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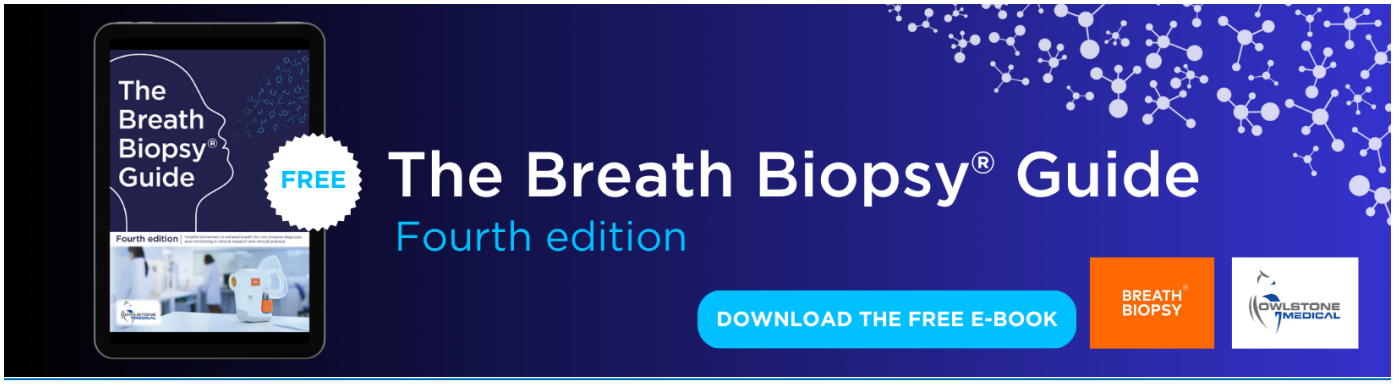

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Impact of climate change on soil nitric oxide and nitrous oxide emissions from typical land uses in Scotland

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Abstract

Soil emissions of NO and N_2O 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 N_2O (range: 157–277 μg N_2O–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 N_2O emissions from both natural and managed ecosystems in the following order: natural Highlands < natural Lowlands < grazed grasslands < natural moorland receiving high NH_3 deposition rates. Largest NO emission rates were observed from natural moorlands exposed to high NH_3 deposition rates. Although soil NO emissions were much smaller (6–660 times) than those of N_2O, their impact on air quality is likely to increase as combustion sources of NO_x 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 N_2O, 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 (NH_3); nitrous oxide (N_2O), 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 extend N_2O 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 NH_3 also led to increased soil water nitrates and N_2O emissions [12, 13].

However, the cumulative impact of soil type, land cover/ use and climate on NO and N_2O emission rates are still not well understood [2], and data on moorland responses to NO and N_2O emissions are scarce [13–15]. Both gases (NO and N_2O) 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_2O 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_2O 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_x emissions at decreasing current trends of NO_x from non-agricultural sources in Europe. In California, US, N fertilized soils have become the dominant source for NO_x pollution as a result of successful mitigation of fuel related NO_x emissions [22]. Still, limited number of long-term datasets derived from *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_2O 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_2O emissions.

2. Methods

2.1. Study sites and soil sampling

Soils were collected in October 2018 at ambient air temperature of *ca.* 10 °C from the sites in the 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 Ecosystem 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/5a04fee1-42aa-47e9-abfc-043a3eda12ac) and LTSER Platform (https://deims.org/1b94503d-285 c-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.acuk) and Whim Bog (W; https://deims.org/c80eaaac-411 f-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_r) deposition as (a) dry deposited NH_3 and (b) wet deposited NH_4^+ (reduced N) and NO_3^- (oxidised N)_are conducted since 2002 [12, 25]. As previous studies [12, 25] have shown high dry N deposition rates caused more damage to ecosystems affecting all vegetation types and induced high N losses (both NO_3^- leaching and N_2O 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_3 deposition experimental area (50–70 kg N ha^{-1} yr^{-1}) (W-MN) and (b) background (control) area (8–11 kg N ha^{-1} yr^{-1}) (W-MB). Also the Auchencorth site received annually around 16.8 kg N ha^{-1} with atmospheric deposition, while the Cairngorm sites received only 4.3 kg N ha^{-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 replicas 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_4^+ and NO_3^-.

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_2O 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_2O 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_2O 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_2O 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_2O 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_2O emissions (ΔEmission) were calculated as:

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

where $\text{Emission}_{\text{after}}$—emission after treatment, $\text{Emission}_{\text{before}}$—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 (ΔWFPS) were calculated as:

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

where $\text{WFPS}_{\text{after}}$—emission after treatment, $\text{WFPS}_{\text{before}}$—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 moistures, 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_2O 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_2O emission rates showed no distinct pattern across the sites. For N_2O the larger emissions ranked in order of W-MB ≈ A-GG > A-MG ≈ A-MH (322–411 μg N_2O–N $m^{-2}\ h^{-1}$), whereas lower emission rates (157–277 μg N_2O–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

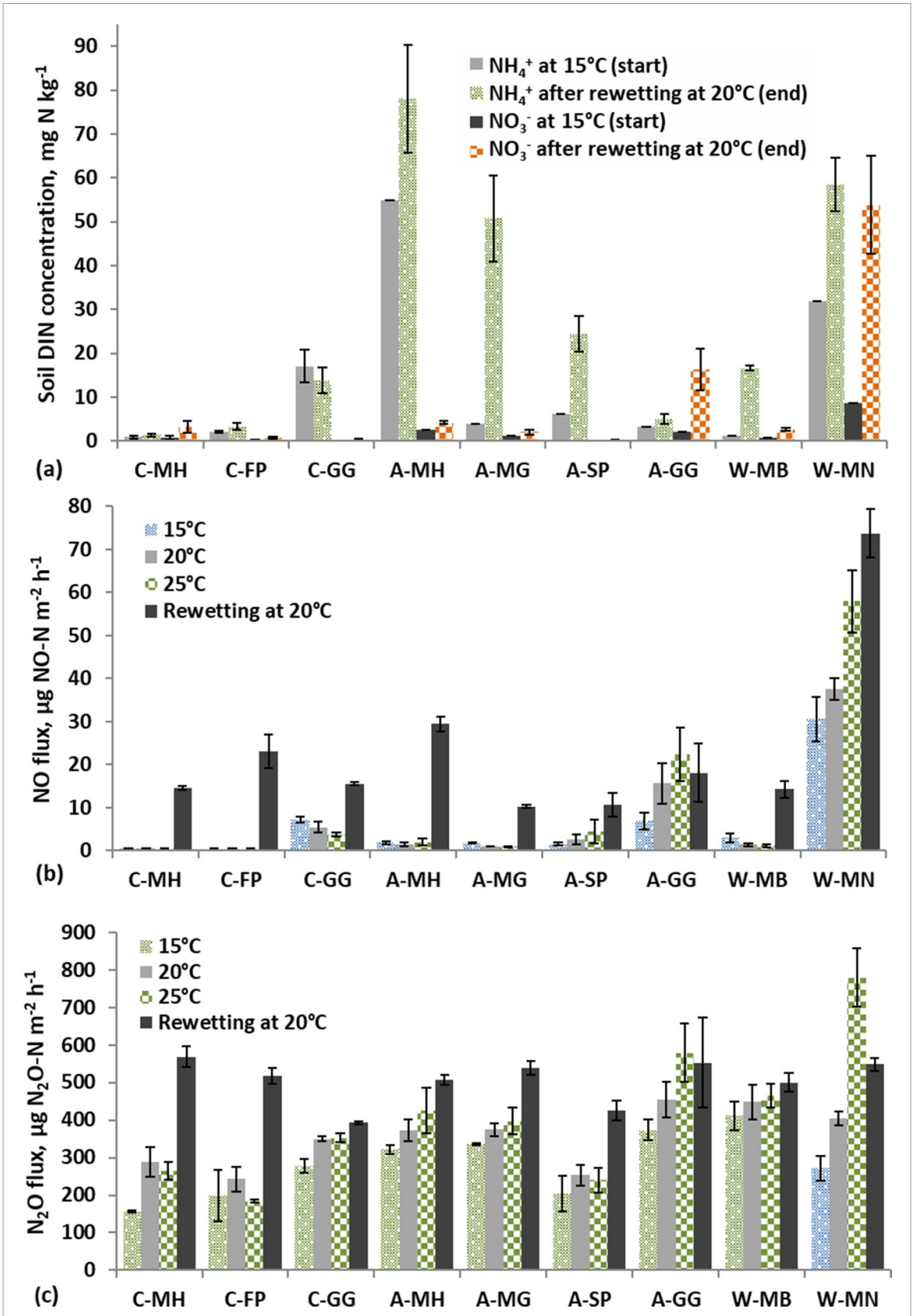

Figure 1. Exchangeable NH_4^+ and NO_3^- concentrations (a), soil NO (b) and N_2O (c) fluxes for Treatments 1–4. (Data are means (± standard error) of four observations. DIN: dissolved inorganic nitrogen; Treatment 1 (T1): 15 °C and drought, no water addition; T2: 20 °C and drought; T3: 25 °C and drought; 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 N_2O were of similar order as in T1. The only exception was W-MN, which was ranked the 3rd highest N_2O emission, however statistically insignificantly different from W-MB, A-GG, A-MG and A-MH (373–453 μg N_2O–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 N_2O emissions were similar to that of NO. Highest N_2O emissions (579–779 μg N_2O–N m^{-2} h^{-1}) were observed from Lowlands receiving high N, while the lowest emissions (184–265 μg N_2O–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 N_2O 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 > C-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 NH_4^+ and NO_3^- concentrations across the soils. Largest NH_4^+ concentrations (50.7–78.1 mg NH_4^+–N kg^{-1}) were found at A-MH, A-MG and W-MN, moderate concentrations (5.0–24.4 mg NH_4^+–N kg^{-1}) were registered in the C-GG, A-GG, A-SP and W-MB sites, while the lowest concentrations (>3.3 mg NH_4^+–N kg^{-1}) were detected in natural Highlands (C-MH, C-FP). At the same time, the highest NO_3^- contents (16.2–53.8 mg NO_3^-–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 NO_3^- in the other soils were significantly smaller, varying over the range of 0.3–4.2 mg NO_3^-–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 N_2O pulses were more uniform across all land uses compared to NO pulses, and varied over a narrow range of 393–569 μg N_2O–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 soil, plant 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 N_2O emissions [8, 23, 30].

4.1. Drivers controlling soil NO and N_2O 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 N_2O 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 N_2O emissions during T1–T3. Largest NO (57.9 ± 7.3 and 22.5 ± 6.2 μg NO–N m^{-2} h^{-1}) and N_2O (779.3 ± 77.3 and 579.3 ± 77.7 μg N_2O–N m^{-2} h^{-1}) emissions for W-MN and A-GG, respectively, coincided with significant increases (628%–757%) in soil NO_3^- concentrations after rewetting ($p < 0.01$, figures 1(a)–(c). The large N_2O emissions at W-MN (fumigated with ca. 70 kg NH_3–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 N_2O 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

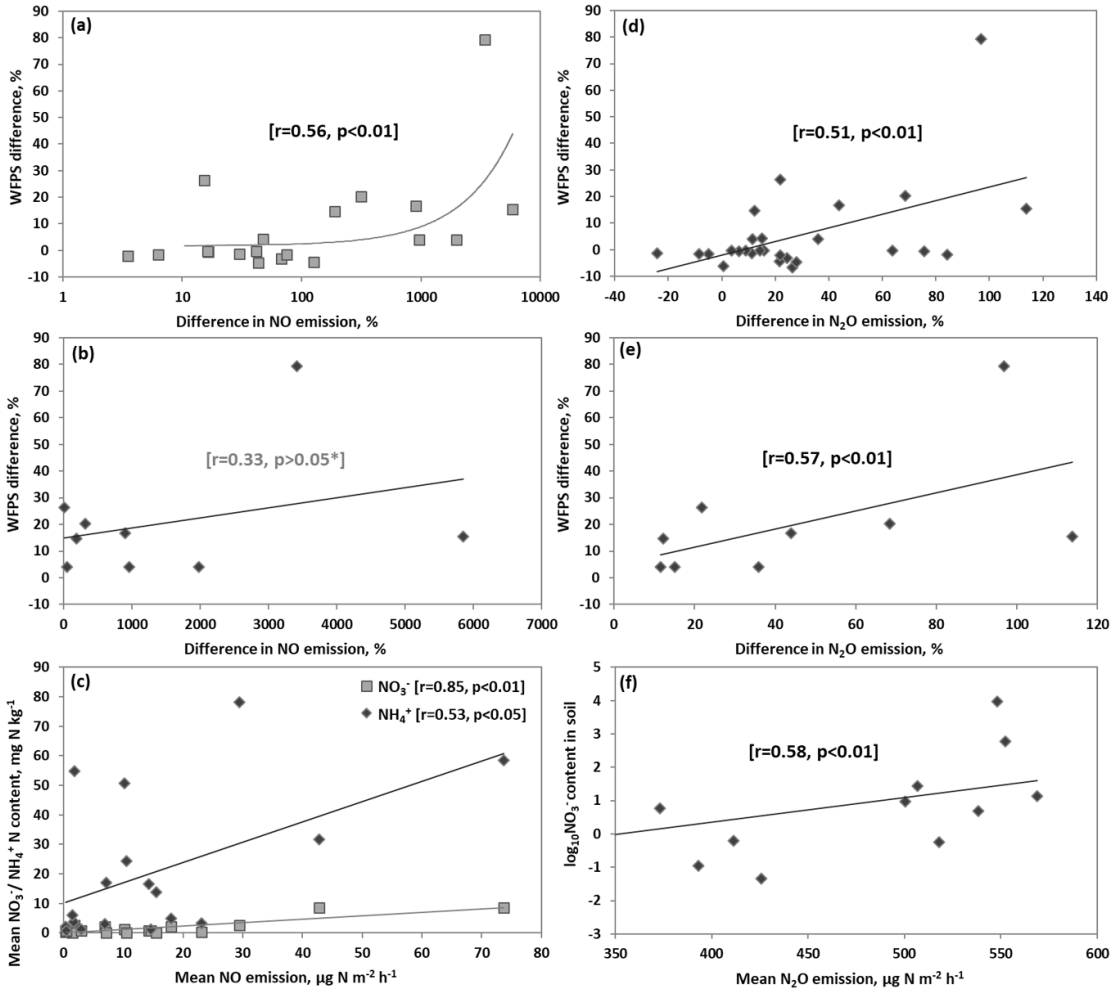

Figure 2. Correlation of differences in water filled pore spaces (WFPS) with differences in NO (a) and N_2O (d) emissions after Treatment 1–4; WFPS differences with NO (b) and N_2O (e) emission differences after Treatment 4; soil NO_3^- and NH_4^+ concentrations with mean NO emissions (c), soil NO_3^- content (expressed via $\log_{10}NO_3^-$) with mean N_2O emission (f) over Treatment 1 and 4 across all studied land uses. (Data are means (± standard error) of four observations. 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.
*Statistically insignificant correlation).

in T3. Release of N_2O was associated ($p < 0.01$) with soil NO_3^- concentrations (figure 2(f)). These apparent contradictions imply rather erratic changes in NO and N_2O 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_2O 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_2O [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_2O 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_2O. However, NO and N_2O 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_2O 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_2O 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_2O 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_2O 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_2O (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_2O emissions [9, 42, 43]. A comprehensive field study in a Californian semi-arid grassland showed a significant contribution of NO_3^- forming NO and N_2O 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_2O emissions in relation to WFPS upon rewetting (figure 2(d)). In addition, N_2O 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_2O 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_2O (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_2O emissions (506 ± 20 μg N_2O–N m^{-2} h^{-1}; CV = 12%). The large N_2O emissions from both, natural and managed lands in Scotland may act as significant sources of N_2O under drought followed by dry–wet transitions. The Birch effect, i.e. the large increase in WFPS upon rewetting induces larger N_2O emissions, which can substantially contribute to the total annual soil N_2O budget [31]. Meanwhile the increase in NO pulses was 31-fold higher compared to N_2O. 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_2O emissions and pathways of their production

Conventionally it is suggested that NO/N_2O ratios may roughly indicate the prevailing contribution

of either nitrification (>1) or denitrification (<1) processes of NO and N_2O 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_2OH-derived NO during nitrification [48], (b) enzymatically under denitrification [36, 37], (c) intracellularly under nitrate ammonification [17]. Besides, in acid soils abiotic pathways and unspecific 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_2O 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_2O emissions were substantially larger than NO emissions, with a ratio of $NO/N_2O \ll 1$. The contribution of NO emissions to the sum of NO + N_2O 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_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_2O, 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_2O, 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_3 deposition rates made the natural moorland a significant NO source, compared to the other sites. Contrary, N_2O 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_2O 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_2O 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_2O 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_2O emissions from both natural and managed ecosystems in the following order natural Highlands < natural Lowlands < GGs < natural moorlands receiving high NH_3 deposition rates. Although soil NO emissions were much smaller (6–660-fold) than those of N_2O, their impact on air quality (especially during dry–wet transitions) is likely to increase relative to combustion sources of NO_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).

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Ethical statement

There are no ethical concerns regarding this data analysis.

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