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Soil-Atmosphere Exchange of NH_3 and NO_x in Differently Managed Vegetation Types of Southern Germany

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Abstract

Ammonia (NH_3) and Nitrogen Oxides ($NO_x = NO + NO_2$) emissions from soils and vegetation, and their subsequent deposition are key factors in global Nitrogen (N) cycling and have important functions in atmospheric and ecosystem degradation processes. To better understand their contribution, NH_3 and NO_x gases were simultaneously measured from differently managed vegetation types using a dynamic-chamber method. Biomass and N yields were higher from unfertilized clover-grass than fertilized oilseed radish. Summer cuts of clover-grass resulted in 137% higher biomass and 2.7-3.7% N concentrations than autumn cuts. Mulching reduced the re-growth and biomass production in clover-grass by 16% compared to cutting. The relative loss of NH_3 through mulching was higher from the clover-grass (2.18%) than in the oilseed radish (0.08%). The total NH_3 release over the four cuts of the clover-grass was 0.58% of the N removed. The influence of biomass-N, either mulched or cut, on the total NO_x emission was temporary, resulted in net deposition (0.02-0.15% of the added/removed biomass-N). The ecosystems acted as sources for NH_3, with the rate being weakly related to the added biomass-N, air temperature and humidity ($R^2 = 0.58$, $p<0.07$), and sinks for NO_x, with the rate influenced significantly by sunshine hours, precipitation and amount of biomass-N added ($R^2 = 0.87$, $p<0.001$). We conclude that cutting clover-grass multiple times could be a good option to reduce the emissions of reactive N species and increase fodder yields with moderate N. Additionally, clover-grass could be superior for soil conservation measures over oilseed radish. Results imply further studies on the annual exchanges of gaseous N between the ecosystems and the atmosphere through long-term measurements.

Keywords

Mulching/Cutting; Forage; Temperate Climate; NO_x Deposition; NH_3 Loss

Introduction

Ammonia (NH_3) and Nitrogen Oxides ($NO_x = NO + NO_2$) play a vital role in global Nitrogen (N) cycling through their emission from soils and vegetation, and their subsequent deposition onto soil-plant systems [1,2]. Both compounds also have important functions for various atmospheric and ecosystem degradation processes. Their deposition onto both terrestrial and aquatic systems results in acidification, eutrophication and a decrease in plant biodiversity [3]. The NO_x is also responsible for direct or indirect contributions to global warming and ozone depletion. There are several factors governing their production, and that the contribution of agriculture to their overall release and the potential for smart management practices to reduce the emissions are complex and multi-faceted.

Compared to global average, the highest NH_3 emission rates are found in many of the regions in Europe and its sources and influencing factors have been well discussed [4]. The average NH_3 emission in Western Europe is 12 kg N ha^{-1} yr^{-1} [5], and emissions from decomposing crops used as mulch are ranging from 17 to 39% of the total N present in the mulch. Gauger et al., reported an N deposition of 24 kg ha^{-1} for Dürnast and 27 kg ha^{-1} for Viehhausen [6], whereas Werner et al., estimated 2.3 kg NO-N ha^{-1} yr^{-1} emissions from grassland systems [7]. Vegetation/grassland can act as sinks of soil-emitted NH_3 and NO_x depending on the soil mineral N concentration [8]. However, agriculture remains the main source of NH_3 volatilized to the atmosphere and that the management of soil-plant systems is equally important to that of animal rearing [1,9].

In addition to the organic matter turnover in the soils, the plants themselves emit NH_3 to the atmosphere via leaf senescence and N remobilization [10-12]. This process is accentuated by the presence of NH_4^+ and/or the application of NH_4^+-based fertilizers, particularly those derived from urea [2]. Both serve as additional major sources of NH_3 and can lead to excessive N absorption by the roots followed by high N concentrations in the foliage [13]. The precise level of NH_3 emission from various systems depends on substrate availability and its chemical composition, soil management and other environmental factors. Moreover, NH_3 volatilization is stimulated by the difference between compensation point over canopy cover and atmospheric mole fraction, and the external N supply [14,15].

Mulching is of particular concern for NH_3 production and that is thought to impact its emission on a par with that arising from live plants from their metabolic processes [11]. Ammonia emission from mulched material probably derives from metabolic enzymatic breakdown, and its potential magnitude depends largely on the concentration of NH_4^+ in the plant tissue [4]. Nitrogen oxides, by contrast, have short atmospheric lifetimes and their real-time concentrations vary depending on their proximity to their sources. For instance, soil represents a net source of reactive oxidized nitrogen as NO_x [16,17], and natural sources represent only 30% of the total emissions of these compounds [18]. The biogenic emission of NO (or NO_x in general) is a surface-related process, with the compounds being formed as intermediates or by-products of nitrification and denitrification processes that are regulated by heterogeneous microbes under both aerobic and anaerobic conditions [2,19]. The amount of substrate/sources and their rates of N turnover, either organic or inorganic, control NO_x production potential and there are opportunities to limit its emissions from agriculture by investing in management practices [20]. This production potential is also influenced by physical and chemical properties of the soil and NO_x partitioning in plant biomass and is highly variable particularly due to natural or anthropogenic disturbances [21].

Agriculture has a potentially important role to play in reducing its contribution to N deposition through the adoption of appropriate management options [4,22]. For example, grassland farming without grazing can impact significantly on N cycling through the process of cutting the grass at predetermined intervals to feed to the animals as either forage or hay. Promisingly, however, strategic management of legumes in an arable-ley rotation to enhance fixation of atmospheric N and recycle the stocked residues in grassland could increase productivity, enrich soil N pool and reduce reactive N species [23] or vice-versa [24,25], and may effective for soil conservation. Finding solutions to the above issues are hindered by the limited amount of data and poor understanding of their functional relations with soil and environmental factors underlying them. To address these deficits, we conducted experiments (i) to evaluate the biomass and N yield benefits from clover-grass mixture (mulching and cut) and oilseed radish receiving inorganic N fertilizer; (ii) to quantify the losses of NH_3 and NO_x from these ecosystems; and (iii) to elucidate those variables related to climatic conditions and to the biochemical composition of the vegetation that affect NH_3 and NO_x emissions.

Material and Methods

Site description

Two separate field experiments were conducted during the vegetation periods in two consecutive years at the Viehhausen and Dürnast research stations of the Institute of Plant Nutrition, Technische Universität München (TUM) in Freising, Bavaria in Germany. Both soils are silt loam from loess (Cambisol) and some of their physical and chemical properties are presented in table 1. The Viehhausen station is located 5 km south of the TUM, where a long-term experiment on clover (*Trifolium repens L.*)-grass (ryegrass mainly: *Lolium perenne L.*) management was established by the Bavarian State Research Center for Agriculture. This site received no fertilizer for the two years preceding this study (Table 2). Prior to that, the crops in Viehhausen were potato (*Solanum tuberosum L.*) and winter wheat (*Triticum aestivum L.*) receiving manure at 200 kg N ha^{-1} and inorganic N as Calcium Ammonium Nitrate (CAN) at 60 kg N ha^{-1}, respectively. The Dürnast station is located 6 km west of the TUM, where an experiment with oilseed radish

(*Raphanus sativus L.*) was set up following the cultivation of winter barley (*Hordeum vulgare L.*). At this site, CAN was applied at 60 kg N ha^{-1} and the straw of the previous crop of winter wheat, receiving cattle slurry at 240 kg N ha^{-1}, was incorporated (Table 2). Prior to the winter wheat, winter barley and maize (*Zea mays L.*) were cultivated, which received mineral N as CAN (60 kg N ha^{-1}) and cattle slurry (200 kg N ha^{-1}), respectively.

Location	Particle size distribution			pH ($CaCl_2$)	C (%)	N (%)	C/N	CEC ($Cmol_c kg^{-1}$)	$CaCO_3$(%)
	% Clay	% Silt	% Sand						
Viehhausen	17	66	17	6.6	1.29	0.14	9.2	13.7	1
Dürnast	20	66	14	6.2	1.2	0.12	10	14.1	0

Table 1: Physical and chemical properties of the two experimental soils, both of which belong to Loess silt loam, Cambisol.

Experiment 1: Viehhausen						
Previous years		Immediately preceding years		Experimental period		
Crops	Fertilization (kg N ha^{-1})	Crops	Fertilization (kg N ha^{-1})	Crops	Fertilization (kg N ha^{-1})	Treatments
Potato	Manure @ 200	Clover-grass	0	Clover-grass	0	A. Periods of harvest: 4 B. Utilizations: (i) Mulching (ii) Cut
Winter wheat	CAN* @ 60					
Experiment 2: Dürnast						
Winter barley	CAN @ 60	Winter barley	CAN @ 60 + Straw of winter wheat	Oilseed radish	CAN @ 40, 80 and 120	Feralization (kg N ha^{-1}) @ (i) 40 (ii) 80 (iii) 120
Maize	CS** @ 200					
Winter wheat	CS @ 240					

Table 2: Land uses, fertilization practices and treatments during the pervious and experimental periods.

* Calcium Ammonium Nitrate (CAN); ** Cattle Slurry (CS)

Experiment 1: NH_3 and NO_x fluxes from a clover-grass mixture: The experiment at the Viehhausen station was established to investigate the N use efficiency of a clover-grass mixture, consisting of 70% white clover, 25% ryegrass and 5% indigenous legumes, in rotations. The clover-grass was harvested four times during the growing season (May 10, June 29, August 16 and October 17), keeping ~5 cm of biomass above the ground. The treatments consisted of the harvested biomass (i) laid on the surface for subsequent mulching i.e., mulched and (ii) removed immediately after cutting i.e., cut. The treatments were arranged in a Randomized Complete Block Design (RCBD) and the data derived from both periods of harvesting and utilizations were analysed by Two-way Analysis of Variance (ANOVA). Representative dry weights of the mulched and cut clover-grass used as fodder were recorded from a whole plot (10 m x 5 m in size) using pseudo-triplicate sub-samples. Pseudo-triplicate plant N and Carbon (C) concentrations were also determined using a C-N analyzer (Vario MAX CNS, Germany). Simultaneous measurements of NH_3 and NO_x were performed over a two-week period by placing three chambers (system details follow) on the soil surface immediately after mulching and cutting for each measurement plot (representing the number of replicates) and period of harvesting.

Experiment 2: NH_3 and NO_x fluxes from oilseed radish: At the Dürnast station, a catch crop (as cover crop cum mulching) of oilseed radish were grown separately following winter-barley cultivation. The treatments consisted of N fertilization applied to the oilseed radish at a rate of 40, 80 and 120 kg N ha^{-1} with CAN two weeks after sowing and arranged in a RCBD. Plots of 10 m x 5 m were selected for each ecosystem/treatment.

The plants were cut three months after sowing (October 20) from the whole plot and mulched. The corresponding biomass and N yields were recorded. Both NH_3 and NO_x fluxes from the ecosystem were measured using a single chamber for each plot over a period of three weeks starting immediately after mulching.

System descriptions and measurement of gases

Both NH_3 and NO_x were measured concurrently using a specially developed dynamic-chamber (area 0.125 m^2, diameter 0.40 m and height 0.40 m) method. The system had six chambers (Figure 1) with a facility to collect ambient air 3 m above soil surface and to ventilate at a continuous airflow, measured daily using a Thermal Mass Flow-Meter (TSI Model 4045, TSI Inc., USA), of ~40 L/min. Each chamber was covered with acrylic glass fitted with a stainless-steel ring and was inserted the sharpened bottom to 3 cm soil depth. An angled inlet and additional ventilator were used to flow the ambient air horizontally 5 cm above the soil surface to mix with the gas emitting from the treatment plots within the chamber. Then it was flowed upward to the outlet having gas sampling point. All tubes (Fluorethylene-propylene Teflon) were insulated and heated along with the chambers to 50°C with an electrical heating cable.

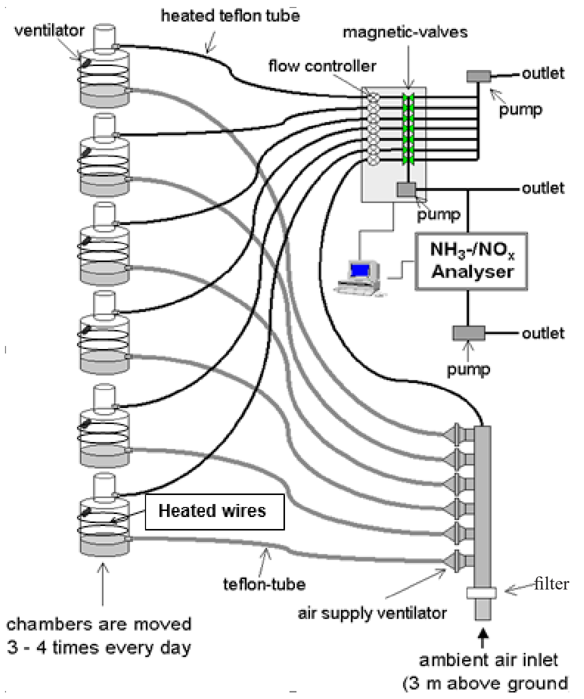

Figure 1: Schematic diagram of the dynamic-chamber method used for the simultaneous measurement of NH_3 and NO_x fluxes.

The continuous gas sampling flow (4 L/min) was verified by a Mass-Flow Controller (AFC 50D, France) before the sample was assayed by a Two-Channel Chemiluminescence NO-Analyser (CLD 700AL, Switzerland) at a flow of 0.7 L/min. In one channel, a stainless-steel thermal converter was used to convert NH_3 + NO_x to NO under a vacuum at 600°C (NO_x + amines), and in another, molybdenum one to reduce NO_2 to NO at 375°C. Ammonia concentrations were calculated as the difference between channels 1 (NO_x + amines) and 2 (NO_x). The NO-analyser was calibrated daily using NO, and a Portable Calibrator (VE3M, Germany) was used to check the efficiencies, ranging from 97 to 99%.

Emissions were continuously measured during the experimental period, representing flushing time as well, with consecutive sampling for 15 minutes and the last point was used for data analysis. The NH_3 and NO_x fluxes were calculated as the difference between the concentrations of the respective gases in the collected ambient air and in the air sample at the chamber outlets. The chambers were moved to a new undisturbed area of the same treatment plot up to three times a day to minimize any possible greenhouse effects (e.g., humidity, temperature) on gas exchange inside the chambers. The system was controlled using a PC via the software NEMO Lite v3.70 (Schmidt Technology, Neufahrn/Munich, Germany), which recorded data for each of NH_3 and NO_x and the airflow.

Statistical analysis and calculation

The ANOVA for each experiment separately and statistical analyses were performed using the computer package JMP v4.0.2 (SAS Inc.). For dry matter and N yields, the probability (p) values were determined by the F statistic and specific differences between pairs (Two-way ANOVA: periods of harvesting and utilizations for clover-grass and one-way ANOVA for oilseed radish) of means were measured using Tukey's Honest Significant Different tests. Total NH_3 and NO_x emissions/depositions were calculated by integrating the daily fluxes, and standard errors. Simple and multiple linear regression analyses were performed for NH_3-N and NO_x-N emissions/depositions (with or without a mathematical transformation) with selected meteorological variables, biomass N and soil temperature.

Result

Dry matter and N yields of clover-grass and oilseed radish

Forage Dry Matter (DM) yields of the clover-grass mixture varied significantly among the four periods ($p<0.0001$) and between the two management strategies/utilizations (i.e., mulching versus cutting; $p<0.001$), but not between the periods and utilizations (Table 3). For the first two of the four cuts (from May to June), the management system influenced the biomass production significantly. The DM yield was significantly higher for the June cut (5.20 t DM ha^{-1}) than for either of the mulched or cut plots. The forage yields for the fourth cut in October were less than half of the three earlier cuts, regardless of the management system. Generally, DM yields of clover-grass for all harvests were higher in the cut plots than in the mulched ones. There was a significant ($p<0.001$) difference in biomass N concentrations for the clover-grass over time, but not for the management systems and their interactions, with increased N concentrations later in the season (August and October cuts). Nitrogen yields differed significantly between periods ($p<0.0001$), utilizations ($p<0.01$) and their interactions ($p<0.01$). The highest value was observed for the mulched plot during third cut (142 kg N ha^{-1}), despite N yields being generally lower in the mulched plots.

Period	1	2	3	4	Mean	Total
Date	10 May	29 June	16 August	17 October		
Utilization	DM yield (t ha^{-1})					
Mulch	3.49^{c}	4.33^{abc}	4.18^{bc}	1.94^{d}	3.49^{A}	13.9^{B}
Cut	4.47^{ab}	5.20^{a}	4.75^{ab}	2.03^{d}	4.11^{A}	16.5^{A}
Mean	3.98^{B}	4.77^{A}	4.47^{AB}	1.99^{C}		
Probability (p) level: Period = <0.0001; Utilization = <0.001 and Period * Utilization = NS						
N concentration (%)						
Mulch	2.7^{cd}	2.5^{d}	3.4^{abc}	3.7^{a}	3.1^{A}	
Cut	$2.8b^{cd}$	2.6^{cd}	2.9^{c}	3.6^{ab}	3.0^{A}	
Mean	2.8^{BC}	2.6^{C}	3.2^{B}	3.7^{A}		
Probability (p) level: Period = <0.0001; Utilization = NS and Period * Utilization = NS						
N yield (kg N ha^{-1})						
Mulch	94^{cd}	108bc	142^{a}	72^{d}	104^{A}	416^{B}
Cut	125^{ab}	135a	138^{a}	73^{d}	118^{A}	471^{A}
Mean	110^{B}	122^{AB}	140^{A}	73^{C}		
Probability (p) level: Period = <0.0001; Utilization = <0.01 and Period * Utilization = <0.01						

Table 3: Dry Matter (DM) and Nitrogen (N) yields of clover-grass that was either mulched or removed after cutting (cut) at four different dates.

Values with the same letter do not vary significantly to each other; NS = Not Significant.

The DM yields of oilseed radish were dependent on the amount of fertilizer applied with the values for 80 or 120 kg N ha^{-1} applied as CAN (6.86 or 7.17 t DM ha^{-1}) being significantly higher ($p<0.01$) than those for 40 kg N ha^{-1} (5.26 t DM ha^{-1}; Table 4). The N concentrations in the oilseed radish were likewise increased from 1.6 to 2.2% with increasing fertilization rates, showing no significant difference, and were lower than that as observed for the clover-grass. The addition of 80 or 120 kg N ha^{-1} to the oilseed radish also significantly ($p<0.001$) increased N yields over the lowest rate. After six months, the total biomass production and N yields from the oilseed radish were two-fold lower than from the clover-grass either mulched or cut. As determined from biomass production, the apparent uptake of soil N in excess of that from the CAN applied to the oilseed radish ranged from 38 to 64 kg N ha^{-1}, with the

Crops	Fertilization (kg N ha^{-1})	Dry matter yield (DM, t ha^{-1})	N concentration (%)	N yield (kg N ha^{-1})	C/N ratio
Oilseed radish	40	5.26^{b}	1.6	84^{b}	26.9^{a}
	80	6.86^{a}	2.1	144^{a}	20.5^{b}
	120	7.17^{a}	2.2	158^{a}	19.6^{b}
Probability (p) level:		<0.01	NS	<0.001	<0.001

Table 4: Dry Matter (DM) and N yields of oilseed radish (grown with or without N fertilizer) and used for mulching. Values with the same letter do not vary significantly to each other; NS = Not Significant.

highest value derived by the application of 80 kg N ha^{-1}.

NH_3 and NO_x emissions/depositions for mulched or non-mulched clover-grass

Ammonia volatilization from the clover-grass plots was consistently influenced by both the measurement period (first through third cuts) and the management systems (Figure 2). The peaks for NH_3 fluxes from the mulched plots (maxima of 198 to 864 g N ha^{-1} d^{-1}) were generally higher than those recorded from the cut plots (57 to 273 g N ha^{-1} d^{-1} from first through third cut). Fluxes for NH_3 differed significantly for most of the measurement days, with the largest peaks appeared within three to nine days after mulching or cutting. An exception was observed after the fourth cut, where the highest peaks occurred later (e.g., the maximum peak of 566 g N ha^{-1} d^{-1} occurred on day 13). The total NH_3 volatilized over the four harvests showed similar trends (Table 5), with the mulched plots emitting about three-fold more NH_3 (9065 g N ha^{-1}) than the cut plots did (2740 g N ha^{-1}).

Period	1	2	3	4	Mean	Total
Date	10 May	29 June	16 August	17 October		
Utilization	Total NH3 flux (g N ha-1)					
Mulch	885^{a}	2483^{a}	3533^{a}	2297^{a}	2300^{A}	9065^{A}
Cut	335^{a}	93^{a}	1479^{a}	833^{a}	685^{B}	2740^{B}
Mean	610^{A}	1288^{A}	2506^{A}	1595^{A}		
Probability (p) level: Period = NS; Utilization = <0.05 and Period * Utilization = NS						
	Total NOx flux (g N ha-1)					
Mulch	6^{a}	4^{a}	-22^{ab}	-194^{b}	-52^{A}	-206^{A}
Cut	1^{a}	-22^{ab}	-76^{ab}	-138^{ab}	-59^{A}	-235^{A}
Mean	3^{A}	-9^{A}	-49^{A}	-166^{B}		
Probability (p) level: Period = <0.01; Utilization = NS and Period * Utilization = NS						
	Weather conditions					
Mean temprature (°C)	14	15	18	10		-
Total preci-pitation (mm)	69	63	16	26		174
Mean relative humidity (%)	53	58	49	80		-

Table 5: Total NH_3 and NO_x fluxes (mean ± standard error) over two-week re-growth periods of clover-grass that was either mulched or removed after cutting (cut).

The annual average ambient concentrations of NH_3 and NO_x was 46.0 ± 5.7 and 9.8 ± 1.2 ppb, respectively (mean ± standard error); NS = Not significant.

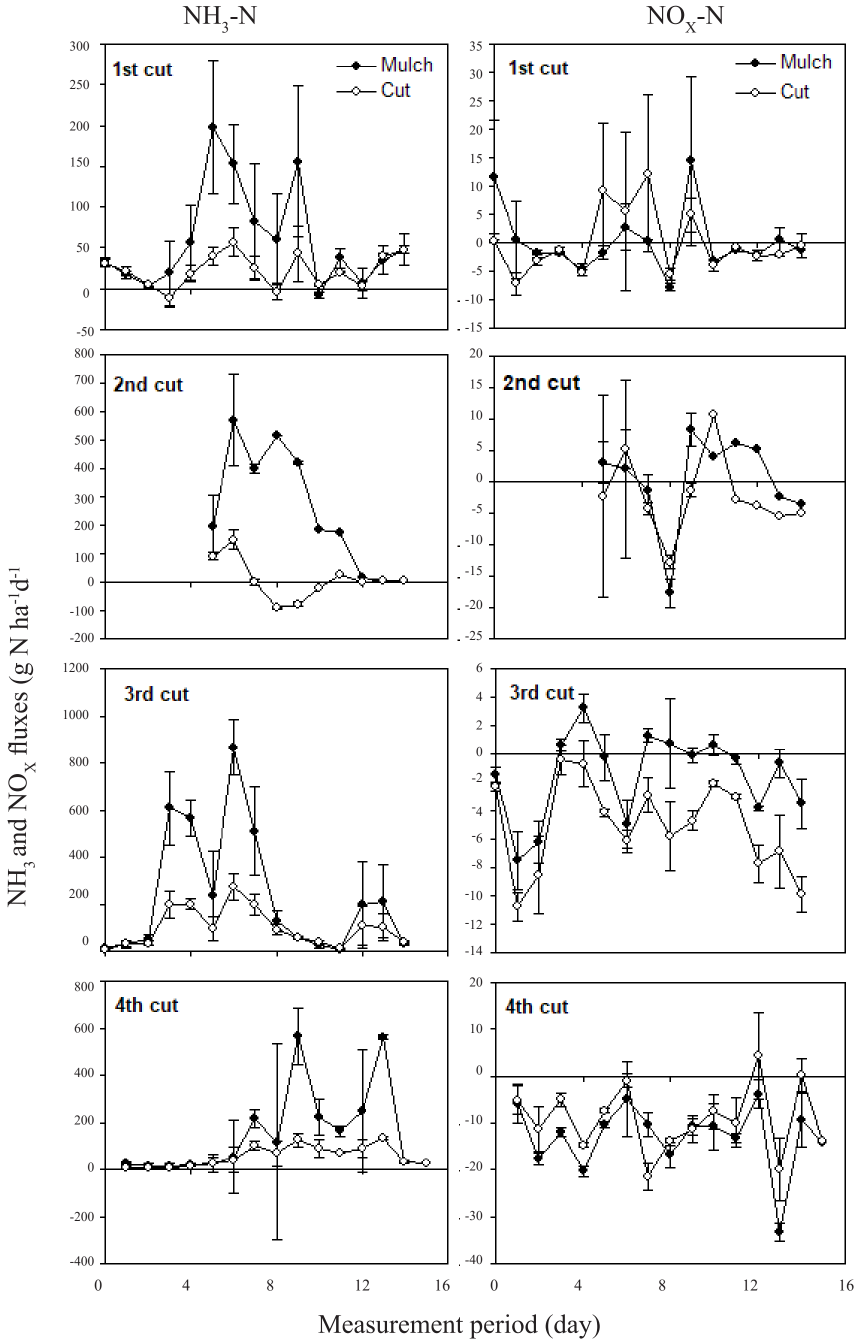

Figure 2: NH$_3$ and NO$_x$ emissions/depositions over a two-week measurement period during the re-growth of clover-grass that was either mulched or removed after cutting (cut).

In contrast, NO$_x$ exchange was dominated by deposition (Figure 3), with the peaks for emissions/depositions being largely inconsistent in their timing between the mulched and cut plots. The exception was after the first cut, in which both management systems produced overall NO$_x$ emissions (mulched: 14.4 g N ha^{-1} d^{-1}; cut: 12.2 g N ha^{-1} d^{-1}). From the second cut onwards, the fluxes decreased substantially, showing only small emission peaks or large depositions. Over all, the net amount of deposition was 206 and 235 g NO$_x$-N ha^{-1} from the mulched and cut clover-grass plots, respectively (Table 5).

NH$_3$ and NO$_x$ emissions/depositions for mulched oilseed radish

Following some short peaks that occurred around day 12, the plots mulched with oilseed radish produced their maximal peaks

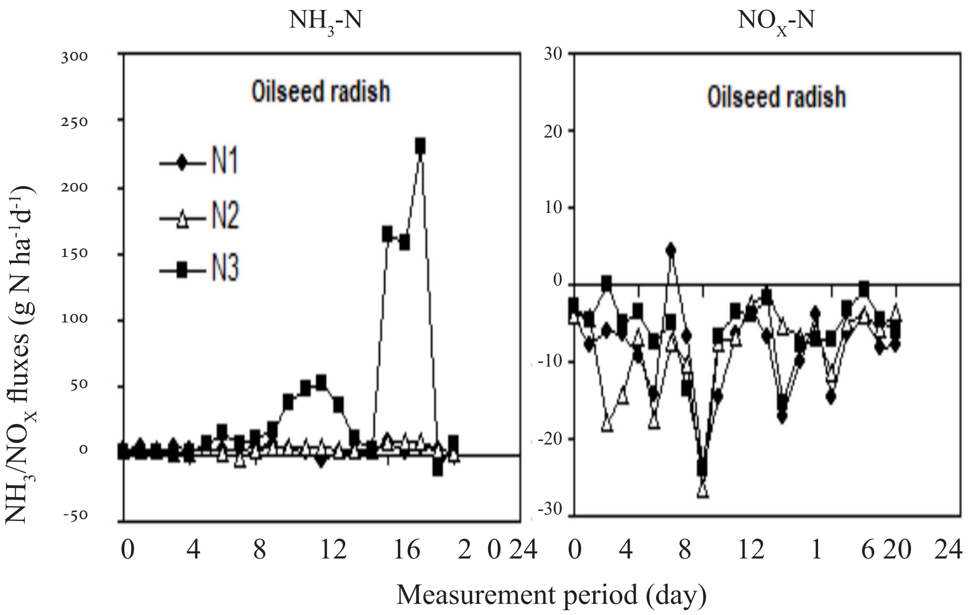

Figure 3: NH_3 and NO_x emissions/depositions over a three-week measurement period on fields that were mulched with oilseed radish after cutting the three-month old plants (N1, N2 and N3 = 40, 80 and 120 kg N ha^{-1}, respectively).

for NH_3 after day 15 (231 g N ha^{-1} d^{-1}) on day 18 for those plots initially received the highest amount of inorganic N (Figure 4). Theapplication of inorganic N at lower rates of 40 and 80 kg ha^{-1} did not show much residual influence on NH_3 volatilization, showing the maximum peaks of only 10.3-10.5 g N ha^{-1} d^{-1}. Over the course of the entire two-week measurement period in the mulched oilseed radish, the highest amount of inorganic N (120 kg N ha^{-1}) released significantly (p<0.01) greater total NH_3 (255 g N ha^{-1}) than other two N treatments (42-47 g N ha^{-1}) (Table 6).

Crop	Fertilization (kg N ha^{-1})	NH_3 emission (g N ha^{-1})	NO_x deposition (g N ha^{-1})	Mean temperature (°C)	Total precipitation (mm)	Mean relative humidity (Ø, %)
Oilseed radish	40	42^b (69)	-128^a (-178)	6.7 (8.1)	25.8 (47.8)	61.1 (73.4)
	80	47^b (87)	-135^a (-175)			
	120	255^a (808)	-103^b (-134)			
Probability (p) level:		<0.01	<0.01			

Table 6: Total NH_3 emissions and NO_x deposition over a two-week period (three-week in parentheses) following mulching of oilseed radish.

Values with the same letter do not vary significantly to each other.

Deposition of NO_x was generally observed into the oilseed radish plots throughout the measurement periods, with the net rate not differing between the management strategies (Figure 4). The only exception was a peak in NO_x emission at day 6 for those plots mulched with oilseed radish that received the lowest amount of inorganic and biomass N. The total NO_x deposition over a two-week period from plots mulched with oilseed radish varied significantly (p<0.01), ranging from 103 to 135 g N ha^{-1} (Table 6).

Influence of meteorological and soil variables on NH_3 and NO_x emissions/depositions

We performed correlation analyses relating the daily NH_3 and NO_x fluxes with the daily changes in soil temperature and selected meteorological variables for all crops, either individually or in combination. All variables, either individually or in combination, showed a very poor fit to the daily NH_3 fluxes. By contrast, daily NO_x fluxes showed significant correlations with

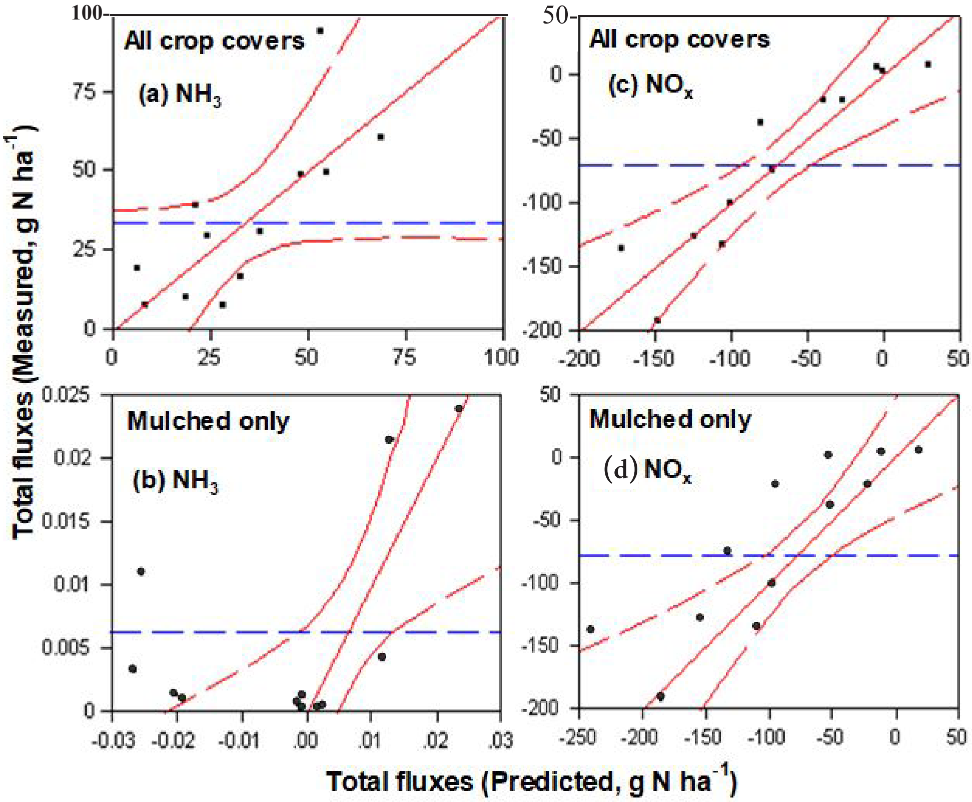

Figure 4: Measured and predicted total NH_3 and NOx fluxes (g N ha^{-1}) over a two-week period with the corresponding regression equations for the dependent variables influencing their emissions/depositions for a pooling of clover-grass, legume mixture and oilseed radish that was either mulched or cut (a; NH_3-N = -142.62 + 0.34 NR + 5.20 AT +1.44 RH, $R^2 = 0.58$, $p<0.07$, n = 12, and c; NO_x-N = -242.10 + 16.46 SH + 1.49 P + 0.33 NR, $R^2 = 0.87$, $p<0.001$, n = 12) and mulched only (b; 1/NH_3-N = -0.0163 + 0.0016 C/N - 0.0002 P, $R^2 = 0.80$, $p<0.05$, n = 12, and d; NO_x-N = -316.63 + 18.06 SH + 0.77 NR + 1.63 P, $R^2 = 0.95$, $p<0.01$, n = 12).

(NR = biomass N added through mulching in kg ha^{-1}; AT = mean Air Temperature in °C; RH = mean Relative Humidity in %; C/N = Carbon and Nitrogen Ratio; P = total Precipitation in mm; SH = mean Sunshine Hours; n = Number of Samples)

some variables, although the predictive levels were generally low (Table 7). For instance, fluxes of NO_x were related to relative humidity and soil temperature for mulched or cut clover-grass (R^2 = 0.13-0.33, $p<0.05$). For the mulched oilseed radish, the best predictive levels obtained with precipitation and air temperature ($R^2 = 0.38$, $p<0.001$).

Correlation analyses were also performed between total NH_3 or NO_x fluxes over the two-week measurement periods with mean values of air temperature, relative humidity, sunshine hours, total precipitation, and the amount of biomass N applied through mulching. Although not correlated at the 5% level, the square root of the total NH_3 flux was positively related to the combination of biomass N rate, mean air temperature and relative humidity with a predictive level of 58% though increased sample size showed a significant relationship (Figure 4a). When the mulched input variables were taken into consideration, the total 1/NH_3 flux showed a strong relationship with C/N ratio of the mulched materials and total precipitation ($R^2 = 0.80$, $p<0.05$; Figure 4b). However, the best fit to the NH_3 flux, either normal or transformed, by any single variable was with %N (R^2 = 0.54-0.59, $p<0.05$, n = 8).

The total NO_x flux for all three crops in combination, by contrast, was best explained by the combination of mean sunshine hours, total precipitation and biomass N rate, showing a predictive level of 87% (Figure 4c). Considering only the mulching effects of the legume species, the predictive level for the total NO_x flux for this combination of variables improved to 95% (Figure 4d). The total NO_x flux was generally not significantly related to any single meteorological variable, although the trends (R^2 = 0.35-0.69, p<0.02-0.13, n = 8) were stronger than those derived from the biochemical characteristics of the biomass (data not shown).

Variables Ecosystems	Simple linear					Multiple linear (step-wise)
	AT (°C)	SH (hour)	P (mm)	RH (%)	ST (°C)	
Clover-grass (mulched, n = 55)	0.24 ***	0.08 *	-0.01	-0.19 ***	0.17 **	= -0.22 - 0.17 RH - 0.83 ST; R^2 = 0.33*
Clover-grass (cut, n = 55)	0.08 *	0.05	0.01	0.12 *	0.02	= 1.24 - 0.12 RH - 0.19 ST; R^2 = 0.13*
Oilseed radish (mulched, n = 63)	-0.17 ***	-0.00	0.21 **	0.01		= 1.73 - 0.50 P - 1.02 AT; R^2 = 0.38***

*, **, *** indicate significance at Probability (p) level of <0.05, 0.01, 0.001, respectively; AT = Air Temperature, SH = Sunshine Hours, P = Precipitation, RH = Relative Humidity, ST = Soil Temperature; n = Number of Samples

Table 7: Correlation coefficients of NO_x fluxes (g N ha^{-1}) with selected meteorological variables and soil temperature as measured during the re-growth of either mulched or cut clover-grass and mulched oilseed radish.

Discussion

Biomass and N yields of clover-grass and oilseed radish

Values for biomass (as either forage or mulch materials) and N yields for clover-grass (70% white clover) from either the mulched or cut treatments differed markedly to those for the oilseed radish. The yields were higher for clover-grass, attributing to a higher N input received through Biological Nitrogen Fixation (BNF), compared to the fertilized oilseed radish. Mulching somewhat decreased the yield benefits for the clover-grass, probably due to the resulting physical barrier, and shading-induced lower temperature compared to cut practices and thereby limited the re-growth of the clover-grass. The oilseed radish apparently exploited up to 64 kg of soil N in excess of inorganic N applied, a value that was several-fold lower than the N (soil + atmospheric) yielded by the clover-grass.

A well-established process of BNF largely compensates for any insufficient application of inorganic N in the production of clover-grass. As typical forage legumes could fix atmospheric N_2 in amounts ranging from 196 to 240 kg ha^{-1} [23]. Moreover, the mineral N derived from decomposition of organic materials, especially following cut practices, might contribute to future N availability, leading to facilitate enhanced N uptake and vegetation growth. This conjecture is supported by other workers for example Herrmann et al., reported a compensation process through BNF when inorganic N was applied at a low rate [26]. The plant components of clover-grass contained higher N than did the oilseed radish and thus yielded more N. Indeed, the biomass and N yields from each cutting of the clover-grass observed here were within the upper limits of recorded ranges [27].

In addition to the advantages of mulching practices for soil conservation measures, legume species can also contribute to enriching the soil pool with nutrients to supply to future crops in rotations. By contrast, application of inorganic N is imperative to boost biomass production of oilseed radish. Oilseed radish can be used mainly as a cover crop and/or mulching material but contains low N and generally shows poor nutrient release over time due to a large C/N ratio [28].

NH_3 volatilization from clover-grass and oilseed radish

Mulching forage materials influenced NH_3 emissions significantly, with large peaks appeared three days after its placement. The levels of volatilized NH_3 from this mulched clover-grass system were three times greater than those found under cut conditions. The precise timeframe, when the maximum peak appeared, varied slightly over the seasons for clover-grass and its delayed appearance for oilseed radish due to its higher C/N ratio. These observations could be ascribed both to the natural variation in the meteorological variables and N immobilization phenomena that reduce NH_3 emissions [25,29,30].

Residual N following the application of inorganic and organic N fertilizers to the previously grown crops might also have contributed to the large NH_3 losses. This contrasts with oilseed radish, which is an exhaustive crop. As such, the amount of fertilized N lost as NH_3 was noticeably the lowest for the mulched oilseed radish (0.03-0.16% or 0.08% on average). The percent of N lost as NH_3 from the mulched clover-grass (2.7% of the N concentration during crop residue decomposition) was either within or exceeded the upper ranges reported by Mannheim et al., [31]. Some researchers, however, observed values that were several-fold higher than ours either in laboratory-based studies using selected parts of various legume species or in long-term field studies [5,25].

In line with other research [25], our findings demonstrate that the mulching of the clover-grass having high N concentrations could significantly increase the atmospheric build-up of NH_3. By contrast, Mannheim et al., stated that NH_3 emissions from crop residues could be reduced substantially through ploughing and mulching [31]. Ploughing could indeed be an effective management strategy [32]. However, the loss of other N species may be high during denitrification [33], whereas mulching-induced N_2O loss could be less than 1% [24,25]. Taking the value of 1.5% added-N lost as NH_3 from CAN into account [29,30], mulching of the oilseed radish seemed to reduce the NH_3 volatilization for prior N application rates of up to 80 kg N ha^{-1} compared to the clover-grass. Riedo et al., also reported reduced emissions 12 days after cut/fertilization events, a result that was even more pronounced after the second cut event compared to the first one [34].

Outright removal of the clover-grass after each of the four cuttings to use as either forage or hay reduced the overall NH_3-N loss three times more than when it was mulched. The re-growth of plants required after cutting enhances ammonium availability in the soil, leading to an increase in apoplastic ammonium (i.e., leaf tissue N) and thereby NH_3 emissions [10,12,35]. However, mulching with legume vegetation might override these processes. As such, NH_3-N emissions from the cut clover-grass were higher than those observed from the mulched oilseed radish. In the former case, this can be attributed primarily to the contribution of the biologically active soil N pool. The N pool generally derives from legumes through microbial symbiosis as well as decomposition of roots and nodules, and/or newly growing leaves [10,12], with a subsequent influence by the air temperature appearing to have a small influence [35]. It was not possible to clearly distinguish the microbes responsible for BNF either directly during the re-growing periods or interactively through NH_3 exchanges during soil C and N mineralization. Under field cutting conditions, the NH_3 emissions between the first and fourth cut were 0.58% of the biomass N removed through cutting, including accounting for the uptake that occurred in some instances. Herrmann et al., however, reported that NH_3 deposition could exceed its emission under field cutting conditions from a clover-grass mixture, even when applying inorganic N fertilizer and assuming a deposition of <1% of the N removed by cutting from the system [26]. The NH_3 levels emitted from the mulched oilseed radish with its higher C/N ratio were very low, which may be attributed to N immobilization and is comparable to the findings of Herrmann et al., [26]. By assuming an estimated loss of NH_3 from the soil N pool of ca. 201 g over a two-week period, a net deposition of NH_3 could be observed from mulched oilseed radish receiving low N rates from either inorganic or organic N sources [2]. This indicates that NH_3 emission from catch crop species after mulching might not exceed the atmospheric concentration of NH_3 or might be close to the canopy compensation points. These could demonstrate either low net emissions or overall deposition if any losses are held to have occurred from the soil N pool.

The NH_3 emissions overriding zero/canopy compensation points were regulated mostly by the quality or biochemical composition of the substrates mulched (as delineated by %N, C/N ratio or biomass N added, either alone or in combination with selected meteorological variables) and relating to the C and N mineralization processes [15,28]. Similarly, Glasener and Palm thought that the high lignin and polyphenol concentrations in N-rich plant materials might be counteractive to NH_3 emission [36]. Moreover, several researchers have indicated the importance of the metabolic enzymatic breakdown of cells/mulched materials for NH_3 emission. Its overall contribution depends largely on the concentration of NH_4^+ in the plant tissue and often exceeding that of the stomata of the plants [10,22]. The C/N ratio of the plant components (considering mulching effects only) in combination with precipitation influenced NH_3 volatilization significantly, and %N as a single variable also contributed to this effect in agreement with the findings of Larsson et al., [25]. Increased NH_3 loss from vegetation having high N concentration, mainly as ammonium in leaves (and in litters), has been reported [12].

We also found that NH_3 emission was inversely, and weakly, related to the water content of the plant components. This result contrasts with those of Mannheim et al., who stated that the plant components of a mixed crop having high water content emitted more NH_3 than did plant parts with high dry matter and N concentration [31]. These could be explained by the differences in moisture content between the mulched materials used in this study being relatively small compared to those used in Mannheim et al., [31]. Our results also indicate that NH_3 emission was influenced by the combination of the amount of added biomass N, air temperature and relative humidity. Thus, interactive effects of the water content of the plant components and meteorological variables could also exist. Similarly, Mastrorilli et al., revealed that, following cover crop (*Vicia faba*) decomposition, NH_3 emission stopped during rainy days and recommenced with the increased amount of solar radiation, soil and air temperatures [37]. Besides, NH_3 emission is high and frequent (occurring about 50% of the time) during warm, dry summer periods. By contrast, deposition is dominant (80% of the time) in wet, cool autumn periods due to small canopy compensation points caused by the low temperatures and generally wet surfaces [15,38]. Soil evaporation, plant transpiration and ambient atmospheric humidity all contribute to humid conditions. Therefore, any dynamic changes of canopy liquid water storage could regulate the internal cycling of NH_3, leading to enhanced deposition or degassing of the highly water-soluble ammonia [4,10]. Our results further reveal that the biochemical composition (C/N ratio, %N) or the amount of biomass N added in association with selected meteorological variables could also significantly influence NH_3 volatilization.

When comparing the different mulched materials, use of oilseed radish seemed the best option to reduce NH_3 emissions. Still, oilseed radish degrades slowly, and the presumed N immobilization would result in a poor supply of nutrients to the crops. Instead, the full NH_3 emission scenario needs to consider both applied inorganic N fertilizers as well as the entire farming system approach being used. Thus, multiple cuttings of the clover-grass, using either as forage and hay or as an N-rich mulching material to improve the soil N pool for the next crop in rotation, might be a better alternative to oilseed radish for ecological farming.

NO_x emissions/deposition from clover-grass and oilseed radish

Deposition of NO_x was dominant for the clover-grass strategy; the only exceptions were after the first harvest (for both mulching and cutting) and after the second harvest when the biomass was cut and removed. The deposition of NO_x was slightly greater for the cutting than for mulching strategy over the two-week measurement periods, indicating only a small influence for added biomass N. The total exchange of NO_x over the course of 2-3 weeks was noticeably higher in the oilseed radish, with deposition increased with decreasing amounts of added N, than in the clover-grass. Although the added N influenced NO_x emission [17,20], both soil and environmental conditions might lead to overall deposition over the short measurement periods used here. Some researchers reported the uptake of NO_x by vegetation canopies from the point of view of N deposition [39], with its consumption through canopy reduction possibly being up to 50% of soil emission [18]. By contrast, Werner et al., estimated a NO emission potential of grasslands of about 2.3 kg N ha^{-1} y^{-1} [7]. Our results suggest that NO_x deposition in the grassland systems might be the dominant process, at least during summer and autumn, and particularly so for either the mulched or cut re-growing grass covers without additional inorganic N input. In line with the observations of other workers [40], the increasing concentrations of ambient NO_x we observed from May to October might be one of the important factors relating to NO_2 uptake by the soil and/or low soil NO emission and canopy resistance. Finally, Ozone (O_3) flux, although not investigated in the present study, is inextricably linked with NO_x exchange [17]. Despite the fact that the interconversion of NO_x and O_3 is complex, deposition of NO_x (i.e., resulting in low NO availability) limits the photochemical dissociation of O_3. The resulting acceleration of the O_3 concentration within the vegetation canopies is followed by soil and stomatal uptake, and possible damage to sensitive plant species [16].

Depending on the management strategy, it was observed that either relative humidity or precipitation along with soil/air temperature inversely regulated NO_x effluxes. Biomass input by mulching might facilitate the immobilization of mineralized N, with the extent of this process presumably depending on the biochemical compositions of the added biomass (e.g., C/N ratio, lignin and polyphenol content; [28]). However, the short-term variation inherent to environmental conditions, including comparatively higher ambient NO_x levels and edaphic conditions, might also be an important contributing factor influencing NO_x emissions/deposition [41]. Similarly, Hou and Tsuruta also reported a small efflux of NO during the post-harvest periods when using incorporated cabbage residues [42]. Despite these findings, a strong relationship between NO_x and both NH_4^+ and NO_3^- concentration has been reported elsewhere [43]. High NH_4^+ concentrations could facilitate NO emissions under aerobic conditions, with nitrification being the dominant process given that it is typically not a major end-product of denitrification under anaerobic conditions or serves as a sink [44-46].

Finally, temperature is generally considered to be an important factor controlling NO_x fluxes, subject to the availability of NH_4^+ or NO_3^-. Yet the influence of temperature might be negligible with either extremely wet or dry soils, which impede the diffusion of NO_x [19]. In our study, total NO_x efflux was positively correlated with the combination of sunshine hours, precipitation, and the biomass N added during the two-week measurement periods, and with a high predictive level (87% or 95% depending on whether input variables from the mulching systems were included or not). However, the daily peaks for NO_x generally followed precipitation events in agreement with observations of Hutchinson et al., who stated that the pulsing intensity and duration of NO_x efflux depended on the size of the precipitation event [41]. Even so, uncertainty still prevails as to the factors, like elevated atmospheric NO_x levels, influencing its deposition. Indeed, the correlation analyses in this research indicated the dominancy of NO_x emission over deposition once the weather conditions were favourable. However, measurements of NO_x flux over longer periods are necessary before any conclusive remarks on the net annual rate of emissions/depositions occurring in the three systems studied here can be made.

Conclusion

Our results indicate that clover-grass species can use Biologically Fixed-N (BNF) to help meet their N requirements during re-growth periods following either mulching or removal after cutting. The mulched clover-grass might release larger amounts of NH_3 into the atmosphere compared to the non-mulched clover-grass or mulched oilseed radish, and that could demonstrate remarkably low NH_3 emissions under field conditions. It appears that the biochemical composition of the added plant material has a large influence on the total NH_3 emissions, whereas sunshine hours and precipitation seem to determine the NO_x fluxes instead. All three management systems under investigation could act as sources of NH_3, but as sinks for NO_x, with NH_3 volatilization being the dominant process. Overall, the clover-grass farming practices could be more beneficial than those involving oilseed radish in temperate climates because clover-grass (i) could compensate for the application of inorganic N through BNF, (ii) demonstrated lower NH_3 and NO_x emissions/depositions, and (iii) could, as an N-rich material, either enrich the soil N pool for the succeeding crop cultivation through mulching or could be used as a forage product after cutting. Results imply that further long-term measurements are desirable, especially to gain insight into the annual exchange of unavoidable gaseous N between each of the ecosystems and the atmosphere. This is to assess air quality and offer technological and policy options to meet significant challenges facing by the world.

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References

1. Flechard CR, Nemitz E, Smith RI, Fowler D, Vermeulen AT, et al. (2011) Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network. Atmos Chem Phys 11: 2703-2728.
2. Khalil MI, Schmidhalter U, Gutser R (2006) N_2O, NH_3 and NO_x emissions as a function of urea granule size and soil type under aerobic conditions. Water Air Soil Poll 175: 127-148.
3. Stevens CJ, Dise NB, Gowing DJG, Mountford JO (2006) Impact of nitrogen deposition on the species richness of grassland. Sci 303: 1876-1879.
4. Sutton MA, Howard CM, Erisman JW, Billen G, Bleeker A, et al. (2011) The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. Cambridge University Press, UK.
5. Kirchmann H, Esala M, Morken J, Ferm M, Bussink W (1998) Ammonia emissions from agriculture: Summary of the Nordic seminar on ammonia emission, science and policy. Nutr Cycl Agroecosys 51: 1-3.
6. Gauger T, Anshelm F, Schuster H, Erisman JW, Vermeulen AT, et al. (2002): Mapping of ecosystem specific long-term trends in deposition loads and concentrations of air pollutants in Germany and their comparison with critical loads and critical levels. Final Report on behalf of Federal Environmental Agency (Umweltbundesamt), Berlin.
7. Werner C, Li C, Papen H, Butterbach-Bahl K (2004) Soils as sources of N-trace gases in Germany. International Conference on the 'Greenhouse Gas Emissions from Agriculture - Mitigation Options and Strategies'. Leipzig, Germany. Pg: 18-24.
8. Yienger JJ, Levy II H (1995): Empirical model of global soil-biogenic NO_x emissions. J Geophys Res 100: 11447-11464.
9. Felix JD, Elliott EM, Gish T, Maghirang R, Cambal L, et al. (2014) Examining the transport of ammonia emissions across landscapes using nitrogen isotope ratios. Atmos Environ 95: 563-570.
10. Burkhardt J, Flechard CR, Gresens F, Mattsson ME, Jongejan PAC, et al. (2008) Modeling the dynamic chemical interactions of atmospheric ammonia and other trace gases with measured leaf surface wetness in a managed grassland canopy. Biogeosci Disc 5: 2505-2540.
11. Loubet B, Milford C, Hill PW, Tang SY, Cellier P, et al. (2002) Seasonal variability of apoplastic NH_4^+ and pH in an intensively managed grassland. Pl Soil 238: 97-110.
12. Mattsson M, Herrmann B, Jones S, Neftel A, Sutton MA, et al. (2008) Contribution of different grass species to plant-atmosphere ammonia exchange in intensively managed grassland. Biogeosci Disc 5: 2583-2605.
13. Schjoerring JK, Husted S, Mattsson M (1998) Physiological parameters controlling plant-atmosphere ammonia exchange. Atmos Environ 32: 491-498.
14. Massad RS, Loubet B, Tuzet A, Cellier P (2008) Relationship between ammonia stomatal compensation point and nitrogen metabolism in arable crops: Current status of knowledge and potential modelling approaches. Environ Poll 154: 390-403.
15. Kruit RJW, Schaap M, Sauter FJ, van Zanten MC, van Pul WAJ (2012) Modeling the distribution of ammonia across Europe including bi-directional surface-atmosphere exchange.

Biogeosci 9: 5261-5277.

16. Dorsey JR, Duyzer JH, Gallagher MW, Coe H, Pilegaard K, et al. (2004) Oxidized nitrogen and ozone interaction with forest. I: Experimental observations and analysis of exchange with Douglas fir. Quart J Royal Met Soc 130: 1941-1955.

17. Oikawa PY, Ge C, Wang J, Eberwein JR, Liang LL, et al. (2015) Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region. Nat Commun 6: 8753.

18. Delmas R, Serça D, Jambert C (1997) Global inventory of NO_x sources. Nutr Cycl Agroecosys 48: 51-60.

19. Ludwig J, Meixner FX, Vogel B, Förstner J (2001) Soil-air exchange of nitric oxide: An overview of processes, environmental factors and modelling studies. Biogeochem 52: 225-257.

20. Almaraz M, Bai E, Wang C, Trousdell J, Conley S, et al. (2018) Agriculture is a major source of NO_x pollution in California. Sci Adv (Appl Ecol) 4: 3477.

21. Sanhueza E, Hao WM, Scharffe D, Donoso L, Crutzen PJ (1990) N_2O and NO emissions from soils of the northern part of the Guayana Shield. J Geophys Res 95: 22,481-22,488.

22. Sutton MA, Milford C, Nemitz E, Theobald MR, Hill PW, et al. (2001) Biosphere-atmosphere interactions of ammonia with grassland: Experimental strategy and results from a new European initiative. Pl Soil 228: 131-145.

23. Hardarson G, Broughton WJ (2001) Maximising the Use of Biological Nitrogen Fixation in Agriculture. Developments in Plant and Soil Sciences, Volume 99, Kluwer Academic Publishers, The Netherlands and FAO/IAEA, Austria.

24. Flessa H, Potthof M, Loftfield N (2002) Greenhouse estimates of CO_2 and N_2O emissions following surface application of grass mulch: importance of indigenous microflora of mulch. Soil Biol Biochem 34: 875-879.

25. Larsson L, Ferm M, Kasimir-Klemedtsson Å, Klemedtsson L (1998) Ammonia and nitrous oxide emissions from grass and alfalfa mulches. Nutr Cycl Agroecosys 51: 41-46.

26. Herrmann B, Jones SK, Fuhrer J, Feller U, Neftel A (2001) N budget and NH_3 exchange of a grass/clover crop at two levels of N application. Pl Soil 235: 243-252.

27. Hopkins A, Gilbey J, Didd C, Bowling PJ, Murray PJ (1990) Response of permanent and reseeded grassland to fertilizer N. I. Herbage production and herbage quality. Grass Forage Sci 45: 43-55.

28. Khalil MI, Hossain MB, Schmidhalter U (2005) Carbon and nitrogen mineralization in different upland soils of subtropics treated with organic materials. Soil Biol Biochem 37: 1507-1518.

29. Weber A, Gutser R, Schmidhalter U (2001a) Field emissions of NH_3 and NO_x following urea application to wheat. In: Horst WJ, Schenk MK, Bürkert A, Claassen N, Flessa H, et al. (eds.). Plant Nutrition - Food Security and Sustainability of Agro-ecosystems. Kluwer Academic Publishers, The Netherlands. Pg: 884-885.

30. Weber A, Gutser R, Schmidhalter U, Henkelmann G (2001b) Unvermeidbare NH_3-Emissionen aus mineralischer Düngung (Harnstoff) und Planzenmulch unter Verwendung einer modifizierten Messtechnik. VDLUFA-Schrift 55: 175-182.

31. Mannheim T, Braschkat J, Marschner H (1997) Ammonia emissions from senescing plants and during decomposition of crop residues. J Pl Nutr Soil Sci 160: 125-132.

32. Thönnissen C, Midmore DJ, Ladha JK, Old DC, Schmidhalter U (2000) Legume decomposition and nitrogen release when applied as green manure to tropical vegetable production systems. Agron J 92: 253-260.

33. Khalil MI, Rosenani AB, Van Cleemput O, Shamshuddin J, Fauziah CI (2002) Nitrous oxide production from an Ultisol treated with different nitrogen sources and moisture regimes. Biol Fertil Soils 36: 59-65.

34. Riedo M, Milford C, Schmid M, Sutton MA (2002) Coupling soil-plant-atmosphere exchange of ammonia with ecosystem functioning in grasslands. Ecol Model 158: 83-110.

35. Herrmann B, Mattsson M, Jones S, Cellier P, Milford C, et al. (2008) Vertical structure and diurnal variability of ammonia exchange potential within an intensively managed grass canopy. Biogeosci Disc 5: 2897-2921.

36. Glasener KM, Palm CA (1995) Ammonia volatilization from tropical legume mulches and green manures on unlimed and limed soils. Pl Soil 177: 33-41.

37. Mastrorilli M, Rana G, Colucci R, Marrone G (1998) Restitution into atmosphere of nitrogen as ammonia from cover crop decomposition (*Vicia faba* - Apulia). Riv di Agron 31: 786-791.

38. Kruit RJW, van Oul WAJ, Otje R, Hofschreuder P, Jacobs AG, et al. (2007) Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new Gradient Ammonia - High Accuracy - Monitor (GRAHAM). Atmos Environ 41: 1275-1287.

39. Johansson C (1989) Fluxes of NO_x above soil and vegetation. In: Andreae MO, Schimel DS (eds.). Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere. John Wiley and Sons, Chichester. Pg: 229-248.

40. Duyzer JH, Dorsey JR, Gallagher MW, Pilegaard K, Walton S (2004) Oxidized nitrogen and ozone interaction with forests. II. Multi-layer process-oriented modelling results and a sensitivity study for Douglas fir. Quart J Royal Met Soc 130: 1957-1972.

41. Hutchinson GL, Vigil MF, Doran JW, Kessavalou A (1997) Modeling the net microbial production and the soil-atmosphere exchange of gaseous NO_x. Nutr Cycl Agroecosys 48: 25-35.

42. Hou AX, Tsuruta H (2003) Nitrous oxide and nitric oxide fluxes from an upland field in Japan: effect of urea type, placement and crop residues. Nutr Cycl Agroecosys 65: 191-200.

43. Hutchinson GL, Brams EA (1992) NO vs. N_2O emissions from an NH_4^+-amended Bermuda grass pasture. J Geophys Res 97: 9889-9896.

44. Russow R, Sich I, Neue H-U (2000) The formation of the trace gases NO and N_2O in soils by the coupled process of

nitrification and denitrification: results of kinetic ^{15}N tracer investigations. Chemos - Gl Ch Sci 2: 359-366.

45. Davidson EA (1993) Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil. In: Oremland RS (ed.). Biogeochemistry of Global Change: Radiatively Active Trace Gases. Chapman and Hall, New York. Pg: 369-386.

46. Remde A, Slemr F, Conrad R (1989) Microbial production and uptake of nitric oxide in soil. FEMS Microb Ecol 62: 221-230.