Revisions on the manuscript: "Land use change associated with urbanization modifies soil nitrogen cycling and increases N_2O emissions"

Editor:

5 Dear Authors

thank you very much for your final responses to the reviews.

I have a few comments:

- 1. please provide a revision with track changes.
- 2. in your responses it will make it easier for us, if you copied the reviewer comment and then let this follow by your response.
- 3. In the revised Figure 4 you speak of an exponential relationship. Could you try log (y) linear x scale, then the exponential nature would figure as a line.

With kind regards,

Andreas Ibrom

15

10

The authors would like to thank Andreas Ibrom for the comments. Figure 4 was updated accordingly, which improved the R² even further. This suggestion was much appreciated.

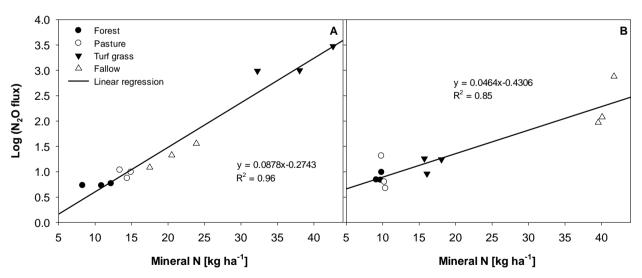


Figure 1: Linear relationship of log transformed N_2O emissions with mineral N content within 20 cm soil depth for each replicate of forest, pasture, turf grass and fallow land use during the establishment phase (A) and the rest of the year (B), with the coefficient of determination \mathbb{R}^2 .

The authors would like to thank both reviewers for their great feedback. We agree on all of the mentioned suggestions and prepared the revised manuscript accordingly. The detailed response is as follows:

Referee 1

20

25

This manuscript reports on a work investigating soil N dynamics and nitorus oxide emissions associated with the change in land-use in a transition from forest to peri-urban turf grass establishment. From an experiment perspective I find that the work has been carried out very thoroughly with careful planning and execution giving rise to a solid set of data on soil N, N2O fluxes and key soil parameters. Data from similar ecosystems are rare, and I support these should be made available to the scientific community and do suggest publication of the current work in BG. Meanwhile, I also find that the data interpretations in some places are exaggerated with a need for modifications before publication can be recommended. As pointed out by the authors the observed N2O emissions from turf grass system is possibly the result of a system in transition characterized by poor root development during the first months after establishment and thus high N2O emissions due to reduced N competition by plants. In a longer time perspective, N2O emissions from turf grass systems may remain at low levels throughout the year once the grasses have been established. Meanwhile, I think this need to be emphasized more strongly in the presentation of the results as generalization from the current data should be avoided.

Thus, I suggest leaving out the correlation plot (Fig. 4) as in this plot you actually compare the established forest and pasture systems with the turf grass supposedly under rapid transition. In this context, I'm also wondering how this correlation analysis can be established on non-transformed data as it is mentioned that data are non-normally distributed. Optionally, the correlation plot may be modified to illustrate partial relationships showing the analysis specifically for the initial transition period.

This recommended modification of correlating the parameters within the establishment phase separately to the rest of the year and changing the N_2O data to log transformed values greatly improved the R^2 value and results in a valuable partial relationship presentation. This suggestion was much appreciated. The figure was furthermore updated according to the editor's comments as mentioned above.

Secondly, the authors conclude that leaching of NO3 took place in the fallow plots. However, this process was not investigated in the current work and although the data may imply water-mediated losses of NO3-N I suggest this statement be modified in the current text.

Statements about leaching was reduced and modified to clarify the focus of the study:

30 Section 4.1, page 8, line 29:"Nutrient mineralisation is often faster in sandy soils but the rapid infiltration and low nutrient holding capacity of the A horizon of the Chromosol decreases the highly mobile NO₃ content substantially after heavy rain events. This amount of NO₃ is not only lost for plant uptake but can pollute groundwater and open waterways resulting in eutrophication."

Section 4.1, page 9, line 28:" These NO₃ peaks together with irrigation, which is particularly needed during turf grass establishment, implies a high N leaching potential in other Australian sandy soils of up to 80 kg N ha⁻¹ y⁻¹ (Barton et al. 2006). With the high potential of heavy rain events in the subtropics, fertilizer rates and timing needs to be considered carefully to avoid excessive N losses in form of NO₃ displacement."

Section 4.1, page 10, line 3:" Despite the fact that mineral N in the fallow soil never dropped back to zero, substantial amounts of NO_3 were lost from the topsoil after heavy rain events, not only as N_2O emissions but also through NO_3 displacement into deeper soil layers."

Section 4.2, page 10, line 14:" The high surface sand content of the Chromosol, combined with the moderate slope, prevents excessive water logging over long periods of time, which limits N₂O gaseous losses from denitrification in saturated soil conditions."

Section 4.3 from line 28:" The results presented here verify that subtropical N_2O emissions positively correlate to mineral N content in the soil and therefore indicate that land use change increases N_2O emissions from the soil, especially after plant cover removal and establishment of fertilized turf grass lawn."

How were the experimental plots situated in the landscape? E.g. were the randomized plots separated by strips of pasture, and what was the distance between plots? More details on the gas-flux chambers should be included in the text, e.g. were chambers transparent or opaque, how did the chambers open/close. Were fluxes obtained from two pseudo-replicate collars per each replicate plot considered a continuous timeseries of measurements, or were they analyzed separately? Please, clarify.

Additional information included into the Materials and Method section:

10

15

20

35

- a. Buffer zones of 0.5 m pasture strips between plots
- b. Pneumatically operated, clear acrylic glass chambers
- c. Fluxes from the two pseudo-replicate frames were analysed continuously as one replicated treatment

Check citations, if more than two authors only first author + et al. should be mentioned (e.g. Barton, Walm and Colmer, 2006 (P 9)).

The bibliography will be updated to make sure the Copernicus output style matches the author's reference list.

In section 4.2 (lines 7 and 14) you refer to a linear increase in N2O emissions with increasing NO3 – where is this shown? Please, clarify.

Clarified into: "However, the linear increase of N_2O emissions with increasing NO_3 content in the soil may be the result of higher denitrification than nitrification rates in the SERF soil."

And sentence added into results section to clarify the linear relationship shown in the updated Figure 4: "However, the linear regression shown in Figure 4 identified a clear increase of N₂O emissions with increasing annual mineral N contents for all treatments during the establishment phase as well as during the rest of the year."

In section 4.3, line 22 it is concluded that land use change results in increased N losses from the soil. Is this statement pointing at the N lost as N2O? Please, clarify

Clarified into: "This study determined that urbanization related land use change results in an accumulation of NO_3^- in fallow topsoil and elevated N_2O emissions, mainly after heavy rain events."

Section 5, conclusions – as pointed out above, I think this section needs to be modified according to the nature of the current study. Also, conclusions about turf grass C sequestration cannot be made from this study and should be removed from this section.

Conclusion section will be modified to clarify the focus of the study:

"This study provides evidence that land use change associated with urbanization accelerates N turnover and increase N₂O emissions from soils by presenting the first high temporal frequency dataset on peri-urban soils in the subtropics for a full year after land use change. These findings demonstrate that GHG emissions from peri-urban areas should be included into future IPCC climate change scenarios and rural to urban land development guidelines need to be established for GHG emission mitigation. Three main factors need to be considered to target N₂O losses from soils during land use change associated with urbanization: (i) previous land use, (ii) duration of development process, and (iii) new land use purpose that it is being changed into, i.e. public or private. The dry sclerophyll forest in this study supports the general hypothesis that forest soils are low N₂O emitters, contrary to expectation that the humid subtropical summer conditions would increase emissions compared to temperate forest soils. The accumulation of NO₃⁻ in fallow soil increases the potential for N₂O emissions and may amplify considering future predictions of rising temperatures and more frequent heavy rain events worldwide. Increased fertilizer application may be required to compensate for these N losses after land use change to keep land uses, such as turf grass, highly productive while altering N cycling in peri-urban environments. The outcomes of this study highlight the substantial NO₃⁻ accumulation in soils during land use change which consequently increases N₂O emissions and should be accounted for in global climate forecasts as urbanization processes are predicted to increase worldwide with increasing population growth."

Referee 2

20

This is a significant contribution to our understanding of the nitrogen cycle in soil-plant systems, and how these are affected by urban development. The manuscript extends work published previously by the team (van Delden et al. (2016)), but as the authors have said the previous work was preliminary data for a shorter period of observation. A much clearer picture is presented in this paper. However, the key point that comes across is that it is the process of land use change rather than the behavior of established turf grass that affects N2O emissions. I think that the title needs to be changed to reflect this. Also, given the very wide range of possibilities covered by the words 'land use change', a phrase that means very different things to different people, the title should be much more focused, so we know that the paper addresses changes in N2O emissions as a consequence of turf grass establishment – for lawns, golf courses, amenity grassland etc., and not a permanent change as a consequence of that change.

The authors agree and suggest a title change into:

"Urbanization related land use change from forest and pasture into turf grass modifies soil nitrogen cycling and increases N_2O emissions"

The behaviour of N depends on the different behaviours of ammonium and nitrate, as explained by the authors. Ammonium is affected by cation exchange, and so is affected by the CEC of the soil and by the mineralogical composition of the soil. While cation exchange is recognized as a process, no data for CEC are presented, and no description of the clay mineralogy of the soil is given. I appreciate that this could be a research project in its own right, but it would help to know what clay

minerals are present – perhaps by reference to other published descriptions. The reason for going on about that is that without knowledge of the CEC (at least) or the mineralogy of the soil, you can't really compare N emissions for different locations, as variation in the clay mineral type could well give rise to different N2O emissions, all other factors being equal. That would be an interesting experiment to conduct.

The authors appreciate the suggested importance of the specific site characteristic CEC and include CEC analysis into the site description (Table 1) for each soil profile horizon.

However, the sandy topsoil showed very low CEC between 0.9 and 4 meq⁺ 100g⁻¹, which suggests a minor effect of CEC on the NH₄⁺ dynamics. Even the subsoil (B horizon) with high clay content barely reached 12 meq⁺ 100g⁻¹. The most occurring clay in the highly weathered soils of Australia is kaolinite with a low CEC of approximately 10 meq⁺ 100g⁻¹ (Moore et al. 1998).

These CEC results are included into the text:

In section 2.4: "The cation exchange capacity (CEC) was determined based on Rayment and Higginson (1992)."

In section 3.1: "The CEC of the sandy topsoil is very low, and slightly higher in the A1 compared to the A2 horizon due to the higher soil organic matter as indicated by the total C and N content."

In section 4.1, page 8, line 24: "Nutrient mineralisation is often faster in sandy soils but the rapid infiltration and low nutrient holding capacity of the A horizon of the Chromosol decreases the highly mobile NO₃ content substantially after heavy rain events."

In section 4.1, page 10, line 11: "The low CEC of the sandy topsoil highlights the minor nutrient holding capacity of this peri-urban environment."

20 I have some more minor comments.

Minor comments are addressed as followed:

1) P2 lines 9 – head or heat?

Heat

2) P2 line 31 – what industry?

25 Turf grass industry

3) P3 line 11: illustrate, not illustrates

Illustrate

4) P4 line 8 – do you mean 2/3 N by mass or by molar proportion?

Two-thirds of the N content by mass

5) Section 2.4. You say measurements were made on 'fresh' soil. Was this dried before analysis? Was the soil dried before LECO analysis? I found this section insufficiently detailed to enable me to reproduce the analysis precisely, and it is not clear how the measured analytes were back calculated to the soil under field conditions. Please clear up this ambiguity.

"Mineral N in form of NH_4^+ and NO_3^- were extracted from the soil using a 1:5 KCl solution with 20 g of fresh soil with additional soil moisture determination at 105°C to identify the dry soil weight for the mineral N calculation as described by Carter and Gregorich (2007))."

"Total C and N content of air dried soil and plant material was determined by dry combustion (CNS-2000, LECO Corporation, St. Joseph, MI, USA) from ground samples."

6) P9 line 26 – possibly, instead of possible?

5 Possibly

20

7) Is it possible to calculate a nitrogen balance for these sites?

We agree on the advantage of a N balance for these systems. However, as reviewer 1 highlighted, this study did not quantify nitrate leaching, which seems to be one of the major N losses in these systems. Therefore, a rough calculated N balance based solely on fertilizer input and N_2O emissions would not be representative but will be subject for further research.

10 The references are a bit of a mess, which is surprising these days. Missing from the bibliography are: P1 line 23: United Nations 2008 P2 line 8: Grimm 2008 – 2 Grimm et al's are given but not cited P2 line 30: United Nations 2013 P2 line 34: AGO 2014 P3 line 2: ABS 2012 and Turf Australia 2012 P3 line 20: Moreton Bay Regional Council 2011 P9 line 29 and P12 line 7: it should be Barton et al P10 line 25: it should be Page et al From the Bibliography the following appear not to be cited (I may have missed some): Grimm et al – 2 references are given Hart et al 1994 Kaye et al 2006 Lorenz and Lal 2009

Community profile 2011, which is out of order Tratalos et al 2007 Newsletter 2012 again out of order We apologise for the mess, the bibliography will be updated to make sure the Copernicus output style matches the author's reference list.

Please find the marked-up manuscript version below:

Urbanization related land use change from forest and pasture into turf grass modifies soil nitrogen cycling and increases N_2O emissions Land use change associated with urbanization modifies soil nitrogen cycling and increases N_2O emissions

5 Lona van Delden, David W Rowlings, Clemens Scheer, Peter R Grace

Queensland University of Technology (QUT), Brisbane, QLD, Australia

Correspondence to: Lona van Delden (lona.vandelden@qut.edu.au)

Abstract. Urbanization is becoming increasingly important in terms of climate change and ecosystem functionality worldwide. We are only beginning to understand how the processes of urbanization influence ecosystem dynamics, making peri-urban environments more vulnerable to nutrient losses. Brisbane in South East Queensland has the most extensive urban sprawl of all Australian cities. This research estimates the environmental impact of land use change associated with urbanisation by examining soil nitrogen (N) turnover and subsequent nitrous oxide (N₂O) emissions with a fully automated system that measured emissions on a sub-daily basis. There was no significant difference in soil N₂O emissions between a native dry sclerophyll eucalypt forest and an extensively grazed pasture, wherefrom only low annual emissions were observed amounting to 0.1 and. 0.2 kg N₂O ha⁻¹ y⁻¹, respectively. The establishment of a fertilised turf grass lawn increased soil N₂O emissions by 18 fold (1.8 kg N₂O ha⁻¹ y⁻¹) with highest emission occurring in the first 2 month after establishment. Once established, the turf grass lawn presented relatively low N₂O emissions after fertilization and rain events for the rest of the year. Soil moisture was significantly higher and mineralised N accumulated in fallow land, resulting in highest N₂O emissions (2.8 kg N₂O ha⁻¹ y⁻¹) and significant nitrate (NO₃) losses of up to 63 kg N ha⁻¹ from a single rain event due to plant cover removal. The study concludes that urbanization processes into peri-urban ecosystems can greatly modify N cycling and increase the potential for losses in form of N₂O and NO₃.

1 Introduction

10

15

20

Global urbanization processes are becoming increasingly important in terms of global warming and ecosystem functionality. Urban populations worldwide have not only exceeded rural populations but are also predicted to account for all future population growth (United Nations 2008). Urban sprawl and increasing population densities are causing severe land use changes from intact biomes and commercially focused agriculture into smaller residential properties with introduced species. This transition from rural to semi-rural, i.e. peri-urban, and urban environments is increasingly associated with development and construction processes and the extensive establishment of turf grass for residential backyards, public parks and sportsgrounds, and golf courses (IPCC 2006). How these urbanization processes influence ecosystem dynamics in

biogeochemical cycling, and therefore contribute to ecosystem vulnerability and global warming is only beginning to be understood.

The consequences of land use change from native to agriculture have been identified by several studies, including a loss in soil quality (structure and nutrient losses) and quantity (erosion), increase greenhouse gas (GHG) emissions, and reduced potential for soil carbon (C) sequestration (Grover et al. 2012; Livesley et al. 2009). On the other hand, changing soils from agricultural to residential use in temperate climates has shown the potential to improve critical ecosystem services by (i) providing stormwater treatment, (ii) acting as a sink for atmospheric nitrogen (N) and (iii) sequestering C (Golubiewski 2006; Raciti et al. 2011a).

Studies on the impact of those land use changes on climate change are few but suggest that urbanization will change the biogeochemical cycling of C and N and associated nutrient turnover (Grimm et al. 2008). These biogeochemical alterations induced by land use change interact with urban effects (Betts 2007); such as creating heated islands through vegetation replacement and surface sealing but also increased local carbon dioxide concentration of over 500 ppm around cities compared to 390 ppm in natural environments (IPCC 2013; Pataki et al. 2007). These changing local climatic conditions and their feedback effects onto natural ecosystems make peri-urban environments more vulnerable to nutrient losses and potential sources of GHG emissions. With these peri-urban areas expanding worldwide it is most likely that these changing local climates will increasingly have an impact on global climate change, making an examination of GHG emissions from peri-urban land uses all the more urgent.

Nitrous oxide (N₂O) along with carbon dioxide (CO₂) and methane (CH₄) is one of the major greenhouse gases with a global warming potential (GWP) nearly 300 times that of CO₂ (IPCC 2013). Nitrous oxide is produced principally by microorganisms during nitrification and denitrification processes from mineral N (NH₄⁺ and NO₃⁻) in the soil. The production of N₂O is influenced by a number of soil parameters including substrate availability, temperature, and availability of oxygen, which is dependent on water content and texture of the soil (Rowlings et al. 2015). With the predicted climatic changes, Australia's ancient and fragile soils will most likely be affected in their balance between GHG gas emissions and consumptions (Baldock et al. 2012). Management practices such as fertilization and irrigation enhance N₂O production in the soil by increasing the mineral N content and limiting the oxygen availability (Rowlings et al. 2013; Scheer et al. 2008). Turf grass is the most highly managed land use of peri-urban environments in terms of fertilization, irrigation and frequent mowing, which therefore has a high potential for N₂O emissions.

Research on urban and peri-urban areas in temperate zones suggests that changes in biogeochemical cycling due to urbanization will substantially affect the global climate comparable to agriculture, with those areas and their intensive management expanding rapidly worldwide (Groffman and Pouyat 2009; Milesi et al. 2005). More than half the world's 7.2 billion population currently occupies 2.4 % of the global terrestrial land surface in urban areas (Potere and Schneider 2007; United Nations 2013). While peri-urban environments are often considered too small to be of consequence, the rapid growth of the <u>turf grass</u> industry as highlighted in the USA covers over 160,000 km² occupied with turf grass, three times more than any other irrigated crop in the country (Groffman and Pouyat 2009; Milesi et al. 2005). In Australia about 60 % of all

30

anthropogenic N₂O emissions come from cropped and grazed soils and the first GHG estimations from turf grass establishment support the emission intensity reported from temperate zones (AGO 2010; van Delden et al. 2016a). The use of turf grass is consistently growing in Australia with up to 17,320 ha in turf grass sales and an approximate gross value production of \$240 million AUD per annum (ABS 2012; Turf Australia 2012). Detailed estimates of turf grass cover, however, currently do not exist for the Australian continent and other subtropical regions like South-east Asia, China, India or Mexico. Urbanization is currently neglected in modelled IPCC climate scenarios, mainly due to limited data on C and N processes in urban and peri-urban environments (IPCC 2006, 2013).

Therefore, this study aims to identify the impact of those land use changes associated with urbanization on annual N_2O emissions and their driving parameters in subtropical peri-urban environments. Following a short-term (80 days) GHG sampling campaign focussing on lawn establishment (van Delden et al. 2016a), a fully automated closed static chamber system was used to continuously monitor N_2O fluxes together with soil biogeochemical processes over a full year to determine the seasonal impact of construction work and conversion from extensively grazed pasture to turf grass lawn. This study's high resolution flux measurements and supporting soil N mineralisation illustrates the vulnerability of ecosystems to urbanization processes and the potential impact on N cycling and N_2O emissions.

15 2 Materials and Method

10

2.1 Site description

The study was conducted at the Samford Ecological Research Facility (SERF) in the Samford Valley, 20 km from Brisbane in South-East Queensland, Australia. The Samford Valley covers an area of approximately 82 km² and is surrounded by mountains to the north, west and south. Mostly cleared in the early 1900s, the valley was developed in the 1960s for dairy and beef cattle as well as intensive agriculture including banana and pineapple. Samford's population density has increased rapidly, almost doubling from 1996 – 2006, causing land use change from predominately rural to residential properties (Moreton Bay Regional Council 2011). As a result, SERF contains the last remnant forest of the valley floor. The valley is influenced by a humid subtropical climate with seasonal summer rain. The long term mean annual precipitation is 1110 mm with mean annual minimum and maximum temperatures of 13 °C and 25.6 °C respectively (BOM). The soil at the experimental site is characterised by a strong texture contrast between the A and B horizon and is classified as brown Chromosol according to the Australian soil classification (Isbell 2002) and Planosol according to the World Reference Base (WRB 2015).

2.2 Experimental design

30

This study examines the impact of land use change from a native forest to well-established pasture, turf grass lawn and fallow soil without plant cover using the same sampling campaign setup as van Delden et al. (2016a). Each land use treatment included 3 replicated plots, 2 m wide by 10 m long and separated by 0.5 m of pasture as a buffer zone. The turf

grass lawn and fallow treatments were established within the well-established pasture to create a randomised plot design, 50 m from the native forest. The SERF native forest (*Dry sclerophyll eucalypt forest*) is a baseline for historical land use and was unmanaged. The well-established *Chloris gayana* pasture represents rural development in the area and has been extensively grazed for the last 15 years. Livestock, however, was excluded over the course of the study and the pasture grass was slashed 5 times during the study to ensure it did not exceed the maximum height of the GHG measurement chamber.

The turf grass lawn was established from the well-established pasture by removing 5 cm of topsoil with grass roots. The soil was rotary hoed twice to a depth of 15 cm and Blue Couch (*Digitaria didactyla*) was planted with 50 kg N ha⁻¹ fertilization (13.6.2013) to aid in establishment. Over the experimental year the turf grass lawn was fertilized twice (26.10.13, 6.3.2014) with 50 kg N ha⁻¹ and irrigated, in all 150 kg N ha⁻¹ y⁻¹ of Prolific Blue AN fertilizer (12.0 % nitrogen, 5.2 % phosphorus, 14.1 % potassium, 1.2 % magnesium) with two-thirds of the N_content by mass in the ammonium form. The turf grass lawn was irrigated to a total of 30 mm during drier months as well as after fertilization. The turf grass was mowed with the clippings removed as soon as the grass grew to the maximum chamber height, once in spring, twice in summer and twice in autumn, and kept free of weeds manually at all times. Fertilization rates were based on half the local industry practices recommendation. Infrequent mowing represents the normal management for residential properties in this region and is normally in response to increased growth in the wetter and warmer summer months.

The fallow treatment simulated the impact of transitional processes such as construction work and plant cover replacement. In the fallow treatment, the grass cover was removed and the bare soil was rotary hoed twice to a depth of 15 cm. The fallow treatment was kept free from plant cover over the full experimental year with a non-selective herbicide (Bi-Active 360g/L Glyphosate) and a broad leaf herbicide (Double Time, 340g/l MCPA + 80g/l Dicambra). During the experimental year, high resolution sub-daily N_2O flux measurements were combined with mineral N analysis and site specific climate and soil moisture measurements.

2.3 N₂O flux measurements

Nitrous oxide fluxes were determined from mid-June 2013 to mid-June 2014 using an automated sampling system as detailed by Scheer et al. (2014), extending the turf grass establishment phase documented by van Delden et al. (2016a) into a full measurement year. The pneumatically operated 50 cm x 50 cm x 15 cm high, clear acrylic glass-static chambers were secured to stainless steel bases, permanently inserted 10 cm into the ground. The chambers were moved each week between two bases per treatment plot, to minimize the influence of the chamber microclimate, while measurements were analysed continuously. The chambers were connected to an automated sampling system and an in-situ gas chromatograph (SRI GC8610, Torrance, CA, USA) equipped with 63Ni Electron Capture Detector (ECD) for N₂O. One replicate chamber from each of the four treatments was closed for one hour, and four headspace gas concentrations measured at 15 minute intervals, followed a known calibration standard (0.5 ppm N₂O, Air Liquide, Houston, TX, USA). This process was repeated for the remaining two replicate chambers over a full cycle of three hours, allowing eight flux measurements to be calculated per day, for each of the 12 chambers.

2.4 Auxiliary measurements

Soil samples were taken fortnightly from all replicated treatment plots over the experimental year and divided into 2 depths (0-10 cm, 10-20 cm). Mineral N in form of NH₄⁺ and NO₃⁻ were extracted from the soil using a 1:5 KCl solution with 20 g of fresh soil with additional soil moisture determination at 105°C to identify the dry soil weight for the mineral N calculation as described by Carter and Gregorich (2007)).NH₄⁺ and NO₃⁻ were extracted from the soil using a 1:5 KCl solution with 20 g of fresh soil. The extract was analysed for NH₄⁺ and NO₃⁻ with an AQ2+ discrete analyser (SEAL Analytical WI, USA). The net mineralisation rate was determined from differences in mineral content between sampling dates (Hart et al. 1994). Soil moisture and temperature for each treatment were collected using a TDR probe (HydroSense CD 620 CSA) and a PT100 probe (IMKO Germany). Soil moisture was then converted with the treatment specific bulk density (BD) to water-filled pore space (WFPS). Soil samples were taken for site characterization with a hydraulic soil corer to 1 m depth, air dried and sieved to 2 mm. Particle size analysis for soil texture as well as BD, pH and electrical conductivity (EC) analysis were undertaken according to Carter and Gregorich (2007). Total C and N content of air dried soil and plant material was determined by dry combustion (CNS-2000, LECO Corporation, St. Joseph, MI, USA) from ground samples.

2.5 Flux calculations and statistical analysis

Fluxes were calculated from the slope of the linear increase or decrease of the 4 concentrations measured over the closure time and corrected for chamber temperature and atmospheric pressure, using the procedure outlined by Knowles and Singh (2003) and Scheer et al. (2014). The linear regression coefficient (r²) was calculated and used as a quality check for fluxes above the detection limit to assure linearity of the gas concentration increase. Flux rates were discarded if r² was < 0.85 for N₂O fluxes (Scheer et al. 2013). Daily fluxes from the automated chambers were calculated by averaging sub-daily measurements for each chamber over the 24 hour period. The detection limit determined for the gas sampling system is ± 1.2 g N₂O ha⁻¹ d⁻¹. Gaps in the dataset were filled by linear interpolation across missing days.

Statistical analysis was undertaken using SPSS Statistics 21.0 (IBM Corp., Armonk, NY). Non-normal distribution meant all cumulative data were log-transformed for ANOVA analysis using Games-Howell as the post-hoc test. Daily N₂O flux differences between treatments were interpreted by plotting 95 % confidence intervals using R studio. A significant difference of p < 0.05 between treatments was assumed in case the confidence intervals of all treatments were not overlapping. A Spearman's rho correlation analysis was used to examine relationships between gas fluxes, soil chemistry, soil moisture and temperature. The significance value (p) is shown for each analysis, as well as the correlation coefficient (r) with its significance level $(p < 0.05^*, p < 0.01^{**})$.

3 Results

3.1 Site characteristics

The site received 740 mm of rain during the experimental year, substantially less than the long term average (Table 1). Wet season rainfall was delayed compared to the historic average, with less than half the rainfall in summer (December to February) compared to autumn (March to May) (Table 2). Substantial out of season rain also fell in the spring with over 200 mm in November alone. Rainfall was highly episodic, with the highest daily rain event of 108.8 mm in March 2014. The mean annual minimum and maximum temperatures for the experimental year were 16.7 °C and 27.1 °C respectively, and light ground frost occurred twice in August. The turf grass and fallow treatment were established within the pasture and therefore share the same soil profile with its characteristics, except for bulk density in the A1 horizon which changed after the turf grass establishment from 1.4 to 1.2 g cm⁻³. Nutrient removal in turf grass clippings added up to 1.8 t C ha⁻¹ y⁻¹ and 30 kg N ha⁻¹ y⁻¹ lost from the system during the experiment year. The turf's biomass production was approximately 6.3 kg C ha⁻¹ d⁻¹ and 0.13 kg N ha⁻¹ d⁻¹ in dry matter but varied widely depending on fertilization and available water and increased up to 10.4 kg C ha⁻¹ d⁻¹.

3.2 Environmental parameters

The lowest WFPS during the experimental year was 13 % in the forest, with the highest occurring in the pasture which briefly reached saturation in March 2014 (Figure 3). In all treatments the lowest WFPS occurred in spring and summer with an average of 33 and 32 % respectively together with the highest average maximum daily temperatures of 28 and 30 °C. While the highest seasonal WFPS for all treatments occurred in winter, the maximum WFPS occurred during autumn after the heavy rain in March 2014. The forest had significantly lower WFPS throughout the experimental year than all other treatments (p < 0.01, Table 3), while the fallow had significantly higher WFPS (p < 0.01). No significant difference in WFPS was observed between pasture and turf grass (p > 0.05) although during spring, summer and autumn turf grass had lower minimum and maximum values than the pasture. Fallow had significantly higher and forest significantly lower WFPS than pasture and turf grass (p < 0.01) throughout the experimental year.

3.3 Temporal variability of mineral nitrogen

Averaged over the experimental year the fallow treatment had the highest NH₄⁺ and NO₃⁻ content across 20 cm soil profile, followed by turf grass, pasture and forest (Table 3). These differences in mineral N were significant for all treatments (p < 0.01) except between pasture and forest (p > 0.05). The 0-10 cm depth had higher average mineral N, NH₄⁺ and NO₃⁻ than the 10 - 20 cm depth for all treatments with significant differences between all treatments (p < 0.01). In 10 - 20 cm soil depth only the fallow had significantly higher mineral N, NH₄⁺ and NO₃⁻ contents (p < 0.01). Soil NH₄⁺ showed relatively little temporal variation and remained consistently above 3 kg NH₄⁺ ha⁻¹ while NO₃⁻ decreased substantially after rain events and fell below detection limit several times in all treatments but the fallow (Figure 1).

Total mineral N in the forest ranged from 8 to 40.1 kg N ha⁻¹ 20 cm⁻¹ throughout the year with marginally higher mineral N content from 0-10 cm than 10-20 cm with 9.7 and 8 kg N ha⁻¹ respectively. Total mineral N in the pasture ranged from 5.1 to 42.4 kg N ha⁻¹ 20 cm⁻¹, with a comparable distribution in depth than the 0-10 cm and 10-20 cm forest soil with 10.7 and 7.8 kg N ha⁻¹ respectively. Total mineral N in the turf grass soil ranged from 9.1 to 127.6 kg N ha⁻¹ 20 cm⁻¹. The turf grass had twice as much mineral N in 0-10 cm than 10-20 cm depths with 20.7 and 10.1 kg N ha⁻¹ respectively. A short term increase in both NH₄⁺ and NO₃⁻ content in the soil was evident after fertilization in June, October and March, which decreased to the background levels after approximately one month. Total mineral N contents in the fallow soil ranged from 19.7 to 160.7 kg N ha⁻¹ 20 cm⁻¹ with about 2/3 of the mineral N being located in the upper 10 cm. All main changes in the fallow until the major rain event in March when it dropped from 95.5 to 32.8 kg N ha⁻¹ 20 cm⁻¹. From the linear increase in mineral N content within the upper 10 cm between January and March 2014 a soil mineralization rate of 0.6 kg N ha⁻¹ d⁻¹ was estimated.

3.4 Temporal variation of N₂O fluxes

Daily N_2O fluxes across all treatments ranged from extended periods close to zero to over 123 g N_2O ha⁻¹ d⁻¹ from the fallow with the highest WFPS after heavy rain events (Figure 2). The N_2O fluxes from turf grass were more often significantly different on daily bases than any other treatment with 76 days (21 %) of the experimental year, 80 % of this difference occurred in the first two months after establishment. This was followed by the forest with 65 days (18 %), fallow with 58 days (16 %) and pasture with 29 days (8 %). Daily N_2O fluxes from the forest soil showed no substantial temporal variation throughout the experimental year, with minor emission peaks up to 8.1 g N_2O ha⁻¹ d⁻¹ after large rain events (> 60 mm) in November and March. From September until October one of the two bases in one pasture replicate emitted substantially more N_2O than the other replicates, however, the exact cause of this is unknown. Without these spatially variable emissions, the annual flux would have been about 40 % lower and therefore comparable to the forest N loss of 0.09 kg N ha⁻¹ y⁻¹. During the initial emission peak between June and August the daily average N_2O flux from the turf grass was 24 g N_2O ha⁻¹ d⁻¹. Excluding this initial emission peak, daily N_2O flux averaged 1.2 g N_2O ha⁻¹ d⁻¹. The highest annual N_2O flux was measured in the fallow from only 3 large peaks over 19, 10, and 44 consecutive days after rain events which together accounted for 85 % of the total N losses. Over a third of the significantly high daily N_2O fluxes in the fallow occurred from the heavy rain event in March 2014.

Annual N_2O losses were highest in the fallow and turf grass treatments totalling 1.78 and 1.15 kg N ha⁻¹ y⁻¹ respectively compared to the pasture and forest losses of 0.15 and 0.09 kg N ha⁻¹ y⁻¹ (p < 0.01, Table 3). About 80 % of the annual N_2O losses in the turf occurred in the first 8 weeks after establishment (Figure 3). Mineral N fertilizer input of 150 kg N ha⁻¹ y⁻¹ and the yearly N_2O -N losses from the turf grass lawn corrected for background emissions (zero N fertilization) from the pasture resulted in an emission factor (EF) of 0.7 % (Kroeze et al. 1997).

3.5 Environmental parameters influencing N₂O fluxes

Mineral N contents in the forest and fallow soils were not significantly correlated to N_2O fluxes on a daily basis (Table 4). However, the linear regression shown in Figure 4 identified a clear increase of N_2O emissions with increasing annual mineral N contents for all treatments during the establishment phase as well as during the rest of the year. However, the linear regression shown in Figure 4 identified a clear increase of N_2O emissions with increasing annual mineral N contents for all treatments. This relationship is supported by the substantial N_2O emissions peaks from the fallow and simultaneous decrease in NO_3 after the two biggest rain events in November 2013 and March 2014, with WFPS above 70 %. The separate linear regression for all land uses with plant cover, i.e. forest, pasture, and turf grass, identified an even stronger relationship of mineral N and N_2O . Forest and turf grass N_2O fluxes were strongly and fluxes from the pasture and fallow moderately correlated to their WFPS. Temperature was moderate negatively correlated to N_2O fluxes as well as mineral N for pasture and turf grass. In the fallow temperature strongly affected mineral N contents but not N_2O fluxes. Mineral N in the fallow soil was strongly negative correlated to its WFPS mostly because of the strong negative correlation of NO_3 with WFPS with r = -0.56**.

4 Discussion

20

30

This study combines the first high frequency estimates of subtropical N₂O fluxes and annual mineral N cycling from dry sclerophyll forests, unfertilized pastures and turf grass lawns, the most common land uses associated with urban and periurban environments. The lack of high frequency field measurements in urban and peri-urban environments makes accurate assumptions and mitigation strategies difficult. Conventional gas sampling methods most likely result in an over- or underestimation of emissions, as the production and release of N₂O can differ in time (Mosier et al. 1998). This research gap together with the strong temporal variability of subtropical heavy rain events underlines the importance of automated high frequency measurements to capture representative soil-atmosphere gas exchange. The subtropical climatic zone represents an often neglected area of research, despite the subtropics covering 3.26 M ha in Australia alone, as well as large areas on the North and South American continent, Africa and Asia. Differences between other climates and the humid subtropics are the heavy summer rains leading to high soil moisture and temperatures favourable for high soil microbial activity. Therefore this study identified mineral N content and WFPS as the main parameters driving N₂O production in the soil while studies from temperate zones report temperature as the main driver (Butterbach-Bahl and Kiese 2005; Fest et al. 2009).

4.1 Mineral N

Mineralised N in form of NH_4^+ and NO_3^- determines the production and loss of N via N_2O and depends on climatic parameters like temperature as well as substrate and oxygen availability. Nutrient mineralisation is often faster in sandy soils but the rapid infiltration and low nutrient holding capacity of the A horizon of the Chromosol decreases the highly mobile NO_3^- content substantially after heavy rain events. This amount of NO_3^- is not only lost for plant uptake but can pollute

groundwater and open waterways resulting in eutrophication. Nutrient mineralisation is often faster in sandy soils but the rapid infiltration of the A horizon of the Chromosol increases the leaching potential of the highly mobile NO₃ into deeper layers of the soil profile after heavy rain events. The leached NO₃ is not only lost for plant uptake but can pollute groundwater and open waterways. In this study mineral N contents from the forest and pasture treatments where driven by annual variation in temperature and moisture contents whereas turf grass lawn and fallow where dominated by management. The negative correlation of temperature in the pasture and turf grass can be most likely explained by the higher plant productivity during the warmer summer and spring resulting in higher plant NO₃ and water uptake with increasing temperature which then reduces soil moisture conditions.

10

Soil mineral N in the SERF forest was generally low and dominated by NH₄⁺, and while less seasonally variable throughout the year than NO₃⁻, still responded to rainfall. The overall mineral N reported from temperate eucalypt forest soils was double the annual SERF average of 17.6 kg N ha⁻¹ with up to 38.1 kg N ha⁻¹ (Fest et al. 2009; Fest et al. 2015a; Livesley et al. 2009). However, the greater NO₃⁻ proportion in the sandy SERF soil of 3.9 kg N ha⁻¹ compared to 0.8 kg N ha⁻¹ of temperate sandy forest soils indicates a higher mineral N availability in the subtropics (Livesley et al. 2009). Average NO₃⁻ contents from other dry sclerophyll forest are even lower with 0.02 kg N ha⁻¹ (Fest et al. 2015a). The higher N availability is most likely due to faster soil organic matter turnover in the subtropical climate with higher temperatures in combination with the main annual rainfall. While in temperate summers it is mostly dry during the high temperatures which limits microbial activity, the humid summers in SEQ not only accelerate N turnover but also water and N uptake by plant, which therefore reduces potential N losses. Subtropical rainforests, on the other hand, present with 97.7 kg N ha⁻¹ up to 6 times higher mineral N contents than the SERF soil, suggesting a lower N turnover associated with the low net primary productivity (NPP) of the dry sclerophyll forests (Rowlings et al. 2012). Overall NH₄⁺:NO₃⁻ ratios from Australian forests indicate higher NO₃⁻ availability in subtropical forest soils (3-4) compared to temperate zones (28-125) (Livesley et al. 2009; Rowlings et al. 2012; Fest et al. 2015a). These differences in N availability suggest that N cycling in forest soils is mainly regulated by the climate as opposed to soil type and NPP.

Ammonium was the dominant mineral N form in the SERF pasture, similar to the forest and in line with other subtropical pastures in Australia (Rowlings et al. 2015). The SERF soil reflects the overall minor annual variability of NH_4^+ compared to NO_3^- across most climates in Australia. The overall mineral N content at the SERF pasture soil was at the lower end of the reported values from both temperate and subtropical pastures which is most likely explained by the lower clay contents at the site which fixes NH_4^+ and higher N inputs by legumes (Livesley et al. 2009; Rowlings et al. 2015). For example, in other extensively used subtropical pastures NH_4^+ annual values did not drop below 55 kg N ha⁻¹, which is three times higher than the SERF annual NH_4^+ average (Rowlings et al. 2015). While NH_4^+ at SERF is comparable to temperate Australian pastures, NO_3^- in the SERF pasture soil is at the lower end (Livesley et al. 2009). This indicates an efficient system from tied up N in organic material to the plant uptake of NO_3^- , which supports the hypothesis of an efficient N cycle within well-established land use.

Annual mineral N variations in the SERF turf grass were mainly controlled by the fertilisation events but rapidly fell back to background levels after each application. The fertilizer mineral N peak was particularly emphasized after the first application, where soil NO₃ was more than double than after subsequent fertilization events. This is possibly due to the undeveloped root system and therefore less N uptake as well as additional plant available N in the added turf grass rolls. These NO₃ peaks together with irrigation, which is particularly needed during turf grass establishment, implies a high N leaching potential in other Australian sandy soils of up to 80 which can account for up to 160 kg N ha⁻¹ y⁻¹ in less than two vears in sandy soils (Barton et al. 2006). With the high potential of heavy rain events in the subtropics, fertilizer rates and timing needs to be carefully considered carefully to avoid excessive N losses in form of NO₃ displacement, to water ways. The fallow soil had the highest WFPS content throughout the year due to plant cover removal and therefore no further water uptake by the roots, creating favourable condition for soil mineralisation and losses (Robertson and Groffman 2007). The moist conditions together with the temperatures of the warmer season resulted in accelerated N turnover and without the N uptake by plants substantial amounts of NO₃ accumulated in the soil. Despite the fact that mineral N in the fallow soil never dropped back to zero, substantial amounts of NO₃ were lost from the topsoillosses occurred after heavy rain events, not only as N₂O emissions but also through NO₃ displacement into deeper soil layers gaseous losses but also most likely due to leaching of NO₃ from the topsoil. The substantial N loss after rain events demonstrates the significant impact of plant cover removal and soil disturbance in peri-urban ecosystems. The low CEC of the sandy topsoil highlights the minor nutrient holding capacity of this peri-urban environment. These potential N losses after heavy rain events demonstrates the significant impact of plant cover removal and soil disturbance in peri-urban ecosystems.

4.2 N₂O fluxes

10

- The study illustrates that land use change associated with urbanization can significantly alter soil N turnover resulting in elevated soil N₂O emissions and increased N losses from the soil. During the experimental year of this study, autumn was the wettest season and therefore had the highest N₂O emissions from all treatments but with different intensity from the different land use systems. Soil N₂O emissions were significantly different between the investigated land use systems with the temporal variations in daily N₂O fluxes and primarily controlled by WFPS. However, the linear increase of N₂O emissions with increasing NO₃ content in the soil may be the result of higher denitrification than nitrification rates in the SERF soil. However, the linear increase of N₂O emissions with increasing NO₃ content in the soil of all four treatments suggest higher denitrification than nitrification rates in the SERF soil. The high surface sand content of the Chromosol, combined with the moderate slope, prevents excessive water logging over long periods of time, which. This limits N₂O gaseous losses from denitrification in saturated soil conditions, but indicates a high potential for NO₃ leaching.
- The daily N_2O average of 0.4 g N_2O ha⁻¹ d⁻¹ from this study's subtropical dry sclerophyll forest is lower than the averages of < 1.2 g N_2O ha⁻¹ d⁻¹ reported from temperate Australian dry sclerophyll forests (Fest et al. 2009; Livesley et al. 2009). This might be explained by the overall low total C and N and the below average rainfall during the experimental year. Considering the positive correlation of N_2O emissions and NO_3^- content in the soil, it was expected that the higher NO_3^-

availability in the SERF forest compared to the temperate dry sclerophyll forest also causes higher N_2O emissions. The low WFPS which was > 40 % for most of the year inhibited denitrification processes and caused therefore lower N_2O emissions compared to the temperate zones as well as increased NO_3^- uptake during the humid subtropical summer. This efficient N cycling together with the low NPP of the dry sclerophyll forest and low clay content at SERF causes also lower N_2O losses compared to subtropical rainforests (Rowlings et al. 2012). This study supports the general hypothesis that forest soils are minor contributors to the global N_2O budget, although other N_2O emission studies of Australian forest soils provide only a limited comparison of temporal N_2O variability due to infrequent or short term measurements (Page et al. 2011; Fest et al. 2009; Fest et al. 2015a).

The annual N₂O emissions from the SERF pasture are comparable to other reported extensive pastures across Australia (1-2 kg N ha⁻¹ y⁻¹) but substantially lower than unfertilized pasture in the northern hemisphere (Dalal et al. 2003). Annual emissions from other studies on subtropical Australian pastures reported to be up to 3.4 kg N₂O ha⁻¹ y⁻¹ and highly interannual variable depending on rainfall (Rowlings et al. 2015). This exceeded the annual N₂O emissions at SERF by nearly 17 times, which may have been limited by the dry year and high sand content.

The first N₂O emission peak after the turf grass's establishment caused the majority of the annual N₂O emissions and was not repeated after two additional fertilization events. This initial N₂O peak can be explained by the underdeveloped root system and consequently a reduced NO₃ uptake by the turf grass, which together with the irrigation stimulated nitrification and denitrification and consequential N₂O emissions. The high N demand from the highly productive turf grass later on results in the immediate uptake of mineral N and therefore minor N₂O emissions. The annual N₂O emissions from the SERF's turf grass are more than double the N₂O emissions from extensive Australian pastures reported in the literature (Dalal et al. 2003). The SERF turf grass lawn emitted about 3.3 times more N₂O on daily average during the experimental year than native pasture from the temperate zones, but only half of the reported values for urban turf grass in the USA which were comparable to intensive agriculture (Kaye et al. 2004). However, compared to Australian intensively managed pastures, N₂O emissions from the SERF turf grass were 50 % lower (Scheer et al. 2011). Differences between reported values and the SERF turf grass are most likely explained by differences in texture and the total N content in the SERF soil being nearly 4 times lower. Reported EFs from temperate pastures also vary substantially between experimental years due to differences in received rainfall (Jones et al. 2005). It could be therefore expected that the SERF's turf grass EF will increase in wetter years. However, in subtropical systems is has been proven that the total amount of annual rainfall received is not as decisive for annual N₂O emissions as rainfall patterns and intensities (Rowlings et al. 2015). These differences between temperate and subtropical N cycling make short term N₂O flux measurements difficult to compare and need further investigation in the global subtropics.

Significantly higher NO_3 contents occurred 3 months after plant cover removal in the fallow soil but only during the warm and wet summer season substantial N_2O emissions were observed. The two significant N_2O emission peaks from the fallow were most likely caused by denitrification processes from the accumulated NO_3 and soil moisture conditions after major rain events. These N_2O emission peaks mirror the NO_3 decrease from the soil after those rain events but cannot completely

30

account for it, suggesting that most NO_3 was leached below 20 cm soil depths or lost via other gases such as N_2 . All other treatments, including the fertilized turf grass, prevented potential N_2O production in the soil by rapid NO_3 uptake from plants. Therefore, plant cover removal makes ecosystems undergoing land use change most vulnerable to substantial N losses under humid subtropical climate conditions.

4.3 Effect of land use change associated with urbanization

10

15

This study determined that urbanization related land use change results in an accumulation of NO₃ in fallow topsoil and elevated N₂O emissions, mainly after heavy rain events. The results presented here verify that subtropical N₂O emissions positively correlate to mineral N content in the soil and therefore indicate that land use change increases N₂O emissions from the soil, especially after plant cover removal and establishment of fertilized turf grass lawn. This study determined that land use change associated with urbanization results in substantially elevated N₂O emissions and increases N losses from the soil. The results presented here verify that subtropical N₂O emissions positively correlate to mineral N content in the soil and therefore indicate that land use change increases N₂O emissions from the soil, especially after plant cover removal and establishment of fertilized turf grass lawns. The annual variation in daily N_2O fluxes confirm that despite soil moisture as the strongest climatic parameter influencing N_2O emissions, the individual land use is the main influence on the soil-atmosphere gas exchange. Extended periods of fallow soil in particular should be avoided during urbanization processes as bare soil is highly vulnerable to N losses due to plant cover removal. Turf grass lawn, as a fertilized and highly managed land cover, leads to significantly changed soil conditions compared to the rural land use types of forest and pasture. However, turf grass lawns in the subtropical climate of SEQ have lower emissions against expectations based on the high emission findings from temperate zones (Grimm et al. 2008; Tratalos et al. 2007; Kaye et al. 2006). Substantial N₂O emissions were only observed within the first 2 months after turf grass establishment, while over the remaining 10 months only minor fluxes occurred even after further fertilization events. While N₂O emissions from the turf grass were reduced substantially over time, emissions from the fallow increased with time due to more available NO₃. Therefore, the N₂O emissions of well-established turf grass lawns need to be considered separately to their production and establishment phase as well as potential N losses from fallow land targeted for the entire duration of land use change, which should be kept as short as possible (Barton et al. 2006; van Delden et al. 2016a).

Research from temperate zones suggests a C sequestration potential from the higher productivity of turf grass lawns (Golubiewski 2006; Lorenz and Lal 2009; Raciti et al. 2011a). Others argue that the positive effect of C sequestration however can easily be offset by the high N demand together with irrigation, resulting in increased N₂O emissions and overall nutrient losses caused by management practices like mowing and clipping removal (Conant et al. 2005; Wang et al. 2014). Australian ecosystems with highly weathered soils, however, are generally low in nutrient stocks and often limited in their C sequestration potential (Livesley et al. 2009). The SERF turf grass, however, presented relatively low N₂O emissions when excluding the establishment phase, which implies the potential to balance GHG-emissions with C sequestration. A full life cycle assessment needs to determine if turf grass lawn in the subtropics is increasing or decreasing the GWP of peri-urban

environments by balancing C sequestration and GHG emissions, not only from the soil but also through the production, distribution and use of fertilizer, fuel and chemicals (Selhorst and Lal 2011).

5 Conclusion

This study provides evidence that land use change associated with urbanization accelerates N turnover and increase N₂O emissions from soils by presenting the first high temporal frequency dataset on peri-urban soils in the subtropics for a full year after land use change. These findings demonstrate that GHG emissions from peri-urban areas should be included into future IPCC climate change scenarios and rural to urban land development guidelines need to be established for GHG emission mitigation. Three main factors need to be considered to target N₂O losses from soils N losses from soils via NO₂ and N_2O during land use change associated with urbanization: (i) previous land use, (ii) duration of development process, and (iii) new land use purpose that it is being changed into, i.e. public or private. Their dry sclerophyll forest in this study supports the general hypothesis that forest soils are low N₂O emitters, contrary to expectation that the humid subtropical summer conditions would increase emissions compared to temperate forest soils. The accumulation of NO₃ in fallow soil increases the potential for N₂O emissions and may amplify considering future predictions of rising temperatures and more frequent heavy rain events worldwide. Increased fertilizer application may be required to compensate for these N losses after land use change to keep land uses, such as turf grass, highly productive while altering N cycling in peri-urban environments. The outcomes of this study highlight the substantial NO₃ accumulation in soils during land use change which consequently increases N₂O emissions and should be accounted for in global climate forecasts as urbanization processes are predicted to increase worldwide with increasing population growth. In the fallow soil the increased N losses via NO₂ leaching and specifically N₂O emissions may be amplified considering future predictions of rising temperatures and more frequent heavy rain events worldwide. Increased fertilizer application may be required to compensate for these N losses after land use change to keep peri urban land such as turf grass highly productive, which subsequently increases GHG emissions. Once established, however, turf grass lawn might offset N losses with potential C sequestration through higher plant productivity. The outcomes of this study emphasize the potential to mitigate N₂O and NO₃ losses through altered management during urbanization processes and turf grass establishment.

25 6 Acknowledgements

This study was undertaken at the Samford Ecological Research Facility (SERF) one of the Supersites in the Terrestrial Ecosystem Research Network (TERN). The study was supported by the Institute for Future Environments (IFE) of the Queensland University of Technology (QUT). The data set "Greenhouse gas emissions from peri-urban land use at SERF, SEQ. 2013-2015" can be found online at the N₂O network under http://www.N2O.net.au/knb/metacat/vandelden.3.3/html.

References

5

10

- AGO. "National Inventory Report 2008": National Greenhouse Account, Australian Greenhouse Office, Commonwealth of Australia, Canberra. 2010.
- Baldock, J. A., I. Wheeler, N. McKenzie and A. McBrateny. "Soils and climate change: potential impacts on carbon stocks and greenhouse gas emissions, and future research for Australian agriculture." Crop & Pasture Science 63 (3): 269-283. <Go to ISI>://WOS:000304489700009. doi: 10.1071/cp11170. 2012.
- Barton, L, GGY Wan and TD Colmer. "Turfgrass (Cynodon dactylon L.) sod production on sandy soils: II. Effects of irrigation and fertiliser regimes on N leaching." Plant and soil 284 (1-2): 147-164. 2006.
- Betts, Richard. "Implications of land ecosystem-atmosphere interactions for strategies for climate change adaptation and mitigation." Tellus B 59 (3): 602-615. 2007.
 - BOM. Commonwealth Bureau of Meteorology, Australian Government. 2015.

ABS. edited by Australian Bureau of Statistics. Canberra. 2012.

- Butterbach-Bahl, Klaus and Ralf Kiese. "Significance of forests as sources for N2O and NO." In Tree species effects on soils: implications for global change, 173-191: Springer. 2005.
 - Carter, R. and E.G. Gregorich. Soil Sampling and Methods of Analysis, Second Edition, edited by Canadian Society of Soil Science: Taylor & Francis. 2007.
- Conant, R. T., K. Paustian, S. J. Del Grosso and W. J. Parton. "Nitrogen pools and fluxes in grassland soils sequestering carbon." Nutrient Cycling in Agroecosystems 71 (3): 239-248. <Go to ISI>://WOS:000229627500003. doi: 10.1007/s10705-004-5085-z. 2005.
- Dalal, R. C., W. J. Wang, G. P. Robertson and W. J. Parton. "Nitrous oxide emission from Australian agricultural lands and mitigation options: a review." Australian Journal of Soil Research 41 (2): 165-195. <Go to ISI>://WOS:000182064800001. doi: 10.1071/sr02064. 2003.

Fest, Benedikt J., Stephen J. Livesley, Matthias Drösler, Eva van Gorsel and Stefan K. Arndt. "Soil-atmosphere greenhouse gas exchange in a cool, temperate Eucalyptus delegatensis forest in south-eastern Australia." Agricultural and Forest Meteorology 149 (3-4): 393-406. http://www.sciencedirect.com/science/article/pii/S0168192308002517. doi: http://dx.doi.org/10.1016/j.agrformet.2008.09.007. 2009.

5

Fest, Benedikt J., Stephen J. Livesley, Joseph C. von Fischer and Stefan K. Arndt. "Repeated fuel reduction burns have little long-term impact on soil greenhouse gas exchange in a dry sclerophyll eucalypt forest." Agricultural and Forest Meteorology 201: 17-25. http://www.sciencedirect.com/science/article/pii/S0168192314002743. doi: http://dx.doi.org/10.1016/j.agrformet.2014.11.006. 2015a.

10

Golubiewski, N. E. "Urbanization increases grassland carbon pools: Effects of landscaping in Colorado's front range." Ecological Applications 16 (2): 555-571. <Go to ISI>://WOS:000237052200011. doi: 10.1890/1051-0761(2006)016[0555:uigcpe]2.0.co;2. 2006.

15

Grimm, Nancy B, David Foster, Peter Groffman, J Morgan Grove, Charles S Hopkinson, Knute J Nadelhoffer, Diane E Pataki and Debra PC Peters. "The changing landscape: ecosystem responses to urbanization and pollution across climatic and societal gradients." Frontiers in Ecology and the Environment 6 (5): 264-272, 2008.

Groffman, P. M. and R. V. Pouyat. "Methane Uptake in Urban Forests and Lawns." Environmental Science & Technology 43 (14): 5229-5235. <Go to ISI>://WOS:000268138000013. doi: 10.1021/es803720h. 2009. 20

Grover, S. P. P., S. J. Livesley, L. B. Hutley, H. Jamali, B. Fest, J. Beringer, K. Butterbach-Bahl and S. K. Arndt. "Land use change and the impact on greenhouse gas exchange in north Australian savanna soils." Biogeosciences 9 (1): 423-437. <Go to ISI>://WOS:000300229000029. doi: 10.5194/bg-9-423-2012. 2012.

25

Hart, Stephen C, John M Stark, Eric A Davidson and Mary K Firestone. "Nitrogen mineralization, immobilization, and nitrification." Methods of Soil Analysis: Part 2—Microbiological and Biochemical Properties (methodsofsoilan2): 985-1018. 1994.

30

IPCC. Chapter 8 Settlements in Guidelines for National Greenhouse Gas Inventories: Agriculture, Forestry and Other Land Use. Edited by Hector Daniel Ginzo (Argentina) Jennifer C. Jenkins (USA), Stephen M. Ogle (USA), Louis V. Verchot (ICRAF/USA), Mariko Handa (Japan), Atsushi Tsunekawa (Japan), Vol. 4. http://www.ipccnggip.iges.or.jp/public/2006gl/pdf/4 Volume4/V4 08 Ch8 Settlements.pdf. 2006.

IPCC, Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Edited by T.F. Stocker, D. Oin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., doi: 10.1017/CBO9781107415324, 2013.

Jones, S. K., R. M. Rees, U. M. Skiba and B. C. Ball. "Greenhouse gas emissions from a managed grassland." Global and

Planetary Change 47 (2-4): 201-211. <Go to ISI>://WOS:000231753100013. doi: 10.1016/j.gloplacha.2004.10.011.

5

Isbell, Raymond. The Australian soil classification. Vol. 4: CSIRO publishing: Collingwood. 2002.

10

Kaye, J. P., I. C. Burke, A. R. Mosier and J. P. Guerschman. "Methane and nitrous oxide fluxes from urban soils to the atmosphere." Ecological Applications 14 (4): 975-981. <Go to ISI>://WOS:000223156600002. doi: 10.1890/03-5115. 2004.

2005.

15

Kaye, Jason P, Peter M Groffman, Nancy B Grimm, Lawrence A Baker and Richard V Pouvat. "A distinct urban biogeochemistry?" Trends in Ecology & Evolution 21 (4): 192-199. 2006.

20

Knowles, T. A. and B. Singh. "Carbon storage in cotton soils of northern New South Wales." Australian Journal of Soil Research 41 (5): 889-903. <Go to ISI>://WOS:000185266100006. doi: 10.1071/sr02023. 2003.

Kroeze, C., A. Mosier, C. Nevison, O. Oenema, S. Seitzinger and O. van Cleemput. Revised 1996 IPCC guidelines for national greenhouse gas inventories: Intergovernmental Panel on Climate Change. 1997.

25

Livesley, S. J., R. Kiese, P. Miehle, C. J. Weston, K. Butterbach-Bahl and S. K. Arndt, "Soil-atmosphere exchange of greenhouse gases in a Eucalyptus marginata woodland, a clover-grass pasture, and Pinus radiata and Eucalyptus globulus plantations." Global Change Biology 15 (2): 425-440. <Go to ISI>://WOS:000262510500011. doi: 10.1111/j.1365-2486.2008.01759.x. 2009.

30

Lorenz, Klaus and Rattan Lal. "Biogeochemical C and N cycles in urban soils." Environment international 35 (1): 1-8, 2009.

Milesi, C., S. W. Running, C. D. Elvidge, J. B. Dietz, B. T. Tuttle and R. R. Nemani, "Mapping and modeling the biogeochemical cycling of turf grasses in the United States." Environmental Management 36 (3): 426-438. <Go to ISI>://WOS:000231959000008. doi: 10.1007/s00267-004-0316-2. 2005.

"Community profile; Regional Council. Samford area." Moreton http://profile.id.com.au/Default.aspx?id=311&pg=101&gid=560&type=enum 2011. Mosier, Arvin, Carolien Kroeze, Cindy Nevison, Oene Oenema, Sybil Seitzinger and Oswald Van Cleemput. "Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle." Nutrient cycling in Agroecosystems 52 (2-3): 225-248. 1998. Page, K. L., R. C. Dalal and R. J. Raison. "The impact of harvesting native forests on vegetation and soil C stocks, and soil CO2, N2O and CH4 fluxes." Australian Journal of Botany 59 (7): 653-668. <Go to ISI>://WOS:000297263400006. doi: 10.1071/bt11207. 2011. Pataki, DE, T Xu, YO Luo and JR Ehleringer. "Inferring biogenic and anthropogenic carbon dioxide sources across an urban to rural gradient." Oecologia 152 (2): 307-322. 2007. Potere, David and Annemarie Schneider. "A critical look at representations of urban areas in global maps." GeoJournal 69 (1-2): 55-80. 2007. Raciti, S. M., P. M. Groffman, J. C. Jenkins, R. V. Pouyat, T. J. Fahey, S. T. A. Pickett and M. L. Cadenasso. "Accumulation of carbon and nitrogen in residential soils with different land-use histories." Ecosystems 14 (2): 287-297. <Go to ISI>://WOS:000288172300009. doi: 10.1007/s10021-010-9409-3. 2011a. Robertson, G. Philip and P. Groffman. "Nitrogen transformations." Paul EA CF, ed. Soil Microbiology, Ecology, and Biochemistry. Oxford, UK: Elsevier Academic Press: 341-364. 2007. Rowlings, D. W., P. R. Grace, R. Kiese and K. L. Weier. "Environmental factors controlling temporal and spatial variability

5

10

15

20

25

30

environment 179: 168-178. 2013.

Rowlings, DW, PR Grace, C Scheer and R Kiese. "Influence of nitrogen fertiliser application and timing on greenhouse gas

in the soil-atmosphere exchange of CO2, CH4 and N2O from an Australian subtropical rainforest." Global Change Biology 18 (2): 726-738. <Go to ISI>://WOS:000299042500027. doi: 10.1111/j.1365-2486.2011.02563.x. 2012.

emissions from a lychee (Litchi chinensis) orchard in humid subtropical Australia." Agriculture, ecosystems &

- Rowlings, DW, PR Grace, C Scheer and S Liu. "Rainfall variability drives interannual variation in N 2 O emissions from a humid, subtropical pasture." Science of The Total Environment 512: 8-18. 2015. Scheer, C., P. R. Grace, D. W. Rowlings, S. Kimber and L. Van Zwieten. "Effect of biochar amendment on the soil-5 atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia." Plant and Soil 345 (1-2): 47-58. <Go to ISI>://WOS:000292999700005. doi: 10.1007/s11104-011-0759-1.2011. Scheer, C., P. R. Grace, D. W. Rowlings and J. Payero. "Soil N2O and CO2 emissions from cotton in Australia under varying irrigation management." Nutrient Cycling in Agroecosystems 95 (1): 43-56. <Go to 10 ISI>://WOS:000314334300003. doi: 10.1007/s10705-012-9547-4. 2013. Scheer, Clemens, David W Rowlings, Mary Firrel, Peter Deuter, Stephen Morris and Peter R Grace. "Impact of nitrification inhibitor (DMPP) on soil nitrous oxide emissions from an intensive broccoli production system in sub-tropical 15 Australia." Soil Biology and Biochemistry 77: 243-251. 2014. Scheer, Clemens, Reiner Wassmann, Kirsten Kienzler, Nazar Ibragimov and Ruzimbov Eschanov. "Nitrous oxide emissions from fertilized, irrigated cotton (< i> Gossypium hirsutum</i> L.) in the Aral Sea Basin, Uzbekistan: Influence of nitrogen applications and irrigation practices." Soil Biology and Biochemistry 40 (2): 290-301. 2008. 20 Selhorst, A. L. and R. Lal. "Carbon budgeting in golf course soils of Central Ohio." Urban Ecosystems 14 (4): 771-781. <Go to ISI>://WOS:000297670700015. doi: 10.1007/s11252-011-0168-5. 2011. Tratalos, Jamie, Richard A Fuller, Philip H Warren, Richard G Davies and Kevin J Gaston. "Urban form, biodiversity 25 potential and ecosystem services." Landscape and urban planning 83 (4): 308-317. 2007. Turf Australia. "Newsletter 2012." https://www.turfaustralia.com.au/.2012. United Nations. "World urbanization prospects: The 2007 Revision", edited by Economics and Social Affairs. United 30 Nations (NY): United Nations Population Division. 2008.
 - <u>United Nations.</u> "World Population Prospects: The 2012 Revision, Highlights ans Advance Tables", edited by Economics and Social Affairs. United Nations (NY): United Nations Population Division. 2013.

- van Delden, Lona, Eloise Larsen, David Rowlings, Clemens Scheer and Peter Grace. "Establishing turf grass increases soil greenhouse gas emissions in peri-urban environments." Urban Ecosystems: 1-14. 2016a.
- Wang, Yi, Cong Tu, Chunyue Li, Lane Tredway, David Lee, Mark Snell, Xingchang Zhang and Shuijin Hu. "Turfgrass Management Duration and Intensities Influence Soil Microbial Dynamics and Carbon Sequestration." International Journal of Agriculture and Biology 16 (1): 139-145, 2014.

5

10

WRB, IUSS Working Group. World Reference Base for Soil Resources 2014, update 2015. Vol. World Soil Resources

Reports No. 106., International soil classification system for naming soils and creating legends for soil maps.: FAO,

Rome. 2015.

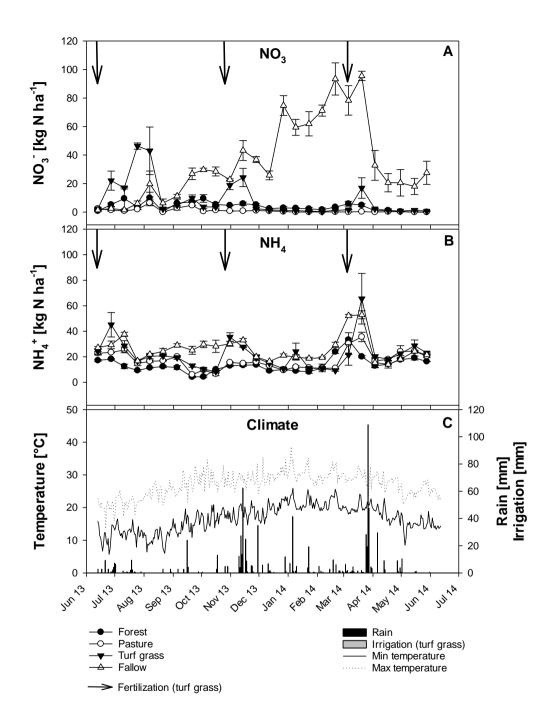


Figure 2: Annual soil $NO_3^-(A)$ and $NH_4^+(B)$ contents variations from forest, pasture, turf grass and fallow averaged across replicates (n = 3) and summed for separate analysed soil depths of 0-10 and 10-20 cm with the climatic conditions (C) for the experimental year 2013/2014 as well as fertilization and irrigation indication for the turf grass treatment.

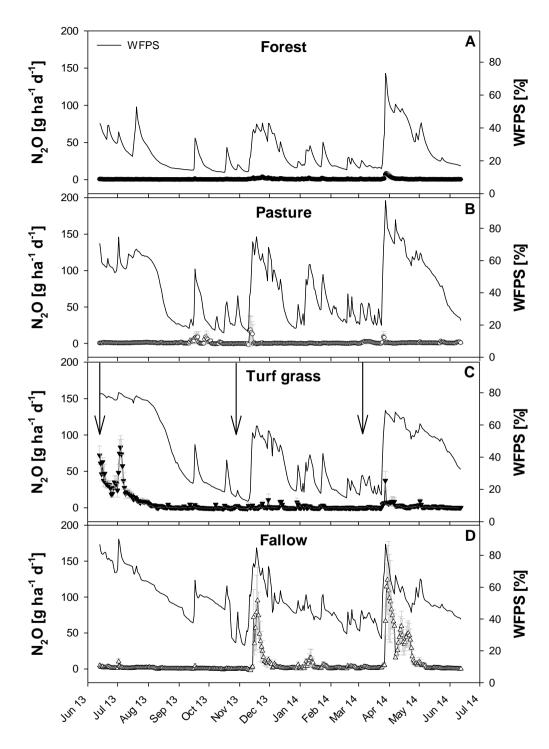


Figure 3: Daily N_2O flux averages (max 8 fluxes per day for 3 replicates each) with standard errors (n =3) over the experimental year 2013/2014 for forest (A), pasture (B), turf grass (C) and fallow (D) with the treatment specific water filled pore space (WFPS).

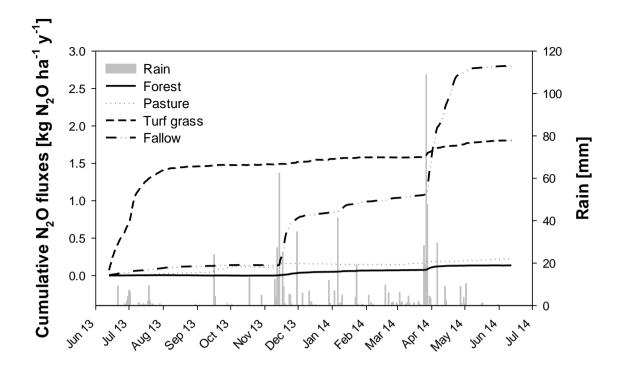


Figure 4: Cumulative daily N_2O fluxes (n = 3) for forest, pasture, turf grass and fallow with rainfall for the experimental year 2013/2014.

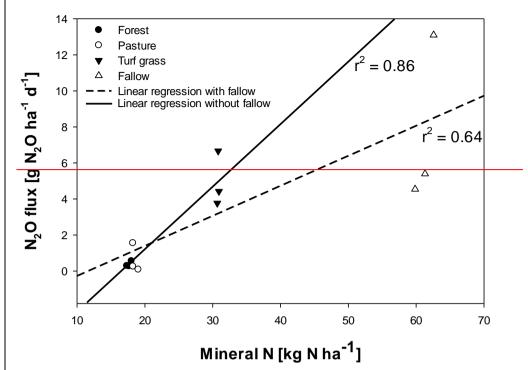


Figure 4: Linear regression and correlation coefficient r^2 for the annual averages of soil mineral N within 20 cm depth (n = 78) and N₂O fluxes (n = 1095) for each replicate of forest, pasture, and turf grass as well as with and without fallow.

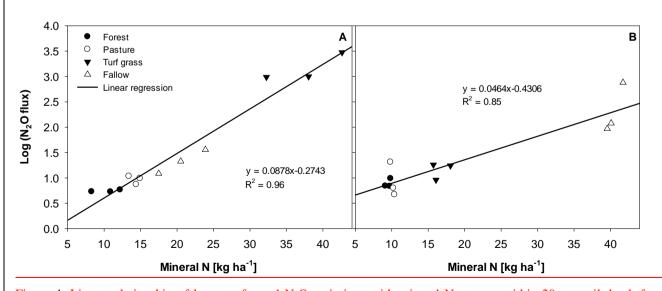


Figure 4: Linear relationship of log transformed N_2O emissions with mineral N content within 20 cm soil depth for each replicate of forest, pasture, turf grass and fallow land use during the establishment phase (A) and the rest of the year (B), with the coefficient of determination R^2 .

Table 1: SERF site characteristics

Parameters	CF site charact	cristics										
Longitude					15	152° 52' 37.3" E						
Latitude					27	27° 23' 22.211" S						
Altitude					60	60 m						
Slope					2°	2°						
Mean annual min temp.					13	13 °C*						
Mean annual max temp.				25.6 °C*								
Mean annual	rain				11	10 mm*						
Soil profile	Horizons**	Depths	Sand	Silt	Clay	BD	рН	EC	Total C	Total N		
		(cm)	(%)	(%)	(%)	(g cm ⁻³)		(μS)	(%)	(%)		
Pasture	A1	0 – 17	70	24	6	1.4	5.4	46	1.5	0.12		
	A2	17 – 45	74	18	8	1.6	6.0	10	0.9	0.07		
	B2	45 – 92	9	18	73	1.8	6.1	31	0.4	0.03		
Forest	A1	0 - 20	75	18	7	1.4	5.5	29	1.8	0.14		
	A2	20 - 47	78	15	7	1.5	5.6	30	1.1	0.08		
	B2	47 - 70	44	39	17	1.7	5.6	30	0.2	0.02		
.		11.5			11 0	(2.01						

^{*}Long term means by Commonwealth Bureau of Meteorology, Australian Government (BOM)

5 Table 2: Seasonal and cumulative rain, number of rain events and seasonal and annual averages of minimum and maximum Temperatures of the experimental year

	Sum Rain	Number of	Avg Temperature (°C)		
	(mm)	rain events*	Min	Мах	
Winter	51.2	0	11.5	22.6	
Spring	248.2	5	16.7	28.2	
Summer	137.2	3	20.7	30.2	
Autumn	303.2	3	17.6	27.5	
	739.8	11	16.7	27.1	

^{*} Rain event if sum > 10 mm per day

^{**}According to the Australian soil classification

Table 3: Annual mineral N averages as NH_4^+ -N and NO_3^- N in 0-20 cm soil depth, WFPS and daily maximum and average N_2O fluxes from all treatments with their cumulative annual fluxes over the experimental year with their standard error

	NH₄ ⁺ -N	NO ₃ -N	WFPS	Max daily flux	Avg daily flux	Annual flux
	(kg ha ⁻¹)	(kg ha ⁻¹)	(%)	(g N₂O ha ⁻¹ d ⁻¹)	(g N₂O ha ⁻¹ d ⁻¹)	(kg N₂O ha ⁻¹ y ⁻¹)
Forest	13.7 ^a ± 1.2	$3.9^{a} \pm 0.6$	23 ^a	8.1	$0.4^{a} \pm 0.1$	$0.1^a \pm 0.03$
Pasture	$17.4^{\text{b}} \pm 1.4$	$1.1^{b} \pm 0.3$	42 ^b	18.3	$0.6^{a} \pm 0.1$	$0.2^{a} \pm 0.2$
Turf grass	21.9 ^{bc} ±2.4	$8.9^{\circ} \pm 2.5$	43 ^b	83.0	$4.9^{b} \pm 0.6$	$1.8^{b} \pm 0.3$
Fallow	$26.0^{\circ} \pm 1.9$	$35.2^{d} \pm 5.6$	55 ^c	123.8	$7.7^{b} \pm 1.0$	$2.8^{b} \pm 1.0$

abcd different letters indicate significant differences between treatments based on p < 0.05

Table 4: Spearman's rho correlation coefficient between N_2O fluxes and mineral N, WFPS and temperature for each treatment

	N₂O			Mineral N		
	Mineral N	WFPS	Temperature	WFPS	Temperature	
Forest	-0.39	0.61**	0.40**	0.07	-0.17	
Pasture	0.49**	0.30**	-0.46**	0.39**	-0.41**	
Turf grass	0.47**	0.78**	-0.45**	0.47**	-0.50**	
Fallow	-0.0	0.43**	0.20**	-0.61**	0.72**	

^{**} correlation coefficient significant with p < 0.01

5