



The impact of atmospheric N deposition and N fertilizer type on soil nitric oxide and nitrous oxide fluxes from agricultural and forest Eutric Regosols

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Abstract

Agricultural and forest soils with low organic C content and high alkalinity were studied over 17 days to investigate the potential response of the atmospheric pollutant nitric oxide (NO) and the greenhouse gas nitrous oxide (N₂O) on (1) increased N deposition rates to forest soil; (2) different fertilizer types to agricultural soil and (3) a simulated rain event to forest and agricultural soils. Cumulative forest soil NO emissions (148–350 ng NO-N g⁻¹) were ~ 4 times larger than N₂O emissions (37–69 ng N₂O-N g⁻¹). Contrary, agricultural soil NO emissions (21–376 ng NO-N g⁻¹) were ~ 16 times smaller than N₂O emissions (45–8491 ng N₂O-N g⁻¹). Increasing N deposition rates 10 fold to 30 kg N ha⁻¹ yr⁻¹, doubled soil NO emissions and NO₃⁻ concentrations. As such high N deposition rates are not atypical in China, more attention should be paid on forest soil NO research. Comparing the fertilizers urea, ammonium nitrate, and urea coated with the urease inhibitor ‘Agrotain®,’ demonstrated that the inhibitor significantly reduced NO and N₂O emissions. This is an unintended, not well-known benefit, because the primary function of Agrotain® is to reduce emissions of the atmospheric pollutant ammonia. Simulating a climate change event, a large rainfall after drought, increased soil NO and N₂O emissions from both agricultural and forest soils. Such pulses of emissions can contribute significantly to annual NO and N₂O emissions, but currently do not receive adequate attention amongst the measurement and modeling communities.

Keywords Atmospheric N deposition · Ammonium nitrate · Urea · Urease inhibitor · Pulsing effect

Introduction

The industrialization of mineral N fertilizer production contributes immensely to global food security, but also shares responsibility for a series of environmental pollution issues. The N use efficiency of crops is rather poor, with a global average of 0.4% in 2010 (Zhang et al. 2015). Excess N fertilizer is largely converted through microbial and chemical reactions to environmentally damaging compounds such as nitrate (NO₃⁻), nitric oxide (NO) and nitrous oxide (N₂O). Surplus N is an acute problem in China. Between 1961 and 2012 China’s

total fertilizer N input has increased by 490% and the N surplus by more than 10 times, from 3.3 Mt in 1961 to 38 Mt in 2012 (Yuan and Peng 2017). Consequently, many natural ecosystems, especially forests in China, experience high atmospheric N deposition rates and commonly exceed critical loads of sensitive ecosystems (Liu et al. 2011). Annual wet deposition rates have increased from 13 kg N ha⁻¹ yr⁻¹ in the 1980s to 21 kg N ha⁻¹ yr⁻¹ in the 2000 (Liu et al. 2013), and forest ecosystems are changing from naturally N-limited to N-saturated systems. This can lead to negative impacts such as soil acidification and changes in the species composition of flora and fauna (Bobbink et al. 2010).

Modern agriculture strives towards maximum productivity to feed our growing population, whilst also reducing the environmental burden of N fertilizer additions. A proportion of the N fertilizer applied is inevitably lost to the atmosphere as NO, N₂O and N₂ (Zhu et al. 2013) and NH₃ (Yan et al. 2011), or leached to the waters as NO₃⁻ and dissolved organic N compounds (Shan et al. 2015). The ratio of these loss products

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and their rates depend on the amount of N fertilizer applied, soil properties and climatic conditions (Zhang et al. 2014). Agricultural ecosystems contribute to about 60% of the global anthropogenic emissions of the greenhouse gas N₂O (IPCC 2013), and can also be an important source of soil NO emissions in rural areas (Almaraz et al. 2018). N research tends to focus on N₂O, NH₃ and NO₃⁻ and especially in relation to fertilizer application, whereas the loss of NO from soils is not sufficiently researched. The reason for this is that soil is a small source of NO_x compared to the main source, fossil fuel combustion. Nitric oxide is a highly reactive air pollutant in the troposphere, and contributes to O₃ production and acid rain (Hertel et al. 2012). It has been estimated that soils in China contribute only to 4% of the total annual NO_x loss to the atmosphere (Gu et al. 2012). However, with the ongoing clean-up of NO_x combustion sources soil NO emissions are becoming increasingly more important as a source of atmospheric ozone in rural areas (Almaraz et al. 2018).

The N input from atmospheric deposition is relatively small compared to N fertilizer application rates (Chen et al. 2014; Liu et al. 2013), even in regions with very large atmospheric N deposition rates. For example, at Yanting research station in the Sichuan Basin, where we collected the soils for this study, the average annual atmospheric bulk N deposition rate for 2008–2013 was 23 kg N ha⁻¹ yr⁻¹, which amounts to less than 10% of the average N fertilizer application in this region (280 kg N ha⁻¹ yr⁻¹) (Song et al. 2017; Zhu et al. 2009). Thus, NO and N₂O emissions in agricultural soils are predominately influenced by N fertilizer application rates (Pfab et al. 2011; Yao et al. 2017). The rates of these emissions are largely determined by soil moisture, soil texture and bulk density, which control the oxygen concentrations (Davidson et al. 2000). In addition, soil pH is of importance as it influences the efficiency of nitrification and the ratio of denitrification products (N₂O and N₂). High soil moisture contents tend to favor N₂O emissions, whereas the opposite is the case for NO emissions (Skiba et al. 1992). Precipitation rate and frequency plays an important role on NO and N₂O emission rates. A large rainfall onto dry soil can trigger a pulse of NO and/or N₂O emissions, even from soils with low mineral N contents. However, effects of such events are poorly understood. They are not uncommon, and can contribute significantly to the overall annual NO and N₂O emission budget (Dick et al. 2006; Medinets et al. 2016a; Sanchez-Martin et al. 2008). The focus of this study is to provide new data of soil NO and N₂O fluxes from an alkaline Regosol, supporting two different ecosystems, a forest and agricultural field, which are adjacent to each other and experience the same climate. By conducting controlled environment laboratory studies, the impact of atmospheric N deposition, N fertilizer type, and the pulsing effect (rewetting dry soil) on NO and N₂O emissions will be addressed simultaneously. Our hypothesis is that investigating NO and N₂O emissions from low N (deposition)

and high N (fertilization) systems under stable soil moisture conditions, varying soil moisture conditions (pulsing effect) and varying N rates from a forest and agricultural ecosystems will provide insight into the relative importance of NO or N₂O emissions of the scenarios to be investigated.

Materials and methods

Site description and soil collection

Soils were collected from the Yanting Agro-ecological Experimental Station for Purple Soils (31°16' N, 105°28' E), which is part of the Chinese Ecosystem Research Network (CERN), Chinese Academy of Sciences, in the center of the Sichuan Basin. The climate is a subtropical monsoon climate, and alkaline Eutric Regosols (locally known as purple soils) occupy 300,000 km² in this region (Wang et al. 2015b). Soils were collected from an agricultural and a forest soil in February, 2016. The agricultural soil originates from a field cropped with wheat, which was sown in October 2015, and fertilized with ammonium carbonate (NH₄HCO₃) at a rate of 130 kg N ha⁻¹ yr⁻¹ by broadcast at sowing stage. The soil is of loamy texture with a sand, silt, and clay content of 27.1%, 51.6% and 22.3%, respectively. The average annual bulk N deposition rate to this agricultural area was 23 kg N ha⁻¹ yr⁻¹ in the period 2008–2013 (Song et al. 2017). Other soil properties are shown in Table 1.

The forest soil was collected from a cypress (*Cyprinus funebris*) plantation forest, and only 3 km away from the agricultural field. The forest was planted approximately 40 years ago, has never received N fertilizer and is representative of plantation forests throughout the central Sichuan Basin. The forest soil is also a purple soil, with a sand, silt, and clay content of 46.5%, 35.8% and 17.7%, respectively. Average total N deposition rates (wet and dry) to Chinese forests have been estimated at 22 kg N ha⁻¹ yr⁻¹ (Du et al. 2016). Other soil properties are shown in Table 1.

Soil was collected randomly from the top 15 cm soil layer of the wheat field and forest. The soil was air-dried in the laboratory, then passed through a 2-mm sieve, and transported by air to the UK Centre for Ecology and Hydrology, Edinburgh, Scotland, where the experiments were conducted.

Soil manipulation studies

Three incubation experiments, measuring fluxes of NO, N₂O, and KCl extractable soil NH₄⁺ and NO₃⁻ concentrations were carried out over a 17 day period.

Experiment 1 The impact of N deposition rate on forest soil was tested, with application rates equivalent to 0 kg N ha⁻¹ (control), 3 kg N ha⁻¹ (low N) and 30 kg N ha⁻¹ (high N), applied in the form of NH₄NO₃.

Table 1 Climate and soil properties of the locations of the soils collected

Ecosystem	Total annual precipitation ^a (mm)	Average annual air temperature ^a (°C)	Vegetation	Fertilizer application rate (kg N ha ⁻¹ yr ⁻¹)	Atmospheric N deposition rate ^b (kg N ha ⁻¹ yr ⁻¹)	Soil Texture	pH (H ₂ O) ^c	Soil bulk density ^d (g m ⁻³)	Soil organic C ^e (g kg ⁻¹)	Total N content ^e (g kg ⁻¹)
Forest	863	16.7	Cypress	0	15	loamy	8.3 ± 0.03	1.4 ± 0.1	21.0 ± 5.3	1.6 ± 0.2
Agricultural	826	17.3	Wheat	130	23	loamy	8.5 ± 0.05	1.6 ± 0.8	12.3 ± 0.4	0.9 ± 0.1

^aPrecipitation and temperature are 10 years (2008–2017) averages (<http://yga.cern.ac.cn/>)

^bN deposition rates are for the period 2008–2013 (Song et al. 2017)

^cValues are from this study and based on 6 replica

^dData for soil bulk density from Wang et al. (2015a)

^eData for soil organic C and total N from Wang et al. (2017)

Experiment 2 The impact of different N fertilizer types on NO and N₂O fluxes from the agricultural soil was investigated. The fertilizer application rate was equivalent to 150 kg N ha⁻¹, which is approximately 0.04 mg N g⁻¹ soil, assuming a soil depth of 0.25 m and a bulk density of 1.5 g cm⁻³. Applying the same principles to the atmospheric N deposition rates (experiment 1) converts the 3 and 30 kg N ha⁻¹ rates to 0.0008 and 0.008 mg N g⁻¹, respectively. The tested fertilizers were: ammonium nitrate (NH₄NO₃), urea, urea coated with the urease inhibitor Agrotain® DRI-MAXX (UI) and no fertilizer (control). The active ingredient of Agrotain® is N-(n-butyl)-thiophosphoric triamide (NBPT; CAS #94317–64-3) 60%, and the inactive ingredients are urea, formaldehyde polymer and pigment, 40%. It is a dry N stabilizer developed by Koch Agronomic Services (2020). A previous study found that the influence of Agrotain® on soil N concentration and N gas emission occurred within approximately two weeks after fertilizer application (Cowan et al. 2019).

Experiment 3 The impact of simulating a ‘pulsing effect’ on NO and N₂O fluxes was investigated for both the agricultural and forest soils. Dry soils were wetted with a weak solution of 0.008 mg NH₄NO₃ g⁻¹, simulating a low atmospheric N deposition event.

The experiments were carried out using clear Perspex cores (20 cm height × 5 cm diameter), which were sealed at the base, and during flux measurements, also at the top with a rubber bung. Close to the top of the cores 5-mm inlet and outlet silicon ports were fitted and equipped with three way taps; the outlet hole was 5 cm above the inlet hole (Sanchez-Martin et al. 2008). Aliquots of 180 g of soil were placed into the cores and compressed to adjust to the field bulk density, which was 1.56 g cm⁻³ for the agricultural soil and 1.42 g cm⁻³ for the forest soil. The headspace above the soil was on average 0.34 l. For the ‘N deposition to forest’ (experiment 1) and ‘fertilizer to an arable crop’ (experiment 2), a pre-incubation was necessary to avoid the interference of pulses of large NO and N₂O emissions, which are typically observed

when wetting dry soil (Dick et al. 2006). The dried soils were therefore brought to a water content of 50% WFPS (water filled pore space) for forest soil and 45% WFPS for agricultural soil, representing the saturated water capacity (Wang et al. 2015a). They were placed in an incubator at a constant temperature of 25 °C for 10 days, and were mixed daily. At the end of the pre-incubation period the soils had lost on average of 9.2 ± 1.6 ml of water from the forest soils and 8.5 ± 0.9 ml from the agricultural soils. This water was replaced with a solution of fertilizer dissolved in deionized water to exactly provide N deposition rates of 3 or 30 kg N ha⁻¹ in experiment 1 and a fertilization rate of 150 kg N ha⁻¹ soil in experiment 2. The soil moisture content was maintained throughout the experimental period by daily reweighing the cores and replacing weight loss with deionized water, after the flux measurements were made.

For experiment 3 dry forest and dry agricultural soils (180 g) were placed into cores and were wetted to field capacity with a solution of NH₄NO₃ simulating a low N deposition rate of 3 kg N ha⁻¹, and then were left to dry out naturally over the next 17 days. The cores were reweighed daily to monitor weight loss, as a proxy for changes in soil moisture. The conversion from weight loss to soil moisture throughout the 17 day study period was inferred from the gravimetric moisture content measured at the start and end of the incubation period, by drying at 105 °C for 24 h. For all three experiments, each lasting 17 days, fluxes were measured on 9 occasions, daily in the first week, and then at 2 to 3 day intervals. All treatments were replicated 3 times.

Soil mineral N concentrations were measured from separate cores, in order not to disturb the soil profile of the flux cores, described above. These cores were treated the same as the flux measurement cores, regarding N and water additions and incubation temperature. Due to limited amount of soil, aliquots of only 100 g of each soil were placed into polyethylene cups of similar dimensions to the Perspex cores used for the flux measurements, and there were 3 replications for each treatment. To avoid too much disturbance, the soil sampling

frequency was reduced to 5 occasions in experiment 1 and 3, and to 4 occasions in experiment 2. The soil moisture content was maintained throughout the experimental period by daily reweighing the cores and replacing weight loss with deionized water, after the flux measurements were made.

All three experiments were carried out at 25 °C, which is the average air temperature of the Yanting area for the months of June to September. On the first day the applications of the N and control treatments were staggered in time, in order to observe the immediate response (approximately 0.5 h after application) in NO, N₂O fluxes. On all subsequent measurement days, samples for N₂O analysis were collected within 1 h from all treatments and before starting with the NO flux measurements, which took between 20 and 30 min for each core. Cores were weighed, and adjusted for water loss (experiment 1 & 2) at the end of the day. The soil samples for NH₄⁺, NO₃ analysis were always collected after adjusting the soil moisture content.

NO and N₂O fluxes measurements

NO fluxes were measured from the soil cores using a gas flow-through system, as described in detail by Dick et al. (2006). Ambient air, filtered through charcoal and aluminum/KMnO₄ to remove O₃ and NO_x, was passed over the headspace of the core into the chemiluminescence analyzer (flow rate 40 ml min⁻¹) to measure NO by using a chemiluminescent analyzer (42C NO-NO₂-NO_x, Thermo Environmental Instruments Inc., Franklin, MA, USA) and O₃ using a UV photometric O₃ analyzer (49C Thermo Environmental Instruments Inc., Franklin, MA, USA). As the NO_x and O₃ analyzer each require a flow rate of 1 l min⁻¹, additional filtered air was supplied. The NO_x and O₃ analyzers were calibrated against a zero air standard before starting this study. Ozone concentrations were only measured to ensure that concentrations were sufficiently low (on average 2.2 ppb) to avoid reactions with NO_x. The flow rates through the core and into the analyzer were monitored using mass flow meters (Aera FC 7700C; Advanced Energy Industries Inc., Fort Collins, CO, USA). NO and O₃ concentrations, air temperature and flow rates were recorded at 10s intervals using a 21x data logger (Campbell Scientific, Shropshire, UK). Typically, measurements from each core lasted approximately 30 min and until the NO concentration recorded was steady. These measurements were interspersed with NO concentration measurements from empty control cores, in order to take into account reactions with chamber walls and lids. The NO flux (ng N g⁻¹ h⁻¹) was calculated as the product of the flow rate of the air stream through the repacked soil core, the increase in NO concentration above the control (empty core) and the dilution rate, by supplying additional air to the analyzer, divided by the soil dry weight (180 g).

N₂O fluxes were always measured within 4 h after measuring the NO fluxes. The cores were sealed with a rubber bung for a period of 20 min, and air samples were extracted from the headspace at time 0, 10 and 20 min, using 10 ml syringes fitted with a luer lock. The extracted gas samples were stored in syringes until analysis of N₂O concentrations within 5 h. Previous tests using standard N₂O concentrations showed that over this time N₂O concentrations remained stable (Drewer, pers. com.). N₂O concentrations were analyzed by gas chromatography using an Agilent Technology 7890B GC system, fitted with an electron capture detector (ECD) (Drewer et al. 2020). The N₂O flux was calculated as the product of the increase in N₂O concentrations above ambient laboratory air and volume of the headspace in the repacked soil core, divided by the time the core was sealed and the soil dry weight in the core.

Soil nutrient analysis

The soil organic matter content was measured using the standard method of loss on ignition (Rowell 1994). To determine soil exchangeable NH₄⁺ and NO₃⁻ content, 15 g of soil were extracted with 50 ml of 1 M KCl solution for 1 h at 100 rpm on an orbital shaker (Stuart Orbital Shaker SSL1 Barloworld Scientific Ltd.). The extract was filtered through Whatman No 42 filter paper and frozen until analysis. Concentrations of exchangeable NH₄⁺ and NO₃⁻ were analyzed by colorimetric methods (Harwood and Huyser 1970; Henriksen and Selmer-Olsen 1970) using the SEAL AQ2 discrete analyzer. Moisture contents were calculated from the weight difference between the wet and oven dried soils.

Statistical analysis

Statistical analyses including multiple comparison were performed using the SPSS software package, version 14.0 (SPSS Inc., Chicago, IL). Pearson correlations, linear regression analyses and significance were evaluated using a significance level (p) of 0.05. Cumulative flux data were interpolated using LOESS smoothing in R. Daily interpolated values were calculated, even when there were no flux measurements and then summed to obtain the cumulative fluxes (Table 2).

Results

The impact of low and high atmospheric N deposition rates on N fluxes and soil mineral N concentrations in forest soil

NO and N₂O fluxes Nitric oxide emissions from the high N treatment were significantly (p<0.01) higher than for the other two treatments during the first 5 days, and emissions peaked

Table 2 Summary of soil NO and N₂O fluxes and KCl exchangeable NH₄⁺-N and NO₃⁻-N content. *Experiment 1*: N application rates are equivalent to an atmospheric N deposition rate of 3 kg N ha⁻¹ (Low N) and 30 kg N ha⁻¹ (High N). *Experiment 2*: N fertilizer applications are

equivalent to 150 kg N ha⁻¹. Nitrogen was not applied to the controls in experiments 1 & 2. *Experiment 3*: The pulsing experiment received a low rate of N (3 kg N ha⁻¹) applied to dry soil

Treatments	NO Average flux ng N g ⁻¹ h ⁻¹	N ₂ O Average flux ng N g ⁻¹ h ⁻¹	NO Cumulative emission ng N g ⁻¹	N ₂ O Cumulative emission ng N g ⁻¹	NH ₄ ⁺ -N Average concentrations μg N g ⁻¹	NO ₃ ⁻ -N Average concentrations μg N g ⁻¹
<i>Experiment 1: Atmospheric N deposition to forest soil</i>						
Control	0.5 ± 0.4 ^a (0.1–1.4)	0.1 ± 0.0 ^a (0.0–0.2)	148.2 ± 8.9 ^a (140.9–158.1)	36.7 ± 2.4 ^a (34.0–38.8)	1.1 ± 1.4 ^a (0.0–6.0)	19.6 ± 6.23 ^a (10.4–32.5)
Low N	0.6 ± 0.5 ^a (0.1–1.5)	0.2 ± 0.1 ^b (0.0–0.4)	188.2 ± 27.3 ^a (164.5–218.0)	63.8 ± 27.0 ^b (42.2–94.1)	2.0 ± 1.8 ^a (0.0–6.7)	22.8 ± 7.0 ^a (8.3–34.9)
High N	1.2 ± 0.9 ^b (0.1–2.7)	0.2 ± 0.2 ^b (0.0–0.8)	349.6 ± 59.3 ^b (287.7–406.0)	69.3 ± 31.9 ^b (62.0–104.2)	1.4 ± 1.5 ^a (0.0–5.2)	54.8 ± 21.8 ^b (22.7–105.0)
<i>Experiment 2: Nitrogen fertilizer application to agricultural soil</i>						
Control	0.1 ± 0.1 ^a (0.0–0.6)	0.1 ± 0.1 ^a (0.0–0.3)	20.9 ± 8.0 ^a (13.9–29.6)	44.6 ± 11.1 ^a (31.9–52.6)	0.3 ± 0.4 ^a (0.0–1.5)	18.3 ± 4.9 ^a (11.4–25.6)
NH ₄ NO ₃	0.9 ± 1.0 ^c (0.0–2.8)	15.6 ± 12.8 ^c (0.1–35.4)	227.2 ± 48.7 ^c (197.4–283.5)	4938.0 ± 1118.4 ^c (4196.8–6224.4)	0.7 ± 0.6 ^a (0.0–2.1)	254.4 ± 106.7 ^b (92.4–430.7)
Urea	1.3 ± 1.4 ^c (0.0–3.9)	22.2 ± 20.9 ^c (0.0–70.2)	375.6 ± 18.8 ^c (362.3–397.1)	8490.9 ± 4953.0 ^c (4646.0–14,080.1)	0.7 ± 0.5 ^a (0.1–1.5)	214.3 ± 84.3 ^b (104.6–329.6)
Urea + Agrotain	0.5 ± 0.2 ^b (0.0–1.0)	6.2 ± 5.5 ^b (0.0–17.9)	158.1 ± 11.9 ^b (145.5–169.2)	2513.5 ± 2028.8 ^b (1435.4–4853.7)	0.6 ± 0.6 ^a (0.0–2.0)	258.0 ± 79.8 ^b (119.5–384.9)
<i>Experiment 3: Impact of the pulsing effect on emissions from forest and agricultural soils</i>						
Agricultural soil	0.4 ± 0.5 ^a (0.0–1.7)	0.5 ± 1.0 ^a (0.0–3.6)	111.9 ± 17.6 ^a (92.0–125.3)	97.0 ± 15.5 ^a (81.7–112.7)	0.3 ± 0.4 ^a (0.0–1.1)	16.0 ± 6.6 ^a (8.4–27.7)
Forest soil	0.7 ± 0.5 ^b (0.2–2.1)	0.1 ± 0.1 ^a (0.0–0.3)	308.3 ± 51.2 ^b (249.2–339.9)	31.6 ± 7.8 ^a (24.4–40.0)	7.0 ± 7.7 ^b (0.5–20.4)	15.2 ± 5.5 ^a (4.9–24.8)

Data shown are average/cumulative ± standard deviation (n = 4) of fluxes / concentrations over the 17 days incubation periods, with minimum and maximum values shown in brackets

Different letters across the columns for each experiment indicate a significant difference between treatments at P < 0.05

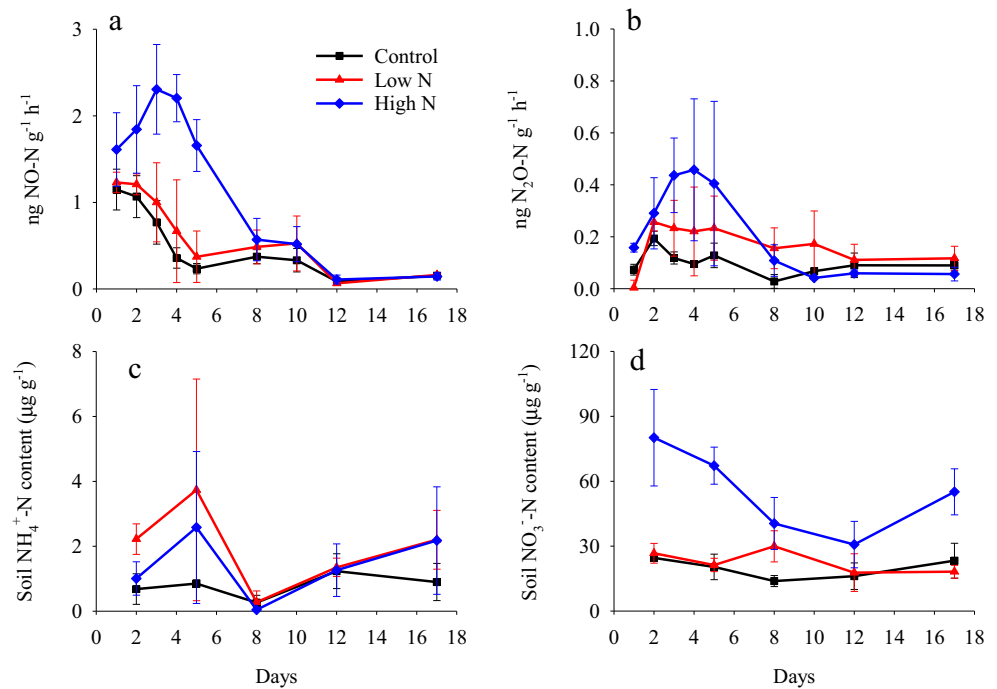
on day 3 followed by a significant (p < 0.01) decrease of about 75% by day 8 (Fig. 1a). Thereafter fluxes were not significantly different from the control and low N treatments. Generally, NO emissions from the control and low N treatments were not significantly different from each other and followed similar emission trends throughout the 17 day measurement period (Table 2, Fig. 1a). For both, NO emissions peaked immediately after N addition, and then declined to significantly (p < 0.01) smaller emissions on day 4 (control) and day 5 (low N). Overall average NO fluxes were 0.5 ± 0.4, 0.6 ± 0.5 and 1.2 ± 0.9 ng NO-N g⁻¹ h⁻¹ for the zero N control, the low N deposition and high N deposition treatments, respectively; and cumulative emissions ranged from 148 to 350 ng N g⁻¹ (Table 2).

Control core N₂O emissions did not change significantly during the 17 day study period, and average emission rates of 0.10 ± 0.03 ng N₂O-N g⁻¹ h⁻¹ were significantly lower (p < 0.05) than for the low and high N deposition rates (0.2 ±

0.2 ng N₂O g⁻¹ h⁻¹) (Table 2). For the low N treatment a significant 26-fold increase in N₂O emissions was observed on day 2, which then remained at a relatively stable value of about 0.2 ± 0.1 ng N₂O-N g⁻¹ h⁻¹. For the high N treatment, a significant 2-fold increase (p < 0.01) in N₂O emission occurred between day 1 and 2 and continued to increase until day 5. Thereafter N₂O declined to the rates of the control and low N treatment, with no significant differences between them (Fig. 1b). Cumulative soil N₂O emissions ranged from 37 to 69 ng N g⁻¹ (Table 2).

Soil mineral N concentrations Forest soil exchangeable NH₄⁺ concentrations remained low during the incubation period. Average concentrations ranged from 1.1 to 2.0 μg NH₄⁺-N g⁻¹, and there were no significant differences between treatments or with time (Fig. 2c). Contrary soil NO₃⁻ concentrations were one order of magnitude higher than exchangeable NH₄⁺ concentrations (p < 0.01). NO₃⁻ contents in the low N

Fig. 1 The impact of atmospheric N deposition to forest soil on fluxes of NO (a), N₂O (b), soil concentrations of exchangeable NH₄⁺ (c) and NO₃⁻ (d) during the 17 days incubation period. Nitrogen application rates were equivalent to atmospheric N deposition rates of 30 kg N ha⁻¹ (High N), 3 kg N ha⁻¹ (Low N) and a zero N Control (Experiment 1). Error bars are the standard deviation for each treatment (n = 4)

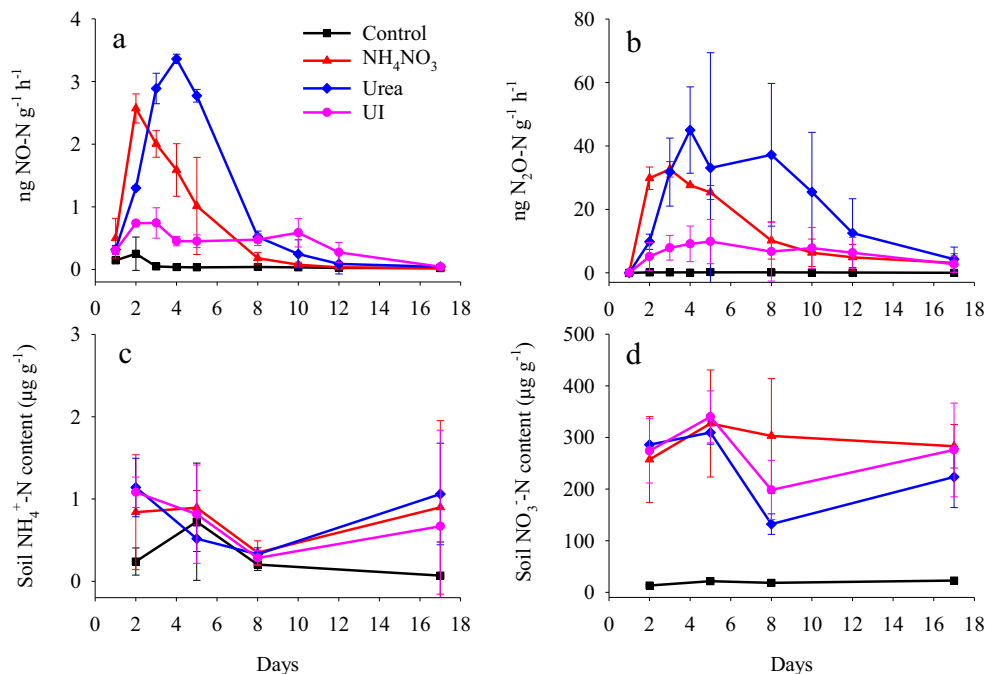


treatment and control cores were not significantly different from each other, and did not change significantly with time. Average concentrations were 19.6 and 22.8 μg NO₃⁻-N g⁻¹. For the high N deposition rate soil NO₃⁻ concentrations were about 2.5 times larger than the control, 2 days after N application. They decreased with time until day 12, and then rose again on the last measurement day 17 (Fig. 2d). Apart from day 12, NO₃⁻ concentrations were significantly (p<0.01) larger than the control and low N treatment.

The effect of different N fertilizer types on soil N fluxes and soil mineral N concentrations in agricultural soil

NO and N₂O fluxes Soil NO emissions were significantly (p<0.01) higher from the N fertilized cores compared to the zero N control. Average fluxes measured during the 17 day period were 0.1 ± 0.1, 0.9 ± 1.0, 1.3 ± 1.4, and 0.5 ± 0.2 ng NO-N g⁻¹ h⁻¹ for the control, NH₄NO₃, urea, and UI,

Fig. 2 The impact of N fertilizer type on fluxes of NO (a) and N₂O (b), and soil concentrations of exchangeable NH₄⁺ (c) and NO₃⁻ (d) during the 17 days incubation period. Fertilizer types were a zero N control, NH₄NO₃, urea and urea with the urease inhibitor Agrotain® (UI) (Experiment 2). The fertilization rate was equivalent to 150 kg N ha⁻¹. Error bars are the standard deviation for each treatment (n = 4)



respectively, with cumulative NO fluxes ranging from 21 to 376 ng N g⁻¹ (Table 2). Overall, there was no significant difference between NH₄NO₃ and urea applications ($p > 0.05$), and both were significantly ($p < 0.01$) higher than the UI treatment. For all N treatments significant increases ($p < 0.01$) in NO emissions were measured by day 2. For NH₄NO₃, NO emissions peaked on day 2 (2.6 ± 0.2 ng NO-N g⁻¹ h⁻¹), at rates about ten times higher than NO emissions from the control, and thereafter declined significantly ($p < 0.01$) to zero by day 8 and not significantly different from the control. For the urea application, NO emissions plateaued at 3.0 ± 0.7 ng NO-N g⁻¹ h⁻¹ from the 3rd to the 5th day. For UI, peak NO emissions occurred the day after fertilizer application (0.7 ± 0.0 ng NO-N g⁻¹ h⁻¹) and were about 70% lower than the peak NO emissions for NH₄NO₃ and urea. A significant decreasing trend occurred from the 4th day onwards (Fig. 2a).

Soil N₂O emissions followed a very similar pattern to NO emissions. N₂O fluxes from the zero N control were significantly smaller ($p < 0.01$) than for the N fertilizer treatments, and average fluxes were 0.1 ± 0.1 , 15.6 ± 12.8 , 22.2 ± 20.9 , and 6.2 ± 5.5 ng N₂O-N g⁻¹ h⁻¹ for the control, NH₄NO₃, urea and UI, respectively, and cumulative N₂O emissions ranged from 45 to 8492 ng N g⁻¹ (Table 2). Differences were not significant ($p > 0.05$) between NH₄NO₃ and urea, but both were significantly ($p < 0.01$) larger than UI. The response of increased N₂O fluxes after NH₄NO₃ application was faster than for the urea application, as also observed for soil NO emissions. By the second day, NH₄NO₃ induced N₂O emissions had increased significantly ($p < 0.01$) from 0.1 ng N₂O-N g⁻¹ h⁻¹ to 29.9 ng N₂O-N g⁻¹ h⁻¹, and further significantly ($p < 0.01$) increased to a peak emission of 32.7 ng N₂O-N g⁻¹ h⁻¹ on the 3rd day. Thereafter emissions declined steadily, and were not significantly different from the control by day 8 ($p > 0.05$). For urea, a significant increase was observed on the 3rd day and peak emissions (45.0 ng N₂O-N g⁻¹ h⁻¹) were achieved on the 4th day after urea application, and remained high until day 8. Thereafter emissions declined significantly ($p < 0.01$), and were statistically the same as the control on the 12th and 17th day ($p > 0.05$). For UI, a small significant ($p < 0.01$) increase of N₂O emission was observed from 0.0 ng N₂O-N g⁻¹ h⁻¹ (day 1) to 9.9 ng N₂O-N g⁻¹ h⁻¹ (day 5) and then returned to same rates as for the control plots (Fig. 2b).

Soil mineral N concentrations Average soil exchangeable NH₄⁺ concentrations ranged from 0.3–0.7 μg g⁻¹ during the incubation period, and did not show significant differences between treatments and with time, except that the exchangeable NH₄⁺ concentration in the urea treatment was significantly ($p < 0.01$) higher than the control on the 2nd day after fertilizer application (Table 2, Fig. 2c). Soil NO₃⁻ concentrations from fertilized cores were more than 2 orders of magnitude higher than soil exchangeable NH₄⁺ concentrations and for the control soil NO₃⁻ concentrations were around 10 fold

higher than soil exchangeable NH₄⁺ concentrations. Average NO₃⁻ concentrations in the control cores were about 18.3 ± 4.9 μg NO₃⁻-N g⁻¹, whereas N fertilizer application had increased NO₃⁻ concentrations to 254.4 ± 106.6 , 214.3 ± 84.3 , 258.0 ± 79.8 μg NO₃⁻-N g⁻¹ for the NH₄NO₃, urea and urea with Agrotain® treatment, respectively. However, there were no statistical significant differences with time and fertilizer type ($p > 0.05$) (Fig. 2d).

The impact of the pulsing effect on N fluxes and soil mineral N concentrations from forest and agricultural soils

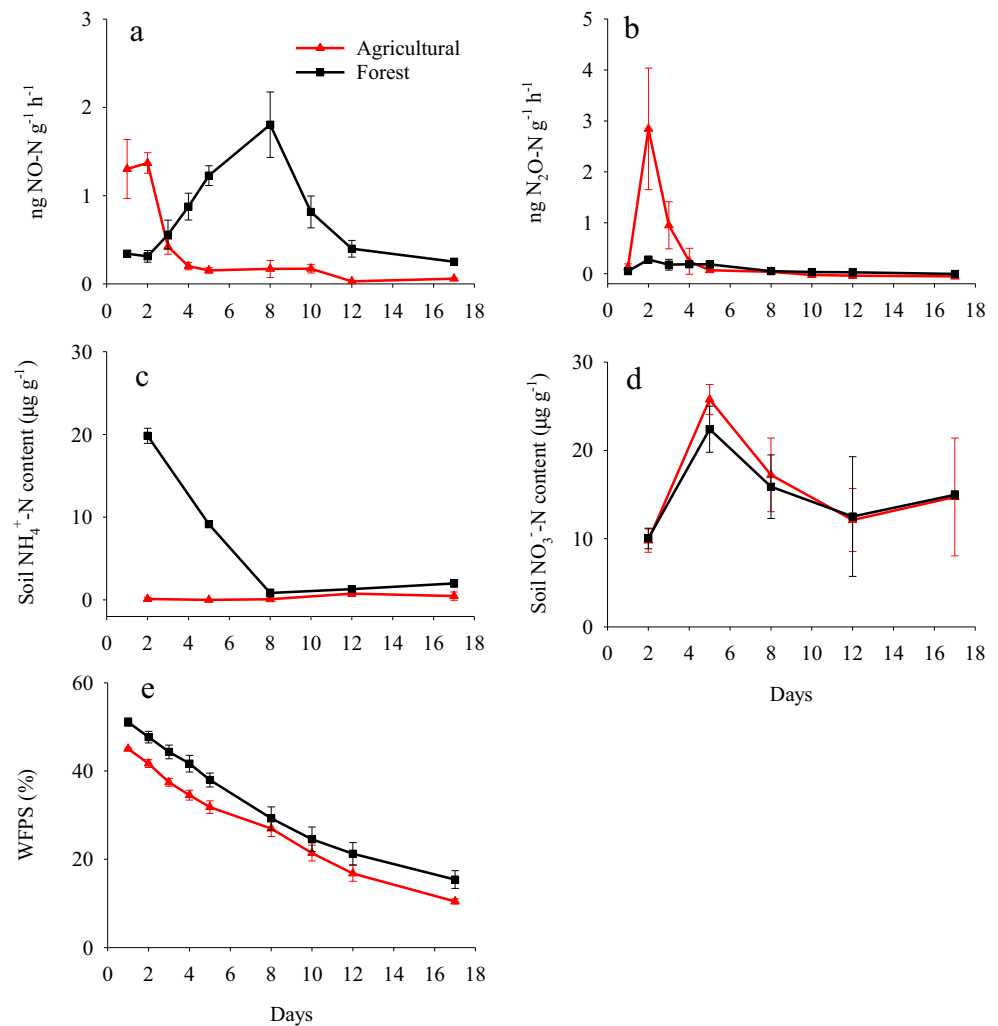
NO and N₂O fluxes At the start of the experiment, the WFPS was adjusted to the saturated soil moisture content in the forest (50%) and in the agricultural field (45%). During the incubation period, the WFPS decreased at a relatively constant rate in both soils. Differences between the soil moisture of the forest and agricultural soil were maintained throughout the study. At the end of the incubation period, the WFPS of the forest and agricultural soil had decreased to 15% and 10%, respectively (Fig. 3e).

The response of NO flux to the pulsing effect was faster in the agricultural soil compared to the forest soil. In the forest soil, NO emissions increased significantly ($p < 0.01$) until the 3rd day of incubation, and further increased significantly to the peak NO emission of 1.8 ng NO-N g⁻¹ h⁻¹ on the 8th day of incubation, after which emissions decreased. For the agricultural soil, NO emissions increased immediately after water addition on the first day, and increased significantly ($p < 0.01$) to peak NO emissions (1.37 ng NO-N g⁻¹ h⁻¹) on the second day of incubation. Significant decreasing trends were observed from the 3rd day onwards (Fig. 3a).

The pulsing effect significantly stimulated N₂O emissions for both, the forest and agricultural soil, and followed a similar trend. N₂O emissions peaked on day two, and was significantly ($p < 0.01$) higher for the agricultural soil compared to the forest soil (2.84 ng N₂O-N g⁻¹ h⁻¹ for agricultural, and 0.28 ng N₂O-N g⁻¹ h⁻¹ for the forest). Thereafter N₂O emissions from the forest and agricultural sites significantly decreased, and on the 5th (agricultural soil) and 8th (forest soil) day N₂O emissions had returned to those on day 1 (Fig. 3b). Cumulative soil NO and N₂O emissions from the agricultural (112 ng NO-N g⁻¹, 97 ng N₂O-N g⁻¹) and forest (308 ng NO-N g⁻¹, 32 ng N₂O-N g⁻¹) soils were within the range of fluxes measured in experiment 1.

Soil mineral N concentrations Forest soil exchangeable NH₄⁺ concentrations were much higher during the first 8 days compared to the agricultural soil and significantly decreased thereafter ($p < 0.01$). In contrast, exchangeable NH₄⁺ concentrations of the agricultural soil increased significantly ($p < 0.01$) in the second week only (Fig. 3c). Soil NO₃⁻ concentrations first

Fig. 3 The impact of the pulsing effect on soil NO fluxes (a), N₂O fluxes (b), exchangeable NH₄⁺ (c) and NO₃⁻ concentrations (d) and WFPS (e) from forest and agricultural soil (Experiment 3). Error bars are the standard deviation for each treatment (n = 4)



showed a significant increasing trend, peaked on day 5 and thereafter declined in both, the forest and agricultural soils (Fig. 3d).

Discussion

The results of this paper have provided interesting observations on soil NO and N₂O emissions from an alkaline Regosol supporting a forest and agricultural system within around 500 m from each other. Both ecosystems received N as atmospheric N deposition to the forest, at a relatively low rate of 30 kg N ha⁻¹ yr⁻¹ compared to N fertilization (150 kg N ha⁻¹ yr⁻¹) to agricultural soils. This N input increases soil N availability and thereby provides substrates for nitrification; and the product of nitrification, NO₃⁻, provides substrates for denitrification (Freedman et al. 2016). Both processes can lead to the production and emission of NO and N₂O.

Drivers of soil NO and N₂O emissions

In the present study much more NO than N₂O was emitted from the forest soil in the N deposition experiment 1, whereas the opposite was the case for the agricultural soil in the N fertilization experiment 2. Over the 17-day measurement period, cumulative fluxes of NO were on average around 4 times larger than of N₂O for the forest soil (experiment 1), whereas about 16 times more N₂O than NO was emitted from the agricultural soil (experiment 2) (Table 2). Interestingly, in the pulsing experiment (experiment 3) NO emissions dominated in both the agricultural and forest soils, with 5 times more NO emissions compared to N₂O emissions. The reason for this difference to experiments 1 and 2 is related to differences in the soil moisture content. In experiment 1 and 2 the soil moisture content was kept at a constant WFPS prior to adding N, in order to avoid the pulsing effect. Contrary, the aim of experiment 3 was to study the pulsing effect, i.e. dry soils were wetted to the same WFPS as in experiments 1 and 2, but then left to dry out (Fig. 3). Thus we may infer that the

pulsing effect can contribute significantly to NO and N₂O emissions from fertilized soils, and should be accounted for in measurements and models.

Many physical and chemical properties influence NO and N₂O emission, by providing conditions that promote either nitrification or denitrification, such as soil C and P content, pH, soil texture, temperature and soil water (Mehnaz et al. 2018). Of these parameters, soil water, often expressed as WFPS, is a key driver in determining the redox potential and thereby oxygen availability (Werner et al. 2007). WFPS is a function of the soil moisture content and the soil bulk density and thereby influences the relative proportions of N₂O and NO emissions (Ludwig et al. 2001). Based on measurements from different ecosystems, Davidson (2000) created a simple model stating that soil NO emissions occur at lower soil WFPS (range 10–60%) than N₂O (range 40–80%). There are of course variations with ecosystems. For example, van Dijk and Meixner (2001) observed maximum NO emission at a WFPS of 27% for a tropical forest soil; and Schindlbacher et al. (2004) reported a maximum N₂O emission at a WFPS of 80% in the temperate boreal forest in Europe. In our pulsing experiment, NO and N₂O emissions from the agricultural soil both peaked on the second day at a soil water content of about 43% (Fig. 3). This supports the Davidson (2000) model, that probably both processes, nitrification and denitrification could be responsible for the emissions. In the pulsing experiment, NO and N₂O emissions increased exponentially with WFPS (Fig. 4 exp. 3d). Contrary, in the forest soil the relationship of WFPS with N₂O was linear but bell shaped for NO (Fig. 4 exp. 3e).

It is reassuring that our observations agree with other laboratory and field studies across the globe. For example, a meta-study by Liu et al. (2017) has shown that on average forests across the global climate zones have larger NO than N₂O emissions; and a review of fertilized agricultural soils, has shown that N₂O emissions prevail over NO emissions (Bouwman et al. 2002). Similarly, lower N₂O emission fluxes from the forest soil and higher N₂O emission fluxes from a cropland were also observed in field studies at the Yanting research station (Zhou et al. 2019).

Atmospheric N deposition to forests

Field measurements from European forests have demonstrated a strong relationship of soil NO emissions with atmospheric N deposition rates, but not for N₂O, because NO was positively correlated with the nitrification process while N₂O was correlated with soil pH and their C/N ratio (Pilegaard et al. 2006). Unlike in this European study (Pilegaard et al. 2006; Schindlbacher et al. 2004) we observed a significant correlation of soil NO and N₂O emissions with each other (Fig. 4 exp. 1a), but only soil NO emissions significantly increased under simulated high N deposition rates (30 kg N ha⁻¹)

(Fig. 1). Atmospheric N deposition has increased substantially in southwest China. For example, over a 6 year period (2008–2013) the bulk wet deposition of N had increased from 17 kg N ha⁻¹ yr⁻¹ to 25 kg N ha⁻¹ yr⁻¹ in the Sichuan province, where our soils originate from (Song et al. 2017). The higher N deposition rate may alleviate short-term nutritional constraints in N limited ecosystems and may increase C sequestration in the above and below ground woody biomass (Schulte-Uebbing and de Vries 2018). However, once such ecosystems reach N saturation further N additions can lead to increased N losses, such as higher NO₃⁻ leaching rates, and increased NO and N₂O emissions (Galloway et al. 2004; Peterjohn et al. 1998). In our study, simulated atmospheric N deposition to the forest soils increased soil NO₃⁻ concentrations, which significantly correlated with NO and N₂O emissions (Fig. 4, exp. 1b, c).

Atmospheric N deposition stimulates N₂O and NO production in the same manner as N fertilizer application, albeit at much lower rates. The molecule NO₃⁻ is the endpoint of the nitrification pathway, and the starting point of denitrification. It is tempting to speculate that the presence of large NO₃⁻ concentrations are an indication of N₂O production by denitrification. However, this may not be the case. The processes nitrification and denitrification occur simultaneously in different microsites within the soil (Dong et al. 2018). Sophisticated isotopic labelling studies have identified many different processes (Butterbach-Bahl et al. 2013), but without isotopic labels it is impossible to identify whether large NO₃⁻ concentration rate are indicative of soil N₂O production by nitrification or denitrification in this study.

N fertilized agricultural soils

Most agricultural soils require large amounts of N fertilizers, either in mineral or organic form, to optimize food production. Urea and NH₄NO₃ are amongst the most widely used N fertilizers worldwide, and are the main cause of N₂O, NH₃ and NO emissions. To reduce these emissions chemicals have been developed to slow down the rate of nitrification to NO₃⁻ and the hydrolysis of urea to NH₃. The delay of both processes increases the chance of fertilizer uptake by roots, and thereby reduce NO₃⁻ leaching and N₂O emissions in the case of the nitrification inhibitors. Urease inhibitors combined with urea, such as the commercially available product ‘Agrotain®’ delay the hydrolysis of urea and increase the time available for sufficient rain to fall and move surface applied urea into the soil and thereby reduce NH₃ loss. Smaller soil NH₄⁺ concentrations would lead to reduced nitrification and denitrification rates (Akiyama et al. 2010). The impact of nitrification inhibitors is well researched (Ruser and Schulz 2015), whereas we hardly know if urease inhibitors can have any influence on nitrification and denitrification rates. This laboratory study did not allow us to measure the impact of

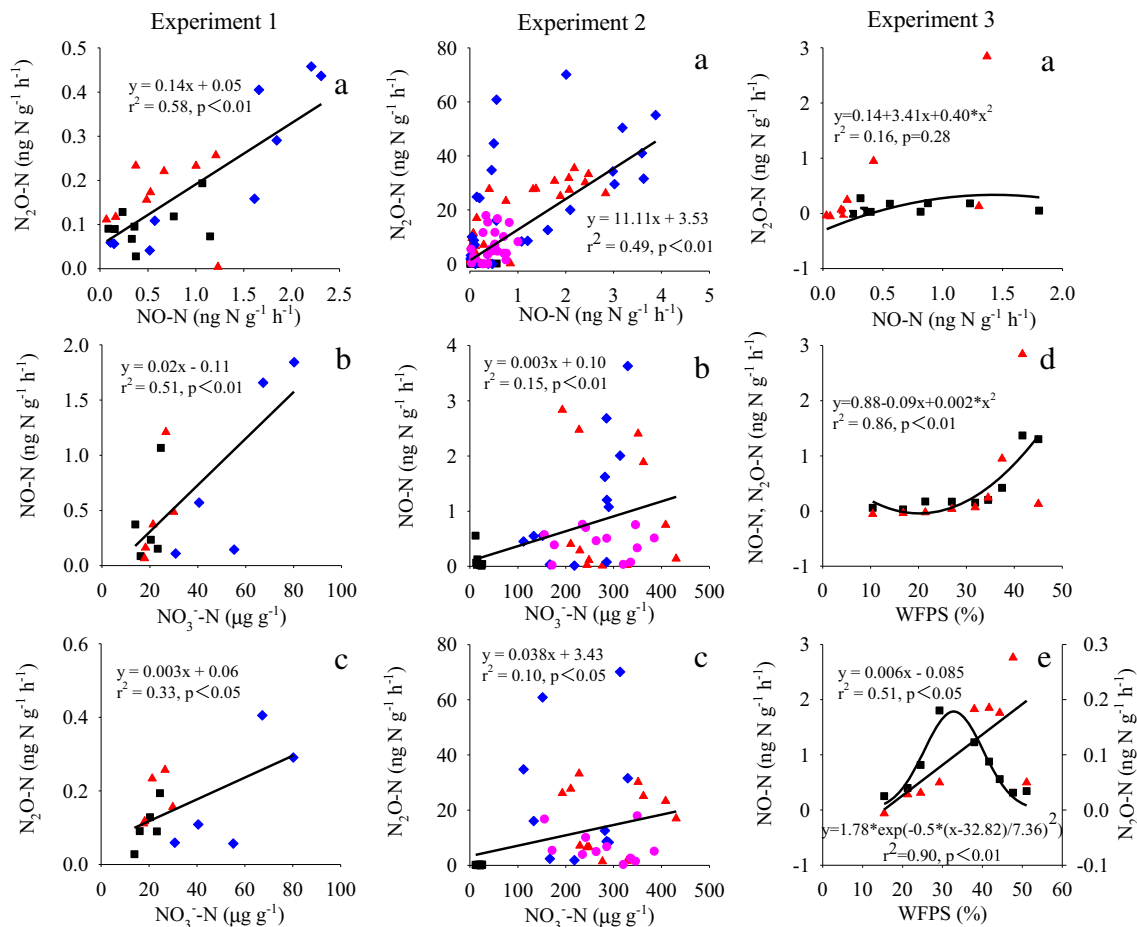


Fig. 4 Significant correlations between the fluxes and variables measured in experiment 1 (left column), experiment 2, (middle column) and experiment 3 (right column) (a) NO vs N_2O fluxes; (b) NO_3^- concentrations vs N_2O fluxes; (c) NO_3^- concentrations vs N_2O fluxes; (d & e) water filled pore space (WFPS) vs NO and N_2O fluxes for agricultural (d) and forest (e) soils. Symbols represent averages of 3 replicate soil cores for

each measurement date. Experiment 1: control (black squares), low N deposition rate (red triangles), high N deposition rate (blue diamonds). Experiment 2: control (black squares), NH_4NO_3 (red triangles), urea (blue diamonds), urea with Agrotain® inhibitor, pink circles). Experiment 3: agricultural soils (red triangles) and forest soils (black squares) in a, and NO (black squares) and N_2O (red triangles) in d and e

fertilizer type on NH_3 losses as the small soil cores used were unsuitable for such measurements; besides the focus of this laboratory study lies on the impact of fertilizer type on NO and N_2O emissions. However, it is very interesting to observe that Agrotain® decreased NO and N_2O emissions significantly, compared to the NH_4NO_3 and urea fertilizers. There were no significant differences between the NH_4NO_3 and urea treatments for both, NO and N_2O emissions. This suggests that adding Agrotain® to urea may have some beneficial effect reducing emissions of N_2O and NO. Similarly, Cowan et al. (2019) and Smith et al. (2012) found that the use of a urease inhibitor in the field can provide some mitigation of N_2O emission both in UK crop and grasslands, and Kuang et al. (2019) reported reduced N_2O emissions from a laboratory study using a sandy loam from North West China. This was also concluded in a global meta-analysis evaluating a range of enhanced-efficiency fertilizers, including fertilizers with urease inhibitors (Akiyama et al. 2010). The conventional

method to reduce soil NO and N_2O emissions is adding nitrification inhibitors or controlled-release N fertilizers, which can achieve substantial emission reductions (Liu et al. 2017).

In contrast to the forest soils, agricultural N_2O emissions were significantly higher than NO emissions for all three fertilizer treatments (Fig. 2a, b). The occurrence of such high N_2O emission in the alkaline agricultural soil could be explained by: 1) excessive N inputs creating an N surplus status which provides more N substrates for microbial N_2O production (McSwiney and Robertson 2005); 2) the high NO_3^- content inhibited the reduction of N_2O to N_2 , because of the decreased N_2O reductase activity (Senbayram et al. 2012, Kuang et al. 2019). Nitric oxide and N_2O fluxes correlated significantly with each other (Fig. 4 exp. 2a), and both correlated significantly with the soil NO_3^- content (Fig. 4 exp. 2b, c), as was also the case for the forest soils. This does not necessarily imply that both gases are products of denitrification. Nitrate concentrations may equally represent the product

formation during nitrification as well as the substrate reduction in denitrification, depending on the redox potential of individual soil microsites. A recent field study at Yanting Research Station, investigated soil N_2O emissions within 3 weeks after application of an organic fertilizer together with analysis of functional genes related to nitrification and denitrification processes, and concluded that denitrification was the main source of N_2O (Dong et al. 2018).

The pulsing effect

In experiment 1 (forest) and 2 (agriculture), the 10 day pre-incubation period prior flux measurements was designed to avoid the pulsing effect, in order not to interfere with the comparison of N fertilizer types or N deposition rates. The ‘Birch’ effect (Birch 1964) - the surge in microbial activity after dormancy, triggered by a rain event after prolonged periods of drought or temperature rise defrosting soil in cool continental climate regions - leads to pulses of gaseous emissions, such as CO_2 , N_2O and NO. The timing and rate of these emission pulses is highly unpredictable, but can be an important contribution to the overall annual flux, especially in regions that experience seasonal freeze/thaw or wet/dry cycles (Dick et al. 2001; Medinets et al. 2016b). The water addition at the start of the pre-incubation period, and prior to the start of the measurements, would have stimulated nitrification and denitrification processes and accompanying N_2O and NO emissions in a similar manner to those observed for the pulsing effect (experiment 3) (Wei et al. 2017). When the actual experiments were conducted, the microbial community would have been sufficiently large to rapidly nitrify the added N, resulting in the large NO_3^- concentrations observed in the N fertilized agricultural soils, but not in the zero N control (Fig. 2d). The same was observed in experiment 1 for the higher rate of atmospheric N deposition applied to the Cypress forest soils (Fig. 1d), albeit NO_3^- accumulation was at a much lower rate compared to the agricultural soil (Fig. 2d). In contrast, in the pulsing study, where only a low rate of N, equivalent to 3 kg N ha^{-1} , was applied to dry forest and agricultural soil, NO_3^- concentrations increased within the first few days after application and then slowly declined in a very similar manner in both soils. Ammonium concentrations remained at background levels.

Previous long-term field studies, conducted at the Yanting agricultural research station also observed that NO_3^- is the dominant form of inorganic N in these purple soils (Wang et al. 2012, 2015 a,b; Zhou et al. 2012; Zhu et al. 2012). A ^{15}N incubation experiment, also using alkaline soil from Yanting station, confirmed that the soil NO_3^- dynamics in this region appear to be governed by nitrification (Wang et al. 2015b); and, as in our study, promote rapid oxidation of NH_4^+ to NO_3^- (Dong et al. 2018; Wang et al. 2015b; Zhang et al. 2016a,b). Most of added soil NH_4^+ transformed to NO_3^-

within 24 h and soil NO_3^- concentrations increased sharply within 48 h because of fast nitrification rates (Wang et al. 2015b). This is also the reason why NO_3^- concentrations in relation to exchangeable NH_4^+ concentrations are disproportionately larger already at the start of the agricultural and forests soils in experiment 1 and 2 (Figs. 1, 2, Table 2).

Microbial pathways

Soil NO/ N_2O emission ratios provide a crude indication of the prevailing nitrification/ denitrification processes, with ratios >1 suggestion that nitrification is the main source, and a ratio of <1 for denitrification (Medinets et al. 2015). This implies that forest emissions are probably driven by nitrification, whereas agricultural emissions by denitrification. Although generally, soil NO emissions are associated with nitrification processes, denitrification could, under some circumstances also be a source of soil NO. For example, Loick et al. (2016) has demonstrated in a He/ O_2 atmosphere, with ^{15}N labeled KNO_3 and glucose additions that denitrification contributed to N loss as NO, in addition to the recognized denitrification products N_2O and N_2 . Abiotic soil NO emissions are mainly associated with acid soils and are unlikely to occur at significant rates in alkaline soils (Medinets et al. 2015). Denitrification is the main pathway for N_2O , but N_2O is also a product of nitrification. The relative emission rates depend largely on the redox potential and soil N availability (Butterbach-Bahl et al. 2013).

It is not easy to identify the underlying pathways responsible for the emissions rates, without using isotopic tracers or studying the gene abundance. However, existing studies within the Sichuan basin on alkaline soil and same climate and agricultural management, could provide insight into the processes responsible for the NO and N_2O emissions in our study. For example, a recent analysis of nitrification and denitrification genes and N_2O emissions from a wheat/maize field in the Sichuan basin on alkaline soil, concluded that both nitrification and denitrification pathways, with denitrification dominating, contributed to the N_2O flux in the first few weeks after N fertilization when mineral N supply in the soil is high (Dong et al. 2018). Contrary, when soil mineral N concentration rates were low, as in our forest soils, nitrification by ammonium oxidizing archaea and bacteria (AOA, AOB) were mostly responsible for the N_2O flux. AOA and AOB are also responsible for soil NO emissions (Behrendt et al. 2017). If we assume that these findings can be translated to our experiment, then one may speculate that in the forest soil the relatively low rates of mineral N compared to the agricultural soil would promote nitrification by AOA and AOB, and possibly AOA would prevail, due to a larger SOM content (Table 1), compared to the agricultural soil. The domination of nitrification would also explain why the forest soil has larger NO emissions than N_2O emissions. The opposite would be the case for the

agricultural soil, were very large soil NO_3^- concentrations (Table 2) would favor denitrification to N_2O and N_2 production. Denitrification to N_2 was not measured in our study, but was measured from the same experimental station at Yanting using the acetylene inhibition method (Dong et al. 2014). They found that overall N_2O and N_2 emissions were of similar order of magnitude, possibly due to large NO_3^- concentrations, which slowed down the reduction of N_2O to N_2 (Dong et al. 2018).

The preference of AOA and AOB in soils with low mineral N concentrations (Dong et al. 2018) may be the reason why in experiment 3 (the pulsing experiment) soil NO emissions prevail over soil N_2O emissions in both, the agricultural and forest soils. In addition, the rapid declining WFPS would promote nitrification (Fig. 3).

In this paper we have demonstrated contrasting soil NO and N_2O fluxes in response to high and low N application rates and soil moisture contents from a forest and agricultural soil. The data highlight the importance of the pulsing effect on soil NO and N_2O emissions in both agricultural and forest soils, and presumably also of other natural ecosystems. One can speculate about the possible microbial pathways involved, however to model NO and N_2O emissions in relation to N deposition rates and soil moisture changes (including the pulsing effect), it is important to include isotopic tracers and/or genetic markers to ascribe the underlying processes.

Conclusion

The controlled environment laboratory studies have successfully demonstrated the impact of atmospheric N deposition, N fertilizer type, and the pulsing effect (rewetting dry soil) on NO and N_2O emissions from an alkaline Regosol, supporting adjacent forest and agricultural ecosystems. Contrasting NO/ N_2O emission ratios, with soil NO dominating forest emissions, and N_2O being the principal emission source in the agricultural soils, have been observed previously. However, what is interesting in this study is the prevalence of soil NO emissions in forests and of N_2O emissions in agricultural soils; and that this is happening in both, the N addition and the pulsing experiments. Overall, soil NO emission rates were not significantly different across the three experiments. Since their impact on atmospheric chemistry is large, one should study not only fertilizer induced agricultural emissions, but focus also on the forest emissions and particularly on hotspot emissions, i.e. a heavy rainfall after drought. Contrary, for N_2O , the fertilizer induced emission rates dwarf the emission pulses after rewetting. Nitric oxide and N_2O emissions increased significantly when fertilized with NH_4NO_3 and urea, but there was no difference in the flux rates between the two fertilizers. Addition of the urease inhibitor ‘Agrotain®’ effectively reduced NO and N_2O emissions,

although it’s main role would be to reduce ammonia emission. The latter was not tested in this study. This observation is interesting, and not well known. Further research is needed to understand the underlying processes of reduced soil NO and N_2O emission when the urease inhibitors ‘Agrotain®’ is applied in the presence and absence of vegetation.

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