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Dynamics of ammonia exchange with cut grassland: strategy and implementation of the GRAMINAE Integrated Experiment

M. A. Sutton¹, E. Nemitz¹, M. R. Theobald¹, C. Milford¹, J. R. Dorsey², M. W. Gallagher², A. Hensen³, P. A. C. Jongejan³, J. W. Erisman³, M. E. Mattsson⁴, J. K.Schjoerring⁴, P. Cellier⁵, B. Loubet⁵, R. Roche⁵, A. Neftel⁶, B. Hermann⁶, S. Jones⁶, B. E. Lehman^{*,†}, L. Horvath⁷, T. Weidinger⁸, K. Rajkai⁹, J. Burkhardt¹⁰, F. J. Löpmeier¹¹, and U. Daemmgen¹²

 ¹Centre for Ecology and Hydrology (CEH), Edinburgh Research Station, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK
 ²University of Manchester (UoM), Oxford Road, Manchester, M13 9PL, UK
 ³Energy research Centre of the Netherlands (ECN), Postbus 1, 1755 ZG Petten, The Netherlands
 ⁴Plant and Soil Science Laboratory, University of Copenhagen (UoC), Faculty of Life Sciences, Thorvaldsensvej 40, 1871 Frederiksberg C, Copenhagen, Denmark
 ⁵Institut National de la Recherche Agronomique (INRA), UMR Environnement et Grandes Cultures, Thiverval-Grignon, 78850, France
 ⁶Agroscope Reckenholz-Tänikon Research Station (formerly FAL-CH ; now ART), Zürich-Reckenholz, 8046 Zürich, Switzerland





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⁷ Hungarian Meteorological Service (HMS), PO Box 39, 1675 Budapest, Hungary (in association with the Forest Research Institute (FRI) of Hungary)

⁸ Eötvös Loránd University (ELU), Dept. Meteorology, 1117 Budapest, Hungary

⁹ Research Institute of Soil Science and Agrochemistry of Hungary (RISSAC), Herman Ottó út 15, 1022 Budapest, Hungary

¹⁰ University of Bonn, Institute for Crop Science and Resource Conservation, INRES-PE, Karlrobert-Kreiten-Str. 13, 53115 Bonn, Germany

¹¹ Agrometeorological Research Station of Deutscher Wetterdienst (DVD), Bundesallee 50; 38116 Braunschweig, Germany

¹² Institut fur Agrarokologie, Bundesforschungsanstalt fur Landwirtschaft (FAL), Bundesallee 50, 38116 Braunschweig, Germany

* formerly at: University of Bern, Hochschulstr. 4, 3012 Bern, Switzerland

[†] deceased

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Correspondence to: M. A. Sutton (ms@ceh.ac.uk)

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Abstract

A major international experiment on ammonia (NH₃) biosphere-atmosphere exchange was conducted over intensively managed grassland at Braunschweig, Germany. The experimental strategy was developed to allow an integrated analysis of different fea-

- ⁵ tures of NH₃ exchange including: a) quantification of nearby emissions and advection effects, b) estimation of net NH₃ fluxes with the canopy by a range of micrometeorological measurements, c) analysis of the sources and sinks of NH₃ within the plant canopy, including soils and bioassay measurements, d) comparison of the effects of grassland management options on NH₃ fluxes and e) assessment of the interactions
 ¹⁰ of NH₃ fluxes with aerosol exchange processes. Additional technical objectives included the inter-comparison of different estimates of sensible and latent heat fluxes, as well as continuous-gradient and Relaxed Eddy Accumulation (REA) systems for NH₃ fluxes.
- The prior analysis established the spatial and temporal design of the experiment, ¹⁵ allowing significant synergy between these objectives. The measurements were made at 7 measurement locations, thereby quantifying horizontal and vertical profiles, and covered three phases: a) tall grass canopy prior to cutting (7 days), b) short grass after cutting (7 days) and c) re-growing sward following fertilization with ammonium nitrate (10 days). The sequential management treatments allowed comparison of sources-²⁰ sinks, advection and aerosol interactions under a wide range of NH₃ fluxes.

This paper describes the experimental strategy and reports the grassland management history, soils, environmental conditions and air chemistry during the experiment, finally summarizing how the results are coordinated in the accompanying series of papers.

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Introduction 1

Atmospheric ammonia (NH₃) is a trace pollutant that has major impacts on terrestrial ecosystems and on the formation of secondary particulate matter. In the atmosphere, ammonia acts as a base, reacting to form ammonium (NH_{4}^{+}) aerosol. By contrast, deposition of both forms of reduced nitrogen (NH_x) can lead to soil acidification (e.g.,

5 van Breemen et al., 1982; Sutton et al., 1993c). In addition, NH, leads to ecological changes through eutrophication as well as through direct effects of gaseous NH₃ (e.g., Achermann and Bobbink, 2003; Erisman et al., 2007; UNECE, 2007).

As a result of reductions in European emissions of sulphur and nitrogen oxides over the last decade, the relative importance of NH₃ has grown substantially, so that it is 10 estimated that NH₃ will be the largest contributor to acidifying deposition in Europe in the next decade (Amman et al., 2005; Simpson et al. 2006). In addition, the role of NH₃ as a precursor for secondary aerosol formation, with effects on human health, visibility and radiative forcing is increasingly being recognized (e.g., Adams et al., 2001; Vayenas et al., 2005; Sutton et al., 2007). 15

The exchange of NH₃ between the land surface and the atmosphere has long been a key uncertainty in quantifying atmospheric budgets and nitrogen deposition (e.g., Eriksson, 1968; Söderlund and Svensson, 1976; Fowler et al., 1989; Langford et al., 1992; Sutton et al., 1993c, 1994; Hertel et al., 2006; Kugler et al., 2008). Biosphere-

- atmosphere exchange of NH₃ is complicated by the existence of bi-directional fluxes 20 for a wide range of land surfaces: the net flux at any time represents the combination of several opposing component fluxes, with leaf surfaces, leaf intercellular matrix, leaf litter and the soil surface (e.g., Denmead et al., 1978; Sutton et al., 1995a,b, 2000b, 2001a; Harper et al., 1996; Wyers and Erisman, 1998; Nemitz et al., 2000a, 2004a;
- Massad et al., 2008). These component fluxes are affected by a range of environ-25 mental, plant, soil and management factors, so that the overall NH₃ flux for a given surface may switch between net emission and net deposition on sub-hourly, diurnal and seasonal scales.

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Grasslands represent a major uncertainty in quantifying regional NH_3 fluxes and parametrizing atmospheric models. This is both due to the large area extent of grasslands and because of the wide range of grassland types and management practices. In the context of bi-directional NH_3 exchange, grasslands are of particular interest. Firstly, intensively managed grasslands are frequently net NH_3 sources (e.g., Sutton

- Firstly, intensively managed grasslands are frequently net NH₃ sources (e.g., Sutton et al., 1993b, 2001a; Bussink et al. 1995; Harper et al. 1996, Plantaz et al., 1997; Milford et al. 2001b; Daemmgen and Webb, 2005; Misselbrook et al., 2005; Kruit et al., 2007), resulting in grasslands impacting on atmospheric NH₃ composition. Secondly, semi-natural grasslands are mainly net NH₃ sinks (Duyzer et al., 1994; Sutton et al., 1993a; Flechard and Fowler, 1998; Spindler et al. 2001; Horváth et al. 2005), resulting
- 1993a; Flechard and Fowler, 1998; Spindler et al. 2001; Horvath et al. 2005), resultin in atmospheric NH₃ impacting on the ecological functioning of grasslands.

Substantial progress has been made in quantifying these exchange processes for grasslands and other ecosystems, particularly through the work of major European Union research projects, such as EXAMINE (Sutton et al., 1995b, 2000b; Meixner et

- ¹⁵ al., 1996; Schjoerring et al. 1998; Wyers and Erisman, 1998; Nemitz et al., 2004a) and the LIFE programme (Flechard and Fowler, 1998; Flechard et al. 1999; Erisman et al., 2001a; Spindler et al., 2001), as well as other international activities (Meyers et al., 2006; Trebs et al., 2006; Walker et al., 2006; Kruit et al., 2007; Sutton et al., 2007; Wolff et al., 2007; Neiryncka and Ceulemans, 2008).
- ²⁰ Complementing these efforts, the EU GRAMINAE (GRassland AMmonia INteractions Across Europe) project has provided a major assessment of the dynamics of NH₃ fluxes with different European grassland types, including a wide network of both intensively managed and semi-natural grasslands (e.g., Sutton et al., 2001a, 2002; Milford et al., 2001a,b; Mosquera et al., 2001; Hill et al., 2001; Horvath et al., 2005; Loubet et al., 2001, 2002, 2006; Mattsson and Schjoerring, 2002, 2003; Riedo et al., 2002).

A limitation of such a dispersed network approach, however, is that it is not economically feasible to consider in an integrated way all of the interacting factors that affect NH_3 exchange at all the individual measurement sites. As part of the GRAMINAE effort, a major experiment was therefore designed to consider the integration of different

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processes affecting NH₃ exchange. The experiment took place at the German Federal Agricultural Research Centre Bundesforschungsanstalt für Landwirtschaft, (FAL) near Braunschweig in 2000, and linked micrometeorological, cuvette and bioassay analyses for NH₃, gas-particle interactions, effects of management practice and the role of advection from agricultural sources on NH₃ fluxes in the rural landscape. Overall, the experiment included fifty scientists in the field.

The present paper describes the objectives, strategy and implementation of the GRAMINAE Braunschweig Experiment. The method developments and prior modelling tasks necessary to refine the measurement strategy are summarized, followed by a description of the spatial and temporal design of the experiment, including the soil

¹⁰ by a description of the spatial and temporal design of the experiment, including the soil and meteorological conditions prevailing during the experiment. Finally, the paper outlines the inter-dependence of the detailed analyses arising from the experiment, and reflects on the merits and challenges of such an integrated approach.

2 Key questions and objectives

- ¹⁵ The GRAMINAE Integrated Experiment addressed five major scientific questions:
 - 1. How do the component sources and sinks of ammonia exchange (leaf surfaces, leaf tissues, plant uptake from soil, litter decomposition) integrate to control net fluxes with the atmosphere?
 - 2. What are the mechanisms by which grassland management events (cutting and
 - N fertilization) affect component and net ammonia fluxes?
 - 3. When does the location of a micrometeorological study site in a real landscape lead to significant quantifiable effects of advection on net ammonia fluxes and their measurement?
 - 4. How much does the near-surface perturbation of the equilibria between ammonia,
 - acid gases and aerosols lead to non-conservation of vertical ammonia fluxes, and



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is this a relevant mechanism for particle formation/growth?

5. To what extend can divergence in vertical ammonia fluxes (either due to advection or chemical reactions) be directly measured by available techniques?

All of these questions are closely linked. Although first attempts to measure NH₃ fluxes by eddy covariance have been made (Shaw et al., 1998; Famulari et al., 2004; White-5 head et al., 2008), most studies have applied the aerodynamic gradient method (AGM), which is based on determination of the vertical concentration profile of NH₃ above the canopy (e.g., Sutton et al., 1993a; Wyers and Erisman, 1993; Kruit et al., 2007; Neirynck and Ceulemans, 2008). The gradient method is not well suited to the guantification of divergence in the vertical flux (compared with the flux at the surface), since 10 it estimates an average vertical flux based on measurements at different heights. Flux measurements methods that require sampling at a single height are therefore preferred (e.g. eddy covariance, EC; relaxed eddy accumulation, REA). Given the challenges for accurate EC measurements of NH₃, a priority was identified to the application of REA for NH₃, with the ultimate goal to deploy several REA systems at different heights and 15 thereby directly measure vertical flux divergence (i.e. the change of the NH₃ flux with

height) where this is significant.

Both advection of NH₃ from nearby sources and reactions with acid gases are possible sources of flux divergence and can lead to errors in the determination of vertical fluxes using micrometeorological methods. The tendency in micrometeorological studies has been to try to avoid such effects through careful selection of field sites and experimental conditions. However, it often proves difficult to estimate the importance of advection and chemical interactions a priori. Advection from nearby sources is often thought to be of minor importance, as long as the flux footprint falls within the study

²⁵ area, while Loubet et al. (2001, 2006) have shown that downwind of ground-level NH_3 point-sources, advection errors can be significant for several hundred metres. Similarly, Nemitz et al. (2004a, b) and Nemitz and Sutton (2004) showed that evaporation of NH_4NO_3 near the ground can alter NH_3 exchange fluxes, even where this effect



might be expected to be insignificant.

In addition, the conscious minimization of advection errors in the choice of field sites means that the "ideal" field sites typically selected by researchers are far from representative. By contrast, such non-stationarities are "real world" issues that need to be quantified rather than avoided. This is particularly relevant for NH₃ where nearby agricultural point sources are often impossible to avoid in many European land-scapes. Advection and chemistry effects are also of scientific interest in their own right as processes that affect the net exchange of NH₃, HNO₃ and NH₄⁺ containing aerosol (e.g. Brost et al., 1988; Milford et al., 2001a; Nemitz et al., 2004a, b; Nemitz and Sutton, 2004; Loubet et al., 2006). The GRAMINAE Braunschweig experiment was therefore designed specifically to investigate the extent of vertical flux divergence due to advection and chemistry effects.

Finally, a core issue of NH₃ bi-directional exchange is the quantification of how different component fluxes interact to generate net NH₃ exchange. To understand these effects requires analysis of the interactions with plant physiology, litter dynamics and interactions with soil conditions. In particular, the vertical structure of a plant canopy can lead to an internal cycle, so that NH₃ released from litter or the soil surface may be recaptured by overlaying leaves (Denmead et al., 1976; Nemitz et al., 2000a, b; Harper et al., 2000). The understanding of these interactions can be also improved by the comparison of fluxes following different crop management decisions, and by the

integration of above-canopy measurements of net NH₃ exchange with cuvette measurements, bioassay determinations and analysis of within-canopy NH₃ fluxes.

Based on the above concerns, the issues relevant to the GRAMINAE experiment are summarized graphically in Fig. 1. These issues were used to develop the main scientific and technical objectives of the Integrated Experiment.

The Primary Scientific Objectives were established as:

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1. to measure the net exchange flux of NH₃ over managed grassland using micrometeorological methods, quantifying the effect of cutting, nitrogen fertilization and environmental controls;

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- to apply bioassay measurements to estimate the foliar NH⁺₄, pH and related parameters and thereby to estimate foliar NH₃ compensations point for different grass species and plant conditions;
- 3. to apply cuvette measurements to quantify the potential for NH₃ emissions from foliage, drying or decomposing leaf litter;

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- 4. to use a comparison of different management treatments with cuvette and bioassay measurements to improve the understanding of controls on NH₃ fluxes;
- 5. to integrate the quantification of component processes and fluxes in the canopy, including measurements of soil N availability/uptake, apoplastic NH₄⁺ concentrations, and within-canopy source/sink distributions;
- 6. to quantify particle size-distributions, particle number fluxes and chemical fluxes of acid gases and inorganic aerosols;
- 7. to quantify the extent of chemical reactions of NH_3 in the air within and immediately above the plant canopy to form or evaporate particulate matter, and to consider the consequence of this process for net NH_3 and particle fluxes;
- 8. to quantify the interactions of NH₃ fluxes with the chemistry of leaf surfaces wetted by dew or rain;
- to determine horizontal concentration gradients of NH₃ downwind of a farm source allowing quantification of the advection error in the vertical flux and analysis of the consequences for net NH₃ fluxes;
- 10. to compare NH₃ emissions from a farm source estimated by plume measurements and inverse dispersion modeling, as a basis to assess inventory-based emission estimates for cattle and pigs.

The Technical Objectives that provide the basis to address primary objectives included:

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- 1. to inter-compare above-canopy estimates of turbulent exchange for momentum, sensible and latent heat, identifying the implications for sampling precision in situations without replication and providing robust estimates for this study;
- to inter-compare estimates of NH₃ fluxes derived from different continuous NH₃ gradient methods, identifying the implications for un-replicated measurements and to provide a robust best-estimate of the net NH₃ flux;

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- to evaluate and inter-compare several continuous REA systems for NH₃ flux measurement and, if sufficiently precise, to deploy these to measure vertical flux divergence;
- to determine the turbulent structure within the grass canopy and to quantify diffusive time-scales, comparing direct turbulence measurements with estimates derived from application of a Radon tracer method;
 - to develop and test a method for estimating total soluble nitrogen concentration of grass leaves as an estimate of "substrate nitrogen" for comparison with ecosystem model estimates;
 - 6. to refine an approach to estimate farm-scale NH₃ emissions (applied to the dairy and pig unit of the FAL) from fixed and mobile NH₃ concentration measurements downwind of the farm coupled with inverse dispersion modelling.

These objectives relate both to the measurements and to the development of a suite of models. Firstly, models were used as analysis tools to derive further measurementbased estimates, e.g., landscape-scale inverse dispersion and advection modelling (Loubet et al., 2001, 2006), within-canopy inverse Lagrangian modelling (Nemitz et al., 2000a), modelling of gas-particle interactions (Nemitz and Sutton, 2004) and the calculation of in-canopy eddy diffusivities from Radon profiles (Lehmann et al., 1999).

²⁵ Secondly, other models were applied with basic site, management and environmental

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input data to compare with the measured results, e.g. soil-vegetation- atmospheretransfer (SVAT) modelling for NH_3 net exchange (Sutton et al., 1995b, 1998; Flechard et al., 1999; Nemitz et al., 2001b), ecosystem modelling of NH_3 exchange with grassland functioning (Riedo et al., 2002; Massad et al., 2008) and aerosol deposition modelling (Gallagher et al., 2002).

3 Prior assessment and development

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Given the interaction of objectives, it was important to design the GRAMINAE experiment so that certain tasks would not compromise others, to refine sampling methods and to establish that the effects of interest would be detectable. Prior modelling focused on the issue of advection, while prior method development aimed to improve continuous REA measurement methods for NH_3 , foliar N bioassays, methods for measurement of acid gases and aerosol and a fast NH_3 sensor for plume measurements.

3.1 Prior modelling of advection effects

The field site at FAL Braunschweig was initially selected because of the good local infrastructure, control of field management, large field size and presence of a nearby farm NH₃ source. Before confirming the exact location of the measurements, it was necessary to show that advection effects would be significant, but not so large as to dominate the flux and uncertainties, which would prevent assessment of other interactions (e.g., particle interactions, internal canopy exchange).

Based on housed animal numbers (120 cows, 130 other cattle, 100 pigs), NH₃ emissions from the farm unit were estimated using standard emissions factors to be 10.1 kg NH₃ day⁻¹. The possible measurement locations in the main grass field ("Kleinkamp") (see Sect. 4.1) were ~400–800 m east of the farm unit, allowing for sufficient fetch in the field under westerly air flow. The MODDAS model (Loubet et al., 2006) was applied to estimate the horizontal gradients in NH₃ concentrations and the advection errors in ver-

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tical NH₃ fluxes ($F_{z(ad)}$) with distance from the farm source (Figs. 2, 3). The modelled concentrations were found to be in reasonable agreement with preliminary measurements of NH₃ concentrations (October–November 1999). Monthly mean NH₃ values at different locations around the farm (see Sect. 4.1) ranged 12–33 μ g m⁻³, while at 240 m east of the farm the measured mean concentration was 3.5 μ g m⁻³ compared with a background of 2.2 μ g m⁻³.

The model analysis showed that advection errors would dominate NH₃ fluxes at distances closer than ~100 m from the farm ($F_{z(adv,2.7 m-hc)}$ >400 ng m⁻² s⁻¹), with the increased values of $F_{z(adv)}$ for larger measurement heights. By contrast, at the furthest measurement distance (780 m) calculated values of $F_{z(adv,2.7 m-hc)}$ were ~20 ng m⁻² s⁻¹, while the value for 550 m was 28 ng m⁻² s⁻¹ (for periods when the measurement sites would be downwind of the farm source). The values at these larger distances are small enough not to be important in periods of high NH₃ emission (e.g. after fertilization), but would be significant for periods of smaller NH₃ fluxes (e.g. prior to cutting). This analysis supported the use of the FAL Braunschweig field, and it was concluded to use two distances for flux measurement (550 m, main site; 780 m second site for comparison, Fig. 4). These flux sites were supported by measurement of NH₃ concentrations closer to the farm.

3.2 Development of relaxed eddy accumulation systems for ammonia

- ²⁰ Continuous systems to measure vertical concentration gradients have largely used wet chemical methods and have become widely available (Wyers et al., 1993; Sutton et al., 1995b, 2007; Neftel et al., 1998). By contrast, although traditional batch sampling techniques have been applied to measure NH₃ fluxes by REA (Zhu et al., 2000), continuous REA systems for NH₃ represent an ongoing challenge. A significant effort was there-
- fore invested in GRAMINAE to refine and test several continuous implementations for REA (e.g., Neftel et al., 1999; Erisman et al., 2001b; Sutton et al., 2001a; Nemitz et al., 2001a, Pryor et al., 2002), which were then compared in the GRAMINAE experiment.



3.3 Development of bioassays of ammonia emission potential

It is well known that "compensation point" concentrations apply to NH_3 exchange with vegetation, these being the air concentrations of NH_3 at which no net flux occurs, with component emission fluxes balancing uptake at different scales (e.g. Farquhar et al.,

⁵ 1980; Sutton et al. 1995b). The stomatal compensation point (χ_s) represents the air concentration in equilibrium with the apoplastic (intercellular) fluids of plant leaves. The temperature dependent value of χ_s can be calculated from the thermodynamic equilibria and the ratio the ratio [NH⁴₄]/[H⁺] in the apoplast, denoted Γ_s (Sutton et al., 2000b; Nemitz et al., 2000b, 2001b), making it of great interest to refine bioassays for
¹⁰ determination of [NH⁴₄] and [H⁺]. A critical experimental evaluation of such methods was therefore made (Husted et al., 2000b), including analysis of practical issues such as the extent of pH buffering on extracted (diluted) apoplastic solutions (Hill et al., 2001).

Prior development of an ecosystem model of coupled grassland C-N cycling and
¹⁵ NH₃ exchange (Sutton et al., 2001a; Riedo et al., 2002) also highlighted the functional importance of different plant N pools, including "substrate nitrogen" being the nitrogen available for plant growth, as compared to that built into plant structures. Although this term represents a model construct, efforts were made to develop a measurement of total soluble nitrogen concentrations in the plant as an estimate of substrate nitrogen, as
well as to measure other soluble nitrogen indicators, such as amines, total foliar ammonium and nitrate (Husted et al., 2000a; Loubet et al., 2002; Mattsson and Schjoerring,

3.4 Measurement of ammonia interactions with particles

2003).

Several fast response optical methods were already available for the measurement
 of particle fluxes, by EC, including condensation particle counters (CPC) and Active
 Scattering Aerosol Spectrometer Probes (ASASP-x) (e.g. Gallagher et al., 1997; Nemitz et al., 2002, 2004b). A key challenge, however is the continuous measurement

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of chemically speciated aerosol fluxes. For this purpose prior efforts were placed to refine a gradient system which was used during a former EXAMINE campaign (Nemitz et al., 2004b). This system is based on the steam jet aerosol collector (SJAC) approach (Khlystov et al., 1995) coupled with a denuder system for acid gases, running with on-line chromatography (Jongejan et al., 1997; Wolff et al., 2007), permitting measurement at two heights simultaneously. In this way, the combined system could be deployed during the GRAMINAE Integrated Experiment to measure mass fluxes of aerosol and acid gases according to the AGM.

4 Field site and measurement strategy

10 4.1 Description of the field site

The site at FAL is located at latitude 52°18′N and longitude 10°26′E, being rather flat at 79 m above mean sea level. FAL is situated at the fringe of the Lower Saxonian city of Braunschweig (Brunswick) with 245 000 inhabitants, 12 km WNW of the city centre. It is therefore subject to mixed agricultural air masses for SW to N wind directions and more urban air masses for easterly winds. The main field of the experiment, "Kleinkamp" (Fig. 4), is surrounded by arable and other managed grassland to the N, woodland, by grassland and sub-urban development to the E and S, and by experimental arable plots and the FAL farm to the west.

The FAL Farm is the main NH₃ point source in the immediate locality, which typically
 houses (according to the prior estimates) 120 dairy cows, 130 other cattle and 100 pigs (50 being in a house fitted with NH₃ scrubbing technology). Based on emission factors for housing and manure storage, 92% of the NH₃ emission was estimated to result from cattle excreta. A further source of NH₃ was liquid cattle manure (slurry) spreading on Field II (see Fig. 4) at ~17:00 GMT 22 May, leading to NH₃ plumes over
 Kleinkamp during spreading and at ~1800 24 May. Emissions from this source ceased on 25 May, following irrigation (with dirty water).

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The Kleinkamp field is 12 ha being ~600 m long and up to 300 m wide (Fig. 4). The soil is sandy, having an upper rooting and ploughing A horizon with a high organic matter content, a yellow C1 horizon with occasional worm and root penetration, and below this a red coloured C2 horizon, including ~20% gravel and flints. Following FAO nomenclature, the soil is a dystric-luvic-cambisol on silty-sandy, cover-sediments overlying gravelly-sandy moranic deposits and glacifluviatile sands. Further details are given in Table 1. A record of the soil conditions during the measurements is provided

in Fig. 12 below.

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The field was sown in March 1996 with 55 kg ha⁻¹ "Country 2010" seed: *Lolium perenne* (6 varieties, 29% by mass), *Festuca pratensis* (2 vars., 33%), *Poa pratensis* (2 vars., 12%), *Phleum pratense* (4 vars., 18%) *Festuca rubra* (3%) and *Trifolium repens* (5%). A further 20 kg ha⁻¹ *Lolium perenne* was intersown on 20 March 2000.

From 1996 to 1999, the field typically received 1 application of liquid animal manure (slurry) each spring (between 25 January and 20 March) at 30–50 tonne ha⁻¹ with ¹⁵ an estimated N content of 1 kg N tonne⁻¹. Annually, the field received 2–4 applications of mineral fertilizer between March and September (usually urea – ammonium nitrate solution, but in 1997 and 1998 calcium ammonium nitrate was used in July and September). Overall, the field received annual mineral fertilizer inputs of 144, 220, 212 and 288 kg N ha⁻¹ for the years 1996, 1997, 1998 and 1999, respectively, with an

- additional average slurry input of 37.5 kg N ha⁻¹ year⁻¹. In order to simplify conditions for the GRAMINAE experiment, no animal manure was applied in 2000 prior to June. Instead only calcium ammonium nitrate was used, with 100 kg N ha⁻¹ being applied on 27 March 2000 and 108 kg N ha⁻¹ being applied on 5 June 2000 (as part of the experiment). The field was ungrazed since sowing, being cut for silage once in June
- 1996, twice in 1997 (May and June), and three times each in 1998–1999 (May, June, August). In 2000 the first cut was made on 29 May 2000 (as part of the experiment). The field was irrigated on 15–17 May, during the set-up stages of the experiment.

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4.2 Spatial measurement strategy

Measurements were made at a series of 7 main sites in order to meet the different objectives of the experiment, as shown in Fig. 4. Mains electricity was provided to all sampling sites, with temporary installations established for the experiment at Sites 1–4.

5 4.2.1 Site 1: Main sampling site

The main flux measurement site was located at 550 m east of the FAL farm in the centre of Kleinkamp. This site was selected on the basis of the prior modelling of advection (Sect. 3.1) as being sufficiently far from the farm to have only moderate advection effects in westerly winds, while being generally suitable for flux measurements (fetch over Kleinkamp of >150 m) when winds were from 20–180° and from 190–360°. The measurements at this site were made in a N-S line 40–80 m from the N edge, and then with two lines (20 m apart) 90–110 m from the N edge of the field (see Figs. 5 and 6). The field measurements at Site 1 were supported by two mobile laboratories (Fig. 5b) for deployment of particle-sampling equipment (UoM Lab., 30 m into the field)
¹⁵ and for chemical preparation (ECN Mobile Lab., at the N edge of the field). Details of the measurements made are given in Sect. 5.

4.2.2 Site 2: Far field site

Site 2 was located at 750 m east of the farm, approximately 25 m from the E edge of Kleinkamp. It was established to permit independent measurement of ammonia fluxes at a site with smaller advection errors than Site 1, due to the larger distance from the FAL farm. A gradient AMANDA system (Wyers et al., 1993) was deployed allowing fluxes to be measured by the AGM, together with measurement of turbulence and sensible heat fluxes by an ultra-sonic anemometer using EC. Fetch was >150 m for the sector 200–290°.

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4.2.3 Site 3: Near-farm transect

A N-S transect was used to measure plumes of NH_3 200–250 m downwind of the FAL farm under westerly flow. At this site, a mobile, fast-response NH_3 analyzer was deployed for transect measurements, together with 3 single-channel AMANDA analyzers fixed at 50, 150 and 250 m from the N edge of the field (Hensen et al., 2008¹).

4.2.4 Site 4: Small plots

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In order to address the effect of different management options on net ammonia exchange (Sect. 4.3), 4 small plots, each of ~10 m×10 m, were marked out from the Kleinkamp field at the start of the experiment. These plots were located at the N edge of the field, NE of Site 1 (Figs. 4 and 5). The main field was designated as Plot 1 (periods A and B), with the small plots designated as Plots A2, A3, B2, B3. In addition, a further 15 m x 20 m was left uncut and unfertilized (Plot C) for determination of vertical profiles of turbulence, temperature and NH₃ within the canopy after the cut (Nemitz et al., 2008²). Measurements in the small plots focused on cuvette measurements of NH₃

²Nemitz, E., Loubet, B., Cellier, P., Lehmann, B., Neftel, A., Jones, S. K., Hargreaves, K. J., and Sutton M. A.: Turbulence characteristics and transport mechanisms in grassland canopies, Biogeosciences Discuss., to be submitted, 2008a.

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¹Hensen, A., Loubet, B., Mosquera, J., van den Bulk, W. C. M., Erisman, J. W., Dämmgen, U., Milford, C., Löpmeier, F. J., Cellier, P., Mikuska, P., and Sutton, M. A.: Estimation of NH₃ emissions from a naturally ventilated livestock farm using local-scale atmospheric dispersion modelling, Biogeosciences Discuss., to be submitted, 2008a. This and the following footnotes refer to the coordinated group of papers for the Special Issue: "Processes controlling the exchange of ammonia between grassland and the atmosphere (GRAMINAE)".

fluxes (David et al., 2008a³, b⁴), and foliar N bioassays in relation to altered soil, vegetation and microclimate (Mattsson et al., 2008a). Site 4 was supported by two further mobile laboratories (Fig. 5b) for apoplastic extractions and plant handling (UoC/FAL-D Lab) and for measurements related to the small plots (INRA Lab).

5 4.2.5 Site 5: FAL Farm buildings

A record was kept of the numbers of different types of livestock in each of the farm buildings during the experiment, allowing detailed calculation of NH_3 emissions according to the inventory approach (Hensen et al., 2008a¹). The sources included both livestock houses and manure stores and the location of the main sources is shown on Fig. 4. Ammonia concentrations were measured at several points around the farm

- using passive samplers, according to the method of Ferm and Rodhe (1997).
 - 4.2.6 Site 6: Tall tower background site

In order to study the effect of surface perturbation of NH₃, HNO₃, HCI and aerosol equilibria, it was desirable to obtain measurements of gas concentrations in the well ¹⁵ mixed atmosphere, well above the surface. For this purpose, a tower building of the German National Metrology Institute (Physikalisch Technische Bundanstalt, PTB) 1 km ENE of Site 1 provided a measuring platform 43 m above ground. An automatic batch wet-denuder (Keuken et al. 1988) was deployed for hourly measurement of NH₃,

⁴David, M., Roche, R., Mattsson, M. E., Sutton, M. A., Dämmgen, U., Schjoerring, J. K., and Cellier, P.: Analysis of ammonia fluxes with intensively managed grassland using dynamic chambers – Part 2: The effects of management options, Biogeosciences Discuss., to be submitted, 2008b.



³David, M., Loubet, B., Cellier, P., Mattsson, M., Nemitz, E., Roche, R., Riedo, M. Schjoerring, J. K., and Sutton, M. A.: Analysis of ammonia fluxes with intensively managed grassland using dynamic chambers – Part 1: Sources and sinks of ammonia at canopy level, Biogeosciences Discuss., to be submitted, 2008a.

 HNO_3 , HCl and SO_2 for key periods during the experiment.

4.2.7 Site 7: Permanent meteorological measurement site

The Kleinkamp field is immediately adjacent to a centre of the German Weather Service (Deutscher Wetter Dienst, DWD), which makes permanent meteorological and agro-meteorological measurements over several canopy types. The main DWD site is \sim 250 m E of the farm, while windspeed and direction (used for the local dispersion modelling, Loubet et al., 2008⁵ and see footnote 1) were measured (10 m) at the NE corner of the "test crop" shown on Fig. 4.

4.3 Temporal measurement strategy

The experiment was divided into three measurement periods of approximately one week to study the effects of cutting and fertilization on ammonia fluxes and exchange processes. The field site was measured out, electricity installed and equipment established on 14–22 May 2000, with measurements started at 12:00 Greenwich Mean Time (GMT) on 22 May. This allowed seven days of measurements before the grass
 ¹⁵ was cut (from ~0.75 to 0.07 m height) at 06:00–10:00 GMT on 29 May. On the morning of 30 May, the grass was turned-over using mechanical "spinners' to help dry it and was then lifted from the field 06:00–10:00 GMT on 31 May. Hand raking of the grass around the sampling equipment at Site 1 was complete by 12:00 GMT.

Seven days after cutting, the field was fertilized with nitrogen at 06:00–07:00 on 5 June (Sect. 4.1), allowing the effects of fertilization of the main field to be followed for 10 days, before measurements were stopped at 12:00 GMT on 15 June.

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⁵Loubet, B., Milford, C., Hensen, A., Dämmgen, U., Erisman, J. W., Cellier, P., and Sutton, M. A.: Advection of ammonia over a pasture field, and its effect on gradient flux measurements, Biogeosciences Discuss., to be submitted, 2008.

4.3.1 Measurement strategy on the main field

Micrometeorological measurements of net NH_3 fluxes were made throughout the experiment using the AGM, while additional resources were deployed to address different questions before and after the cut. Before the cut, particular attention was given

- to measuring within-canopy turbulence and NH₃ concentration profiles (Nemitz et al., 2008a²) investigating the nature of canopy sources and sinks of NH₃. This also included attention to vertical profiles of apoplastic bioassays (Hermann et al., 2008⁶) and differences between plant species (Mattsson et al., 2008b). After the cut, the NH₃ detection systems (ECN, FAL-CH) used for within-canopy profiles, were deployed
- in the intercomparison of REA methods (Hensen et al., 2008⁷), while bioassay measurements focused on measuring the consequences of different management options using the small plots (Sect. 4.4.2) and on determining the extent of diurnal variability of apoplastic [NH₄⁺] and [H⁺] and total tissue NH₄⁺ and NO₃⁻. Diurnal courses of 3-hourly bioassay sampling were made on 26–27 May, 4–5 June and 12–13 June (Herrmann et al., 2008⁶).

4.3.2 Measurement strategy of the small plots

Measurements on the small plots and comparison with the main field allowed the effects of hay/silage management, different levels of N supply, and the longer term effects after cutting to be tested. The following 10 m×10 m plots were defined:

⁷Hensen, A., Nemitz, E., Flynn, M., Blatter, A., Jones S. K., Sørensen, L. L., Hensen, B., Pryor, S., Jensen, B., Otjes, R. P., Cobussen, J., Loubet, B., Erisman, J. W., Gallagher, M. W., Neftel, A., and Sutton M. A.: Inter-comparison of ammonia fluxes obtained using the Relaxed Eddy Accumulation technique, Biogeosciences Discuss., submitted, 2008b.

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⁶Herrmann, B., Mattsson, M. E., Jones, S. K., Cellier, P., Milford, C., Sutton, M. A., Schjoerring, J. K., and Neftel, A.: Vertical structure and diurnal variability of ammonia emission potential within an intensively managed grass canopy, Biogeosciences Discuss., submitted, 2008.

- Plot A1: Main field not cut,
- Plot A2: Cut early on 24 May, subsequent lifting (for silage) and no N fertilization,
- Plot A3: Cut early on 24 May, grass left to dry (as hay) and no N fertilization;
- Plot B1: Main field cut 29 June and fertilized 5 June with $\sim 100 \text{ kg N} \text{ ha}^{-1}$,
- Plot B2: Cut 30 June (split into two: silage and hay) and no fertilization,
- Plot B3: Cut 30 June and fertilized 5 June with \sim 200 kg N ha⁻¹.
- While cuvette NH_3 flux measurements focused sequentially on Plots A1-3 and then Plots B1-3 (David et al., 2008a³, b⁴), the bioassay measurements allowed the responses of Plots A2 and A3 to be followed for up to 3 weeks after cutting (Mattsson et
- ⁵ al., 2008a). In addition, supplementary plots (C1, C2, C3) were delineated during the experiment with an additional cut on 10 June (with cut grass removed), the following conditions:
 - Plot C1: Regrowth of grass, no fertilization,
 - Plot C2: As C1, but bare soil from 12 June,
 - Plot C3: As C1, but bare soil from 12 June, plus green leaves added to surface.
 - 4.4 Data acquisition and reporting
- The Integrated Experiment naturally included a very wide range of measurement types, with different acquisition systems being applied by different groups according to data type. Continuous datasets were logged on instrument dataloggers or PC-based systems by each of the research groups. To ensure comparability of the measurements, data were collected and reported according to common standards: a) for continuous measurements, data were collected on a 15 min basis (or hourly basis, where this was not possible), b) stated sample times refer to the end-time of the sampling period (i.e., 1230 would denote 1215–1230); c) all measurements were recorded according to GMT (being the Universal Time Constant), which equated to local time minus 2 h. The consolidated datasets were provided as a CD and on a shared file server to participants
 20 (Sutton et al., 2001b).

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4.5 Quality assurance and quality control

2008b⁸).

Many of the measurements made during the experiment are known to be very challenging, especially for continuous determination (e.g. NH₃, HNO₃, NH₄⁺ and anion aerosols, apoplastic bioassays etc.) and when considering fluxes and gradients rather than just concentrations. In addition to following good experimental practice, the availability of different scientists on-site allowed for regular trouble-shooting and repair of instruments. A key QA element was the use of replicated measurement of the same parameter by different groups using either the same or similar sampling methods. Thus the determination of turbulent exchange parameters (Nemitz et al., 2008⁸) was made using 9 different ultra-sonic anemometers (see Sect. 4.5), as well as wind/temperature 10 profiles etc. Similarly, the AGM for NH₃ fluxes was applied using 4 independent NH₃ detectors (Milford et al., 2008⁹), while assessment of NH₃ fluxes by REA also used 4 independent NH₃ detectors (Hensen et al., 2008b⁷). The continuous measurements of trace gas and aerosol concentrations were also supported by FAL permanent daily denuder/filterpack measurements (300 m N of Site 3). Such inter-comparisons en-15 abled screening of the datasets for outliers, while standard filters were applied for flux calculations (e.g. low windspeed, atmospheric stability and flux footprint, Nemitz et al.,

Gas-phase calibrations were used for CO_2 and SO_2 measurements. However, such calibration is uncertain for NH₃ (as well as aerosol chemistry), and in this case liquid

⁹Milford, C., Theobald, M. R., Nemitz, E., Hargreaves, K. J., Horvath, L., Raso, J., Dämmgen, U., Neftel, A., Jones, S. K., Hensen, A., Loubet, B., and Sutton, M. A.: Ammonia fluxes in relation to cutting and fertilization of an intensively managed grassland derived from an inter-comparison of gradient measurements, Biogeosciences Discuss., to be submitted, 2008.

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⁸Nemitz, E., Hargreaves, K. J., Neftel, A., Loubet, B., Cellier, P., Dorsey, J. R., Flynn, M., Hensen, A., Weidinger, T., Meszaros, R., Horvath, L., Fruehauf, C., Sutton, M. A., and Gallagher, M. W.: Inter-comparison of measurements and assessment of the turbulent exchange and energy balance of an intensively managed grassland, Biogeosciences Discuss., to be submitted, 2008b.

phase calibration of the chemical detectors used was applied, using common aqueous standards for all groups. At three times during the experiment, "mystery solutions" were provided blind to test the performance of the different analysis systems for aqueous NH_4^+ .

5 4.6 Summary of measurement methods applied

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As noted above, a large number of sampling systems were applied by the different groups. These are summarized in Table 2, which also notes where the methods are described in more detail. Overall, 14 continuous NH₃ measurement systems with online chemical analysis and 2 automatic batch systems were applied during the experiment, relating to 9 different methods/implementations. Four optical measurement systems were used for aerosol physical properties and number concentrations/fluxes, plus two chemical methods. Ten systems (inc. EC, AGM and energy balance methods) were compared for calculation of sensible heat flux, of which four also provided assessment of latent heat fluxes.

Within-canopy micrometeorological measurements included the application of a micro-ultra sonic anemometer and its comparison with a ²²²Radon tracer method to estimate within-canopy turbulence and exchange coefficients (Nemitz et al., 2008a²). A wide range of other surface parameters were measured including temperature profiles, leaf temperatures (by attached sensors as well as infra-red detection), soil tempera tures and leaf wetness, using leaf surface conductivity (Burkhardt and Eiden, 1994).

Soil moisture was sampled continuously using TDR (Time Domain Reflectometry) probes, as well as a theta capacitance probe and by regular gravimetric measurements, focusing on the A horizon at 0–10 cm and 10–30 cm. Finally, plant material was sampled for N bioassays being prepared and extracted on-site (UoC lab), including pressure impregnation and extraction of apoplastic extracts using a cooled centrifuge (4°C) and measurement of apoplastic pH (Mattsson et al., 2008a). Leaf extracts for analysis of NH₄⁺ and other N components were frozen in liquid nitrogen and subsequently stored on site at –18°C.

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5 Results

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5.1 Synoptic meteorology during the experiment

The meteorology was characterized by mainly W flow, plus shorter periods of S and SE flow, with several frontal systems passing during the experiment (Table 3). The NOAA HYSPLIT model was used to calculate daily 24-h back-trajectories for air masses ar-

⁵ HYSPLIT model was used to calculate daily 24-h back-trajectories for air masses arriving at 1200 and 0000 GMT (Czik et al., 2000). Changing conditions on 22 May were followed by W flow on 23–27 May. Surface air masses (50 m height on arrival) on 23–27 May were estimated to originate over NW Germany while higher air masses (1000, 1500 m on arrival) originated from S England and NW France. Warm fronts passed on 23 and 26 of May, followed by a cold front on 27 May.

Following a brief period of S flow on 28 May, W flow resumed on 29–30 May with surface air masses (50 m) originating 24 hours previously over the Benelux countries, while higher air masses originating over N England. A further period of change on 31 May, was followed by 5 days (1–4 June) of SW flow, with surface air originating 24 h previously over Germany and higher air masses originating over N France. Warm fronts passed on 1 and 3 June.

The flow changed on 5 June associated with a cold front, to be followed by WNW flow on 6–8 June from over the Netherlands, with higher air masses originating 24 previously over the North Sea. For air masses arriving on 9–10 June, the flow was from

the SE over the Czech Republic and S Germany, with a cold front and associated rain on 10 June. Finally, following change on 11 June, W flow was resumed for 12–15 June, with variable 24 h back-trajectory origins of surface (50 m) air being over NW Germany, while higher air masses (1000, 1500 m) originated from the S North Sea and S England.

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An overview of the environmental conditions immediately prior to and during the experiment is shown in Fig. 7. Before the experiment (2–17 May) the conditions were largely dry and sunny, with maximum air temperature (2 m, DWD data) between $20-30^{\circ}$ C, with

- ⁵ the farmer irrigating Kleinkamp on 15–17 May. Conditions were more mixed during the experiment, with in excess of 5 mm precipitation on 7 days, and maximum temperatures ranging from 14°C on 29 May to 31°C on 10 June. Mean daily windspeeds during the experiment ranged 2.0–5.4 m s⁻¹ (overall mean 3.4 m s⁻¹), with mean daily relative humidity in the range 49–83%. Mean daily sunshine was 7 h during the experiment.
- The hourly structure of global radiation, wind direction (10 m), friction velocity (*u*_{*}) and air/canopy temperatures are shown in Fig. 8. The main features of the local wind direction are in accord with the larger scale meteorological flow, including the periods of change on 22 and 31 May, although there was a larger occurrence of surface E winds, such as on 3 and 5 June. This may be related to substantial shear in the atmospheric flow, as identified by the back-trajectory calculations. The most turbulent conditions occurred prior to the cut, associated with cool day-time temperatures. The highest canopy temperatures occurred on 1–4 and 10 June, with values being larger after cutting due to lower transpiration fluxes (Nemitz et al., 2008b⁸).

5.3 Air chemistry during the experiment

The different air-mass origins and local meteorological and environmental conditions provided a wide range of air chemistry conditions during the experiment. This was of great benefit for the experiment, allowing consideration of interactions of gases and aerosols under situations of both potential aerosol growth and evaporation, as well as of differing leaf-surface and biological interactions in the presence of altering amounts of acidic (HNO₃, SO₂) and basic (NH₃) gases.

The time course of aerosol and gaseous pollutant concentrations during the experiment is shown in Fig. 9. The three physical measurements of particle number concen5, 3347-3407, 2008

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trations reflect different particle sizes, with categories presented in Fig. 9a including the fractions 0.01–3 μ m (CPC), 0.1–3 μ m (ASASP-x) and 0.5–2.5 μ m (APS). Since these are number concentrations, the values are dominated by the smallest particle sizes in each range. Thus, the CPC counts are dominated by the nucleation and Aitken

- ⁵ modes, the ASASP-x reading by the smaller accumulation mode particles and the APS concentration by the larger accumulation mode. These differences help interpret the aerosol processes occurring at different times. For example on 5 June, surface air was moving little (Table 3) with regional pollution providing a high correlation between accumulation (APS) and Nucleation/Aitken mode (CPC) aerosol. By contrast, on the
- ¹⁰ 9 June, flow from the SE over S. Germany and the Czech Republic (Table 3) brought SO₂- and HNO₃-rich air masses with a low APS reading over Braunschweig to the site, apparently favouring regional nucleation of new particles. The aerosol appears to age over the 10 June, with higher values in the larger size classes. This interpretation is supported by the results of the Differential Mobility Particle Sizer (DMPS), which
- recorded particle size spectra throughout the experiment. Following a period of small concentrations on 8 June, a nucleation event occurred at 9 a.m. on 9 June, followed by particle growth (through coagulation and condensation) from 8 nm at 00:00 9 June to 100 nm by 12:00 10 June (Fig. 10). The "chimney" or "banana" shape of the event on the three-dimensional presentation is consistent with nucleation events observed around the globe (e.g., Kulmala et al., 2004).

The ASASP-x's provided the size categories that are most consistent with the mass concentrations of aerosol recorded by the SJAC (Fig. 9b). Although there is a reasonable correlation with SO_4^{2-} mass concentrations, this makes up only 46% of the measured inorganic anion aerosol mass on average, with NO_3^{-} being the largest com-

²⁵ ponent, with the SJAC recording only small concentrations (<1 μ g m⁻³) of Cl⁻ and NO₂⁻ aerosol. The highest NO₃⁻ concentrations were associated with the SE and S flow on 10 June, with high values also at the start of the experiment 23 May under SW flow, which passed over the industrial Ruhr area of Germany.

These peaks are clearly reflected in the SO₂ and HNO₃ concentrations (Fig. 9c),

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which were rather similar, at up to $6-8 \mu \text{g m}^{-3}$ on the 23 May, 9 and 10 June, while the latter event was also associated with high O₃ mixing ratios of up to 70 ppbv indicating significant photochemical activity. These peaks may be contrasted with cleaner periods (e.g. 5–6 June) with only 0.8 and 0.4 $\mu \text{g m}^{-3}$ SO₂ and HNO₃, respectively.

- ⁵ The "best estimate" of NH₃ from the continuous gradient measurements (Milford et al., 2008⁹) was interpolated to 1 m above canopy, based on the mean of up to four instruments (Fig. 9d). There was some doubt about the performance of two of the AMANDA denuders on selected days (due to disagreement with the two other systems), and for this reason an "alternative estimate" (Milford et al., 2008⁹) is also shown.
- ¹⁰ The 1 m NH₃ surface air concentrations agree very closely with the background air at 43 m prior to 29 May, while after 5 June, the NH₃ concentrations at 1 m are much larger. This illustrates how, prior to 29 May, NH₃ concentrations at 1 m were largely controlled by external sources, while the later larger values, especially after the 5 May, are mainly due to NH₃ emissions from the field itself. The increased NH₃ concentrations following
- ¹⁵ cutting and fertilization thus provide the opportunity to investigate consequent interactions with the acid gases and aerosols. Not surprisingly, the time course of NH⁺₄ aerosol follows that of aerosol anions, and for much of the time (esp. 22–25 May, 4 June, 8– 10 June) completely neutralized the equivalent anions (average neutralization 94%).

While there were clear relationships of the aerosol concentrations to air mass origin, there was only a weak relationship to local (10 m) wind direction (Fig. 11) indicating a significant contribution from long-range transport. By contrast, NH₃, SO₂ and HNO₃ were largest for SE winds, with the latter linked to the episode on 8–10 June, indicating pollution of more local/regional origin.

5.4 Plant and soil conditions during the experiment

At the time of cutting the grass was 0.75 m tall, with a single sided Leaf Area Index (LAI) of 3.06. Cutting reduced the sward to 0.07 m tall with a LAI of 0.14. Ample soil moisture was available for plant growth, due to the prior irrigation and 5, 3347-3407, 2008

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rain events at several times during the experiment. Figure 12 shows the time course of volumetric soil water content, with values in the range 10-18% vol. according to TDR measurements at 0.15 m, and 12-20% vol. by gravimetric determination for 0-0.1 m, with a similar range from theta probe measurements. These values represent

46–91% of field capacity (Table 1), with averages of 63% (TDR) and 73% (gravimetric) field capacity for the experiment. The moisture content at 0.1–0.3 m was only slightly higher at 66% (TDR, 0.3 m) and 76% field capacity (gravimetric, 0.1–0.3 m). The TDR results are considered the more reliable and outlier gravimetric results (> field capacity) for wet conditions on 23 May are excluded from these means. TDR values for the C1 horizon were in the range 12.8–16.5, representing 77–99% field capacity.

A survey of soil moisture across the field (theta probe, 0–0.1 m depth, 50 m intervals, 3–4 June) showed no major E-W gradients ($11.5\pm2.5\%$ vol., \pm SD), although the field was slightly drier at the N edge of Kleinkamp, E of Site 1, and at the S edge, E of the DWD. This did not significantly affect the flux foot-prints of Sites 1 and 2, but resulted in a slightly drier soil (9.4% vol.) at Site 4.

The cutting and fertilization had major effects on the plant and soil N status conditions, providing a significant perturbation for NH₃ exchange processes. Figure 13 shows that cutting the sward had no significant effect on soil NH₄⁺, although soil NO₃⁻ (0–0.1 m) increased from 5 to 18 mg N g¹ dry soil after 4–5 days, with a smaller increase for 0.1–0.3 m). Much larger responses were recorded following fertilization, with soil NH₄⁺ and NO₃⁻ (0–0.1 m) increasing to 139 and 146 mg N g⁻¹ dry soil, respectively, 3 days after fertilization. The decrease by 10 June may be due to plant uptake and microbial immobilization, while rain later on 10–11 June may have led to remobilization, increasing NH₄⁺ and NO₃⁻ values on 12–14 June. Even 9 days after fertilization, a strong vertical profile was present, with ~200 mg N g⁻¹ each of NH₄⁺ and NO₃⁻ for the layer 0–0.02 m. This contrasts with 1 June where there was little gradient in the layer

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0-0.1 m.

While there was little effect of cutting on available soil N, a clearer effect was recorded for total N content of grass foliage. Before cutting, the mature leaves contained 2.0%

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N, and, where the grass was left uncut and unfertilized, this decreased slightly to 1.8%. By contrast, the short re-growing sward (0.13–0.18 m) measured on 2–4 June had a N content of 3.0–3.4% N, presumably to N re-mobilization within the cut plants. Foliar N increased further following fertilization, with the values representing a balance between the effects of soil N uptake and growth dilution. A further increase occurred following

the effects of soil N uptake and growth dilution. A further increase occurred following the rain and increased soil N mobilization after 10 June.

6 Discussion and conclusions

This paper has introduced the rationale, questions and objectives of the GRAMINAE
 Braunschweig experiment. It has described the strategy taken to address these mul tiple objectives in an integrated way, the nature of the measurements made, and the environmental, plant and soil conditions achieved during the experiment.

Integration is one of the key challenges in understanding environmental processes. Because there are so many interactions, addressing them necessarily increases the scale of the required effort. At the same time, increasing the number of interlinked ob-

jectives leads to the danger that the conditions required to meet some objectives may compromise others. Careful design of the GRAMINAE experiment was therefore essential. In particular, some would say that it is unwise to address advection issues in an experiment that also examines sources and sinks, net NH₃ biosphere/atmosphere exchange and its interactions with aerosol chemistry. However, this misses the challenge faced: that these are real world issues to be addressed rather than avoided.

To allow consideration of advection effects, distances were therefore selected based on the prior modeling (Sect. 3.1) so that these would not dominate fluxes. In addition, it was recognized that advection effects would only occur for selected wind directions during the experiment. By contrast to the potential for conflict, addressing multiple questions also has the benefit that the researcher cannot anticipate which measurements will be least and most successful.

The basic site conditions presented here of synoptic meteorology, micrometeorolog-

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ical conditions, air chemistry, soil and plant conditions, show that the experimental set up was successful in obtaining a wide range of conditions to assess NH_3 exchange processes. Firstly, the prevailing meteorology provided the range of turbulence, temperatures, wetness needed to address the interaction of plant physiological, leaf sur-

- face and canopy exchange processes. Secondly, different air mass origins provided a range of air chemistry, including conditions for both formation and evaporation of NH⁺₄ aerosol, while varying local wind direction allowed comparison of periods with and without NH₃ significant advection errors in the vertical fluxes. Thirdly, the management of the main field and the management treatments provided a major perturbation to the grassland N cycling, allowing the processes of NH₃ fluxes to be investigated in great
- detail.

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The present paper provides the necessary background and introduction to the resulting series of papers arising from the experiment, presented in this special issue. A logical overview of the different paper contributions (current May 08) is provided in Fig. 13. These can be considered in four groups: 1) Micrometeorology and net NH_3

- fluxes, 2) Biospheric controls, including within canopy turbulent exchange, 3) Interactions with acidic and other gases at the canopy surface, and 4) aerosol fluxes and NH_3 gas-particle interactions.
 - 6.1 Micrometeorology and net NH₃ fluxes
- The quantification of turbulent exchange fluxes and the energy balance is fundamental to any micrometeorological assessment. This is analyzed by Nemitz et al., 2008b⁸, who use an inter-comparison of the different measurement systems applied to provide "best estimates" of the exchange terms for the experiment. At the same time, they provide an assessment of the uncertainty in such measurements when (as in most studies) they are not replicated. Using these turbulent exchange estimates, Milford et al., 2008⁹ compare the different AGM implementations for measurement of net NH₃ fluxes, deriving both best estimates and uncertainties in the measured fluxes. Milford et al. thus provide a robust quantification of the response of NH₃ exchange to environ-

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mental conditions and the grassland management events. These robust ammonia flux estimates by the AGM provide a reference for the assessment of four continuous REA systems for NH_3 by Hensen et al., $2008b^7$.

Two papers address NH₃ emission from the adjacent FAL farm. Firstly, Hensen et al., 2008a¹ apply the plume NH₃ measurements to estimate the farm NH₃ emissions, in comparison with the inventory approach. Secondly, Loubet et al., 2008⁵ apply the NH₃ concentrations measured at Sites 1, 2 and 3 in a Lagrangian stochastic dispersion model (MODDAS) to quantify the effects of the farm, and the emitting field itself, on advection errors in measured vertical fluxes.

10 6.2 Biospheric controls on NH₃ exchange

The bioassay measurements of potential for NH₃ emission are reported by Mattsson et al., 2008a, b and Hermann et al., 2008⁶. The interaction of plant N bioassays with changing soil conditions through the experiment, including determination of Γ_s from apoplastic extractions, is presented by Mattsson et al., 2008a. Hermann et al., 2008⁶ then report on vertical changes within the plant canopy, while Mattsson et al., 2008b 15 describe the inter-species differences in plant N bioassays and NH₃ emission potential. The effects of the grassland management options on bioassays are reported by Mattsson et al., 2008a, while David et al., 2008b⁴ address the effects on net NH₃ fluxes using the cuvette approach. David et al., 2008a³ also use this approach to investigate the nature of the NH₃ sources and sinks within the grass canopy. The cuvette approach 20 is complemented by the investigation of within-canopy micrometeorology by Nemitz et al., 2008a². Their investigation applies the measured vertical profiles of radon activity to estimate within-canopy exchange and estimates turbulent and heat exchange using measurements from a micro-sonic anemometer and hotwire anemometer located in the tall grass canopy. These approaches provide the basis to estimate within-canopy 25 NH₃ fluxes for selected periods.

The integration of biospheric and micrometeorological conditions in defining net NH₃



fluxes is considered by Personne et al., 2008¹⁰ and by Sutton et al., 2008¹¹. Firstly, Personne et al., 2008¹⁰ apply the "canopy compensation point" resistance modelling approach (Sutton et al., 1995b; Nemitz et al., 2001b) to described the measured net NH₃ fluxes, deriving stomatal resistances and values of Γ_s , Γ_{soil} and the leaf cuticular uptake resistance for NH₃ (R_w). Secondly, Sutton et al., 2008a¹¹ apply the coupled grassland C-N and NH₃ exchange model, PASIM (Riedo et al., 2002) to the conditions of the experiment, comparing the results with the measured net NH₃ fluxes. Together with the foregoing analyses, these examine the canopy scale trade-offs that define net NH₃ fluxes.

10 6.3 Interactions with acidic and other trace gases

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The performance of the profile SJAC system for measuring concentrations and fluxes of acidic and basic species is summarized by Sutton et al., 2008^{12} The species measured included gaseous SO₂, HNO₃, HCl, HNO₂, NH₃ and aerosol SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺. The availability of data on NH₃, the acidic gases and aerosols, together with the results of dew chemistry sampling during the experiment allowed the leaf surface

¹⁰Personne, E., Loubet, B., Herrmann, B., Mattsson, M. E., Schjoerring, J. K., Nemitz, E., Sutton, M. A., and Cellier, P.: SURFATM-NH₃: a model combining the surface energy balance and the bi-directional exchanges of ammonia at the field scale, Biogeosciences Discuss., to be submitted, 2008.

¹¹Sutton, M. A., Campbell, C., Milford, C., Mattsson, M. E., Schjoerring, J. K., Herrmann, B., and Riedo, M.: Application of a coupled grassland - gas exchange model to investigate the interactions between grassland management and ammonia fluxes Biogeosciences Discuss., to be submitted, 2008a.

¹²Sutton, M. A., Nemitz, E., Milford, C., Erisman, J. W., Hensen, A., Cellier, P., David, M., Loubet, B., Personne, E., Schjoerring, J. K., Mattsson, M. E., Dorsey, J., Gallagher, M., Horvath, L., Weidinger, T., Dämmgen, U., Neftel, A., Herrmann, B., Lehman, B., and Burkhardt, J.: Dynamics of ammonia exchange with cut grassland: Synthesis of results and conclusions, Biogeosciences Discuss., to be submitted, 2008b.



and flux interactions to be addressed by Burkhardt et al., 2008 using a canopy compensation point model that incorporates mixed chemistry dynamics on leaf surfaces (Flechard et al., 1999). In parallel, the measurements of CO_2 and O_3 exchange, and their relationship to grassland management are presented by Mészáros et al., 2008¹³.

 $_{\rm 5}$ 6.4 Aerosol fluxes and NH₃ gas – particle interactions

The large NH_3 emissions observed after fertilization of the grass, as well as the warm canopy temperatures, provide conditions with the potential for both formation/growth and evaporation of NH_4^+ -containing particles. Nemitz et al., 2008¹⁴ investigate the aerosol dynamics including the size resolved EC measurements of physical particle fluxes. They then combine these data with the results of the NH_3 and NH_4^+ aerosol fluxes to assess the interactions between NH_3 fluxes and gas-particle inter-conversion.

6.5 Conclusions

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This introduction and the series of papers noted above demonstrates the multiple interactions that occur in defining net NH_3 fluxes between the biosphere and atmosphere. The GRAMINAE Braunschweig experiment was designed to assess many of these in an integrated way, providing substantial synergy between different measurement groups and scientific issues being addressed. The experiment was successfully implemented with measurements over a 25-day period, covering a range of meteorological conditions and atmospheric chemistry, as well as plant and soil conditions associated

¹⁴Nemitz, E., Dorsey, J. R., Flynn, M. J., Gallagher, M. W., Hensen, A., Owen, S., Dämmgen, U., and Sutton, M.A.: Aerosol fluxes and gas-to-particle conversion above grassland following the application of NH₄NO₃ fertilizer, Biogeosciences Discuss., to be submitted, 2008c.



¹³Mészáros, R., Horváth, L. Weidinger, T., Neftel, A., Nemitz, E., Hargreaves, K.J., Dämmgen, U., Cellier, P., and Loubet, B.: Measurement and modelling ozone and carbon dioxide fluxes over grassland during the GRAMINAE experiment, Braunschweig, Biogeosciences Discuss., to be submitted, 2008.

with management perturbation of the grassland nitrogen cycle. It is shown how such an integrated strategy can be developed, which allows multiple objectives to be addressed through careful placement of sampling locations and timing of the different activities.

- The detailed papers resulting provide the most comprehensive analysis of NH₃ exchange processes that has been attempted to date. These cover issues of a) quantifying net NH₃ fluxes in a real landscape and using new methods, b) the biospheric controls on NH₃ fluxes, using a combination of flux measurement approaches, bioassays and models, c) the interactions that occur with acidic gases at the canopy surface, and d) the potential for NH₃ fluxes to interact with particle fluxes within and immediately above a grassland canopy. The results of these detailed analyses are brought together at the end of this Special Issue in the synthesis presented by Sutton et al., 2008.
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 Table 1.
 Soil conditions the main study field of the GRAMINAE integrated experiment ("Kleinkamp").

	Horizon A	Horizon C1	Horizon C2
Horizon depth (cm) ^a	0-27	27-71	71–80
Bulk soil density (g dry soil cm ⁻³) ^a	1.73	1.61	1.58
Clay/Silt/Sand fraction (%) ^a	3/34/63	3/31/66	-
Volumetric saturated water content (%) ^a	37.1	42.2	45.6
Volumetric water content at field capacity pF2 (%) ^a	21.90	16.70	19.30
Saturated hydraulic conductivity (mm d ⁻¹) ^a	47.0	382	586
Cation Exchange Capacity (mgee/100 g soil) ^a	6.85	3.94	6.78
Soil Organic Carbon $(g C kg^{-1})^{bc}$	21.2/8.9	3.9	_
Soil Organic Nitrogen (g N kg ⁻¹) ^{bc}	1.56/0.60	0.22	_
Soil pH (in 0.01 M CaCl ₂) ^b	6.35/6.85	_	_

^a Sampled on 5 June 2000.

^b Using soil layers 0–10/10–30 & 30–60 cm, where available.

^c From a full analysis in 1984.

Table 2. Summary of measured parameters, sampling methods and sampling location of sampling during the GRAMINAE Integrated Experiment.

Approaches applied	Parameter (number measurement points)	Methodology	Sampling site [Fig. 4] (Sampling frequency)	Contributing teams [See Fig. 6] (method reference)
Vertical concentration profiles (0–3 m)	NH ₃ (3)×2 systems	Continuous AMANDA denuders with triple denuder inlets	Site 1 (7.5 min)	FAL-D, FRI (Wyers et al., 1993)
	NH ₂ (5)	Continuous mini-WEDD	Site 1 (7.5 min)	FAL-CH (Neftel et al., 1998)
	NH ₃ (3)	Continuous AMANDA denuders with triple denuder inlets	Site 2 (7.5 min)	CEH (Wyers et al., 1993)
	Gaseous HNO ₃ , SO ₂ , HONO, HCI, NH ₃ ; particulate NH ₄ ⁺ , NO ₂ ⁻ , NO ₂ ⁻ , SO ₂ ⁻ , Cl ⁻ (2)	Continuous GRAEGOR with Steam Jet Aerosol collection & on-line IC	Site 1 (30 min)	ECN (Khlystov et al., 1995; Oms et al., 1996)
	SO ₂ (3)	Pulsed chemiluminescence ana- lyzer	Site 1 (1 min over 15 min)	CEH (Thermo Environment 43S, Franklin MA, USA)
Ammonia transect (1 m)	NH ₃ (1)×3 systems	Continuous AMANDA denuders with single denuder inlets	Site 3 (a, b, c) (7.5 min)	ECN (Wyers et al., 1993)
	$\ensuremath{NH}\xspace_3$ (mobile across transect) (1)	Fast response mini wet-denuder with AMANDA detector.	Site 3 (transect) (30 s)	ECN (Erisman et al., 2001b), Petten, NL.
Background air (43 m)	NH ₃ , HNO ₃ , SO ₂ , HCl (1)	Automatic batch wet annular	Site 6 (40 min/h)	CEH, University of Kiel (Keuken et al., 1988)
Conditional sampling for REA (1.5 m)	NH ₃ (2 channel)	Continuous membrane denuder	Site 1 (15 min)	ECN (Erisman et al., 2001b; Hensen et al., 2008b ⁷)
		Continuous mini-WEDD	Site 1 (7.5 min)	FAL-CH (Neftel et al., 1998)
		AMANDA with vertical parallel plate wet denuders	Site 1 (7.5 min)	CEH, UoM (Nemitz et al., 2001a)
		Continuous mini-WEDD	Site 1 (15 min)	RISO (Sørensen et al., 2003)
Cuvette concentrations	NH ₃ (1)	AMANDA with single inlet	Site 4 (15 min)	INRA (Wyers et al., 1993)
	NH ₃ (1)	TULIPA wet denuder	Site 4 (1 and 2 h)	INRA (David et al., 2006a)
Physical aerosol measurement (2 m)	Size distribution of particle numbers (2.9 nm< D_p <0.45 μ m)	Differential mobility particle-sizer (DMPS)	Site 1 (10 min)	UoM (Williams, 1999; Coe et al., 2001)
				(with TSI UCPC 3025 & TSO CPC 3010)
	Particle number for EC flux measurements: Total Number N for sizes >11 nm (detection range of CPC 11 nm c0 <3 um)	Condensation Particle Counter (CPC)	Site 1 (20 Hz over 15 min)	UoM (TSI Model 3010 CPC; TSI Inc., Minneapolis, USA)
	Size distribution and EC of particle numbers $(0.1 < Dp < 3 \mu m) -$	Active Scattering Aerosol Spectrometer Probe (ASASP-X)	Site 1 (10 Hz over 15 min)	UoM (PMS Model ASASP-XS, Boulder, USA;
	Optical scattering diameter. (2	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		Gamey & Pinnick, 1983; Gallagher et al., 2002).
	systems: 0.7 m, 2.86 m)			
	Size distribution and EC of particle numbers $(0.5 < D_n < 20 \ \mu m)^*$	Aerodynamic Particle Sizer (APS)	Site 1 (15 min)	UoM (APS 3320, TSI Inc. Minneapolis, USA;
	, р,,			Armendariz & Leith, 2002).
Other concentration measurements (2 m)	Size segregated particle chemistry	Micro-orifice uniform deposition impactor (MOUDI)	Site 1 (2-3 days)	CEH (Model 100, MSP Corp., Minneapolis, USA)
	Instantaneous ozone for eddy co- variance	Fast-response fluorescence detector	Site 1 (10 Hz, 15 min)	ELU, FRI (NOAA, 1996; Mészáros et al., 2008 ¹³)
	NO, NO_2 , O_3 reference concentrations	Continuous analyzers	Boitzem, 5 km S of FAL	FAL-D

Notes: D_p =electrical mobility diameter;

*, Time of Flight Aerodynamic Diameter.



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Table 2. Continued.

Approaches applied	Parameter (number measurement points)	Methodology	Sampling site [Fig. 4] (Sampling integn. pe- riod)	Contributing teams [See Fig. 6] (method reference)
Micrometerological measurements	Horizontal wind speed (5)×2 systems	Cup anemometers	Site 1 (15 min)	CEH & FRI/ELU (Vector Instruments, Clywd, UK)
inducationitie	Instantaneous windspeed (<i>u</i>) and temperature (<i>T</i>) fluctuations (8 systems)	Ultrasonic anemometers	Site 1 (15 min)	CEH, INRA, ECN, FAL-CH, ELU, FRI, UoM (Nemitz et al., 2006)
	Instantaneous <i>u</i> and <i>T</i> fluctuations (1 system)	Ultrasonic anemometer	Site 2 (15 min)	CEH (Nemitz et al., 2006)
	Instantaneous water vapour (E) fluctuations (2 systems)	Krypton hygrometer	Site 1 (15 min)	CEH, UoM (KH2O, Campbell Scientific, Loughborough, UK)
	Instantaneous CO ₂ and E (2 systems)	Licor 6262 IGBA	Site 1 (15 min)	CEH, INBA
	Mean E, T and air pressure	Humicap, PRT100 thermistor, Baromet- ric pressure transducer	Site 1 (15 min)	UoM (Vaisala)
	T and E profiles (2 heights), net radiation (Rn), total solar radiation (S _t), ground heat flux (G) and precipitation (2 sys-	Campbell "Bowen Ratio" systems (fine thermocouples, dewpoint meter and additional parameters)	Site 1 (15 min)	CEH, FRI/ELU (Campbell Scientific, Loughborough, UK)
	Standard meteo. inc. $u(10 \text{ m})$, S _t , direction, PAR, long-wave radiation, E, T,	Suite of permanent instruments	Site 5 (hourly & daily)	Deutscher Wetter Dienst
	precip. etc			
Within canopy micromet.	Instantaneous u and T fluctuations in plant canopy (1 system)	Kayo Denki micro ultrasonic- anemome- ter	Site 1 (15 min)	CEH (Kayo Denki corp, Japan; Nemitz et al., 2006b)
measurements	Ground wetness (2 systems)	Besistance plate	Site 1 (15 min)	EBI Univ Bonn
	Leaf wetness (4 sampling points)	BESI (leaf surface resistance)	Site 2 (15 min)	Univ Bonn (Burkhardt & Fiden 1994)
	Bain chemistry and dew chemistry	Analysis by ion-chromatography	Site 1 (event basis)	FAL-D UoC Univ Bonn
	T profile in canopy & leaf T (10 sensors)	Thermocouples, inc. leaf clips	Site 1 (15 min)	INRA
	Radiative canopy temperature	Infrared temperature sensor	Site 1 (15 min)	UoM (KT19 IR pyranometer)
	Leaf level water vapour conductance	Leaf cuvette	Site 1 (key periods)	U ₀ C
	²²⁰ Radon and ²²² Radon (3 heights)	22×Radon analvzer	Site 1 (15 min)	UoB. FAL-CH (Lehmann et al., 1999)
Foliage measurements	Canopy height meter	Herbometer	Site 1 (daily)	INRA
	Leaf apoplastic concentrations and other	Hydraulic extractor, cooled centrifuge, pH	Site 1 (daily, selected	UoC, FAL-CH, CEH (Husted et al., 2000;
	foliar N parameters	micro-electrode etc.	diurnal profiles)	Mattsson et al., 2006a)
Soil measurements	Soil moisture	Time Domain Reflectometry	Site 1	Univ. Bonn (Imko Trime-T3 tube access probe, www.imko.de)
		Gravimetric determinations	Site 1, Site 2	RISSAC, FAL-D
	Soil profile (1)	Classical soil assessment	Site 1	RISSAC
	Soil temperature and soil heat flux (2)	Part of Campbell "Bowen Ratio System" measurements	Site 1	ELU, CEH (Campbell Scientific, Lough- borough, UK).
	Soil available NH ₄ ⁺ & NO ₃ ⁻ (0-0.1,0.1- 0.3 m)	Extracts in KCI	Site 1	UoC, INRA
	Soil bulk density and other physical mea- surements.	Range of methods	Site 1 and map of site	INRA (see Table 1)

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Table 3. Summary of daily air-mass back-trajectories (arriving at the field site 12:00 GMT) and fronts, from calculations of Czik et al. (2000).

Trajectory arrival date	Direction of flow and indicative position of air mass 24 h previously	Latitude (N) and longitude (E, -W) of air mass 24 h prior to arrival at 12:00 GMT: for different air mass arrival heights				Fronts passing the site		
		50 m 1000 r		00 m) m 1500 m			
		Lat	Long	Lat	Long	Lat	Long	
22-May-2000	100 km NW (6 h), local circulation before	52.8	9.9	52.8	9.6	51.9	9.1	
23-May-2000	WSW over Germany (50 m) and S Netherlands	51.9	7.7	51.4	4.8	51.3	2.8	Warm front
24-May-2000	SW over Ruhr (50 m); From WSW over Brittany (1500 m)	49.9	7.8	48.5	2.9	48.0	-4.6	
25-May-2000	SSW over Germany (50 m); From WSW over	49.8	9.1	47.1	2.1	45.9	-6.5	
26-May-2000	W over Belgium (50 m) and S England (1000, 1500 m)	50.9	4.3	50.5	-2.3	50.8	-5.8	Warm front
27-May-2000	WSW over NE France (50 m) and Brittany (1000, 1500 m)	48.6	6.3	49.7	-5.2	48.5	-8.2	Cold front
28-May-2000	S over Germany (50 m); From SW over N Spain (1500 m)	49.1	9.2	45.9	4.8	42.9	-5.5	
29-May-2000	WSW over Belgium (50 m); From W over N England (1000, 1500 m)	50.5	3.0	52.0	-2.1	54.9	-3.0	
30-May-2000	WSW over Netherlands (50 m); From WNW over NE England (1000, 1500 m)	51.8	5.3	53.1	1.4	54.5	-1.2	
31-May-2000	NNW over Germany (50, 1000 m); From WNW over Germany (1500 m)	53.7	10.0	54.2	8.3	53.3	7.4	
01-Jun-2000	SSW over Germany (50 m); From SW from NE	5.5	9.3	49.5	6.5	49.7	2.8	Warm front
02-Jun-2000	SW over Ruhr (50 m); From SW over N France	50.2	8.0	49.0	4.4	48.2	0.3	
03-Jun-2000	NW over Germany (50 m); From WSW over NL (1000 m) and N France (1500 m)	53.1	9.0	52.0	5.6	49.8	0.8	Warm front
04-Jun-2000	100 km SE (50 m); From SW over Germany (1000 m) and France (1500 m)	51.8	11.7	49.7	7.3	48.5	2.1	
05-Jun-2000	150 km N, but looping E (50 m); 200 km W (1000 m) and LU (1500 m)	52.7	9.6	52.0	8.1	49.5	7.0	Cold front
06-Jun-2000	WNW over German Bight of N Sea (all heights)	53.9	6.1	54.7	5.7	54.4	4.2	
07-Jun-2000	WNW over NL (50 m) and N Sea (1000, 1500 m)	52.5	4.9	53.9	1.9	54.9	-0.2	
08-Jun-2000	WNW over NL (50 m) and N Sea (1000, 1500 m)	52.9	7.2	53.6	4.2	53.2	2.7	
09-Jun-2000	SSE over CZ (50 m) and S over Germany (1000, 1500 m)	50.5	13.6	48.9	11.6	48.9	8.1	
10-Jun-2000	SE over CZ (all heights)	50.6	13.5	49.1	14.4	49.5	13.0	Cold front
11-Jun-2000	WNW over German Bight (50, 1000 m); from S over Germany (1500 m)	54.1	6.2	52.4	4.0	50.0	9.6	
12-Jun-2000	W over NL (50 m), S England (1000 m) and Wales (1500 m)	52.1	5.9	50.9	0.1	52.0	-5.3	
13-Jun-2000	WSW over Ruhr (50 m) and Belgium (1000, 1500 m)	51.3	8.0	50.7	5.6	51.8	3.4	
14-Jun-2000	NW over Germany (50 m); WNW over NL (1000 m); W over S England (1500 m)	53.1	7.5	52.6	4.0	51.0	-1.8	
15-Jun-2000	NW over Germany (50 m) and N Sea (1000, 1500 m)	53.3	7.1	54.3	4.7	54.8	-1.0	

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with plant N uptake & NH₃ fluxes

Fig. 1. Overview of issues addressed by the GRAMINAE Integrated Experiment.

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Fig. 2. Prior modelling of the effect of upwind farm NH₃ emissions on NH₃ concentrations and total vertical fluxes. Advection errors in the vertical flux represent the difference in the vertical flux between canopy height (h_c =1 m above ground) and specified heights above ground. Advection errors are substantial in the first 100–200 m from the source, but decrease to values smaller than typical NH₃ fluxes (50–100 ng m⁻² s⁻¹) at distances larger than 400 m from the farm. Results of the MODDAS model (Loubet et al., 2006) using a farm source height of 1–4 m, windspeed (10 m) of 4.5 m s⁻¹, and background NH₃ of 1 µg m⁻³.







Fig. 3. Prior modelling of the potential effect of upwind farm NH_3 emissions on changes in the vertical flux with height using the MODDAS model. Model values are as specified for Fig. 2. The horizontal arrow shows the divergence in the vertical flux (the advection error, $F_{z(ad)}$) between a flux measurement made at 3 m above ground and the flux at the canopy surface (1 m above ground) for an example where fluxes are measured 780 m from the downwind edge of the farm.

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Fig. 4. Site map of the GRAMINAE Braunschweig Experiment on the site of the FAL. Sites: 1, Main micrometeorological flux measurement site; 2, Micrometeorological NH_3 flux measurement at increased distance from the farm; 3, N-S transect for mobile NH_3 plume measurements including three fixed points; 4, Small plots (each 10 m x 10 m) for comparison of grass management options; 5, FAL farm buildings; 6, Tower of the PTB for measurement of background air at 43 m above ground; 7, Meteorological measurement site of the Deutscher Wetter Dienst. Axes in metres.

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Fig. 5. Aerial photographs of the GRAMINAE Braunschweig Experiment during lifting of the grass, \sim 08:00 GMT 31 May 2000: **(a)** the main field looking from the ENE with the main field site in the centre and the DWD station in the top left, **(b)** Close up of Sites 1 and 4, looking from the S.

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Fig. 6. Detailed plan of Sites 1 and 4. Notes: EC, eddy covariance system; BR, Campbell Scientific Bowen Ratio System; REA, Relaxed Eddy Accumulation system for ammonia; SJAC, gradient Steam Jet Aerosol Collector system; AMANDA, gradient continuous NH_3 wet denuder system; WEDD, wet effluent diffusion denuder system for NH_3 . Key instrumentation and facilities operated by different institutes are shown.



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Fig. 9. Air concentrations of particles and mixing ratios of gases during the GRAMINAE Braunschweig Experiment. **(a)** Aerodynamic Particle Sizer (APS) (2.5 m); Condensation Particle Counter (CPC) (2 m); Axially Scattering Aerosol Spectrometer Probe (ASASP-X) (mean of 2 instruments at 0.7 and 2.9 m). **(b)** Steam Jet Aerosol Collector (SJAC), including SO_4^{2-} , NO_3^- , CI^- and NO_2^- (2 m); ASASP-X overlain for comparison. **(c)** SO_2 and HNO_3 by denuder linked to SJAC (mean of 0.3, 2 m); Ozone (5 km south of field site). D. NH₃ by automatic batch wet denuder (with off-line analysis) at Site 6; Best estimate NH₃ derived (1 m) vertical profiles of 4 gradient continuous denuders; Alternative NH₃ estimate (1 m), reflects uncertainty in selected denuders at certain times (Milford et al., 2008⁹); NH₄⁺ by SJAC as in (b).

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Fig. 10. Changing particle diameter (d_p, nm) distribution from the Differential Mobility Particle Sizer (DMPS) during a regional nucleation event following a period of clean air from the SE on 8–10 June 2000. Increasing particle numbers (N), represented as blue to green to red, are expressed as $d \text{ N}/d \log(d_p)$ (cm⁻³).

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Fig. 11. Dependence of hourly gas mixing ratios (ppbv) and aerosol concentrations (μ g m⁻³) on local wind direction (10 m) during the GRAMINAE experiment (22 May–15 June). Methods as in Fig. 9. The N sector 320°–40° is less certain for SO₄²⁻, NO₃⁻, HNO₃ and HCl with <30 hours of data. Based on between 281 (SO₂) to 420 (NH₃) hours of measurement.







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Fig. 13. Overview of the specific analyses emerging from the GRAMINAE Integrated Experiment. Paper numbers indicate the logical order of the papers in the GRAMINAE Special Issue, the present paper being P1. The superscripts refer to the footnote references. [The numbers will be amended pending peer review].

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