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Dinitrogen emissions and the N_2:N_2O emission ratio of a Rendzic Leptosol as influenced by pH and forest thinning

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ABSTRACT

Reduction of nitrous oxide (N_2O) to dinitrogen (N_2) by denitrification in soils is of outstanding ecological significance since it is the prevailing natural process converting reactive nitrogen back into inert molecular dinitrogen. Furthermore, the extent to which N_2O is reduced to N_2 via denitrification is a major regulating factor affecting the magnitude of N_2O emission from soils. However, due to methodological problems in the past, extremely little information is available on N_2 emission and the N_2:N_2O emission ratio for soils of terrestrial ecosystems. In this study, we simultaneously determined N_2 and N_2O emissions from intact soil cores taken from a mountainous beech forest ecosystem. The soil cores were taken from plots with distinct differences in microclimate (warm-dry versus cool-moist) and silvicultural treatment (untreated control versus heavy thinning). Due to different microclimates, the plots showed pronounced differences in pH values (range: 6.3–7.3). N_2O emission from the soil cores was generally very low (2.0 ± 0.5–6.3 ± 3.8 μg N m^{-2} h^{-1} at the warm-dry site and 7.1 ± 3.1–57.4 ± 28.5 μg N m^{-2} h^{-1} at the cool-moist site), thus confirming results from field measurements. However, N_2 emission exceeded N_2O emission by a factor of 21 ± 6–220 ± 122 at the investigated plots. This illustrates that the dominant end product of denitrification at our plots and under the given environmental conditions is N_2 rather than N_2O. N_2 emission showed a huge variability (range: 161 ± 64–1070 ± 499 μg N m^{-2} h^{-1}), so that potential effects of microclimate or silvicultural treatment on N_2 emission could not be identified with certainty. However, there was a significant effect of microclimate on the magnitude of N_2O emission as well as on the mean N_2:N_2O emission ratio. N_2:N_2O emission ratios were higher and N_2O emissions were lower for soil cores taken from the plots with warm-dry microclimate as compared to soil cores taken from the cool-moist microclimate plots. We hypothesize that the increase in the N_2:N_2O emission ratio at the warm-dry site was due to higher N_2O reductase activity provoked by the higher soil pH value of this site. Overall, the results of this study show that the N_2:N_2O emission ratio is crucial for understanding the regulation of N_2O fluxes of the investigated soil and that reliable estimates of N_2 emissions are an indispensable prerequisite for accurately calculating total N gas budgets for the investigated ecosystem and very likely for many other terrestrial upland ecosystems as well.

1. Introduction

Production of inert dinitrogen (N_2) via denitrification in soils removes reactive nitrogen from the biosphere and thus contributes to closing the global N cycle (Galloway et al., 2003). For terrestrial upland ecosystems, the complete reduction of nitrate or nitrite via nitric oxide (NO) and nitrous oxide (N_2O) to N_2 by classical denitrification is thought to be the quantitatively most important process leading to N_2 production. Cycling of reactive nitrogen in ecosystems has been accelerated due to the approximate doubling of inputs of reactive nitrogen to the biosphere via increased growing of N fixing crops, NO_x production during anthropogenic fossil fuel combustion and inorganic N fertilizer production (Galloway et al., 2003). The conversion of reactive N back to N_2 by denitrification (and anaerobic ammonium oxidation) is thought to represent the largest uncertainty of the N cycle at all scales (Galloway et al., 2004). Unlike N_2, reactive nitrogen gases (NO, NO_2 and N_2O) affect atmospheric physics and chemistry. Throughout the last decades, the exchange of reactive nitrogen gases between upland soils and the atmosphere has been investigated across a wide range of terrestrial ecosystems due to both the outstanding importance of soils as sources within the respective global budgets and the importance of these atmospheric trace gases for atmospheric chemistry and global warming. These studies have been facilitated by the

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comparably elementary detection techniques and measuring system setups for reactive nitrogen gases. However, extremely little information is available on the emission of N_2 from upland soils. This is mainly due to methodological constraints, which did not allow a reliable quantification of actual N_2 emission from soils against the high background of 78% in the atmosphere (Groffman et al., 2006). Thus, knowledge of N_2 emissions from upland soils is so far based mainly on the use of inhibitors of N_2O reduction to N_2 and on ^{15}N tracing experiments, which require physical soil disturbance and substrate addition (Groffman et al., 2006).

The lack of reliable measurements of N_2 emissions from terrestrial ecosystems does not only limit our understanding of the significance of the single permanent sink for reactive nitrogen, but also impedes the quantification and comprehension of the denitrification process as a whole (Davidson and Seitzinger, 2006; Groffman et al., 2006) and hinders closing of N gas budgets in biogeochemical models (Butterbach-Bahl et al., 2002a; Boyer et al., 2006). Limited understanding of N_2 emissions from soils even limits our understanding of N_2O release and/or uptake in soils (Chapuis-Lardy et al., 2007) since N_2 production via denitrification is catalyzed by the enzyme N_2O reductase (NOR). This enzyme utilizes N_2O as substrate, and is thus critical for the regulation of net N_2O fluxes between pedosphere and atmosphere. Consequently, the discrepancy between ecological significance and limited knowledge of N_2 fluxes from soils as well as the urgent need for reliable N_2 flux measurements across a wide range of ecosystems and environmental conditions has recently been emphasized (Davidson and Seitzinger, 2006; Groffman et al., 2006).

Recently, a new method has been introduced that allows simultaneous quantification of the emissions of N_2O and N_2 from intact soil cores (Butterbach-Bahl et al., 2002a). This method is based on the replacement of the soil atmosphere by an artificial, nearly N_2-free atmosphere and the subsequent evaluation of the increase of N_2 and N_2O concentration in the headspace above the cores. In the present study, this method has been applied to investigate the effects of microclimate, pH and forest thinning on the emissions of N_2 and N_2O as well as on the N_2:N_2O emission ratio of a shallow calcareous soil in a mountainous beech forest. As for most forest ecosystems, no reliable data on pedogenic N_2 emissions and N_2:N_2O emission ratios have been available for this ecosystem. Furthermore, to our knowledge no study has investigated the effect of forest management and microclimate on N_2 emissions and the N_2:N_2O emission ratio yet. The objectives of the present study were to provide general knowledge on the significance and magnitude of N_2 fluxes and N_2:N_2O ratios of the investigated ecosystem, and, furthermore, to evaluate the effects of microclimate and forest management (thinning). Since the different microclimates and treatments of the investigated plots lead to a wide range of pH values, soil water contents and soil temperatures, we additionally investigated the effect of these potential environmental controls on N_2 emissions, N_2O emissions and the N_2:N_2O emission ratio.

2. Material and methods

2.1. Site characteristics

The study sites are located in the Swabian Jura, a low mountain range in southern Germany (Tuttlingen Research Station, longitude 8°45′E; latitude 47°59′N) at an altitude between 760 and 820 m a.s.l. Mean annual air temperature is approximately 6.6 °C and the average annual precipitation amounts to 856 mm. The study site is exposed to a comparatively low N deposition of <10 kg N ha^{-1} year^{-1}. The two experimental sites are located on the steep slopes (23–30° inclination) of a narrow valley facing southwest (abbreviation "S") and northeast (abbreviation "N"). The sites in Tuttlingen were established in order to obtain a gradient of climate for a comprehensive interdisciplinary ecosystem research project. Due to the differing exposure, the sites are characterized by pronounced differences in radiation, air temperature, soil temperature and soil moisture leading to a cool-moist microclimate at the N site and a warm-dry microclimate at the S site (Geßler et al., 2001; Holst et al., 2004, 2005; Dannenmann et al., 2006, 2007b). The soil profiles are characterized as Rendzic Leptosols (WRB-classification, ISSU/ISRIC/FAO, 1998) derived from limestone and marls. At both sites, soil profiles are shallow ($\approx$20 cm of topsoil), followed by parent rock or periglacial layers containing >45% gravel and stones. The finer grained soil fraction of the uppermost 8 cm of the Ah layer is characterized by high C content (range: 8.2–11.2%) and high clay content (range: 37.4–45.5%) (Dannenmann et al., 2007a). The different microclimates lead to different water supply resulting in different status in decarbonisation of the Ah layer, and thus, different pH values (Dannenmann et al., 2006). Consequently, pH values are higher at the site characterized by warm-dry microclimate.

Beech (*Fagus sylvatica* L.) is the dominant species constituting >90% of the total basal area of adult trees. At both sites, adjacent 70 m × 70 m plots were created in March 1999: untreated control plots (mean basal area of the stands: approximately 25 m^2 ha^{-1}, abbreviation "C") and thinned plots, where the basal area of the stands was evenly reduced to approximately 10 m^2 ha^{-1} (abbreviation "T") by selected cutting. Two replicated plots for each treatment at each site were sampled (=8 plots). The combinations of differing microclimates and silvicultural treatments lead to pronounced variations in soil pH values, soil water content and soil temperature at the plot scale.

2.2. Soil sampling

Soil sampling was performed by use of stainless steel cores (length 20 cm, inner diameter 12.5 cm) which were closed with pin-holed parafilm after sampling and stored at 4 °C before start of the N_2/N_2O flux measurements. Sampled soil cores contained 1–5 cm of forest floor and the underlying Ah horizon. Sampling was performed in a 30 m × 30 m core zone of the plots to avoid edge effects. The eight research plots were sampled during six campaigns in April, August and October 1999 and May, July and October 2000, thus covering spring, summer and autumn seasons of the first 2 years following thinning. Four soil cores per plot were collected during each sampling campaign. However, for capacity reasons of the measuring system, measurements could be performed with on average only three of the cores. For measurements, the soils were incubated at the mean soil temperatures that were measured during 5 days prior to sampling at a depth of 5 cm in the mineral soil. Soil water content was not manipulated for the measurements.

Soil pH values (0.01 M $CaCl_2$) and gravimetric soil water contents were determined according to Dannenmann et al. (2006) after finishing measurements.

2.3 . N_2 and N_2O flux measurements

Soil cores of adjacent control and thinned plots were in general measured within the same run of the measuring system having a capacity of two soil cores. We used the same incubation temperature for control and thinned plots since mean soil temperature across adjacent control and thinned plots is very similar at the investigated sites (Holst et al., 2004; Dannenmann et al., 2007a).

The measurement system for simultaneous detection of N_2 and N_2O fluxes was custom-made at the labs of IMK-IFU and described in detail by Butterbach-Bahl et al. (2002a). The principle of the measurement system is the replacement of the soil atmosphere by an artificial, helium-based, nearly N_2-free atmosphere (20% O_2, 0.5% CO_2, 350 ppbv N_2O and 10 ppmv N_2) and the subsequent evaluation