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N_2O, NO, N_2 and CO_2 emissions from tropical savanna and grassland of northern Australia: an incubation experiment with intact soil cores

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Abstract. Strong seasonal variability of hygric and thermal soil conditions are a defining environmental feature in northern Australia. However, how such changes affect the soil–atmosphere exchange of nitrous oxide (N_2O), nitric oxide (NO) and dinitrogen (N_2) is still not well explored. By incubating intact soil cores from four sites (three savanna, one pasture) under controlled soil temperatures (ST) and soil moisture (SM) we investigated the release of the trace gas fluxes of N_2O, NO and carbon dioxide (CO_2). Furthermore, the release of N_2 due to denitrification was measured using the helium gas flow soil core technique. Under dry pre-incubation conditions NO and N_2O emissions were very low ($< 7.0 \pm 5.0$ µg NO-N m^{-2} h^{-1}; $< 0.0 \pm 1.4$ µg N_2O-N m^{-2} h^{-1}) or in the case of N_2O, even a net soil uptake was observed. Substantial NO (max: 306.5 µg N m^{-2} h^{-1}) and relatively small N_2O pulse emissions (max: 5.8 ± 5.0 µg N m^{-2} h^{-1}) were recorded following soil wetting, but these pulses were short lived, lasting only up to 3 days. The total atmospheric loss of nitrogen was generally dominated by N_2 emissions (82.4–99.3 % of total N lost), although NO emissions contributed almost 43.2 % to the total atmospheric nitrogen loss at 50 % SM and 30 °C ST incubation settings (the contribution of N_2 at these soil conditions was only 53.2 %). N_2O emissions were systematically higher for 3 of 12 sample locations, which indicates substantial spatial variability at site level, but on average soils acted as weak N_2O sources or even sinks. By using a conservative upscale approach we estimate total annual emissions from savanna soils to average 0.12 kg N ha^{-1} yr^{-1} (N_2O), 0.68 kg N ha^{-1} yr^{-1} (NO) and 6.65 kg N ha^{-1} yr^{-1} (N_2). The analysis of long-term SM and ST records makes it clear that extreme soil saturation that can lead to high N_2O and N_2 emissions only occurs a few days per year and thus has little impact on the annual total. The potential contribution of nitrogen released due to pulse events compared to the total annual emissions was found to be of importance for NO emissions (contribution to total: 5–22 %), but not for N_2O emissions. Our results indicate that the total gaseous release of nitrogen from these soils is low and clearly dominated by loss in the form of inert nitrogen. Effects of seasonally varying soil temperature and moisture were detected, but were found to be low due to the small amounts of available nitrogen in the soils (total nitrogen < 0.1 %).

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1 Introduction

Tropical savanna ecosystems are one of the most important biomes of the earth and cover approximately 27.6 million km^2 (Hutley and Setterfield, 2008) or 11.5 % of the global surface (Scholes and Hall, 1996). However, it is often difficult to find concise and clear criteria to define the spatial extent of this biome, and thus scientists often use a wide range of areal estimates leading to substantial uncertainties in calculating the total contribution of this biome to the global soil–atmosphere exchange of nitrogen (Davidson and Kingerlee, 1997). On a continental scale these areas can be constrained much better. Northern Australian tropical savannas cover about 2 million km^2 (approximately 12 % of the global extent of the biome) and are located north of 20° S in Western Australia, the northern part of the Northern Territory and northern Queensland (e.g., Lehmann et al., 2009; Williams et al., 2005). In addition to these natural and semi-natural landscapes, farmers have introduced improved pastures in northern Australia since the 1880s to increase productivity and their area expanded by approximately 2500 $km^{-2}\,yr^{-1}$ during the 1980s (Lonsdale, 1994).

Savanna systems experience pronounced intra-annual variability of rainfall (dry season conditions from 2 to 9 months) in addition to substantial inter-annual climatic fluctuations (Frost et al., 1986). In the tropical savanna zone of Australia the wet season is controlled by the Asian monsoon and occurs from October to March. Precipitation ranges from over 2000 $mm\,yr^{-1}$ at coastal areas to $< 400\,mm\,yr^{-1}$ inland (e.g., Russell-Smith and Yates, 2007) and declines by approximately 1 $mm\,yr^{-1}$ per kilometer inland (Cook and Heerdegen, 2001). In addition to strong hygric variability savannas are also shaped by high fire frequencies (~ 20 % burned annually, Dwyer et al., 2000). Tropical savanna of the coastal belt of northern Australia was found to burn even more frequently than the global average (up to 35 %, Russell-Smith et al., 2007).

Climatic conditions as well as fire activity control soil conditions and nutrient turnover in tropical savanna ecosystems as they affect soil temperature, soil moisture levels and thus oxygen availability in the soil matrix and availability as well as structure of organic matter other than inorganic nutrients. Biogenic N trace gases are produced in soils through the microbial processes of nitrification and denitrification (Conrad, 1996), two key processes of N cycling in terrestrial ecosystems. The mineralization of organic material leads to the formation of ammonium (NH_4^+), which serves as a substrate for autotrophic and/or heterotrophic nitrification. Under aerobic conditions, autotrophic and/or heterotrophic nitrifying organisms oxidize NH_4^+ via hydroxylamine (NH_2OH) and nitrite (NO_2) to nitrate (NO_3^-). Anaerobic conditions in the soil or in micro-sites promote the denitrification process, using NO_3^-/NO_2 as alternative electron acceptors. Depending on environmental conditions, NO_3^- is reduced stepwise via NO_2, nitric oxide (NO) and N_2O to inert nitrogen (N_2). N_2O as well as NO emissions from soils depend on the rates of nitrification and denitrification and underlying environmental conditions. Both processes can occur simultaneously in the soil due to the heterogeneity of soils with regard to gas diffusion and metabolic activity, which can create anaerobic micro-sites even in well aerated soil. The primary controls of N_2O as well as NO production and emission are the availability of NH_4^+ and NO_3^-, the content of decomposable organic substrate and the soil aeration status, whereas soil temperature and pH are secondary controls (see Baggs 2008 and Butterbach et al., 2013 for a summary of these processes and their functions). The significant variability of environmental factors (soil, vegetation and hydrological properties) across space and time (e.g., Davidson, 1991; Papen and Butterbach-Bahl, 1999) has often been demonstrated to control the magnitude and variability of N_2O and NO emissions from soils. Soil water status mainly regulating soil aeration conditions was found to act as the main driver for N_2O emissions in most tropical soils (e.g., Butterbach-Bahl et al., 2004b; Davidson, 1991; Grover et al., 2012; Linn and Doran, 1984; Werner et al., 2007b), although, due to the complexity of interacting environmental controls, it is difficult to obtain relationships of predictive value (Andersson et al., 2003). As savanna regions are characterized by climates with distinct wet and dry seasons (see above), the biogeochemical processes and associated trace gas exchange can be expected to also exhibit strong seasonal patterns following the hygric regime (e.g., Andersson et al., 2003; Eamus and Prior, 2001) – a feature also reported for other tropical ecosystems (seasonal tropical rainforest ecosystems: Breuer et al., 2000; Butterbach-Bahl et al., 2004b; Werner et al., 2007b, 2006). Most data sets of N trace gas emissions from savanna soils show a substantial variation of N_2O and NO emissions on a seasonal-scale following the hygric conditions (e.g., Castaldi et al., 2004, 2006; Pinto et al., 2002), whereas on a site-scale emissions are mostly controlled by the variability of soil properties (Castaldi et al., 2004, 2006). As fire is a characteristic forcing in all savanna ecosystems (Bond and Keeley, 2005), it also affects the nitrogen cycle in a direct (pyrodenitrification loss of nitrogen) and indirect (conversion of part of the organic N to mineral N, which is added to the soil surface) way.

While literature can be found investigating the soil–atmosphere exchange of NO, N_2O and CO_2, reliable information about the release of N_2 via microbial denitrification is unavailable for savanna systems and still scarce for other terrestrial ecosystems (Butterbach-Bahl et al., 2013; Dannenmann et al., 2011; Groffman et al., 2006). This is, in part, due to the reluctantly accepted, but currently well-proven fact, that the previously widely used acetylene-inhibition technique fails to accurately quantify N_2 loss from soil (e.g., Felber et al., 2012).

The major problem in recording the loss of N_2, the final product of the microbial transformation process

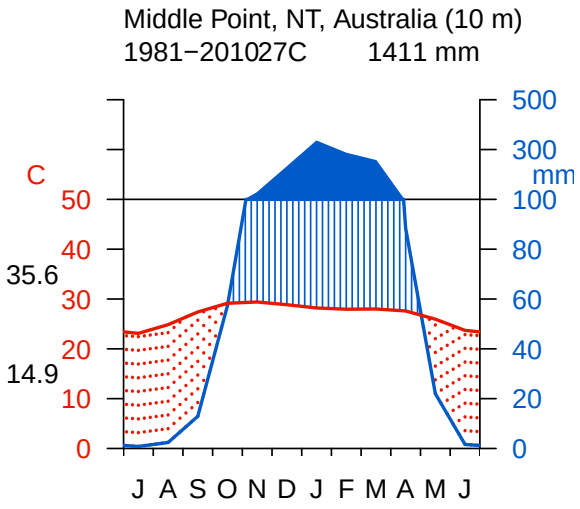

Figure 1. Climatic conditions at sampling sites (data: Bureau of Meteorology, Australia, http://www.bom.gov.au, years 1981–2010).

denitrification, is its abundance in the atmosphere and thus, precise measurements of N_2 production of soil have to be carried out with great sophistication. High-quality measurements are commonly only available from laboratory measurements under a controlled atmosphere using the gas-flow helium incubation method (Butterbach-Bahl et al., 2002) or by tracking the fate of ^{15}N-labelled substrate (e.g., Rolston et al., 1978). However, both methods are costly and time-consuming, and thus severely limiting the feasibility of large-scale replication experiments. As a consequence measurements of N_2 emissions from soils of terrestrial ecosystems remain scarce (Butterbach-Bahl et al., 2013). Nevertheless, reliable N_2 measurements are a valuable tool in understanding the nitrogen mass balances and biochemistry (Butterbach-Bahl et al., 2013).

In order to investigate gaseous emissions of C (CO_2) and N (N_2O, NO, N_2) compounds from tropical savanna and grassland systems in northern Australia, we extracted intact soil cores from various field sites and performed a range of incubation experiments under controlled thermal and hygric conditions.

For our study we hypothesize that NO and N_2O gas fluxes from the investigated savanna systems are generally low (below 0.1 kg N ha^{-1} yr^{-1}), and that re-wetting events have a significant importance not only for NO but also for N_2O fluxes at annual scale. Moreover, we hypothesized that N_2 fluxes should only occur at soil moisture levels greater 60 % water-filled pore space (WFPS).

The scope of the study was thus (a) to assess the magnitude of trace gas release under a range of environmental conditions typical for tropical savanna systems of northern Australia, (b) to deduce environmental regulators leading to the observed emissions and (c) to contrast the findings from natural savanna soil cores to samples derived from an improved pasture site. We furthermore aim to describe the total annual gaseous loss of nitrogen for such soil and the role of short-lived pulse emissions.

2 Material and methods

2.1 Site description and soil core sampling

In this study we investigated two field sites approximately 30 km east of Darwin, Northern Territory, Australia, and extracted intact soil cores for our laboratory incubation experiments. The first site is located at 12°30′ S, 131°05′ E at 18–22 m a.s.l., Girraween. Vegetation was *Eucalyptus tetrodonta* and *Eucalyptus miniata* dominated open-forest savanna with a grass layer composed of *Shorgum* spp. and *Heteropogon contortus*. The second site was established on managed grassland at Beatrice Hill Farm, Middle Point, located at 12°36.5′ S, 131°18′ E, approximately 25 km south-east of the savanna site. The farm estate is a long-term state-owned research station, operated by the Department of Primary Industry and Fisheries, Northern Territory.

This part of the Australian north is characterized by a strong seasonality of precipitation, with a pronounced dry season ranging from May to September. The dry season is followed by a period of intense convective thunderstorms (buildup), which marks the start of the wet season (Cook and Heerdegen, 2001). The long-term annual mean of precipitation for the closest climate station (Middle Point) is 1411 mm (data: http://www.bom.gov.au, years 1981–2010; see Fig. 1 for a Walter and Lieth climatic diagram of this station). The dominant amount of annual precipitation (91 %) is received in the wet season, often as heavy afternoon thunderstorms. Due to the strong rainfall intensities, a substantial amount of this water does not penetrate the soil and is transported away via overland flow.

The intensity of the wet season, as well as the total amount of rainfall, varies substantially from year to year. The annual average temperature is 27 °C and the seasonal temperature variability is less pronounced with a mean daily temperature of 23.1 °C during the dry season and up to 29.4 °C (monthly means) during the buildup. The daily temperature amplitude varies much stronger with a maximum daily amplitude in July–August and a minimum in February.

At the first site (Girraween, savanna site), a transect of sampling positions was established (Transect 1, T1), stretching approximately 500 m slightly downslope into a small topographical depression (altitudinal difference less than 4 m over the transect distance). At five positions, spaced approximately 100 m, sampling positions were established. Soil cores were extracted at positions P1, P3 and P5 (positions P2 and P4 were not used for this analysis, but to ensure consistent naming, the original position identifiers are used). P1 was located at the upper-most position of the topographic gradient, P3 250 m downslope and P5 at the lowest position.

The individual sampling positions are referenced as T1P1, T1P3 and T1P5 in the manuscript.

Site T1 is representative of many savanna sites found in the region under comparable hygric conditions (see e.g., Grover et al., 2013; Liveseley et al., 2011) and the typical natural fire regime is a fire for 2 out of 3 years (Hutley et al., 2011). The site was located in a peri-urban environment where fire management in recent years reduced fire frequency (a general phenomena observed for settlements in this region; Elliott et al., 2009) and woody cover was $\sim$ 10 to 20 % higher at this site than the extensive surrounding savanna that is burned more frequently. Managed fires are usually lit frequently (fire return interval approximately 2–3 years) as low-intensity fires early in the dry season reducing the risk of higher intensity late dry season fires (P3, P5). The site P1 was privately owned and was not burned for more than 6 years (D. Georges, personal communication, 2010). Tree cover was highest at P1, while the landscape was more open towards the center of the transect. Tree cover increased again at P5 due to higher water availability at the bottom of the slope (cover approx. 40–50 %).

The improved pasture at the second site was established in the 1960s by clearing savanna vegetation and ploughing and seeding of pangola grass (*Digitaria eriantha*). The area was fertilized annually or every second year with approximately 50 kg phosphorus, 100 kg superphosphate and 100 kg urea in single fertilization events. Buffalo (*Bubalus bubalis*) graze the improved pasture during the wet season and for 3–4 weeks during the dry season (grazing intensity: 1 beast ha^{-1} or 0.7 livestockunits ha^{-1}), and a herd grazed the site until the soil cores were extracted. The site is referenced as T3P1 throughout the manuscript. This site is representative of floodplain-based grasslands of the Northern Territory, but soil textural composition differs slightly from site T1 (the difference is within site variance encountered in the area and thus deemed acceptable). Furthermore, in contrast to other sites in the area, land use history is well documented.

At each position 12 soil cores were extracted for the incubation experiments under dry season conditions in 2010 and air dried immediately. For this, plastic cylinders (height: 20 cm, diameter: 14 cm) were driven into the soil and the surrounding soil removed. The cores were then carefully lifted from the ground and the bottom of the cylinder sealed with appropriate pipe caps, packed and sent to the laboratory at IMK-IFU, Karlsruhe Institute of Technology (Garmisch-Partenkirchen, Germany) for analysis. The extracted soil cores were divided into three groups of four cores for each sample position. The three groups were used for independent analysis with different moisture levels (WFPS: 25 %, 50 %, 75 %; see section incubation setup for details) and each analysis was replicated with three cores. One soil core was kept as a spare for each position.

2.2 Soil analysis

Soil organic carbon, total nitrogen, soil texture and soil pH were analyzed by a commercial laboratory for all sampling positions (Dr. Janssen, Gillersheim, Germany). Microbial C and N were measured using the chloroform fumigation-extraction technique (Brookes et al., 1985). We sampled and sieved soil from cores of each field position. Three sub-samples were immediately extracted with 60 mL 0.5 M K_2SO_4, while another three samples were fumigated with chloroform vapor for 24 h and extracted similarly. Total organic carbon (TOC) and total chemically bound nitrogen (TNb) were measured using a TOC analyzer (DIMATOC 2000, Dimatec Analysentechnik GmbH, Essen, Germany) and a coupled chemoluminescence detector, respectively. See Dannenmann et al. (2006) for more details.

2.3 Incubation setup and detection of N_2O, NO, N_2 and CO_2

In order to investigate the C and N trace gas exchange of the soil samples under a variety of environmental controls, we designed an incubation experiment. Soil water content of the stored cores was determined prior to the experiment gravimetrically by drying samples derived from the spare replicate core. The samples were dried at 105 °C for 24 h. Bulk density of the samples was also measured (approximately at 10 cm depth, $n = 3$) and used to calculate the pore volume and consequently the amount of water required to reach 25, 50 and 75 % WFPS.

$$\mathrm{WFPS}[\%] = \frac{W_{\mathrm{vol}}}{\left(1 - \frac{\mathrm{BD}}{2.65}\right)}$$

$W_{\mathbf{vol}}$ volumetric water content,

BD bulk density [$g\,cm^{-3}$],

2.65 particle density [$g\,cm^{-3}$].

The cores were first exposed to 20 °C temperature for pre-incubation before the air-dried samples were wetted to the desired soil moisture levels of 25 % WFPS (M25), 50 % WFPS (M50) and 75 % WFPS (M75). To avoid a bias of follow-up measurements, all three soil moisture levels were analyzed with independent cores. The moisture content was adjusted bi-daily by weighing the cores and adding evaporated water at least 1 hour prior to the measurements. Note that the reported average trace gas fluxes were derived by excluding measurements immediately after temperature adjustments (day 0–3 after temperature change) in order to exclude transition effects from raising temperatures. Soil cores were sealed with gas-permeable foil immediately after the sampling procedure to minimize the evaporative loss of water. During the course of the incubation period, the temperature was stepwise increased from 20 to 30 and to 40 °C. In-between measurement events, all soil cores were incubated in

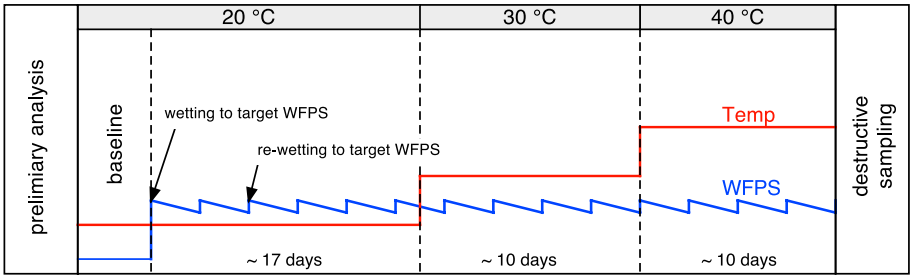

Figure 2. Schematic of the incubation setup. The soil moisture level of the cores was kept constant be readding water every second day, the temperature was raised stepwise from 20 °C, to 30 °C, and finally 40 °C. The incubation outlined in this figure was performed three times for separate soil cores (once for each of the three soil moisture levels, WFPS: water-filled pore space).

thermostat cabinets (Lovibond ET 651-8, Tintometer GmbH, Dortmund, Germany) at the prescribed incubation temperature. The cabinets were ventilated with low-flow pumps to prevent CO_2 enrichment or temperature gradients.

The air-dried soil cores were measured for up to 10 days prior to the initial wetting at each incubation run to record the baseline emission and to test the detection setup. N_2O, NO and CO_2 emissions were measured approximately every second to third day. After the initial wetting, soil cores were incubated and measured until the initial pulse event leveled off and flux rates approached a relatively stable emission level. Afterwards, the temperature was raised to 30 °C and measurements continued. After approximately 10 days of incubation at 30 °C, the temperature was increased again by 10 °C to 40 °C. A schematic of the incubation and measurement schedule is given in Fig. 2 (note that due to laboratory access limitations we did not measure the 40 °C incubation step in the M25 run).

The static chamber technique (e.g., Smith et al., 1995) was used to measure N_2O and CO_2 fluxes. The soil cores were closed with gas-tight lids equipped with a port and septum for gas sampling. The headspace of each of the 12 soil cores (T1P1, T1P3, T1P5 and T3P1; $n = 3$) was determined individually (average headspace volume 1.54 L). Four gas samples of 5 mL chamber air were drawn from the port at 0, 20, 40 and 60 min after closure using 20 mL plastic syringes fitted with three-way stop-cocks and injected into vacuumed sampling veils. The sample veils and a set of veils with standard gas mixture for calibration (0.4 ppmv N_2O, 400 ppmv CO_2; Air Liquide, Düsseldorf, Germany) were placed into two auto-sampler systems (HT280T, HTA s.r.l., Brescia, Italy) attached to gas chromatograph (SRI 8610C, SRI Instruments, Torrance, CA, USA) systems equipped with a ^{63}Ni electron detector (ECD) for N_2O analysis and an flame ionization detector and methanizer for CO_2 analysis. We used high-purity N_2 as carrier gas and installed Ascarite® filter to exclude any interference of CO_2 on N_2O detection. Flux rates of N_2O and CO_2 were calculated from the observed linear increases of sampled chamber air using linear regression (e.g., Papen and Butterbach-Bahl, 1999).

Nitric oxide emissions were measured immediately after sampling for N_2O/CO_2 analysis using a dynamic chamber technique (e.g., Yamulki et al., 1997) and chemoluminescence detector (CLD 770 AL ppt, Ecophysics AG, Durnten, Switzerland). A sealing lid with inlet and outlet fittings was attached to the soil core, and synthetic air (79 % N_2, 21 % O_2) was pumped through the headspace. The NO flux was calculated from the inlet/outlet NO concentrations in a dynamic equilibrium with constant gas flow rate. Steady-state conditions were reached approximately after 20–25 min, and the average detected flow rate over 5 min after this grace period was used to determine the flux. The detector was periodically calibrated in the laboratory with standard gas and a calibration unit (for details see, Butterbach-Bahl et al., 1997).

Following N_2O, CO_2 and NO flux measurements of an incubation run (M25, M50 and M75 incubation runs, respectively), soils from the experiments were finally used to measure N_2 fluxes by the helium gas flow technique (Butterbach-Bahl et al., 2002). For this any three replicated soil cores of one sample site were destructively subsampled (2–3 samples per individual core) and stored in the compartments of one helium soil core incubation vessel. The gas flux measurements were conducted after, once again, wetting the soil material to the required moisture level. The closed vessels were then exposed to a series of temperature settings (20 °C, 30 °C and 40 °C).

The custom-build system developed for soil core incubation is described in detail in Dannenmann et al. (2011). The system consists of two vessels for N_2 and N_2O emissions measurements, and each vessel holds seven soil cores of 4 cm height and 100 cm^3 volume each, which are incubated together in order to account for soil spatial heterogeneity. Prior to flux measurements, the soil and headspace atmosphere in the vessels are replaced by an artificial gas mixture (20 ppm N_2, 400 ppb N_2O and 20 % O_2 in helium) by 2 days of gas flushing from bottom to top through the soil cores. The required extreme gas tightness of the vessels against intrusion of atmospheric N_2 is ensured by double sealings purged with helium, and by placing the incubation vessels with its tubing connections under water (Dannenmann et al., 2011). After

the soil and headspace flushing period, N_2 and N_2O concentrations are measured hourly in the headspace over a period of 8 h in order to allow for calculation of N_2 and N_2O gas fluxes (Butterbach-Bahl et al., 2002). Similar to previous use of the system (Dannenmann et al., 2011), regular measurements with empty vessels showed no increase of N_2 in the system over the measurement period.

2.4 Data analysis and presentation

All analysis and plotting was carried out using R 2.15 (R Development Core Team, 2011). Differences between measured gas fluxes at the various incubation settings and tests for comparable air-dried soil conditions were investigated using a multiple comparison of means procedure (Herberich et al., 2010), as group sizes and distributions varied substantially in the comparison. Relative importance of environmental factors controlling trace gas emissions was assessed using multiple linear regression analysis and a tool for variance decomposition (proportional marginal variance decomposition, R package relaimpo; see Grömping, 2007). Statistical significance is given at the 95 % difference level ($p \leq 0.05$), and error bars denote standard deviation if not specified otherwise. N_2O uptake rates are presented as negative emissions.

3 Results

3.1 Soil analysis

Physicochemical properties of the sampled soil cores are given in Table 1. All cores had a very sandy texture composition (T1 > 80 %, lower for cores sampled at T3 = 68 %), but the pasture site T3 had a higher fraction of clay (15 %). Note that this discrepancy is within the landscape variability encountered in this area. Bulk density was highest at position T1P5 (1.7 $g\,cm^{-3}$) and in a range of 1.4 to 1.5 $g\,cm^{-3}$ for the other soil cores. Soil pH was ranging from 4.4 to 5.1. At 0.8 and 0.7 %, total organic carbon was very low for sites T1P3 and T1P5, respectively, higher at the grassland site T3P1 (1.5 %) and highest for site T1P1 (2.8 %). Total nitrogen concentrations were also low and ranged between 0.04 % and 0.1 %. The C/N ratios were also widest for site T1P1 (24.1) and most narrow for site T1P5 (15.5). With 222.1 $\mu g\,C\,g^{-1}$ soil dry weight (sdw) microbial carbon and 35.7 $\mu g\,N\,g^{-1}$ sdw microbial nitrogen, the samples from the improved pasture site were approximately 2.3–3.6 times (carbon) and 4.7–7.8 times (nitrogen) richer, respectively, in microbial nitrogen than the samples from natural savanna (T1).

Ammonium concentrations were low for the soil samples from the savanna transect positions ranging from 2.4 to 3.9 $\mu g\,N\,g^{-1}$ sdw, but almost a magnitude higher for the sampled grassland site (23.6 $\mu g\,N\,g^{-1}$ sdw). Nitrate concentrations did not vary significantly between the two sampled sites (T1: 5.5–12.1 $\mu g\,N,\ g^{-1}$ sdw, T3: 9.7 $\mu g\,N,\ g^{-1}$ sdw).

3.2 Gas fluxes

3.2.1 CO_2 emissions

The CO_2 baseline emissions during pre-incubation (unwatered, 20 °C) were $0.1 \pm 2.7\,mg\,C\,m^{-2}\,h^{-1}$ (T1) and $1.0 \pm 3.8\,mg\,C\,m^{-2}\,h^{-1}$ (T3) and not significantly different between transect positions or transects. Immediately after watering the soil cores, CO_2 emissions rose for all three watering levels (M25, M50 and M75) and all replicates (see Fig. 3). Peak emissions generally occurred immediately after watering (day 0 of incubation section: D0), and emissions at the following day (D+1) dropped to 70 % (M25), 38 % (M50) and 37 % (M75) of the initial pulse emission response recorded at D0. After 2 days (D+2), CO_2 emissions declined further to levels of 26–34 % before stabilizing at those levels and eventually increasing again (see Fig. 3). During the pulse emission event (D0−D+2), the average CO_2 emission was $62.8 \pm 43.7\,mg\,C\,m^{-2}\,h^{-1}$ (min: $7.7\,mg\,C\,m^{-2}\,h^{-1}$, max: $195.1\,mg\,C\,m^{-2}\,h^{-1}$). Pulse intensity was found to differ significantly between natural savanna soil cores of transect T1 ($55.5 \pm 39.8\ mg\,C\,m^{-2}\,h^{-1}$) and improved pasture at transect T3 ($75.1 \pm 46.4\,mg\,C\,m^{-2}\,h^{-1}$), but not between individual transect positions. After the initial pulse event, CO_2 emissions remained relatively stable for all three moisture levels at 20 °C soil temperature (Fig. 3). The immediate emission after initial watering indicates that the release is predominately a physical displacement rather than microbially driven. Average CO_2 emissions at 20 °C (after the pulse event) were $19.2 \pm 6.4\,mg\,C\,m^{-2}\,h^{-1}$ (M25), $23.1 \pm 6.9\,mg\,C\,m^{-2}\,h^{-1}$ (M50) and $36.2 \pm 18.5\,mg\,C\,m^{-2}\,h^{-1}$ (M75), indicating a direct link between soil moisture and CO_2 emission strength. Fluxes recorded at M75 were significantly higher than those obtained at M25 and M50 ($p < 0.001$). In contrast to the pulse emission, CO_2 emissions from T3 ($30.5 \pm 16.2\,mg\,C\,m^{-2}\,h^{-1}$) were not significantly higher than those from T1 ($25.2 \pm 13.9\,mg\,C\,m^{-2}\,h^{-1}$). No significant difference between individual transect positions was detected. It is noteworthy that CO_2 emissions for some individual cores (T1P1R1, T1P3R1; R1 being the replicate number to identify a individual core) were substantially higher for M75 conditions than those from the other two replicates, resulting in high standard deviations. At 30 °C soil temperature, average CO_2 emissions were again not found to differ significantly between T1 ($36.0 \pm 17.2\,mg\,C\,m^{-2}\,h^{-1}$) and T3 ($43.3 \pm 20.8\,mg\,C\,m^{-2}\,h^{-1}$, $n = 45$), but moisture levels were again significantly correlated with higher emissions (M25: $34.1 \pm 14.5\,mg\,C\,m^{-2}\,h^{-1}$, M50: $35.6 \pm 20.4\,mg\,C\,m^{-2}\,h^{-1}$, M75: $44.0 \pm 18.6\,mg\,C\,m^{-2}\,h^{-1}$). No significant differences were recorded for CO_2 fluxes from cores originating from different transect positions, indicating that physicochemical soil properties did not have a major influence on CO_2 emissions. Since no data is available from the 40 °C incubation temperature run with M25 cores, we do not report results

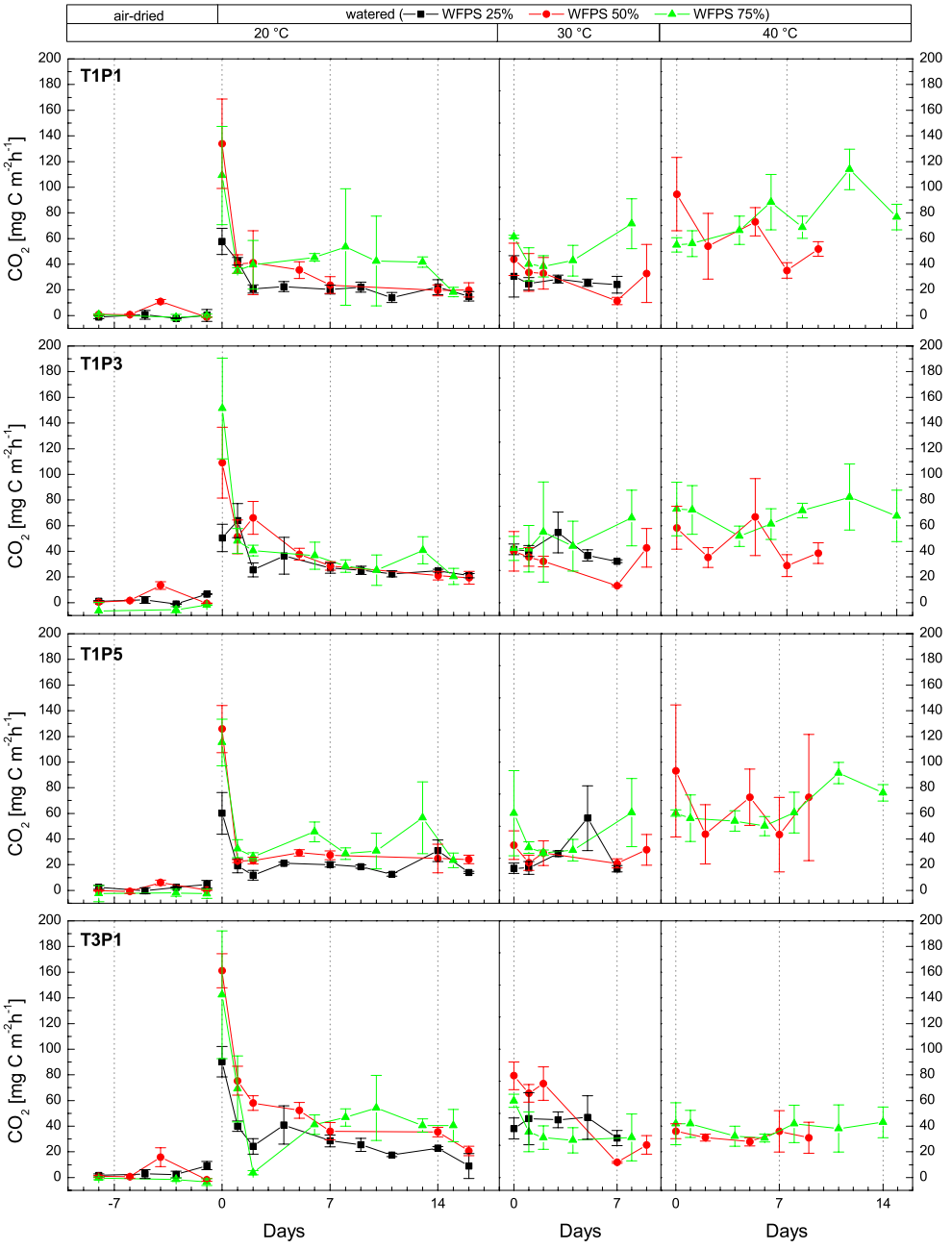

Figure 3. Average CO_2 emission per site (savanna: T1P1, T1P3, T1P5; grassland: T3P1) for three soil moisture (black: 25 % water-filled pore space (WFPS), red: 50 % WFPS, green 75 % WFPS) and three temperature levels (*x* axis days since incubation change/negative values indicate pre-incubation period; error bars: standard deviation; $n = 3$).

for transect positions or transects, as the higher moisture levels (M50 and M75 only) lead to biased mean fluxes due to the strong response of CO_2 fluxes to moisture levels. See the discussion section for an in-depth analysis of temperature effects on emissions.

3.2.2 N_2O emissions

Nitrous oxide emissions under pre-incubation conditions were low and did not differ significantly between transect positions or transects (T1: $0.0 \pm 1.4\,\mu g\,N\,m^{-2}\,h^{-1}$, T3: $-0.2 \pm 1.9\,\mu g\,N\,m^{-2}\,h^{-1}$). We measured low N_2O uptake or zero N_2O flux for 8 out of 12 cores at pre-incubation conditions (min: $-6.2\,\mu g\,N\,m^{-2}\,h^{-1}$), but variance ranged from

Table 1. Physicochemical properties of the sampled soil and mean microbial biomass (sampling depth 0–20 cm; * μg C/N g [dry weight] $soil^{-1}$; BD: bulk density).

Land use	Pos.	Soil texture (%)			BD	Org. C	Total N	pH	Microbial biomass (*)		NH_4^+	NO_3^-
		Sand	Silt	Clay	($g\,cm^{-3}$)	(%)	(%)		C	N	(*)	(*)
Natural	T1 P1	81	12	7	1.4	2.8	0.1	5	97.5	18.4	3.1	12.1
savanna	T1 P3	87	8	5	1.5	0.8	0.04	4.4	81.8	21.0	3.9	7.2
	T1 P5	87	10	3	1.7	0.7	0.05	5.1	61.0	14.5	2.4	5.5
Pasture	T3 P1	68	17	15	1.5	1.5	0.1	4.6	222.1	23.3	23.6	9.7

0.3 to 3.6 $\mu g\,N\,m^{-2}\,h^{-1}$. Increased N_2O emissions were detected immediately after watering the cores (D0), but average emissions during the defined peak event (D0 – D+2) were relatively modest for 33 out of 36 cores sampled at T1 (avg.: $3.2 \pm 3.1\,\mu g\,N\,m^{-2}\,h^{-1}$, max: $13.7\,\mu g\,N\,m^{-2}\,h^{-1}$) and T3 (avg.: $4.9 \pm 6.2\,\mu g\,N\,m^{-2}\,h^{-1}$, max: $24.2\,\mu g\,N\,m^{-2}\,h^{-1}$), but the results for T1 and T3 were not significantly different. Very strong N_2O emissions were recorded for three individual cores at M75 (T1P1R1: $85.8\,\mu g\,N\,m^{-2}\,h^{-1}$, T1P1R2: $106.2\,\mu g\,N\,m^{-2}\,h^{-1}$, T1P3R1: $180.2\,\mu g\,N\,m^{-2}\,h^{-1}$) after a delay of 2 or 6 days and remained systematically higher throughout the incubation experiment (see Fig. 4). Due to their distinctly different emission patterns, those three cores are excluded from further analysis here and discussed in detail at the end of this section. Intensity of pulse emissions correlated positively with saturation levels (M25: $2.7 \pm 3.2\,\mu g\,N\,m^{-2}\,h^{-1}$, M50: $3.2 \pm 4.1\,\mu g\,N\,m^{-2}\,h^{-1}$, M75: $5.8 \pm 5.0\,\mu g\,N\,m^{-2}\,h^{-1}$). After the initial pulse, N_2O emissions at 20 °C were $1.2 \pm 3.8\,\mu g\,N\,m^{-2}\,h^{-1}$ (T1) and $0.6 \pm 1.0\,\mu g\,N\,m^{-2}\,h^{-1}$ (T3), and no significant differences were detected for transect positions or transects. At 30 °C, N_2O emissions increased slightly to $1.4 \pm 1.8\,\mu g\,N\,m^{-2}\,h^{-1}$ (T1) and $2.6 \pm 5.1\,\mu g\,N\,m^{-2}\,h^{-1}$ (T3). At 40 °C, N_2O emission substantially increased over the results obtained at 30 °C, but due to missing results for the M25 incubation run, we do not report site averages here.

3.2.3 NO emissions

Pre-incubation emissions were $6.7 \pm 4.3\,\mu g\,N\,m^{-2}\,h^{-1}$ (T1) and $7.0 \pm 5.0\,\mu g\,N\,m^{-2}\,h^{-1}$ (T3), and no significant differences were detected between the transect positions or transects. Large NO emission pulses of 27.7–306.5 $\mu g\,N\,m^{-2}\,h^{-1}$ were recorded after the addition of water at D0 (see Fig. 5). Furthermore, NO emission strength was negatively correlated with water saturation (M25: $141.2 \pm 70.9\,\mu g\,N\,m^{-2}\,h^{-1}$, M50: $48.4 \pm 26.6\,\mu g\,N\,m^{-2}\,h^{-1}$, M75: $22.1 \pm 15.2\,\mu g\,N\,m^{-2}\,h^{-1}$), and pulse strength did not significantly differ between transects. NO emissions on the following day (D+1) dropped sharply to 16 % (M25), 40 % (M50) and 28 % (M75) of the initial pulse emission response at D0. After 2 days (D+2), NO emissions further decreased to 10–26 % of the emission of D0. After the initial pulse, average NO emissions at 20 °C were below pre-incubation levels and ranged from 3.2 ± 1.8 to $5.8 \pm 2.9\,\mu g\,N\,m^{-2}\,h^{-1}$ for the four transect positions being $4.9 \pm 2.7\,\mu g\,N\,m^{-2}\,h^{-1}$ at T1 and $3.2 \pm 1.8\,\mu g\,N\,m^{-2}\,h^{-1}$ at T3 (differences not significant). NO emissions increased at 30 °C incubation temperature to $6.7 \pm 4.3\,\mu g\,N\,m^{-2}\,h^{-1}$ (T1) and $6.5 \pm 6.9\,\mu g\,N\,m^{-2}\,h^{-1}$ (T3). At 40 °C, a marked increase of NO emission was observed for the majority of soil cores watered to 50 % WFPS (for 5 of the 12 cores increase from 30 to 40 °C >200 %, for 11 of 12 cores >60 %) while NO emissions at 75 % WFPS only increased slightly or remained constant (see Fig. 5). Again, as no M25 measurements are available, we do not give site averages for 40 °C, but the significant increase of NO emissions can be highlighted when M50 and M75 NO emissions obtained at 40 °C are compared to the fluxes measured under 30 °C. NO emissions under medium moisture levels (M50) increased from $6.7 \pm 5.1\,\mu g\,N\,m^{-2}\,h^{-1}$ at 30 °C to $52 \pm 87.5\,\mu g\,N\,m^{-2}\,h^{-1}$, while high moisture levels (M75) only led to an increase of $5.0 \pm 4.9\,\mu g\,N\,m^{-2}\,h^{-1}$ to $11.5 \pm 13.7\,\mu g\,N\,m^{-2}\,h^{-1}$. A negative correlation between moisture levels and NO emission strength was observed for all episodes of the incubation experiment. We did not detect significant differences between both land use types for temperatures up to 30 °C, but at 40 °C, NO emission was significantly higher at the savanna transect than at the improved pasture.

3.2.4 N_2 emissions

An incubation setup with the same number of replications as performed for N_2O, NO and CO_2 measurements was not feasible due to the time required to perform a single N_2 measurement (see Sect. 2.3). We thus report results as transect averages (T1, $n = 3$) and single measurement incubation results (T3). However, in each measurement cycle, soil from all replicate cores was pooled in the sampling cuvette and thus, the results are based on multi-core soil conditions (in case of T3 without true measurement replication). Dinitrogen emissions varied between 16.7 and 2350.4 $\mu g\,N\,m^{-2}\,h^{-1}$. As shown in Table 2, N_2 emissions were strongly influenced by water saturation. Average N_2 emissions increased from M50 to M75 by a factor of 11 to 16 for savanna soil (T1), whereas emission strength did not differ between M25 and

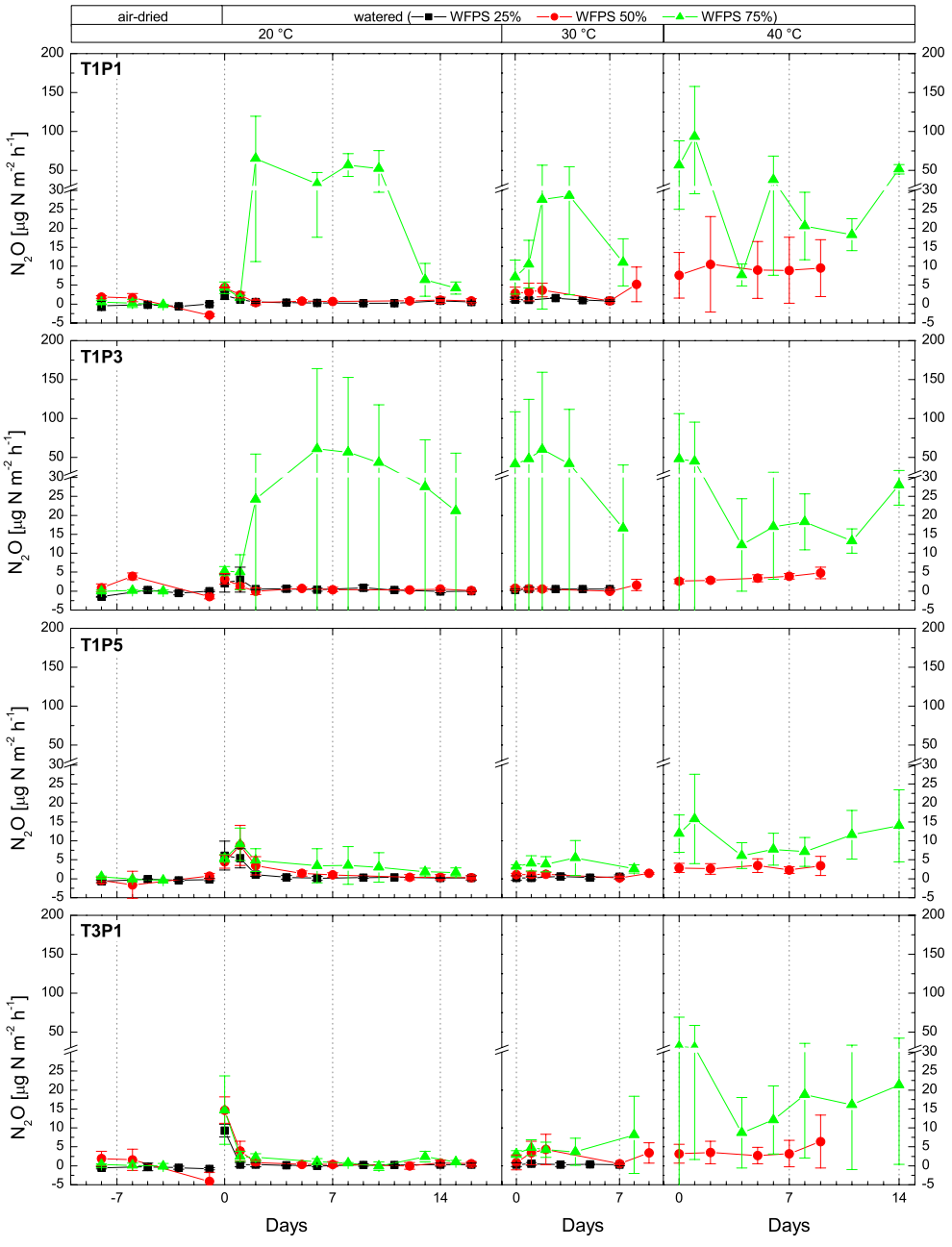

Figure 4. Average N_2O emission per site (savanna: T1P1, T1P3, T1P5, grassland: T3P1) for three soil moisture (black: 25 % water-filled pore space (WFPS), red: 50 % WFPS, green 75 % WFPS) and three temperature levels (x axis days since incubation change/negative values indicate pre-incubation period, error bars: standard deviation, $n = 3$).

M50. Although no true replication is available for T3 results, a similar pattern can be observed, but we do not contrast results from the two transects due to differences in sample numbers.

In general, N_2 emissions dominate the gaseous nitrogen losses at T1 (see Table 3). While N_2O emissions only account for 0.3–3.6 % of gaseous N losses, N_2 emissions represent up to 99.3 %. Note that inclusion of N_2O outlier emissions reduced the share of N_2 losses only by one percent (Table 3). NO emissions contributed to 5.6–16.5 % at low to medium soil saturations and 20 to 30 °C soil temperatures. Only at 40 °C and medium soil saturation (M50) did NO emissions account for a substantial fraction of total N losses to the atmosphere (43.2 %). At high water saturation, NO emissions were insignificant and contributed only 0.3–1.1 %.

Table 2. Average CO_2, N_2O, NO and N_2 emission at different moisture and temperature incubation settings (fluxes reported post-pulse; [a] value excluding outliers/brackets including outliers; [b] N_2: T1 $n = 3$, T3: no replicates; NA: not available).

		WFPS [%]			Transect
		25	50	75	
carbon dioxide (mg CO_2-C m^{-2} h^{-1})					
Temperature [°C]	20	19.7 ± 6.8	21.5 ± 5.6	33.3 ± 18.7	T1
		17.6 ± 5.0	28.1 ± 8.7	45.1 ± 15.9	T3
	30	32.0 ± 15.9	25.4 ± 15.5	66.1 ± 20.2	T1
		38.8 ± 14.4	18.6 ± 8.7	31.3 ± 18.3	T3
	40		53.6 ± 26.0	75.8 ± 30.3	T1
			31.6 ± 10.8	38.4 ± 12.4	T3
nitrous oxide (µg N_2O-N m^{-2} h^{-1})[a]					
Temperature [°C]	20	0.3 ± 0.4	0.5 ± 0.6	3.6 ± 7.2 (13.7 ± 29.0)	T1
		0.3 ± 0.3	0.5 ± 0.7	1.1 ± 1.4	T3
	30	0.6 ± 0.4	1.5 ± 2.4	3.1 ± 1.2 (9.6 ± 12.4)	T1
		0.4 ± 0.2	1.9 ± 2.3	8.2 ± 10.2	T3
	40		5.4 ± 4.8	13.7 ± 9.4 (19.6 ± 15.3)	T1
			4.1 ± 4.4	17.1 ± 14.5	T3
nitric oxide (µg NO-N m^{-2} h^{-1})					
Temperature [°C]	20	6.4 ± 2.4	4.9 ± 2.1	3.4 ± 2.6	T1
		3.6 ± 1.7	4.2 ± 1.7	1.7 ± 1.1	T3
	30	9.1 ± 4.8	6.1 ± 3.1	3.5 ± 2.4	T1
		3.2 ± 1.5	8.4 ± 9.0	9.5 ± 8.2	T3
	40		65.0 ± 97.8	13.2 ± 15	T1
			12.9 ± 11.0	6.1 ± 6.7	T3
dinitogen (µg N_2-N m^{-2} h^{-1})[b]					
Temperature [°C]	20	107.6 ± 82.8	65.3 ± 26.5	1041.1 ± 255.8	T1
		400.6	110.1	1281.2	T3
	30	45.4 ± 33.2	56 ± 13	627.4 ± 789.1	T1
		311.3	118.9	348.3	T3
	40	NA	79.9 ± 11.5	1201 ± 1625	T1
			207.0	614.4	T3

4 Discussion

4.1 CO_2 emissions

Decomposition of organic matter and root respiration leads to the emission of CO_2 from the soil, but since the soil cores were removed from the field and any existing fine roots were cut, the observed fluxes represent only soil respiration CO_2 efflux. Even though our major focus was on the emission of nitrogen gases, CO_2 emissions can also be useful as a proxy to identify the relative availability/production of substrate for the microbial processes responsible for N_2O, NO and N_2 losses.

Carbon dioxide emissions increased with rising temperature and high moisture levels (Table 2), and soil temperature was identified to have the highest relative importance, followed by soil moisture variations, in explaining the observed CO_2 emissions (Fig. 6). The strong temperature dependency of decomposition and associated CO_2 emissions, given a certain moisture level, is well known in the literature and was

Table 3. Fractional contribution of N_2O, NO and N_2 to total gaseous N losses of savanna soil at T1 (units: % of total gaseous N loss, $N_2O : NO : N_2$, [a] value excluding outliers/brackets including outliers, NA: not available).

		WFPS [%]		
		25	50	75 [a]
Temp. [°C]	20	0.3 : 5.6 : 94.1	0.7 : 6.9 : 92.4	0.3 : 0.3 : 99.3 (1.7 : 0.3 : 98)
	30	1.1 : 16.5 : 82.4	2.4 : 9.6 : 88.1	0.5 : 0.6 : 99.0 (1.6 : 0.5 : 97.9)
	40	NA	3.6 : 43.2 : 53.2	1.1 : 1.1 : 97.8 (1.7 : 1.1 : 97.3)

reported for many ecosystems (Raich and Schlesinger, 1992). In general, CO_2 emissions from tropical savanna in northern Australia were found to increase through the seasons (dry, wet–dry transition, wet), but due to relatively minor seasonal variations in temperature, changes in soil moisture are considered to be the dominant control in these ecosystems (Grover et al., 2012). This was also reported for African savannas (Brümmer et al., 2009a) and the wet–dry tropics of the Amazon Basin (Davidson et al., 2000). Strong break-of-season (pulse) emissions ranging between 100 and 250 $mg\,C\,m^{-2}\,h^{-1}$ were previously reported for natural savanna in Africa (Brümmer et al., 2009a) and are in-line with our observations. We found no significant differences in average CO_2 emissions between pasture cores and cores from the natural savanna site.

4.2 N_2O emissions

Measurements of gaseous nitrogen losses from tropical savanna are still scarce in the literature (e.g., Castaldi et al., 2006; Dalal and Allen, 2008; Stehfest and Bouwman, 2006; Steinkamp and Lawrence, 2011) and to our knowledge no previous study investigated the emission of N_2O, NO and N_2 simultaneously. Annual N_2O emissions from tropical savanna systems were reported to range from 0.06 to 1.46 $kg\,N\,yr^{-1}$ (mean: 0.6 $kg\,N\,yr^{-1}$) and to be lower for Australian savannas (0.06–1.08 $kg\,N\,yr^{-1}$, median: 0.19 $kg\,N\,yr^{-1}$) due to drier conditions and smaller amounts of N deposited from the atmosphere (Dalal and Allen, 2008). From previous in situ measurements at an area close to transect T1, it was calculated that soils only acted as minor sinks or sources for N_2O annually (-0.015 $kg\,N\,ha^{-1}\,yr^{-1}$; Livesley et al., 2011), a result also found to be true for savanna soils of the Daly River south of our site, which receives substantially less annual precipitation (0.02 $kg\,N\,ha^{-1}\,yr^{-1}$, Grover et al., 2012).

For total site exchange, it has to be noted that termite mounds have been identified as hotspots of N_2O emissions in savannas (e.g., Brümmer et al., 2009b) and are abundant in savannas of tropical Australia (Dawes-Gromadzki, 2008), but the total contribution to the soil–atmosphere exchange is highly variable in space. It was also reported that below-ground termite activity can (often only temporarily) add to on-site variability of measured in situ fluxes (Livesley et al., 2011). Very low N_2O emission or even soil N_2O uptake was also previously reported for tropical savanna soils under dry season conditions (Andersson et al., 2003; Castaldi et al., 2006; Donoso et al., 1993; Livesley et al., 2011; Sanhueza et al., 1990), and low mineral N content was considered to be a major controlling factor (Rosenkranz et al., 2006), although many other controls and processes are discussed (Chapuis-Lardy et al., 2007).

We also observed very low N_2O emissions and occasional N_2O uptake by the soil cores with a maximum soil uptake rate of -6.2 $\mu g\,N\,m^{-2}\,h^{-1}$ during pre-incubation measurements of our air-dried soil samples at 20 °C. At low (M25) and medium (M50) moisture conditions, average N_2O emissions ranged from 0.3 to 5.4 $\mu g\,N\,m^{-2}\,h^{-1}$ and were in-line with the low N_2O emissions previously observed from nearby sites (Grover et al., 2012; Livesley et al., 2011). The observed N_2O uptake rates are also in-line with the reported range of -1.0 to -10 $\mu g\,N\,m^{-2}\,h^{-1}$ for upland soils (Schlesinger, 2013).

The N_2O emissions, observed for the improved pasture site under dry to medium moisture levels, were also low and did not differ significantly to the natural savanna site, which was to be expected as the analysis of physicochemical properties did not reveal significant differences between the two plots either (Table 1). This similarity is somewhat remarkable as the improved pasture site did receive substantial amounts of P and N over 40 years. Similar results were reported for young and old pastures under dry season conditions in the Daly region, Northern Territory, Australia, but emissions from old pasture under wet conditions were higher (> 25 $\mu g\,N\,m^{-2}\,h^{-1}$). A direct comparison is difficult, however, as the soil water content reported (dry: ~ 5 % WFPS, medium: ~ 37 % WFPS, wet: ~ 53 % WFPS) does not align with our incubation setup. However, the general range of reported in situ flux measurements from savanna and pasture shows good agreement with our laboratory results (Grover et al., 2012).

As stated before, we excluded the results for three of the nine savanna soil cores measured with 75 % WFPS from the previous discussion as they clearly

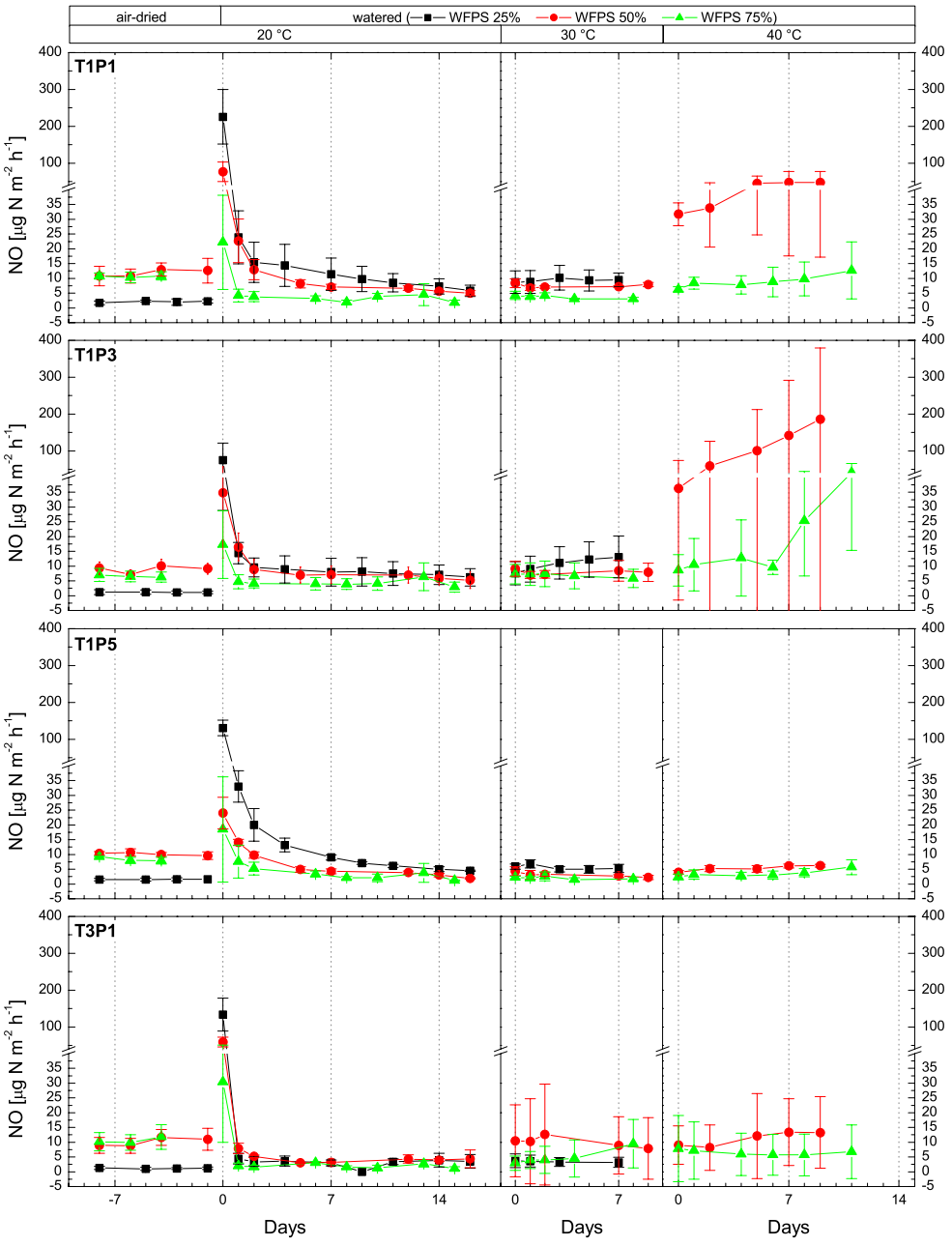

Figure 5. Average NO emission per site (savanna: T1P1, T1P3, T1P5; grassland: T3P1) for three soil moisture (black: 25 % water-filled pore space (WFPS), red: 50 % WFPS, green 75 % WFPS) and three temperature levels (*x* axis days since incubation change/negative values indicate pre-incubation period; error bars: standard deviation; n=3).

exhibiteddifferent emission patterns. In contrast to the other cores, N_2O emission increases of those cores were delayed by 2–3 days, and strong N_2O emissions (T1P1R1: $33.7 \pm 29.8\,\mu g\,N\,m^{-2}\,h^{-1}$, T1P1R2: $26.3 \pm 17.8\,\mu g\,N\,m^{-2}\,h^{-1}$, T1P3R1: $52.3 \pm 37.0\,\mu g\,N\,m^{-2}\,h^{-1}$, $n = 8$) were measured throughout the incubation run. If those outlier results are included (see Table 2), average N_2O emissions are 1.4–3.8 times higher and thus substantially higher than those reported for savanna soil and on par with reported pasture fluxes under wet conditions (see, Grover et al., 2012). Although the cause for these substantially different emission patterns could not be determined, we hypothesize that small-scale mineralization hotspots (e.g., due to availability of organic material from dead soil fauna or plant residuals) account for this observation. These findings underline the importance of taking spatial heterogeneity into account when designing field samplings, and it is a strong indication that more spatial replicates would help to fully assess

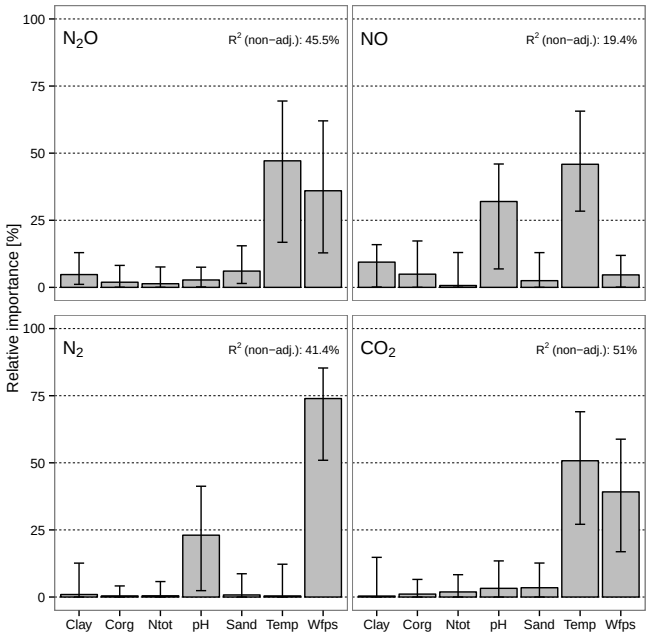

Figure 6. Relative importance of environmental factors clay, organic carbon (Corg), total nitrogen (Ntot), sand, temperature and water-filled pore space (WFPS) on N_2O, NO, N_2 and CO_2 emissions (based on proportional marginal variance decomposition, R^2 values give total predictability of each model).

site-scale soil–atmosphere fluxes. However, the nature of incubation experiments (i.e., the need for timely replicate sampling, laboratory constrains and climate controlled storage) severely limits the number of samples, though the gas pooling technique may offer ways to overcome spatial heterogeneity (Arias-Navarro et al., 2013; Morris et al., 2013).

Nitrous oxide emissions were positively correlated with temperature and soil moisture (see Table 2), and their variations were found to explain 58.6 and 41.3 %, respectively, of the variance of N_2O emissions if a simple linear two-parameter regression model was used (proportional marginal variance decomposition (PMVD) method, total variance: 46.0 %). Inclusion of soil properties did not further improve the linear model (see decomposition plot, Fig. 6). Previous results also show a positive correlation between soil temperature and N_2O emissions (Castaldi et al., 2010), but other authors found no clear linear correlation (Brümmer et al., 2008; Scholes et al., 1997), although observing clear diurnal patterns (Brümmer et al., 2008). Previous studies from tropical savanna and seasonally dry tropical forest sites identified changes in WFPS to dominate the N_2O emission patterns (Brümmer et al., 2008; Castaldi et al., 2010; Davidson et al., 1993; Grover et al., 2012; Rees et al., 2006), but in general, N_2O emissions from undisturbed savanna soil ranked lowest for seasonally dry ecosystems due to low nutrient availability and soil textures favoring quick drainage (Castaldi et al., 2006). In accordance, significant positive correlations were reported for clay content and soil volumetric water content (Castaldi et al., 2004), factors which strongly determine the pore space and water saturation and thus soil aeration and anaerobiosis. It is well established that oxygen saturation in the soil air controls the level of aerobic nitrification and anaerobic denitrification microbial activity (Davidson et al., 1993) and thus nitrogen pathways and process rates. Compared to tropical biomes of seasonally dry or humid tropical forests (e.g., Butterbach-Bahl et al., 2004b; Gharahi Ghehi et al., 2012; Kiese et al., 2003; Werner et al., 2007b), the annual N_2O emissions from savanna soils seem to be substantially lower, which is hypothesized to originate from N depletion via pyrodenitrificatory losses (bush fires), shorter wet periods with prevailing denitrificatory conditions in combination with well-drained soils and lower amounts of total nitrogen cycling within the system (Castaldi et al., 2006; Davidson et al., 2001). Other studies have not found significant effects of soil moisture on N_2O emissions under in situ conditions (Livesley et al., 2011), and is assumed that a lack of seasonality and low nitrogen levels provide the rationale for this observation.

4.3 NO emissions

Nitric oxide emissions measured at low moisture conditions (M25) and 20 to 30 °C soil temperature were 6.4 ± 2.4 and $9.1 \pm 4.8\,\mu g\,N\,m^{-2}\,h^{-1}$, respectively, and therefore higher than the fluxes reported for African sites during the dry season ($1.6–2.2\,\mu g\,m^{-2}\,h^{-1}$; Meixner et al., 1997; Serça et al., 1998) but comparable to dry season conditions observed in Venezuela (Cárdenas et al., 1993). A link between the magnitude of NO emissions from savanna soil and soil water content and nutrient availability has been postulated by various authors (Cárdenas et al., 1993; Feig et al., 2008; Parsons et al., 1996; Poth et al., 1995; Rondón et al., 1993). It was reported that soil moisture is the dominant factor whenever it is not limiting the NO flux, but emission strength is modulated by daily variation of soil temperature (Meixner et al., 1997). A significant correlation of NO emissions with soil pH was also reported (Poth et al., 1995), and it is in agreement with the outcome of our relative importance analysis where pH scored second after soil temperature in explaining observed NO emissions post pulse (Fig. 6). The low score of soil moisture in this analysis can be explained by the nonlinear response of NO to changing soil moisture levels and is also reflected in the low total explanatory power of 19.4 %. High soil temperatures (40 °C) in combination with medium moisture levels (M50) resulted in the strongest NO emissions ($65.0 \pm 97.8\,\mu g\,N\,m^{-2}\,h^{-1}$), with high intra-core variability. This indicates a substantial importance of aerobic ammonia oxidation-based pathways for NO emission (Butterbach-Bahl et al., 2013). Previous studies from African savannas on sandy soils suggest that maximum NO emissions occur at a narrow WFPS range between 10 and 25 % WFPS (Aranibar et al., 2004; Feig et al., 2008; Otter et al., 1999) and

that a strong linear increase of NO emissions occurs with increasing temperatures starting at 25 to 30 °C (Aranibar et al., 2004). It was also reported that NO emission decreases again at a soil temperature exceeding 40 °C (Passianoto et al., 2004), but such extreme soil temperatures were not included in our experimental setup. In accordance with this, the analysis of site T1 cores (savanna) showed strongest emissions for pulsing after the initial rewetting and the following incubation steps for the lowest soil moisture treatment (M25). It is noteworthy that pulse emissions again were slightly stronger at M25 conditions for pasture cores; the following measurements revealed no difference in emission strength between the three moisture levels at the first temperature interval. At 30 °C soil temperature, emissions for the driest cores remained low but M50 cores exhibited higher NO emissions (see Fig. 5).

Unfortunately, no measurements were conducted for low moisture conditions (M25) and high soil temperatures (40 °C) during the first incubation sequence of our work; thus, we can only speculate that NO emissions at low moisture levels (M25) would have even exceeded our maximum NO emissions recorded due to nitrification activity peaking at moisture levels below 50 % WFPS (see literature citations above).

4.4 N_2 emissions and total gaseous nitrogen losses

Dinitrogen emissions varied greatly between the different incubation setups (17–2350 $\mu g\,N\,m^{-2}\,h^{-1}$), and this range is comparable to results reported for temperate forests (Butterbach-Bahl et al., 2013; Dannenmann et al., 2008). The N_2 emission rates were clearly dominated by soil saturation (see Table 2 and Fig. 6). Average N_2 emissions for savanna soil below 50 % WFPS and under any implemented temperature setting were ranging from 45 to 108 $\mu g\,N\,m^{-2}\,h^{-1}$, while average N_2 emissions with highest water saturation (M75) were ranging from 627 to 1201 $\mu g\,N\,m^{-2}\,h^{-1}$. It is thus not surprising that the analysis of relative importance revealed that approximately 75 % of the variance of N_2 emissions was explained by changes in WFPS. Variations in pH accounted for another 23 % of variance (Fig. 6), while the other factors contributed considerably less to explain the observed N_2 emissions. The dominance of WFPS is in line with common knowledge about the functioning of denitification, given that N_2 production is catalyzed by the enzyme N_2O–reductase, which in turn is up-regulated by low oxygen concentrations (Spiro, 2012). From calculating fractions it is clear that N_2 is the dominant compound of gaseous losses, often exceeding N_2O and NO emissions by several magnitudes (Table 3). N_2 accounted for 82–99 % of all gaseous N losses from savanna soils for the investigated incubation intervals, except for the 50 % WFPS/40 °C setup, where strong NO emissions were accounting for 43 % of all N emissions.

The N_2-dominated N gas product ratios across all soil moisture levels might appear surprising at first, since strong N_2 soil emission has been associated with strictly anaerobic soil conditions and the investigated sandy soil textures may facilitate good aeration and thus impair formation of anaerobic microsites. It is, however, increasingly recognized that our previous knowledge on rather low N_2 loss from ecosystems is falsified by systematic but irreproducible underestimation of N_2 emission estimates due to the failure of the widely applied acetylene inhibition technique to indirectly estimate N_2 loss (Butterbach-Bahl et al., 2013). In contrast, the few available reliable direct measurements of N_2 emission from upland soil obtained with state-of-the-art methods, such as the helium soil core incubation technique, generally revealed large ecosystem N_2 losses (Butterbach-Bahl et al., 2013). This is in line with recent evidence about unexpectedly large abundance and diversity of the N_2O reducing microbial community in soil, not restricted to denitrifiers (Jones et al., 2013; Sanford et al., 2012). The latter findings could provide a microbiological explanation for high importance of N_2 loss in upland soil in general and probably also for the savanna soils investigated in this study.

4.5 Pulse emissions

Significant N_2O pulse emissions following the first rains after a dry season, often with a small temporal delay, have been reported for different seasonally dry (sub-)tropical ecosystems (Brümmer et al., 2008; Davidson et al., 1993; Scholes et al., 1997; Werner et al., 2007a) and are often preceded by significant CO_2 emissions immediately after the soil is re-moistured. We also measured significant CO_2 pulse emissions for all three watering levels immediately after water addition, but emissions dropped significantly in the following days. It has been stated that this pattern is caused by water-induced activation of soil microbes after pronounced dry season periods leading to immediate mineralization of accumulated organic material and subsequent consumption of freshly produced NH_4^+ / NH_3^- trough nitrification (Davidson et al., 1993).

The initial watering led to N_2O pulse emissions with peak emissions immediately after water addition, but they were, with 3 days duration, only short lived (a pattern that was previously reported for African savanna soil; Brümmer et al., 2008; Scholes et al., 1997). The occurrence of N_2O pulsing emissions was previously reported by Grover et al. (2012) for in situ measurements at a nearby savanna site, but emissions were, in accordance with our laboratory results, several magnitudes below reported break-of-seasons pulse emissions reported for tropical rainforests (Butterbach-Bahl et al., 2004b; Werner et al., 2007b). We did observe a positively correlated increase of N_2O pulse emissions with watering intensity, but with an average pulse emission of $5.8 \pm 5.0\ \mu g\,N\,m^{-2}\,h^{-1}$ for our highest watering intensity (M75), the amount of N released to the atmosphere was still minor. It has to be noted that, due to experimental design restrictions (consecutive incubation variations of temperature), we only measured initial

pulse emissions under rather low temperature settings, and given the observed positive correlation of N_2O emissions with temperature, pulse emissions at higher temperatures would have been even more pronounced.

Strong NO pulse emissions were reported for many sites from seasonally dry tropics (Brümmer et al., 2008; Levine et al., 1996; Scholes et al., 1997) and rainforests with seasonality (Butterbach-Bahl et al., 2004b) and are now an essential part in models simulating global NO emissions (Steinkamp and Lawrence, 2011; Yan et al., 2005; Yienger and Levy, 1995). The immediate emission of NO after watering was also observed by Pinto et al. (2002), who measured up to 100-fold increased NO emissions above pre-watering levels to 105 $\mu g\,N\,m^{-2}\,h^{-1}$, but noted that results varied substantially between collars. These results are in-line with our observed peak pulse emissions, which also varied between 27.7 and 306.5 $\mu g\,N\,m^{-2}\,h^{-1}$. In contrast to N_2O peak emission, the response was negatively correlated with moisture saturation. For soils of seasonally dry tropical rainforests in Mexico and Australia, high rates of NO emissions and quick temporal responses to the first rainfall events were observed (Butterbach-Bahl et al., 2004b; Davidson et al., 1993, 1991). The authors also state that rainfall events during the wet season triggered only minor emission events, providing pointers that the duration and severity of antecedent dry periods ultimately determine the magnitude of response of NO emissions to wetting events (Butterbach-Bahl et al., 2004a; Davidson et al., 1993). Thus, these pronounced pulse emissions events are thought to contribute substantially to the annual total of NO emissions (Butterbach-Bahl et al., 2004b; Ludwig et al., 2001).

Due to incubation design and the required destructive sampling of soil cores for N_2 analysis, pulsing effects on N_2 emission were not investigated (N_2 analysis for the various incubation conditions was carried out after the N_2O, NO and CO_2 incubation runs were completed).

4.6 Estimate of annual emission potentials

In order to estimate the potential annual soil–atmosphere exchange of N_2O, NO, N_2 and CO_2 from savanna soil, we used daily soil moisture and soil temperature records from a long-term eddy flux tower site (Howard Springs) located within 6 km from site T1 to extrapolate our results. The soil properties of the flux tower site are comparable to site T1 and sensors were placed at 10 cm depth (data provided by L. Hutley for years 2001–2013).

The site data was discretized into classes of soil moisture (SM) and soil temperature (ST) to link with the incubation setup classification. Annual fluxes are the sum of daily emission for the existing SM/ST condition at this day. Finally, the annual estimates were averaged to acknowledge the inter-annual variability of hygric conditions of this region. On average, 58 % of a year was assigned to class M25T30 (ST: 25 °C, SM: 37.5 % WFPS), followed by 36 % of class M50T30 (ST: 25–35 °C, SM: 37.5–62.5 % WFPS). For only 14 days per year WFPS levels exceeded 62.5 % (M75 conditions), indicating that these extreme moisture conditions only play a minor role for the annual budget (see Table 4 for a detailed annual classification).

In the following we present upscaled flux rates without pulse emission contribution as a minimum scenario as we did not investigate the effect of consecutive watering–drying cycles in our incubation setup. Based on climate data for the 13 year period, the average of annual emissions (excluding pulse emissions) is estimated to amount to $0.12 \pm 0.02\,kg\,N\,ha^{-1}\,yr^{-1}$ (N_2O), $0.68 \pm 0.02\,kg\,N\,ha^{-1}\,yr^{-1}$ (NO), $6.65 \pm 1.07\,kg\,N\,ha^{-1}\,yr^{-1}$ (N_2) and $2718.96 \pm 72.33\,kg\,C\,ha^{-1}\,yr^{-1}$ (CO_2). Thus, N_2 emission dominates the total annual gaseous nitrogen loss (89 %), and N_2O and NO only contribute 1.6 % and 9.3 %, respectively. In addition to these base emission levels we can estimate additional losses per pulse emission event. Given our data, we estimate an additional release of $1.2\,g\,N\,ha^{-1}\,yr^{-1}\,event^{-1}$ (N_2O), $37.9\,g\,N\,ha^{-1}\,yr^{-1}\,event^{-1}$ (NO) and $22.2\,kg\,C\,ha^{-1}\,yr^{-1}\,event^{-1}$ (CO_2). Since the actual number of pulse events is not known, we use a range of 1–5 three-day pulse events. This leads to the conclusion that pulse emission may only contribute 0.8–3.9 and 1.0–4.8 % to annual CO_2 and N_2O emissions, respectively. The strong pulse emissions observed for NO are reflected in the potential contribution to annual NO emissions. For 1–5 pulse emission events they could contribute between 5.3 and 21.8 % to the annual release of NO from soil. Due to experimental restrictions we cannot report N_2 pulse emissions.

The numbers indicate that on average savanna soils release approximately $7.5\,kg\,N\,ha^{-1}\,yr^{-1}$ to the atmosphere. In contrast, it is estimated that approximately $2\,kg\,N\,ha^{-1}\,yr^{-1}$ are deposited in remote rural areas of Australia (Meyer et al., 2001), but biological nitrogen fixation rates and nitrogen leaching are currently unknown and thus a qualified statement can not be made if the nitrogen cycle at this site is in equilibrium.

5 Conclusion

We reported the N_2O, NO, N_2 and CO_2 emission response of intact soil cores from tropical savanna and pasture to a range of climatic conditions. The laboratory analysis of intact soil cores allows for an analysis under controlled soil moisture and temperature conditions while largely preserving the structural components of the soil column, although influence of flora and macro-fauna is lost compared to in situ measurements.

Key findings of our analysis are

1. Soil–atmosphere exchange of NO and CO_2 under late dry season conditions was very low and for N_2O often even negative.

Table 4. Annual emission of N_2O, NO, N_2 and CO_2 from savanna soil (excluding contribution from pulse emission events). The number of days per year with a given soil temperature (ST) and soil moisture (SM) are presented in addition to the resulting annual emission.

	SM [% WFPS]	25	25	25	50	50	75	75	Annual flux [kg C / N ha^{-1} yr^{-1}]			
	ST [°C]	20	30	40	20	30	20	30	N_2O	NO	N_2	CO_2
Year	2001	0	205	0	0	152	0	8	0.10	0.68	5.48	2627.9
	2002	0	226	12	0	117	1	9	0.10	0.70	5.77	2691.8
	2003	0	223	13	0	99	1	29	0.14	0.69	8.52	2884.0
	2004	0	223	5	3	118	0	17	0.12	0.69	6.66	2748.0
	2005	0	213	2	0	147	0	3	0.09	0.69	4.77	2594.9
	2006	0	203	7	1	132	3	19	0.14	0.67	7.69	2748.0
	2007	0	233	0	0	111	2	19	0.13	0.69	7.39	2783.5
	2008	0	219	5	0	124	0	18	0.12	0.68	6.80	2754.2
	2009	0	223	7	0	120	0	15	0.11	0.69	6.38	2735.9
	2010	0	172	0	0	175	0	18	0.13	0.65	6.94	2673.3
	2011	10	176	0	0	156	3	20	0.14	0.65	8.03	2691.2
	2012	0	225	23	0	107	0	11	0.10	0.71	5.78	2724.0
	2013	0	207	0	0	144	0	14	0.12	0.67	6.30	2689.7
		1	211	6	0	131	1	15	0.12 ± 0.02	0.68 ± 0.02	6.65 ± 1.07	2718.96 ± 72.33

2. Total atmospheric loss of nitrogen was dominated by N_2 emissions under all but one tested soil climatic condition (82.4–99.3 % of total gaseous N loss), but NO emissions contributed almost 43.2 % to the total gaseous loss at 50 % WFPS and 30 °C soil temperature.

3. N_2O emissions were substantially higher for 3 out of 12 soil cores investigated and indicate substantial spatial variability at site level (maximum N_2O emission rate: 180 $\mu g\,N\,m^{-2}\,h^{-1}$). This has implications for site-scale estimates and extrapolation of soil–atmosphere exchange rates.

4. Pulse emissions were observed for N_2O, NO and CO_2 immediately after water addition, but they were only short lived (24–72 h). The magnitude of pulse emissions was positively correlated with soil moisture addition for CO_2 and N_2O, but negatively correlated for NO. Three of the cores displayed a different N_2O emission pattern with no initial pulse response, but prolonged elevated N_2O after the first days. However, pulse emissions may only contribute significant amounts to the annual emission budget of NO (5.3–21.8 %).

5. Upscaling to annual total suggests that savanna soil from this ecosystem only emits 0.12 $kg\,N_2O - N\,ha^{-1}\,yr^{-1}$. The estimated total annual emission of NO and N_2 was 0.68 $kg\,N\,ha^{-1}\,yr^{-1}$ and 6.65 $kg\,N\,ha^{-1}\,yr^{-1}$, respectively (data excluded contribution from pulse emissions).

6. We did not detect significant differences in emission magnitudes and patterns for our soil samples derived from savanna and pasture despite differing textural composition, higher carbon content in microbial biomass, higher NH_4^+ concentrations and the on-going fertilization of the pasture (note that only one pasture site was investigated versus three savanna sites).

7. Major controls on emission levels were soil moisture and temperature for N_2O and CO_2 emissions, soil temperature and pH for NO (soil moisture effect was not detected due to nonlinear response in the analysis) and soil moisture and pH for N_2.

The results indicate that the gaseous loss of nitrogen in savannas from northern Australia is largely controlled by NO emissions at high soil temperatures and low moisture conditions and N_2 losses, whereas the soil–atmosphere exchange of N_2O is generally low or even negative after pronounced dry periods. We did encounter strong N_2O emissions for a few individual cores, but no explanation for this emission pattern could be detected from the soil physicochemical properties of these cores. This indicates that a higher replication or larger sample areas are required to determine the N_2O exchange of these systems more reliably.

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