Ammonia sources and sinks in an intensively managed grassland using dynamic chambers

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Abstract

Grassland is a canopy with a complex structure where sources and sinks of ammonia 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-sinks relationship at the canopy level as well as the interaction with the atmosphere. There is therefore a need to better understand the exchanges of ammonia between grasslands and the atmosphere, especially regarding the locations of sources and sinks and their magnitudes.

Fluxes of atmospheric ammonia (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 “litter leaves”, and the functioning “green leaves”. A set of 6 field experiments and 6 laboratory experiments were performed in which the different compartments were either added or removed from the cuvettes.

This study shows that the cuvette measurements agree with the extraction technique in ordering the strength of compartment sources. It suggests that in the studied grassland the green leaves are mostly a sink for NH$_3$ with a compensation point around 0.1–0.4 µg m$^{-3}$ NH$_3$ and an NH$_3$ flux of 6 to 7 ng m$^{-2}$ s$^{-1}$ NH$_3$. 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 compensation point up to 1000 µg m$^{-3}$ NH$_3$ and an NH$_3$ flux up to 90 ng m$^{-2}$ s$^{-1}$NH$_3$. The litter was found to be a much smaller NH$_3$ source when dried ($C_p=160$ µg m$^{-3}$NH$_3$ and $F_{NH_3}=35$ 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 ($C_p=320$ µg m$^{-3}$ NH$_3$
and $F_{\text{NH}_3} = 60 \text{ ng m}^{-2} \text{ s}^{-1} \text{NH}_3$), although always relatively smaller than the litter source. The soil NH$_3$ emissions were, however, not lasting more than one day, and were not observed with sieved soil. Soil emissions 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.

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 difference between the atmospheric concentration and the stomatal compensation point concentration (Sutton et al., 1993a; Schjoerring et al., 2001; Massad et al., 2008). A significant quantity 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 by decomposing litter leaves. They showed by inverse lagrangian technique that the above-attached leaves recaptured almost all the ammonia emitted by the litter leaves, while at the top of the canopy, the siliques were emitting NH$_3$, leading to a net emission from the crop.

Grassland has 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. On the opposite, 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 lying. Based on the literature, four compartments may be considered in grassland canopies regarding NH$_3$ exchange: the soil, the litter (senescing attached leaves, dead or decomposing detached leaves), the flowers/ears and the green (photosynthesising) leaves. The purpose of the present work was to assess the NH$_3$ emission potential of the soil, the litter and the green leaves compartments in a grassland canopy in Braunschweig (Germany). The study is based on the use of a set of dynamic chambers under field or controlled conditions, operated simultaneously on plots with different experimental treatments in order to evaluate the emissions from the soil, the litter and the green leaf compartments. 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, 2008), and 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 under controlled conditions.

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 $\mu$m-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 evaporative fluxes and, therefore, larger risks of condensation on the chamber walls for a given flow rate in the chamber. A 20 cm $\times$ 20 cm square was chosen for tall plants and a 30 cm $\times$ 30 cm square for cut plants or plants with small LAI. The top of the bag was held in position by attaching it to a metallic frame which was also used to support the ammonia sensors.
The volume of the chamber ranged between 20 and 65 l depending on the frame size and sward height.

During the field experiments, the air was pumped from a point at 2.5 m above the ground surface at a flow rate between 30 and 40 l min\(^{-1}\). At this height, the air was expected to have more constant and lower content in water vapour and ammonia than near the soil surface. In order to have zero-ammonia air, it was blown 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 went through a cooling unit to dry and cool the air coming into the chamber in order to avoid condensation in the chamber and limit 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). Others radiators were positioned on the warm side of the Peltier elements and ventilated by a fan to evacuate 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 an additional increase in air temperature in tubes.

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 equal at least to one chamber air volume every two minutes, ensuring satisfactory air mixing in the chamber. Air in excess went out through leaks in the chamber and there was a slight over-pressure inside the chamber which prevented intrusion of air from the outside.

The C2 chambers were made of a flat stainless steel box (L=30 cm; l=20 cm; h=6 cm). Air at the inlet was cleaned for ammonia 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 temperature was controlled in the climatic chamber.

These chamber measurements are based on the mass balance technique, with the particularity that inlet NH\(_3\) concentration is forced to zero with the acid traps, therefore
requiring only measurements of the outlet NH$_3$ concentration to determine NH$_3$ fluxes. The NH$_3$ concentration was measured either with an AMANDA analyser (ECN, Petten, NL) or a wet effluent denuder called TULIPA (Cellier et al., 2000). The flow rate was measured with mass flow meter (Bronkhorst, Netherland). Temperatures were monitored with thin thermocouples (Thermoelectric, Limeil Brevannes, France) mounted in the chamber (soil at a depth of 5 cm and soil surface when available, plants surface and 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 pyradiometer (type S1, Swisstec 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 (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., 2008). 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. A plot of 10×10 m was settled, on which the three C1 chambers were installed, operated simultaneously and moved around regularly.

The main aim of the field experiment was to identify the potential sources of NH$_3$ in the grassland canopy after cutting, by comparison of the 3 chambers. One chamber contained cut grassland and no litter, 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 compare NH$_3$ emissions from three different grassland soils (CS1-CS3), and (ii) to investigate the effects of air relative humidity and litter water content on emissions from litter leaves (CL1-CL2) (See Table 2). The three soils compared in
CS1-CS3 are described in Table 4. The CS1 soil was sandy with 8% water content, taken from the field experiment (F1-F6) in Braunschweig (Germany); CS2 was a clay-silt soil with 28% water content, taken from a French grassland field in Mirecourt (France); CS3 was a silt-clay soil with 16% water content, taken from a low fertilised sward in the INRA experimental farm in Grignon (France). Roots were removed from the soils and the soils were sieved and homogenised. Soils CS1 and CS2 were frozen at −18°C for transportation and kept frozen until used for experimentation, while soil CS3 was taken in the field before each experiment. 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.

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$_3^-$) concentration as well as total nitrogen and pH. The bulk extracts were obtained by grinding the plant tissues in liquid nitrogen and adding up water before freezing in liquid nitrogen, prior to 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., 2008). 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). Drying was performed 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., 2008).

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 experi-
ment. The leaves were immediately frozen in liquid nitrogen and kept in a deep-fryer. 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 (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 NH₄⁺ analysis by conductivity (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 ammonium and nitrate concentrations were measured in the top 10 cm using 5 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 ammonium and nitrate concentrations by the Berthelot method and for pH in CaCl₂ as described by Mattsson et al. (2008). During field measurements (F1-F6), samples were taken at 7 dates following cutting, while during laboratory measurements (CS1-CS3), samples were taken once.

2.5 Ammonia emission potentials

The NH₃ emission potential of bulk plant extracts, soil and stomatal extracts was estimated and is hereafter designated Γplant, Γsoil and Γstom, respectively. The NH₃ emission potential in each compartment was defined as:

\[
Γ = \frac{[\text{NH}_4^+]}{[\text{H}^+]} \tag{1}
\]

where \([\text{NH}_4^+]\) is the NH₄⁺ concentration in the extract and \([\text{H}^+]\) the proton concentration in the extract (\([\text{H}^+] = 10^{-pH}\)). The compensation point concentration (\(C_p\), in µg m⁻³)
NH$_3$) for a compartment at a given temperature $T$ (°C) is defined as (see e.g. Fléchard, 1998):

$$C_p = \Gamma 10^{-3.4362+0.0508T}$$

(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 plants, respectively. The litter leaves in the cut grassland (re-growing plants of approx. 5 cm height) showed much higher bulk NH$_4^+$ concentration (23.9±1.6 µmol g$^{-1}$ FW) than the green leaves (2.6±1.5 µmol g$^{-1}$ FW) or the stems (1.7±0.8 µmol g$^{-1}$ FW) (Table 3). This difference was not observed for bulk NO$^-_3$ concentration: 28.0±1.6 µmol g$^{-1}$ FW for litter leaves, 27.0±1.5 µmol g$^{-1}$ FW for green leaves and 16.8±0.8 µmol g$^{-1}$ FW for the stems in cut grassland (Table 3). In the main field, having with a canopy consisting of 34–40 cm high plants, there was more NO$_3$ and less NH$_4^+$ in the litter than observed in the cut grassland (F1-F6) which were performed in a 100 m$^2$ plot at the periphery of the main field. 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 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 whereas the pH of the green leaves was 6.0 and 6.4 for tall grassland and hay, respectively.

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) (10.3±0.6 and 5.2 ±0.3 µmol g$^{-1}$ FW for CL1 and CL2, respectively). Moreover, the bulk NH$_4^+$ concentration in the litter decreased by more than 50%
in 4 days for moisturized litter (CL1), and decreased by about 30% in 7 days for 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.

The plant NH$_3$ emission potential, $\Gamma_{\text{plant}}$, was largest for litter leaves. It was smaller in the main field ($\sim$140 000), than in the cut grassland F1-F6 ($\sim$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). $\Gamma_{\text{plant}}$ 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 $\Gamma_{\text{plant}}$ obtained for the excised green leaves of the hay (>23 000) suggests that these leaves were starting senescing. The flowers in the hay had a $\Gamma_{\text{plant}}$ twice as large as the stems.

The soil moisture content (Table 4) was quite constant during field experiments with cut grassland F1-F6 (11 to 14% dry weight), while it was pronouncedly different between CS1, CS2 and CS3 (8 to 28% 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 $\mu$g N-NO$_3^-$ g$^{-1}$ DW and 24 to 38 $\mu$g N-NH$_4^+$ g$^{-1}$ DW) while it was markedly different between soils (CS1, CS2 and CS3) (5 to 31 $\mu$g N-NO$_3^-$ g$^{-1}$ DW and 0.2 to 3.1 $\mu$g N-NH$_4^+$ g$^{-1}$ DW). The soil [NO$_3^-$] and [NH$_4^+$] changed a lot between field conditions (F1-F6) and later controlled conditions (CS1), probably because nitrification occurred during the storage of the samples between the two set of experiments. Indeed, the mineral nitrogen content (sum of NO$_3^-$ and NH$_4^+$ soil s) were 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 two other soils from Mirecourt (CS2) and Grignon (CS3) had significantly lower mineral nitrogen content, which is partly explained by the nitrogen fertilisation, which was smaller in Grignon and Mirecourt than in Branschweig (Table 2).
pH was relatively constant through F1–F6 and CS1 (ranging from 6.1 to 6.5).

The soil NH$_3$ emission potential $\Gamma_{\text{soil}}$ 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. $\Gamma_{\text{soil}}$ 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, $\Gamma_{\text{soil}}$ was markedly smaller in controlled conditions and in Grignon and Mirecourt soils CS1-CS3 (300 to 6000), reflecting the small ammonium concentration in these soils.

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 higher than those observed above cut grassland, especially just after excising the shoots (Fig. 1). During the following night and the following day, 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. 2), although in this case the emission from bare soil increased one day after excising the shoots as opposed to the first experiment (Fig. 1) where it immediately increased. Moreover, in Fig. 2, fluxes were smaller in magnitude: 75 ng NH$_3$ m$^{-2}$ s$^{-1}$ above the bare soil and 50 ng NH$_3$ m$^{-2}$ s$^{-1}$ above grassland, as a maximum. 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 to 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 in climatic chambers at about 20°C from three soils (CS1-CS3), showed low NH$_3$ fluxes, which on average ranged from 11 to 16 ng NH$_3$ m$^{-2}$ s$^{-1}$. Maximum emissions were of 50 ng m$^{-2}$ s$^{-1}$ (Table 5). The NH$_3$
fluxes were comparable for the three soils, although they received contrasting amounts of nitrogen and had differing levels of $\text{NH}_4^+$ content and $\Gamma_{\text{soil}}$. The $\text{NH}_3$ fluxes were often near the detection limit of the measurement system, which might explain why no difference appeared between the soils, but which also indicates that the fluxes were very small compared to what was measured just after excising the shoots under field conditions.

3.3 Emissions of $\text{NH}_3$ from leaf litter

Measurements under field conditions of $\text{NH}_3$ 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. 1, in comparison with emissions from cut grassland (5 cm high plants). Emissions from litter leaves themselves were similar to emissions from cut grassland during the period (37 ng $\text{NH}_3$ m$^{-2}$ s$^{-1}$ on average), apart during the first hour, where litter leaves were emitting more $\text{NH}_3$ (75 ng $\text{NH}_3$ m$^{-2}$ s$^{-1}$). Conversely, after adding water, the litter leaves started emitting $\text{NH}_3$, and emissions increased up to 185 ng $\text{NH}_3$ m$^{-2}$ s$^{-1}$, which was almost 10 times larger than the $\text{NH}_3$ emissions simultaneously measured above cut grassland (Fig. 1). The emissions from moisturized litter leaves increased continuously over 24 h, indicating that decomposition of organic nitrogen might have taken place. During the night, while the surface temperature did not exceed 18°C, relatively high fluxes occurred above the dead material with an average of 92 ng $\text{NH}_3$ m$^{-2}$ s$^{-1}$ during the whole period. Although the maximum $\text{NH}_3$ emission in F7 was of the same order 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 $\text{NH}_3$, 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 themselves (Fig. 2). A diurnal variation was observed with very low fluxes during night and fluxes increasing during the day with temperature
Under controlled conditions, the effect of air relative humidity on NH₃ emissions from moisturized (CL1, CL3) or dry litter leaves (CL2) was studied at constant temperature. Figure 3 shows the ammonia fluxes and the relative humidity monitored above moisturized litter leaves (CL1, 56% FW; Table 3) over 4 days. The NH₃ emissions was 41 ng m⁻² leaf area s⁻¹ NH₃ on average, and maximum 95 ng m⁻² leaf area s⁻¹ NH₃ (Table 5), which is much smaller in magnitude than fluxes measured in (F6) and (F7), although the mass of plants was also smaller (8.2 g FW as compared to 22 g FW). These smaller fluxes may be explained by the lower nitrogen fertilisation in CL1-CL3 than in F1-F6, which is shown by the N content being smaller (1.1% N DW in CL1-CL3 versus 2.1% N DW in the field). 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 (CL1) and (CL3), with moisturized leaves, the NH₃ emissions changed after each change in RH: the NH₃ flux first increased during about 3 h 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 where smaller on average (35 ng m⁻² leaf area s⁻¹ NH₃ Table 5). No sharp increase after a change in RH was observed with dry leaves, as opposed to moisturized leaves (Fig. 3).

4 Discussion

The measured fluxes of NH₃ in plant or soil cuvettes as well as the compensation point estimates from NH₄⁺ concentration and pH measured in bulk extracts (Table 5) can be used to analyse the potential sources and sinks of NH₃ in the grassland canopy by comparing the experiments F1-F6, CS1-CS3 and CL1-CL2. The NH₃ 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 (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 µg NH₃ m⁻³) was in the range of the smallest reported values. For instance, in *Luzula sylvatica* (Huds.) the compensation point determined by gas exchange measurements ranged between 0.51 and 1.10 µg NH₃ m⁻³ (Hill et al., 2001). In grass sward the compensation point measured in the lab with mini wind-tunnel was between 0.5 and 1.9 µg NH₃ m⁻³ (Ross and Jarvis, 2001). For *Lolium perenne* L. in a grassland, it ranged from 0.04 to 0.5 µg NH₃ m⁻³ between fertilisation periods (Loubet et al., 2002). Using the infiltration technique, Van Hove et al. (2002) observed larger emissions over *Lolium perenne* L., with values in the range 0.5–4.0 µg NH₃ m⁻³ and median values between 1.5 and 2.0 µg NH₃ 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 to 29.7 µg NH₃ m⁻³, with an average of 7.0 µg NH₃ m⁻³. These high values were interpreted as caused by high nitrogen input in the past and high atmospheric deposition from local sources, as well as high temperature during the summer period. Moreover, 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 NH₃ fluxes in the cuvettes above cut grassland (F1, F3, F4). Clearly, the cut grassland with litter removed (F4) showed the smallest flux of NH₃ 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 any immediate effect on the bulk and stomatal emission potential (Γ_{plant} and Γ_{stom}).
4.2 Ammonia emissions from bare soil

Bare soil 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. However, in this study, the bare soil was found to have a large $\Gamma_{\text{soil}}$ 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 $\Gamma_{\text{soil}}$ was large, may be explained by the recapture of NH$_3$ by the functioning “green” leaves, which had a much lower $\Gamma_{\text{plant}}$, a process clearly demonstrated by Nemitz et al. (2000).

However, Fig. 2 suggests that the NH$_3$ emissions after shoot excision only last a 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). Another 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 can be 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 NH$_4^+$ 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 $\Gamma_{\text{soil}}$ measured in F5, which decreased in F6 and F7, seems however to suggest that the
emission was really linked with a large quantity of available \( \text{NH}_4^+ \) in the soil itself.

In the laboratory, much lower emissions and \( \Gamma_{\text{soil}} \) were found on the same soil after freezing and sieving (CS1) (Tables 4 and 5). The latest effect is probably due to ammonium being nitrified as shown by the \( \text{NH}_4^+ \) concentration being almost zero in CS1 whereas it was about 30 \( \mu \text{g N-NH}_4^+ \text{ g}^{-1} \text{ DW} \) in the field, while in the mean time the sum of \( \text{NO}_3 \) and \( \text{NH}_4^+ \) content was only diminished by 25%. The missing fraction of nitrogen might have been lost by volatilisation during storage or immobilisation on the soil mineral or organic matter (Darrah et al., 1983).

Finally, this analysis suggests that the bare soil can be a significant source of \( \text{NH}_3 \) 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 \( \Gamma_{\text{plant}} \) of green leaves (even recently cut) may favour re-absorption of \( \text{NH}_3 \) emitted by soil.

4.3 Litter \( \text{NH}_3 \) emissions and relative humidity

The litter, which was composed of both senescing and litter 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 \( \Gamma_{\text{plant}} \) (Tables 3 and 5) and \( \text{NH}_3 \) flux measurements in cuvettes both in the lab (CL1-CL3) or 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 crop (Schjoerring et al., 1998; Nemitz et al., 2000; Mattsson and Schjoerring, 2003). The \( \Gamma_{\text{plant}} \) 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 the \( \text{NH}_3 \) source larger than for bare soil (Table 5).

The emission from the litter is however diminished by the presence of 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 \( \text{NH}_3 \)
emitted by the litter.

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. 3–4). Indeed lower NH$_3$ fluxes and $\Gamma_{\text{plant}}$ were observed for dry litter than for moisturized litter (except for CL3 $\Gamma_{\text{plant}}$ for unexplained reasons). Moreover, experiment under controlled conditions (CL1-CL3, Figs. 3–4) shows that the emission of NH$_3$ increases 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. section d in Fig. 3). 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. 3).

4.4 Emission potentials ($\Gamma_{\text{soil}}, \Gamma_{\text{plant}}$) and NH$_3$ fluxes measured with the cuvettes

The results in Fig. 4 show a comparison of the NH$_3$ compensation point concentration ($C_P$) estimated from $\Gamma_{\text{soil}}, \Gamma_{\text{plant}}$ and $\Gamma_{\stom}$, with the fluxes of NH$_3$ per square unit of ground measured with the cuvettes (remind that the cuvettes imposed a zero NH$_3$ concentration at the inlet, hence they 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 order the different plant compartments NH$_3$ source strength.

Figure 5 also shows 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 $\Gamma$ are the potential sources and the lowest are 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 in 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 management and in several parts of the canopy, allow to compare 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) 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 $\Gamma$ up to $\sim$400,000;

- the soil was also identified as a strong potential source ($\Gamma$ 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). Shoot extrusion was shown to be insufficient to explain the observed emissions;

- the green (or photosynthesising) leaves were a clear sink of NH$_3$ before or after cutting the grass, with a bulk $\Gamma$ being an order of magnitude (at least) lower than the other compartments (from $\sim$50 to $\sim$2600);
Emissions from litter leaves showed a peak both after a step decrease or a step increase of air relative humidity, due to 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 observed fluxes.

Acknowledgements. These measurements were made in the context of the EU project “GRAMINAIE” (contract ENV4-CT98-0722), while the final analysis was supported by the EU “NitroEurope IP”. National funding was received from the French Ministries of Agriculture, Research, and Education, from the UK Natural Environment Research Council, and from the Faculty of Life Sciences, University of Copenhagen, Denmark. The authors gratefully acknowledge the Institute of Agroecology of the German Federal Research Centre for Agriculture at Braunschweig-Völkenrode for access to the field site and provision of excellent site infrastructure.

References


http://www.biogeosciences-discuss.net/5/2749/2008/.


Pilbeam, D. J. and Kirby E. A.: Some aspects of the utilization of nitrate and ammonium by
Ammonia sources and sinks in an grassland

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Table 1. Characteristics of the dynamic chambers. Chambers C1 refers to chambers in polythene films (25 µm width), whereas C2 are stainless steel chambers. Three size 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.

<table>
<thead>
<tr>
<th>Chamber name</th>
<th>Usage</th>
<th>Surface</th>
<th>Volume</th>
<th>Flow rate</th>
<th>Residence time</th>
<th>Cooling/ Drying</th>
<th>Analysis</th>
<th>Sampling time</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-20</td>
<td>Tall grass</td>
<td>0.04</td>
<td>20</td>
<td>30–40</td>
<td>&lt;1</td>
<td>YES</td>
<td>TULIPA</td>
<td>60–120</td>
</tr>
<tr>
<td>C1-65</td>
<td>Cut grass, soil, litter</td>
<td>0.09</td>
<td>65</td>
<td>30–40</td>
<td>~2</td>
<td>YES</td>
<td>TULIPA</td>
<td>60–120</td>
</tr>
<tr>
<td>C1-S</td>
<td>Soil</td>
<td>0.0338</td>
<td>20</td>
<td>29–47</td>
<td>&lt;1</td>
<td>NO</td>
<td>TULIPA</td>
<td>60–120</td>
</tr>
<tr>
<td>C2</td>
<td>Litter</td>
<td>–</td>
<td>3.6</td>
<td>35–40</td>
<td>&lt;1</td>
<td>NO</td>
<td>AMANDA</td>
<td>2</td>
</tr>
</tbody>
</table>

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.
Table 2. Experimental conditions. Three types of experiments were conducted: a field experiment in 2000 in Braunschweig (F1-F6), where all conditions are compared to the reference case (F1, cut grassland without hay), a laboratory experiment to compare different soil emissions (CS1-CS3) 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. Details of the treatments are; F1, grass cut the day before, at a height of approximately 5 cm, hay removed; F2, grass remained uncut, approximately 40–50 cm height; F3, the hay from cutting was put on top of the cut grass; F4, cut grassland, with the dead attached leaves and the litter leaves at the ground removed; F5, 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; F6, 22.2 g FW (16.7 g DW) of litter picked up outside the chambers were put on top of the bare soil (F5); F7, 1 mm of water was added on the litter previously cited to investigate the effect of an increase in litter wetness on NH₃ exchange; CS1, sandy soil, 8% water content, taken from the field experiment F1-F6 in Braunschweig (Germany); CS2, clay-silt soil, 28% water content, taken from a French grassland field in Mirecourt (France); CS3, silt-clay soil, 16% water content, taken from a low fertilised sward in the INRA experimental farm in Grignon (France). Roots were removed from the all sieved homogenised soils, soils CS1 and CS2 were kept frozen at −18°C before experimentation; CL1 and CL3 litter leaves moisturized by applying water droplets at their surface; CL2, dry litter leaves. The air temperature and relative humidity ranges are also given.

<table>
<thead>
<tr>
<th>Name</th>
<th>Conditions</th>
<th>Chamber type</th>
<th>Treatment details</th>
<th>N fertilisation status</th>
<th>Period</th>
<th>Temp. range °C</th>
<th>RH air range %</th>
<th>Other specific conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Field, Braunschweig C1-65</td>
<td>Cut grassland, without hay (reference)</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>all dates F2-F6 indicated below</td>
<td>11–31</td>
<td>42–67</td>
<td>max 490 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>Field, Braunschweig C1-20</td>
<td>Tall grassland</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>31/05/00–01/06/00</td>
<td>3–20</td>
<td>43–78</td>
<td>max 510 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>Field, Braunschweig C1-65</td>
<td>Cut grassland, with hay</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>31/05/00–01/06/00</td>
<td>11–31</td>
<td>42–67</td>
<td>max 490 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>Field, Braunschweig C1-65</td>
<td>Cut grassland, litter withdrawn</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>13/06/00–14/06/00</td>
<td>14–33</td>
<td>28–75</td>
<td>max 530 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>Field, Braunschweig C1-65</td>
<td>Bare soil after shoot excision</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>03/06–04/06/00 and 12/06–14/06/00</td>
<td>9–37</td>
<td>35–59</td>
<td>max 560 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F6</td>
<td>Field, Braunschweig C1-65</td>
<td>Bare soil and litter</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>04/06/00–05/06/00</td>
<td>11–25</td>
<td>36–56</td>
<td>max 330 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>F7</td>
<td>Field, Braunschweig C1-65</td>
<td>Bare soil and litter, 1 mm water added</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>06/06/2000</td>
<td>11–22</td>
<td>51–73</td>
<td>max 330 W m⁻²</td>
<td></td>
</tr>
<tr>
<td>CS1</td>
<td>Climatic chamber C1-65</td>
<td>Braunschweig soil (sandy)</td>
<td>300 kg ha⁻¹ y⁻¹ N</td>
<td>20/02–22/02/01</td>
<td>17–20</td>
<td>37–53</td>
<td>no light</td>
<td></td>
</tr>
<tr>
<td>CS2</td>
<td>Climatic chamber C1-65</td>
<td>Mirecourt soil (clay-silt)</td>
<td>~200 kg ha⁻¹ y⁻¹ N</td>
<td>20/02–22/02/01</td>
<td>17–20</td>
<td>37–53</td>
<td>no light</td>
<td></td>
</tr>
<tr>
<td>CS3</td>
<td>Climatic chamber C1-65</td>
<td>Grignon soil (silt-clay)</td>
<td>~50 kg ha⁻¹ y⁻¹ N</td>
<td>20/02–22/02/01</td>
<td>17–20</td>
<td>37–53</td>
<td>no light</td>
<td></td>
</tr>
<tr>
<td>CL1</td>
<td>Climatic chamber C2</td>
<td>Moisturized litter leaves</td>
<td>low Nitrogen status</td>
<td>06/09–10/09/01</td>
<td>17–23</td>
<td>53–97</td>
<td>no light</td>
<td></td>
</tr>
<tr>
<td>CL2</td>
<td>Climatic chamber C2</td>
<td>Dry litter leaves</td>
<td>low Nitrogen status</td>
<td>10/09–17/09/01</td>
<td>17–21</td>
<td>55–92</td>
<td>no light</td>
<td></td>
</tr>
</tbody>
</table>
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 $\Gamma_{plant}=\frac{[\text{NH}_4^+]}{10^{-\text{pH}}}$. 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.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Observation</th>
<th>Fresh weight</th>
<th>Water content</th>
<th>N content</th>
<th>[NO$_3^-$]</th>
<th>[NH$_4^+$]</th>
<th>pH bulk</th>
<th>$\Gamma_{plant}$</th>
<th>Rep</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1–F6 (hay)</td>
<td>Flowers</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.8</td>
<td>0.1</td>
<td>3.2</td>
<td>0.1</td>
<td>6.4$^a$</td>
</tr>
<tr>
<td></td>
<td>Litter</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>18.0</td>
<td>0.5</td>
<td>36.9</td>
<td>0.5</td>
<td>7.0$^c$</td>
</tr>
<tr>
<td></td>
<td>Green leaves</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.2</td>
<td>0.3</td>
<td>10.0</td>
<td>0.3</td>
<td>6.4$^a$</td>
</tr>
<tr>
<td></td>
<td>Stems</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.3</td>
<td>0.5</td>
<td>1.7</td>
<td>0.5</td>
<td>6.4$^a$</td>
</tr>
<tr>
<td>F1–F6 (cut grass)</td>
<td>Litter</td>
<td>–</td>
<td>70</td>
<td>–</td>
<td>28.0</td>
<td>1.6</td>
<td>23.9</td>
<td>1.6</td>
<td>7.0$^c$</td>
</tr>
<tr>
<td></td>
<td>Green leaves</td>
<td>–</td>
<td>25</td>
<td>–</td>
<td>27.0</td>
<td>1.5</td>
<td>2.6</td>
<td>1.5</td>
<td>6.0$^c$</td>
</tr>
<tr>
<td></td>
<td>Stems</td>
<td>–</td>
<td>69</td>
<td>–</td>
<td>16.8</td>
<td>0.8</td>
<td>1.7</td>
<td>0.8</td>
<td>6.4$^a$</td>
</tr>
<tr>
<td>(main field)</td>
<td>Tall grass</td>
<td>–</td>
<td>–</td>
<td>2.1</td>
<td>1.0</td>
<td>0.0</td>
<td>1.1</td>
<td>0.1</td>
<td>6.4$^c$</td>
</tr>
<tr>
<td></td>
<td>Cut grass</td>
<td>–</td>
<td>–</td>
<td>3.2</td>
<td>14.8</td>
<td>1.7</td>
<td>1.3</td>
<td>0.1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>Hay</td>
<td>–</td>
<td>–</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Litter</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>59.3</td>
<td>10.3</td>
<td>13.2</td>
<td>3.1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>Stems</td>
<td>–</td>
<td>–</td>
<td>2.1</td>
<td>22.5</td>
<td>2.0</td>
<td>1.1</td>
<td>0.0</td>
<td>6.4$^a$</td>
</tr>
<tr>
<td></td>
<td>Roots</td>
<td>–</td>
<td>–</td>
<td>1.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CL1</td>
<td>Litter (start)</td>
<td>8.2</td>
<td>56</td>
<td>1.1</td>
<td>–</td>
<td>–</td>
<td>10.3</td>
<td>0.6</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>Litter (end)</td>
<td>5.2</td>
<td>26</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.3</td>
<td>0.6</td>
<td>7.4</td>
</tr>
<tr>
<td>CL2</td>
<td>Litter (start)</td>
<td>10.0</td>
<td>21</td>
<td>1.1</td>
<td>–</td>
<td>–</td>
<td>5.2</td>
<td>0.3</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>Litter (end)</td>
<td>11.1</td>
<td>47</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.3</td>
<td>0.2</td>
<td>7.3</td>
</tr>
<tr>
<td>CL3</td>
<td>Litter (start)</td>
<td>12.1</td>
<td>61</td>
<td>1.1</td>
<td>–</td>
<td>–</td>
<td>2.4</td>
<td>0.1</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>Litter (end)</td>
<td>8.5</td>
<td>14</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.3</td>
<td>0.7</td>
<td>6.6</td>
</tr>
</tbody>
</table>
Table 4. Soil characteristics for each experiment: granulometric composition, soil moisture content, soil nitrate \([\text{NO}_3^-]\) and ammonium \([\text{NH}_4^+]\) concentration expressed in equivalent nitrogen per mass of dry weight of soil (DW), as well as soil pH, and soil NH$_3$ emission potential $\Gamma_{\text{soil}}=\frac{[\text{NH}_4^+]}{10^{-\text{pH}}}$. In CS1-CS3, roots were removed from the sieved homogenised soils prior to experiment, whereas in F1-F6 dynamic chambers were put on the ground. Soils CS1 and CS2 were frozen at $-18°\text{C}$ for transportation and kept frozen before experimentation, while soil CS3 was taken in the field before each experiment, which would explain the differences observed in \([\text{NO}_3^-]\) and \([\text{NH}_4^+]\) concentrations between F1-F6 and CS1. The bold pH (CS2-CS3) were assumed equal to the pH in CS1 to allow estimation of the emission potential $\Gamma_{\text{soil}}$.

| Name | Granulometric composition (clay %, silt %, sand %) | Soil moisture % dry soil | Soil \([\text{NO}_3^-]\) & \mu g N-NO$_3^-$ g$^{-1}$ DW mean & SE | Soil \([\text{NH}_4^+]\) & \mu g N-NH$_4^+$ g$^{-1}$ DW mean & SE | Soil mineral N & \mu g N g$^{-1}$ DW mean | Soil pH | $\Gamma_{\text{soil}}$ | Rep |
|------|-------------------------------------------------|--------------------------|-----------------------------|------------------|------------------|------------------|-----------------|--------|-----------------|-----|
| F1   | 3 34 63                                          | 11                       | 11                          | 0.4              | 28               | 2.3              | 40              | 6.5    | 85 808          | 4   |
| F2   | 3 34 63                                          | 14                       | 8                           | 0.6              | 24               | 0.5              | 32              | 6.4    | 61 898          | 7   |
| F3   | 3 34 63                                          | 13                       | 10                          | 0.3              | 34               | 0.5              | 44              | 6.4    | 84 923          | 14  |
| F4   | 3 34 63                                          | –                        | –                           | –                | –                | –                | –               | –      | –               | –   |
| F5   | 3 34 63                                          | 11                       | 12                          | 1.0              | 38               | 1.0              | 50              | 6.4    | 104 883         | 3   |
| F6   | 3 34 63                                          | 12                       | 13                          | –                | 32               | –                | 46              | 6.4    | 75 958          | 1   |
| F7   | 3 34 63                                          | 11                       | 12                          | –                | 37               | –                | 49              | 6.1    | 51 356          | 1   |
| CS1  | 3 34 63                                          | 8                        | 31                          | –                | 0.2              | –                | 31              | 6.3    | 357             | –   |
| CS2  | 49 43 8                                          | 28                       | 5.0                         | –                | 3.1              | –                | 8               | 6.3    | 5482            | –   |
| CS3  | 30 57 13                                         | 16                       | 6.8                         | –                | 0.5              | –                | 7               | 6.3    | 937             | –   |
Table 5. Averaged NH$_3$ fluxes, and water vapour fluxes ($E$), as well as air temperature and humidity in the chamber ($T_a$ and RH$_a$ respectively), surface temperature ($T_{surf}$), and solar radiation above the chambers. The NH$_3$ emission potential ($\Gamma$) 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 $\Gamma$ chosen was: F1, $\Gamma_{\text{plant}}$ (green leaves), as litter was still there; F2, $\Gamma_{\text{stom}}$ (tall green leaves); F3, $\Gamma_{\text{plant}}$ (average of green leaves cut and hay); F4, $\Gamma_{\text{stom}}$ (cut green leaves); F5, $\Gamma_{\text{soil}}$(F5); F6, mean of $\Gamma_{\text{plant}}$(CL2) and $\Gamma_{\text{soil}}$(F6) assuming half cover of dry litter; F7: $\Gamma_{\text{plant}}$ (litter leaves). Mean or median and standard deviations or maximum are given for each experiment. NH$_3$ fluxes in the climatic chamber were related 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.

<table>
<thead>
<tr>
<th>Name</th>
<th>Treatment details</th>
<th>$T_{surf}$ $^\circ$C</th>
<th>$T_a$ $^\circ$C</th>
<th>RH$_a$ %</th>
<th>NH$_3$ Flux ng NH$_3$ m$^{-2}$ s$^{-1}$</th>
<th>Diff with ref ng NH$_3$ m$^{-2}$ s$^{-1}$</th>
<th>$E$ $\mu$m h$^{-1}$</th>
<th>Solar radiation W m$^{-2}$</th>
<th>$\Gamma$ µg NH$_3$ m$^{-3}$</th>
<th>$C_p$ ($T_{surf}$) µg NH$_3$ m$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 Cut grassland, hay removed (reference)</td>
<td>16.9  54.3  15.9  38.0  42–67  13  31  145  0.0</td>
<td>10.0  44  80  825  2627  6.9</td>
<td>F2 Tall grassland</td>
<td>12.6  20.2  14.3  26.7  43–78  6  15  50  –7.0</td>
<td>106  88  97  910  46  0.1</td>
<td>12.4  22.2  11.8  27.8  42–67  16  30  125  3.0</td>
<td>60  58  82  826  13076  20</td>
<td>17.0  41.3  17.1  35.5  28–75  7  9  38  –7.0</td>
<td>48  34  101  769  159  0.4</td>
<td>18.2  49.7  16.3  37.2  30–59  64  45  180  51</td>
</tr>
<tr>
<td>CS1 Braunschweig soil (sandy)</td>
<td>16.4  19.0  18.8  19.7  38–53  11  12  50  –2.0</td>
<td>26  12  –  –  357  0.9</td>
<td>CS2 Mirecourt soil (clay-silt)</td>
<td>17.3  19.6  19.2  19.7  39–52  16  9  38  3.0</td>
<td>22  12  –  –  5482  15</td>
<td>19.1  21.2  19.1  21.2  53–97  41  16  95  28</td>
<td>3  8  –  –  259031  884</td>
<td>19.0  20.9  19.4  20.8  55–92  35  20  108  21</td>
<td>2  5  –  –  45953  162</td>
<td>19.2  19.9  19.2  19.9  62–97  42  49  184  28</td>
</tr>
</tbody>
</table>

Reference: M. David et al.
**Fig. 1.** 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 and plant temperatures, as well as the solar radiation 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 the 3/06/2000, then 22 g of litter leaves were added the 4/06/2000, and 1 mm of double deionised water was added on the 06/06/2000.
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; closed squares) and cut grassland with the litter removed (F4; open triangles). The soil and plant temperatures, as well as the solar radiation are also given in the bottom graph. Note that roots and stumps were still present in the bare soil. The shoots were excised the 12/06/2000 at about 12:00 in F5, and the litter was removed from F4 at the same date.
Ammonia emissions from moisturized litter leaves, measured with a dynamic chamber and an AMANDA (CL1). The measurements were performed in a growth climatic chamber (20°C), 06–10/09/2001, Grignon, France. (a), (b), (c) and (d) relate to changes in air relative humidity, which is shown on the secondary axis.
Fig. 4. 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.