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Ammonia fluxes over
intensively managed
grassland

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Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements

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Abstract

Quantification of ammonia (NH_3) land-atmosphere exchange is required for atmospheric modelling and assessment of nitrogen deposition, yet flux measurement methods remain highly uncertain. To address this issue, a major inter-comparison of ammonia fluxes over intensively managed grassland was conducted during the GRAMINAE Integrated Experiment held in Braunschweig, Germany. In order to provide a robust dataset of ammonia exchange with the vegetation, four independent continuous flux gradient systems were operated. Three independently operated continuous wet denuders systems (AMANDA) were compared with a Wet Effluent Diffusion Denuder (mini-WEDD) system. Measurements were made at two distances from an adjacent livestock farm, allowing effects of advection to be quantified in a real landscape setting. Data treatment included filtering for instrument failure, disturbed wind sectors and unsuitable micrometeorological conditions, with corrections made for storage and advection errors.

The inter-comparison demonstrated good agreement in measured ammonia concentrations and fluxes (<20% difference) for some periods, although the performance of the ammonia analyzers was variable, with much poorer agreement on particular days. However, by using four systems, the inter-comparison was able to provide a robust mean estimate of continuous ammonia fluxes through the experiment. The observed fluxes were: a) small bi-directional fluxes prior to cutting (-64 to $42\,\mathrm{ng\,NH_3\,m^{-2}\,s^{-1}}$), b) larger diurnally-varying emissions following cutting (-49 to $703\,\mathrm{ng\,NH_3\,m^{-2}\,s^{-1}}$) and c) much larger emissions following fertilizer application (0 to $3820\,\mathrm{ng\,NH_3\,m^{-2}\,s^{-1}}$). The results are a salutary reminder of the uncertainty in unreplicated ammonia flux measurements, while the replication of the present study provides a uniquely robust dataset for the evaluation of ammonia exchange processes. It is clear that consistently reliable determination of ammonia concentrations remains the major measurement challenge.

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1 Introduction

Measurements of ammonia exchange with vegetation using micrometeorological methods have been conducted since the 1970s (e.g. Denmead et al., 1974, 1976; Dabney and Bouldin, 1985; Harrison et al., 1989; Flechard et al., 1998; Warland et al., 2001; Phillips et al., 2004). The measurements have been conducted over a range of agricultural systems as well as semi-natural systems (e.g. Erisman and Wyers, 1993; Sutton et al., 1993b; Duyzer, 1994; Nemitz et al., 2004), including grasslands (e.g. Horvath, 1982; Harper et al., 1983; Horvath et al., 2005). Initially, the motivation for measurement of ammonia was to quantify N losses from agricultural systems. The first measurements used techniques such as bubblers/acid traps (Denmead et al., 1974), filter packs (Harrison and Kitto, 1990) or denuder tubes (e.g. Ferm, 1979). All these methods operated at a time resolution of at least 1 h and required significant operator effort for changing over samples and off-line analysis. As a consequence, most early measurements were for short field-campaigns only, of a few days or weeks (e.g. Sutton et al., 1993b; Duyzer, 1994).

As interest in ammonia (NH_3) as an atmospheric pollutant has grown, so too has the range of measurement techniques available. Developments in continuous measurement-techniques enabled much longer time periods of measurements to be conducted. In particular, the continuous flow denuder (AMANDA) developed by Wyers et al. (1993), achieved the balance between reasonable cost, a wide operating concentration range (0.02–100 μg m^{-3}) and on-line analysis with short time resolution (<5 min). The AMANDA utilises wet chemistry techniques, stripping ammonia from the air in an acidic capture solution. Other similar instruments have been developed which also operate via wet chemistry methods, for example the Wet Effluent Diffusion Denuder (WEDD) technique (Vecera and Dasgupta, 1991), as well as recent more automated implementations of the AMANDA technique (Trebs et al., 2006; Kruit et al., 2007). Although these techniques have been proven to measure NH_3 successfully, there are limitations; in particular they cannot be used for eddy correlation measure-

ments where a sensor with a time response of typically at least 4 Hz is needed. Shaw et al. (1998), Famulari et al. (2004) and Whitehead et al. (2008) have reported eddy correlation measurements of NH_3 fluxes, using a tandem mass spectrometer and tunable diode laser technology, but substantial further developments (and cost reductions) are required before eddy correlation becomes more widely used for NH_3 flux measurement.

An alternative micrometeorological flux measurement technique is the relaxed eddy accumulation method (REA). This method has the advantage of not requiring a fast response analyser. REA flux measurements of NH_3 have been conducted in recent years (e.g. Neftel et al., 1999; Nemitz et al., 2001a; Meyers et al., 2006) and constitute an area of ongoing research.

Ammonia has been recognised as contributing to eutrophication and acidification of ecosystems (Fangmeier et al., 1994; Krupa et al., 2003). To assess these effects, reliable models of ammonia deposition are needed (Hertel et al., 2006). Currently, there are only crude parameterisations of NH_3 exchange present in national and European deposition models and measurements are needed to improve these parameterisations. A European project GRAMINAE (GRassland AMmonia INteractions Across Europe) was therefore initiated to improve quantification and parameterisation of NH_3 exchange with grasslands across Europe (Sutton et al., 2001a, 2007).

In addition to the interest in contrasting ecosystem types (e.g. Horvath et al., 2005; Walker et al., 2006; Kugler et al., 2008), large rates of NH_3 emission have been observed following cutting of intensively managed grassland, from the sward itself (Sutton et al., 1997, 2001a; Milford et al., 2001b), with this effect being modelled by Riedo et al. (2002). There is, however, a shortage of studies investigating this emission source, while Bussink et al. (1996) observed the opposite, i.e. an apparent increase in deposition flux immediately after cutting. Emission of NH_3 from senescing and decomposing vegetation has also been investigated (Whitehead and Lockyer, 1989; Mannheim, 1997), but this is rather distinct from the enhanced emissions from a re-growing canopy following cutting noted above. Emission of volatile organic compounds (VOCs) has

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been detected from cut grassland and attributed to a "wounding" of the vegetation (Gouw et al., 1999). Other work has investigated the effect of cutting regimes on the health, yield and species diversity of swards (Smith et al., 1996a, b; Blum et al., 1997; Evans et al., 1998), but not the effect on NH_3 exchange. Much research has been
conducted on NH_3 volatilisation following N fertilization applied to grassland (e.g. Pain et al., 1989; Thompson et al., 1990a, b, 1991; van der Weerden and Jarvis, 1997; Sommer et al., 2004), but little research has been conducted to quantify the contributions from direct fertilizer emission of NH_3 and indirect NH_3 emission from the plants themselves.

To address some of these issues, the GRAMINAE Integrated Experiment was held in Braunschweig, Germany, over intensively managed grassland (Sutton et al., 2008b). In order to provide a robust dataset of NH_3 exchange with the vegetation, four independent continuous flux gradient systems were operated. Although there have been many inter-comparisons of ammonia concentration measurements (e.g. Gras, 1984; Appel et al., 1988; Harrison and Kitto, 1990; Wiebe et al., 1990; Sutton et al., 2001b; Schwab et al., 2007) there have been much fewer inter-comparisons of ammonia flux measurements (Sutton et al., 2000; Whitehead et al., 2008). This paper presents the results of a major inter-comparison of continuous NH_3 flux measurements over intensively managed grassland. The best estimates of NH_3 flux and concentration from this inter-comparison are subsequently used to investigate the effect of cutting and fertilizing on NH_3 exchange fluxes. These best estimates of NH_3 concentrations and fluxes were also provided to other participants in the experiment as a basis for further analyses, for example in quantifying advection fluxes (Loubet et al., 2008), assessing the relaxed eddy accumulation technique (Hensen et al., 2008b), modelling the dynamics of ammonia fluxes (Burkhardt et al., 2008; Personne et al., 2008; Sutton et al., 2008a) and quantifying production of particulate ammonium aerosol (Nemitz et al., 2008a).

2 Materials and methods

2.1 Micrometeorological theory

The NH_3 flux measurements were made using the aerodynamic gradient method, following the approaches described in Fowler and Duyzer (1989), Monteith and Unsworth (1990) and Sutton et al. (1993). The flux (F_z)is calculated from the friction velocity (u_*) and concentration scaling parameter (χ_*):

$$F_z = -u_*\chi_* \tag{1}$$

with emission fluxes denoted as being positive. χ_* is calculated as:

$$\chi_* = k\frac{\partial \chi}{\partial[\ln(z-d)-\Psi_H]} \tag{2}$$

where k is von Karman's constant (=0.41), z is height above the surface, d is zero plane displacement, χ is NH_3 concentration and Ψ_H is the integrated stability correction function for scalar properties, calculated from the Monin-Obukhov length (L) according to the description of Sutton et al. (1993). Although u_* can be calculated from profiles of windspeed in an equation analogous to Eq. (2), in this instance it was obtained from ultrasonic anemometry using eddy covariance (Moncrieff et al., 1997). u_* and all other meteorological parameters were measured by several institutes in the experiment. These estimates have been compared and evaluated by Nemitz et al. (2008b), who provided a consensus dataset for use in the flux calculations here.

The basic calculations of NH_3 fluxes derived here assume stationarity and homogeneity of the atmospheric conditions, such that the vertical flux results entirely from turbulent transfer in the vertical and that errors related to local advection (horizontal heterogeneity), storage (temporal instationarity) and chemical production or consumption in the surface layer are ignored. Strictly, this assumption cannot always be maintained, with the result that the vertical flux is not constant with height:

$$\frac{\partial F_z}{\partial z} = -\frac{\partial \chi_a}{\partial t} - \frac{\partial F_x}{\partial x} + Q_{chem}. \tag{3}$$

In the case of ammonia, where exchange fluxes are relatively large in proportion to concentration, the flux divergence due to storage ($\partial \chi_a / \partial t$) can generally be ignored as trivial (Sutton et al., 1993a). However, the resulting difference in the vertical flux due to storage (the storage error, $\Delta F_{z,\text{sto}}$) may be found from:

$$\Delta F_{z,\text{sto}} = \int_0^{z-d} \frac{\partial \chi_a}{\partial t} dz \tag{4}$$

which is approximately equal to:

$$\Delta F_{z,\text{sto}} = (z-d)\frac{\partial \chi_a}{\partial t}. \tag{5}$$

The horizontal flux divergence $\partial F_x / \partial x$ may be more significant for NH$_3$, particularly where large NH$_3$ sources exist in the vicinity, causing large local horizontal concentration gradients in the direction of the wind ($\partial \chi_a / \partial x$) (Loubet et al., 2001, 2006; Milford et al., 2001a). Estimates of the difference in the vertical flux due to advection (the advection error, $\Delta F_{z,\text{adv}}$) are usually not made, due to lack of information on $\partial \chi_a / \partial x$. This issue was, however, given special attention in the Braunschweig Experiment, with both measurements and modelling of $\partial \chi_a / \partial x$ being conducted (Loubet et al., 2008). On this basis, where relevant, derived $\Delta F_{z,\text{adv}}$ were applied to correct the measured fluxes at 1 m ($F_z(1\,\text{m})$) and provide estimates of the fluxes at the canopy surface ($F_z(z_o)$).

Chemical production or consumption (Q_{chem}) may also be significant for ammonia where either evaporation of ammonium containing aerosol, or production of aerosol, respectively, occur in the surface layer. The difference in the vertical flux due to these effects ($\Delta F_{z,\text{che}}$) is assessed separately by Nemitz et al. (2008a).

2.2 Ammonia measurement techniques and implementation

Ammonia concentrations were determined in gradient configuration at four locations using two different measurement techniques. At three out of the four sites the continuous flow wet denuder system "AMANDA" (Ammonia Measurement by ANnular Denuder

sampling with online Analysis) was deployed (Wyers et al., 1993). This technique captures gaseous ammonia in a continuous-flow horizontal annular denuder using a stripping solution of 3.6 mM sodium hydrogen sulphate ($NaHSO_4$) and determines the aqueous ammonium concentration online by conductivity analysis. The time resolution of this method can be set to 1 min, however, in this instance, concentrations were measured sequentially for 150 s at each of three heights (including liquid-flow delay loops), resulting in a full profile measurement every 450 s. These concentrations were averaged to 15 min periods for flux calculation. The air-flow rate of the AMANDAs was approximately 25 l min^{-1} and the liquid flow rate through the denuders was approximately 1 ml min^{-1}; the detection limit was about 0.02 μg NH$_3$ m^{-3}. The heights of the concentration measurements were varied throughout the measurement campaign according to the canopy height, but the maximum height and minimum heights above ground were 2.37 m and 0.32 m, respectively. The three AMANDA systems were maintained by the Centre for Ecology and Hydrology (CEH-UK), the German Federal Agricultural Research Institute (FAL-D) and the Hungarian Forest Research Institute (FRI), the last being in collaboration with the Hungarian Institute of Atmospheric Physics (IAP).

A second continuous ammonia measurement technique utilised miniaturised Wet Effluent Denuders (mini-WEDD), which are silica-coated glass tubes (length 125 mm) positioned vertically, with continuous flow of a stripping solution in a membrane tube analysed online by a four-channel fluorescent analyser (e.g. Neftel et al., 1998; Vecera and Dasgupta, 1991). The mini-WEDDs were maintained by ART the former Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH) and placed at four heights (0.15 m, 0.3 m, 0.6 m and 1.2 m above ground). However, the lowest mini-WEDD concentration was not used in the flux calculations as it was judged to be too close to the canopy. An air-flow rate of 600 ml min^{-1} and a liquid flow rate of 0.12 ml min^{-1} were used. The detection limit was 0.1 μg NH$_3$ m^{-3}. Calibration of both systems was conducted with aqueous standards of 0, 50 and 500 mg kg^{-1} NH$_4^+$. A summary of the different NH$_3$ measurement systems applied and acronyms used in the intercomparison is provided in Table 1.

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During the experiment, aqueous calibration standards were prepared centrally and distributed amongst the ammonia analyser operators. In addition, unknown quality control standards were distributed on 3 occasions to test the accuracy of the analysers. On each occasion, 2 unknown standards were distributed and the difference in concentration measured by each analyser was compared with the actual concentration difference.

2.3 Field site and instrument locations

A full site description and diagram are given in Sutton et al. (2008b). The field site was intensively managed grassland of approximately 12 ha and the principal micrometeorological measurement location (Site 1) was 380 m from the western edge of the field, this being the main wind direction during the experiment. There was a second micrometeorological measurement location (Site 2), which was 210 m east of Site 1 and 36 m from the eastern edge of the field. Measurements were made at Site 2 in order that any advection of NH_3 emitted from a farm located 610 m west of Site 1 (Hensen et al., 2008a) could be identified and quantified (see Sect. 2.5). Two gradient AMANDAs (each consisting of 3 denuder inlets linked to a common ammonium detector) were deployed at Site 1 (FAL-D, FRI), as well as the mini-WEDD system (FAL-CH), while one gradient AMANDA (CEH) was deployed at Site 2. The field was cut for silage on the morning of 29 May 2000 (starting at 06:00 GMT), with grass removed from the field on the morning of 31 May 2000. The field was fertilized with $108 \, kg \, N \, ha^{-1}$ calcium ammonium nitrate on the morning of 5 June 2000 (06:00–07:00 GMT).

2.4 Data processing procedures

The complexities of data processing are increased by the availability of the 4 independent estimates of NH_3 concentration profiles. The following procedure was applied:

1. Any periods of calibration or obvious malfunctioning of each instrument were removed from the dataset of measured concentrations.

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2. Fluxes F_z(1 m) of NH_3 and concentrations at 1 m (χ(1 m)) were calculated according to Sect. 2.1. Flux measurements were rejected during periods when the fetch was obstructed by other equipment or by the edge of the field (see below for details).

3. Once F_z(1 m) and χ(1 m) estimates were available for the different systems, these were compared to identify any further periods where one system had malfunctioned or underperformed which had not yet been identified. These data were then removed.

4. Given the different estimates of the 4 systems, gaps in the data create an artificial change in the mean estimate when one system goes offline or comes back online. To avoid this artefact, gaps of <6 h in each instrument were filled for F_z(1 m) and χ(1 m) according to the technique described below.

5. As the flux measurements were made at two sites, different vertical flux divergence will apply due to horizontal advection where local sources are present. The advection corrections for 1 m above d were calculated by Loubet et al. (2008) for the Sites 1 and 2 measurements and applied to the measured fluxes, resulting in an estimate of the fluxes at the canopy surface ($F_z(z_o)$) (see Sect. 3.3). No corrections to the data for the potential effect of chemical production or consumption are made here, as this effect is assessed by Nemitz et al. (2008a).

6. The "mean gradient estimate" (subscript mg) was calculated for ($F_z(z_o)$) and χ(1 m), as the arithmetic mean of all the remaining individual measurements. At the same stage, corrections for storage errors were also applied.

7. The data were filtered according to the passing or failing of a set of defined micrometeorological criteria (see below). Data failing these criteria were retained in the dataset, but distinguished as being of lower reliability.

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There was a substantial amount of measurement equipment at Site 1, concentrated on a N-S axis, as well as three mobile laboratories in the N direction (see site description in Sutton et al., 2008b). As a result, flux measurements from the FAL-D and FRI gradient systems were rejected for wind directions from both the N and S direction (0° to 20° and 180° to 190° rejected), whilst flux measurements were rejected for winds from the NNE direction (10° to 45°) for the FAL-CH gradient system. Due to the close proximity of the edge of the field to the east of Site 2, flux measurements were rejected at this site for wind direction 0° to 170°.

The gapfilling technique applied for each instrument involved calculating the ratio of the individual flux measurement to the mean estimate at the start and the end of the gap and then interpolating this ratio. This interpolated ratio was then multiplied by the available mean estimate to fill in missing data. This method propagates the deviations from the mean present at the start and end of the gap, and limits the occurrence of step changes in the flux when individual analysers fail or are restored in the dataset. Only gaps of <6 h were filled.

Finally, the data were filtered according to micrometeorological criteria to identify periods where the fluxes are estimated with less certainty. These micrometeorological criteria were: $u(1\,\mathrm{m})<0.8\,\mathrm{m\,s^{-1}}$, $|L|<5\,\mathrm{m}$ and cumulative normalised footprint function (CNF) <67%. The cumulative normalised footprint function was calculated using the Kormann and Meixner (2001) formulation as described in Nemitz et al. (2008b).

3 Results

3.1 Data processing

The data processing procedures ensured that high data coverage at individual sites was achieved even after periods of malfunctioning and obstructed wind sectors were removed (Table 2). Having four estimates of the flux lead to a "mean gradient estimate" of the flux with an overall data coverage of 98%. This highlights the advantage of

having a number of independent systems to achieve a robust estimate of the flux. The data coverage was reduced to 69% if the fluxes which were calculated with less certainty were removed, showing that meteorological conditions (low windspeed, stable conditions) were the main limitation to obtaining a complete flux dataset. Data on the
5 gapfilling procedure revealed that FAL-CH had the greatest number of gaps filled and that the median gap length varied from 15 min (FAL-D) to 90 min (CEH).

3.2 Temporal inter-comparison of gradient measurements

The range of NH_3 concentrations at 1 m and fluxes from the 4 different systems are shown for example days from the pre-cutting, post-cutting and post-fertilizing periods
10 (Figs. 1 and 2). These figures show that there were periods of close agreement (e.g. 6 and 7 June 2000) and periods of substantial divergence (e.g. 8 June 2000). It can be seen that for certain periods (31 May–2 June 2000) there were consistent concentration differences between the different instruments with FAL-D generally reading higher concentrations than CEH and FAL-CH.
15   The blind testing of the aqueous ammonium Quality Control standards by the different analysers did indicate periods of significant concentration differences (Table 3). In particular, the result of FAL-D over-reading by 41% on 31 May 2000 is consistent with Fig. 1b. However, the small number of aqueous quality tests meant that it was not possible to adjust the concentrations in an objective manner and so the quality tests
20 were used for interpretation rather than adjustment.
        The flux intercomparison highlights the changing pattern of NH_3 exchange during the experiment; before the cutting of the grass the flux was predominantly deposition to the surface. After cutting of the grass, the NH_3 exchange changed to predominantly emission with emission fluxes of up to 760 ng m^{-2} s^{-1}, whilst after fertilization the fluxes
25 according to individual analyzers increased up to 6000 ng m^{-2} s^{-1}. The emission fluxes peaked in the daytime and were generally close to zero during nighttime. As with the comparison of ammonia air concentrations, there were periods of close agreement (e.g. 6 and 7 June 2000) and periods of substantial disagreement (e.g. 1 and 8 June

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2000). However, generally the fluxes from the different systems showed a similar structure and response to the management activities on the field. The larger flux values (e.g. FAL-D on 1 and 2 June 2000) were generally coupled with larger concentrations at 1 m, although this was not always the case (e.g. FAL-D and FRI in the early hours of 8 June 2000). Scatter plots comparing the NH_3 concentration and flux for the different systems are presented in Sect. 3.4.

3.3 Assessment of advection corrections

Estimates of the difference in the vertical flux due to advection (the advection error, $\Delta F_{z,\text{adv}}$) were derived from both measurements and modelling by Loubet et al. (2008). The modelled estimates of $\Delta F_{z,\text{adv}}$ were applied to correct the flux measurements ($F_z(1\,\text{m})$) in order to provide an estimate of the fluxes at the canopy surface ($F_z(z_o)$). Examples of the magnitude of the advection errors in relation to the flux measurements for particular periods are given in Loubet et al. (2008). The modelled advection errors during the pre-cut period due to the farm 610 m from Site 1 estimated by Loubet et al. (2008), ranged between 0 to $27\,\text{ng m}^{-2}\,\text{s}^{-1}$. However, relatively few periods of advection from the farm were observed due to winds occurring directly from the W occurring for only a small period of the time, and accounted on average for 32% of the measured flux. As well as advection due to the farm emissions, advection errors also occurred due to NH_3 emissions from the field itself, which were largest following fertilization of the field. Although these were larger in absolute terms (-209 to $13\,\text{ng m}^{-2}\,\text{s}^{-1}$), they represented a smaller percentage of the measured fluxes at 1 to 2%. For the week following 29 May 2000 (post-cut period), the farm and field advection errors amounted on average to +3% and −4% of the measured fluxes, respectively (Loubet et al., 2008).

3.4 Regression analysis of gradient measurements

3.4.1 Regressions of $\chi(1\,\text{m})$ and $F_z(z_o)$ against FAL-CH

FAL-CH was chosen as the reference for a preliminary analysis and comparisons of $\chi(1\,\text{m})$ and $F_z(z_o)$ for each instrument versus FAL-CH were conducted. FAL-D, $\chi(1\,\text{m})$ and $F_z(z_o)$ agreed well with FAL-CH across the data range for some of the time (Fig. 3). However, there were a considerable number of data points which greatly overestimated the concentration and flux compared with FAL-CH. The fact that this was not evident for the whole period suggests that there was some variation in the accuracy of the FAL-D analyser throughout the measurement period. For example, this could be due to variation in the accuracy of the calibration. Inaccuracies in the measurement could be exacerbated in the large concentration range, where the calibration is no longer as robust. In addition, temperatures inside the analysers reached 40°C on some days. Although the concentration measurements were corrected for temperature, inaccuracies in the temperature correction could lead to overestimation of concentrations. A similar effect was seen in some periods for the FRI AMANDA data of $\chi(1\,\text{m})$ and $F_z(z_o)$ (data not shown). CEH AMANDA $\chi(1\,\text{m})$ and $F_z(z_o)$, underestimated the FAL-CH mini-WEDD values, but did not show the variation in agreement demonstrated by FAL-D and FRI.

3.4.2 Regressions of $\chi(1\,\text{m})$ and $F_z(z_o)$ against mean gradient estimate

After the data processing procedures were conducted as detailed in Sect. 2.4 the "mean gradient estimate" was calculated for $F_z(z_o)$ and $\chi(1\,\text{m})$ ($F_z(z_o)_{mg}$ and $\chi(1\,\text{m})_{mg}$), this is the arithmetic mean of all available individual measurements remaining in the dataset. These data include the corrections for advection. A comparison of $\chi(1\,\text{m})_{mg}$ versus the individual systems was conducted (Fig. 4a and b), the regression results are presented in Table 4.

Data from 3, 8, 9 and 10 June 2000 were not included in the regression because on these days there was significant disagreement between the systems with FAL-D and FRI giving higher estimates compared with the CEH and FAL-CH estimates. To include the FAL-D and FRI estimates for these days in the regression would bias the regression towards FAL-D and FRI and might give a false impression of the overall dataset.

With data from 3, 8, 9 and 10 June removed, Fig. 4a and b demonstrate that there was close agreement of $\chi(1\,m)$ between each individual system and the mean estimate across the full concentration range. As indicated by the temporal graphs, FAL-D and FRI showed slightly higher concentrations than the best estimate, whilst FAL-CH and CEH showed slightly lower. The r^2 value for all the regressions was high (>0.93; Table 4) which gives confidence in the 4 systems and the values of $\chi(1\,m)_{mg}$.

The regression of $F_z(z_o)_{mg}$ versus $F_z(z_o)$ from the individual systems (Fig. 5a and b) demonstrates that once the four uncertain days (3, 8, 9 and 10 June) were removed from the regression then FAL-D tended to underestimate the flux slightly compared with the mean gradient estimate, as did CEH. By contrast, FRI and FAl-CH both overestimated the mean gradient flux by about 10% compared with the mean gradient estimate.

As a result of the disagreement between systems on the 3, 8, 9 and 10 June an "alternative gradient estimate" for $\chi(1\,m)$ and $F_z(z_o)$ was proposed for these days. The alternative gradient estimate (subscript ag) consisted of the mean of the two systems (CEH and FAL-CH). It was not considered that there was sufficient justification to remove the high measurements from the mean dataset. However, it was suspected that on these days the two high systems might not have been operating correctly. Therefore, this alternative estimate was also provided to other end-users of the data.

3.5 NH_3 concentration and flux in relation to management activities

The resulting mean gradient concentrations of NH_3 at 1 m ($\chi(1\,m)_{mg}$) and flux ($F_z(z_o)_{mg}$) for the whole period (Fig. 6) demonstrate clearly the effect of the management activities (cutting and fertilizing) on the concentration and flux. In addition to the

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mean gradient estimate, Fig. 6 also shows the alternative gradient estimate for $\chi(1\,\text{m})$ and $F_z(z_o)$ on 3, 8, 9 and 10 June. Statistics for the mean gradient estimate of $\chi(1\,\text{m})$ and $F_z(z_o)$ were calculated for the three periods: i) pre-cutting; ii) post-cutting/pre-fertilizing and iii) post-fertilizing (Tables 6 and 7). These data have been corrected for
5 both advection and storage errors.

It can be seen that the median concentrations and fluxes for all periods were slightly smaller than the mean values, reflecting a log normal distribution of both $\chi(1\,\text{m})$ and $F_z(z_o)$. The effect of the data filtering for micrometeorological restrictions (Sect. 2.4, step vii) is illustrated, with slightly larger $\chi(1\,\text{m})$ and $F_z(z_o)$ from the filtered dataset.
10 This reflects a bias in the filtered dataset, that more data were excluded from night-time conditions, when $\chi(1\,\text{m})$ and $F_z(z_o)$ were smallest.

3.5.1 Pre-cutting

Prior to cutting of the grass, the flux was predominantly deposition to the surface (see Fig. 2 for typical diurnal course). The mean flux of the pre-cutting period was
15 $-5.8\,\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$ if all data were included and $-6.0\,\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$ if only data which passed the micrometeorological criteria were included. Any emission which was observed was generally small, the maximum emission observed over the period was $42\,\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$. The intensive grassland was generally acting as a sink for NH_3 during this period.

3.5.2 Post-cutting, pre-fertilizing

20 Immediately after cutting (29 May 2000 06:00 GMT) the NH_3 flux switched to emission. The emission had a diurnal pattern with very small fluxes during night-time and emission fluxes increasing during the daytime; daily peak emission values were 135 to 700 $\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$. The mean flux during the cutting period was $100\,\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$ (all data) or $138\,\text{ng}\,\text{m}^{-2}\,\text{s}^{-1}$ (only data which passes the micromet criteria). These values are
25 equivalent to 71 and 98 $\text{g}\,\text{N}\,\text{ha}^{-1}\,\text{day}^{-1}$, respectively.

3.5.3 Post-fertilizing

There was a rapid increase in NH_3 flux observed following the fertilization with N (5 June 2000 06:00 GMT), with values peaking at $3820\,ng\,m^{-2}\,s^{-1}$. During the first two nights after fertilization (5 and 6 June) there were mean nocturnal emissions of $1050\,ng\,m^{-2}\,s^{-1}$ and $150\,ng\,m^{-2}\,s^{-1}$, respectively. The mean flux over the whole post-fertilizing period was $474\,ng\,m^{-2}\,s^{-1}$ (all data) or $559\,ng\,m^{-2}\,s^{-1}$ (only data which passed the micrometeorological criteria). These values are equivalent to 337 and $398\,g\,N\,ha^{-1}\,day^{-1}$, respectively. The emission flux decreased on 11 June 2000, but was still up to $565\,ng\,m^{-2}\,s^{-1}$, 13 days after cutting.

The accumulated flux was -0.03, 0.50 and $3.41\,kg\,N\,ha^{-1}$ for the pre-cutting, post cutting and post fertilizing periods, respectively. This accumulated flux up to 10 days after the fertilization represented 3.2% of the N applied, or an equivalent of 3.6% if the post-cutting emissions were included.

3.5.4 Inter-instrument differences for $\chi(1\,m)$ and $F_z(z_o)$ for main management periods

It is relevant to consider the statistics of $\chi(1\,m)$ and $F_z(z_o)$ between the different ammonia analyzers for the main management periods. With longer-averaging periods the uncertainties between the different systems decreased (Table 8). For the four different measurement systems, the relative standard error in $\chi(1\,m)$ was similar for the three measurement periods at 15–20%. By contrast, the relative standard error in $F_z(z_o)$ varied substantially between the three measurement periods. This was as expected, with better agreement between the different ammonia analyzers being found for the periods with larger fluxes.

3.6 Time-course of uncertainties in the mean estimates of $\chi(1\,m)$ and $F_z(z_o)$

The availability of up to four parallel measurements of the ammonia concentrations and fluxes enabled an assessment of the uncertainty in the mean estimates of $F_z(z_o)$ and

$\chi(1\,\mathrm{m})$. The standard error (SE) of the mean 15 min values was calculated as $\sigma_{n-1}/\sqrt{n}$, where σ_{n-1} is the sample standard deviation and n is number of estimates available for a given 15 min period. Hence the magnitude of the SE depended on both the level of agreement of the denuders and the number of denuders operating at a given time. The time course of the SE is presented for $F_z(z_o)$ and $\chi(1\,\mathrm{m})$ (Fig. 7a and b). The SE of the 15 min values in the pre-cut period with substantial bi-directional exchange was typically around 60%, with absolute SE values of 10 to 20 ng m^{-2} s^{-1} (Fig. 7a). Following cutting, the errors differed diurnally with daytime SE in the flux typically 40%. The % SE was smallest following fertilization with daytime values typically 15%, increasing to typically 30% from 10 June. The overall median uncertainty in the 15 min estimates of $\chi(1\,\mathrm{m})$ was 18%, with values mostly in the range 5 to 50% (Fig. 7b). Regarding the storage and advection calculations, for much of the period these were rather small, but they were important in specific instances. The storage errors were generally less than 10% of the measured flux, although individual values occurred in the range 25–125% during periods of rapidly changing $\chi(1\,\mathrm{m})$ (Fig. 7c). The advection errors (Fig. 7d) were a similar magnitude to those for storage, with most values being less than 10% of F_z. Although larger absolute advection errors were observed post cutting and post fertilizing, the values as a percentage of the measured flux were smaller for these periods than for the pre cutting period.

4 Discussion

4.1 Inter-comparison of gradient measurements

Overall, the inter-comparison of gradient measurements was encouraging, with three of the flux measurements being within 11% of the mean estimate and the other within 32% (Table 5). There was also close agreement achieved across the concentration range, except for some days where overestimation of concentration is suspected to have occurred in some of the systems, possibly due to high operating temperatures

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and concentrations measured out of the calibration range. The inter-comparison high-lighted the need for regular calibration of flux gradient systems and regular quality standard checks. As concluded by Harrison and Kitto (1990), operator differences can induce the same amount of variation in NH_3 measurements as different measuring techniques and, although techniques such as AMANDA and the WEDD have been shown to be reliable in measuring NH_3, operators have to be vigilant in their running of these systems. A reliable clean deionised water supply, regular changing of pump tubing and regulation of instrument operating temperature are all essential to maintain the reliability of these systems.

Having four independent systems did result in a robust final dataset with an extremely high data coverage of NH_3 concentrations and fluxes of 98%. The main restriction on estimates was a filter according to strict micrometeorological criteria, which reduced the flux data coverage to 69% if these filter criteria were applied. With typically 50–70% data coverage of concentration and 30–50% for flux being more common in other NH_3 studies (e.g. Erisman et al., 1998; Sutton et al., 2001b; Horvath et al., 2005) and with the continuous record of uncertainty from the replicate systems, it is clear that this dataset is unique in coverage and robustness. As such it provides an important resource for interpretation of ammonia fluxes in relation to bioassays, models and in-teractions with other atmospheric components (Sutton et al., 2008a).

The availability of replicate instruments in the present experiment also highlight the need for caution when interpreting results from the more usual situation of a single ammonia flux detection system. Table 8 shows that the different instruments used here agreed to within 20% (standard error) for ammonia concentrations in the three man-agement periods. By contrast, while the flux by the three systems had a standard error of 20% for the post-fertilization period (when fluxes were largest and easiest to detect), the uncertainties were larger for the pre-fertilization periods. This indicated an uncertainty of 33% for the post-cut period and 76% for the pre-cut period. As demon-strated by Fig. 2, the uncertainties can be even larger for 15 min measurements (even leading to uncertainties in flux direction). As a result, great caution is needed when

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interpreting such NH_3 flux data when only one system is available. In this situation, it is thus essential to perform regular calibration and zero-flux tests (e.g. by bringing inlets to a common height and demonstrating that the measured flux is zero, Sutton et al., 1993a). Intercomparisons of measured ammonia fluxes with process models must similarly recognize the substantial uncertainty in the measured fluxes.

4.2 Influence of management activities on NH_3 flux

The present measurements support previous findings of enhanced emissions following grass cutting (Sutton et al., 1997, 2001a; Milford et al., 2001), with a mean flux of $98\,g\,N\,ha^{-1}\,day^{-1}$ after cutting compared with measurements of predominantly deposition before cutting. These emissions appear to be a consequence of altered N processing in the remaining sward rather than the lying cut grass (Sutton et al., 1997; David et al., 2008; Mattsson et al., 2008). The modelling of Sutton et al. (2001) and Riedo et al. (2002) explained this on the basis of a larger ammonia compensation point of the remaining plant (Riedo et al., 2002) and these interactions are further investigated by Burkhardt et al. (2008), Personne et al. (2008) and Sutton et al. (2008a).

As expected, emissions were also enhanced following fertilization, with a mean flux of $398\,g\,N\,ha^{-1}\,day^{-1}$. These fluxes are somewhat larger in magnitude to those observed earlier (Sutton et al., 1997; Milford et al., 2001). Expressed as the % emission of fertilizer N applied, in the present case 3.2% of the N (applied as calcium ammonium nitrate) was lost as ammonia within 10 days of application. The emission factor for ammonium nitrate fertilizer applied to grasslands in the UK is 1.6% of the applied N (van der Weerden and Jarvis, 1997). By comparison using AMANDA flux measurement, Milford et al. (2001) also estimated that 1.6% of fertilizer N (as ammonium nitrate) was lost as ammonia from a Scottish grassland. Strictly, the value from Milford et al. (2001) is not comparable with the present study, since their estimate referred to total emissions (including from grass cutting). Hence if the present losses following cutting are included, this gives an equivalent loss of 3.6% of the nitrogen, further emphasizing the larger values of this study. The larger emissions measured here are possibly a

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result of the high temperatures which were observed, particularly in the latter period of the campaign. The mean air temperature at 1 m was 17.6°C during 5–15 June 2000, although daily maximums reached 39°C (Nemitz et al., 2008b). The potential for NH_3 emission increases with increasing temperature due to the dependence of solubility of NH_3 on temperature, which affects the stomatal compensation point (Farquhar et al., 1980) as well as the NH_3 gaseous concentration at the soil and litter surface (Nemitz et al., 2001b, 2004).

The diurnal pattern of ammonia emission following fertilization is quite typical for the chainging patterns of environmental conditions, with largest fluxes occurring during the day. Substantial emission also occurred at night immediately after fertilizer application (5–6 June), demonstrating the importance of surface emissions from the soil and litter surface. However, nocturnal emissions ceased after this date, and therefore process models and other measurements (David et al., 2008) are needed to interpret the contribution of different sources and sinks.

5 Conclusions

An inter-comparison of four NH_3 gradient measurement systems was conducted over intensively managed grassland during a four week period in May–June 2000 as part of the GRAMINAE Integrated Experiment. The inter-comparison was encouraging, with three of the flux measurements being within 11% of the mean and the other within 32%. The inter-comparison highlighted the need for regular calibration of flux gradient systems and regular checks against quality standards. Operating four systems resulted in exceptionally high data coverage of measured ammonia fluxes (98%) and provided a continuous record of the uncertainty of the data. The measurements supported previous findings of enhanced emissions from grass cutting with a mean daily flux of 98 g N ha^{-1} day^{-1} after cutting compared to measurements of predominantly deposition before cutting. Emissions were also enhanced following fertilization, with a mean flux of 398 g N ha^{-1} day^{-1}. The results of this intercomparison provide a robust dataset for the

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evaluation of the processes controlling ammonia exchange, while indicating the need for caution in interpreting unreplicated ammonia flux measurements. It is clear that measurement of ambient ammonia concentration and flux still remains a challenge and future research should focus on continuing to improve ammonia measurement techniques and the reliability of flux measurements.

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Table 1. Summary of the different continuous ammonia concentration profile sampling systems used to calculate ammonia fluxes in the present study.

System acronym	System description	Location
FRI	AMANDA (3 point profile) operated by the Hungarian Forest Research Institute (FRI) in collaboration with the Hungarian Institute of Atmospheric Physics (IAP).	Site 1
FAL-CH	Mini-WEDD(3 point profile) operated by the former Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH).	Site 1
FAL-D	AMANDA (3 point profile) operated by the German Federal Agricultural Research Institute (FAL-D)	Site 1
CEH	AMANDA (3 point profile) operated by the Centre for Ecology and Hydrology (CEH) UK.	Site 2

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Table 2. Results of processing procedures for the ammonia flux data, from 21 May 2000 10:00–15 June 2000 12:00 GMT.

Proceedure	No. of valid (15-min) F_z data points remaining					Data coverage (%)				
Instrument	CEH	FRI	FAL-D	FAL-CH[a]	Mean estimate	CEH[b]	FRI[b]	FAL-D[b]	FAL-CH[c]	Mean estimate
Field Site number	2	1	1	1		2	1	1	1	
i) Periods of calibration or obvious malfunctioning of the instruments removed.	1912	1510	1893	1037		79	63	79	69	
ii) Measurements from obstructed wind sectors removed.	1400	1451	1841	1012		58	60	76	68	
iii) Gap-filling No. of valid data points remaining after gapfilling	1496	1531	1968	1372						
Number of gaps filled	23	13	31	71		62	64	82	92	
Median gap length (mins)	90	30	15	30						
Std. dev. of gap length (mins)	67	107	87	83						
iv) Mean gradient estimate, all data	-	-	-	-	2350	-	-	-	-	97.5
v) Data passing micromet criteria	-	-	-	-	1652	-	-	-	-	68.5

[a] FAL-CH gradient data comences on 30 May 2000 22:15, up until 30 May the system measured within-canopy profiles.

[b] % data coverage calculated for period 21 May 2000 10:00–15 June 2000 12:00.

[c] % data coverage calculated for period 30 May 2000 22:15–15 June 2000 12:00.

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Table 3. Results of the blind testing of aqueous ammonium Quality Control standards. The blind standards were prepared by a separate laboratory (ECN, the Netherlands). On each occasion two standards were distributed and the difference in concentration measured by each analyser was compared with the actual concentration difference to give an indication of the performance across the full measurement range. The % difference shown was calculated as $(100-(100\Delta[NH_4^+]_{lab}/\Delta[NH_4^+]_{QCstd}))$.

Date of test	$[NH_4^+]_{aq}$ of QC standard 1 $(mg\,l^{-1})$	$[NH_4^+]_{aq}$ of QC standard 2 $(mg\,l^{-1})$	% difference in concentration compared with the unknown standards			
			FRI	FAL-D	FAL-CH	CEH
25 May 2000	22	84	44[*]	13	21	16
31 May 2000	16	98	16	41	n/a	10
6 June 2000	273	38	4	21	n/a	−3

[*] This test was conducted on 22 May 2000 for FRI and a contaminated stripping solution container was found to be the cause; n/a: not available.

Table 4. Summary of linear regression results of $\chi(1\,\text{m})$ of the individual systems versus the value for the mean gradient ($\chi(1\,\text{m})_{mg}$) expressed in $\mu\text{g}\,\text{m}^{-3}$. The regression is given as: $\chi(1\,\text{m})_{\text{individ}} = c\chi(1\,\text{m})_{mg} + b$. The estimates are derived from the data shown in Fig. 4. Data from 3, 8, 9 and 10 June are excluded.

	c (slope)	c 95% confidence limits	b (intercept)	b 95% confidence limits	n	r^2
$\chi(1\,\text{m})_{\text{FAL}-\text{D}}$	0.99	[0.98, 1.01]	1.28	[1.19, 1.37]	1525	0.94
$\chi(1\,\text{m})_{\text{CEH}}$	0.82	[0.81, 0.83]	−0.21	[−0.27, −0.15]	1256	0.93
$\chi(1\,\text{m})_{\text{FRI}}$	1.15	[1.13, 1.17]	−0.70	[−0.81, −0.59]	1097	0.95
$\chi(1\,\text{m})_{\text{FAL}-\text{CH}}$	0.92	[0.91, 0.94]	−0.32	[−0.44, −0.20]	990	0.94

Table 5. Summary of linear regression results of $F_z(z_o)$ of the individual systems versus $F_z(z_o)_{mg}$ expressed in $\mathrm{ng\,m^{-2}\,s^{-1}}$, given as $F_z(z_o)_{\mathrm{individ}} = cF_z(z_o)_{mg} + b$. The estimates are derived from the data shown in Fig. 5.

	c (slope)	c 95% confidence limits	b (intercept)	b 95% confidence limits	n	r^2
$F_z(z_o)_{\mathrm{FAL-D}}$	0.89	[0.88, 0.90]	33.45	[28.68, 38.22]	1525	0.95
$F_z(z_o)_{\mathrm{CEH}}$	0.68	[0.67, 0.69]	−8.86	[−10.75, −6.97]	1256	0.96
$F_z(z_o)_{\mathrm{FRI}}$	1.08	[1.07, 1.09]	−5.36	[−9.16, −1.55]	1097	0.98
$F_z(z_o)_{\mathrm{FAL-CH}}$	1.10	[1.09, 1.11]	−5.58	[−11.16, 0.00]	990	0.98

Table 6. Variations in 15 min measurements of NH_3 concentration at 1 m from the mean gradient, $\chi(1\,\text{m})_{mg}$, throughout different measurement periods, before and after micromet filtering.

Period	Dataset	Mean $\mu\text{g m}^{-3}$	Stdev $\mu\text{g m}^{-3}$	Median $\mu\text{g m}^{-3}$	Min $\mu\text{g m}^{-3}$	Max $\mu\text{g m}^{-3}$	n	Data coverage (%)
Pre-cutting	All data	3.22	2.06	2.64	0.29	15.00	705	93.6
Pre-cutting	After filtering	3.25	2.03	2.64	0.35	10.81	592	78.6
Post-cutting/ Pre-fertilizing	All data	4.32	2.15	3.96	0.58	12.32	675	98.7
Post-cutting/ Pre-fertilizing	After filtering	4.50	2.46	3.86	0.58	12.32	393	57.5
Post-fertilizing	All data	8.38	5.55	6.78	0.92	31.52	970	99.7
Post-fertilizing	After filtering	9.21	5.76	7.38	0.92	31.52	667	68.6

Pre-cutting: 21 May 10:00–29 May 06:00; Post-cutting/Pre-fertilizing: 29 May 06:00–5 June 06:00; Post fertilizing: 5 June 06:00–15 June 12:00.

Table 7. Variations in 15 min measurements of mean gradient net NH_3 flux ($F_z(z_o)_{mg}$) throughout different measurement periods, before and after micromet filtering.

Period	Dataset	Mean $ng\,m^{-2}\,s^{-1}$	Stdev $ng\,m^{-2}\,s^{-1}$	Median $ng\,m^{-2}\,s^{-1}$	Min $ng\,m^{-2}\,s^{-1}$	Max $ng\,m^{-2}\,s^{-1}$	n	Data coverage (%)
Pre-cutting	All data	−5.8	13.1	−6.0	−64.2	42	705	93.6
Pre-cutting	After filtering	−6.0	13.9	−6.7	−64.2	42	592	78.6
Post-cutting/ Pre-fertilizing	All data	99.8	131.7	52.4	−54.3	703	675	98.7
Post-cutting/ Pre-fertilizing	After filtering	138.2	143.7	97.6	−49.2	703	393	57.5
Post-fertilizing	All data	474.0	611.0	191.7	−2.2	3821	970	99.7
Post-fertilizing	After filtering	559.4	603.5	304.5	1.4	3821	667	68.6

Pre-cutting: 21 May 10:00–29 May 06:00; Post-cutting/Pre-fertilizing: 29 May 06:00–5 June 06:00; Post fertilizing: 5 June 06:00–15 June 12:00.

Table 8. Standard errors (SE) and % standard errors in the concentration and flux estimates between the 4 ammonia sampling systems according to the different management periods (for the full dataset).

Variable	Pre-cutting	Post-cutting	Post-fertilizing
Mean $\chi(1\,\text{m})$	3.22	4.32	8.38
SE in $\chi(1\,\text{m})$	0.55	0.81	1.24
% SE in $\chi(1\,\text{m})$	17.0	18.7	14.8
Mean $F_z(z_o)$	−5.8	99.8	474.1
SE in $F_z(z_o)$	4.4	33.1	93.7
% SE in $F_z(z_o)$	76.2	33.2	19.8
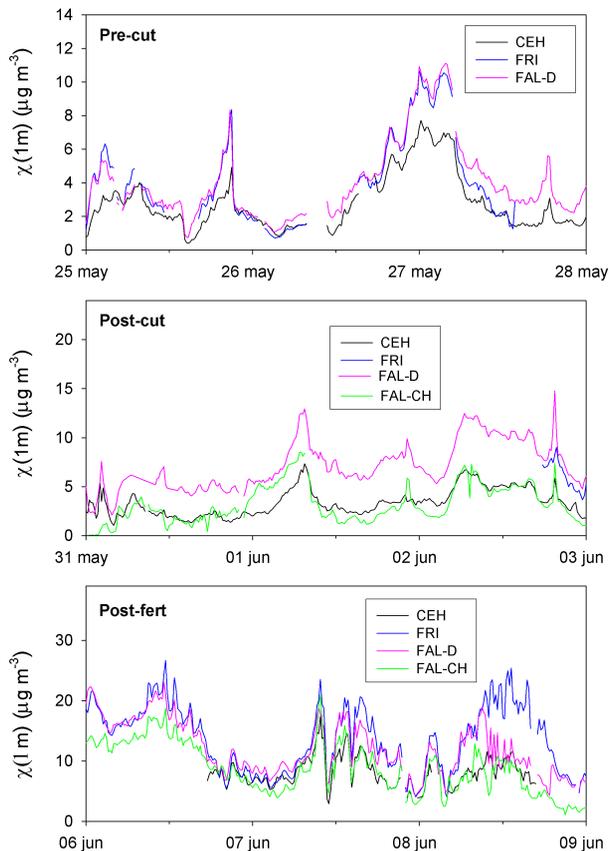
Fig. 1. Examples of $\chi(1\,\mathrm{m})$ for NH_3 from the four different systems for pre-cutting, post-cutting and post-fertilizing periods. Centre for Ecology and Hydrology (CEH), Hungarian Forest Research Institute (FRI), German Federal Agricultural Research Institute (FAL-D) and Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH). FAL-CH gradient data comences on 30 May 2000. Tick labels mark 00:00 GMT.

Fig. 2. Example of NH_3 fluxes (F_z) from the 4 different systems for pre-cutting, post-cutting and post-fertilizing periods. Centre for Ecology and Hydrology (CEH), Hungarian Forest Research Institute (FRI), German Federal Agricultural Research Institute (FAL-D) and Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH). FAL-CH gradient data comences on 30 May 2000. Tick labels mark 00:00 GMT.

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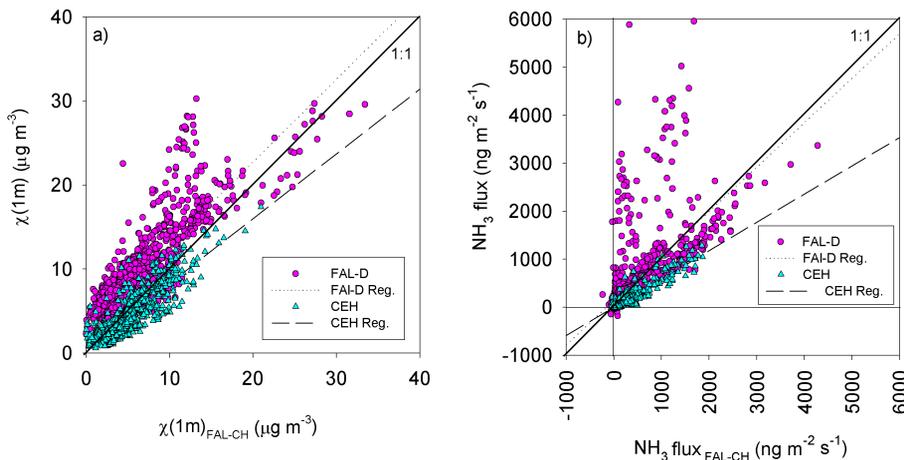
Fig. 3. Regression of **(a)** $\chi(1\,\mathrm{m})$ and **(b)** NH_3 flux at z_o (corrected for advection) measurements. German Federal Agricultural Research Institute (FAL-D), Centre for Ecology and Hydrology (CEH) and Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH).

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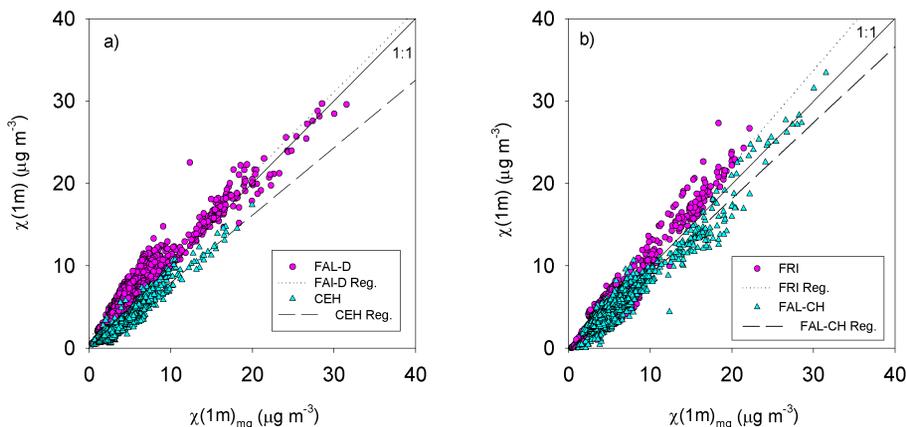
Fig. 4. Regression of $\chi(1\,\mathrm{m})$ from each system against mean gradient concentration, $\chi(1\,\mathrm{m})_{mg}$, for **(a)** German Federal Agricultural Research Institute (FAL-D) and Centre for Ecology and Hydrology (CEH) and **(b)** Hungarian Forest Research Institute (FRI) and Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH). Data from 3, 8, 9 and 10 June 2000 are not included.

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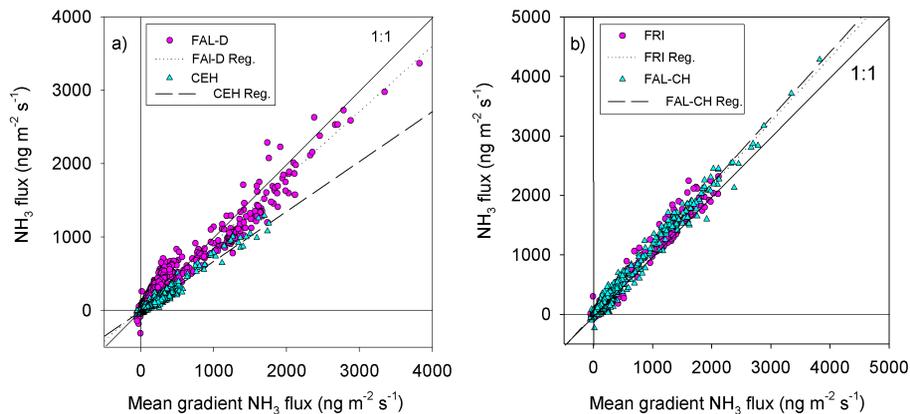
Fig. 5. Regression of NH$_3$ flux from each system against mean gradient flux for **(a)** German Federal Agricultural Research Institute (FAL-D) and Centre for Ecology and Hydrology (CEH) and **(b)** Hungarian Forest Research Institute (FRI) and Swiss Federal Research Station for Agroecology and Agriculture (FAL-CH). Data from 3, 8, 9 and 10 June 2000 are not included.
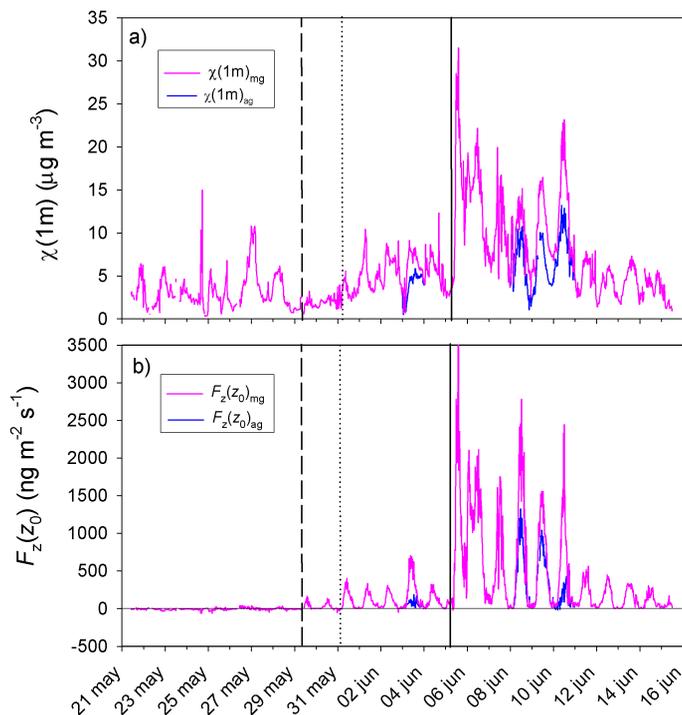
Fig. 6. Mean gradient estimate of **(a)** $\chi(1\,\text{m})_{mg}$ and **(b)** net NH_3 flux ($F_z(z_o)_{mg}$) showing response to management activities. The alternative gradient estimate is also shown ($\chi(1\,\text{m})_{ag}$ and $F_z(z_o)_{ag}$) on 3, 8, 9 and 10 June 2000, these are days with high instrument uncertainty (see text). Vertical lines indicate cutting (dashed line), removal of the grass from the field (dotted line) and $NH_4^+NO_3^-$ fertilization (solid line).

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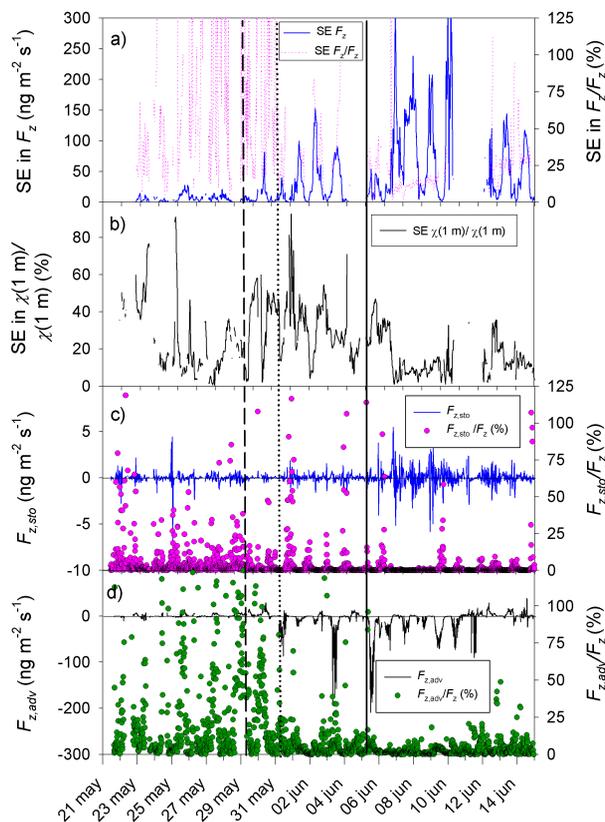
Fig. 7. Time-course of the uncertainty in mean $F_z(z_o)$ and $\chi(1\,m)$ presenting 1 h running medians of the 15 min estimates, shown together with the magnitude of advection and storage errors: **(a)** Percentage and absolute Standard Error (SE) in the measured ammonia flux, **(b)** % SE in $\chi(1\,m)$, **(c)** absolute storage error ($F_{z,sto}$) and $F_{z,sto}$ as a % of $F_z(1\,m)$, **(d)** absolute advection error ($F_{z,adv}$), sum of the modelled advection errors at $z=1\,m$ due to the experimental field and farm and $F_{z,adv}$ as a % of $F_z(1\,m)$. Vertical lines indicate cutting (dashed line), removal of the grass from the field (dotted line) and $NH_4^+NO_3^-$ fertilization (solid line).