ENVIROMENTAL RESEARCH LETTERS

LETTER

Impact of climate change on soil nitric oxide and nitrous oxide emissions from typical land uses in Scotland

S Medinets1,2,* , S White3, N Cowan4, J Drewer2, J Dick1, M Jones1, C Andrews2, D Harvey1 and U Skiba1

1 Regional Centre for Integrated Environmental Monitoring, Odesa National I. I. Mechnikov University, Odesa, Ukraine
2 Department of Agroecology, Aarhus University, Tjele, Denmark
3 UK Centre for Ecology and Hydrology, Edinburgh, United Kingdom
* Author to whom any correspondence should be addressed.
E-mail: s.medinets@gmail.com

Abstract

Soil emissions of NO and N2O from typical land uses across Lowland and Highland Scotland were simulated under climate change conditions, during a short-term laboratory study. All locations investigated were significant sources of N2O (range: 157–277 µg N2O–N m−2 h−1) and low-to-moderate sources of NO emissions (range: 0.4–30.5 µg NO–N m−2 h−1), with a general tendency to decrease with altitude and increase with fertiliser and atmospheric N inputs. Simulated climate warming and extreme events (drought, intensive rainfall) increased soil NO pulses and N2O emissions from both natural and managed ecosystems in the following order: natural Highlands < natural Lowlands < grazed grasslands < natural moorland receiving high NH3 deposition rates. Largest NO emission rates were observed from natural moorlands exposed to high NH3 deposition rates. Although soil NO emissions were much smaller (6–660 times) than those of N2O, their impact on air quality is likely to increase as combustion sources of NOx are declining as a result of successful mitigation. This study provides evidence of high N emission rates from natural ecosystems and calls for urgent action to improve existing national and intergovernmental inventories for NO and N2O, which at present do not fully account for emissions from natural soils receiving no direct anthropogenic N inputs.

1. Introduction

Agriculturally managed soils, including grazed grasslands (GGs), receiving high nitrogen (N) input are known to be significant sources of the atmospheric pollutant ammonia (NH3); nitrous oxide (N2O), a powerful greenhouse gas (GHG) in the troposphere and a strong stratospheric ozone depletion agent; and nitric oxide (NO), an atmospheric pollutant and a precursor of tropospheric ozone [1, 2]. Besides, natural and semi-natural ecosystems located in the vicinity of agricultural activities may be exposed to increased deposition rates of N gases and aerosols [3–5]. It is well documented that N deposition may increase carbon sequestration in forest ecosystems until N saturation status is reached [6]; thereafter forests may turn into a significant source of NO and to a lesser extent N2O emissions [7–9]. Natural grassland ecosystems are more vulnerable to N critical loads resulting in biodiversity loss [4]. In Scotland, fragile moorland (peatland) habitats cover ca. 40% of the land surface area, and are strongly affected by climate change and atmospheric N pollution [10, 11]. Excessive N deposition to a typical peatland ecosystem (Whim Bog, South East Scotland) altered bryophyte growth, species dominance, and enhanced Sphagnum decomposition rates [11], while dry deposition of NH3 also led to increased soil water nitrates and N2O emissions [12, 13].

However, the cumulative impact of soil type, land cover/use and climate on NO and N2O emission rates are still not well understood [2], and data on moorland responses to NO and N2O emissions are scarce [13–15]. Both gases (NO and N2O) can be produced in the soil profile microbially and abiotically under aerobic and anaerobic conditions. To date,
nitrification and denitrification are still considered as the main microbial pathways for NO and N\textsubscript{2}O production, although other processes have been recently discovered [16–18]. It is assumed that a source of N input, temperature and the water filled pore space (WFPS) are likely crucial drivers [17, 19]. In general, highest NO rates are emitted from dry and well-aerated soils in contrast to N\textsubscript{2}O emissions, which are favored by anaerobic conditions [16, 17, 20].

Newly published assessments by Skiba et al [21] highlighted the increasing importance of soil related NO\textsubscript{x} emissions at decreasing current trends of NO\textsubscript{x} from non-agricultural sources in Europe. In California, US, N fertilized soils have become the dominant source for NO\textsubscript{x} pollution as a result of successful mitigation of fuel related NO\textsubscript{x} emissions [22]. Still, limited number of long-term datasets derived from \textit{in situ} soil NO emission measurements is the crucial drawback in both understanding the ecosystem response and improving atmospheric pollution forecast [9, 21, 23, 24].

The aim of this study is to identify soil NO and N\textsubscript{2}O emission rates from typical land uses across Lowland and Highland regions of Scotland and estimate potential impacts of climate change, hypothesizing that warmer climate with irregular rain patterns (specifically longer drought periods followed by intensive rains) will entail larger NO and N\textsubscript{2}O emissions.

2. Methods

2.1. Study sites and soil sampling
Soils were collected in October 2018 at ambient air temperatures of ca. 10 °C from the sites in the Scottish Highlands and Lowlands of Scotland (covering nine typical land uses; SI figure S1 (available online at stacks.iop.org/ERL/16/055035/mmedia)), which are included in the European Long-Term Ecological Research network (eLTER). Soil physicochemical properties upon sampling can be found in SI table S1.

From the Highland Cairngorms (C) LTER site (https://deims.org/5a0f4ee1-42aa-47e9-abfc-043a3eda12ac) and LTser Platform (https://deims.org/1b94503d-285c-4028-a3db-bc78e31dea07), soil cores were collected from three land use types: (a) fertilized GG (C-GG), (b) heather moorland (C-MH), (c) mature semi-natural pine woodland (C-FP).

The Lowland sites comprise of two sub-areas: Auchencorth Moss (A; www.auchencorth.ceh.ac.uk) and Whim Bog (W; https://deims.org/c80eaaac-411f-4e8f-a2c8-5ee7797576db). Four land uses were selected for soil core collection at Auchencorth: (a) fertilized GG (A-GG), (b) grass dominated moorland (A-MG), (c) heather moorland (A-HM) and (d) a small shelterbelt of pine trees (A-SP) separating the moorland and the fertilized GG (SI figure S1). Whim Bog is a lowland Calluna—Eriophorum blanket bog where a unique field simulation of elevated reactive N (N\textsubscript{r}) deposition as (a) dry deposited NH\textsubscript{3} and (b) wet deposited NH\textsubscript{4}\textsuperscript{+} (reduced N) and NO\textsubscript{3}\textsuperscript{−} (oxidised N) are conducted since 2002 [12, 25]. As previous studies [12, 25] have shown high N deposition rates caused more damage to ecosystems affecting all vegetation types and induced high N losses (both NO\textsubscript{3}\textsuperscript{−} leaching and N\textsubscript{2}O emission) compared to those of increased wet N deposition, which reduced moss species cover only and triggered no significant N losses. Therefore, we chose the peatland area exposed to high dry N deposition rates, which (a) simulates the real world condition when an intensive agricultural spot is located upwind and (b) may cause stronger potential damages, in a response to drought and wetting (intensive rain simulation). Soil samples were collected from the heather covered areas from (a) the high dry NH\textsubscript{3} deposition experimental area (50–70 kg N ha\textsuperscript{-1} yr\textsuperscript{-1}) (W-MN) and (b) background (control) area (8–11 kg N ha\textsuperscript{-1} yr\textsuperscript{-1}) (W-MB). Also the Auchencorth site received annually around 16.8 kg N ha\textsuperscript{-1} with atmospheric deposition, while the Cairngorm sites received only 4.3 kg N ha\textsuperscript{-1} (www.apis.ac.uk). Average annual precipitation rates were very similar (~1000 mm) across studied locations [26].

In total, 36 undisturbed soil cores (Ø = 15 cm, h = 10 cm) including their vegetation were collected from the top 10 cm of nine typical land uses across Scotland (four replicates per site) using PVC tubes and transported to the laboratory for soil incubation studies. Additionally, 108 soil samples (three samples in a vicinity per each soil core) were collected using the same soil corer for determination of field soil moisture, pH, bulk density and KCl extractable NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−}.

2.2. Soil incubation experiments
Four incubation treatments, using the same soil cores, were carried out in sequence. To avoid emission spikes (pulsing effect) caused by excavation of the intact soil cores and acclimatization, all cores were pre-incubated in two cooled incubators MIR-554 (Panasonic Healthcare Co., Ltd, Japan) set to 10 h of daylight at 15°C for 3 d (initial 3 d of drought), then the following treatments were applied:

(a) Treatment 1 (T1): ‘dry period at summer average’. Soil cores were incubated at average summer temperatures of 15 °C without replenishing soil moisture losses for 3 d prior measurements (6 d of drought in total).

(b) Treatment 2 (T2): ‘drought with increased temperature’. Soil cores were incubated at 20 °C for 5 d, without replenishing soil moisture losses, then N\textsubscript{2}O and NO fluxes were measured (11 d of drought in total).

(c) Treatment 3 (T3): ‘drought with extreme temperature increase’. Soil cores were exposed to
25 °C for 3 d without replenishing moisture losses, then N$_2$O and NO fluxes were measured (14 d of drought in total).

(d) Treatment 4 (T4): ‘intensive rainfall after a prolonged drought’. Soil cores were exposed to 4 d of drought at 20 °C (18 d of drought in total) followed by a single rewetting event (simulating intensive rain over ca. 20–30 s), equivalent to 8 mm of rain (deionized water), representing a three times larger than the average daily rainfall for the two regions. N$_2$O and NO fluxes were measured immediately after rewetting.

2.3. Flux measurements

A modified soil core gas-flow-through incubation system [27] was used to determine soil NO and N$_2$O fluxes at different temperatures (15 °C, 20 °C, 25 °C) and soil moisture contents (SMCs) (reduction and rewetting) as described in the four treatments above. Emission measurements are described in SI text S1.

The NO and N$_2$O fluxes ($\mu$g N m$^{-2}$ h$^{-1}$) were calculated as the product of the flow rate of the air stream through the undisturbed soil core, the change in gas concentration above the empty core control (converted into gas mixing ratio corrected with temperature) divided by the core area (0.0181 m$^2$). The differences in NO and N$_2$O emissions ($\Delta$Emission) were calculated as:

$$\Delta\text{Emission}(\%) = \frac{\text{Emission}_{\text{after}} - \text{Emission}_{\text{before}}}{\text{Emission}_{\text{before}}} \times 100\% - 100\%,$$

where Emission$_{\text{after}}$—emission after treatment, Emission$_{\text{before}}$—emission before treatment. Positive values indicate increase, negative values—decrease.

2.4. Soil analysis

Soil exchangeable NH$_4^+$ and NO$_3^-$ concentrations were determined at the beginning (from soil samples taken in the vicinity of soil cores) and at the end of experiment (from soil cores) using the standard procedure (SI text S2).

SMCs were calculated from the weight difference between the wet and oven dried soils (105 °C). SMCs were also quantified as the percentage WFPS accounting for the different bulk densities of the soils. The difference in WFPS ($\Delta$WFPS) were calculated as:

$$\Delta\text{WFPS}(\%) = \frac{\text{WFPS}_{\text{after}} - \text{WFPS}_{\text{before}}}{\text{WFPS}_{\text{before}}} \times 100\% - 100\%,$$

where WFPS$_{\text{after}}$—emission after treatment, WFPS$_{\text{before}}$—emission before treatment. Positive values indicate increase, negative ones—decrease.

Determination of soil pH, bulk densities and total C and total N are described in SI text S2.

2.5. Statistical analysis

All statistical analyses were carried out with the STATISTICA 7.0 (StatSoft Inc., USA).

3. Results

3.1. Variation of soil properties across the studied land uses

Prior to the start of the treatments lowest WFPS values were detected from the tree-growing areas (C-FP: 30.6%; A-SP: 32.0%). Both GGs having similar gravimetric soil moisture, significantly differed in their WFPS (C-GG: 35.6%; A-GG: 107.9%) due to substantial differences (1.7-fold) in bulk densities (SI tables S1 and S2). Moorland sites at Auchencorth Moss and Whim Bog had the largest WFPS (130.7%–149.5%), except a grass dominated moorland (A-MG: 87.0%). WFPS very gradually decreased over T1–T3 until rewetting (T4) (SI table S2).

Soils from all land uses were acidic, varying from pH 3.4–3.9 (C-FP, W-MN, W-MB, A-MH, A-MG) and pH 4.1–6.0 (A-SP, C-MH, C-GG, A-GG). Soil exchangeable concentrations of NH$_4^+$ differed significantly across the land uses (0.9–54.8 mg NH$_4^+$–N kg$^{-1}$), however in all samples NH$_4^+$ concentrations were higher than those of NO$_3^-$ (figure 1(a), SI table S2). The latter varied within narrow limits (0.1–8.6 mg NO$_3^-$–N kg$^{-1}$) compared to NH$_4^+$. C/N ratios (<20) were smaller in the GGs (C-GG and A-GG) and the shelterbelt (A-SP), while the remaining sites had larger soil C/N ratios of 23–35 (SI table S2).

3.2. Variation of soil NO and N$_2$O fluxes and their response to drought and increased temperature across different land uses

After a 3 d pre-incubation period (at summer average temperature of 15 °C) followed by a 3 d period at 15 °C, without replenishing soil moisture losses, (T1) soil NO emissions were significantly higher (6.9–30.5 μg NO–N m$^{-2}$ h$^{-1}$) from sites receiving large N inputs, such as C-GG and A-GG. NO emissions from the moorland with simulated high N deposition rates (W-MN) were approximately four fold larger than from C-GG and A-GG. Moderate NO emissions (1.5–3.0 μg NO–N m$^{-2}$ h$^{-1}$) were emitted from natural/semi-natural sites surrounded by agricultural activities in the Lowlands (A-SP, A-MG, A-MH, W-MB). Natural Highlands (C-MH and C-FP), receiving reduced N deposition (2–4-fold lower) than the Lowlands, had lowest NO emission rates (0.4–0.5 μg NO–N m$^{-2}$ h$^{-1}$) from soils (figure 1(b)). In contrast, N$_2$O emission rates showed no distinct pattern across the sites. For N$_2$O the larger emissions ranked in order of W-MB ≈ A-GG > A-MG ≈ A-MH (322–411 μg N$_2$O–N m$^{-2}$ h$^{-1}$), whereas lower emission rates (157–277 μg N$_2$O–N m$^{-2}$ h$^{-1}$) from the other land were not significant. (figure 1(c)).

After a 5 d incubation at 20 °C (T2) highest NO emissions (5.4–37.6 μg NO–N m$^{-2}$ h$^{-1}$) were still detected for GGs and W-MN (experimental exposure to N fumigation), although...
Figure 1. Exchangeable NH$_4^+$ and NO$_3^-$ concentrations (a), soil NO (b) and N$_2$O (c) fluxes for Treatments 1–4. (Data are means (± standard error) of four observations. DIN: dissolved inorganic nitrogen; Treatment 1 (T1): 15 °C and drought, no water addition; T2: 20 °C and drought; T3: 25 °C and drought; T4: 20 °C and intensive rainfall (rewetting) of 8 mm. Cairngorms: C-MH, heather moorland; C-FP, Pine forest; C-GG, fertilized grazed grassland. Auchencorth Moss: A-MH, heather moorland; A-MG, grass dominated moorland; SP, Pine shelterbelt; A-GG, fertilized grazed grassland. Whim Bog: W-MB: peatland (background N deposition); W-MN: peatland (simulated high N deposition)).
emissions from C-GG were ca. three-fold smaller than that of A-GG (figure 1(b)). Moderate NO emission rates were measured in the lower range (1.0–1.3 µg NO–N m⁻² h⁻¹) for natural lowland sites (A-MH, W-MB), whereas at the upper range (2.6 ± 1.2 µg NO–N m⁻² h⁻¹) for A-SF. Lowest NO emissions (0.4–0.5 µg NO–N m⁻² h⁻¹) were measured from the Cairngorm sites (figure 1(b), SI table S3), whereas emissions of N₂O were of similar order as in T1. The only exception was W-MN, which was ranked the 3rd highest N₂O emission, however statistically insignificantly different from W-MB, A-GG, A-MG and A-MH (373–453 µg N₂O–N m⁻² h⁻¹, figure 1(c)).

Continuous drought over the next 3 d, at an increased temperature of 25 °C (T3) resulted in contrasting differences between sites. Lowland sites receiving high N input (A-GG, W-MN) emitted significantly (p < 0.01) higher NO emissions (22.5–58.0 µg NO–N m⁻² h⁻¹) than the remaining sites (figure 1(b), SI table S3). On average, NO emissions from natural Lowlands and GG in the Cairngorms were moderate, varying from 0.9 ± 0.1 µg NO–N m⁻² h⁻¹ at A-MG to 4.5 ± 2.8 µg NO–N m⁻² h⁻¹ at A-SP. Smallest NO emissions (0.4–0.5 µg NO–N m⁻² h⁻¹) were emitted from the natural Highland C-MH and C-FP. The response patterns of N₂O emissions were similar to that of NO. Highest N₂O emissions (579–779 µg N₂O–N m⁻² h⁻¹) were observed from Lowlands receiving high N, while the lowest emissions (184–265 µg N₂O–N m⁻² h⁻¹) were detected from natural Highlands as well as from the unmanaged shelterbelt area (figure 1(c), SI table S3).

3.3. The response of soil NO and N₂O fluxes and changes in soil dissolved inorganic N concentrations on elevated wetting after drought across the different land uses

After the 18 d drought period (end of T4) the WFPS had decreased in all soils. Largest WFPS reductions (7.4%–30.2%) were observed for C-GG > A-GG > A-SP > A-MH > C-FP, while losses (<1.9%) were negligible for the water-saturated moorlands (W-MN > W-MB > A-MH) (SI table S2). Simulation of an intensive rainfall (8 mm over ca. 30 s), at 20 °C in T4, changed the distribution of exchangeable NH₄⁺ and NO₃⁻ concentrations across the soils. Largest NH₄⁺ concentrations (50.7–78.1 mg NH₄⁺–N kg⁻¹) were found at A-MH, A-MG and W-MN, moderate concentrations (5.0–24.4 mg NH₄⁺–N kg⁻¹) were registered in the C-GG, A-GG, A-SP and W-MB sites, while the lowest concentrations (>3.3 mg NH₄⁺–N kg⁻¹) were detected in natural Highlands (C-MH, C-FP). At the same time, the highest NO₃⁻ contents (16.2–53.8 mg NO₃⁻–N kg⁻¹) were observed in the Lowland soils (W-MN and A-GG) receiving large N inputs (figure 1(a), SI table S1). Concentrations of NO₃⁻ in the other soils were significantly smaller, varying over the range of 0.3–4.2 mg NO₃⁻–N kg⁻¹.

All studied soils responded to the simulated rainfall event (T4) with peak NO emissions (figure 1(b), SI table S3). The largest pulses (73.6 ± 5.7 µg NO–N m⁻² h⁻¹) were measured from W-MN (with high N deposition), whereas for the other soils NO emission ranged from 10.2 to 29.5 µg NO–N m⁻² h⁻¹. After around 60–90 min, pulse emissions decreased to 1–12-fold lower than during the pulsing event (SI figure S3). Rates of N₂O pulses were more uniform across all land uses compared to NO pulses, and varied over a narrow range of 393–569 µg N₂O–N m⁻² h⁻¹ slightly decreasing up to 1.3-fold during the 60–90 min period (SI figure S3).

4. Discussion

We have investigated the biogeochemical response of soil-plant biomes from natural and N-enriched sites to changes in temperature and soil moisture, simulating climate change, for the temperate region, Scotland. It is well known that the gradual increase of soil-surface temperature affects soils, plants and animal communities [28], and that the perturbation of rainfall patterns can lead to prolonged periods of drought followed by intensive rainfall. The latter causes the pulsing (‘Birch’) effect, which results in the increase of microbial activity after dormancy [29] accompanied by pulses of NO and N₂O emissions [8, 23, 30].

4.1. Drivers controlling soil NO and N₂O emissions under drought with increased temperature in different land uses

In this short incubation study, we have shown that typical land use categories in the Lowland and Highland regions responded differently to soil NO emissions, compared to N₂O emissions when subjected to simulated drought conditions and changes in temperature (figures 1(b) and (c)). For the Lowland moorland receiving high N deposition rates (W-MN) and the fertilized A-GG increasing drought and temperature steadily increased NO and N₂O emissions during T1–T3. Largest NO (57.9 ± 7.3 and 22.5 ± 6.2 µg NO–N m⁻² h⁻¹) and N₂O (779.3 ± 77.3 and 579.3 ± 77.7 µg N₂O–N m⁻² h⁻¹) emissions for W-MN and A-GG, respectively, coincided with significant increases (628%–757%) in soil NO₃⁻ concentrations after rewetting (p < 0.01, figures 1(a)–(c)). The large N₂O emissions at W-MN (fumigated with ca. 70 kg NH₄–N ha⁻¹ yr⁻¹), relative to background emissions (W-MB), are in agreement with previous field measurements [12].

In this laboratory study, the response to drought and temperature in T1–T3, were rather mixed. Significantly larger N₂O emissions from the low N-input W-MB were measured after T1 compared to the N-enriched W-MN. Contrary, the opposite was the case.
Figure 2. Correlation of differences in water filled pore spaces (WFPS) with differences in NO (a) and N\textsubscript{2}O (d) emissions after Treatment 1–4; WFPS differences with NO (b) and N\textsubscript{2}O (e) emission differences after Treatment 4; soil NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} concentrations with mean NO emissions (c), soil NO\textsubscript{3}\textsuperscript{-} content (expressed via log\textsubscript{10} NO\textsubscript{3}\textsuperscript{-}) with mean N\textsubscript{2}O emission (f) over Treatment 1 and 4 across all studied land uses. (Data are means (± standard error) of four observations. Treatment 1 (T1): 15 \textdegree C and drought, no water addition; T2: 20 \textdegree C and drought; T3: 25 \textdegree C and drought; T4: 20 \textdegree C and intensive rainfall (rewetting) of 8 mm. *Statistically insignificant correlation).

in T3. Release of N\textsubscript{2}O was associated (p < 0.01) with soil NO\textsubscript{3}\textsuperscript{-} concentrations (figure 2(f)). These apparent contradictions imply rather erratic changes in NO and N\textsubscript{2}O production rates.

In contrast, drought and temperature reduced NO emission (>2-fold) from the water-saturated natural Lowland moorlands (W-MB and A-MG), whereas N\textsubscript{2}O emissions increased only by 1.3–1.6 times between T1 and T3. This can be explained by a stronger and rapid response of NO emissions to drying out of surface soil layer than that in N\textsubscript{2}O [9, 30, 31].

The opposite response of NO emissions, increasing for A-GG but decreasing for C-GG to drought and temperature (T1), was likely related to the much lower WFPS for C-GG (35.9%), being close to sub-optimal levels for NO release [23] compared to 107.9% for A-GG. The high moisture losses (totally 30.2% of the initial WFPS) over 14 d drought, may have increased hydrologically isolated microsites, suppressed microbial activity and (bio)chemical interactions [32, 33]. Soil NO emission rates are known to respond rapidly to soil moisture changes, as in the well aerated top soil layer [9, 34], but has less impact on N\textsubscript{2}O mainly produced in lower layers [16].

The heather moorlands (C-MH and A-MH) responded to drought and temperature (T1–T3) with statistically insignificant changes of NO fluxes, but significant (p < 0.05) increases in N\textsubscript{2}O. However, NO and N\textsubscript{2}O emissions did not increase from the adjacent shelterbelts (C-FP and A-SP) (figure 1 (b) and (c)). At all times, lower NO and N\textsubscript{2}O emission rates were detected from the Highlands compared to the similar land uses in the Lowlands. This might be explained by the fact that Cairngorms were exposed to 2.2 and 3.9 times lower N deposition rates than Whim Bog (W-MB) and Auchencorth (all sites), respectively. In the long-term, higher N loads impact
soil N availability and microbial community composition/activity (e.g. [35]). Recently Barrat et al [31] have conceptualized that the way how microbial community utilizes substrate and its bioavailability, rather than its bulk content, control soil N transformation and emission.

We showed that changes in NO and N$_2$O emission rates (T1–T4) were always controlled by WFPS differences before and after the series of treatment (figures 2(a) and (d)). Our data are supported by a recent meta-analysis of the impact of drought and rewetting, which identified WFPS and N fertiliser rate as important drivers [31]. Nitric oxide emission rates correlated with NO$_3^−$ and NH$_4^+$ concentrations, whereas only NO$_3^−$ correlated with N$_2$O emissions (figures 2(c) and (f)). These results agree well with previous studies [7, 36–38].

4.2. Dry-wet pulses

The ‘Birch’ effect, caused by dry–wet cycles, is well known to contribute substantially to soil NO and N$_2$O annual emissions in both managed and natural ecosystems [9, 23, 30]. In dry periods, the accumulation of N substrates is suggested to occur in soil microsites, which are hydrologically disconnected from those where microbial C and N immobilization takes place, and as a result of reduced N uptake by plants [33, 39, 40]. The onset of rainfall restores hydrological connectivity and enables the dormant microbial community to mineralize accumulated organic matter, as also observed in our study. It is well documented that even a slight rainfall after drought induces high NO pulses from soils [23, 30, 34, 41], whereas larger water additions may stimulate a rapid short-term increase followed by a fast decline in NO emissions, because under anaerobic condition NO produced is mostly reduced to N$_2$O (and N$_2$) [17, 20, 36]. Rewetting of the cores (T4) significantly ($p<0.01$) increased soil dissolved inorganic nitrogen (DIN; DIN = NH$_4^+$+NO$_3^−$) concentrations in relation to DIN concentrations at the beginning of the study (figure 1(a)), apart from a non-significant increase of NH$_4^+$ concentrations for C-MH and C-GG. Particularly in soils with high carbon (>40% total carbon) and moisture contents (84%–147% WFPS prior wetting), rewetting increased DIN concentrations 1.4–10.5 fold, providing the substrates for microbial nitrification and denitrification, with consequential NO and N$_2$O emissions [9, 42, 43].

A comprehensive field study in a Californian semiarid grassland showed a significant contribution of NO$_3^−$ forming NO and N$_2$O pulses immediately after rewetting, with later involvement of NH$_4^+$ in post-wetting emissions [33]. This may also be the case in our study, where significant positive correlations between soil NO$_3^−$ concentrations with NO emission (figure 2(c)) and WFPS (SI figure S3) was observed. The latter relationship requires further targeted studies to investigate the underlying processes as currently, to the best of our knowledge, available literature could not give the reliable explanation for this. We could not find significant relationships between changes in NO and WFPS following wetting (figure 2(b)). Perhaps higher resolution measurements are needed to register rapid evolution of both parameters. However, we did observe a small increase in N$_2$O emissions in relation to WFPS upon rewetting (figure 2(d)). In addition, N$_2$O emissions were negatively correlated with the amount of water draining through the soil cores ($r=−0.79, p<0.01$; SI figure S4), which is known to be tightly depended on soil texture, and water retention potential [44]. Although we did not measure N concentrations in the leachate, it is highly likely that NO$_3^−$ concentrations will be large, based on [45]. Their mesocosm experiments demonstrated that N fertilization during drought can lead to significant increases of NO$_3^−$ leaching rates.

Surprisingly, rewetting (8 mm) stimulated much higher increases of NO emissions in natural moorlands (964%–3421%) and tree-growing areas (313%–5851%) rather than from GG (15%–189%) and the moorland (96%) receiving high N inputs (figure 1(b)). The N$_2$O increase, stimulated by the pulsing effect, was much smaller than for NO (figure 2(e)); higher emission rates were found for pine woodland (114%) and natural moorland (97%) in the Highlands as well as for Lowland shelterbelt area (69%). Other lands responded to wetting with lower increases of N$_2$O (12%–44%). We hypothesize that this may be connected to the plant composition. Those soils dominated by grass appear to have (a) higher resilience to temperature increase [46], (b) better adaptation to drought and high N input, by having a higher capacity of N uptake and accumulation in their tissues compared to bryophytes (SI figure S5), and apparently succeeded in the competition for nitrogen with the microbes upon wetting [47].

In general, mean NO emissions (23.3 ± 6.6 μg NO–N m$^2$ h$^{-1}$) induced by wetting across all study sites were 21-fold lower, and with a large coefficient of variation (CV = 85%) compared to N$_2$O emissions (506 ± 20 μg N$_2$O–N m$^2$ h$^{-1}$; CV = 12%). The large N$_2$O emissions from both, natural and managed lands in Scotland may act as significant sources of N$_2$O under drought followed by dry–wet transitions. The Birch effect, i.e. the large increase in WFPS upon rewetting induces larger N$_2$O emissions, which can substantially contribute to the total annual soil N$_2$O budget [31]. Meanwhile the increase in NO pulses was 31-fold higher compared to N$_2$O. This large increase may substantially impact on tropospheric ozone concentration in rural areas causing negative effect on vegetation and human health [17, 48].

4.3. Ratios of NO and N$_2$O emissions and pathways of their production

Conventionally it is suggested that NO/N$_2$O ratios may roughly indicate the prevailing contribution
of either nitrification (>1) or denitrification (<1) processes of NO and N\textsubscript{2}O emission [17]. This assumption is rather ambiguous, taking into account recent insights that NO is an obligate intermediate, rather than a by-product of nitrification [49] and denitrification [36]. Nitrous oxide may also be produced (a) non-enzymatically by reaction with NH\textsubscript{2}OH-derived NO during nitrification [48], (b) enzymatically under denitrification [36, 37], (c) intracellularly under nitrate ammonification [17].

Besides, in acid soils abiotic pathways and unspcific enzyme-oxidative mechanisms might be relevant for both gases production [17, 18, 50].

Emission rates are suggested to mainly depend on soil N (bio)availability, WFPS, redox potential (as a function of soil characteristics), microbial (and plant) composition and their functional gene activities [16, 17, 31]. Many studies demonstrated that changes in emission rates were mainly driven by WFPS as shown in this study (figures 2(a) and (d)) [8, 23, 33, 41, 51]. However, the accurate identification of processes contributing to NO and N\textsubscript{2}O production and release during drought/temperature increase and rewetting is hardly possible without isotopic and metagenomics studies.

In all experiments, and across all studied soils N\textsubscript{2}O emissions were substantially larger than NO emissions, with a ratio of NO/N\textsubscript{2}O ≪ 1. The contribution of NO emissions to the sum of NO + N\textsubscript{2}O after drought/temperature treatments were ranked as follows: natural Highlands (0.15%–0.24%) < natural Lowlands (0.49%–0.69%) < GGs (2.17%–2.43%) ≪ natural moorland (W-MN) exposed to high NH\textsubscript{3} deposition (6.92%–13.63%). Upon rewetting this contribution substantially increased and reached a similar threshold (3.14%–3.49%) across all sites, except for W-MN (11.9%), which hardly changed prior rewetting.

Our data have demonstrated that both natural and managed land uses can be significant sources of N\textsubscript{2}O, as confirmed in previous studies [12, 14, 15], but only a low-to-moderate source of NO. Whereas, the contribution of Scotland soils to global emission of N\textsubscript{2}O, a potent GHG and a strong agent depleting tropospheric ozone, could increase under warming climate and extreme events (drought, intensive rainfall). In general, both fluxes tended to decrease their rates with elevation, increased WFPS pulses and N input, as observed in previous studies [16, 17].

Surprisingly, rewetting stimulated higher NO emissions from natural Highlands compared to the natural and grazed Lowlands. A possible explanation may be lower soil bulk densities, providing high soil aeration need for NO emissions to the land uses MH, FP, GG in the highlands compared to the lowlands, and similarly observed in [20].

Perturbation of the biogeochemical N cycling caused by the long-term exposure to high NH\textsubscript{3} deposition rates made the natural moorland a significant NO source, compared to the other sites. Contrary, N\textsubscript{2}O emission rates were similar for the high N (W-MN) and background (W-MB) moorlands, albeit at much larger concentrations than NO. As this bog is by far the wettest site (~147% WFPS) it is unlikely that NO was produced by nitrification. The combination of a large organic matter content and high acidity implies abiotic NO production, denitrification or nitrate ammonification [17].

Across all sites stepwise drought/temperature changes and rewetting resulted in large NO losses, which were comparable to emission rates from temperate arable lands [23, 34].

It is noteworthy that presently natural soils receiving no direct N inputs (i.e. mineral fertilizers, manure, plant residues) have been accounted in recent global and national models estimating soil NO emission [52–54], but are still underrepresented in most national N\textsubscript{2}O and NO inventories and not fully considered as sources within inventories of intergovernmental bodies, such as the European Monitoring and Evaluation Programme (EMEP) under the Convention on Long-range Transboundary Air Pollution (CLRTAP), the Food and Agriculture Organization of the United Nations (FAO), the Intergovernmental Panel on Climate Change (IPCC) [21]. This is of high concern for existing official national inventory improvement in order to account for the contribution of high background NO and/or N\textsubscript{2}O emissions from natural ecosystems (often induced by atmospheric N deposition) especially for forests [7–9, 55] and moorlands [12, 14, this study].

5. Conclusions

Typical land uses in Scotland are significant sources of N\textsubscript{2}O and low-to-moderate sources of NO emissions to the atmosphere. Climate warming and extreme events, such as drought and intensive rain events appear to increase soil NO pulses and N\textsubscript{2}O emissions from both natural and managed ecosystems in the following order natural Highlands < natural Lowlands < GGs < natural moorlands receiving high NH\textsubscript{3} deposition rates. Although soil NO emissions were much smaller (6–660-fold) than those of N\textsubscript{2}O, their impact on air quality (especially during dry–wet transitions) is likely to increase relative to combustion sources of NO\textsubscript{x}, which are declining as a result of successful mitigation strategies.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
Acknowledgments

This study was facilitated by the Transnational Access project ‘HONO–NO–N2O’ funded by the EU Horizon 2020 eLTER project, supported by UK CEH (www.ceh.ac.uk) and the GEF-UNEP funded project ‘Towards INMS’ (see www.inms.international). UK CEH authors were supported by the Natural Environment Research Council Award Number NE/R016429/1 as part of the UK-SCAPE programme delivering National Capability. We are grateful to Dr Yuk Sim Tang (UK CEH) for her valuable comments and information provided.

Ethical statement

There are no ethical concerns regarding this data analysis.

ORCID iDs

S Medinets https://orcid.org/0000-0001-5980-1054
N Cowan https://orcid.org/0000-0002-7473-7916
J Drewer https://orcid.org/0000-0002-6263-6341
J Dick https://orcid.org/0000-0002-4180-9338
M Jones https://orcid.org/0000-0003-3480-7980
C Andrews https://orcid.org/0000-0003-2428-272X
U Skiba https://orcid.org/0000-0001-8659-6092

References

[1] IPCC 2019 Agriculture, Forestry and Other Land Use (vol 4) 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories Eds E Calvo Buendia, K Tanabe, A Kranjc, J Baasansuren, M Fukuda, S Nigari, A Osako, Y Pyrozhko, P Shermanau and S Federici (Switzerland: IPCC) (available at: https://www.ipcc-nggip.iges.or.jp/public/2019rf/vol4.html)
[2] Sutton M A, Howard C M, Erismann J W, Billen G, Bleecker A, Glennfält P, van Grinsven H and Grizzetti B 2011 The European Nitrogen Assessment (Cambridge: Cambridge University Press)
[3] Cape J N, van der Eerden J J, Sheppard J I, Leith I D and Sutton M A 2009 Evidence for changing the critical level for ammonia Environ. Pollut. 157 1033–7
[4] Bobbink R et al 2010 Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis Ecol. Appl. 20 30–59
[5] Medinets S et al 2020 Rates of atmospheric nitrogen deposition to agricultural and natural lands within the Lower Dniester catchment Monitoring of Geological Processes and Ecological Condition of the Environment (November 2020) (European Association of Geoscientists & Engineers) (https://doi.org/10.3997/2214-4609.202056053)
[6] Schulte-Uebbing I and de Vries W 2018 Global-scale impacts of nitrogen deposition on tree carbon sequestration in tropical, temperate, and boreal forests: a meta-analysis Glob. Change Biol. 24 416–31
[7] Liu S, Lin F, Wu S, Ji C, Sun Y, Lin Y, Li S, Li Z and Zou J 2017 A meta-analysis of fertilizer-induced soil NO and combined NO+NO3 emissions Glob. Change Biol. 23 2520–32
[8] Medinets S, Gasche R, Skiba U, Schindlbacher A, Kiese R and Butterbach-Bahl K 2016b Cold season soil NO fluxes from a temperate forest: drivers and contribution to annual budgets Environ. Res. Lett. 11 114012
[9] Medinets S, Gasche R, Kiese R, Rennenberg H and Butterbach-Bahl K 2019 Seasonal dynamics and profiles of soil NO concentrations in a temperate forest Plant Soil 445 335–48
[10] Van Der Wal R, Bonn A, Monteith D, Reed M, Blackstock K, Hanley N, Thompson D, Evans M and Alonzo I 2011 Mountains, moorlands and heaths In the UK National Ecosystem Assessment Technical Report (Cambridge: UK National Ecosystem Assessment, UNEP-WCMC) pp 105–60
[11] Levy P, van Dijk N, Gray A, Sutton M, Jones M, Leeson S, Dice N, Leith I and Sheppard L 2019 Response of a peat bog vegetation community to long-term experimental addition of nitrogen J. Ecol. 107 1167–80
[12] Sheppard L J, Leith I D, Leeson S R, van Dijk N, Field C and Levy P 2013 Fate of N in a peatland, Whim bog: immobilisation in the vegetation and peat, leakage into pore water and losses as N2O depend on the form of N Biogeoosciences 10 149–60
[13] Leeson S R et al 2017 Nitrous oxide emissions from a peat bog after 13 years of experimental nitrogen deposition Biogeoosciences 14 5753–64
[14] DREWER J et al 2010 Comparison of greenhouse gas fluxes and nitrogen budgets from an ombrotrophic bog in Scotland and a minerotrophic sedge fen in Finland Eur. J. Soil Sci. 61 640–50
[15] Skiba U et al 2013 Comparison of greenhouse gas fluxes from extensive and intensive grazing in a temperate maritime climate Biogeoosciences 10 1251–41
[16] Butterbach-Bahl K, Baggs E M, Dannenmann M, Kiese R and Zechmeister-Boltenstern S 2013 Nitrous oxide emissions from soils: how well do we understand the processes and their control Phil. Trans. R. Soc. B 368 20130122
[17] Medinets S, Skiba U, Rennenberg H and Butterbach-Bahl K 2015 A review of soil NO transformation: associated processes and possible physiological significance on organisms soil Biol. Biochem. 80 92–117
[18] Heil J, Vereecken H and Brüggemann N 2016 A review of chemical reactions of nitrification intermediates and their role in nitrogen cycling and nitrogen trace gas formation in soil Eur. J. Soil Sci. 67 23–39
[19] Skiba U, Hargreaves K J, Fowler D and Smith K A 1992 Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate Atmos. Environ. 26 2477–88
[20] Skiba U and Ball B 2002 The effect of soil texture and soil drainage on emissions of nitric oxide and nitrous oxide Soil Use Manage. 18 56–60
[21] Skiba U, Medinets S, Cardenas L, Carnell E, Hutchings N and Amon B 2021 Assessing the contribution of soil NOx emissions to European atmospheric pollution Environ. Res. Lett. 16 025009
[22] Almaraz M, Bai E, Wang C, Trousdell J, Conley S and Falloon I 2018 Agriculture is a major source of soil NOx pollution in California Sci. Adv. 4 eaao3477
[23] Medinets S, Gasche R, Skiba U, Medinets V and Butterbach-Bahl K 2016a The impact of management and climate on soil nitric oxide fluxes from arable land in the Southern Ukraine Atmos. Environ. 137 113–28
[24] Song L, DREWER J, Zhu B, Zhou M, Cowan N, Levy P and Skiba U 2020 The impact of atmospheric N deposition and N fertilizer type on soil nitric oxide and nitrous oxide fluxes from agricultural and forest Eutric Regosols Biol. Fertil. Soils 56 1077–90
[25] Sheppard L J, Crossley A, Leith I D, Hargreaves K J, Carrafe J A, van Dijk N, Cape J N, Sleep D, Fowler D and Raven J A 2004 An automated wet deposition system to compare the effects of reduced and oxidised N on ombrotrophic bog species: practical considerations Water Air Soil Pollut. 4 197–205
[26] Coyle M et al 2019 Meteorological measurements at Auchencorth Moss from 1995 to 2016 Geosci. Data J. 6 16–29
[27] Drewer J, Braban C F, Tang Y S, Anderson M, Skiba U M, Dragosits U and Trathan P 2015 Surface greenhouse gas fluxes downwind of a penguin colony in the sub-Antarctic Atmos. Environ. 123 9–17
[28] Lembrechts J J et al 2020 SoilTemp: a global database of near-surface temperature Glob. Change Biol. 26 6616–29
[29] Birch H F 1964 Mineralisation of plant nitrogen following alternate wet and dry conditions Plant Soil 20 43–69
[30] Kim D G, Vargas R, Bond-Lamberty B and Turetsky M R 2012 Effects of soil rewetting and thawing on soil gas fluxes: a review of current literature and suggestions for future research Biogeosciences 9 2459–83
[31] Barrat H A, Evans J, Chadwick D R, Clark I M, Le Cocq K M and Cardenas I 2020 The impact of drought and rewetting on N₂O emissions from soil in temperate and Mediterranean climates Environ. J. Soil Sci. (https://doi.org/10.1111/ejs.13015)
[32] Manzoni S, Schimel J P and Porporato A 2012 Responses of soil microbial communities to water stress: results from a meta-analysis Ecology 93 930–8
[33] Leitner S, Homyak P M, Blankinship J C, Eberwein J, Jenerette G D, Zechmeister-Boltenstern S and Schimel J P 2017 Linking NO and N₂O emission pulses with the mobilization of mineral and organic N upon rewetting dry soils Soil Biol. Biochem. 115 461–6
[34] Laville P, Lehuger S, Loubet B, Chaumartin F and Cellier P 2011 Effect of management, climate and soil conditions on N₂O and NO emissions from an arable crop rotation using high temporal resolution measurements Agric. For. Meteorol. 151 228–40
[35] Andersen R, Chapman S J and Artz R R E 2013 Microbial communities in natural and disturbed peatlands: a review Soil Biol. Biochem. 57 979–94
[36] Russow R, Stange C F and Neue H U 2009 Role of nitrate and nitric oxide in the processes of nitrification and denitrification in soil: results from 15N tracer experiments Soil Biol. Biochem. 41 785–95
[37] Loick N et al 2016 Denitrification as a source of nitric oxide emissions from incubated soil cores from a UK grassland soil Soil Biol. Biochem. 95 1–7
[38] Loick N et al 2021 Application of a triple 15N tracing technique to elucidate N transformations in a UK grassland soil Geoderma 385 114644
[39] Parker S S and Schimel J P 2011 Soil nitrogen availability and transformations differ between the summer and the growing season in a California grassland Appl. Soil Ecol. 48 185–92
[40] Homyak P M, Blankinship J C, Marchus K, Lucero D M, Sickman J O and Schimel J P 2016 Aridity and plant uptake interact to make dryland soils hotspots for nitric oxide (NO) emissions Proc. Natl Acad. Sci. USA 113 2608–16
[41] Williams E J, Hutchinson G L and Fehsenfeld F C 1992 NO₂ and N₂O emissions from soil Global Biogeochem. Cycles 6 351–88
[42] Sanchez-Martin L, Vallejo A, Dick J and Skiba U M 2008 The influence of soluble carbon and fertilizer nitrogen on nitric oxide and nitrous oxide emissions from two contrasting agricultural soils Soil Biol. Biochem. 40 142–51
[43] Stirling E, Fitzpatrick R and Mosley L M 2020 Drought effects on wet soils in inland wetlands and peatlands Earth Sci. Rev. 210 103387
[44] Li X, Chang S X and Salifu K F 2014 Soil texture and layering effects on water and salt dynamics in the presence of a water table: a review Environ. Rev. 22 41–50
[45] Klaus V H, Friedritz L, Hamer U and Kleinebecker T 2020 Drought boosts risk of nitrate leaching from grassland fertilization Sci. Total Environ. 726 137877
[46] Jassey V E et al 2013 Above- and belowground linkages in Sphagnum peatland: climate warming affects plant-microbial interactions Glob. Change Biol. 19 811–23
[47] Moreau D et al 2015 Plant traits related to nitrous oxide emission in a plant-microbe competition Ecology 96 2300–10
[48] Emberson L 2020 Effects of ozone on agriculture, forests and grasslands Phil. Trans. R. Soc. A 378 20190527
[49] Caranto J D and Lancaster K M 2017 Nitric oxide is an obligate bacterial nitrification intermediate produced by hydroxylamine oxidoreductase Proc. Natl Acad. Sci. USA 114 8217–22
[50] Kesik M et al 2005 Inventories of N₂O and NO emissions from European forest soils Biogeosciences 2 353–75
[51] Flechard C et al 2007 Effects of climate and management intensity on nitrous oxide emissions in grassland systems across Europe Agric. Ecosyst. Environ. 121 135–52
[52] Steinkamp J and Lawrence M G 2011 Improvement and evaluation of simulated global biogenic soil NO emissions in an AC-GCM Atmos. Chem. Phys. 11 6063–82
[53] Hudman R C, Moore N E, Meibust A K, Martin R V, Russell A R, Valin I C and Cohen R C 2012 Steps towards a mechanistic model of global soil nitric oxide emissions: implementation and space-based-constraints Atmos. Chem. Phys. 12 7779–95
[54] Rasool Q Z, Zhang R, Lash B, Cohan D S, Cooter E J, Bash J O and Lamsal L N 2016 Enhanced representation of soil NO emissions in the Community multiscale air quality (CMAQ) model version 5.0.2 Geosci. Model Dev. 9 3177–97
[55] Luo G J, Brüggemann N, Wolf B, Gasche R, Grote R and Butterbach-Bahl K 2012 Decadal variability of soil CO₂, NO, N₂O, and CH₄ fluxes at the Höglwald Forest, Germany Biogeosciences 9 1741–65