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Cold season soil NO fluxes from a temperate forest: drivers and contribution to annual budgets

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E-mail: klaus.butterbach-bahl@kit.edu**Keywords:** nitric oxide, N₂O, CO₂, freeze-thaw, snowSupplementary material for this article is available [online](#)

Abstract

Soils, and here specifically acidic forest soils exposed to high rates of atmospheric nitrogen deposition, are a significant source for the secondary greenhouse gas nitric oxide (NO). However, as flux estimates are mainly based on measurements during the vegetation period, annual NO emissions budgets may hold uncertainty as cold season soil NO fluxes have rarely been quantified. Here we analyzed cold season soil NO fluxes and potential environmental drivers on the basis of the most extensive database on forest soil NO fluxes obtained at the Högwald Forest, Germany, spanning the years 1994 to 2010. On average, the cold season (daily average air temperature <3 °C) contributed to 22% of the annual soil NO budget, varying from 13% to 41% between individual cold seasons. Temperature was the main controlling factor of the cold season NO fluxes, whereas during freeze-thaw cycles soil moisture availability determined NO emission rates. The importance of cold season soil NO fluxes for annual NO fluxes depended positively on the length of the cold season, but responded negatively to frost events. Snow cover did not significantly affect cold season soil NO fluxes. Cold season NO fluxes significantly correlated with cold season soil carbon dioxide (CO₂) emissions. During freeze-thaw periods strong positive correlations between NO and N₂O fluxes were observed, though stimulation of NO fluxes by freeze-thaw was by far less pronounced as compared to N₂O. Except for freeze-thaw periods NO fluxes significantly exceeded those for N₂O during the cold season period. We conclude that in temperate forest ecosystems cold season NO emissions can contribute substantially to the annual NO budget and this contribution is significantly higher in years with long lasting but mild (less frost events) cold seasons.

1. Introduction

Nitric oxide (NO) is a main precursor of tropospheric ozone (O₃) (Ludwig *et al* 2001), which is an important short-lived greenhouse gas (GHG) and a key compound affecting the oxidizing capacity of the troposphere (Delon *et al* 2008, Steinkamp *et al* 2009). Sources of tropospheric NO are not only energy

generation processes, but also soils. NO emissions from soils have been reported for agriculturally managed and natural ecosystems. Emissions are a result of microbial and physicochemical soil N cycling processes (Schindlbacher *et al* 2004, Medinets *et al* 2015). Despite that NO fluxes from soils are generally low (<2–10 kg NO-N ha⁻¹ yr⁻¹), the large areal extent of agricultural land and forests results in a

significant contribution of soils to regional and global budgets (Butterbach-Bahl *et al* 2009, FAO 2015). Therefore, for further improving estimates, an accurate assessment of the magnitude and drivers of soil NO fluxes is required.

In recent years understanding of the diverse abiotic and biotic NO sources and sinks in soil has increased considerably (Medinets *et al* 2015, Heil *et al* 2016), and resulted in improvements of process descriptions in biogeochemical models (Butterbach-Bahl *et al* 2009, Pilegaard 2013). However, the uncertainty of annual soil NO budgets from temperate ecosystems is still considerable as NO fluxes from soil during the non-vegetation period are rarely quantified (Yao *et al* 2010, Kim *et al* 2012, Medinets *et al* 2016).

During the cold season, low soil temperatures decrease the activity of soil microorganisms and accordingly the process rates of microbial N transformations. Therefore, cold season soil NO fluxes were often considered as negligible (Yao *et al* 2010, Kim *et al* 2012, Medinets *et al* 2016). It, however, has been shown that cold season soil carbon dioxide (CO₂) fluxes contribute significantly to the annual soil C budget (*e.g.*, Chen *et al* 2013, Schindlbacher *et al* 2014) and that nitrous oxide (N₂O) fluxes from soil can even peak during the cold season (*e.g.*, De Bruijn *et al* 2009, Filippa *et al* 2009, Goldberg *et al* 2010, Yanai *et al* 2011). Therefore, microbial breakdown of organic matter and associated N cycling during the cold season could result in significant fluxes of NO. If cold period emissions are not accounted for, annual NO fluxes from ecosystems which experience seasonal climate may be underestimated.

There is evidence of significant NO emission during freeze/thaw periods in temperate cropland and grassland soil (Yao *et al* 2010, Laville *et al* 2011). Cold season NO emission pulses were observed from arable soil in Southern Ukraine (Medinets *et al* 2016) and from snow-covered soils in temperate and polar regions (*e.g.* Peterson and Honrath 2001, Davis *et al* 2004, Helmig *et al* 2009). While most of these studies are covering one or two seasons (Helmig *et al* 2009, Kim *et al* 2012, Medinets *et al* 2016), longer time series are required for a better quantification of the cold season soil NO contribution to annual budgets and for a determination of emission drivers and controls.

Here we use the unique soil NO flux measurements of the Höglwald Forest research site covering 16 years for characterizing cold season NO fluxes. Postulating that the dynamics of soil NO fluxes at the Höglwald Forest are representative of forest soil NO fluxes in the temperate zone, we hypothesize that (i) forest soils in temperate continental climate zones have significant NO fluxes during the cold season, (ii) soil NO emissions increase with soil temperatures and peaks occur during freeze-thaw periods, (iii) that NO emissions are more closely correlated with soil N₂O than soil CO₂ emissions.

2. Methods

2.1. Study site

The Höglwald (HGW) research site (48°30'N 11°11'E, 540 m a.s.l) is a temperate mature spruce forest in an agricultural area with high atmospheric nitrogen (N) deposition (20–30 kg N ha⁻¹ yr⁻¹) (Butterbach-Bahl *et al* 1997, 2002, Luo *et al* 2012, 2013). The climate is suboceanic with an annual bulk precipitation rate of 932 mm (including snow water equivalent) and an annual mean air temperature of 8.6 °C (observation period of 1994–2010; Luo *et al* 2012). The soil is a Typic Hapludalf (Soil Taxonomy 2014) (WRB (2015): Dystric Cambisol) with an acidic pH (CaCl₂) of 2.9–3.2 in the organic layer and 3.6–4.0 in the uppermost mineral soil layer (Kreutzer 1995). Main characteristics of the study site are summarized in table 1.

2.2. Flux measurements

At the Höglwald Forest site (HGW) soil-atmosphere trace gas fluxes were continuously measured for the period 1994–2010, though, due to instrument failures, no data were available for 1998–1999. Methods and measurements have been described earlier (*e.g.*, Butterbach-Bahl *et al* 1997, Gasche and Papen 1999, Luo *et al* 2013). Briefly, five static chambers (0.5 × 0.5 × 0.2 m) were used for N₂O flux measurements via immediate on-line (*in situ*) determination by gas chromatography (using Shimadzu GC 14, Duisburg, Germany). Fluxes of soil NO and CO₂ were measured using a dynamic chamber system approach, consisting of 5 flux chambers and one control chamber placed onto a PTFE sheet to account for NO/NO₂ interactions with the chamber walls. Chamber dimensions were the same as for the static chamber. Flowrate of ambient air through the chambers was 50 l min⁻¹. NO/NO₂ concentrations in sample air of the five chambers were measured using a chemiluminescence NO/NO₂ detector (CLD 770 AL ppt with converter PLC 760 or CLD 88p with photolytic NO₂ converter PLC 860, Eco Physics AG, Switzerland). CO₂ fluxes were determined using an infrared gas analyzer (BINOS 100, Rosemount, Hanau, Germany). N₂O fluxes were measured every 2 h, and NO and CO₂ fluxes were measured at hourly resolution. During snow cover, snow volume (snow water equivalent) in the chambers (derived from regular snow height and snow density measurements) was taken into account for flux calculations. The gas ports of the chambers were situated 15 cm above the soil surface. We removed snow if snow depth was >15 cm to avoid malfunctioning of the chambers and gas sampling. This, however, was rarely the case at this our site, while the mean snow depth was 4.6 cm. *I.e.* snow pack height rarely exceeded the >15 cm threshold (approx. 1.6 days per year on average) over the entire observation period and was only necessary on a few occasions in 2003, 2005 and 2006.

Table 1. Main characteristics of the Höglwald Forest site^a.

Parameter	Characteristic
Location	48 °30'N and 11 °11'E
Climate	suboceanic
Height above sea level (m)	540
Annual temperature (°C)	8.6 (1994–2010)
Annual bulk precipitation (mm)	932 (1994–2010)
Annual throughfall (mm)	ca. 600 (1994–2010)
Mean snow cover period ^b (days)	40 (1994/95–2009/10)
Mean snow depth ^b (cm)	3.8 (2007–2010) ^c /4.6 (1994–2010) ^d
Vegetation type	<i>Picea abies</i>
Annual N deposition (kg N ha ⁻¹ yr ⁻¹)	20–30
Soil type	Typic Hapludalf
Soil parent material	Pleistocene loess over tertiary sand deposits
Soil layer morphology and thickness (cm)	
Organic layer	(7–8)
L	1
Of1	2
Of2	1–2
Oh	2–3
A horizon	(0–40)
Aeh	0–5
Al	5–40
pH (CaCl ₂)	
Organic layer	2.9–3.2
Uppermost A horizon ^e	3.6–4.0
Bulk density (g cm ⁻³)	
Organic layer	0.108–0.287
Uppermost A horizon ^e	1.033–1.092
C/N ratio	
Organic layer	20–25
Uppermost A horizon ^e	18–19
C content (%)	
Uppermost A horizon ^e	1.63–2.87
Soil texture (%) of uppermost A horizon ^e	
Sand	50–64
Silt	30–38
Clay	5–11

^a Data compiled from Kreutzer (1995), Kreutzer and Weiss (1998), Butterbach-Bahl *et al* (2002), Rothe *et al* (2002), Wu *et al* (2010) and Luo *et al* (2012).

^b This study data.

^c HGW data; directly measured in the HGW site.

^d German Weather Service (GWS) data; measured in open area close to the HGW site.

^e 0–10 cm mineral soil depth.

2.3. Soil and meteorological measurements

Chamber air temperature, organic layer (3.5 cm depth from the soil surface) and mineral layer soil temperature (5 cm mineral soil depth) were measured with PT100 probes (IMKO GmbH, Germany).

Volumetric soil moisture content was determined using horizontally installed TDR probes (IMKO GmbH, Germany) for organic and mineral soil (5 cm depth). All the data were measured at 10 s resolution and logged on a hard drive using IDASw software. Snow cover was irregularly measured at HGW. We therefore used a linear relationship ($r^2 = 0.64$, $p < 0.01$) between snow cover at HGW and the nearest German Weather Service (GWS) climate station Augsburg-Mühlhausen to estimate snow cover during measurement gaps.

2.4. Definition of the cold season and freeze/thaw period

In our study the 'cold season' is defined in agreement with the definition of the non-vegetation period by the Swedish Meteorological and Hydrological Institute (SMHI 2015) as the period when the daily average air temperature is below 3 °C. To minimize biases due to short-term (singular days) temperature fluctuations, we used a 5-day moving average approach. Thus, in our study the cold season started as the five day moving average of air temperature fell below 3 °C for the first time and ended as it exceeded this threshold. The rest of the time was defined as the 'warm' period. The cold season ranged between 126 and 167 days (table S1).

Freeze-thaw events were defined as periods with changes from sub-zero to above-zero temperature of the organic soil layer. Only periods with available simultaneous N₂O and NO data were used to establish relationships between gases and environmental parameters during freeze-thaw cycles.

2.5. Seasonal and annual NO budgets

Using daily NO fluxes (Luo *et al* 2012), annual NO budgets were calculated from 1 July to 30 June of the following year to cover the corresponding cold season. Cold season NO budgets consisted of the entire cold season period, i.e. started from the beginning of cold season in autumn and finished at the end of cold season in spring of the following year (table S1). LandscapeDNDC, a biogeochemical model capable of simulating soil N trace gas fluxes, was used to gap-fill missing data (Haas *et al* 2013, Molina-Herrera *et al* 2016).

NO budgets were only calculated for years where less than 20% of data were missing. Therefore, the periods 10.97/03.98–12.01/04.02, 10.03/03.04 and 11.06/03.07–10.08/03.09 had to be excluded from the annual budget calculation (figure S1).

2.6. Statistical analysis

Correlation, as well as multiple regression analyses were performed to investigate relationships between NO, N₂O and CO₂ fluxes, soil moisture, soil and organic layer temperatures, air temperature and precipitation at high resolution (hourly or bi-hourly). Time periods with significant (>20%) gaps of daily

observations of soil NO measurements were excluded from this analysis. Missing soil environmental data were gap filled by a machine-learning technique (support vector machine, SVM), which is based on a statistical learning algorithm according to the procedure described in Wu *et al* (2010).

To reveal relationships between inter-seasonal dynamics of NO fluxes and other variables (e.g., cold season duration, air temperature, frost event period, snow covered period) the cold season mean data were used for the regression analysis. As the length of the cold season varied substantially between years, the seasonal mean data were normalized by time (per month basis) to be fitted for this analysis, when required (e.g. frost event period, snow covered period).

All analyses were carried out with STATISTICA 7.0 (StatSoft Inc., USA) and SPSS 20.0 (SPSS Inc., USA). Graphs and diagrams were created using MS Excel 2010 (Microsoft Corp., USA) and STATISTICA 7.0 (StatSoft Inc., USA).

3. Results

3.1. Meteorology during the cold season

Air temperature fluctuated from -14.9°C to $+12.8^{\circ}\text{C}$ with an average value of $0.6 \pm 2.0^{\circ}\text{C}$ during the 15 cold periods (table 2). The daily mean volumetric SMC was $31.1 \pm 15.3\%$ varying from 11.2% to 74.9%, with moisture levels being affected by precipitation amount ($r^2 = 0.014$, $p < 0.05$) and thawing (incl. snow melting). The average number of frost days (daily mean air temperature $< 0^{\circ}\text{C}$) was 55 days ranging from 16 to 108 days in the cold seasons of 2006/07 (3 November–25 March) and 1995/96 (3 November–16 April), respectively (table 2). The wettest cold season was in 1994/95, when 414 mm of precipitation was recorded for the period of 30 November–15 April and the driest was in 1997/98 (24 October–26 March) with 180 mm only. The average of the 15 cold seasons was 264 mm. The mean number of days with snow cover was 40, ranging from 10 days (2006/07) to 65 days (2004/05). The mean snow depth directly measured at the HGW site for 2007–2010 was 3.8 cm with the absolute maximum of 15.2 cm. Meanwhile, data derived at the German Weather Service site Mühlhausen (close to HGW) showed an average snow depth of 4.6 cm and an absolute maximum of 27 cm in the period 1994–2010. However, a snow cover > 15 cm was only observed rarely (*ca.* 1.6 days per year on average), namely in 2002/03 (3 days), 2004/05 (19 days) and 2005/06 (5 days).

3.2. Cold season NO, N₂O and CO₂ fluxes

The average NO flux over the 15 cold seasons was $53.0 \pm 15.7 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$ (table 2) and daily average soil NO emissions ranged from -4.4 to $182.9 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$. Whilst NO fluxes from snow covered soil was found to be lower (mean:

$31.2 \pm 9.9 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$) and varied from -4.4 to $127.6 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$. N₂O fluxes in this period were approx. three times smaller ($17.2 \pm 23.9 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$) than the NO fluxes. However, strong freeze-thaw N₂O emission events were observed in 1995/96 and 2005/06 and were more than 3.7 times larger than the average cold season flux ($63.3 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ and $66.5 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$, respectively; table 2). Maximum daily soil N₂O flux of $487.3 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ was observed in conjunction with freezing-thawing. Average cold season soil CO₂ fluxes varied from $44.6 \text{ mg CO}_2\text{-C m}^{-2} \text{ h}^{-1}$ to $86.4 \text{ mg CO}_2\text{-C m}^{-2} \text{ h}^{-1}$ with a mean value of $64.1 \pm 18.4 \text{ mg CO}_2\text{-C m}^{-2} \text{ h}^{-1}$ (table 2).

3.3. Contribution of cold season NO fluxes to annual soil NO budgets

In seven out of 15 years the number of missing data was $< 20\%$, which was considered to be sufficient to accurately assess the contribution of the cold period to annual soil NO emission budgets (figure 1). The average cumulative cold period NO flux was $1.8 \pm 0.7 \text{ kg NO-N ha}^{-1}$. For these years the total annual cumulative soil NO flux (warm and cold period fluxes) ranged between $7.3\text{--}10.2 \text{ kg NO-N ha}^{-1}$ with an average of $8.5 \pm 1.0 \text{ kg NO-N ha}^{-1}$. The mean contribution of cold periods to the annual NO budget was $22.3 \pm 10.2\%$ with a minimum of 12.8% in 2005/06 and a maximum of 41.3% in 1994/95 (figure 1).

Significant positive relationships between mean NO flux and mean cold season air temperature ($r^2 = 0.69$, $p < 0.05$; figure 2(b)) as well as less significant between individual year cold season NO flux and duration of the cold season ($r^2 = 0.43$, $p < 0.1$; figure 2(a)) could be demonstrated. While a negative dependence of time normalized (monthly) quantity of frost events ($r^2 = 0.56$, $p < 0.05$; figure 2(c)) on cold season NO flux was observed, a show significant relationship of cold season NO flux with snow cover was not existing.

3.4. Relationship between soil NO flux and environmental drivers

Hourly variations in soil NO fluxes for the entire cold season dataset significantly ($p < 0.001$) positively correlated with air ($r^2 = 0.17$), organic layer ($r^2 = 0.18$; figure 3(a)) and mineral soil temperatures ($r^2 = 0.12$). Similar relationships were found for the entire cold season data set, if fluxes observed during freeze-thaw events were excluded. There were no correlations between soil NO fluxes and soil moisture content (SMC) at both organic and mineral soil layers for the whole cold season observation period. However during periods of freeze-thaw events positive relationships were observed (organic layer SMC: $r^2 = 0.08$, $p < 0.05$ and mineral layer SMC: $r^2 = 0.27$, $p < 0.0001$).

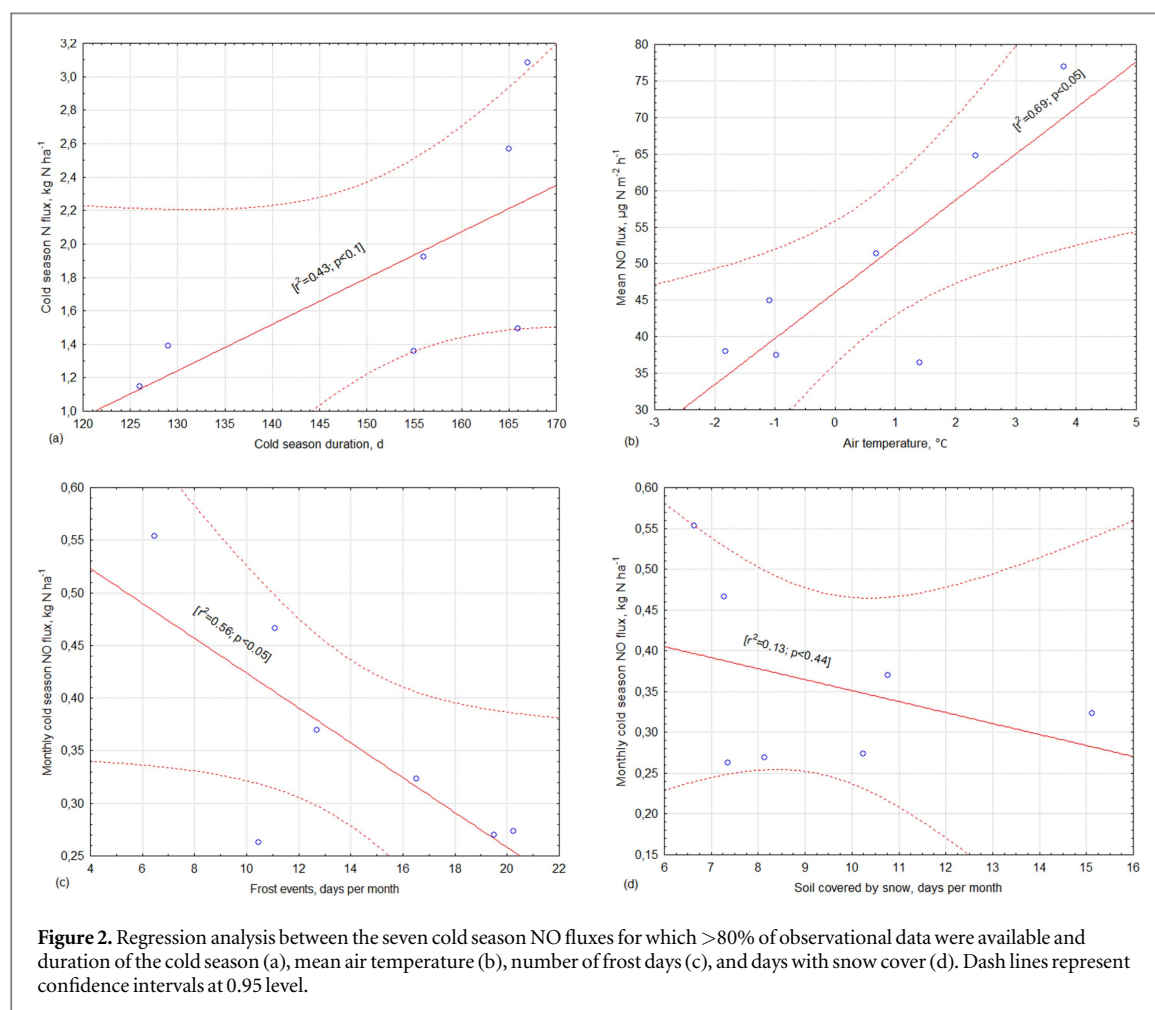
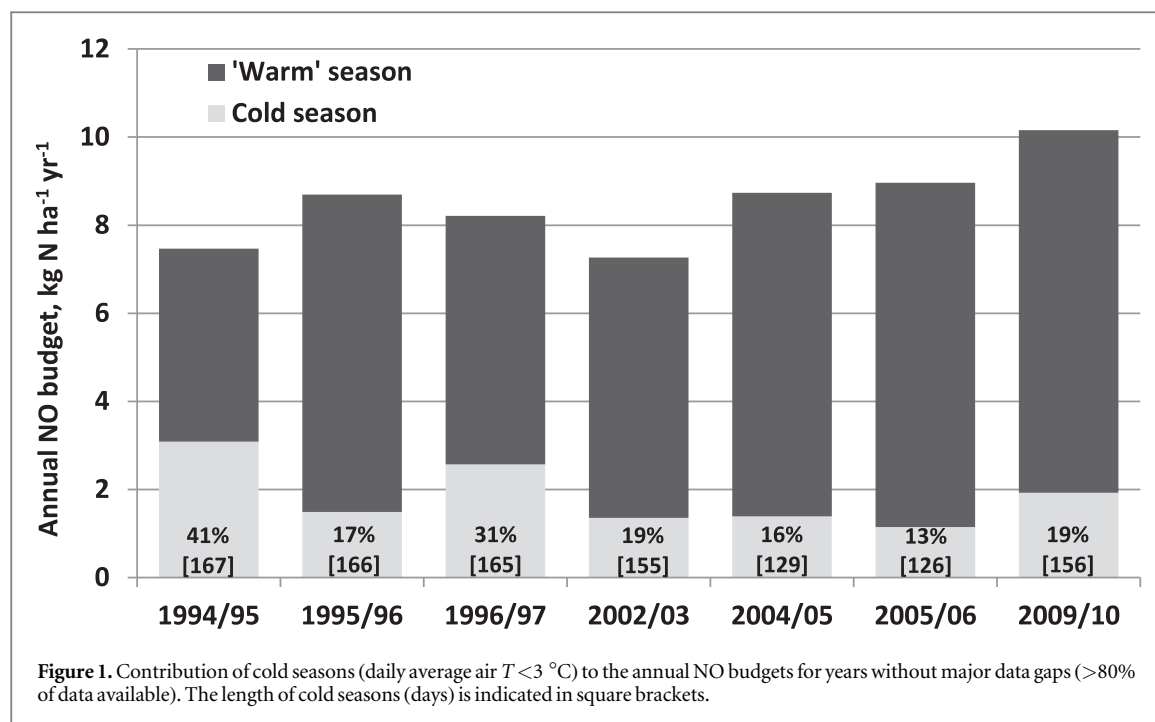
Table 2. Average annual soil NO, N₂O and CO₂ fluxes, temperatures (*T*), soil moisture content (SMC) and precipitation, days of frost (air *T* < 0 °C), frozen soil organic/mineral (5 cm) layers (*T* < 0 °C) and snow cover in each of the 15 cold seasons, 1994–2010.

Cold season	Length of cold season, d	CO ₂ flux, mg CO ₂ -C m ⁻² h ⁻¹	N ₂ O flux, μg N ₂ O-N m ⁻² h ⁻¹	NO flux, μg NO-N m ⁻² h ⁻¹	NO missed data, %	Gap filled NO flux, μg NO-N m ⁻² h ⁻¹	Air temperature, °C	Organic layer soil temperature, °C	Mineral (5 cm) layer soil temperature, °C	Precipitation, mm	SMC in organic layer, %	Frost days	Frozen period (organic), d	Frozen period (mineral), d	Days with snow cover
1994/95	167	86.4	5.7	79.1	2	76.9	3.8	2.3	3.3	414	60.5	36	23	18	37
1995/96	166	44.6	63.3	38.8	7	37.4	−1.0	0.8	0.8	210	56.8	108	78	80	45
1996/97	165	54.4 ^a	13.0	66.5	4	64.8	2.3	1.9	2.3	219	n/a ^b	61	46	44	40
1997/98	154	33.1	3.9	67.4	57	42.4	2.7	4.2	4.4	180	n/a	40	n/a	n/a	n/a
1999/00	116	10.8	3.0	69.0	44	50.2	0.7	0.2	1.3	241	n/a	44	39	14	n/a
2000/01	126	54.5	5.6	40.1	36	34.7	2.8	0.6	1.5	380	29.3	29	57	24	n/a
2001/02	140	61.9	2.9	42.0	21	38.9	1.3	1.8	2.9	312	29.2	53	41	n/a	38
2002/03	155	n/a	8.3	38.7	16	36.5	1.4	2.5	3.8	280	30.3	54	23		38
2003/04	161	43.5	2.1	45.0	52	33.9	1.8	n/a	n/a	340	27.1	50	n/a	n/a	50
2004/05	129	52.3	2.5	46.2	5	44.9	−1.1	n/a	n/a	215	n/a	71	n/a	13	65
2005/06	126	70.8	66.5	42.2	18	38.0	−1.8	0.8	0.3	218	n/a	85	24	21	43
2006/07	143	71.2	4.9	62.6	11	59.1	4.0	3.3	4.3	207	17.6	16	11	n/a	10
2007/08	160	40.7	5.1	54.9	43	42.3	2.5	2.7	3.3	291	22.7	43	11	n/a	13
2008/09	149	49.3	14.2	45.0	78	23.4	0.3	0.5	1.4	206	19.2	67	81	65	39
	156	57.1	3.5	59.4	20	51.3	0.7	5.5	3.1	252	18.5	66	n/a	44	56

Table 2. (Continued.)

Cold season	Length of cold season, d	CO ₂ flux, mg CO ₂ -C m ⁻² h ⁻¹	N ₂ O flux, μ g N ₂ O-N m ⁻² h ⁻¹	NO flux, μ g NO-N m ⁻² h ⁻¹	NO missed data, %	Gap filled NO flux, μ g NO-N m ⁻² h ⁻¹	Air temperature, °C	Organic layer soil temperature, °C	Mineral (5 cm) layer soil temperature, °C	Precipitation, mm	SMC in organic layer, %	Frost days	Frozen period (organic), d	Frozen period (mineral), d	Days with snow cover
2009/10															
Mean ^c	148	52.2	13.6	53.1	28	45.0	1.4	2.5	2.8	264	31.1	55	39	36	40
Mean ^d	152	64.1	17.2	53.0	10	50.0	0.6	2.4	2.6	258	41.5	69	39	37	46

^a Italic values indicate data sets with gaps >20%.^b Data is not available.^c Average of all years.^d Average of years without major data gaps, *i.e.* >80% of measuring data for CO₂, NO and N₂O were available.



3.5. Relationships between soil NO fluxes and soil fluxes of N_2O and CO_2

Fluxes of NO and CO_2 had similar positive response to soil temperature increase (figure 3(a)) resulting at

cross-correlation between those fluxes ($r^2 = 0.10$, $p < 0.0001$; figure 4(a)). NO and N_2O fluxes were not correlated (figure 4(a)) across the entire cold season, though during freeze-thaw events (figure 4(b)) NO

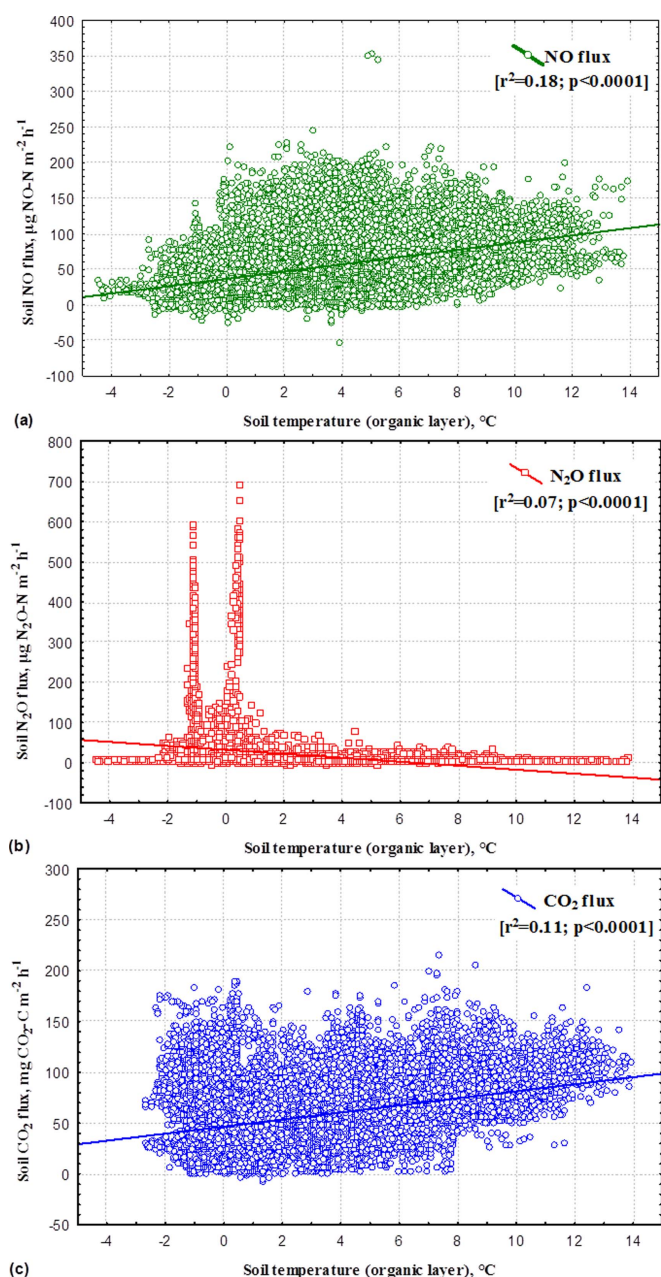


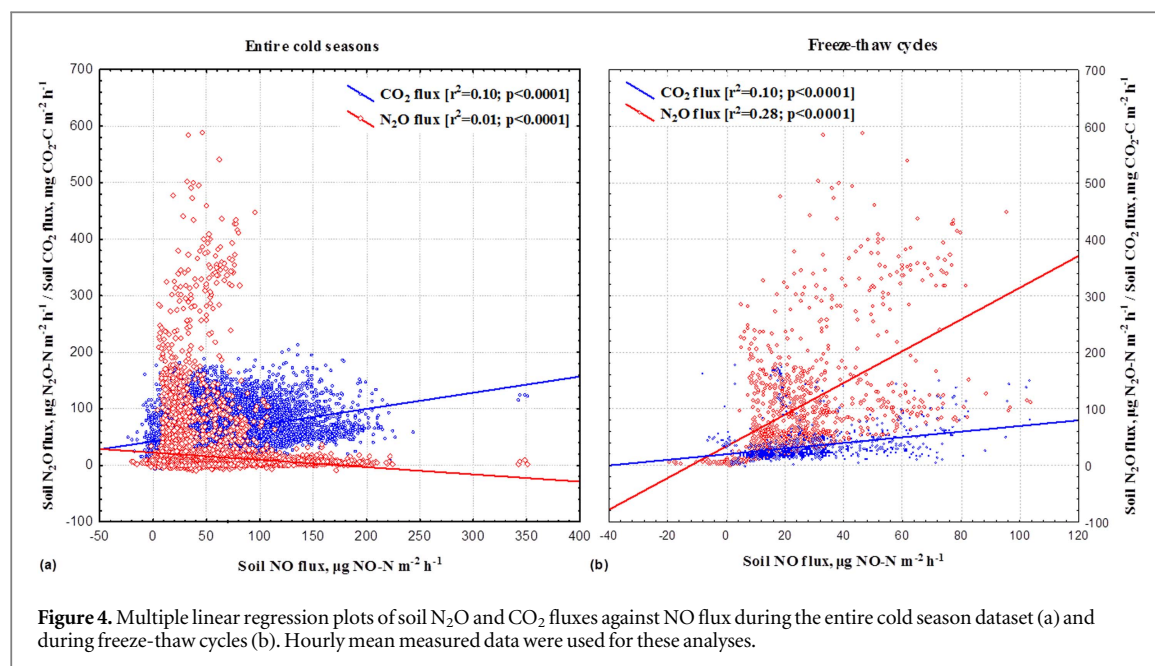
Figure 3. Linear regression plots of soil NO (a), N₂O (b) and CO₂ (c) fluxes against the organic layer soil temperature during the entire cold season dataset. Hourly mean measured data were used for these analyses.

flux correlated with N₂O flux ($r^2 = 0.28$, $p < 0.0001$) and was weakly related to CO₂ fluxes ($r^2 = 0.10$, $p < 0.0001$) too.

4. Discussion

Cold season NO flux contributed on average 22% (1.8 kg NO-N ha⁻¹) to the total annual NO budget at our observation site the Högwald Forest. Postulating that the forest is representative for the dynamic of soil NO fluxes of temperate forests this confirms our hypotheses (i) that temperate forest soils can emit significant amounts of NO during the cold season. The contribution of cold season NO flux to the annual budgets varied considerably between years (13%–

41%) and was positively correlated to the duration of the cold seasons and the mean cold season air temperatures. This suggests that, cold season NO emissions were higher in years with longer lasting cold periods during spring and/or autumn (periods, which fell below the <3 °C threshold in our study) and that such periods should not be ignored when measuring soil NO fluxes. The lowest contribution of cold season NO emissions (13%–17%) occurred in those seasons where mean air temperature was below zero (range: −1.8 to −1.0 °C) and frost periods were well above 71 days (table 2, figure 1). This suggests that soil NO emissions during short and cold winters were comparatively low. Nevertheless, even during these years, cold season emissions still contributed more than 10%



to the annual budget and therefore should not be treated as negligible.

At the Höglwald Forest cold season NO emissions were mostly larger than the N₂O fluxes in this period. Soil NO emissions showed a positive relationship to soil temperature (confirming hypotheses (ii)), an observation which is in line with previous studies (e.g., Ludwig *et al* 2001, Butterbach-Bahl *et al* 2004, Laville *et al* 2011, Medinets *et al* 2016). However none of these studies had specifically focused on the cold periods. Contrary N₂O fluxes did not correlate significantly with soil temperature, but responded very distinctively to freeze thaw cycles (figure 3(b)). The very large freeze thaw emission peaks as for N₂O (e.g., Luo *et al* 2012) were not observed for NO (rejecting hypotheses (iii)). But, freeze-thaw cycles, did raise NO emissions slightly above background (figure 4(b)).

Thawing frozen soil increases the soil moisture content and thereby rehydrates microbial and plant cells, mobilizes and releases soil nutrients and stimulates the metabolic activity of dormant microbial communities (Kemmitt *et al* 2008, De Bruijn *et al* 2009, Kim *et al* 2012). All of these activities can lead to soil NO and N₂O emission pulses (Yao *et al* 2010, Laville *et al* 2011, Yanai *et al* 2011, Kim *et al* 2012). During freeze-thaw in our study, N₂O fluxes significantly exceeded NO fluxes. Due to the relatively minor contribution of freeze-thaw events to the overall cold season period and the comparatively small freeze-thaw impact on NO emissions, freeze-thaw did not significantly affect the magnitude of the overall cold season NO emission. This is further confirmed by the inverse relationship of the number of frost events with cold season NO fluxes (figure 2(c)). This suggests, that the quantity and duration of the frozen period, which is an important aspect for N₂O pulse emissions (Papen and Butterbach-Bahl 1999, De Bruijn *et al* 2009, Wu

et al 2010, Yanai *et al* 2011) had an opposite impact on NO flux by lowering its release in absolute values compared to the rest of the cold season. As freeze-thaw seems quantitatively less important regarding NO emissions, but also with regard to soil CO₂ emissions (Luo *et al* 2012), cold season NO emissions correlated with cold season soil CO₂ flux (figure 4(a)), which showed the typical dependency on wintertime soil temperature (Schindlbacher *et al* 2014).

In spite of snow cover not being identified as a driver for cold season NO fluxes, snow cover may reduce NO release to the atmosphere. Snow melting causes topsoil over-saturation by water (Wolf *et al* 2012), which restricts gas diffusion and thereby also suppresses immediate NO release (Kiese and Butterbach-Bahl 2002, Mu *et al* 2012, Wu *et al* 2014). Furthermore, following snow melt soils often do not reach WFPS optimum conditions for NO release (Wu *et al* 2014). Whilst, abiotic transformations of NO occurring in snowpack and between snow and air which are possible and still not completely understood. E.g., Medinets *et al* (2016) observed weak net uptake of NO during snow cover periods at an agricultural site in the Ukraine. However, contradicting results have been published with regard to NO fluxes from snow covered soils as i) according to Henry's constant for NO (Sander 2015), it does not interact with snow (Bartels-Rausch *et al* 2013) and soil originated NO can be emitted via snowpack to the atmosphere (e.g., Helmig *et al* 2009), ii) snow is considered as a source of NO (France *et al* 2012) which can be produced via photolysis of NO₂⁻, NO₂ and NO₃⁻ as a by-product together with NO₂ (Seok *et al* 2015 and references therein). With our chamber design, we measured trace gas fluxes from/ to the snow surface and it therefore was not possible to distinguish if the NO was produced in the soil or in the snow layer. However, since NO efflux

was similar during snow free periods and periods with snow cover (at similar soil temperatures), we attribute the NO production primarily to soil processes. With this regard, it also should be noted that our chamber system operated only until snow depth of max. 15 cm. We therefore, occasionally, had to remove snow to keep this 15 cm threshold. As the mean snow depth at our site was (ca. 4.6 cm) and snow depth exceeded the threshold of 15 cm depth for only 1.6 days per year on average, we do not expect the snow removal having any significant effect on annual NO budgets. It is further noteworthy, that other reported NO fluxes from snow covered soil and from the snowpack itself are low $0.25\text{--}0.40\text{ }\mu\text{g NO-N m}^{-2}\text{ h}^{-1}$ (Helmig *et al* 2009; high elevation alpine forest) and $0.21\text{--}0.35\text{ }\mu\text{g NO-N m}^{-2}\text{ h}^{-1}$ (France *et al* 2012; onshore and offshore coastal Alaskan snowpacks), when compared to the mean cold season flux from snow covered soil ($31.2 \pm 9.9\text{ }\mu\text{g NO-N m}^{-2}\text{ h}^{-1}$) at our temperate forest site, which in turn was 1.7 time lower than the average cold season flux ($53.0 \pm 15.7\text{ }\mu\text{g NO-N m}^{-2}\text{ h}^{-1}$). Overall, our results indicate that snow cover itself plays a less dominant role in regulating cold season soil NO emissions at the temperate forest studied. As snow cover is mostly shallow, frost can penetrate the topsoil even during periods of snow-cover. This may be one reason for the poor relationship between snow cover and NO emissions. However, a further decrease of snow cover depth and snow cover duration, ahead with concurrent climate warming (Kreyling and Henry 2011, Klein *et al* 2016), is thus unlikely to lead to colder soils in a warmer world (Groffman *et al* 2001) but to result in warmer soils and higher soil NO emissions.

5. Conclusions

We conclude that cold season soil NO emissions can contribute significantly to the annual NO emissions of a temperate forest soil. Therefore, cold season emissions should not be neglected in annual emission budgets of these ecosystems. Compared to N₂O, NO showed little response to freeze-thaw and NO emissions were not distinctively affected by snow cover. Since cold season NO fluxes showed a strong positive relationship to air and soil temperature, these environmental drivers should receive priority, when modeling NO fluxes during winter.

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