small taking spatial heterogeneity into account, the results indicate that gaseous N loss is a small portion of the external N input to the ecosystem on an annual basis.

The NO3-N concentrations measured upon thaw in the incubated cores were two orders of magnitude higher than the early season field extractions from the site and from previous investigations (Rasmussen et al., 2020, 2021). This unexpected difference highlights how taking even intact topsoil cores to the lab changes conditions under which microbes function. In this case, the lack of drainage from and through the topsoil combined with the lack of plant N uptake in the incubation study could be the reason for this discrepancy between the lab and the field, illustrating the potential importance of landscape hydrological connectivity and plants in regulating soil water chemistry.

However, despite the larger NO3 availability for denitrification, N2O fluxes in the incubations were not significantly larger than in the in situ measurements, and are at a level with other dry to moist pristine permafrost soils (Voigt et al., 2020). The increase in NO3 availability did thus not lead to a pulse of N2O production, as seen in the field (Rasmussen et al., 2021; Kolstad et al., 2021).

4.2. NO3 as regulator of N2O emissions

Decoupling between NO3 and N2O production seen in the lab is contrary to other controlled studies, which have shown a substrate limitation on N2O production (Voigt et al., 2020; Butterbach-Bahl et al., 2013 and studies therein). It suggests that denitrification was not the dominating source for N2O during thaw at our site, perhaps because other factors limited denitrification (e.g. redox conditions connected to soil moisture (Mekonnen et al., 2021; Rasmussen et al., 2022) or labile C substrate (Kolstad et al., 2021)), but that NO3 was rather taken up and immobilized by microbes as observed by Rasmussen et al. (2021). The fact that NO3/N2O ratios decreased with time at the bottom of the slope (Reception area) suggests that the denitrification that did occur here was more complete in the early season, where soil moisture was also highest (Butterbach-Bahl et al., 2013). At the top of the slope (Top), and keeping the decrease in soil moisture with time in mind, the increase in N2/N2O ratios with time suggests a shift to nitrification as source of N2O.
65% to about 45% vol. in the lab thaw experiment, which supports the hypothesis that near-surface soil layers become drier after snowmelt and that aerobic nitrification takes over from anaerobic denitrification as the main source of N\textsubscript{2}O. As nitrification is temperature sensitive as well as oxygen dependent (Butterbach-Bahl et al., 2013), the increasing soil temperatures with season progression may contribute to increases in N\textsubscript{2}O emission rates as time passes after thaw.

The trend was found in the lab incubations without plants, but also in the SEM patterns based on the field measurements that included plants. Here, similarly to the lab observations, NO\textsubscript{3} concentrations decreased unconnected to a simultaneous N\textsubscript{2}O emission increase with time after thaw (DAST), while a negative trend in soil moisture (p = 0.051) was observed impacting NO\textsubscript{3} concentrations. In the field measurements, each point on the slope is hydrologically connected along the slope. NO\textsubscript{3} leaching inputs from upslope, which flow in the near-surface soil layers only in the early growing season (Rasmussen et al., 2021) may therefore help explain NO\textsubscript{3} decrease from early to mid-growing season, as the leaching input moves to deeper soil layers. In the mid- and late growing seasons, however, the decrease in NO\textsubscript{3} content rather suggests that N-uptake from both microbes (such as seen in the lab experiment) and plants increases with higher temperature and lower soil moisture as the season progresses. In spite of different absolute soil water NO\textsubscript{3} content, the patterns observed after first thaw were thus similar in the controlled lab environment and in the field study, and the most important explaining factor for soil solution NO\textsubscript{3} concentration was in fact season progression, DAST, through its influence on soil moisture.

### 4.3. Plants as regulators of NO\textsubscript{3} and indirectly N\textsubscript{2}O emissions

Lack of plant N uptake impacted the incubation thaw period soil water chemistry, leaving more NO\textsubscript{3} in solution. In the field, NO\textsubscript{3}-N content depended on NH\textsubscript{4}+-N content, which by a tendency (p = 0.053) was related to NDVI (as proxy for plant biomass). Plant size is related to plant N demand (e.g., Sturm et al., 2001; Eckersten et al., 2007), and higher plant uptake with higher NDVI can be a regulating factor of NO\textsubscript{3} availability through their NH\textsubscript{4}+ acquisition, because nitrification is then limited by NH\textsubscript{4}+ availability. With no correlation between NO\textsubscript{3} and N\textsubscript{2}O fluxes, the plants did not regulate N\textsubscript{2}O emissions via N-uptake. On the contrary, NDVI and N\textsubscript{2}O fluxes had a significantly positive relationship, which is counter-intuitive because of N competition between plants and denitrifiers. Such a link could suggest that there are underlying, not measured processes, which are missing from the SEM. This could be a measure of root exudation, which could give labile C for denitrification as proposed for the same site by Kolstad et al. (2021), increased transpiration rates, which have been linked to N\textsubscript{2}O emission increase (Pihlatie et al., 2005), or general microbial activity, which could increase NH\textsubscript{4}+ content and NDVI, but also provide substrate for nitrification, possibly the dominating source of N\textsubscript{2}O production as the season progresses.

DAST did not affect Total Dissolved N (TDN) content, which is mainly made up by organic N compounds. This suggests that mineral N content is more affected by season, because of its attractiveness as N source for plants and microbes (Liu et al., 2018; Sistla et al., 2012), and that plants and microbes are the regulators of NO\textsubscript{3} content as growing season progresses (e.g. Buckeridge et al., 2016; Semenchuk et al., 2015; Binfield et al., 2021).

### 4.4. Day after soil thaw as temporal variable for understanding ecological processes

There were significant patterns of seasonal progression (significant decrease in NO\textsubscript{3} concentrations and increase in N\textsubscript{2}O emissions) in the incubation experiment, which represented top soils across the entire slope. In the field, where seasonality was also spatially normalized to the DAST, season progression (DAST) was in fact the variable in the SEM with most explanatory power over the most ecological, chemical and physical variables measured. DAST was a stronger explainer of NDVI than plant nutrient availability and explained much of the variability in soil moisture content, soil temperature, N\textsubscript{2}O flux and NO\textsubscript{3} concentrations in situ.

The impact of season progression on the ecosystem is indirect, because the fact that time passes after soil thaw in itself does not cause e. g., NO\textsubscript{3} decrease. Rather, plants react to light availability and temperature in spring, and their N uptake, which will increase after snowmelt, soil thaw and the beginning of their growing season (Billings et al., 2000), thus impacts soil NO\textsubscript{3} content. The variability of e.g., soil moisture and soil temperature are aligned in such a way that they have a direction of a general decrease in soil moisture after snowmelt (modified by precipitation) and a general increase in soil temperature (e.g. Miller, 1982). The fact that the variabilities of the ecosystem variables are
significantly correlated with season progression may be the cause of the considerable explanatory power held by the DAST variable, and an argument for its usefulness in a SEM that aims to tease out ecological relationships in an ecosystem. For example, soil temperature had no significant impact on N\textsubscript{2}O emissions or NO\textsubscript{3} content, likely because temperature is impacted by many other things than season progression. Using DAST in the SEM could account for only the variation in temperature that is season-dependent and therefore show a temperature impact on e.g., N\textsubscript{2}O emissions through DAST.

4.5. Normalizing thaw season onset in terms of space

Variation in snowmelt timing between years and in a heterogeneous landscape can confound otherwise general biogeochemical patterns because of its impact on growing season onset, soil moisture and temperature, N release and thus soil biogeochemical processes (Kępski et al., 2017; Niittynen et al., 2020). This means that statistically significant seasonal patterns can be difficult to identify across several years and in space (e.g. Mastepanov et al., 2013; Rasmussen et al., 2020; Kolstad et al., 2021) when working with Day Of Year. Using spatial difference in thaw season onset to normalize time to the first day of soil thaw does not solve all variability related to spatial position, but aligning variations to season onset may help to understand other spatial variability more clearly, as well as temporal patterns that were otherwise overprinted by strong snowmelt variability effect. Snowmelt date has for example long been seen as the beginning of summer by tundra biologists, as the disappearance of snow allows plants to start photosynthesizing (Khor-san Rosa et al., 2015; Assmann et al., 2019). The results of this study suggest that a time variable based on timing of snow disappearance and soil thaw is useful when studying plant-soil interactions and biogeochemical processes across a slope with a marked snow patch development. A significant increase in N\textsubscript{2}O emission over the season, spanning the whole slope and two very different growing seasons, was revealed, and this was not visible without the spatial normalization of the temporal driving variable. In the future, with more variation in seasonal climate (Westergaard-Nielsen et al., 2018), and with climate change possibly altering snow melt timing (Cooper, 2014), normalizing based on snowmelt and soil thaw timing could reduce variation and enable comparison across years.

5. Conclusions

The first thaw after snowmelt can result in a release and downslope transport of nitrate across Arctic hillslopes. Here, we show that only 1–2% of this nitrate flux is converted into a gaseous N flux dominated by N\textsubscript{2}O (about 80%), and N\textsubscript{2}O only plays a minor role. When normalizing the temporal patterns in terms of spatial differences and inter-annual variability in snow melt date, we conclude that the thaw pulse of NO\textsubscript{3} did not seem to provide substrate for additional denitrification. In fact, as the growing season progressed, decreasing soil moisture suggests that nitrification became the most important source of N\textsubscript{2}O, coinciding with N\textsubscript{2}O emissions increasing over the summer along with the soil temperature increase.

The SEM model demonstrated the complexity of biologically available inorganic dissolved N compounds and the link to plant N uptake and N\textsubscript{2}O production. The model suggested that nitrate is made available through nitrification throughout the growing season, but only a minor fraction ends up being denitrified as the majority is taken up by plants and microbes.

By using the Day After Soil Thaw as temporal variable in the SEM, we showed how seasonal progression was the strongest explanatory power in the model, and the method provides the opportunity to study other ecological and biogeochemical relationships otherwise hidden by spatial and inter-annual differences in growing season onset. The approach thus is useful, although relating Day After Soil Thaw to Day After Snow Melt site-specifically is necessary for a low-cost, easily applicable normalization variable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found at https://doi.org/10.1016/j.soilbio.2022.108840.

References
