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Emissions of atmospherically reactive gases nitrous acid and nitric oxide from Arctic permafrost peatlands

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Keywords: Arctic ecosystem, soil nitrogen cycle, HONO and NO, nitrification, denitrification, atmospheric chemistry

Supplementary material for this article is available online

Abstract

Soils are important sources of nitric oxide (NO) and nitrous acid (HONO) in the atmosphere. These nitrogen (N)-containing gases play a crucial role in atmospheric chemistry and climate at different scales because of reactions modulated by NO and hydroxyl radicals (OH), which are formed via HONO photolysis. Northern permafrost soils have so far remained unexplored for HONO and NO emissions despite their high N stocks, capacity to emit nitrous oxide (N_2O), and enhancing mineral N turnover due to warming and permafrost thawing. Here, we report the first HONO and NO emissions from high-latitude soils based on measurements of permafrost-affected subarctic peatlands. We show large HONO (0.1–2.4 μg N m^{-2} h^{-1}) and NO (0.4–59.3 μg N m^{-2} h^{-1}) emissions from unvegetated peat surfaces, rich with mineral N, compared to low emissions ($\leqslant$0.2 μg N m^{-2} h^{-1} for both gases) from adjacent vegetated surfaces (experiments with intact peat cores). We observed HONO production under highly variable soil moisture conditions from dry to wet. However, based on complementary slurry experiments, HONO production was strongly favored by high soil moisture and anoxic conditions. We suggest urgent examination of other Arctic landscapes for HONO and NO emissions to better constrain the role of these reactive N gases in Arctic atmospheric chemistry.

1. Introduction

Traditionally, high-latitude soils have been considered negligible sources of nitrogenous gases to the atmosphere. Cold and often wet soil conditions slow down the decomposition and mineralization processes (Robinson 2002), thus limiting the availability of mineral nitrogen (N) for microbial pathways producing N-containing gases. However, a recent synthesis shows that nitrous oxide (N_2O) emissions commonly occur in permafrost-affected soils and can reach high rates in soils with high N availability, for example, as a consequence of disturbed or completely lacking vegetation cover or input of additional N from permafrost thaw (Voigt *et al* 2020). These observations suggest that, in addition to N_2O release, other N-containing gases might occur from permafrost-affected soils, but they have never been studied.

Particularly important in this context are nitrous acid (HONO) and nitric oxide (NO), atmospherically reactive gases which are emitted from soils (Kubota and Asami 1985, Galbally *et al* 1987, Su *et al* 2011, Oswald *et al* 2013) (figure 1). The photolysis of HONO generates the hydroxyl radical (OH), a key atmospheric oxidant that initiates the removal of pollutants, such as carbon monoxide (CO) and the potent greenhouse gas methane (CH_4) (Lelieveld *et al* 2004). OH participates in the formation of secondary organic aerosols by oxidizing volatile organic compounds (VOCs), which further trigger cloud formation (Claeys 2004). Nitric oxide, on the other hand, regulates the ozone (O_3) cycle in the atmosphere as

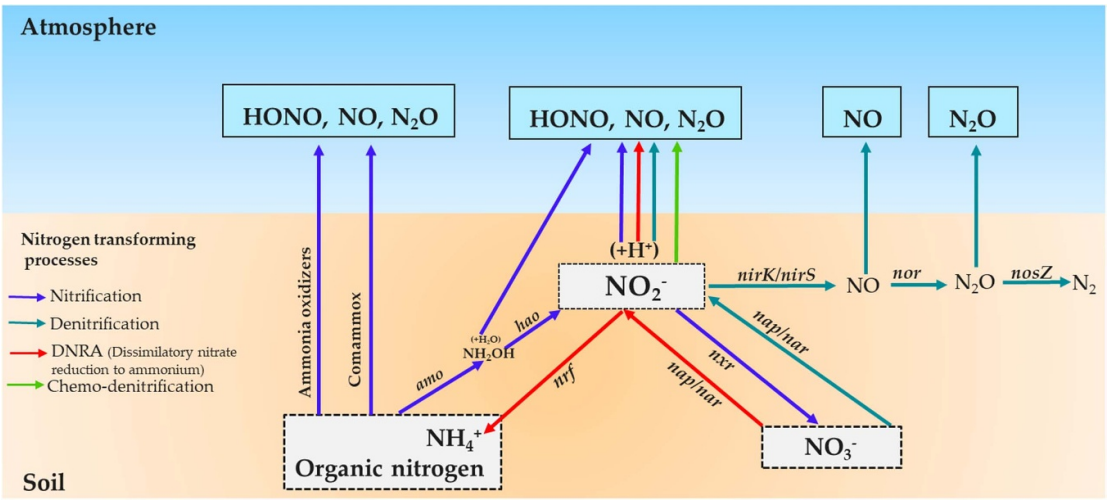

Figure 1. Nitrogen transforming processes release nitrous acid (HONO), nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2) from soil to the atmosphere. HONO, NO, and N_2O is produced in aerobic ammonia (NH_4^+) oxidation (blue arrows) by chemolithotrophic bacteria, archaea, and comammox organisms (complete ammonia oxidation to nitrate) (Oswald *et al* 2013, Ermel *et al* 2018, Han *et al* 2021). Ammonia oxidation can also support HONO formation via abiotic reactions between hydroxylamine (NH_2OH) and water (Ermel *et al* 2018). The denitrification process (turquoise arrows) contributes to soil NO and N_2O emissions during the sequential reduction of nitrate (NO_3^-) under anaerobic conditions (Knowles 1982). Soil nitrite (NO_2^-) produced via nitrification, denitrification, and dissimilatory nitrate reduction to ammonium (DNRA, red arrows) can be converted chemically in the presence of reduced metals (e.g. Fe^{+2}) and organic substances (e.g. humic acid) into gaseous NO and N_2O in the process called chemo-denitrification (green arrow) (Coby and Picardal 2005). Nitrite can also react chemically with proton (H^+) to form HONO and NO (Cleemput and Samater 1995, Su *et al* 2011, Bhattarai *et al* 2021). The italic terms above the colored arrows indicating nitrogen transforming processes denote the genes encoding enzymes carrying out the respective processes. The *amo* is ammonia monooxygenase oxidizing NH_4^+ to NH_2OH, *hao* is hydroxylamine oxidoreductase oxidizing NH_2OH to NO_2^-, *nxr* is nitrite oxidoreductase oxidizing NO_2^- to NO_3^-, *nap* and *nar* are periplasmic and cytoplasmic enzymes respectively reducing NO_3^- to NO_2^-, *nrf* is formate-dependent dissimilatory nitrite reductase converting NO_2^- to NH_4^+, *nirK*, and *nirS* are copper and cytochrome-*cd1* based enzymes respectively reducing NO_2^- to NO, *nor* is heme or heme-copper based enzyme reducing NO to N_2O, and *nosZ* is nitrous oxide reductase reducing N_2O to atmospheric N_2.

well as the formation of another atmospheric oxidant, the nitrate (NO_3^-) radical (Atkinson 2000). Therefore, HONO and NO have a crucial role in atmospheric chemistry and climate, and understanding their emission sources is paramount.

Numerous studies have reported substantial HONO and NO emissions from agricultural soils (Davidson and Kingerlee 1997, Stehfest and Bouwman 2006, Su *et al* 2011, Maljanen *et al* 2013, Oswald *et al* 2013, Scharko *et al* 2015, Wu *et al* 2019, Bhattarai *et al* 2021), where fertilization and other management practices lead to the high availability of mineral N. The global emissions of NO_x ($NO + NO_2$) from agricultural soils (3.7 Tg N yr^{-1}) are dominated by NO emissions (Ciais *et al* 2013). Agricultural soils are also globally significant sources of the potent greenhouse gas N_2O (3.8 Tg N yr^{-1}) (Tian *et al* 2020), suggesting that the production mechanisms of HONO, NO, and N_2O are interlinked and related to high N turnover rates in soil (Maljanen *et al* 2013, Bhattarai *et al* 2018, 2019, Wu *et al* 2019). Indeed, studies have clearly shown the role of microbial N-transformation pathways, most importantly nitrification and denitrification, behind N_2O, HONO, and NO production (Oswald *et al* 2013, Scharko *et al* 2015, Ermel *et al* 2018, Wu *et al* 2019, Bhattarai *et al* 2021, Han *et al* 2021) (figure 1). In addition to reports from agricultural soils, a few studies have reported HONO and NO emissions from soils under natural vegetation, such as biocrust (Weber *et al* 2015) and forest soils (Mushinski *et al* 2019). However, pristine Arctic soils have so far remained entirely unexplored concerning HONO (Bhattarai *et al* 2021) and NO (Davidson and Kingerlee 1997) emissions, despite their well-documented capability to emit N_2O and extensive soil N stocks, which are becoming increasingly vulnerable to mobilization (Voigt *et al* 2020) as a consequence of warming and permafrost thaw (Meredith *et al* 2019).

Some of the highest N_2O emissions from permafrost-affected soils have been found in peatlands (Voigt *et al* 2020). Permafrost-affected peatlands cover up to 46% (1.7×10^6 km^2) of the Northern Hemisphere peatland and are important storehouses of soil organic carbon (185 Pg C) and N (10 Pg N) (Hugelius *et al* 2020). Permafrost-affected peatlands in the Arctic region have surfaces uplifted by permafrost, the so-called palsas and peat plateaus (Seppälä 2011, figure 2). These are common geographical features occurring in discontinuous and sporadic permafrost zone (Sannel and Kuhry 2011, Borge *et al* 2017). They are formed by permafrost aggradation, which lifts the peat surface, leading to drier conditions than the surrounding unfrozen peatland surface (Seppälä 2003). As a result of wind abrasion, parts of the palsas and peat plateaus lack

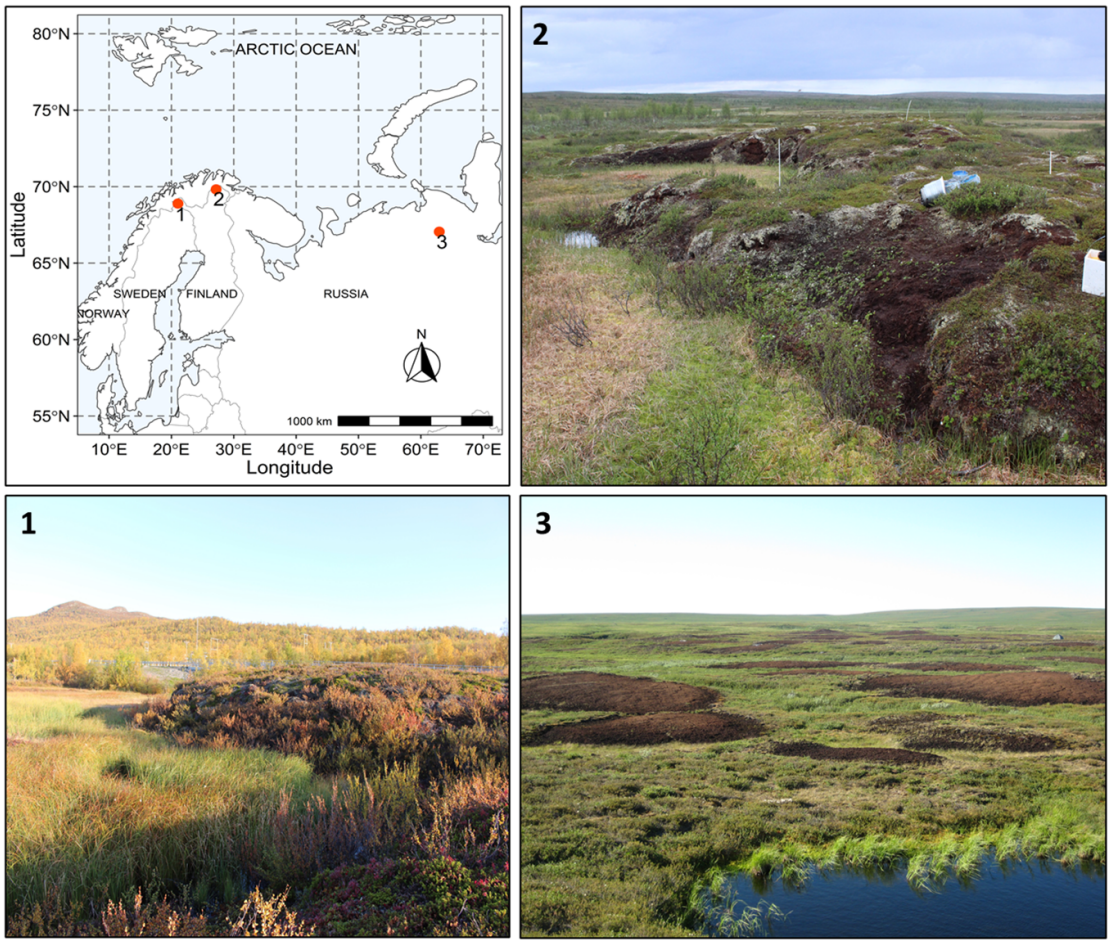

Figure 2. Sampling sites were assessed for nitrous acid (HONO) and nitric oxide (NO) emissions. (a) Map showing the sampling sites with numbered red dots, 1—Kilpisjärvi, 2—Kevo, and 3—Seida. The field view photos are numbered accordingly and show the topography and dominant vegetation of the sampling sites. A detailed explanation about sampling sites is presented in the material and methods, and a close view of the studied peat surfaces is provided in figure S1. Photo credit: 1. First author, 2. Richard E Lamprecht, and 3. Maija E Marushchak.

vegetation (Seppälä 2003). These unvegetated (bare) peat surfaces, due to well-drained conditions and lack of competition for N between plant and soil microbes, possess high total N content, high mineral N content, and low C/N ratio (Marushchak *et al* 2011, Kaverin *et al* 2016).

Due to the high availability of mineral N, unvegetated peat surfaces on permafrost peatlands are known to emit substantial amounts of N_2O *in-situ* (Repo *et al* 2009, Marushchak *et al* 2011, Siljanen *et al* 2019), and N_2O emissions have been shown to increase with permafrost thaw and climate warming (Voigt *et al* 2017a, 2017b). Such high mineral N content and high N_2O emission rates from permafrost-affected peatlands indicate a high potential for HONO and NO emissions, as these N-containing gases are an integral part of the soil N cycle (figure 1). Here, we hypothesized that Arctic permafrost peatlands are sources of HONO and NO, as they are of N_2O, with higher emissions from unvegetated compared to vegetated surfaces due to better mineral N availability for the microbial N cycle because of lack of competition for mineral N between plant and soil microbes. To address our hypothesis, we assessed HONO and NO fluxes from intact peat cores from permafrost peatlands collected from Seida (NW-Russia), Kevo, and Kilpisjärvi (N-Finland) under laboratory conditions and N_2O fluxes *in-situ* from all sampling sites except that in Kilpisjärvi. Furthermore, we conducted complementary slurry experiments to explore the effect of soil moisture on HONO and N_2O production. We also assessed the changes in HONO and NO emissions induced by permafrost thawing by measuring intact cores sampled from collapsing palsa edges.

2. Materials and methods

2.1. Site description

To test our hypothesis, we collected intact peat cores (0–0.1 m depth) from unvegetated and vegetated palsa and peat plateau surfaces (figures 2 and S1 available online at stacks.iop.org/ERL/17/024034/mmedia) in three subarctic peatlands in northern Finland and northwestern Russia (figure 2). We collected only the surface peat layer for our study because these layers connect

the peatlands with the atmosphere, thus playing a vital role in the exchange (emissions or uptake) of gases between the atmosphere and peatland. Of the three studied subarctic permafrost peatlands, two were palsa mires in the sporadic permafrost zone in northern Finland: Peera palsa located in Kilpisjärvi (68.88° N, 21.05° E, 496.5 m a.s.l.) and Vaisjäeggi palsa mire located in Kevo (69.82° N, 27.17° E, 295 m a.s.l.); and the third was the Seida peat plateau (67°030 N, 62°550 E, 100 m a.s.l.) with discontinuous permafrost located in northwestern Russia. The mean annual temperature and precipitation in Kilpisjärvi, Kevo, and Seida are −1.9 °C and 487 mm, −1.3 °C and 433 mm, and −5.6 °C and 501 mm, respectively (Repo *et al* 2009, Pirinen 2012). Additional details are provided in the supplementary material.

2.2. Peat core sampling and transportation

Intact peat cores were sampled from unvegetated (bare) peatland surfaces and adjacent vegetated surfaces (figure S1). We collected 14 (five vegetated and nine unvegetated), 19 (12 vegetated and seven unvegetated), and six (three vegetated and three unvegetated) intact peat cores in Kilpisjärvi, Kevo, and Seida, respectively. The vegetated cores included ground vegetation and small vascular plants. The dominant vegetation species were *Rubus chamaemorus* L. and *Empetrum nigrum* subsp. *hermaphroditum* in Kilpisjärvi, *E. nigrum* subsp. *hermaphroditum* and *R. chamaemorus* L. in Kevo, and mosses, *Sphagnum Dicranum* sp. and lichen, *Cladina* sp. in Seida. Six had only lichens but no vascular plants among the 12 vegetated peat cores from Kevo (figure S1). Among the nine unvegetated peat cores from Kilpisjärvi, four were collected from collapse scars, which are common microtopographic features at this site (figures 2 and S1). In Kilpisjärvi and Kevo, intact peat cores were sampled using polyvinylchloride (PVC) rings ($h = 0.12$ m, Ø = 0.1 m). A circular boundary (exact size as PVC area) was cut to the peat surface to a depth slightly deeper than the PVC ring by a sterilized knife (70 vol.% alcohol) during the peat core sampling. The cylindrical peat core was then extracted and inserted into the PVC core, after which extra depth (>0.1 m) was removed. This step was done to avoid peat compaction and to maintain the *in-situ* bulk density. The peat cores from Kilpisjärvi and Kevo were transported in cold conditions (+7 °C–8 °C) to the laboratory at the University of Eastern Finland (UEF) and further stored at +4 °C before the measurements. In Seida, surface peat samples with dimensions of 0.1 × 0.05 m (width × depth) were sampled with a sterilized knife, frozen within 24 h after sampling, and transported in zipper bags to UEF, Finland, where they were stored at −18 °C ± 2 °C until the analyses. The samples from the remote Seida study site were transported in frozen condition since that was the only way to ensure that the sample stayed cold during the shipment, which took several days.

2.3. Flux measurement of HONO, NO, and N_2O and soil analyses

Before the HONO, NO, and N_2O flux measurements, we pre-incubated the peat cores at +13 °C for 4 d to acclimatize the soils to near *in-situ* summer conditions. After unfreezing and inserting into the PVC rings described above, the Seida peat cores were stored at +4 °C for 9 d before the pre-incubation at +13 °C. An incubation temperature of +13 °C was selected because it was close to the ambient air temperatures during the sampling (Kilpisjärvi = 12.0 °C, Kevo = 15.4 °C, Seida = 13.3 °C). Moisture loss from the peat cores during the incubation period was compensated daily by adding Milli-Q water, thus maintaining the moisture content (table S1) close to the *in-situ* condition.

The HONO and NO fluxes from the intact peat cores were measured in the laboratory at room temperature (21 °C) in the dark using a dynamic chamber (made from Teflon, Polytetrafluoroethylene, (PTFE)), $V = 0.034$ m^3) system (Bhattarai *et al* 2018). This method represents the current state-of-the-art HONO and NO measurements due to the major technical challenges associated with *in-situ* HONO and NO measurements, particularly in remote areas such as the Arctic. The N_2O fluxes were measured using a static chamber system in the laboratory (Maljanen *et al* (2018) and *in-situ* (Repo *et al* 2009, Siljanen *et al* 2019) conditions. After the gas flux measurements, intact peat cores were homogenized and processed for peat physiochemical properties (table S1). More details are provided in the supplementary material.

2.4. HONO production under oxic and anoxic slurry conditions

In addition to *in-situ* moisture conditions, we further explored the role of high moisture (∼100% water holding capacity (WHC)) on HONO emissions in a soil incubation experiment under oxic and anoxic conditions. The effect of moisture on HONO production was tested with unvegetated Seida peat because it had the highest HONO and NO emissions under the *in-situ* moisture content, indicating an efficient mineral N cycling associated with HONO and NO production. Here, we assessed only HONO (not NO) as influenced by moisture because gaseous N loss via HONO was 25 times less (μg HONO–N vs μg NO–N) compared to NO from the intact cores with low moisture content (gravimetric water content (GWC), 1.7 g H_2O g^{-1}, ∼37% water filled pore space (WFPS), table S1) and we wanted to assess if an increase in moisture would increase HONO emissions or not. Additionally, we investigated the role of abiotic (chemical) HONO production by repeating the slurry experiment with Seida peat sterilized by autoclaving to stop any microbial activities. To relate the HONO production with N_2O production in peat slurries, we also followed the N_2O production over the same measurement period.

More details are provided in the supplementary material.

2.5. Statistics

Unless otherwise specified, statistical analysis and graphical presentations were done using R statistical software (R version 4.0.5), except for figure 1 and the conceptual model in figure 4, which were created with PowerPoint and a graphic software Inkscape (version 1.0.1), respectively. Before statistical testing, data distribution was assessed using the Shapiro–Wilk test, *Q*–*Q* plots, and histograms. Non-normally distributed data were transformed ($\log_{10}$ or square root) when required to achieve a normal distribution. We used one-way analysis of variance followed by Bonferroni's post hoc test on normally distributed data, whereas a non-parametric Kruskal–Wallis test followed by Dunn's post hoc test on data showing a non-normal distribution. More details are provided in the supplementary material.

3. Results and discussion

3.1. Magnitude and drivers of HONO and NO emissions

We found HONO and NO emissions from the studied permafrost peatlands (figure 3(a)). Emission rates varied considerably between (Seida > Kevo > Kilpisjärvi) and within (unvegetated > vegetated) the study sites (figure 3(a)), which is typical for N cycling processes and N gas emissions from soils in general (Butterbach-Bahl *et al* 2013). As hypothesized, the unvegetated peat surfaces had a higher mineral N content (figure 3(b)), and they emitted HONO (between 0.1 and 2.4 μg N m^{-2} h^{-1}) and NO (between 0.4 and 59.3 μg N m^{-2} h^{-1}) at higher rates compared to the vegetated surfaces (HONO, $\chi^2(1) = 7.391$, $P = 0.0065$ and NO, $\chi^2(1) = 10.542$, $P = 0.0011$, figure 3(a), table S1). The low HONO and NO emissions in the vegetated surfaces ($\leqslant$0.2 μg N m^{-2} h^{-1}; figure 3(a), table S1) were associated with lower mineral N content than in the unvegetated surfaces ($F(1,37) = 5.47$, $P = 0.0248$). The HONO emissions measured from permafrost peatlands are smaller than the global median (18 μg N m^{-2} h^{-1}) (Bhattarai *et al* 2021), but within the range reported for boreal peatlands drained for agriculture (1.7–6 μg HONO–N μg m^{-2} h^{-1}) (Maljanen *et al* 2013). Notably, the mean NO emission from the unvegetated peat surfaces of the highest emitting Seida site (59.3 μg N m^{-2} h^{-1}; table S1) is almost two-fold the global mean NO emission (30.8 μg N m^{-2} h^{-1}) (Davidson and Kingerlee 1997) and more than two-fold the mean N_2O emission (24.8 μg N m^{-2} h^{-1}) from peatlands across the permafrost region (Voigt *et al* 2020), highlighting the importance of this newly revealed N gas emissions from Arctic permafrost peatlands.

The HONO and NO emissions in the studied palsa and peat plateau surfaces were strongly interlinked ($r_s = 0.84$, $P < 0.05$, figure S2), implying common production pathways with similar environmental regulatory factors like N availability (figure 1). Both HONO and NO emissions correlated negatively with the C:N ratio ($r_s = -0.41$ for HONO and $r_s = -0.47$ for NO, $P < 0.05$, figure S2) and positively with the total mineral N content ($NH_4^+ + NO_3^-$, $r_s = 0.74$ for HONO and $r_s = 0.84$ for NO, $P < 0.05$, figure S2). These correlations reflect the tight linkage between N gas production and N mineralization in these pristine soils where, in the absence of external N inputs (low N deposition (Bobbink *et al* 2010) and biological N_2 fixation (Stewart *et al* 2014)), mineralization of organic matter is a dominant source of mineral N needed in microbial HONO and NO production. The association of low C:N ratios with high N mineralization rates (Liu *et al* 2017) and N_2O emissions (Klemedtsson *et al* 2005) has been demonstrated in previous studies.

From the two mineral N species determined, NO_3^- exhibited particularly high positive correlations with HONO and NO emissions ($r_s = 0.83$ and $r_s = 0.97$, respectively, $P < 0.05$, figure S2), while the correlations were weaker with NH_4^+ ($r_s = 0.35$ for both HONO and NO, $P < 0.05$, figure S2). The strong correlations between HONO and NO emissions and NO_3^- suggest that nitrification is of great importance for HONO and NO production, either as a direct pathway of HONO and NO production (Oswald *et al* 2013, Scharko *et al* 2015, Ermel *et al* 2018) (figure 1) or via NO_3^- supply for denitrification, where it serves as an electron acceptor. While there is accumulating evidence for the importance of denitrification as a HONO and NO source (Wu *et al* 2019, Bhattarai *et al* 2021) (figure 1), this process is strongly dependent on nitrification in pristine soils without external NO_3^- input (Siljanen *et al* 2019).

Based on the measurements from the peat cores, it is not possible to draw solid conclusions about the contribution of nitrification and denitrification to HONO and NO production or the effect of soil moisture on the production pathways. Soil moisture content in the unvegetated peat surfaces was highly variable (GWC 1.7–2.7 g H_2O g^{-1}, table S1). The HONO and NO emissions tended to be higher in drier soils ($r_s = -0.42$ for HONO and $r_s = -0.46$ for NO, $P < 0.05$, figures 3(a), S2 and table S1). This implies the high importance of nitrification (see above), which is an aerobic process requiring well-drained oxic soil. However, in our slurry incubation experiment with unvegetated Seida peat, we observed a significantly higher HONO ($\chi^2(1) = 12.403$, $P = 0.0004$; figures 3(c), S4 and table S2) and N_2O ($\chi^2(1) = 4.23$, $P = 0.0376$, figure S4) production under anoxic than oxic conditions. This points towards an important role of the reductive microbial

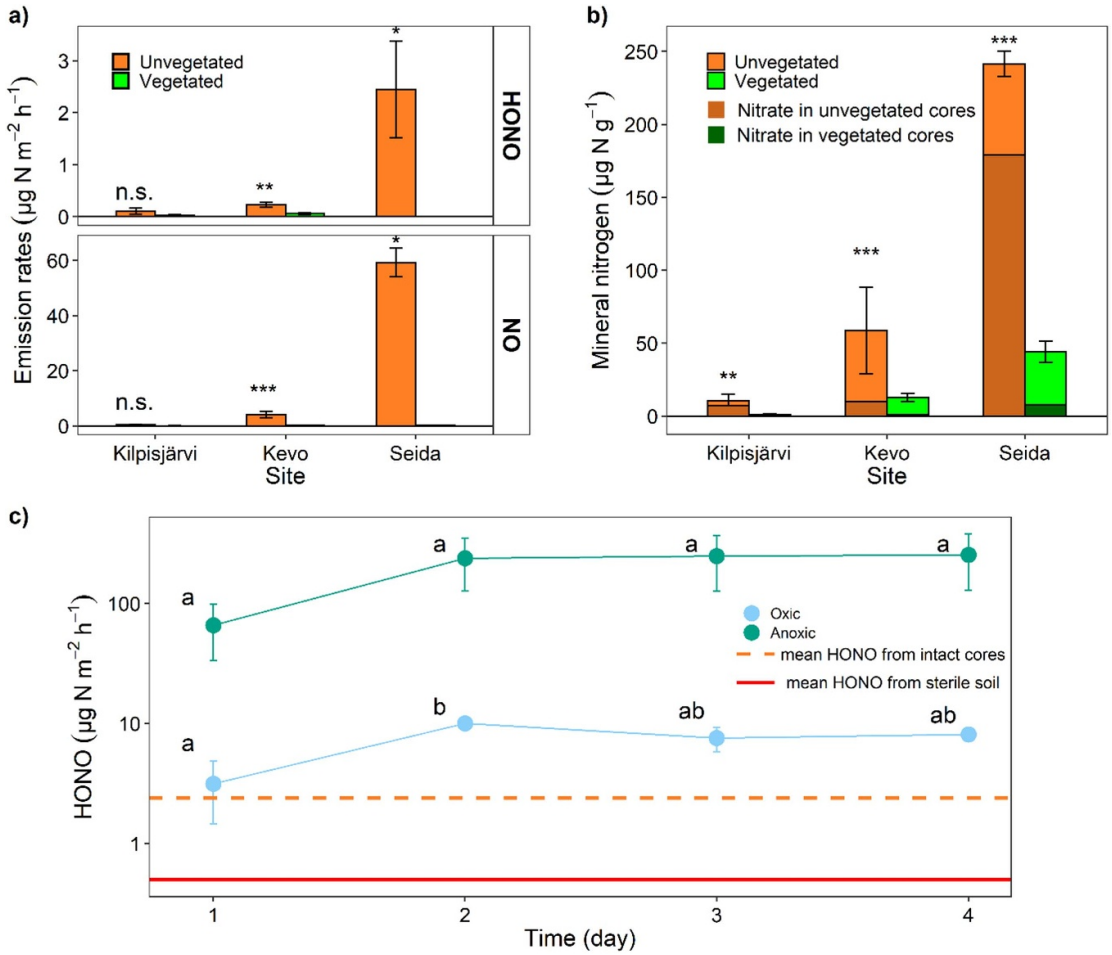

Figure 3. Nitrous acid (HONO) and nitric oxide (NO) emissions and mineral nitrogen (N) content. (a) HONO and NO emissions (μg N m^{-2} h^{-1}) from unvegetated (orange) and vegetated (green) peat cores sampled from palsa and peat plateau surfaces of three permafrost peatlands. (b) Extractable mineral N (ammonia (NH_4^+) + nitrate (NO_3^-) + nitrite (NO_2^-)) content in vegetated and unvegetated peat cores with the proportion of NO_3^- shown with darker orange and the green color within the bars. (c) HONO emission quantified over a 4 d slurry experiment with unvegetated Seida peat under oxic (sky-blue) and anoxic (turquoise) headspace. The orange dashed line represents the mean HONO emission from the Seida intact peat cores with *in-situ* moisture content (~36% WFPS). In (c) the solid red line represents the abiotic mean HONO emission (0.5 μg N m^{-2} h^{-1}, $n = 3$) quantified under anoxic conditions from sterilized (autoclaved) Seida peat slurry. The data are mean values with standard errors. The number of replicates in (a) and (b): Kilpisjärvi—$n = 5$ biologically independent samples for vegetated, $n = 9$ for unvegetated; Kevo—$n = 12$ for vegetated, $n = 7$ for unvegetated; Seida—$n = 3$. In (c), $n = 3$ laboratory replicates. Note: in (a), the scale on the y-axis is different for HONO and NO, and in (c), the y-axis has a $\log_{10}$ scale. Asterisks show statistical significances between the peat surfaces in (a) and (b). The levels of significance are: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$, and n.s. denotes statistically non-significant difference. The lowercase letters in (c) represent statistically significant differences ($P < 0.05$) in HONO emissions between the sampling days in oxic and anoxic conditions.

pathways (Wu *et al* 2019), such as denitrification, in the HONO production (Bhattarai *et al* 2021).

The results of the slurry experiment (⩾100% WHC), where anoxic conditions promoted HONO production (mean emission rates 66–254 μg N m^{-2} h^{-1} and 3–10 μg N m^{-2} h^{-1} in anoxic and oxic conditions, respectively, figure 3(c) and table S2) may seem to conflict with the results from the peat core measurements where the highest HONO emissions (2.4 μg N m^{-2} h^{-1}, figure 3(a)) were observed under low soil moisture content (table S1). However, this kind of non-linear moisture dependence can be easily explained by the multiple pathways contributing to HONO production in soils and their distinct moisture dependencies (figure 1). The double peak of HONO and NO production in soils as a factor of soil moisture, one at a low soil moisture content (20%–30% WHC) and another at a high soil moisture content (~100% WHC), has been reported previously (Wu *et al* 2019). The important implication of the wide range of soil moisture contents supporting HONO and NO production in permafrost peatlands is that these gases can be produced in variable environmental conditions, with high mineral N availability as a key prerequisite (figures 3 and S2).

3.2. Lack of association with N_2O emissions and importance of the whole peat profile for N gas production

The HONO and NO emitting unvegetated Seida cores were also emitting N_2O (0.36 μg N m^{-2} h^{-1}, table S1) under laboratory conditions, as was expected based on previous studies which have reported a close link between these nitrogenous gases (Maljanen *et al* 2013, Bhattarai *et al* 2018, 2019). Interestingly, the same was not true for the unvegetated peat cores from Kevo: these cores showed net uptake of atmospheric N_2O despite their high HONO and NO emissions. The N_2O uptake was even higher in the vegetated cores (figure S3). This N_2O uptake is in contrast with the substantial N_2O emissions from unvegetated permafrost peatland surfaces measured *in-situ* in this study (Kevo, figure S3), as well as in previous studies (Marushchak *et al* 2011, Gil *et al* 2017, Voigt *et al* 2017a, 2017b). This discrepancy between N_2O emissions in the field and the laboratory may be because the latter measurements included only the top layer (0.1 m) of the peat core. The moisture content in the cores (median WFPS 53%) was mostly below the optimum (WFPS 65%–100%) for the N_2O emissions (Voigt *et al* 2017b). Indeed, in previous studies on such permafrost peatlands, the highest soil pore gas N_2O concentrations have been observed in the middle of the seasonally thawing active layer at ~30–55 cm, indicating maximum N_2O production in the deeper and moist peat layers (Gil *et al* 2017, Voigt *et al* 2017a, 2017b). Also, the lower N_2O emissions in laboratory conditions compared to the *in-situ* from Seida (figure S3) can be explained by the importance of the deeper peat layers for N_2O production. Although the consumption of atmospheric N_2O usually occurs in water-logged soils (Hallin *et al* 2018), this process has also been found in dry soils under oxic conditions (Wu *et al* 2013, Siljanen *et al* 2020), including high-arctic soils (Brummell *et al* 2014, Wagner *et al* 2019). Furthermore, the *nosZ* gene encoding the N_2O reductase enzyme, which carries out N_2O reduction to N_2, has been detected in the surface layer of uplifted permafrost peatlands, similar to those studied here (Palmer and Horn 2012, Hetz and Horn 2021). Usually, N_2O reduction occurs when the energetically more favorable electron acceptor NO_3^- is not available. In agreement with this, the unvegetated Kevo peat with net N_2O uptake had a much lower NO_3^- content (9.9 μg N g^{-1}, 16.8% of all mineral N) than the N_2O emitting Seida peat (178.9 μg N g^{-1}, 74.1% of all mineral N) (figure 3(b)). Under *in-situ* conditions, a part of N_2O diffusing from the deeper layers may be consumed in the surface layer by organisms capable of N_2O reduction. The same microbes may switch to using atmospheric N_2O when disconnected from the deeper peat profile.

So, how can we explain continuous HONO and NO emissions despite the observed N_2O uptake in the unvegetated peat cores from Kevo (figures 3(a) and S3)? From the possible HONO and NO precursors (figure 1), NO_2^- is the first product to be formed in both oxidative (i.e. nitrification) and reductive (i.e. denitrification or DNRA) microbial pathways of the soil N cycle. This microbially produced NO_2^- can be lost as gaseous HONO and NO (a primary precursor for N_2O) via various biotic and abiotic reactions (figure 1) before it is used in, for example, the reduction steps towards N_2O production in denitrification. Thus, substantial HONO and NO production can consume the mineral N species (NO_3^- and NO_2^-), which serve as N_2O precursors, thereby effectively reducing the potential for N_2O production (figure 1). Indeed, continuous NO emissions were observed while N_2O flux ranged from zero to N_2O uptake in a grassland soil (Werner *et al* 2014), which is a phenomenon that could also be occurring for HONO.

4. Emissions of HONO and NO from Arctic soils at present and in future

Our results suggest that HONO and NO emissions can have importance for the total loss of nitrogenous gases from permafrost-affected peatlands, adding significantly to the previously discovered gaseous N release in the form of N_2O emissions (Voigt *et al* 2020). Because of the tight linkage between mineral N availability (figure S2), we have good reasons to believe that the HONO and NO emissions from Arctic peatlands will increase with warming and the associated increase in N mineralization (figure 4). This will have several consequences to atmospheric chemistry (figure 4), including the cooling effects associated with oxidation of the potent greenhouse gas CH_4 and secondary aerosol formation and further cloud formation, also associated with a cooling effect (Emmons *et al* 1997, Atkinson 2000, Schmale *et al* 2021). Indeed, in an *in-situ* warming experiment at the Seida study site, warmer temperatures led to enhanced N_2O emissions from unvegetated peat surfaces and triggered N_2O emissions from vegetated peat that had negligible N_2O emissions under ambient temperatures (Voigt *et al* 2017a). The increase in N_2O emissions reflects enhanced N turnover and might well be associated with increased HONO and NO emissions, but this is yet to be proven in future studies.

Furthermore, permafrost thaw may also promote HONO and NO release in Arctic permafrost peatlands through the input of other mineral N together with moisture changes induced by ground collapse associated with the thaw. We, indeed, observed higher NO emissions (figure S5) associated with higher moisture content from collapsing palsa surfaces than from stable ones without signs of permafrost degradation. It has to be noted that since HONO (figures 3(c), S4 and table S2) and NO

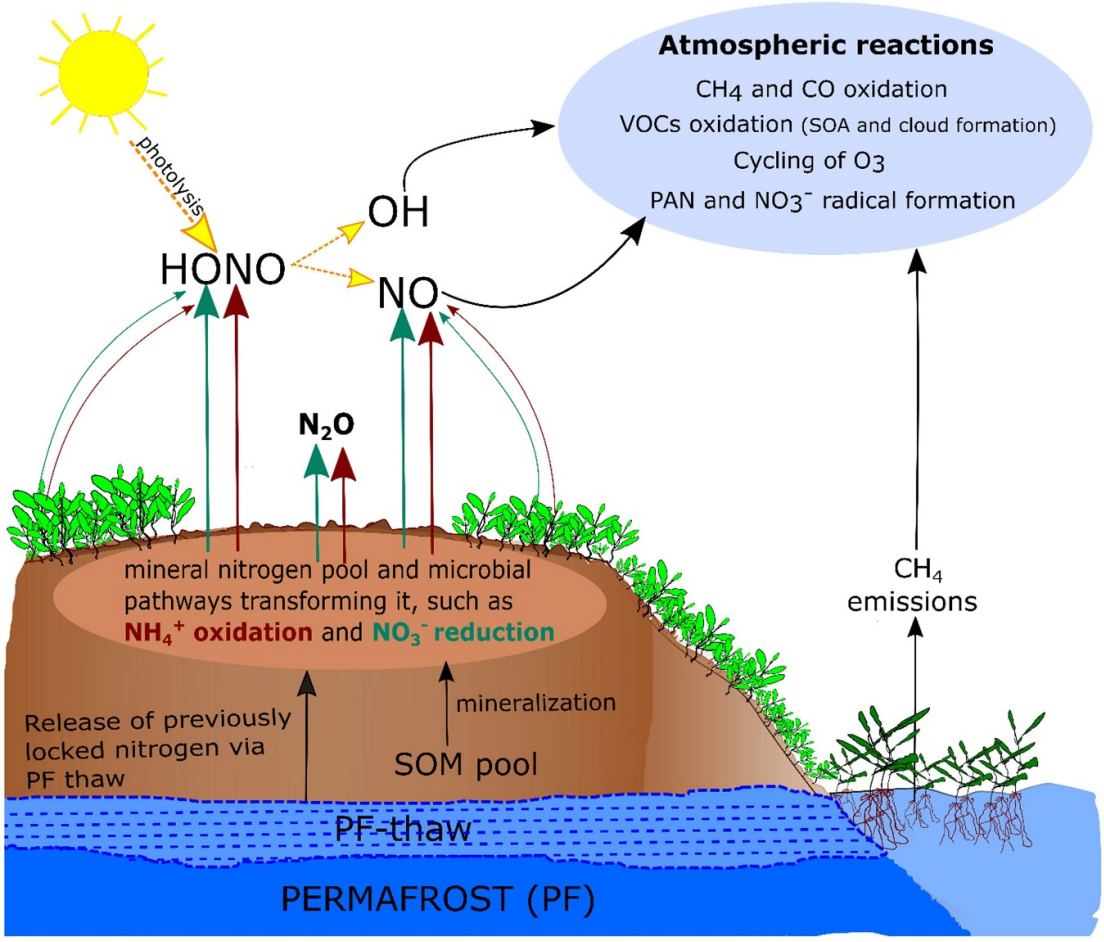

Figure 4. A conceptual model for nitrous acid (HONO) and nitric oxide (NO) emissions from permafrost-affected Arctic peatlands. Under present Arctic conditions, high HONO, NO, and nitrous oxide (N_2O) emissions are occurring from unvegetated (thick arrows) but not from vegetated (thin arrows) peat surfaces. The emissions originate from microbial and chemical transformation pathways (see figure 1 for detail) of mineral nitrogen (N), such as ammonia (NH_4^+) oxidation (dark red color) and nitrate (NO_3^-) reduction (turquoise color). The emissions of HONO and NO from both unvegetated and vegetated surfaces may increase with climate warming, causing enhanced N mineralization from soil organic matter (SOM), as well as with climate change-induced disturbances such as permafrost-thaw, thermokarst, extreme weather events, and wildfires (Voigt *et al* 2020). Upon photolysis (dotted yellow arrow), hydroxyl radicals (OH) and nitric oxide (NO) are produced from HONO, which together with NO participate in various atmospheric reactions (Atkinson 2000) (light blue oval), thus influencing the chemical balance of the Arctic atmosphere. CO—carbon monoxide, VOCs—volatile organic compounds, SOA—secondary organic aerosols, O_3—ozone, and PAN—peroxyacetyl nitrate in the light blue oval. The longer arrows for HONO and NO compared to those for N_2O are used to highlight their relevance with regards to atmospheric reactions and do not represent the magnitude of the emissions of the different gases.

(Wu *et al* 2019) production is enhanced by wetter soil conditions, occurring in the deeper peat layers, the emissions observed in our peat core measurements are likely lower than those occurring *in-situ*. This should be tested by future studies with deeper peat profiles or, preferably, by *in-situ* measurements when it will become technically feasible in places like the Arctic.

5. Conclusions

We have shown that permafrost peatlands in remote Arctic regions emit atmospherically important nitrogenous gases, HONO and NO. In urban areas, the production of NO_x (NO_2 + NO) (Delmas *et al* 1997) and HONO (NO_2 + organic soot particles) (Stemmler *et al* 2006) are primarily related to fuel combustion. Still, this emission source is very limited in remote Arctic regions with minimal anthropogenic influence. Under these circumstances, emissions of OH precursors, such as HONO and NO, from Arctic soils can be crucial for atmospheric chemistry, especially when the same ecosystems are known to emit substantial amounts of VOCs (Kramshøj *et al* 2016, Seco *et al* 2020). Because OH, NO and VOCs jointly participate in atmospheric reactions (Atkinson 2000) (figure 4), their frequent availability in the Arctic atmosphere likely plays a crucial role in the O_3 budget and for aerosol-climate interactions, which can be of global significance (Schmale *et al* 2021). However, our current knowledge about OH, NO, and VOCs sources and sinks in the Arctic region remains poorly understood (Emmons *et al* 1997, Schmale *et al* 2021). In addition, our observations of substantial

NO emissions from permafrost peatlands suggest that the current estimate of the contribution of natural soils to global NO_x emissions (15%), where Arctic soils are not considered yet, might be an underestimate (Ciais *et al* 2013). To better understand the Arctic aerosol-climate interactions and the regional O_3 and the global NO_x budget, we stress the importance of studying the HONO and NO emissions more thoroughly from Arctic peatlands and mineral soils not studied here. Only when a solid understanding of the magnitude of HONO and NO emissions and their regulatory factors (e.g. dry–wet cycles) have been established, it will become feasible to make predictions of how their emissions from the Arctic will change with warming and how they will affect the atmospheric chemistry and climate (figure 4). Therefore, we conclude that a better assessment of diverse Arctic landscapes for HONO and NO emissions are urgently needed.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors and also from the link, https://doi.org/10.5281/zenodo.5864117.

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Author contributions

The idea of assessing HONO and NO from Arctic peatlands was conceived by H R B and supported by H S, C B, and M M H R B conducted the sampling in Kevo and Kilpisjärvi, and J R assisted in the latter. R E L conducted the sampling in Seida. H R B did all the measurements and laboratory analyses, processed the data, and performed the statistical test. H R B wrote the first version of the manuscript, after which H R B and M E M finalized the text with contributions from all the other authors.

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