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Ammonia sources and sinks in an intensively managed grassland canopy

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Abstract. Grasslands represent canopies with a complex structure where sources and sinks of ammonia (NH_3) may coexist at the plant level. Moreover, management practices such as mowing, hay production and grazing may change the composition of the sward and hence the source-sink relationship at the canopy level as well as the interaction with the atmosphere. There is therefore a need to understand the exchange of ammonia between grasslands and the atmosphere better, especially regarding the location and magnitude of sources and sinks.

Fluxes of atmospheric NH_3 within a grassland canopy were assessed in the field and under controlled conditions using a dynamic chamber technique (cuvette). These cuvette measurements were combined with extraction techniques to estimate the ammonium (NH_4^+) concentration and the pH of a given part of the plant or soil, leading to an estimated ammonia compensation point (C_p). The combination of the cuvette and the extraction techniques was used to identify the potential sources and sinks of NH_3 within the different compartments of the grassland: the soil, the litter or senescent "litter leaves", and the functioning "green leaves". A set of six field experiments and six laboratory experiments were performed in which the different compartments were either added or removed from the cuvettes.

The results show that the cuvette measurements agree with the extraction technique in ranking the strength of compartment sources. It suggests that in the studied grassland the green leaves were mostly a sink for NH_3 with a compensation point around 0.1–0.4 $\mu g\,m^{-3}$ and an NH_3 flux of 6 to 7 $ng\,m^{-2}\,s^{-1}$. Cutting of the grass did not increase the NH_3 fluxes of the green leaves. The litter was found to be the largest source of NH_3 in the canopy, with a C_p of up to 1000 $\mu g\,m^{-3}$ NH_3 and an NH_3 flux up to 90 $ng\,m^{-2}\,s^{-1}$. The litter was found to be a much smaller NH_3 source when dried (C_p=160 $\mu g\,m^{-3}$ and F_{NH3}=35 $ng\,m^{-2}\,s^{-1}$ NH_3). Moreover emissions from the litter were found to vary with the relative humidity of the air. The soil was a strong source of NH_3 in the period immediately after cutting (C_p=320 $\mu g\,m^{-3}$ and F_{NH3}=60 $ng\,m^{-2}\,s^{-1}$), which was nevertheless always smaller than the litter source. The soil NH_3 emissions lasted, however, for less than one day, and were not observed with sieved soil. They could not be solely explained by xylem sap flow extruding NH_4^+. These results indicate that future research on grassland-ammonia relationships should focus on the post-mowing period and the role of litter in interaction with meteorological conditions.

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1 Introduction

Ammonia (NH_3) exchange between the vegetation and the atmosphere is bidirectional. Some ammonia can either be emitted or taken up by the leaves through stomatal opening, depending on the relative magnitudes of the atmospheric concentration and the stomatal compensation point concentration (Sutton et al., 1993a; Schjoerring et al., 2001; Massad

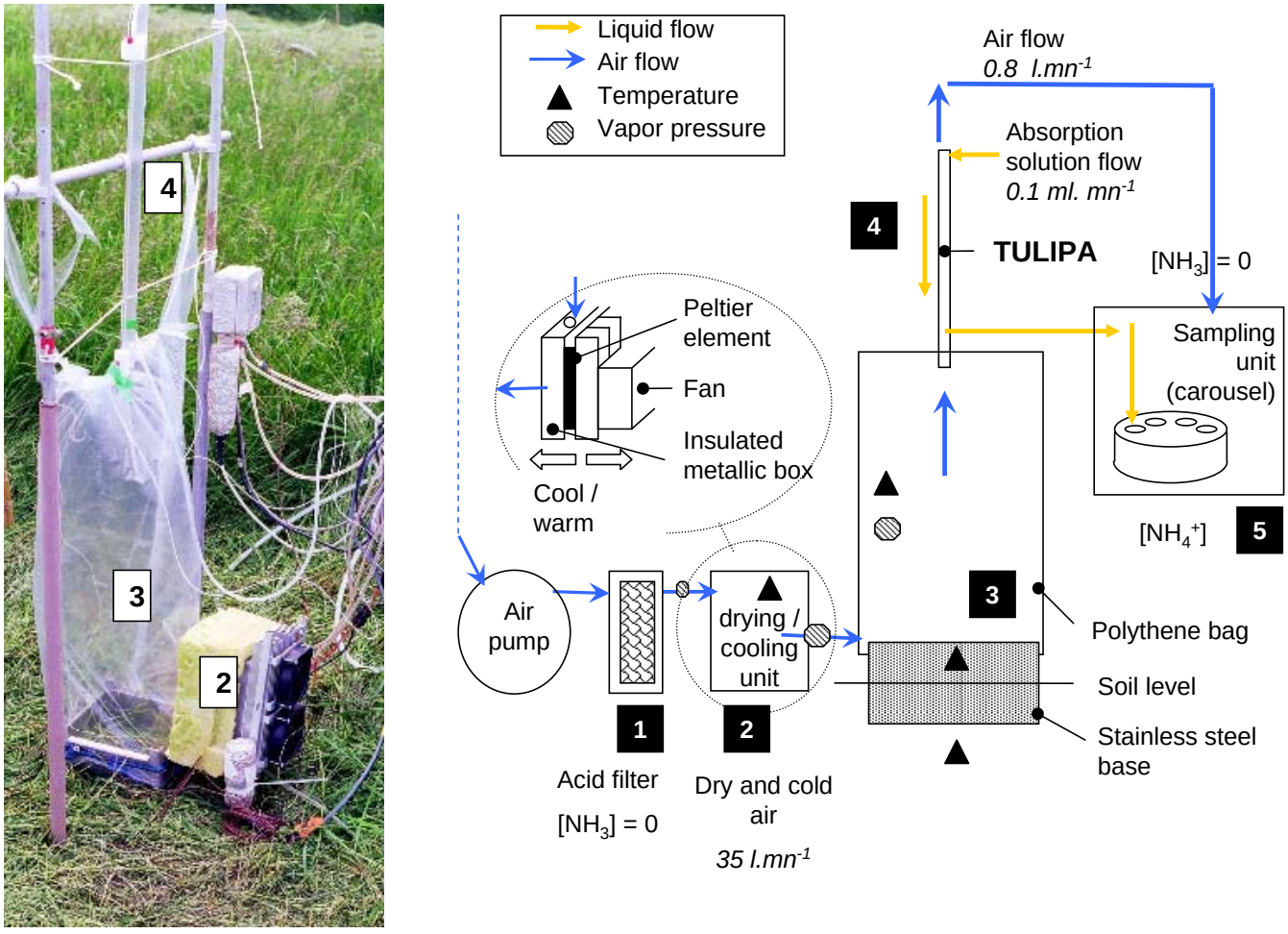

Fig. 1. Photograph and diagram of the dynamic chamber: acid filter (1), cooling unit (2), dynamic chamber itself (3) with the location of temperature and water vapour pressure sensors, TULIPA sensor (4) and sampling-storage unit (5). The blue arrows indicate the air flow and the yellow arrows the liquid flow.

et al., 2008). A significant amount of ammonia can also be deposited to or lost from the water at the surface of the vegetation (Fléchard, 1998). Moreover, NH_3 is emitted from fertilised soils (Génermont et al., 1997) and decomposing litter leaves (Nemitz et al., 2000; Mattsson et al., 2003). Most field studies have investigated the net ammonia exchange – i.e. the balance between emission and deposition – between a canopy and the atmosphere. However, the flux above the canopy results from a complex interaction of sources and sinks at the canopy scale. Nemitz et al. (2000) observed large ammonia concentrations near the ground of an oilseed rape canopy, which were interpreted as emissions from decomposing litter leaves. They showed, using an inverse Lagrangian technique, that the overlying foliage recaptured almost all the NH_3 emitted by the litter leaves, while at the top of the canopy, the siliques (seed cases) emitted NH_3, controlling the net emission from the crop.

Grasslands have been shown to behave either as a source or a sink of NH_3. Measurements by Sutton et al. (1993b) of NH_3 concentration gradients in a 0.85 m tall grassland canopy indicated that the leaves were a source of NH_3 rather than the soil. By contrast, Denmead et al. (1976) observed large NH_3 concentrations just above the ground surface in a grassland, indicating a source at the ground where the litter was located. Based on the literature, four compartments may be considered in grassland canopies regarding NH_3 exchange: the soil, the litter (hereafter defined as senescing attached leaves, dead or decomposing detached leaves), the flowers/ears and the green (photosynthesising) leaves. The purpose of the present work was to check how NH_3 fluxes integrate at the canopy scale in such a complex canopy as grassland. More specifically, this work aimed at assessing the hypotheses, suggested by former studies, that also in grass canopies NH_3 would be emitted by the litter and recaptured by overlying leaves, and check whether the

Table 1. Characteristics of the dynamic chambers. Chambers C1 refers to chambers constructed in polythene film (25 μm width), whereas C2 are stainless steel chambers. Three sizes of C1 chambers were used referred to as C1-20, C1-65 and C1-S. When used in the field, the incoming air was dried and cooled in order to counteract the plant transpiration and the soil evaporation. NH_3 concentration was measured with either an AMANDA analyser (ECN, Petten, NL; Wyers et al., 1993), or a TULIPA sensor (Cellier et al., 2000), both being wet effluent denuder systems, but with different geometries and response time.

Chamber name	Usage	Surface m^2	Volume L	Flow rate L min^{-1}	Residence time min	Cooling/ drying	Analysis	Sampling time min
C1-20	Tall grass	0.04	20	30–40	<1	YES	TULIPA	60–120
C1-65	Cut grass, soil, litter	0.09	65	30–40	∼2	YES	TULIPA	60–120
C1-S	soil	0.0338	20	29–47	<1	NO	TULIPA	60–120
C2	Litter	–	3.6	35–40	<1	NO	AMANDA	2

soil itself was a source or not. For this, we assessed the NH_3 emission potential of the soil, the litter and the green leaves compartments in a grassland canopy near Braunschweig (Germany). The study was based on the use of a set of dynamic chambers under field or controlled conditions, operated simultaneously on plots with different experimental treatments. The dynamic chambers were supplied with ammonia-free air in order to derive an emission under standardized conditions that could be considered as an emission potential and best compared to emission potentials estimated from plant apoplast extracts (Mattsson et al., 2009). Most of this study was carried out in a field experiment within the European project GRAMINAE (GRassland AMmonia INteractions Across Europe) (Sutton et al., 2001, 2009), which was subsequently complemented by two experiments under controlled conditions.

2 Material and methods

2.1 Dynamic chambers

Two types of dynamic chambers were used to measure NH_3 fluxes: a polythene chamber referred to as C1 was used under field and controlled conditions, and a chamber made of stainless steel, referred to as C2, was used only for the measurements under controlled conditions. A photograph and a diagram of the dynamic chamber system C1 are presented in Fig. 1.

The C1 chamber was composed of a square stainless steel frame (15 cm high), inserted into the soil to a depth of 5 cm, and covered with a 25 μm-thick polythene bag attached to the outside part of the base. The chamber surface was adapted to the amount of vegetation inside since more plants create larger evapotranspiration fluxes and, therefore, larger risks of condensation on the chamber walls for a given flow rate in the chamber. A square base area of 20 cm×20 cm was chosen for tall plants and an area of 30 cm×30 cm for cut plants or plants with small leaf area index (LAI) (Table 1). The top of the bag was held in position by attaching it to a metallic frame which was also used to support the NH_3 sensors. The volume of the chambers ranged between 20 and 65 l depending on the frame size and sward height.

The air injected into the chambers was scrubbed of NH_3 for two reasons: to avoid discrepancies between experiments, so that the results would not be influenced by the concentration of ambient air, and to estimate a reference emission. As a matter of fact, the compensation point of vegetation such as grasslands is often on the same order as the ambient concentration in agricultural areas. Moreover, this allowed for better precision in flux measurement and a simpler system since only one NH_3 concentration measurement was required in the chamber. Under such conditions, only emissions can be measured in the chamber. Ammonia free air was generated by blowing air through an ammonia-trapping unit made of a filtration cartridge commonly used for water filtering with a 20 μm pore-size filter coated with citric acid (40 g per cartridge). Then the air flow passed through a cooling unit with condensation trap to dry and cool the air coming into the chamber in order to avoid condensation in the chamber and limit the temperature increase. The cooling unit was made of an aluminium box (17 cm×12 cm×5.5 cm) including a radiator to increase the exchange surface. This box was cooled with two 12 V/18.1 W Peltier elements (Melcor, USA). Other radiators were positioned on the warm side of the Peltier elements and ventilated by a fan to extract extra-heat. The condensed water inside the box could be removed through an opening at the bottom of the box. This cooling unit was attached directly to the chamber to avoid any additional increase in air temperature in tubes between the cooling unit and the chamber.

During the field experiments, the air was pumped at a flow rate between 30 and 40 l min^{-1} from a point at 2.5 m above the ground surface. At this height, the air was expected to have more constant and lower content in water vapour and NH_3 than near the soil surface.

Incoming air was blown from the base of the chamber into the plant canopy. The flow rate was controlled with a mass flow meter (Bronkhorst Hi-Tec BV, the Netherlands), and chosen to exchange the chamber air volume at least once every two minutes, ensuring satisfactory air mixing in the

chamber. There was a slight over-pressure inside the chamber which prevented intrusion of air from the outside, with excess air escaping through leaks in the chamber.

The C2 chambers were made of a flat stainless steel box (L=30 cm; D=20 cm; H=6 cm). Air at the inlet was scrubbed of NH_3 using the same system as in C1, but it was not dried/cooled because it was used only over relatively dry soil and plant samples, and the temperature was controlled in the climatic chamber.

These chamber measurements are based on the mass balance technique, with the particularity that the zero NH_3 inlet concentration meant that only a measurement of the outlet NH_3 concentration was needed to determine NH_3 fluxes. The NH_3 concentration was measured either with an AMANDA analyser (ECN, Petten, NL) (Wyers et al., 1993) or a wet effluent denuder called TULIPA (Cellier et al., 2000). Temperatures were monitored with thin thermocouples (Thermoelectric, Limeil Brevannes, France) mounted in the chamber (within the soil at a depth of 5 cm, at the soil surface when available, at the plants surface and in the air), as well as outside when operated in the field. The vapour pressure was measured in the inlet and the outlet of the chamber using a capacitive hygrometer (HMP35, Vaisala, Helsinki, Finland) to infer the water vapour flux. When operated outside, net radiation was measured at 2 m height with a differential pyrradiometer (type S1, Swissteco Instrument, Oberriet, Switzerland) near the plots. The main characteristics of chambers C1 and C2 are given in Table 1.

2.2 Experimental conditions and treatments

The field study (experiments F1-F6 in Table 2) was conducted from 20 May to 16 June 2000 on a grassland field located near Braunschweig (Lower Saxony, Germany), at the Federal Agricultural Research Centre (Sutton et al., 2009). The soil was sandy and the vegetation was a tall grass canopy dominated by *Lolium perenne*, which was sown in 1996 and had received 300 kg N ha^{-1} y^{-1} since. At the periphery of the main experimental field, a plot of 10 m×10 m was set aside, on which the three C1 chambers were installed, operated simultaneously and moved around regularly. The management of the main field included cutting on 29 May, removal of the cut grass for silage on 31 May and fertilisation on 5 June (Sutton et al., 2009).

The main aim of the chamber measurements was to identify the potential sources of NH_3 in the grassland canopy after cutting, by comparison of the three chambers. One chamber contained cut grassland (hay has been removed) while in the two other chambers the grassland was managed as indicated in Table 2.

Two experiments were conducted later in a controlled temperature room at around 20°C in order (i) to estimate NH_3 emissions from the soil alone under controlled conditions (CS1), and (ii) to investigate the effects of air relative humidity (RH) and litter water content on emissions from litter leaves (CL1–CL2) (see Table 2). The CS1 soil was taken from the field experiment (F1-F6) in Braunschweig (Germany). Due to its texture, the soil had a low volumetric water content (8%). Roots were removed from the soils and the soils were sieved and homogenised. The CS1 soil was frozen at −18°C for transportation and kept frozen until used for experimentation. The litter leaves used in CL1–CL2 came from a *Lolium perenne* experimental sward in Grignon (France). In CL1, the leaves were moisturized by applying double deionised water droplets at their surface, resulting in a water content of 56% on a fresh weight basis. In CL2, dry litter leaves were used, which had 21% fresh weight water content. These leaves were put in a stainless steel chamber for 4 and 10 days, during CL1 and CL2, respectively.

Due to experimental constraints, it was not possible to run more than three chambers at a time. Consequently we could not make replicates for the different treatments in order to circumvent a possible effect of e.g. soil heterogeneity. However, to address the issue of the measurement precision, the chambers were tested prior to the field experiment in a greenhouse using a calibrated NH_3 source. The estimated NH_3 flux was within 10% of the input from the source. Moreover throughout the experimental period, one treatment (F1) was taken as a reference to ensure comparability between the different experimental runs. Additionally, for some analyses, it was a change in conditions of one treatment (i.e. in one chamber) which was studied rather than a comparison between chambers. In this case, the problem of local heterogeneity and the need of replicates do not have the same level of importance. Finally, 4 replicates in time were performed for treatment F1 and 3 replicates for treatment F5, which showed variability of the order of 20%–30% (Table 5).

2.3 Plant N parameters

In order to analyse the potential for emissions from the different compartments of the canopy, the dead and green leaves, the flowers, and stems were separated, weighed and all analysed for bulk ammonium (NH_4^+) and nitrate (NO_3^-) as well as total nitrogen and pH. The bulk extracts were obtained by grinding the plant tissues in liquid nitrogen and adding water before freezing in liquid nitrogen until analysis. The apoplastic NH_4^+ concentration and the pH were also determined on green leaves (F1–F4) after extraction by the vacuum infiltration technique (Mattsson et al., 2009). During experiments F1–F6, all the plant material above the soil surface was harvested at the end of each experiment to measure leaf area, fresh and dry weights (FW and DW, respectively), after drying at 80°C for 24 h. The NH_4^+ analyses were performed with a flow injection system after extraction in a solution of formic acid (Mattsson et al., 2009).

In experiments CL1–CL2, the bulk tissue NH_4^+ and NO_3^- concentrations were determined in an aliquot of the litter leaves at the beginning and at the end of each experiment. The leaves were immediately frozen in liquid nitrogen and

Table 2. Experimental conditions. Three types of experiments were conducted: a field experiment in 2000 in Braunschweig (F1–F6), where all conditions are compared with the reference case (F1, cut grassland without hay), a laboratory experiment to compare different soil emissions (CS1) and another one to estimate the influence of relative humidity on emissions from litter (CL1–CL2). In the two laboratory experiments, the dynamic chambers where placed in a climatic chamber. The air temperature and relative humidity ranges are also given.

Name	Conditions	Chamber type	Treatment details	N fertilisation status	Period	Temp. range °C	RH air range %	Other specific conditions (solar radiation)
F1	Field, Braunschweig	C1-65	Cut grassland, without hay (reference). grass cut the day before, at a height of approximately 5 cm, hay removed	300 kg ha^{-1} y^{-1} N	all dates F2–F6 indicated below	11–31	42–67	max 490 W m^{-2}
F2	Field, Braunschweig	C1-20	Tall grassland. Grass remained uncut, approximately 40–50 cm height	300 kg ha^{-1} y^{-1} N	31 May 2000–1 Jun 2000	3–20	43–78	max 510 W m^{-2}
F3	Field, Braunschweig	C1-65	Cut grassland, with hay. The hay from cutting was put on top of the cut grass	300 kg ha^{-1} y^{-1} N	31 May 2000–1 Jun 2000	11–31	42–67	max 490 W m^{-2}
F4	Field, Braunschweig	C1-65	Cut grassland, litter withdrawn. Cut grassland, with the dead attached leaves and the litter leaves at the ground removed	300 kg ha^{-1} y^{-1} N	13 Jun 2000–14 Jun 2000	14–33	28–75	max 530 W m^{-2}
F5	Field, Braunschweig	C1-65	Bare soil after shoot excision. The shoots were excised at the soil surface. Roots were left present into the soil and the grass stumps were apparent at the soil surface	300 kg ha^{-1} y^{-1} N	3 Jun–4 Jun 2000 and 12 Jun–14 Jun 2000	9–37	35–59	max 560 W m^{-2}
F6	Field, Braunschweig	C1-65	Bare soil and litter. 22.2 g FW (16.7 g DW) of litter picked up outside the chambers were put on top of the bare soil (F5)	300 kg ha^{-1} y^{-1} N	4 Jun 2000–5 Jun 2000	11–25	36–56	max 330 W m^{-2}
F7	Field, Braunschweig	C1-65	Bare soil and litter, 1 mm water added. One mm of water was added on the litter previously cited to investigate the effect of an increase in litter wetness on NH3 exchange	300 kg ha^{-1} y^{-1} N	6 Jun 2000 11–22	51–73	max 330 W m^{-2}	
CS1	Climatic chamber	C1-65	Braunschweig soil (sandy).	300 kg ha^{-1} y^{-1} N	20 Feb–22 Feb 2001	17–20	37–53	no light
CL1	Climatic chamber	C2	Moisturized litter leaves Litter leaves moisturized by applying water droplets at their surface	low Nitrogen status	6 Sep–10 Sep 2001	17–23	53–97	no light
CL2	Climatic chamber	C2	Dry litter leaves.	low Nitrogen status	10 Sep–17 Sep 2001	17–21	55–92	no light
CL3	Climatic chamber	C2	Moisturized litter leaves. Litter leaves moisturized by applying water droplets at their surface	low Nitrogen status	24 Sep–28 Sep 2001	17–20	62–97	no light

kept in a deep-freezer. They were then ground in liquid nitrogen into a thin powder. Approximately 0.1 g FW was then put into 8 ml of deionised water, and left 5 min for equilibration, before filtration with a glass filter (pore size approx. 5 μm) under vacuum. The samples were then diluted in de-ionised water (1:5 v/v) and frozen in liquid nitrogen prior to NH_4^+ analysis by conductometry (AMFIA, ECN, The Netherlands) and pH-measurement (WTM 340, Limonest, France). The total nitrogen content of the litter leaves was measured by the Dumas method (NA 1500, Fisons-Instrument, Thermo Finnigan, Les Ulis, France).

2.4 Soil N parameters

During the field campaign (F1–F6), the soil NH_4^+ and NO_3^- concentrations were measured in the top 10 cm using five samples taken randomly in the field. The soil samples were mixed and immediately frozen. A first sub-sample was analysed for moisture content, and a second sub-sample was extracted and analysed for soil NH_4^+ and NO_3^- concentrations by the Berthelot method and for pH in $CaCl_2$ as described by Mattsson et al. (2009). During field measurements (F1–F6), samples were taken at seven dates following cutting, while during laboratory measurements (CS1), samples were taken once.

2.5 Ammonia emission potentials

The NH_3 emission potential of bulk plant extracts, soil and apoplastic extracts was estimated and is hereafter designated Γ_{plant}, Γ_{soil} and Γ_{stom}, respectively. The NH_3 emission potential in each compartment was defined as:

$$\Gamma = \frac{[NH_4^+]}{[H^+]} \quad (1)$$

where $[NH_4^+]$ is the NH_4^+ concentration in the extract and $[H^+]$ the proton concentration in the extract ($[H^+]=10^{-pH}$).

Table 3. Characteristics of the plant material during each experiment in the chamber as well as the main field characteristics for comparison: fresh weight (FW), water content as percentage of fresh weight, nitrogen (N) content as percentage of dry weight (DW), nitrate [NO_3^-] and ammonium [NH_4^+] concentration in the bulk extracts, pH in the bulk extract, and the NH_3 emission potential Γ_{plant}=[NH_4^+]/10^{-pH}. The number of repetitions (Rep) is also given. The pH values shown in bold are assumed from other measurements: [a] green leaves, stems and flowers of the hay and stems of the cut grassland were assumed to have identical pH as the main field tall grassland; [b] green leaves in the cut grassland was assumed to have the same pH as the main field cut grass; [c] litter leaves in hay and cut grassland were assumed to have the same pH as the litter leaves in the main field. SE is the standard error of the measurements over the number of replicates.

Experiment	Observation	Fresh weight	Water content	N content	[NO_3^-]		[NH_4^+]		pH bulk	Γ_{plant} mean	Γ_{plant} SE	Rep
	–	g	% FW	% DW mean	μmol g^{-1} FW mean	SE	μmol g^{-1} FW mean	SE	–	–	–	–
F1–F6	Litter	–	70	–	28.0	1.6	23.9	1.6	7.0[c]	256 000	16 670	14
(cut grass)	Green leaves	–	25	–	27.0	1.5	2.6	1.5	6.0[b]	2600	1490	14
	Stems	–	69	–	16.8	0.8	1.7	0.8	6.4[a]	3900	1780	14
(main field)	Tall grass	–	–	2.1	1.0	0.0	1.1	0.1	6.4	2600	240	4
	Cut grass	–	–	3.2	14.8	1.7	1.3	0.1	6.0	1320	70	6
	Hay	–	–	2.0	–	–	–	–	–	–	–	3
	Litter	–	–	–	59.3	10.3	13.2	3.1	7.0	142 000	33 680	6
	Stems	–	–	2.1	22.5	2.0	1.1	0.0	6.4[a]	2680	100	5
	Roots	–	–	1.1	–	–	–	–	–	–	–	1
F1–F6	Flowers	–	–	–	0.8	0.1	3.2	0.1	6.4[a]	7480	280	6
(hay)	Litter	–	–	–	18.0	0.5	36.9	0.5	7.0[c]	396 000	4870	5
	Green leaves	–	–	–	4.2	0.3	10.0	0.3	6.4[a]	23 500	650	7
	Stems	–	–	–	8.3	0.5	1.7	0.5	6.4[a]	3940	1280	6
CL1	Litter (start)	8.2	56	1.1	–	–	10.3	0.6	7.6	410 000	23 890	2
	Litter (end)	5.2	26	–	–	–	4.3	0.6	7.4	108 000	15 070	2
CL2	Litter (start)	10.0	21	1.1	–	–	5.2	0.3	6.7	26 100	1500	2
	Litter (end)	11.1	47	–	–	–	3.3	0.2	7.3	65 800	3990	2
CL3	Litter (start)	12.1	61	1.1	–	–	2.4	0.1	6.4	6030	250	2
	Litter (end)	8.5	14	–	–	–	8.3	0.7	6.6	33 000	2790	2

The compensation point concentration (C_p) for a compartment at a given temperature T (°C) is defined as (e.g. Loubet et al., 2002):

$$C_p = \Gamma 10^{-3.4362+0.0508T} \quad (2)$$

3 Results

3.1 Plant and soil NH_4^+, NO_3^- and pH

Hereafter, the terms "litter leaves", "green leaves" and "hay" will refer to the litter leaves, attached or not, at the bottom of the plant, to the active leaves and to the cut plant parts, respectively. The litter leaves in the cut grassland (re-growing plants of approx. 5 cm height) showed much higher bulk NH_4^+ concentration than the green leaves or the stems (Table 3). This difference was not observed for bulk NO_3^- concentration. In the main field, having a canopy consisting of 60–75 cm high plants, there was more NO_3^- and less NH_4^+ in the litter than observed in the cut grassland of our experiments (F1–F6) which were located at the periphery of the main field (Sutton et al., 2009). But the litter concentrations of both NO_3^- and NH_4^+ were still higher than in the other plant compartments. In the hay (excised plants), which probably had started mineralising, the bulk NO_3^- concentration was lower than in the re-growing plants in all compartments, and the bulk NH_4^+ concentration was larger except for the stems. The pH of the litter was 7.0, that of the green leaves of the tall grassland was 6.0 and that of the hay was 6.4.

During the laboratory experiments on litter (CL1–CL2), the bulk NH_4^+ concentration of the litter leaves at the start of each experiment was much smaller than in the field experiments (F1–F7). Moreover, the bulk NH_4^+ concentration in the litter decreased by more than 50% in four days for moisturized litter (CL1), and decreased by about 30% over seven days for the dry litter (CL2). The water content of the moisturized leaves decreased during the experiments from 56% to 26% FW for moisturized litter (CL1), whereas it increased from 21% to 47% FW for the dry litter (CL2). Similarly, the pH decreased in the moisturized leaves (CL1) and increased in the dry litter (CL2) during the experiment. The total N content of the dry and moisturized leaves was similar, allowing the comparison between the treatments.

Table 4. Soil characteristics for each experiment: granulometric composition, soil moisture content, soil nitrate [NO_3^-] and ammonium [NH_4^+] concentration expressed in equivalent nitrogen per mass of dry weight of soil (DW), as well as soil pH, and soil NH_3 emission potential Γ_{soil}=[NH_4^+]/10^{-pH}. In CS1 roots were removed from the sieved homogenised soils prior to experiment, whereas in F1–F6 dynamic chambers were put on the ground. Soils CS1 were frozen at −18°C for transportation and kept frozen before experimentation, which would explain the differences observed in [NO_3^-] and [NH_4^+] concentrations between F1–F6 and CS1.

Name	granulometric composition			soil moisture	Soil [NO_3^-]*		Soil [NH_4^+]*		NO_3^- and NH_4^+	soil pH	Γ_{soil}	Rep
	clay	silt	sand		μg N-NO_3^- g^{-1} DW		μg N-NH_4^+ g^{-1} DW		μg N g^{-1} DW			
	%	%	%	% dry soil	mean	SE	mean	SE	mean	–	–	–
F1	3	34	63	11	11.1	0.4	28.4	2.3	39.5	6.5	85 800	4
F2	3	34	63	14	7.6	0.6	24.1	0.5	31.7	6.4	61 900	7
F3	3	34	63	13	9.6	0.3	34.1	0.5	43.7	6.4	84 900	14
F4	3	34	63	–	–	–	–	–			–	–
F5	3	34	63	11	12.5	1.0	37.5	1.0	50.0	6.4	104 900	3
F6	3	34	63	12	13.3	–	32.4	–	45.7	6.4	76 000	1
F7	3	34	63	11	11.9	–	37.2	–	49.1	6.1	51 400	1
CS1	3	34	63	8	30.9	–	0.2	–	31.1	6.3	360	–

The plant NH_3 emission potential, Γ_{plant}, was largest for litter leaves. It was smaller in the main field (∼140 000), than in the cut grassland F1–F6 (∼260 000), and the hay F1–F6 (400 000). In controlled conditions (CL1–CL3), it ranged from very small in CL3 (6000) to the largest observed value in CL1 (410 000). Γ_{plant} was around 3000–4000 in the stems (main field, cut grassland or hay), and ranged from 1300 to 2600 in the green leaves. The large value of Γ_{plant} obtained for the excised green leaves of the hay (>23 000) suggests that these leaves were starting to senesce. The flowers in the hay had a Γ_{plant} twice as large as the stems.

The soil moisture content (Table 4) was quite constant during field experiments with cut grass F1–F6 (11 to 14% dry weight). Similarly, the soil [NO_3^-] and [NH_4^+] concentration was roughly similar in all experiments with cut grassland (F1–F6) (8 to 13 μg N-NO_3^- g^{-1} DW and 24 to 38 μg N-NH_4^+ g^{-1} DW). The shift in [NO_3^-] and [NH_4^+] between field condition (F1–F6) and controlled conditions (CS1) suggests that nitrification occurred during sample storage and freezing/defreezing. Indeed, the mineral nitrogen content (sum of NO_3^- and NH_4^+ soil) was of the same order in the field F1–F6 and in the later controlled conditions, whereas the NH_4^+ was much larger in F1–F6 than in CS1. The soil pH was relatively constant through F1–F6 and CS1 (ranging from 6.1 to 6.5).

The soil NH_3 emission potential Γ_{soil} was the largest in the bare soil with excised shoots (∼100 000 in F5), possibly denoting a direct emission from the xylem extruded by the shoots. Γ_{soil} was a little bit smaller during the cut grassland experiments (85 000 in F1 and F3), declined further in the uncut grassland soils (60 000 in F2), and was comparable to uncut grassland in bare soil with litter (50 000 and 75 000 in F7 and F6, respectively). However, Γ_{soil} was markedly smaller in controlled conditions CS1 (300 to 6000), reflecting the decrease in NH_4^+ concentration between the sampling and the experiment.

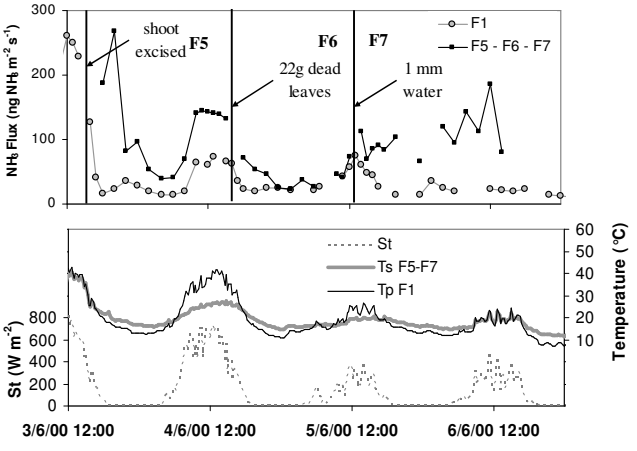

Fig. 2. Time course of NH_3 emissions from the Braunschweig grassland after cutting (F1; open circles), together with NH_3 emissions from bare soil (F5), litter leaves (F6), and moisturized litter leaves (F7) (closed squares). The soil (Ts) and plant (Tp) temperatures, as well as the solar radiation (St) are also given in the bottom graph. Note that roots and stumps were still present in the bare soil. In the bare soil treatment (F5–F7), the shoots were excised on 3 June 2000, then 22 g of litter leaves were added on 4 June 2000, and 1 mm of double deionised water was added on the 6 June 2000.

3.2 Measured NH_3 emissions from soils

The NH_3 emission from the bare soil (including roots and stumps of grass plants excised at the soil surface) was

Table 5. Average NH_3 fluxes and water vapour fluxes (E), as well as air temperature (T_a), relative humidity (RH_a), surface temperature (T_{surf}), and solar radiation above the chambers. The NH_3 emission potential (Γ) for plant, soil or stomata is also reported from Tables 3 and 4, and the equivalent compensation point concentration (C_p) is evaluated at the surface temperature. The value of Γ chosen was: F1, Γ_{plant}(green leaves), as litter was still there; F2, Γ_{stom} (tall green leaves); F3, Γ_{plant} (average of green leaves cut and hay); F4, Γ_{Stom} (cut green leaves); F5, Γ_{soil} (F5); F6, mean of Γ_{plant} (CL2) and Γ_{Soil} (F6) assuming half cover of dry litter; F7: Γ_{plant} (litter leaves). Mean or median and standard deviations or maximum are given for each experiment. NH_3 fluxes in the climatic chamber were scaled to the surface using the LAI measured during the field experiment. The NH_3 flux expressed as a difference with the reference run (F1) is also given. The number of replicated measurements (in time) is given (rep). SE is the standard error of the measurements over the number of replicates.

Name	Treatment details	rep	T_{surf} °C			T_a °C			RH_a %	NH_3 flux ng NH_3 m^{-2} s^{-1} [a]				Diff with ref ng NH_3 m^{-2} s^{-1}	
		–	mean	max	SE[b]	mean	max	SE[b]	range	median	sdev	max	SE[b]	median *	SE[b]
F1	Cut grassland, hay removed (reference)	4	16.9	54.3	0.3	15.9	38.0	0.3	42–67	13	31	145	2	–	–
F2	Tall grassland	1	12.6	20.2		14.3	26.7		43–78	6	15	50		−7	
F3	Cut grassland, with hay	1	12.4	22.2		11.8	27.8	42–67	16	30		125		3	
F4	Cut grassland, litter removed	1	17.0	41.3		17.1	35.5	28–75	7	9		38		−7	
F5	Bare soil	3	18.2	49.7	2.0	16.3	37.2	1.7	35–59	64	45	180	18	51	13
F6	Bare soil and litter	1	18.2	23.5		15.4	21.2	36–56	37	25		73		24	
F7	Bare soil and litter, 1 mm water added	1	17.0	23.7		15.6	22.9	51–73	92	49		185		79	
CS1	Braunschweig soil (sandy)	1	16.4	19.0		18.8	19.7	38–53	11	12		50		−2	
CL1	Moisturized litter leaves	1	19.1	21.2		19.1	21.2	53–97	41	16		95		28	
CL2	Dry litter leaves	1	19.4	20.8		19.4	20.8	55–92	35	20		108		21	
CL3	Moisturized litter leaves	1	19.2	19.9		19.2	19.9	62–97	42	49		184		28	

Name	Treatment details	E μm h^{-1}			Solar radiation W m^{-2}			Γ –		C_p (T_{surf}) μg NH_3 m^{-3}
		mean	sdev	SE[b]	mean	max	SE[b]	mean	SE[b]	mean
F1	Cut grassland, hay removed (reference)	39	44	4	80	825	3	2600	860	6.8
F2	Tall grassland	106	88		97	910		50	10	0.1
F3	Cut grassland, with hay	60	58		82	826		13 050	1070	20
F4	Cut grassland, litter removed	48	34		101	769		160	17	0.4
F5	Bare soil	29	21	3	93	741	24	105 000	3	325
F6	Bare soil and litter	12	5		17	379		61 000	1373	187
F7	Bare soil and litter, 1 mm water added	28	22		34	483		396 000	4870	1058
CS1	Braunschweig soil (sandy)	26	12		–	–		360	–	0.9
CL1	Moisturized litter leaves	3	8		–	–		259 000	19 480	884
CL2	Dry litter leaves	2	5		–	–		46 000	2745	162
CL3	Moisturized litter leaves	8	6		–	–		19 500	1520	68

higher than those observed above cut grassland, especially just after excising the shoots (Fig. 2). During the night and day following the cut, fluxes from the bare soil were roughly twice those from the cut grassland with approx. 5 cm high plants remaining. A repetition of this experiment under field conditions gave similar results (Fig. 3), although in this case the emission from bare soil increased one day after excising the shoots as opposed to the first experiment (Fig. 2) where it increased immediately. Moreover, in Fig. 3, fluxes were smaller in magnitude: with a maximum of 75 ng NH_3 m^{-2} s^{-1} above the bare soil and 50 ng NH_3 m^{-2} s^{-1} above grassland. On average, emissions from the bare soil in field conditions, just after shoot excision, were in the range 45 to 180 ng NH_3 m^{-2} s^{-1}, with a median of 65 ng NH_3 m^{-2} s^{-1}, as compared with 15 ng NH_3 m^{-2} s^{-1} for the cut grassland during the same period. The maximum surface temperature was markedly different between the different runs (Table 5).

Conversely, measurements of NH_3 emissions from the soil in climatic chambers at about 20°C (CS1) showed low NH_3 fluxes, which on average was 11 ng NH_3 m^{-2} s^{-1}. Maximum emissions were 50 ng m^{-2} s^{-1} (Table 5). The NH_3 fluxes were comparable to cut grassland with litter removed (F4), but much less than bare soil with excised shoots (F5). The NH_3 fluxes were often near the detection limit of the measurement system, which indicates that the fluxes were very small compared to what was measured just after excising the shoots under field conditions.

3.3 Emissions of NH_3 from leaf litter

Measurements under field conditions of NH_3 emissions from 22 g FW of litter leaves left on bare soil (F6) and the same leaves after adding 1 mm of deionised water (F7) are shown in Fig. 2, in comparison with emissions from cut grassland (5 cm high plants). During this period, emissions from litter

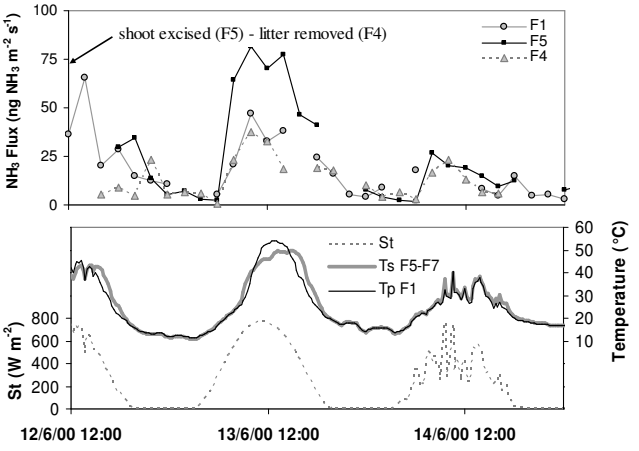

Fig. 3. Time course of NH_3 emissions from the Braunschweig grassland after cutting (F1; open circles), together with NH_3 emissions from bare soil (F5; closed squares) and cut grassland with the litter removed (F4; open triangles). The soil (Ts) and plant (Tp) temperatures, as well as the solar radiation (St) are also given in the bottom graph. Note that roots and stumps were still present in the bare soil. The shoots were excised the 12 June 2000 at about 12:00 in F5, and the litter was removed from F4 at the same date.

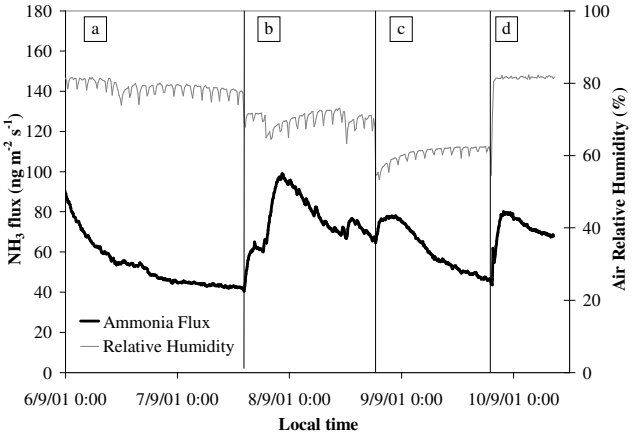

Fig. 4. Ammonia emissions from moisturized litter leaves, measured with a dynamic chamber and an AMANDA (CL1). The measurements were performed in a climatic chamber (20°C), 6–10 September 2001, Grignon, France. **(a)**, **(b)**, **(c)** and **(d)** relate to changes in air relative humidity, which is shown on the secondary axis.

leaves themselves were similar to emissions from cut grassland (37 ng $NH_3\,m^{-2}\,s^{-1}$ on average), apart from the first hour, during which litter leaves were emitting more NH_3 (75 ng $NH_3\,m^{-2}\,s^{-1}$). Conversely, after adding water, the litter leaves started emitting NH_3, and emissions increased up to 185 ng $NH_3\,m^{-2}\,s^{-1}$, which was almost ten times larger than the NH_3 emissions simultaneously measured above cut grassland (Fig. 2). The emissions from moisturized litter leaves increased continuously over 24 h, indicating that decomposition of organic nitrogen might have taken place. During the night, during which the surface temperature did not exceed 18°C, relatively high fluxes occurred above the dead material with an average of 92 ng $NH_3\,m^{-2}\,s^{-1}$ averaged over the whole period. Although the maximum NH_3 emission in F7 was of the same order of magnitude as emissions above bare soil (F5), the maximum surface temperature was a little bit smaller, suggesting that moisturized litter leaves may be a potentially large source of NH_3, comparable or even larger than bare soil after shoot excision.

Emissions from the cut grassland, with the litter removed (F4), were virtually equal to emissions from cut grassland after hay removal (F1) (Fig. 3). A diurnal variation was observed with very low fluxes during night and fluxes increasing during the day with temperature and/or solar radiation.

Under controlled conditions, the effect of air relative humidity on NH_3 emissions from moisturized (CL1, CL3) or dry litter leaves (CL2) was studied at constant temperature. Figure 4 shows the ammonia fluxes and the relative humidity monitored above moisturized litter leaves (CL1, 56% FW; Table 3) over four days. For comparison with F1–F6 data, the fluxes measured under controlled conditions were scaled to the LAI measured in the field. The NH_3 emissions were 41 ng $m^{-2}\,s^{-1}$ NH_3 on average, and maximum 95 ng $m^{-2}\,s^{-1}$ NH_3 (Table 5), which is similar in magnitude to fluxes measured in (F6) and (F7), although the N content was smaller (Table 4). In run CL3 (data not shown) the magnitude of the fluxes was similar, while the leaf water content was even larger at the beginning (61% FW). Under controlled conditions with moisturized leaves (CL1 and CL3), the NH_3 emissions changed after each change in RH: the NH_3 flux first increased for about three hours and then decreased. This behaviour was observed when RH either increased or decreased. Stationary conditions were never reached, even for the longest treatment (>36 h).

In CL2, the leaves were dry when put in the chamber (21% DW), and the fluxes were smaller on average (35 ng m^{-2} leaf area s^{-1} NH_3 Table 5). No sharp increase was observed after a change in RH with dry leaves, as opposed to moisturized leaves (Fig. 4).

3.4 Emission potentials (Γ_{soil}, Γ_{plant}) and NH_3 fluxes measured with the cuvettes

The results in Fig. 5 show a comparison of the NH_3 compensation point concentration (C_p) estimated from Γ_{soil}, Γ_{plant} and Γ_{stom}, with the fluxes of NH_3 per square unit of ground measured with the cuvettes. Bearing in mind that the cuvettes imposed a zero NH_3 concentration at the inlet, these give an indication of the NH_3 emission potential. Although the scatter is important, there is a clear relationship between C_p and the NH_3 fluxes, which enforces the confidence in both the cuvette and the bulk extraction methods as to their ability to adequately rank the different plant compartments with respect to their NH_3 source strength.

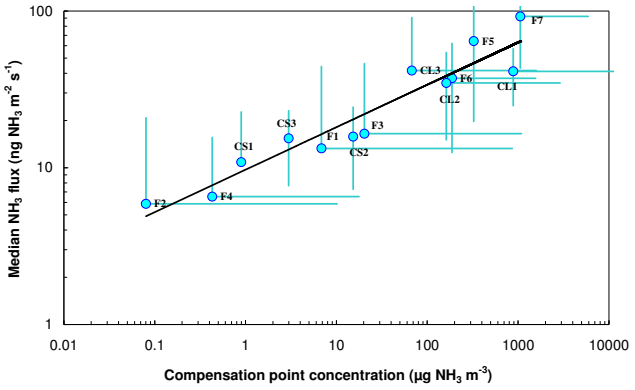

Fig. 5. Median flux of NH_3 in the cuvettes as a function of the NH_3 compensation point concentration estimated from bulk NH_4^+ concentration and bulk pH of the different compartments of the plants and the soil under the conditions of Table 2. Error bars are Standard errors in x and standard deviations in y. The regression line equation is: y=9.71$x^{0.27}$.

4 Discussion

The measured fluxes of NH_3 in plant or soil cuvettes as well as the compensation point estimates from the measurement of NH_4^+ concentration and pH in bulk extracts (Table 5) can be used to analyse the potential sources and sinks of NH_3 in the grassland canopy by comparing the experiments F1–F6, CS1 and CL1–CL2. Even though no replicates could be made for the different trials, most of the results showed significant differences or a clear trend after a change in (Fig. 2) conditions. Moreover the F1 treatment which was applied over all the periods on different places showed little variations, which give an indication that time and spatial variability was certainly not large in the context of this field. The same applies for the treatment F5, which was applied twice on two different locations and gave similar trend when compared to F1. This gives confidence in the effects that were observed. The NH_3 emission potential of the soil, litter, and green leaves compartments are discussed in the following.

4.1 Green leaves

The ammonia stomatal compensation point of green leaves has been reported to be lower than the one of the senescent leaves in previous studies (Husted et al., 1996; Nemitz et al., 2000; Mattson et al., 2003). Under our experimental conditions and before cutting, the ammonia stomatal compensation point in green leaves of tall grass ($0.55\,\mu g\,m^{-3}$) was in the range of the smallest values reported in the literature. For instance, in *Luzula sylvatica* (Huds.) the compensation point determined by gas exchange measurements ranged between 0.51 and 1.10 μg $NH_3\,m^{-3}$ (Hill et al., 2001). In a grass sward, the compensation point measured in the lab with a mini wind-tunnel was between 0.5 and 1.9 μg $NH_3\,m^{-3}$ (Ross and Jarvis, 2001). For *Lolium perenne* L. in a grassland, it ranged from 0.04 to 0.5 μg NH_3 m^{-3} between fertilisation periods (Loubet et al., 2002). Using the vacuum infiltration technique, Van Hove et al. (2002) determined larger emission potentials for *Lolium perenne* L., with compensation points in the range 0.5–4.0 μg $NH_3\,m^{-3}$ and median values between 1.5 and 2.0 μg $NH_3\,m^{-3}$. Using the aerodynamic gradient method over non-fertilized grassland, Wichink-Kruit et al. (2007) observed much larger values, with canopy compensation point varying from 0.5 up to 29.7 μg $NH_3\,m^{-3}$, with an average of 7.0 μg $NH_3\,m^{-3}$. These high values were interpreted as caused by high nitrogen input in the past and high atmospheric deposition from local sources. However the comparison is not straightforward, as one part of the variation may be due to variation in temperature, especially with high temperature during the summer period. Moreover, most of these values at canopy level also include emission from litter.

The emission potential of the green leaves after cutting remained small, as indicated by the small Γ_{plant} as well as by the small NH_3 fluxes in the cuvettes above cut grassland (F1, F3, F4). Clearly, the cut grassland with litter removed (F4) showed the smallest flux of NH_3 of all experiments (Table 5). The Γ_{plant} of the green leaves after cutting were of the same order of magnitude as before cutting which confirms the results of Loubet et al. (2002), who showed that cutting did not have an immediate effect on the bulk and stomatal emission potential (Γ_{plant} and Γ_{stom}).

4.2 Ammonia emissions from the soil

Soil below vegetation has seldom been shown to be an ammonia source, neither below a grassland canopy in summer time (Sutton et al., 1993b), below a barley crop (Schjoerring et al., 1993), or below an oilseed rape canopy (Nemitz et al., 2000). Neftel et al. (1998) even suggested by directly measuring NH_3 concentration in the soil, that soil could be a sink for ammonia in a triticale field. However, in this study, bare soil was found to have a large Γ_{soil} under field conditions (Table 4), but only showed large emissions in the cuvette just after shoot excision (F5) (Table 5). The fact that small emissions were found above grassland (F1–F4) as compared to bare soil (F5), even though the Γ_{soil} was large, may be explained by the recapture of NH_3 by the functioning "green" leaves of the grassland, which had a much lower Γ_{plant}, a process clearly demonstrated by Nemitz et al. (2000).

However, Figs. 2 and 3 suggest that the NH_3 emissions after shoot excision only lasted one day or so. This transient NH_3 emission may be promoted by rapid evaporation of soil water following the cut. Indeed, the evaporation in F5 is of the same order as the evaporation after adding 1 mm of water on litter leaves (F7), but is twice the evaporation in F6 (bare soil with litter but without water). An alternative explanation would be an NH_3 flux driven by the xylem sap flow bleeding through the cut stems. The sap flow is driven by the root

pressure and is known to be able to last from several hours to one day (Smith, 1970; Barthes et al., 1996). The xylem contains NH_4^+ concentrations as high as several mM (Pilbeam and Kirby, 1992; von Wirén et al., 2001; Schjoerring et al., 2002). The emission from the sap flow was estimated as the measured water evaporation multiplied by the NH_4^+ concentration of the xylem sap assumed to equal the bulk NH_4^+ concentration in the stems (1.5 mM). This evaluation results in a calculated flux of 8.5 ng NH_3 m^{-2} s^{-1} on average, which only amounts to about 10% of the measured NH_3 flux in the chamber (F5, Table 5). It may be argued that the emission pulse observed just after shoot excision may be due to NH_4^+ at the soil surface that were left by the litter which was in contact with it just before removal. The large Γ_{soil} measured in F5, which decreased in F6 and F7, however, seems to suggest that the emission was really linked with a large quantity of available NH_4^+ in the soil itself.

In the laboratory, much lower emissions and Γ_{soil} were found on the same soil after freezing and sieving (CS1) (Tables 4 and 5). This is probably due to NH_4^+ being nitrified during transport and storage as shown by the NH_4^+ concentration being almost zero in CS1 whereas it was about 30 μg N-NH_4^+ g^{-1} DW in the field, while in the mean time the sum of NO_3^- and NH_4^+ content was only diminished by 25%. The missing fraction of nitrogen might have been lost by volatilisation, denitrification or assimilation during storage (Darrah et al., 1983).

Finally, this analysis suggests that the bare soil can be a significant source of NH_3 only for a limited period and only when the cut vegetation is removed but not if the soil surface remains covered by the grass. In the latter case, the low Γ_{plant} of green leaves (even recently cut) may favour recapture of NH_3 emitted by soil.

4.3 Litter NH_3 emissions and relative humidity

The litter, which was composed of both senescing and dead leaves, either lying free on the ground surface or attached at the base of the plants, had a large emission potential under all situations as shown by bulk extraction estimation of Γ_{plant} (Tables 3 and 5) and NH_3 flux measurements in cuvettes both in the lab (CL1–CL3) and in the field (F6–F7) (Table 5). This result is similar to what was observed for litter of wheat (Harper et al., 1987), an old cultivar of barley (Husted et al., 1996), perennial ryegrass (Whitehead and Lockyer, 1989) or rape-seed crops (Schjoerring et al., 1998; Nemitz et al., 2000; Mattsson and Schjoerring, 2003). The Γ_{plant} of litter or litter leaves was typically a hundred times that of green leaves and 5 to 8 times that of the soil. Moreover, as the litter is more accessible to the open-air, it makes it a larger NH_3 source than bare soil (Table 5).

However, the emissions from the litter is a complex process, which seems to depend on the litter water content, as shown by the difference between dry (F6, CL2) and moisturized litter leaves (F7, CL1–CL3) (Table 5, Figs. 4–5). The degradation process leading to NH_3 emission is due to biochemical and microbial processes the leaf surface and inside the leaf (Farquhar et al., 1979), but it was not possible in this study to make the share between these two contributions. Indeed, lower NH_3 fluxes and Γ_{plant} were observed for dry litter than for moisturised litter (except for Γ_{plant} in CL3 for unexplained reasons). Moreover, experiments under controlled conditions (CL1–CL3, Figs. 4–5) show that the emission of NH_3 increased systematically after a change in relative humidity. The time constant of this process could not be estimated precisely, but it was of the order of several hours. This might be due to two contradictory effects. When air relative humidity increases, it might increase plant water content and hence promote organic matter mineralization and NH_4^+ production (see e.g. Fig. 4d). When relative humidity decreases, it promotes evaporation and decreases plant water content, thus increasing NH_4^+ concentration and NH_3 volatilisation (see section b in Fig. 4). This is consistent with the findings of Nemitz et al. (2000) who demonstrated with a simple dynamical model that shrinking liquid pools within the leaf litter lead to more concentrated NH_4^+ pools and increased emissions.

4.4 Source-sink relationships at canopy level

The contribution of emission from the litter to the net canopy flux is however diminished by the recapture by green leaves as shown by the small emissions in F1 (cut grassland with litter). Similarly as for soil emissions, the low emission potential of green leaves suggests a recapture of the NH_3 emitted by the litter. This is consistent with the source/sink analysis of NH_3 in the Braunschweig grass canopy which suggests that a ground level source (presumably from the litter leaves) was re-captured within the tall canopy prior to cutting (Nemitz et al., 2009).

Figure 5 showed that an estimate of $\Gamma=[NH_4^+]/[H^+]$ from either the bulk extract of the plants or the soil or the stomatal extract may be sufficient to identify the main sources and sinks within a canopy: the highest values of Γ identify the potential sources, while the lowest values identify the potential sinks. The ability of the canopy to emit or absorb then depends on the relative location of the sources and sinks and on the aerodynamic resistances between the layers: if the sources are at the bottom of the canopy (litter and soil) and the sinks above (case of the tall grassland), the canopy may be a net sink, but if some sources are at the top of the canopy (as were the siliques of a flowering oilseed rape studied by Nemitz et al., 2000), the canopy may be a net source of NH_3. This point is illustrated by experiments F1–F6, which indicates that the litter and the soil may both act as a source when the grass is removed but that the observed net emissions of NH_3 are small when the grass is present.

5 Conclusions

The cuvette experiments and the extractions performed in this study for different grassland managements and in several parts of the canopy allowed the measured NH_3 fluxes (the cuvettes had a forced zero NH_3 concentration at the inlet, hence they give a potential for NH_3 emission which enables better comparison between experiments and treatments) to be compared with the NH_3 compensation point concentration (C_p) evaluated from extraction of the bulk, soil or stomatal NH_4^+ and pH. The combination of the two methods provides a useful means to identify the main sources or sinks of NH_3 in the canopy:

- The wet litter leaves were found to be the main potential source of NH_3 within the grassland canopy with a bulk Γ of up to $\sim$400 000.
- The soil was also identified as a strong potential source (Γ up to $\sim$100 000), but only directly after excision of shoots for a short period and only for fresh soil (after freezing and sieving the soil, the emissions were low). Sap extrusion from the shoot was shown to contribute but to be insufficient to explain the observed emissions.
- The green (or photosynthesising) leaves were a clear sink of NH_3 before and after cutting the grass, with a bulk Γ being an order of magnitude (at least) lower than the other compartments ($\sim 50 < \Gamma < \sim 2600$).

Emissions from litter leaves showed a peak both after a step decrease or a step increase of air relative humidity, due to change either increased mineralization or increased evaporation. This latter process as well as the reasons for observed soil emissions after shoot excision should however be further studied to better understand the contribution of litter to the NH_3 net flux and its dependence on meteorological conditions.

In terms of grassland management, cutting grassland under wet conditions should be avoided, which is consistent with the conditions which are sought for hay drying in the field, but less for silage production or hay drying in barn. However, the best way to decrease NH_3 emission is to leave sufficient green leaves after cutting, to promote ammonia recapture by the active vegetation. This would mean more frequent grass cutting over the growth cycle.

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