

Agricultural ammonia in the atmosphere: transport, monitoring and environmental impacts

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Fast alles
ist leichter begonnen
als beendet...

Johann Wolfgang von Goethe

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Zusammenfassung

Die Landwirtschaft, speziell die Tierproduktion, ist die Hauptquelle für anthropogen erzeugte Ammoniakemissionen in Europa. Der Grund dafür liegt in einem erhöhten Nahrungsbedarf einer stetig wachsenden Weltbevölkerung. Diese Ammoniakemissionen besitzen einen direkten Einfluss auf die angrenzende Umwelt und führen zur Beeinträchtigung der Luftqualität bis hin zu massiver Geruchsbelästigung.

Ein Ziel dieser Dissertation ist es, die Transport- und Ausbreitungsprozesse von Ammoniak (NH_3) zu beschreiben sowie damit verbundene Monitoring-Methoden und auftretende Umwelteinflüsse zu charakterisieren. Um grundlegende Faktoren zu bestimmen, die einen regulierenden Einfluss auf NH_3 -Konzentrationen haben, wurden Umweltbedingungen, meteorologische Aspekte und die Betriebsbedingungen der Stallanlagen berücksichtigt. Ein weiterer Aspekt dieser Arbeit liegt in der Untersuchung der Beziehung zwischen NH_3 -Konzentrationen und der auftretenden Vegetation in unterschiedlichen Entfernungen einer Stallanlage.

Für das Monitoring von NH_3 -Konzentrationen in landwirtschaftlich genutzten Gebieten wurden unterschiedliche Messtechniken entwickelt. Aufgrund der großen Vielzahl an NH_3 -Messmethoden wurden Vergleichsmessungen unter typischen Feldbedingungen initiiert, um geeignete Geräte für exakte Messungen zu finden. Der hier präsentierte Vergleich umfasst elf Geräte zur Detektion von atmosphärischen NH_3 -Konzentrationen, die auf acht unterschiedlichen Messmethoden basieren. Die Messungen fanden auf einer intensiv bewirtschafteten landwirtschaftlichen Weidefläche statt. Trotz der überaus guten Übereinstimmung der mit den unterschiedlichen Geräten gemessenen durchschnittlichen NH_3 -Konzentrationen, bleibt die kontinuierliche Erfassung von NH_3 -Konzentrationen ein herausforderndes Vorhaben.

Transport- und Ausbreitungsprozesse von atmosphärischem NH_3 werden durch viele lokale Faktoren beeinflusst. Während der durchgeführten Feldmessungen wurden Hauptfaktoren ausgewählt und evaluiert, die sowohl die Umweltbedingungen und die meteorologischen Aspekte als auch die Betriebsbedingungen der Stallanlagen charakterisieren.

Als Untersuchungsobjekt wurde eine große Broilermastanlage gewählt, die typisch für die landwirtschaftliche Landschaft in Deutschland und Europa ist. Mittels multipler linearer Regressionsanalyse (MLR) wurde die Beziehung zwischen zehn Haupteinflussfaktoren und den gemessenen NH_3 -Konzentrationen analysiert. Hinsichtlich der Anwendung geeigneter Monitoring-Methoden stellt die Wahl des

Standortes für die Beobachtungspunkte einen entscheidenden Aspekt dar, um wirklich belastbare und sinnvolle Messergebnisse zu erzielen. Das emittierte NH_3 wird durch die auftretenden Windrichtungen stark beeinflusst. Dennoch weisen die Ergebnisse der MLR auf einen rück- bzw. abwärtsgerichteten Transport der NH_3 -angereicherten Luft zum Beobachtungspunkt hin, auch wenn der Wind aus einer Richtung ohne NH_3 -Quelle weht. Diese Ergebnisse zeigen einen starken Einfluss der durch das vorhandene Lüftungssystem bedingten Austrittshöhe der Abluft aus den Schornsteinen.

Während weiterer Versuche an derselben Broilermastanlage wurden die NH_3 -Emissionen und die daraus resultierenden atmosphärischen NH_3 -Konzentrationen an fünf Beobachtungspunkten quantifiziert. Zusätzlich erfolgte eine Analyse der auftretenden Vegetation entlang eines Transekts durch ein sich anschließendes Waldgebiet. Die Broilermastanlage als Emissionsquelle bewirkt einen signifikanten Anstieg der atmosphärischen NH_3 -Konzentrationen in der unmittelbaren Umgebung. Diese erfassten atmosphärischen NH_3 -Konzentrationen wurden stark durch die auftretenden Windrichtungen beeinflusst. Es ist anzunehmen, dass das unmittelbar angrenzende Waldgebiet eine weiträumige Ausbreitung der Luftverunreinigungen durch die NH_3 -Emissionen verhindert. Jedoch wird der Wald innerhalb eines Abstandes von ~400 m von der Broilermastanlage durch den erhöhten Eintrag von NH_3 -Konzentrationen nachteilig beeinträchtigt. Diese Ergebnisse verdeutlichen eine Notwendigkeit von Waldstreifen als Schutzpflanzungen. Sie zeigen aber auch, dass die Umsetzungen weiterer Maßnahmen zur Minderung von NH_3 -Emissionen notwendig sind.

Abstract

Agriculture and especially the livestock industry is the major source of anthropogenic emissions of ammonia (NH_3) in Europe. Ammonia emissions are likely to increase due to the pressure on the food production industry to keep pace with the growing world population. These emissions affect the air quality can cause odour nuisance and have direct impacts on the environment.

This thesis focuses on the investigation of transport and dispersion processes of atmospheric NH_3 . Further aspects take into account the evaluation of relevant monitoring methods and the characterisation of the direct environmental impacts of NH_3 . The processes involved in transport and dispersion of NH_3 are complex. In order to fully understand the underlying and influencing factors, environmental conditions, meteorological aspects and the operational mode of the animal production facilities were considered. The relationship between atmospheric NH_3 concentrations and the abundance and diversity of vegetation with increasing distance from the NH_3 source was a further issue.

For monitoring atmospheric NH_3 in agricultural used areas, various different techniques have been developed. Owing to this wide variety of methods, a comparison under typical field conditions was initiated to identify the most suitable instruments for accurate measurements of atmospheric NH_3 concentrations above an intensively managed agricultural field. The study presented here included eleven instruments based on eight different measurement methods. Despite the overall good agreement between the average NH_3 concentrations measured with the various instruments, a truly continuous NH_3 measurement remains a challenging enterprise.

The process of dispersion and transport of NH_3 is influenced by various local factors. During a field experiment, selected major factors which characterise the atmospheric and meteorological conditions as well as the operational parameters of an animal production facility were evaluated. The animal production facility is represented by a huge broiler farm which is typical for agricultural landscapes in Germany and Europe. By implementing multiple linear regression (MLR) analyses, the relationship between factors-of-influence (FOI) and the measured atmospheric NH_3 were analysed. In terms of applying suitable monitoring methods, the location of a monitoring point is essential for a successful and accurate investigation outcome. The emitted NH_3 was strongly influenced by the actual wind direction. The sensor at the monitoring point detected NH_3 in the air even when the wind blew over an area without sources of NH_3 . This

observation implied that NH_3 -enriched reverse winds blew back in the direction of the monitoring tower. It also implied that a downward flow of NH_3 -enriched air reached the measuring device and was detected. These partially unexpected processes should be considered in any future studies focusing on the spatial dispersion of NH_3 in the air.

For the same broiler farm, NH_3 emissions and resulting atmospheric NH_3 concentrations at five monitoring points in the immediate vicinity have been quantified. Additionally, vegetation along a transect through an adjacent woodland were analysed. Strongly affected by the occurring wind direction, the broiler farm as a source of NH_3 emission significantly increased NH_3 concentrations in the immediate vicinity.

The adjacent woodland had a positive effect because it may help to retain the air pollution in a small local area. Nevertheless, vegetation was adversely affected within a ~400 m distance from the farm. The outcome of this study illustrates the positive effect of tree belts for a reduction of NH_3 concentrations in the vicinity of agricultural sources. It also attempts the need for further implementation of abatement efforts to minimise NH_3 emissions.

1 Introduction

Nitrogen is an essential element for the growth of plants, and the most abundant component of the atmosphere. Reduced nitrogen, such as ammonia (NH_3) plays a crucial role in ecology and environment (Erismann et al., 2007). Ammonia is revealed as a compound of key human interests through the centuries. A review of its role in the environment, in agricultural science and in air chemistry is described in detail by Sutton et al. (2008). Ammonia is a highly reactive gas which can cause odour nuisances in the vicinity of sources and represents the only soluble alkaline substance with significant atmospheric concentrations (Warneck, 1988; Duyzer et al., 1994; Moeller, 2003). In the atmosphere, NH_3 reacts mainly with acidic compounds and neutralises a substantial part of the acids, resulting from sulphur dioxides (SO_x), nitrogen oxides (NO_x) and hydrochloric acid (HCl). These processes form secondary particulate matter, including ammonium sulphates, ammonium nitrate and chloride. As a result, ammonium (NH_4^+) is a major component of atmospheric aerosols (Duyzer et al., 1994; Asman, 1998).

Currently, in Europe more than 90% of atmospheric NH_3 stems from agricultural activities, significantly contributing to the perturbation of the nitrogen cycle (Erisman et al., 2008). In this case, the balance between reduced and oxidised forms of nitrogen is disturbed (Erisman et al., 2007). The human demand for food production requires the intensive use of nitrogen containing fertilisers on crops. Moreover, large-scale animal production in modern livestock facilities is necessary (Aneja et al., 2008). The livestock farms create significant local hotspots of elevated atmospheric NH_3 concentrations (Theobald et al., 2004). In this context animal housing and waste storage (Bussink and Oenema, 1998), land spread manure (Asman et al., 2004) and grazing animals (Beusen et al., 2008) can be identified as main agricultural NH_3 sources (31-55%, 23-38% and 17-37%, respectively). These NH_3 sources are hotspots in the sense that they occur intensely with spatial (point source, such as livestock facilities) or with temporal (application of manure) variability (Fowler et al., 1998; Loubet et al., 2009). The combination of hotspots and deposition processes leads to sources and sinks of atmospheric NH_3 which are distributed spatially heterogeneous at a local scale of a square kilometre (Sutton et al., 1998; Dragosits et al., 2002). The emissions of NH_3 from animal housings strongly depend on thermal and humidity conditions, the current pH-value, the ventilation system, the condition of animals (age, weight, diet, health) and the operational parameters of the farm (Demmers et al., 1999; Redwine et al., 2002; Seedorf and Hartung, 2002; Mosquera et al., 2005). In general, NH_3 is formed by the break down of nitrogenous wastes (undigested proteins and excretory uric acids) in

manure by microorganisms (Atapattu et al., 2008). In winter lower atmospheric NH_3 concentrations occur due to the reduced volatility, lower air temperatures and the generally higher relative humidity (Seethapathy et al., 2008). Thus, atmospheric NH_3 concentrations vary in time. Interpretation of measured NH_3 emissions and corresponding atmospheric NH_3 concentrations relies on a rigorous understanding of relevant processes and factors. Thus, it is important to investigate the processes governing the occurrence of atmospheric NH_3 concentrations.

This thesis was initialised by the Leibniz Institute for Agricultural Engineering Potsdam-Bornim (Germany). All aspects concerning agricultural issues were answered with the support of scientist of this institute. In terms of meteorological approaches, this thesis was supervised by the Chair of Climatology from the Technische Universität Berlin (Germany). The participation in an extensive comparison study of different atmospheric NH_3 measurement techniques was enabled by a research exchange at the Centre for Ecology and Hydrology in Edinburgh (UK).

The present thesis consists of this introductory section, followed by an overview of the current knowledge on the fate of atmospheric NH_3 . Thereby, in *Sections 1.1 to 1.3*, main aspects of NH_3 transport and dispersion processes, monitoring the occurrence and investigating the environmental impacts of atmospheric NH_3 concentrations are reviewed. It was shown that in spite of significant advances during recent years, still many scientific aspects are unresolved. One of the important open questions addressed in this work is focused on the different temporal and spatial monitoring approaches of atmospheric NH_3 concentrations. Furthermore, various factors have influence toward the dispersion of atmospheric NH_3 . In the present work, major factors affecting the NH_3 content in the air were evaluated. In *Section 1.4*, main issues related to NH_3 concentrations in the atmosphere are summarised and the objectives of this thesis are defined. The relevant methods used in this thesis are shortly characterised in *Section 2*. The description and interpretation of the presented results are summarised in *Section 3*. In more detail, the results are shown in the papers collected in the Appendix A to C, containing two published and one submitted paper, all in peer-reviewed journals. Finally, the main outcomes of this work and future plans are outlined in *Section 4*. Appendix D summarises the own contribution of the doctoral candidate and the contribution of the involved co-authors in completing the publications included in this thesis (Paper I-III).

1.1 Emission and atmospheric transport

Gaseous NH_3 has a relatively short atmospheric lifetime (hours to days) before converted to NH_4^+ or deposited by dry deposition to surfaces with a substantial fraction of 20-40% (Aneja et al., 2001). In contrast, NH_4^+ has a lifetime of several weeks, before being washed out by precipitation (wet deposition) (Fig. 1). As a consequence, NH_3 is deposited near a pollution source (within ~50 km), whereas NH_4^+ can be transported over much longer distances (within ~400 km) (Ferm, 1998; Aneja, 2001; Erismann et al., 2007).

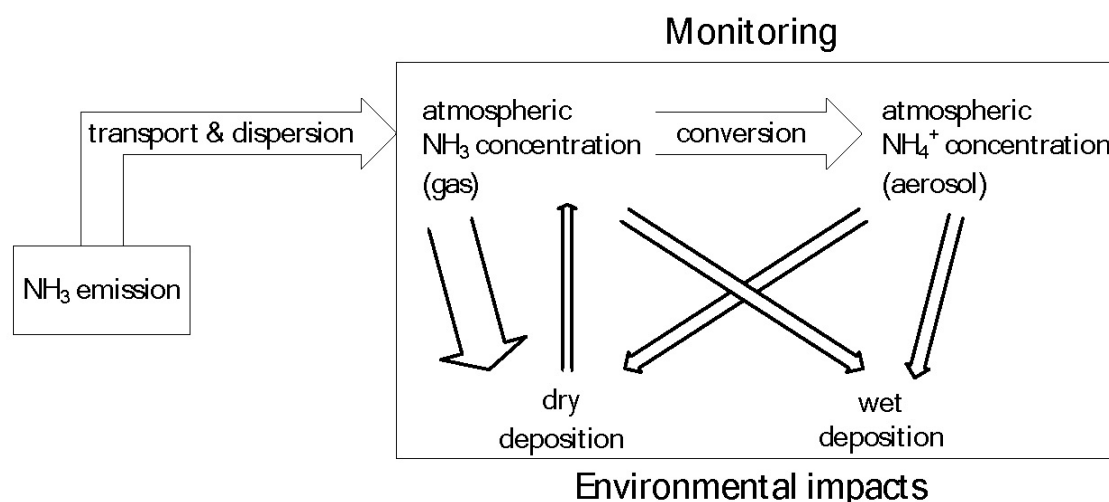


Fig. 1 Relevant atmospheric processes which determine the occurrence of NH_3 in the atmosphere. The thickness of the arrows shows the ratio of the process (Moeller, 2003; van Pul et al., 2009 - modified).

Concerning the quantification of NH_3 emissions from housed livestock facilities, a large variety of scientific results have been published (Aneja et al., 2001; Mosquera et al., 2005; Welch et al., 2005; Blunden et al., 2007; Gates et al., 2007). By the approach to define a particular emission factor for each animal species and other individual sources, it is possible to quantify the strength of emission sources (Asman, 1992; Misselbrook et al., 2006). The development of accurate emission factors is still difficult, due to a lack of data with adequate temporal and spatial resolution (Aneja et al., 2008). However, it is important to specify emission factors for controlling and establishing emission abatement strategies (Ferm, 1998). Various technologies for reducing NH_3 emissions exist or are under consideration, such as feeding practices, manure and slurry treatments and ventilation rates (Angus et al., 2006; Webb et al., 2009). By using different litter and bedding materials, the NH_3 emissions can be reduced and the welfare of animals improved (Atapattu et al., 2008).

Several studies attempted to identify main aspects responsible for affecting atmospheric NH_3 . Important to be considered are the design and the operational parameters of housed livestock facilities and their ventilation system (Demmers et al., 1999; Mosquera et al., 2005).

Between emission and deposition of NH_3 , atmospheric transport and dispersion occur (Fig. 1). Atmospheric transport processes take place within the planetary boundary layer (PBL) which ranges from 100 to 3000 m. It is defined as the part of the atmosphere which reacts to changes at the surface within an hour or less (Stull, 1988). As a consequence, its structure is strongly influenced by heating and cooling of the surface of the earth. Transport and dispersion of substances depend on the state of the atmosphere which itself is influenced by various variables, such as wind with its components (u = component with the wind, v = lateral component, w = vertical component), air humidity, air pressure and air density.

The description of atmospheric transport processes is typically based on the assumption of turbulent fluxes, called “eddy-fluxes” and is calculated by covariance between two variables.

Another approach, the “Reynolds averaging”, leads to a quantification of these turbulent processes by separating the mean and turbulent component of a variable (Davidson, 2004). Both components take place in horizontal and vertical directions. The turbulent fluxes are relatively uniform within the surface layer (20 to 200 m) of the PBL. Thus, this surface layer is known as the constant flux layer. The micrometeorological theories of PBL and Reynolds averaging have been intensively described by various authors (Stull, 1988; Garratt, 1992; Kaimal and Finnigan, 1994; Oke, 1997; Ayra, 2001). Moreover, vertical mixing processes within the PBL can be limited to a certain height, called mixing height. This mixing height shows diurnal and seasonal variations and can be either affected by mechanical or thermal turbulence. The existence of this mixing height is important for transport and dispersion processes at regional and local scale. Furthermore, it is necessary to consider surface roughness and buildings as factors influencing dispersion processes of substances (Erisman et al., 2005; Skiba et al., 2006).

1.2 Monitoring approaches

In general, two complementary sampling approaches are used for measuring and monitoring atmospheric NH_3 concentrations in the immediate vicinity of sources. A monitoring with low time resolution provides information on spatial dispersion patterns. Concerning its simplicity and cost effectiveness, passive sampling is a widely used practical technique for detecting spatial dispersion patterns of NH_3 (Kirchner et al., 1999; Namiesnik et al., 2005; Seethapathy et al., 2008). The second complementary strategy is to conduct highly time-resolved measurements at one location. A variety of different NH_3 measurement techniques which use different methodologies exist, summarised and compared in Mennen et al. (1996); Erisman et al. (2001); Clemitshaw (2004); Schwab et al. (2007); Norman et al. (2009). Owing to several factors, measuring atmospheric NH_3 concentrations is difficult. Ammonia concentrations may widely vary from 500 ppbv near sources (Krupa, 2003) to 5 pptv in remote regions (Janson et al., 2001; Sutton et al., 2001). Based on its chemical character, NH_3 occurs in different phases (gaseous, particulate and liquid), which further complicates its measurement (Warneck, 1988). In addition, NH_3 is “sticky” and interacts with surfaces of materials, often leading to slow inlet response times (Yokelson et al., 2003).

Monitoring studies of emission, dispersion and deposition of NH_3 are crucial for providing information about trends and loads of it toward the environment. The processes involved in measuring NH_3 concentration and the variability of NH_3 dispersion patterns are complex. Therefore, various computer models have been used for simulated measurements. These models can be used to extend the interpretation of these complex processes with higher geographical resolutions or to estimate environmental impacts of NH_3 at locations not covered by a monitoring station. However, models require correct knowledge about meteorological processes and atmospheric conditions (Asman et al., 2001). Regarding NH_3 dispersion, an accurate EU-wide quantitative assessment is still difficult to make (Loubet et al., 2009). By developing local scale models (e.g. Hill, 1998; Sutton et al., 1998), description of information on the spatial dispersion patterns of NH_3 and on the atmospheric transport, deposition and impacts of NH_3 is possible (Dragosits et al., 2002; Cellier et al., 2009). An overview of currently available models at a national or regional scale is given by van Pul et al. (2009). Nevertheless, modelling transport and deposition of atmospheric NH_3 is still a challenge due to the complexity of occurring processes (Asman et al., 1998; Hertel et al., 2006).

The aspects of emission, dispersion and deposition remain of central importance to the NH_3 issues of today (Asman et al., 1998; Sutton et al., 1998; Dragosits et al., 2006; Aneja et al., 2008).

1.3 Environmental impacts

Emissions of NH_3 are responsible for various aspects of air pollution. They can cause odour nuisances (Blanes-Vidal et al., 2009) which are even more important since a growing number of people settle down in agricultural used areas. Further, emitted NH_3 can have negative effects to plants and ecosystems vitality if deposited in amounts above critical levels.

In 1992 the United Nations Economic Commission for Europe (UNECE) sets the average critical annual amount for NH_3 in Europe to $8 \mu\text{g m}^{-3}$. But several studies suggest to reassessing the critical annual amount to lower NH_3 concentrations for sensitive ecosystems (Sheppard et al., 2008; Cape et al., 2009). The conversion of NH_3 to NH_4^+ significantly causes the formation of particulate matter (Erisman et al., 2007; Wu et al., 2007).

Depending on the environmental setting, an over-enrichment of NH_3 in an ecosystem can lead to acidification of soils, enhanced eutrophication of water bodies, forest decline or decreasing of biological diversity (Sutton et al., 1993; Fangmeier et al., 1994; Sutton et al., 1995; Ferm, 1998; Krupa, 2003; Bobbink et al., 2004). In many parts of Europe, the flora has shown shifts towards nitrophilous species (Fangmeier et al., 1994; Pitcairn et al., 1998; Skiba et al., 2006).

Consequently, the release of NH_3 from crop or livestock facilities into the atmosphere recently became the subject of intense scientific research and political agreements: UNECE (UNECE, 1999), the European Union National Emissions Ceilings Directive (2001/81/EC) and the EU Directive on Integrated Pollution Prevention and Control (IPPC, 2008/1/EC). According to the targets set by the European National Emission Ceilings Directive (NECD) 2001/81/EG, Germany has to reduce its NH_3 emissions from 764 kt yr^{-1} in 1990 to 550 kt yr^{-1} in 2010. This equates to a decrease of 28%. The National Inventory Report revealed that Germany's Greenhouse Gas Inventory (1990-2008) exceeded the allowable limit by 11% (UBA, 2010).

For the year 2020 and beyond, deposition from NH_3 emissions will be the main contribution to acidification and eutrophication in many regions in Europe (Sutton et al., 2009). Ammonia from animal buildings contributes substantially to atmospheric nitrogen loading and may yield the same order of magnitude as emissions of NO_x in some areas (Aneja et al., 2001). This is even more the case, since NO_x and SO_2 emissions from combustion sources considerably decreased due to the implementation of emission control legislation (Erisman et al., 2007).

The transport and dispersion of NH_3 vary according to several factors such as meteorology, vegetation and environment. Further, it is closely linked to agricultural management practices (Erisman et al., 2005). Owing to the variation of atmospheric NH_3 concentrations over time, which, in turn, depends on season and atmospheric conditions, a suitable monitoring of atmospheric NH_3 is urgently necessary.

1.4 Open issues and objectives of the thesis

Based on the current knowledge described above, the following aspects have been identified as the prime open issues regarding the NH_3 content in the air.

- ✓ One of the main aspects in the above context is the high spatial and temporal variability of atmospheric NH_3 concentrations, depending on the respective agricultural NH_3 source. For studying the dispersion and transport of atmospheric NH_3 , it is crucial to measure its concentrations precisely, reliably and repeatably. Various measurement techniques exist, based on different methodological approaches. But unfortunately, their results are hardly comparable.
- ✓ Another issue is represented by the lack of knowledge on the factors underlying the processes of transport and dispersion of atmospheric NH_3 . To investigate these dynamic processes, it is necessary to specify the most influencing factors.
- ✓ For a comprehensive evaluation of the fate of the NH_3 content in the air, it is absolutely essential to consider all parts of atmospheric processes which determine the occurrence of atmospheric NH_3 (Fig. 1). Within different detailed studies each occurring process was investigated separately, without focusing on their relationship and connection of them simultaneously.

Accordingly, the objectives of the thesis have been defined as follows:

1. The first objective is focused on the identification of techniques which are most suitable for precisely monitoring atmospheric NH_3 concentrations under typical field conditions. For this purpose, the most often applied measurement techniques are implemented. These techniques are able to record with high temporal-resolution at one location. Concerning the wide variety of atmospheric NH_3 measurement techniques, an inter-comparison under typical field conditions was aimed to find out suitable instruments for accurate measurements (Paper I). For evaluating the spatial dispersion patterns of atmospheric NH_3 , other monitoring approaches are required (Paper III).
2. Several aspects are considered for identifying major factors affecting transport and dispersion of NH_3 in the air, originated from agricultural sources. This work focuses on an adequate selection of factors that are known to exert a strong influence on the emission and dispersion of NH_3 in the air. Moreover, the choice of a meaningful statistical method to distinguish and verify the relationship between selected influencing factors and measured atmospheric NH_3 concentrations has been another important prerequisite (Paper II).
3. A further objective has been addressed to a comprehensive evaluation, which includes all relevant atmospheric processes determining the occurrence of atmospheric NH_3 . Following issues are identified: quantifying the NH_3 emission source, considering the dispersion processes of the emitted NH_3 into the atmosphere, monitoring the NH_3 concentrations in the air and detecting their impacts toward the immediate environment (Paper III).

In order to achieve these aims, the investigations were aimed at a practically orientated approach. Therefore, field experiments in agricultural used environment were conducted.

2 Materials and methods

This Section gives a short overview of the main methods used in this thesis. In more detail these methods are described in the respective papers.

2.1 Study sites

Three field experiments in agriculturally used areas were performed. Concerning the first objective (Paper I), an extensive inter-comparison study of different atmospheric NH_3 measurement techniques took place over a grassland area (Easter Bush), located in Southern Scotland which has been used for cattle and sheep grazing in recent years (Fig. 2). The Easter Bush site is located about 1 km to the west of the Pentland Hills with peaks of up to 500 m (Milford et al., 2001; Whitehead et al., 2008). The site is divided into two fields, each approximately 5 ha, more than 90% is covered by *Lolium perenne* (perennial ryegrass). The dividing line between the fields runs NW to SE. In the following analysis the fields to the NE and SW of the measurement equipment are referred to as N field and S field, respectively.

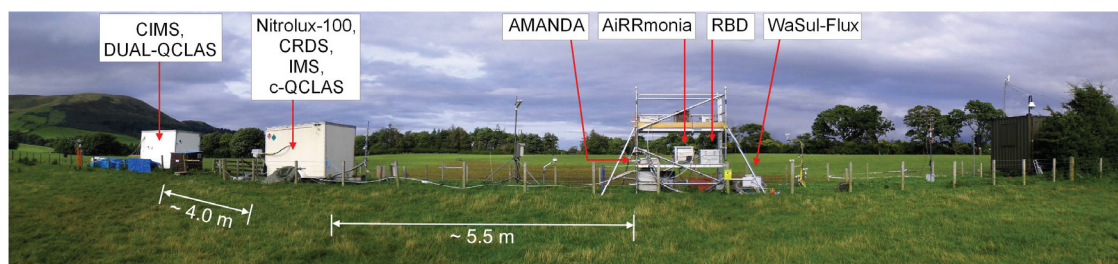


Fig. 2 Intensively managed grassland site with instruments, looking from the S field towards the N field - taken from Paper I, Appendix A, Fig. 1.

All instruments were placed along the boundary between the two fields and deployed with an inlet height of 1.1 m above ground. The inter-comparison experiment took place from 20 August to 4 September 2008. To test the instruments over a wide range of NH_3 concentrations, both N and S field were fertilised with 35 kg N ha^{-1} in the form of urea on 28 August 2008.

The other field studies (Paper II and III) were conducted on the area of a broiler farm. This farm is located to the southeast of Berlin (Germany) and covers an area of about 6 ha. It is surrounded mostly by pine woodland, with trees of approximately 8-10 m in height. There is open space to the northeast, where the road leading to the farm' entrance lies (Fig. 3).

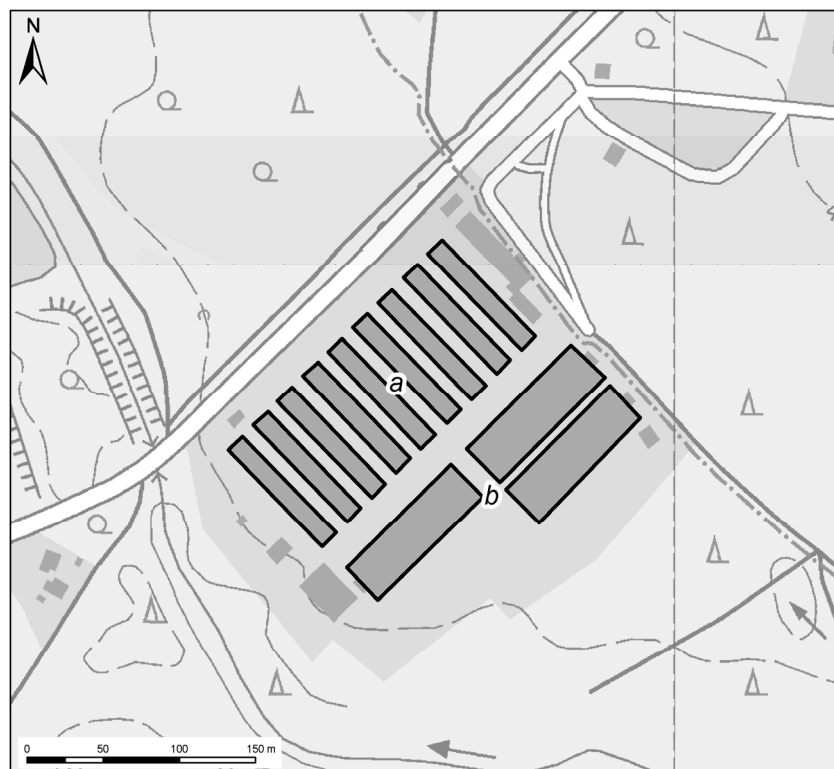


Fig. 3 The investigated broiler farm, where “a” and “b” represent the small and the big broiler barns, respectively.

The broiler installation consists of nine small barns (length: 88 m, width: 12 m and height: 3.5 m), each containing 21,800 broilers (see “a” in Fig. 3). There are also three big barns (length: 93 m, width: 29 m and height: 4.5 m) with 62,000 broilers each (see “b” in Fig. 3). In total, around 382,200 broilers are raised during a growing cycle. The nine small broiler barns are equipped with side-forced ventilation. In contrast, the three big barns have 18 rooftop stacks with controlled fans. Each of these rooftop stacks has a diameter (d_s) of 0.65 m and a height of 1 m above the roof. The operation of the fans is controlled by the inside air temperature of the broiler barns. In each of the seven to eight annual growing cycles, the broilers were kept in the barns for 36 days with a market mass of approximately 1.5-1.8 kg. The broilers shared a common genetic pool and therefore produced the same type of NH_3 . Thus, the measurements taken in one barn would be comparable in the NH_3 concentrations to those taken in any other barn on the farm. Each growing cycle starts simultaneously in all of the barns. The bedding material is sawdust. The barns are cleaned and sterilized during the 7-day service periods between the growing cycles. Additionally to the study site in and around the barns of the farm, measurements were performed along a transect through the adjacent woodland (Paper III).

2.2 Measurements

Ammonia emissions

To meet the demands of the objectives stated in Section 1.4, a quantification of the NH_3 sources, i.e. the broiler barns, was required. Thus, inside NH_3 concentration (c_{in}), air-volumetric flow rate (q) and inside air temperature (T_{in}) were measured close to the exhaust air outlets of one of the large broiler barns (62,000 broilers). With this knowledge, it was possible to calculate the NH_3 -mass-flow which affects the adjacent environment (Paper II and III).

The NH_3 -mass-flow (kg h^{-1}) was calculated (Eq. (1)) as:

$$m = c_{in} * q \quad (1)$$

Further, the exhaust air height out of the stacks of the broiler barns was considered (Paper II). For this calculation, the plume rise calculation after Briggs (1972) was applied.

Atmospheric NH_3 concentrations

Monitoring of atmospheric NH_3 concentrations presents a central aspect in all studies, performed in the context of this thesis. One major issue was the evaluation of different monitoring approaches to find out the method most suitable for precisely monitoring of atmospheric NH_3 concentrations under typical field conditions.

During the extensive inter-comparison of atmospheric NH_3 measurement techniques under typical field conditions, described in Paper I, eight different methods implemented in eleven instruments were evaluated. This study was initialised by the Centre for Ecology and Hydrology (UK). The instruments deployed included three wet-chemistry systems, one with offline analysis (annular rotating batch denuder, RBD) and two with online-analysis (Annular Denuder sampling with online Analysis, AMANDA; AiRRmonia), two Quantum Cascade Laser Absorption Spectrometers (a large-cell dual system; DUAL-QCLAS, and a compact system; c-QCLAS), two photo-acoustic spectrometers (WaSul-Flux; Nitrolux-100), a Cavity Ring Down Spectrometer (CRDS), a Chemical Ionisation Mass Spectrometer (CIMS), an ion mobility spectrometer (IMS) and an Open-Path Fourier Transform Infra-Red (OP-FTIR) Spectrometer (Paper I).

Passive sampling was used for assessing the spatial dispersion patterns of atmospheric NH_3 concentrations at a lower time resolution. Badge-type passive

samplers were installed at 2 m height above ground. The monitoring took place at five points around the broiler farm (one week exposure time) and along a transect (three weeks exposure time) through the adjacent woodland (Paper III). To meet the second objective, concerning the investigation of factors influencing the transport of atmospheric NH_3 , high temporal-resolution of NH_3 measurements was required. Thereby, a chemiluminescence NH_3 analyser (NO_x converter; Breitenbach and Shelef, 1973) detected every 15 s atmospheric NH_3 by sampling the air via a PTFE-hose, attached to a monitoring tower at 10.5 m height above ground (Paper II).

Meteorological factors and environmental conditions

Eleven instruments were compared above an intensively managed agricultural field in late summer 2008 in Scotland (Paper I). The above average wet August in eastern Scotland in 2008, with twice as much rainfall as the long-term average, led to the formation of a “pond” near the measurement site in the N field. Although the accumulating water was pumped away on several occasions, the associated rotting vegetation is likely to have created an additional and heterogeneous NH_3 source near the instruments, for NE wind directions. The few occurrences of this wind direction were therefore excluded from further analyses.

Paper II focused on the investigation of factors affecting the NH_3 content in the air surrounding a broiler farm. A monitoring tower was used to detect the occurring meteorological situation around the farm at 10.5 m height above ground. At this monitoring tower, the three-dimensional wind components (u , v , w) and the acoustic temperature (T) were measured by an ultrasonic anemometer (VDI 3786, 1994). From these datasets, hourly mean values as well as horizontal wind speed (ws) and wind direction (wd) were calculated. In addition, precipitation (P) and outside air temperature (T_{2m}) were measured at 1.5 m and 2 m above ground, respectively. Atmospheric transport processes are defined based on turbulent fluxes, called “eddy-fluxes”. The “Reynolds averaging” approach is used to quantify these turbulent processes by separating the mean and turbulent component of a variable as follows (Kaimal & Finnigan, 1994):

$$x(t) = \bar{x} + x'(t) \quad (2)$$

where $x(t)$ represents the sum of \bar{x} as the means over an interval of time (1 h in this study) and $x'(t)$ the turbulent component. Eddy-covariance defines the flux as the average product of the instantaneous deviations of vertical wind velocity (w') and the

deviations of a scalar χ' from its mean value ($\overline{w'\chi'}$). This technique has already been extensively described in the literature of this field (e.g. Stull, 1988; Foken, 2008). The vertical (σ_w) and the horizontal (σ_{ws}) turbulent components of wind, the friction velocity (u_*) and the sensible heat flux (H) were derived directly from the eddy-covariance measurements. The atmospheric stability was parameterised through the Monin-Obukhov length (L) (Oke, 1987).

In Paper III, the weather conditions were documented by wind direction (wd), temperature (T) and relative air humidity (RH), provided as hourly data by a weather station in Lindenberg (52°22' N, 14°12' O, 98 m a.s.l.) conducted by the German Meteorological Service (Deutscher Wetterdienst – DWD).

Vegetation surveys

At three sites (255 m²; 25 m x 25 m) in different distances (45, 205 and 415 m) from the broiler farm, vegetation surveys were performed (Paper III). The surveys along this transect focused on quantifying the frequency and degree of cover of the major plant species. Thereby, flora species were graded into tree layer, shrubs, herbs and mosses. Defoliation and needle yellowing were observed on six representative pines (*Pinus sylvestris*) at each investigated site. Forest vitality was assessed according to damage classes used for rating of forests in German lowlands (Kallweit and Böttinger, 2001).

Chemical analysis

The correct running of the RBD instrument during the extensive inter-comparison (Paper I) was the contribution of the candidate of this thesis. From the deployed three wet-chemistry systems during the inter-comparison campaign, the RBD instrument is the most “manual” technique included here, using batch sampling and off-line analysis. In the RBD (Keuken et al., 1988), air is pumped at 27 l min⁻¹ through two horizontal concentric rotating glass tubes. These glass tubes are wetted with a thin layer of collecting liquid, which contains 2.0 g l⁻¹ NaOH, 3.4 ml l⁻¹ >98% formic acid and 0.5 mg l⁻¹ thymol as biocide. Ammonia is absorbed into this thin layer of collection liquid over a sampling time of 40 min within each hour, after which the sample (10 to 15 ml) is pumped into an auto sampler holding 20 ml test tubes. All samples were analysed for NH₄⁺ offline on an NH₃ Flow Injection Analyser (AMFIA, ECN, Petten, NL), based on analysis by selective ion membrane and conductivity measurement (Genfa and Dasgupta, 2000). For analysis, 0.5 M NaOH solution is added to the sample, resulting

in the conversion of NH_4^+ to NH_3 in solution. As the solution then passes a semi-permeable Teflon membrane, NH_3 permeates the membrane and is dissolved in a counter stream of deionised water. Here NH_3 is re-ionised to NH_4^+ and is detected by conductivity (Sutton et al., 2000a).

2.3 Statistical analyses

Linear regression analysis

By linear regression analysis, the deployed instruments during the inter-comparison (Paper I) were compared with each other and with the ensemble average of made NH_3 observations ($\text{NH}_{3\text{-ens}}$). Thereby, the ensemble average was computed as the average over all instruments that were operational at a given time, excluding the OP-FTIR, for which too few data points were available. The data from each instrument was block-averaged to hourly values in order to match the time resolution of the slowest instrument (RBD). To test the instruments over a wide range of NH_3 concentrations, the field was fertilised midway through the experiment. The regression analysis was performed for atmospheric NH_3 over the entire NH_3 concentration range and separately, below 10 ppbv to assess the performance at low NH_3 concentrations in more detail.

Multiple linear regression analysis

Regarding the second objective, a multiple linear regression (MLR) analysis was selected as a meaningful statistical method to comprehensively evaluate the relationship between selected factors and the NH_3 content in the air (Paper II). Multiple regression analyses were performed to generate linear regression models. These related the natural logarithms of measured atmospheric NH_3 concentration (c_{out}) to ten factors-of-influence (FOI), without applying an intercept. These FOI characterise the atmospheric and meteorological conditions as well as the operational parameters of the broiler barns. The aim of the MLR analyses where to comprehensively evaluate the relationship between c_{out} and FOI. This led to the following formula:

$$\log_e(c_{out})_i = a_1x_{i1} + a_2x_{i2} + a_3x_{i3} + a_4x_{i4} + a_5x_{i5} + a_6x_{i6} + a_7x_{i7} + a_8x_{i8} + a_9x_{i9} + a_{10}x_{i10} \quad (3)$$

Following the computer-generated MLRs, all values where the probability was greater than $p > 0.05$ (no significant influence) were deleted manually. All statistical analyses of Paper II were carried out using SAS v.9.2 (SAS Institute, Cary, NC, USA).

Bias and time response

During the inter-comparison of different instruments (Paper I) the bias between two instruments is defined accordingly to Eq. (4), where m is the slope of the regression analysis forced through zero:

$$bias = (m - 1) * 100 \quad (4)$$

The bias was calculated as the percentage difference of the entire NH_3 concentration range (overall bias) and the range for NH_3 concentrations < 10 ppbv (10 ppbv bias). For analysing the time response of the different instrument setups, a short time-series of each instrument was compared against data of a well-performing fast-response instrument, for which the 1 min data from the c-QCLAS was chosen. Then, a running mean was calculated from the c-QCLAS data as:

$$c'(t) = fc(t) + (1 - f)c'(t - 1) \quad (5)$$

where $c'(t)$ is the smoothed concentration, $c(t)$ is the measured concentration and f is a smoothing factor defined below, which would be unity for an instrument that is equally as fast as the c-QCLAS. For each instrument a factor (f) was determined by fitting the smoothed c-QCLAS time-series to the data reported by the instrument. The Eq. (5) simulates the response of a concentration measurement which is subject to a memory effect, which may be either due to the turnover time in an air volume, liquid pool or due to adsorption/desorption in inlet lines.

Time-series analysis

The time-series analysis focuses on the description of data characteristics and was applied in the processing of all objectives within this thesis (Paper I, II, and III). During the inter-comparison in Paper I, the additional capture of NH_3 variations of instruments with higher time resolution were shown by analysing the different time-series.

In Paper II, the differences between the time-series of the build-up of NH_3 concentrations inside and outside a large broiler barn facility over an entire growing cycle were explored. The quantification of the NH_3 -mass-flows of three different growing cycles of broilers was possible by conducting of time-series (Paper III).

3 Results and discussion

3.1 Monitoring of atmospheric NH₃

The first objective of this thesis is focused on the identification of techniques for precisely monitoring of atmospheric NH₃ concentrations under typical field conditions. Owing to the high spatial and temporal variability of atmospheric NH₃ concentrations it is challenging to measure reliable concentrations of it (Sutton et al., 2001). The inter-comparison of eleven instruments is a unique attempt because it represents the largest inter-comparison measuring atmospheric NH₃ under typical field conditions to date (Paper I).

Figures 4a and 4b show the time-series of measured NH₃ of all instruments, detected with different temporal resolution (1 min to 1 h) (see Section 2.3). In addition, the wind direction is indicated at the top. Different vertical scales were used to present the time-series before and after the fertilisation on 28 August 2008. For increased clarity, the instruments are presented in two groups, separating wet-chemistry analysers and spectroscopic techniques. The absolute NH₃ concentrations of all instruments revealed the same features within the time-series and agreed closely with each other. In contrast, the different time resolution of the instruments resulted in slightly different features of the temporal NH₃ structure. This additional capture of NH₃ variations of instruments with higher time resolution was consistent with the observations of Norman et al. (2009). The early NH₃ peaks and some periods of disagreement coincided with periods when the wind came from the rotting vegetation source in the northern directions as indicated by the shaded areas in Figs. 4a and 4b.

For the regression analyses, sampled data during wind directions from the North were excluded (see Section 2.2). Overall, a good agreement of hourly average NH₃ concentrations with $R^2 > 0.84$, compared with the average of all instruments used (NH_{3-ens}) was achieved (see Section 2.3). Measurements of RBD, AMANDA, AiRRmonia, WaSul-Flux and c-QCLAS were within $\pm 25\%$ for NH₃ concentrations of 10 to 120 ppbv. The correlation worsens if only concentrations < 10 ppbv were considered which were done to assess the performance of the instruments for lower NH₃ concentrations. These results are in line with previous studies which illustrated the challenges involved in measuring low atmospheric NH₃ concentrations (William et al., 1992; Mennen et al., 1996; Schwab et al., 2007; Norman et al., 2009). During this inter-comparison, the wet-chemistry instruments (RBD, AMANDA, AiRRmonia) showed good long-term stability (see Section 2.2).

The overall bias for all instruments described in Paper I were reasonably small, ranging from -12.9% (CIMS) to 10.9% (AiRRmonia) except for the DUAL-QCLAS (-32.1), whereas the <10 ppbv biases showed more variability (see Section 2.3).

The calculated time response for the instruments was higher than stated by the manufacturers. This is particularly true for the AMANDA system which reports 7.5 min data, but it appeared to take 32.2 ± 3.7 min for a 95% response. The replacement of the liquid pool in the denuder appears to limit this time response of the instrument. A similar observation was made for the RBD. The AiRRmonia seemed to have the least time delays in the system: 14.4 ± 4.0 min to obtain 95% of the signal was only slightly slower than the 10 min measurement cycle (see Section 2.3). A similar observation was made by Thomas et al. (2009). One reason for the variability within the measured NH_3 concentrations between the tested instruments can be explained by the “sticky” nature of NH_3 which interacts with surfaces of materials and partly explain the under-estimate in NH_3 at peak concentrations (Shaw et al., 1998; Whitehead et al., 2008).

Concerning the investigation of the relationship between selected factors-of-influence (FOI) and measured atmospheric NH_3 , a NO_x converter with high temporal-resolution was used (Paper II). Unfortunately, this measurement technique which is based on the chemiluminescence method was not included in the inter-comparison of Paper I. Therefore, a statement concerning the agreement with the tested instruments of the inter-comparison was not possible.

The measurements of the NH_3 concentrations in the air were conducted at one location at the monitoring tower. Thus, the proper location of the tower was essential for a successful and accurate outcome of the study. The importance of finding an optimal monitoring location is emphasised in Paper II. Nevertheless, the aspect of an improvement of more accurate information of the spatial dispersion patterns of NH_3 in the air was pointed out.

In Paper III, this fact was taken into consideration by the approach of using passive samplers with one week exposure time at various locations. The spatial dispersion patterns of atmospheric NH_3 surrounding the broiler farm were quantified at five monitoring points over three different growing cycles in 2007 and 2008. Concerning its simplicity and cost effectiveness, passive sampling is a widely used practical technique (Namiesnik et al. 2005; Seethapathy et al. 2008). Compared to monitoring techniques described in Paper I and II, the time resolution using passive samplers was reduced. In turn, improved information about the spatial dispersion patterns of NH_3 in the air was available.

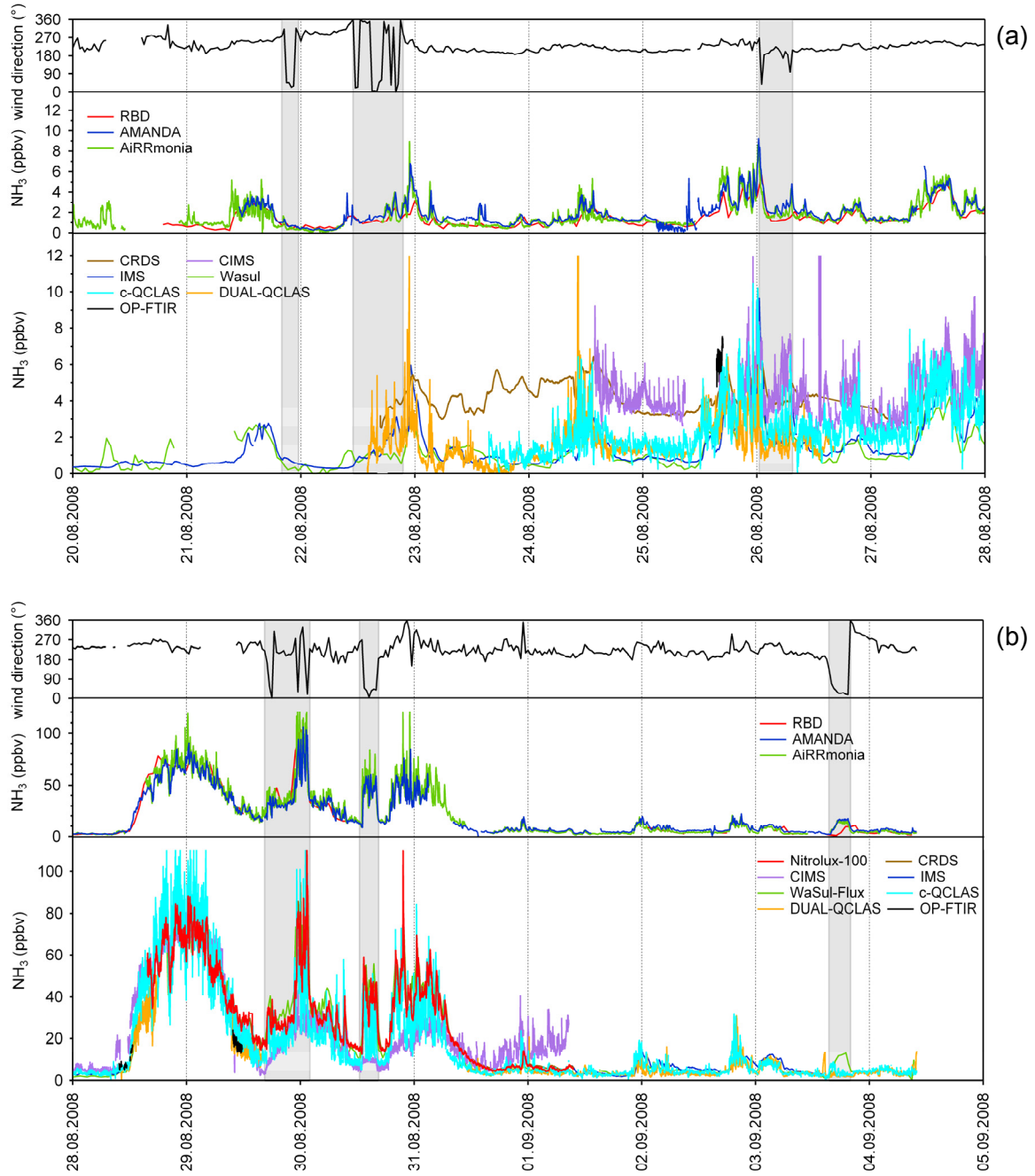


Fig. 4 Times-series of NH_3 concentrations for all instruments ($z = 1.1$ m) with occurring wind direction for the data (a) before fertilisation and (b) after fertilisation on 28 August 2008. The shaded areas indicate periods during which the wind came from the N field. AiRRmonia (green), AMANDA (blue), RBD (red); Nitrolux-100 (red), CRDS (brown), CIMS (purple), IMS (blue), c-QCLAS (cyan), WaSul-Flux (green), DUAL-QCLAS (orange), OP-FTIR (black) - taken from Paper I, Appendix A, Figs. 3a and 3b.

The disadvantage in using passive samplers is caused by the lack of information about the temporal variability of the NH_3 concentrations during the one week exposure time. Thus, it was not possible to observe certain NH_3 concentration peaks as encountered

in Paper I. Also, the transport of NH_3 -laden air above the monitoring device by reverse or downwards winds as mentioned in Paper II, was not possible to detect by using passive samplers.

During the three sampling periods in Paper III, atmospheric NH_3 concentrations increased over time due to rising NH_3 emissions out of the broiler barns. Thereby, the NH_3 concentrations were higher in summer than in winter. This observation agreed well with studies of Buijsman et al. (1998) and Thöni et al. (2004). The observed dispersion patterns of NH_3 in the air varied due to the spatial locations of the monitoring points relative to the surrounding broiler barns and the prevailing wind direction. This fact was consistent with the results of Paper II, where a complex interaction of factors determines the NH_3 content in the air.

According to the particular purpose of monitoring, different methods with high temporal (Paper I and II) or high spatial resolution (Paper III) should be applied. The respective use of monitoring methods attends different aspects of interpretations and evaluations, bearing in mind the constraints of each technique.

3.2 Selected factors-of-influence (FOI)

Agricultural livestock facilities present a major source of NH_3 emissions. The field experiments in Paper II and III took place on the same area of a broiler farm and its adjacent environment. The farm presents a huge animal production facility which is typical for agricultural used landscapes in Germany and Europe. In the near future, more of these facilities will arise due to the pressure on food production industry in our society (Aneja et al., 2008).

Paper II emphasises the different patterns of the NH_3 -mass-flow (m ; Eq. (1)) out of the barns and the outside measured NH_3 concentration (c_{out}) over an entire growing cycle of the broilers (Fig. 5). Concerning the variations of m and c_{out} , five different phases could be identified; these are indicated in the upper part of Fig. 5. The comparison of m and c_{out} resulted in a weak coefficient of determination of $R^2 = 0.18$. This fact implied that external factors were strongly influential and had to be taken into consideration.

Thus, Paper II focuses on an adequate selection of factors-of-influence (FOI) that are known to exert strong effects on the emission and dispersion of NH_3 in the air. For this selection of appropriate FOI, several studies and aspects were considered (Oke, 1987; Kaimal and Finnigan, 1994; Redwine et al., 2002; Demmers et al., 2005; Mosquera et

al., 2005). The combination of operational mode parameters of the broiler barns (ventilation system, NH_3 -mass-flow, exhaust air height, day-of-growing cycle, inside air temperature) with atmospheric and meteorological aspects (mean and turbulent mixing components, outside air temperature and atmospheric stability) turned out as a suitable choice. In addition to c_{out} , all atmospheric and meteorological data were detected with instruments mounted at the monitoring tower.

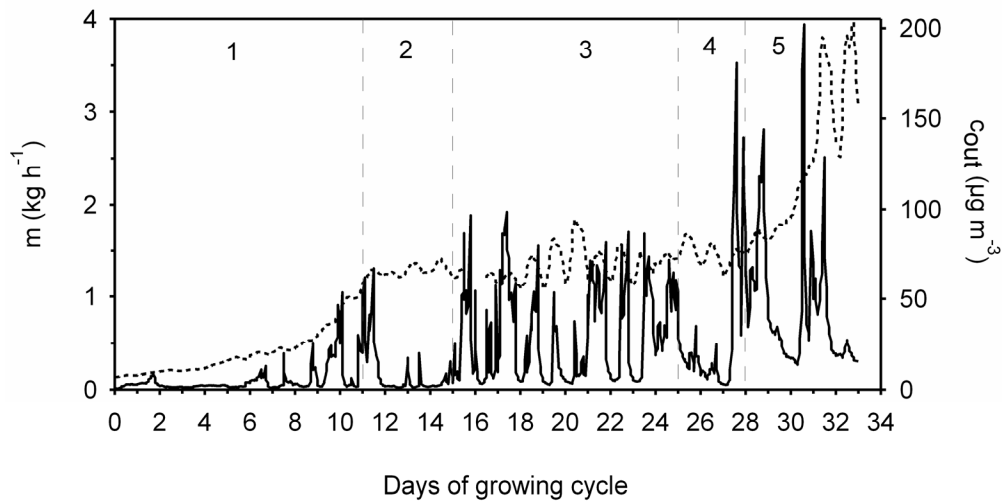


Fig. 5 Ammonia-mass-flow (m) out of twelve broiler barns with 382,200 broilers in total (dashed line) and measured NH_3 concentration in the air (c_{out}) in 10.5 m height (solid line) during one growing cycle. The numbers 1-5 mark phases during which different patterns of m and c_{out} occurred - taken from Paper II, Appendix B, Fig. 4.

The relationship between all mentioned FOI and observed atmospheric NH_3 concentrations was analysed by implementing a multiple linear regression (MLR) analysis as an appropriate method (see Section 2.3). Different approaches of MLRs were applied, considering the entire data range and subsets of data to determine a general model and other more restrictive models. Overall, the precision of the predictive models of the MLRs, based on different datasets, was satisfactory ($R^2 > 0.83$). Thereby, the general non-restrictive model used could interpret 89% of the total variance of c_{out} by using six FOI. This evidence suggested that the decision to use these FOI in the models was justified.

In nearly all models of Paper II, the negative mean vertical wind component ($-\bar{w}$) was observed and proved to be the most important influential factor. This fact supported the assumption that the height of the air coming out of the stacks of the broiler barns strongly influenced the elevation of the exhaust fumes. Considering the effects of the

ventilation system, it can be assumed that emitted NH_3 plumes rose above the height of the monitoring tower. The sensor at the monitoring tower detected NH_3 in the air even when the wind blew over an area without NH_3 sources (wooded area surrounding the farm). This observation implied that NH_3 -enriched reverse winds blew back in the direction of the monitoring tower. It also suggested that a downward flow of NH_3 -enriched air reached the measuring device and was detected. These partially unexpected aspects are the most important outcomes of Paper II.

Further, by monitoring specific FOI, it is possible to apply models for predicting atmospheric NH_3 concentrations. It is important to note that the models presented here used data that were based on one particular growing cycle. Future work will be required to further enhance the models and improve the accuracy of predicting the NH_3 concentrations in the air.

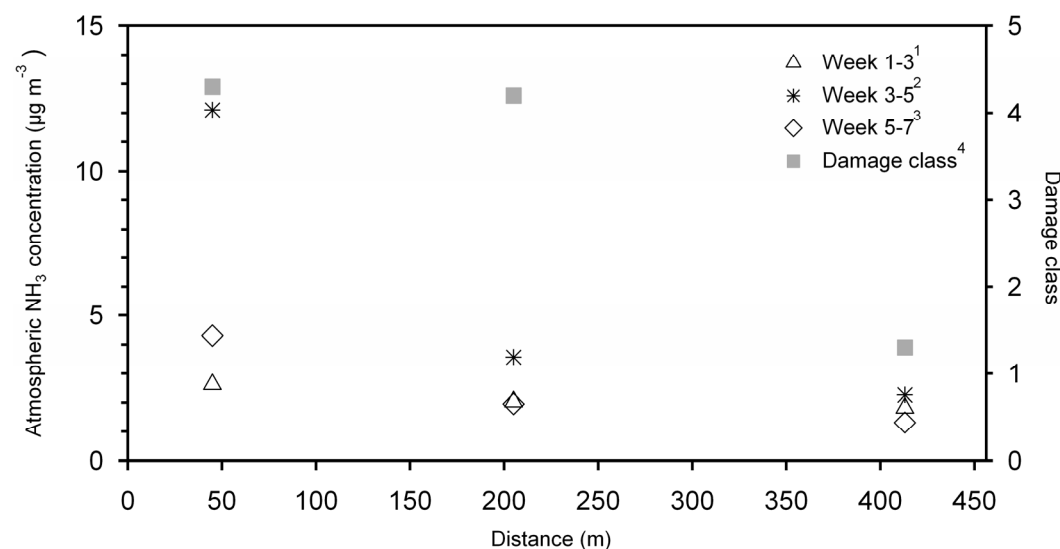
3.3 Comprehensive evaluation

For a sensible evaluation of the fate of atmospheric NH_3 in the environment, it is necessary to consider all aspects of atmospheric processes which determine the occurrence of NH_3 in the air. Therefore, Paper III aimed to obtain a way of a comprehensive evaluation by quantifying the NH_3 emission source, considering the dispersion processes of the emitted NH_3 in the atmosphere, monitoring the atmospheric NH_3 concentrations and detecting the impacts on the immediate environment (see third objective in Section 1.4).

The NH_3 emissions from the described large broiler farm were observed over three growing cycles. At the same time, the spatial dispersion patterns of NH_3 in the air were monitored by passive samplers. During one growing cycle, measurements of NH_3 in the air and vegetation surveys along a transect in the woodland, adjacent to the farm were conducted (see Section 2.2). Owing to the same processes of broiler rearing, the NH_3 -mass-flow (m) out of the broiler barns increased to the same degree throughout the three growing cycles. This rise resulted from the growth of the broilers and their increased activity. As a consequence, higher ventilation rates were required to guarantee the desired inside air temperatures, whereby the NH_3 -mass-flow increased.

In the vicinity of the farm, a significant increase of atmospheric NH_3 concentrations was observed. This increase was strongly influenced by the prevailing wind direction. At three sites along a transect (45, 205 and 415 m) through the adjacent woodland the

NH₃ concentrations in the air decreased with increasing distance from the farm (Fig. 6). The trend of decreasing NH₃ concentrations with increasing distance from the source was consistent with the observations of Fowler et al. (1998) and Skiba et al. (1998, 2006).



¹ Beginning of growing cycle

² Centre of growing cycle

³ End of growing cycle including service period

⁴ According to Kallweit and Böttinger (2001)

Fig. 6 Atmospheric NH₃ concentration and damage class at corresponding distance from the broiler farm at 45, 205 and 415 m - taken from Paper III, Appendix C, Fig. 3.

The forest vitality was assessed according to damage classes, whereas the lower the class the better the vitality. Within a distance up to 205 m from the farm a mean damage class of 4 was observed. Despite the fact that the atmospheric NH₃ concentration was below the current critical threshold for NH₃ in Europe (8 µg m⁻³), visible damages of trees (*Pinus sylvestris*) with defoliations (>60%) and discolorations (<60%) of needles were detected. At increased distance (~400 m) from the farm, the forest vitality could be characterized as vital and barely damaged, with a damage class of 1.3. This finding of a decline of elevated atmospheric NH₃ concentrations over a relative short distance to background concentrations (<3 µg NH₃ m⁻³) confirmed the results of Tyndall et al. (2007) and Adrizal et al. (2008).

This outcome of Paper III suggests the use of tree belts and woodland close to agricultural sources which may help to retain the air pollution in a small local area.

All three sites at the different distances (45, 205 and 415 m) from the farm were dominated by nitrophilous species (*Pinus sylvestris*, *Avenella flexuosa*, *Calamagrostis epigejos*). According to van der Eerden (1982), Fangmeier et al. (1994) and Krupa

(2003), these species react with an intermediate or low susceptibility to acute NH_3 injury. The detected moss species (*Pleurozium schreberi*, *Scleropodium purum*) were as like as the ones in the studies of Pitcairn et al. (1998, 2002), where woodland flora in the vicinity of livestock farms in the UK was investigated.

Species with sensitive susceptibility to acute NH_3 injury (*Vaccinium myrtillus*, *Pleurozium schreberi*) became more abundant at increased distance from the farm (~400 m). This observation agreed with the study of Pitcairn et al. (2009). Many species considered as nitrogen indicators still existed in the distance of ~400 m from the farm, but their fraction declined.

The results of Paper III illustrate the impacts of an animal production facility as a source for elevated NH_3 emissions toward adjacent ecosystems. A demand still exists to find viable emission abatement strategies. Otherwise, a risk of loss and change in biodiversity of the surrounding ecosystem of farms impends. Therefore, a detection of accurate NH_3 emissions, atmospheric NH_3 concentrations and their impacts toward the ecosystem is required.

On the other hand, the results of this study highlight the planting of trees and woodland areas close to agricultural sources which may help to retain the air pollution in a small local area. Thus, the transport of emitted NH_3 into the air over a longer distance may be reduced.

4 Conclusions and outlook

In the frame of the presented thesis, the aspect of an accurate monitoring of atmospheric NH_3 concentrations was a prime prerequisite.

An extensive inter-comparison of eleven atmospheric NH_3 measurement techniques was conducted, representing the largest inter-comparison under typical field conditions to date (Paper I). The instruments used, reported differences in the NH_3 concentrations, but overall a high coefficient of determination of $R^2 > 0.84$ of hourly average of atmospheric NH_3 concentrations was detected. Calibration and the provision of a reliable calibration source was a sensible aspect and need to be performed frequently for all instruments evaluated. Despite the wide variety of advanced atmospheric NH_3 measurement techniques, the continuous measurement of atmospheric NH_3 concentrations remains a challenging enterprise.

Furthermore, this thesis was related to the question which selected factors exert strong effects on the emission and dispersion of NH_3 in the air. For the selection of these factors-of-influence (FOI), the combination of operational mode parameters of the broiler barns with atmospheric and meteorological aspects turned out as a suitable choice. The relationship between the FOI and the observed atmospheric NH_3 concentrations was analysed by implementing a multiple linear regression (MLR) analysis as statistical approach (Paper II).

Overall, the precision of the predictive models of the MLRs was satisfactory ($R^2 > 0.83$) and suggested that the decision to use the selected FOI was justified. In principle, by monitoring specific FOI, it is possible to apply models for predicting atmospheric NH_3 concentrations. Future work will be required for upgrading the data records to further enhance the accuracy of the models.

An idea for a further experiment could be focussed on controlling the operational mode of animal production facilities (ventilation system) in respect to occurring atmospheric conditions which cause high atmospheric NH_3 concentrations. By doing this, the emission source of NH_3 would be reduced in situations which negatively affect the dispersion and transport processes. Thereby, optimal conditions for the animal welfare inside the barns have to be fulfilled. This integration of special FOI in the operational mode of animal barns (e.g. wind speed, wind direction) could help farmers to satisfy certain critical thresholds required by law. Further, the air quality could be improved in situations when atmospheric conditions supporting odour nuisances in the inhabited vicinity of the farm.

In Paper II, the measuring device detected NH_3 in the air even when the wind blew over an area without sources of NH_3 (wooded area surrounding the farm). This finding implied that NH_3 -enriched air reached the measuring device by reverse and downward blowing winds. These partly unexpected processes should be considered in future studies which are focused on the dispersion of NH_3 in the air. Atmospheric models based on local-scale can be further improved and evaluated by stronger focusing on the fact of reverse and downward blowing winds which contribute essentially to the atmospheric transport of NH_3 .

When measuring at one particular point, the proper location of this monitoring point is essential for a successful outcome (Paper II). Detecting the atmospheric NH_3 concentrations at various spatial points simultaneous should be an attempt in future studies. In turn, this improves the accuracy of information about the spatial dispersion patterns.

Within the study, described in Paper III, the fact of measuring at various locations was taken into consideration by the approach of using passive samplers with one week exposure time. The possible disadvantage of a reduction of the time resolution in using passive sampling has to be considered. Bearing in mind the particular method constraints, a combination of both monitoring strategies should be aimed at in future studies.

By consideration of all relevant atmospheric processes which determine the occurrence of NH_3 in the atmosphere, a comprehensive assessment of the fate of the emitted NH_3 into the atmosphere was possible (Paper III). Although the description of vegetation was a first approach, the investigated farm as a NH_3 emission source showed a clear effect towards the number of nitrophilous species which increased with decreasing distance to the farm. This fact illustrated the significant impact of NH_3 emissions from agricultural sources on sensible ecosystem. One outcome of Paper III highlights the planting of trees and woodland areas close to agricultural sources which may help to retain the air pollution in a small local area. Thus, the transport of emitted NH_3 into the air over a longer distance may be reduced.

This thesis underlines that the results of the practical field experiments were achieved by a close collaboration of agricultural and meteorological approaches. Thus, the outcomes derived from the realised studies of the Papers I–III can be act as an assistance for practical research approaches.

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Appendix

Appendix A: Paper I

Field inter-comparison of eleven atmospheric ammonia measurement techniques

Appendix B: Paper II

Factors affecting the ammonia content in the air surrounding a broiler farm

Appendix C: Paper III

Ammonia emissions from a broiler farm: spatial variability of concentrations in the vicinity and impacts on adjacent woodland

Appendix D: Contribution of author to included papers

Appendix E: Acknowledgements

Appendix A:

Paper I Field inter-comparison of eleven atmospheric ammonia measurement techniques

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Field inter-comparison of eleven atmospheric ammonia measurement techniques

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Abstract. Eleven instruments for the measurement of ambient concentrations of atmospheric ammonia gas (NH_3), based on eight different measurement methods were inter-compared above an intensively managed agricultural field in late summer 2008 in Southern Scotland. To test the instruments over a wide range of concentrations, the field was fertilised with urea midway through the experiment, leading to an increase in the average concentration from 10 to 100 ppbv. The instruments deployed included three wet-chemistry systems, one with offline analysis (annular rotating batch denuder, RBD) and two with online-analysis (Annular Denuder sampling with online Analysis, AMANDA; AiRRmonia), two Quantum Cascade Laser Absorption Spectrometers (a large-cell dual system; DUAL-QCLAS, and a compact system; c-QCLAS), two photo-acoustic spectrometers (WaSul-Flux; Nitrolux-100), a Cavity Ring Down Spectrometer (CRDS), a Chemical Ionisation Mass Spectrometer (CIMS), an ion mobility spectrometer (IMS) and an Open-Path Fourier Transform Infra-Red (OP-FTIR) Spectrometer. The instruments were compared with each other and with the average concentration of all instruments. An overall good agreement of hourly average concentrations between the instruments ($R^2 > 0.84$), was observed for NH_3 concentrations at the field of up to 120 ppbv with the slopes against the

average ranging from 0.67 (DUAL-QCLAS) to 1.13 (AiRRmonia) with intercepts of -0.74 ppbv (RBD) to $+2.69$ ppbv (CIMS). More variability was found for performance for lower concentrations (< 10 ppbv). Here the main factors affecting measurement precision are (a) the inlet design, (b) the state of inlet filters (where applicable), and (c) the quality of gas-phase standards (where applicable). By reference to the fast (1 Hz) instruments deployed during the study, it was possible to characterize the response times of the slower instruments.

1 Introduction

Ammonia (NH_3) plays an important role in atmospheric chemistry. It represents the major alkaline gas and is therefore important for the neutralization of acidic gases and the formation of particulate matter (Duyzer et al., 1994; Asman et al., 1998). Deposition of atmospheric NH_3 to ecosystem can lead to effects such as eutrophication and acidification of soils, contributing to forest decline and a decrease in biological diversity (Fangmeier et al., 1994; Sutton et al., 1995; Ferm, 1998). As a consequence, many measurement methods for NH_3 have been developed. Ambient measurement of NH_3 concentrations is difficult due to several factors: ambient levels vary widely, from 5 pptv in remote regions (Janson et al., 2001; Sutton et al., 2001) to 500 ppbv



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near sources (Krupa, 2003). Ammonia occurs in gaseous, particulate and liquid phases which add further complexity to its measurement (Warneck, 1988), since the measurement technique should be specific to the gas-phase and not modify the gas-aerosol equilibrium which depends on environmental conditions (Mozurkewich, 1993). In addition, NH₃ is “sticky” and interacts with surfaces of materials, often leading to slow inlet response times (Yokelson et al., 2003). Finally, NH₃ is emitted by people, increasing the potential for sample contamination (Sutton et al., 2000b).

Currently, bulk denuder techniques are the most widely used method for sampling NH₃ and operate by stripping the gas phase NH₃ from the air stream (Ferm, 1979; Keuken et al., 1988). The main disadvantages of this manual sampling method are the low temporal-resolution, and when high-frequency measurements (e.g. hourly) are needed, the manpower required becomes considerable. Moreover, the manual handling, including sample preparation, wet-chemical analysis and sample storage, increase the chances of sample contamination. In the 1980s systems were developed, based on wet effluent diffusion denuder (WEDD) techniques, to collect stripping solution at regular intervals into test tubes (e.g. Keuken et al., 1988), this automated the process of sample preparation and extraction, while still retaining the need for manual off-line analysis. In a next step, in the 1990s these WEDDs and mist chambers were coupled to NH₄⁺ online analysers in the field (Simon et al., 1991; Simon and Dasgupta, 1993; Wyers et al., 1993; Blatter et al., 1994; Erisman et al., 2001).

In parallel, spectroscopic techniques for NH₃ were developed, such as the use of chemiluminescence NO_x monitors with NH₃ converters (e.g. Breitenbach and Shelef, 1973), Differential Optical Absorption Spectroscopy (DOAS; Gall et al., 1991), Tunable Diode Laser Absorption Spectroscopy (TDLAS; Grisar et al., 1987; Warland et al., 2001) and Fourier Transform Infra-Red spectroscopy (FTIR; Galle et al., 2000). While many of these techniques have been deployed successfully to measure concentrations and emissions downwind of strong sources, it has only been over the past 15 years that spectroscopic techniques have gradually become sufficiently sensitive and robust for field application at typical ambient concentrations (0.1 to 10 ppbv). Approaches more recently applied for NH₃ measurements include photoacoustic spectroscopy (e.g. Harren et al., 2000; Pushkarsky et al., 2002), Chemical Ionization Mass Spectrometry (CIMS; e.g. Norman et al., 2007; Nowak et al., 2007), quantum cascade laser absorption spectrometers (QCLAS; e.g. McManus et al., 2002) and Ion Mobility Spectrometry (IMS; e.g. Myles et al., 2006).

Some experiments have been carried out to compare NH₃ measurement techniques. Wiebe et al. (1990) reported a test of four methods: FTIR, filter-pack, denuders (simple and annular) and a transition flow reactor. Williams et al. (1992) conducted an inter-comparison of five instruments: a photofragmentation/laser-induced fluorescence

(PF/LIF) instrument, a molybdenum oxide annular denuder sampling/chemiluminescence detection (MOADS) system, a tungsten oxide denuder sampling/chemiluminescence detection (DARE) system, a method based on citric acid coated denuder sampling coupled with ion chromatographic analysis (CAD/IC), and a method using an oxalic acid coated filter pack sampling coupled with colorimetric analysis (FP/COL). For selection within the Netherlands National Air Quality Monitoring Network (NAQMN) six analysers were studied by Mennen et al. (1996): a wet-annular rotating denuder, a WO₃-coated thermodenuder, a V₂O₅-coated thermodenuder, a DOAS system, a photoacoustic monitor and a chemiluminescence NO_x monitor with NH₃ converter. In addition, there were smaller inter-comparisons between two instruments: a field study on Tenerife by Milford et al. (2000) included an AMANDA instrument (see below) and a diffusion scrubber flow injection analyzer (DS-FIA). Fehsenfeld et al. (2002) reported a comparison of a CIMS with a citric acid denuder and a molybdenum oxide (MoO₃) converter. Nowak et al. (2006) compared two different CIMS instruments in the field: a NOAA chemical Science Division (NOAA-CSD) apparatus and the Georgia tech (GT) low pressure reactor.

The development of new continuous measurement approaches has motivated two major inter-comparison campaigns in recent years: a laboratory inter-comparison of gaseous NH₃ with seven instruments were performed by Schwab et al. (2007): a TDLAS, a wet scrubbing long-path absorption spectrometer (LOPAP), a WEDD system, an IMS, a photo-acoustic absorption analyzer, and a modified chemiluminescence analyzer. The emphasis of this short inter-comparison was on the accuracy and time-response of these approaches under laboratory conditions while sampling from a common manifold. In addition, Norman et al. (2009) realised an inter-comparison of three instruments at a Swiss grassland site: a modified Proton Transfer reaction Mass Spectrometer (PTR-MS; Norman et al., 2007) and two wet chemistry techniques, based on a horizontal denuder technique (GRAEGOR; Thomas et al., 2009), and a diffusion membrane sampler (AiRRmonia; Erisman et al., 2001). Further, Whitehead et al. (2008) made measurements between a QCLAS, a TDLAS and an AMANDA instrument.

The work presented here included eight different atmospheric NH₃ measurement methods implemented in eleven different instruments, focussing on comparison of the techniques under typical field conditions. Ammonia was measured over intensively managed grassland in Scotland, between 20 August and 4 September 2008. The field was fertilised on 28 August 2008 to stimulate emission from the field and test the instrumentation over a wide concentration range, including regimes that are typical for moderately agricultural mixed land use and also near-sources. The aim was to assess instrument performance and characterise the instrument response times. In addition to the description of time-series, we used regression analyses for concentrations over the entire

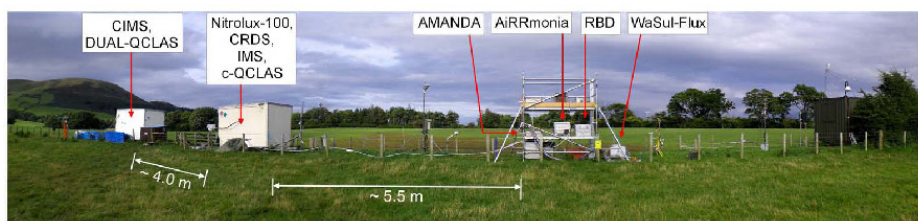


Fig. 1. Intensively managed grassland site (Easter Bush) with instruments, looking from the S field towards the N field.

concentration range and, separately, below 10 ppbv to assess the performance at low concentrations in more detail. Three of the instruments were also used for micrometeorological flux measurements based either on the flux gradient technique (AMANDA, WaSul-Flux) or eddy-covariance (DUAL-QCLAS), but these results will be presented elsewhere.

2 Methodology

2.1 Site description

The measurements were made at a micrometeorological field site in Southern Scotland ($55^{\circ}52' \text{ N}$, $3^{\circ}2' \text{ W}$, 190 m a.s.l.) on an intensively managed grassland area (Easter Bush), located about 1 km to the west of the Pentland Hills with peaks of up to 500 m (see Milford et al., 2001; Whitehead et al., 2008). The Easter Bush site is divided into two fields, each approximately 5 ha, more than 90% of which is covered by *Lolium perenne* (perennial ryegrass). The dividing line between the fields runs NW to SE, and in the following analysis the fields to the NE and SW of the measurement equipment are referred to as N field and S field, respectively. The Pentland Hills channel the wind so that on average 60% of the wind comes clearly from the S field and 19% clearly from the N field (Milford et al., 2001). Both fields receive the same management and have been used for cattle and sheep grazing in recent years. Easter Bush is an intensive flux monitoring site of the NitroEurope IP measurement programme (Sutton et al., 2007) and has hosted several studies on NH_3 flux measurements (Milford et al., 2001; Whitehead et al., 2008). The inter-comparison experiment took place from 20 August to 4 September 2008 with the instruments placed along the boundary between the two fields (Fig. 1). All instruments were deployed with an inlet height of 1.1 m above ground, with the exception of the DUAL-QCLAS (1.95 m), as this was also used for eddy-covariance flux measurements.

Fertilisation took place on 28 August 2008 on both the N and S field, with 35 kg N ha^{-1} in the form of urea.

2.2 Environmental conditions during the field experiment

Figure 2 presents the time-series of hourly data of precipitation, temperature and relative humidity. The wind direction and speed are represented by the direction and length of the arrows, respectively. The mean wind speed was around 3 m s^{-1} . Several rain events occurred during the campaign with the maximum amount being 4.9 mm h^{-1} on 20 August 2008. There was no rain during the fertilisation on 28 August 2008 and therefore no NH_3 was washed into the ground immediately after fertilisation (see Sect. 3.1). The relative humidity never decreased below 58%. The mean temperature was 12.8°C . Overall, August 2008 was wet in Eastern Scotland, receiving about twice as much rainfall compared with the long-term average (mean since 1961; values for Leuchars; Eden, 2008). This high level of precipitation led to the formation of a “pond” near to the measurement site in the N field. Although the accumulating water was pumped away on several occasions, the associated rotting vegetation is likely to have created an additional and heterogeneous NH_3 source near the instruments, for NE wind directions. The few occurrences of this wind direction were therefore excluded from the regression analysis presented below.

Figure 2 also includes a time-series of NH_4^+ aerosol in $\text{PM}_{2.5}$ measured with a MARGA instrument, similar to GRAEGOR (Thomas et al., 2009), except that it deploys on-line cation analysis rather than FIA and a $\text{PM}_{2.5}$ inlet cyclone, at the Auchencorth EMEP site, 10 km south of Easter Bush. From previous simultaneous measurements, there is close ($\pm 20\%$) agreement between NH_4^+ concentrations at Auchencorth and Easter Bush. This time-series is included because it is possible that some of the NH_3 measurement techniques deployed here may show some cross-sensitivity to NH_4^+ aerosol. Ammonium concentrations were below $1 \mu\text{g m}^{-3}$ except for 30 and 31 August 2008.

2.3 Measurement techniques

The characteristics of the NH_3 measurement systems deployed in the inter-comparison are summarised in Table 1, and can be described as followed.

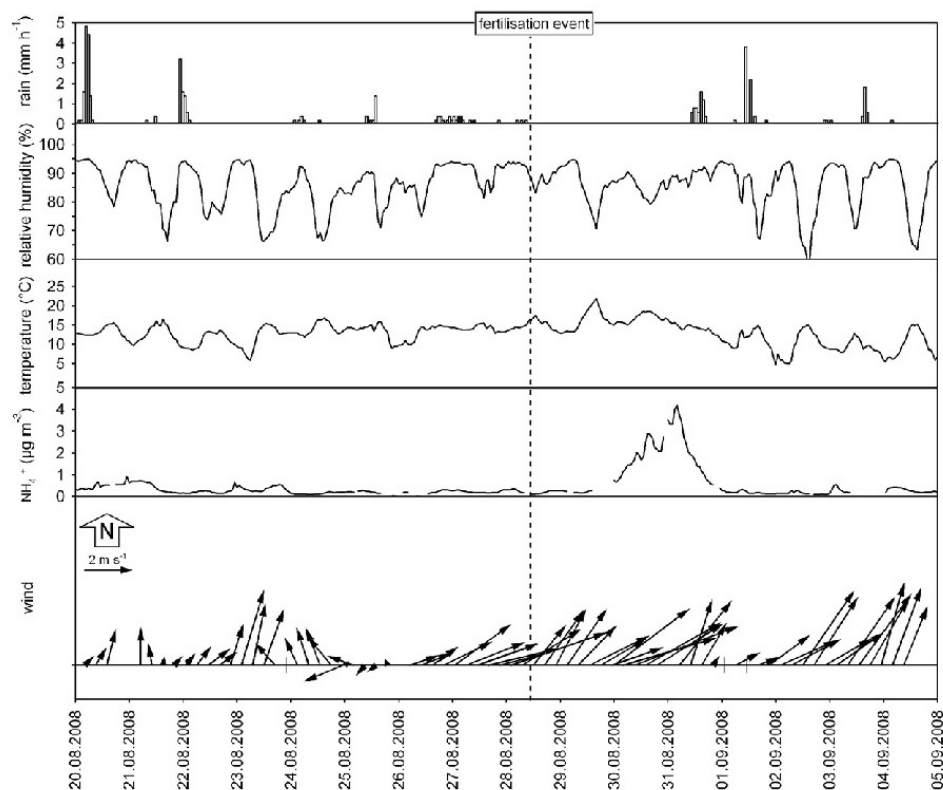


Fig. 2. Time-series of hourly data from selected meteorological variables during the campaign. The aerosol NH_4^+ concentration was measured using a MARGA monitor (see text) at the Auchencorth EMEP site, 10 km south of the Easter Bush field site. The wind panels show both magnitude and direction.

2.3.1 Wet-chemistry analysers

Two of three wet chemistry instruments deployed (RBD, AMANDA) are based on the denuder principle described by Fern (1979), whereby gas phase NH_3 is stripped from the air stream through diffusion to the denuder glass walls, without collecting the NH_4^+ aerosol phase, since gas molecules diffuse quicker than particles to a moistened/acidified tube wall. In a third instrument (AiRRmonia), a diffusion membrane was used to strip the gas phase from the air stream. All three instruments were developed by the Energy Research Foundation of the Netherlands (ECN, Petten, NL). The instruments were housed in weather proof enclosures and placed at the measurement height, with inlets of <0.1 m length.

Annular rotating batch denuder (RBD)

In the RBD instrument (Keuken et al., 1988), air is pumped at 271 min^{-1} through the annulus formed by two horizontal concentric rotating glass tubes (with a diameter of 45 mm)

and a 25 cm long HDPE (High Density Polyethylene) inlet (12 mm diameter). The glass tubes are wetted with a thin layer of collecting liquid, which contains 2.0 g l^{-1} NaOH, 3.4 ml l^{-1} $>98\%$ formic acid and 0.5 mg l^{-1} thymol as biocide. Ammonia is absorbed into this thin layer of collection solution over a sampling time of 40 min within each hour, after which the sample (10 to 15 ml) is pumped off to an autosampler holding 20 ml test tubes. All samples were analysed for NH_4^+ offline on an NH_3 Flow Injection Analyser (AMFIA, ECN, Petten, NL), based on analysis by selective ion membrane and conductivity measurement (Genfa and Dasgupta, 2000). For analysis, 0.5 M NaOH solution is added to the sample, resulting in the conversion of NH_4^+ to gas-phase $\text{NH}_3(\text{g})$ in solution. As the solution then passes a semi-permeable Teflon membrane, $\text{NH}_3(\text{g})$ permeates the membrane and is dissolved in a counter stream of deionised water. Here NH_3 is re-ionised to NH_4^+ and is detected by conductivity (Sutton et al., 2000a; Erismann et al., 2001; Milford et al., 2001). This technique is precise

Table 1. Summary of the characteristics of the instruments.

Instrument	Manufacturer	Air flow rate [l min ⁻¹]	Used time resolution/used time average [s]	Precision [ppbv]	Range [ppbv]	Accuracy [%]
RBD	Energy Research Foundation of the Netherlands (ECN) (Keuken et al., 1988)	27	2400/3600	0.02	not specified	not specified
AMANDA	Energy Research Foundation of the Netherlands (ECN) (Wyers et al., 1993)	28	450/450	0.02	0.02–500	not specified
AiRRmonia	R&R Mechatronics	1	600/60	0.05	0.04–500	±3 ¹
DUAL-QCLAS	Aerodyne Research, Inc. (ARI) (Whitehead et al., 2008)	15	0.2/60	0.018	not specified	±5 ²
c-QCLAS	Aerodyne Research, Inc. (ARI) (McManus et al., 2007)	8.9	1/60	0.05	not specified	±10 ¹
WaSul-Flux	Hilase Ltd.	4	300–1800/ 300–1800	0.25	0.25–1 000 000	not specified
Nitrolux-100	Pranalytica Inc. (Cowen et al., 2004)	1.2–1.6	3/300	0.1	0.1–200	±4 ³
CRDS	Enviro Sense1000 Analyzer, Picarro (Berden et al., 2000)	1	3/300	0.07	0.07–25	±7 ³
CIMS	Georgia Institute of Technology CIMS team (Nowak et al., 2007)	19.5	1/60	0.94	not specified	±4 ⁴
IMS	Bruker Daltonik	0.4	4/60	not specified	Variable, dependent on other substances present	not specified
OP-FTIR	MIDAC Corp.	n/a	8/120	not specified	not specified	not specified

¹ based on manufacturer specification² based on the statistical standard deviations of the reported mixing ratios during calibration³ based on the statistical standard deviations (twice) of hourly data, referenced against AiRRmonia inter-comparison dataset⁴ based on the calibration during the experiment

and reasonably specific, but it has been shown to be somewhat cross-sensitive to selected amines at high concentrations (Husted et al., 2000). In addition to NH₃ it is possible to use the RBD to capture other water soluble inorganic trace gases like HNO₃, HCl, SO₂ and H₂O₂ (Keuken et al., 1988), which would need to be quantified by a different analytical technique such as anion chromatography.

AMANDA

The technique of NH₃ Measurement by ANnular Denuder sampling with online Analysis (AMANDA) was developed by Wyers et al. (1993). The system used here consists of three annular wet rotating denuder inlets, similar to that used in the RBD, located at different heights (0.39 m, 1.07 m, and 2.20 m). Unlike in the RBD, however, the stripping solution (0.5 g l⁻¹ NaHSO₄ containing 0.2 ml l⁻¹ 37% HCHO

as a biocide) is continuously pumped from the denuders to a common detector block, where the three concentrations are analysed sequentially by the same selective ion membrane/conductivity technique as deployed in the AMFIA. In the denuders a constant liquid level is maintained by the use of an independent peristaltic pump, controlled by a conductivity measurement along the denuder. This particular instrument has been upgraded with a newer detection block, using two conductivity measurements. One conductivity cell monitors the initial conductivity of the deionised water, while a second conductivity cell monitors the NH_4^+ content after the membrane exchange. The difference in both readings of the conductivity cells is a measure for the original NH_3 content in the sampled air. This approach takes into account changes in the water quality during longer service intervals. The instrument reports one concentration gradient every 7.5 min, but the overall instrument response time is limited by the exchange of the stripping solution within the denuder (see Sect. 3.3 below).

AiRRmonia

The AiRRmonia is a further development of the AMANDA technique. As with the AMANDA, it was originally developed by ECN (Energy Research Centre of the Netherlands, Petten, NL), but has been further improved and commercialised (Mechatronics Instruments b.v., Hoorn, NL) to provide a sensitive, easy-to-use NH_3 monitor (Erisman et al., 2001). Unlike the RBD and AMANDA, the instrument uses a Teflon membrane to strip the NH_3 from the airflow into a deionised water flow. The detection system of NH_3 is similar to that of the AMANDA, also using the double conductivity measurement. Precision and stability of this instrument are further improved through the use of syringe pumps for reagents and solutions, which undergo less variation due to changes in pump tubing and temperature than the peristaltic pumps used in the AMANDA. The AiRRmonia inlet consists of stainless steel with a length of 5 cm and a diameter of 3.2 mm.

2.3.2 Quantum cascade laser absorption spectroscopy (QCLAS)

QCLAS is an infrared absorption technique that makes use of the rich spectral absorption region in the mid-infrared, in which most species of interest in the atmosphere have resolvable absorption features. Both laser systems used here were produced by Aerodyne Research Inc. (Billerica, MA, USA), and operate with the light source of a thermoelectrically cooled pulsed Quantum Cascade (QC) laser (Alpes Lasers, Neuchâtel, Switzerland). Their design was similar to the closed path configuration described by McManus et al. (2002). These lasers scan over a narrow range of wave numbers chosen to contain an absorption feature of the trace gas of interest, which for NH_3 is at a wavelength of 10.3 μm .

Both instruments use astigmatic Herriott multipass absorption cells, to increase the effective path length, while providing a fast spot measurement. They operate at cell pressures of around 40 Torr as a balance between minimising line broadening, maximising time response and achieving good sensitivity.

In the data acquisition protocol chosen for this study, the spectra were recorded and averaged over the data acquisition time of one second, with the resulting spectra fitted to known spectral line profiles from the HITRAN (High-resolution TRANsmision) molecular spectroscopic database (Rothmann et al., 1998). In principle, this approach provides an absolute measurement.

DUAL-QCLAS

The DUAL-QCLAS uses two separate thermoelectrically cooled pulsed Quantum Cascade (QC) lasers for the potential measurement of two trace gases at different wave lengths. The two beams are brought together (with the pulses separated in time) and directed into either one of two astigmatic Herriott multipass absorption cells where they undergo 238 reflections, before leaving the cell and arriving at a cryogenically cooled HgCdTe infrared detector. The large (5 l) cell provides an effective path length of 210 m, while the small (0.3 l) cell provides a path length of 56 m. The large cell is used for higher precision measurement applications whilst the small cell (used here) provides the fast time response required for eddy-covariance flux measurements. Data were recorded at a rate of 5 Hz to be averaged up in post-processing for the purpose of the concentration inter-comparison reported here. Background measurements were made typically every 15 min and background spectra were subtracted from the measurements prior to the wave fit. For this purpose, NH_3 free air was generated using a customized $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst heated to 300 °C, in an attempt to determine the background at a relative humidity as close to ambient as possible. The $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst has been shown to have a negligible effect on the water concentration of the background air (Wert et al., 2002). The inlet was a 2 m length of 6.4 mm (OD) PFA tube, which was co-located with an ultrasonic anemometer (model HS; Gill Instruments Ltd., Lymington, UK) for the purpose of flux measurements. A general calibration factor of 1.23 was applied to the DUAL-QCLAS data based on the field based calibration. For more information and studies of the DUAL-QCLAS see Whitehead et al. (2008).

Compact QCLAS (c-QCLAS)

The c-QCLAS uses a single QC laser and a single cell with a volume of 0.5 l and an effective path length of 76 m. Air was drawn into the optical cell through a short (<0.1 m) quartz inlet that was heated to 40 °C and coated with a hydrophobic siloxyl coating. The inlet contains a critical orifice that drops

the pressure in the optical cell to approximately 45 Torr while keeping a constant flow rate of approximately 9 l min⁻¹. Following the critical orifice, the flow is split into two branches with 90% of the flow making a sharp turn and being pulled through the optical cell. The other 10% is pulled directly to the pump, relying on inertia to remove more than 50% of particles larger than 300 nm. This design was chosen to minimize surface interactions for gas phase NH₃ while reducing possible positive artefacts in the measurements from particle volatilization. The quartz inlet was connected to the optical cell via ~3 m and 9.5 mm PFA tubing. Background measurements were performed every 30 min by flushing the quartz inlet using dry nitrogen. Standard addition calibrations were performed every two hours with a permeation tube standard, added either into ambient air or dry nitrogen. The permeation rate was determined gravimetrically by the manufacturer (Kin-Tek) as 100 ng min⁻¹ at 40 °C. The rate was confirmed as 100 ± 5 ng min⁻¹ at 40 °C by passing a flow of permeation tube standard through citric acid filters for 24 h, followed by extraction with deionized water and analysis using ion chromatography.

2.3.3 Photoacoustic spectroscopy

Two instruments measured NH₃ concentration using photoacoustic spectroscopy. A light source is tuned to an absorption feature of the target species and molecules are excited to a higher quantum state. Modulating the light source results in a periodic temperature change, giving rise to a periodic pressure change that equates to an acoustic signal if the modulation frequency is in the acoustic range. The intensity of the acoustic signal, which can be detected by a sensitive microphone, is proportional to the concentration of the light-absorbing species (Harren et al., 2000).

Diode laser based photoacoustic system (WaSul-Flux)

This new instrument combines near-infrared photoacoustic spectroscopy with pre-concentration sampling as described in more detail elsewhere (Pogány et al., 2008). The instrument is built into a 48.3 cm 6U temperature controlled instrument box and has an additional waterproof housing. The photoacoustic detection unit consists of a fibre-coupled DFB diode laser light source (FOL15DCWD-A82-19560-A, Furukawa Inc.) with ~40 mW output light power at 1532 nm, and an acoustically optimized photoacoustic cell with an electret microphone (Knowles, EK 3029) for measuring the photoacoustic signal. Ammonia is concentrated from the sampled air by a tungsten (VI) oxide coated preconcentration unit. The instrument has three gas inlets and is therefore suitable for measuring NH₃ concentration at three different heights above the ground. The sampling lines were 6 m long Teflon tubes with 8 mm inner diameter, heated to ~50 °C by self-regulating heating tape and included filters which were replaced weekly. The pre-concentration time can

be adjusted to match the air concentrations. Here the integration time was varied between 15 and 45 min according to the actual concentration. Before fertilization all three inlets were placed at the same height and the reported data are the averages of the three measurements. After fertilization, the inlets were operated in gradient configuration and the reported data represent the measurement of the middle height.

Nitrolux-100

The Nitrolux-100 (Pranalytica Inc., Santa Monica, CA, USA) is an ambient NH₃ analyser that uses resonant photoacoustic spectroscopy and a line-tunable CO₂ laser to provide continuous or on-demand measurements (Pushkarsky et al., 2003). The excited NH₃ molecules undergo collisional deactivation, which converts the absorbed energy into periodic local heating at the modulation frequency of the laser. The resulting acoustic waves are detected with minimal interferences by other compounds at typical concentrations in a non-polluted atmosphere (Cowen et al., 2004). The instrument was originally developed for clean room applications in the semiconductor industry, but has been more widely used for ambient measurements. It is operated with an inlet filter to remove dust and NH₄⁺, with a manufacturer recommended lifetime of three months, while the instrument should be calibrated by the manufacturer every six months. The Nitrolux-100 was calibrated just before the beginning of the inter-comparison (8 August 2008). The uncertainty associated with that calibration was a zero intercept of -0.006 ppbv, a linearity check with $R^2=0.999$ and a system response time (under dry conditions) of 90% in 2 min. The Nitrolux-100 was operated with a 4 m and 6.4 mm OD Teflon inlet which was insulated and heated to ~35 °C. The inlet was sheltered by an inverted plastic funnel.

2.3.4 Cavity Ring Down Spectroscopy (CRDS)

Cavity Ring Down Spectroscopy (CRDS) is a direct absorption technique, which uses pulsed or continuous light sources and has a significant higher sensitivity than other conventional absorption spectroscopy (Berdn et al., 2000). The EnviroSense 1000 Analyzer (Picarro Inc., Sunnyvale, CA, USA) monitors NH₃ in air using this approach. Cavity Ring Down Spectroscopy uses a pair of mirrors facing each other. A brief pulse of laser light is injected into the cavity, and it passes back and forth between the mirrors, while a fraction leaks through the mirror. Ammonia absorbs some of the light and thus the amount of light in the cavity decreases faster-it makes fewer passes. A CRDS setup measures how long it takes for the light to drop to a certain percentage of its original intensity, and this “ringdown time” is used to calculate the concentration of the absorbing substance in the gas mixture in the cavity. Like the Nitrolux-100, the Picarro CRDS uses an inlet filter and is calibrated by the manufacturer subsequent (~2 months) to its most recent calibration. The

CRDS was operated with a 4 m and 6.4 mm OD Teflon inlet which was insulated and warmed with heating tape ($\sim 35^\circ\text{C}$). Again, the inlet was sheltered by an inverted plastic funnel. For detailed information see Rella (2008).

2.3.5 Chemical Ionisation Mass Spectrometry (CIMS)

Chemical Ionisation Mass Spectrometry (CIMS) techniques use ion-molecule reactions to selectively ionize and detect trace species of interest in ambient air with high sensitivity and fast time response. The CIMS method uses a reagent ion to ionise a neutral species, and the product ion resulting from this process is identified and quantified by a quadrupole mass analyser. The distinction between chemical ionization mass spectrometry and other mass spectrometry techniques is the use of ion molecule reactions for the selective ionization of compounds of interest in the complicated matrix of ambient air. In the system deployed here, NH₃ was detected using H⁺(C₃H₆O)₂ as a reagent ion (Nowak et al., 2007). The configuration of the CIMS deployed here is described elsewhere (Slusher et al., 2004; Neuman et al., 2006; Kim et al., 2007; Nowak et al., 2007). The instrument sampled air through a 0.1 m long and 9.5 mm O.D. PFA inlet, temperature controlled to $40 \pm 1^\circ\text{C}$. Inlet flow was 19.5 l min^{-1} , with 0.88 l min^{-1} being subsampled through a 0.65 mm pin-hole into the ionization region, where reaction of NH₃ with H⁺(C₃H₆O)₂ proceeds. The instrumental signal was calibrated every hour using a standard addition from a calibrated permeation tube oven and an instrument background was taken hourly.

2.3.6 Ion mobility spectrometer (IMS)

Ion mobility spectrometers separate chemical substances on the basis of velocity of gas-phase ions in an electrical field (Eiceman and Karpas, 1994). Ions are introduced into an electrical field and the time of flight is measured. The sample molecules are first ionized by β -radiation from a ⁶³Ni source. The formation of positive ions is dominated by the proton-transfer reaction (Sunner et al., 1988) from water clusters to substances that have proton affinity higher than water (697 kJ mol^{-1}), which includes NH₃ (854 kJ mol^{-1}). The charged ions are pulsed through a shutter grid into the drift region, where they are separated by mobility and detected at the end of the drift tube by an electrometer. The instrument is not very specific and the NH₃ measurement can suffer from the cross sensitivity of other compounds of similar mobility if they also have a proton affinity greater than water, while the quantification can be compromised by competing ion reactions. More details on the IMS technique are given in Hill et al. (1990) and Bacon et al. (1998). In this field study the commercial ion mobility spectrometer RAID I was used (Bruker Daltonik GmbH, Bremen, Germany). Sampling gas flow was 0.41 l min^{-1} and the sampling line was 2 m non-heated Teflon tubing. Heating was not applied to avoid contamination from

the evaporation of NH₄⁺ aerosols, although the response time to the concentration peaks might be improved with a heated sampling line.

2.3.7 Open-path Fourier Transform Infra-Red (OP-FTIR) spectroscopy

Fourier Transform Infra-Red (FTIR) spectroscopy can be used to identify and quantify substances by their molecular absorption of infra-red radiation at specific wavelengths. An open-path configuration permits the estimation of path-integrated average concentrations of a gas species of interest over path lengths of up to 1 km. OP-FTIR has been shown to be a useful tool for the measurement of NH₃ from agricultural sources (e.g. Griffith and Galle, 2000). In the present study, a MIDAC M4401 portable FTIR spectrometer with Stirling cooled MCT detector module was used in conjunction with a 50.8 cm infra-red (IR) source in a bi-static open-path configuration (path length of 102 to 105 m). Both the FTIR spectrometer and IR source were aligned at 1.3 to 1.4 m above ground. The spectrometer was operated at a resolution of 0.5 cm^{-1} and eight sample scans were co-added for each spectrum.

Measured spectra were analysed for NH₃ using the NH₃ infra-red absorption features at 968 cm^{-1} and 932 cm^{-1} (accounting for interference by H₂O and CO₂ absorption). Concentration retrievals were performed using the MALT software (Griffith, 1996). MALT iteratively computes synthetic spectra (convolved to the spectrometer line shape) from the HITRAN absorption line database (Rothman et al., 1998) until the mean-squared difference between the synthetic and measured spectra is minimised. The resultant concentrations used for the best-fit synthetic spectrum yield the path-integrated NH₃ (as well as H₂O and CO₂) mixing ratios (in ppbv) for the measured open-path.

2.4 Calibration and treatment of aerosol components

The wet chemistry instruments were calibrated weekly with individual liquid standards and a common liquid standard was run on all analytical systems. The CIMS and c-QCLAS were calibrated regularly with their own gas-phase standards. As noted above, the Nitrolux-100 and CRDS were calibrated by manufacturers and operated within the specified calibration intervals. The WaSul-Flux and IMS were calibrated by the operating groups prior to the campaign by comparison against wet-chemistry reference systems.

An inter-comparison calibration (standard addition to ambient air) from a common NH₃ gas cylinder took place during the campaign. The cylinder was a standard of nominally 21 ppmv NH₃ in N₂ (BOC, UK). During the experiment presented here the actual concentration was determined as $20.2 \pm 1.4 \text{ ppmv}$ by bubbling the gas through acid adsorption solution which was then analysed for NH₄⁺ by flow injection analysis, following the procedure described by

Table 2. Correlation of hourly NH₃ concentrations less than 10 ppbv ($z=1.1$ m) between each instrument and the NH₃_{ens}. Also shown are the bias for the entire data range and the data <10 ppbv, as well as the gas and liquid standard biases for all instruments.

Instrument	< 10 ppbv regression				Overall bias [%]	Gas Std. bias [%]	Liquid Std. bias [%]
	Slope	Intercept [ppbv]	R^2	Bias [%]			
RBD	0.89	−0.33	0.85	−20.1	+5.65	+13.37	+2.62
AMANDA	1.02	−0.08	0.85	+0.62	−0.63	−24.71	+0.85
AiRRmonia	0.83	−0.02	0.90	−17.7	+10.9	−18.3	−2.96
CIMS	0.95	+1.93	0.65	+54.5	−12.9	−0.26	N/A
c-QCLAS	0.72	+0.71	0.81	−12.8	−4.02	−23.2	N/A
DUAL-QCLAS	0.86	−0.19	0.66	−20.6	−32.1	0*	N/A
WaSul-Flux	0.81	−0.15	0.85	−22.0	+1.27	−	N/A
Nitrolux-100	0.42	+3.42	0.52	+2.51	+1.69	−	N/A
CRDS	0.50	+3.14	0.56	+26.0	+5.10	−12.48	N/A
IMS	1.15	−0.61	0.87	−2.63	−2.90	−	N/A

* After calibration using this gas standard.

Thomas et al. (2009). The concentration range and number of step increases varied between instruments. A similar calibration scheme is described in Schwab et al. (2007). For each instrument a calibration bias from a NH₃ gas cylinder and a corresponding measured NH₃ concentration (gas std. bias) was calculated (see Table 2). This gas-phase measurement was used only as a check for most instruments, except for the DUAL-QCLAS, for which it provided the primary calibration, yielding a calibration factor of 1.23.

As outlined in the instrument descriptions above, the wet chemistry systems strip the gas phase from the sample stream, while the aerosol phase passes through the sampling system. The c-QCLAS uses a virtual impactor to prevent most of the particles from entering the detection cell. The Nitrolux-100, CRDS and WaSul-Flux employ filters to prevent aerosol components from contaminating the detection cell. This has the potential to lead to artifacts due to aerosol dynamics on the filter. Indeed, the Nitrolux-100 was initially operated with a used filter and reported elevated NH₃ concentration levels compared with the other instruments (the deviation correlating with temperature), suggesting that the NH₃ originated from NH₄NO₃ volatilisation from the filter. Following replacement of this filter, the Nitrolux-100 measurements were found to agree with the other techniques sharing the same inlet line. The early data were therefore excluded from the data analysis. It appears that, for ambient measurements, the filters provided by the manufacturer have a much shorter lifetime than stated by the manufacturer. The stated lifetime is possibly more appropriate for the clean room applications for which the instrument had originally been developed.

3 Results

3.1 Time-series analysis

Figure 3a and b show the time-series of measured NH₃ during the inter-comparison period of all instruments, measured at different temporal resolutions (1 min to 1 h). Different vertical scales were used to present the time-series before (Fig. 3a) and after (Fig. 3b) the fertilisation on 28 August 2008. The NH₃ traces from the instruments at their individual time resolution (Table 1) are presented in two groups for increased clarity, separating wet chemistry analysers and spectroscopic techniques. In addition, the wind direction is indicated at the top of Fig. 3a and b. Before the fertilisation (Fig. 3a), there were brief NH₃ peaks in the time-series of the DUAL-QCLAS and CIMS of up to 18 ppbv. Except for these individual events, the NH₃ level measured by all instruments ranged up to 10 ppbv before the fertilisation event on 28 August 2008. After fertilisation (Fig. 3b), NH₃ concentrations increased up to 120 ppbv, with such high concentrations continuing until 29 August 2008 around 14:00. The early NH₃ peaks and some periods of disagreement coincided with periods when the wind came from the rotting vegetation source in the N field as indicated by the shaded areas in Fig. 3a and b.

Overall, the absolute NH₃ concentrations of all instruments revealed the same features and agreed closely with each other. By contrast, the different time resolution of the instruments resulted in slightly different features of the temporal NH₃ structure. Of the wet chemistry instruments, the 1 minute data of the AiRRmonia analyser shows additional NH₃ variations during the fertilisation peak (29 August 2008), which the AMANDA and RBD failed to capture because of their lower time resolution. Similar differences can be seen in the comparison of the spectrometric techniques.

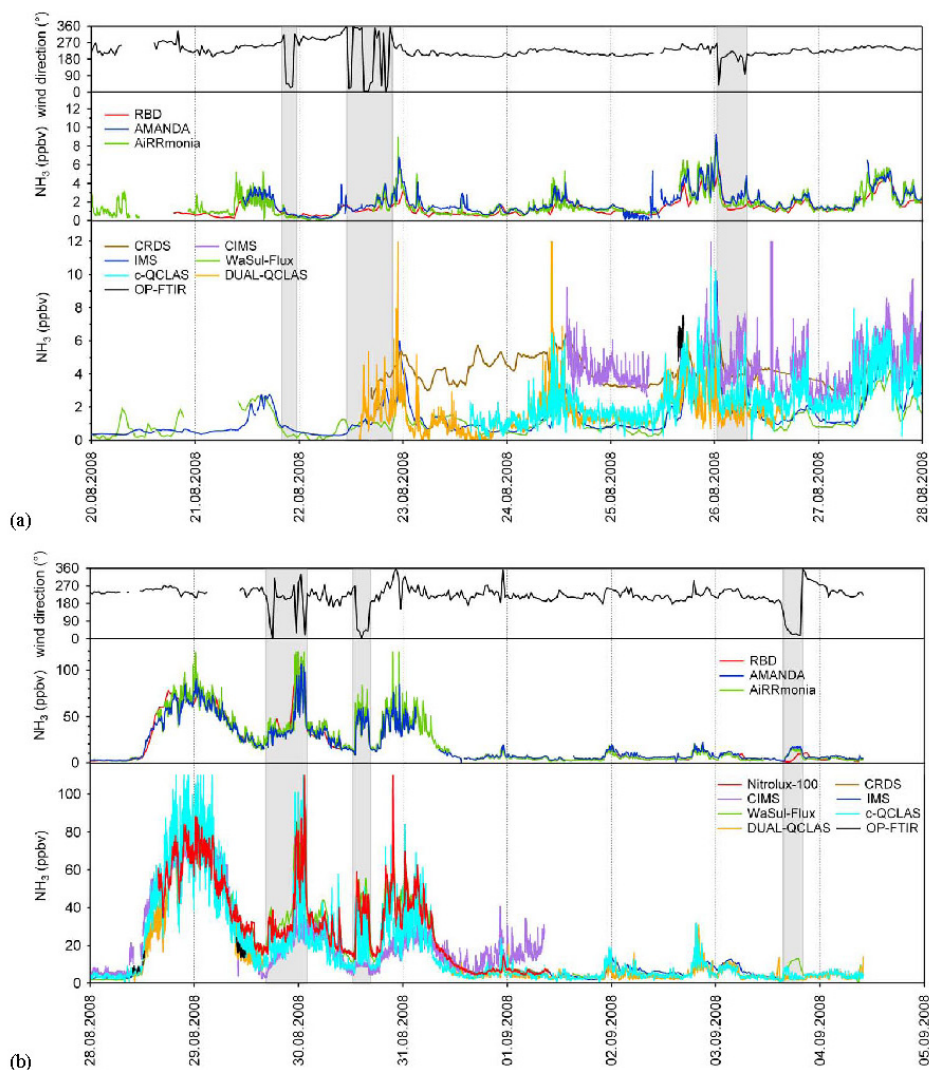


Fig. 3. Time series of NH_3 for all instruments ($z=1.1$ m) with occurring wind direction for the data (a) before fertilisation and (b) after fertilisation on 28 August 2008. The shaded areas indicate periods during which the wind came from the N field. RBD (red), AMANDA (blue), AiRRmonia (green), Nitrolux-100 (red), CRDS (brown), CIMS (purple), IMS (blue), WaSul-Flux (green), c-QCLAS (cyan), DUAL-QCLAS (orange), OP-FTIR (black).

3.2 Instrument inter-comparison

For the regression analysis data from each instrument was block-averaged to hourly values in order to match the time resolution of the slowest instrument (RBD). In addition, wind directions from the sectors 0° to 150° and 310° to 360° were excluded from the analysis, due to the heterogeneous source from the rotting vegetation in the N field.

Figure 4a–j depict NH_3 concentrations from each instrument compared with the ensemble average of measured NH_3 observations ($\text{NH}_{3-\text{ens}}$), together with the results of the linear regression analysis. The $\text{NH}_{3-\text{ens}}$ was computed as the average over all instruments that were operational at a given time, excluding the OP-FTIR, for which too few data points were available. Additionally, the horizontal error bars on $\text{NH}_{3-\text{ens}}$

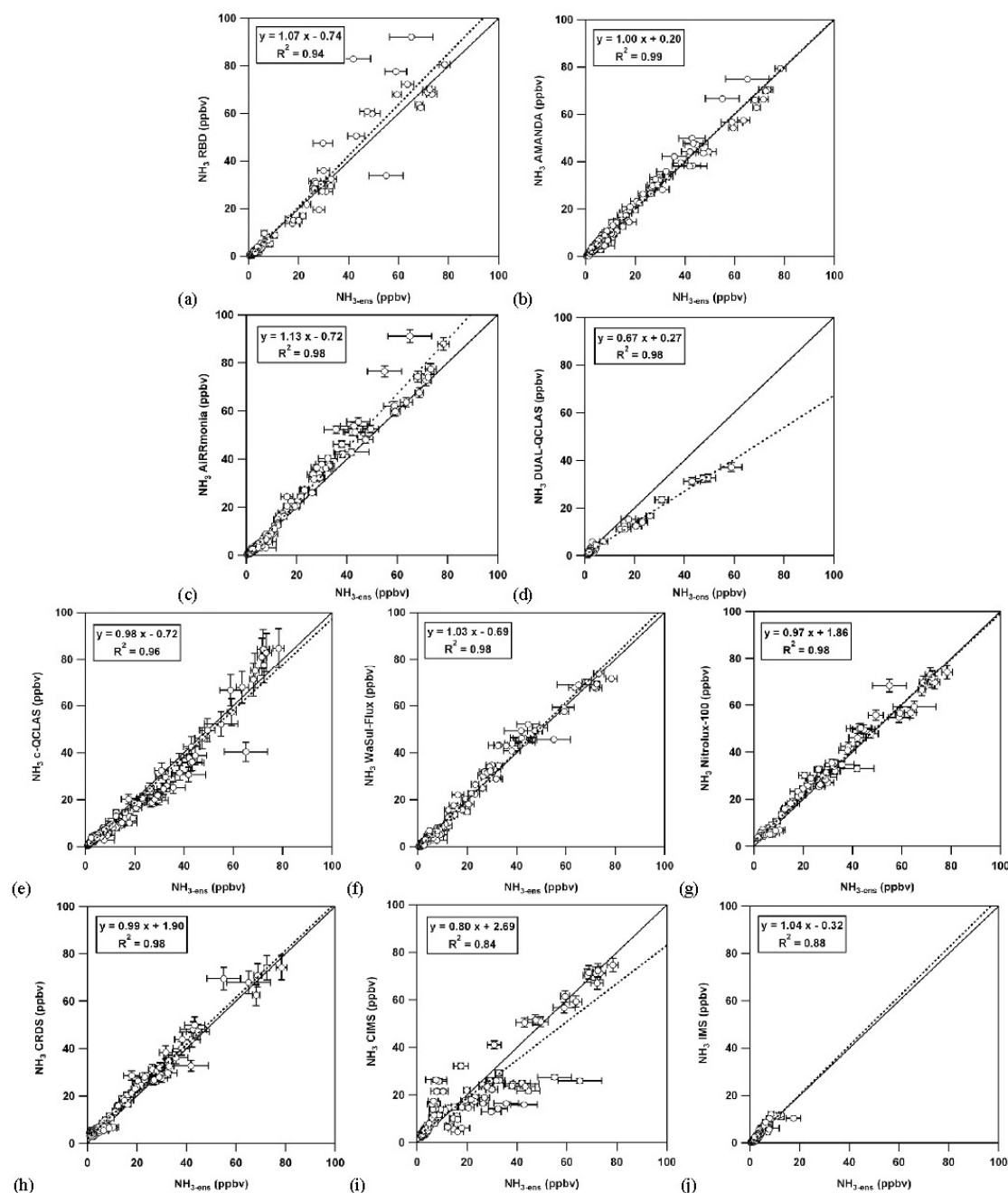


Fig. 4. Scatter plots showing correlation of hourly NH_3 concentrations ($z=1.1$ m) between all instruments and the NH_3 -ens screened for wind direction ($150\text{--}310^\circ$). The horizontal error bars calculate the statistical standard error. For AiRRmonia, DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS the vertical error bars mark the estimated accuracy (Table 1). The solid line gives the 1:1 line and the dashed line the result of the axis regression.

show the statistical standard error (SE) of the different readings from the instruments that went into the calculation of each value of NH_{3-ens}. Further, the estimated accuracy for the AiRRmonia, DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS (Table 1) is shown as vertical error bars.

Overall, a high correlation between all instruments is observed, with $R^2 > 0.84$. The DUAL-QCLAS, c-QCLAS, Nitrolux-100, CRDS and CIMS comparisons with NH_{3-ens} have a slope < 1 (Fig. 4d, e, g, h, i), with the DUAL-QCLAS and the CIMS lowest at 0.67 and 0.80, respectively. The RBD, AiRRmonia, WaSul-Flux and IMS comparisons with the NH_{3-ens} have a slope > 1 , but have negative intercepts of -0.74 ppbv (RBD) to -0.32 ppbv (IMS) (Fig. 4a, c, f, j). The AMANDA instrument was closest to NH_{3-ens}, with a slope of 1 and an intercept of 0.20 ppbv (Fig. 4b). Relatively high intercepts were observed by the CIMS, CRDS and Nitrolux-100 compared with the other instruments. It is thought that the CRDS and Nitrolux-100 intercept might be due to a local contamination source which was either on the sampling post, sample tubing (both came from the same batch of tubing) or most likely the inlet filters. It should be noted that for the IMS, only data from before fertilisation and after the fertilisation plume had diminished could be used, because above about 30 ppbv the IMS becomes strongly non-linear due to the consumption of the parent ions and the formation of clusters, which shifts the mobility. The consequence was a reduced dataset, biased towards smaller concentrations.

Accurate measurement of NH₃ at typical ambient background levels is more challenging. For this reason, the linear regression for periods when NH_{3-ens} < 10 ppbv was calculated separately (Table 2). The R^2 against NH_{3-ens} varied from 0.52 (Nitrolux-100) to 0.90 (AiRRmonia). The slope of AMANDA and IMS against NH_{3-ens} were > 1 and all others were < 1 , e.g. 0.42 (Nitrolux-100) to 0.95 (CIMS) with intercepts from -0.61 to 3.42 ppbv. The highest intercept values were measured for CIMS, CRDS and Nitrolux-100 and again for the latter two inlet/filter contamination are thought to be the cause.

The bias (%) between two instruments is defined according to Eq. 1, where m is the slope of the regression analysis when forced through zero.

$$\text{bias} = (m - 1) * 100 \quad (1)$$

The biases reported in Table 2 represent the percentage difference of the full range NH₃ concentration (overall bias) and the bias derived from concentrations < 10 ppbv (10 ppbv bias). The overall bias for all instruments were reasonably small, ranging from -12.9% (CIMS) to 10.9% (AiRRmonia) except for the DUAL-QCLAS, whereas the 10 ppbv biases showed more variability. Also included in Table 2 is the bias of a reading based on a calibration through standard addition from an NH₃ calibration cylinder. It turned out not to be easy to provide a common, reliable and portable gas-phase calibration standard suitable for the large range of flow rates of the different instruments. Because these are based on

Table 3. Summary of linear regression results of the OP-FTIR against c-QCLAS, DUAL-QCLAS and CIMS at 2 min time resolution from the data shown in Fig. 5.

	Slope	Intercept (ppbv)	R^2
c-QCLAS	0.54	4.39	0.97
DUAL-QCLAS	0.82	3.74	0.92
CIMS	0.43	5.37	0.63

standard additions to ambient air, they only reflect the error on the response (slope) and do not include the intercept. Calibration results were more variable than the slopes derived from the regression analysis and should therefore be treated with caution.

For the wet-chemistry analysers a liquid intercalibration was performed using common 50, 100 and 500 ppbv aqueous standard on the three analytical systems and the outcome is again the regression with the measured percentage difference. For the three wet-chemistry instruments the used liquid standards showed excellent agreement concerning the liquid standard bias (Table 2).

The OP-FTIR was operated manually in the field and the dataset is much reduced compared with the other instruments (9 h). Thus, it is not included in the hourly data analysis. Instead, Fig. 5 compares the OP-FTIR data at 2 min time resolution against the other fast response instruments (c-QCLAS, DUAL-QCLAS and CIMS).

The data of the OP-FTIR agreed best with the DUAL-QCLAS (Fig. 5) with a slope of 0.82 (Table 3), which was reading lower compared to the other instruments (Fig. 4d) with the c-QCLAS providing the best match with the reference here. Further, the regression analysis revealed for the OP-FTIR a high intercept of > 3.74 ppbv compared with all other instruments.

While for graphical representation the analysis of an individual instrument against a common NH_{3-ens} provides a digestible overview over the results, the full information of the inter-comparison is only revealed through correlation between each of the eleven instruments with each other. Tables 4 and 5 show the results of the regression analysis of all hourly data, while Tables 6 and 7 show the results of the regression confined to data points where both instruments reported concentrations of less than 10 ppbv. Each of the four tables contains two separate diagonal parts with information for the instruments. For the top half of the table (grey) the regression provided is the vertical axis (row) against the horizontal axis (column). Concerning the bottom half it switches to horizontal axis (column) against vertical axis (row).

For example, the regression analysis of the RBD against the AMANDA for the entire data range is:

$$\text{RBD} = 0.86 * \text{AMANDA} + 1.41 \text{ ppbv},$$

$$R^2 = 0.93,$$

$$\text{bias} = -11.1\%$$

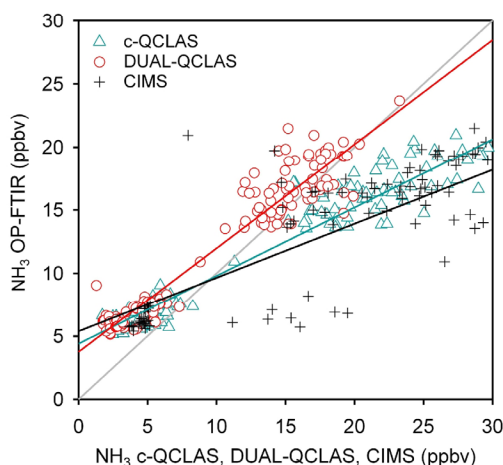


Fig. 5. Scatter plots of OP-FTIR against c-QCLAS, DUAL-QCLAS and CIMS at 2 min time resolution, including regression lines and the 1:1 line (grey).

while the results of the regression analysis of the AMANDA vs. RBD are not included. Although derived from the regression fit of $y = ax$, the bias does not always fully represent a clear picture of the combined effects of the average discrepancy between two instruments specify by slope and intercept. For example, due to a lack of data and high intercept values for some instruments, the datasets in these scatter plots showed a distributed appearance and the linear regression line was difficult to draw (Table 8). Thus all four parameters need to be considered when interpreting the performance of two instruments against each other.

For the overall data range the slopes of the AMANDA, AiRRmonia, c-QCLAS, WaSul-Flux, Nitrolux-100 and CRDS varied by $\pm 20\%$ with each other (Table 4). For the data limited to <10 ppbv the slopes between RBD, AiRRmonia, WaSul-Flux and IMS were all within $\pm 20\%$ of unity (Table 6). High intercepts were found for correlations of CIMS, Nitrolux-100 and CRDS with all other instruments (Bold numbers in Tables 4 and 6), with values from 1.60 to 6.14 ppbv for the full data range and from 1.22 to 3.92 ppbv for data <10 ppbv. For the full data range, R^2 values <0.90 were limited for inter-comparisons involving RBD, CIMS or IMS (Table 5). For <10 ppbv, an $R^2 > 0.80$ was achieved for any comparison between AMANDA, AiRRmonia and c-QCLAS (Table 7). The DUAL-QCLAS (italic numbers in Tables 5 and 7) was biased towards lower values, compared with all other instruments.

Table 8 contains two separate diagonal parts with information and presents a visual support to the results from Tables 4 to 7. The results provided are for the regression of the instrument on the vertical axis (row) against the instrument on the horizontal axis (column) for the entire data range (white).

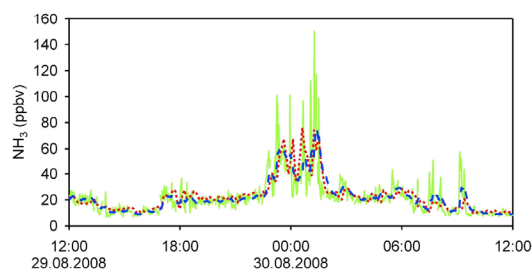


Fig. 6. Comparison of the time-series of the AMANDA (red/dotted) and the c-QCLAS (green) for a 24 h period on 29 to 30 August 2008. The c-QCLAS smoothed concentration $c'(t)$ (blue/dashed) was calculated with $f=0.08$, selected by eye as a fit to the AMANDA data.

The grey diagonal part shows the plots for NH₃ concentration <10 ppbv and it is to read from the instruments in the horizontal axis (row) against instruments in the vertical axis (column). For more visibility and detailed information see the supplemental material (<http://www.atmos-meas-tech.net/3/91/2010/amt-3-91-2010-supplement.pdf>).

3.3 Characterisation of the instrument time responses of the slow response instruments

For analysing the time response of the different instrument setups (including inlets) a short time-series of each instrument was compared against data of a well-performing fast-response instrument, for which the 1 min data from the c-QCLAS was chosen. A running mean was calculated from the c-QCLAS data as:

$$c'(t) = fc(t) + (1-f)c'(t-1) \quad (2)$$

where $c'(t)$ is the smoothed concentration, $c(t)$ is the measured concentration and f is a smoothing factor defined below, which would be unity for an instrument that is equally as fast as the c-QCLAS. Equation (2) simulates the response of a concentration measurement which is subject to a memory effect, which may be either due to the turnover time in an air volume, liquid pool or due to adsorption/desorption in inlet lines. For each instrument f was determined by fitting the smoothed c-QCLAS time-series to the data reported by the instrument. This approach is demonstrated in Fig. 6, where f is adjusted for the smoothed c-QCLAS time-series to match the data from the AMANDA.

The e-folding time of the instrument was determined as $\tau_{1/e} = 1/f$ min, which is reported in Table 9 together with the 50 and 95% response times (τ_{50} , τ_{95}). The corresponding deviation is also stated.

The AMANDA reports 7.5 min data, but it appeared to take 32.2 ± 3.7 min for a 95% response. The replacement of the liquid pool in the denuder appears to limit this time response of the instrument. A similar observation was made

Table 4. Inter-comparison of linear correlations between each instrument for the entire data range. Slopes are given in the bottom half and intercepts are indicated by the top (grey) of the matrix. Bold numbers indicate noticeable non-zero intercepts (>1.5 ppbv).

	RBD	AMANDA	AiRRmonia	CIMS	c-QCLAS	DUAL-QCLAS	WaSul-Flux	Nitrolux	CRDS	IMS
	Intercept [ppbv]									
RBD	–	1.41	0.70	3.65	1.17	1.09	0.55	6.14	3.63	0.10
AMANDA	0.86	–	–1.08	3.51	–0.62	0.34	–0.86	1.82	2.27	0.04
AiRRmonia	0.97	1.12	–	3.92	0.34	0.57	0.16	2.65	2.93	0.02
CIMS	0.74	0.76	0.65	–	–2.46	–0.38	–1.07	4.12	1.60	0.78
c-QCLAS	0.86	0.96	0.83	1.09	–	0.64	0.47	5.73	3.25	0.10
DUAL-QCLAS	0.54	0.69	0.59	0.64	0.65	–	–1.13	2.46	1.81	0.40
WaSul-Flux	0.90	1.02	0.90	1.06	1.00	1.55	–	3.09	3.02	0.19
Nitrolux-100	0.77	0.96	0.85	0.97	0.90	1.53	0.92	–	–0.03	–2.22
CRDS	0.81	0.93	0.83	1.09	1.04	1.60	0.92	1.00	–	–1.13
IMS	1.12	0.88	1.11	0.30	0.93	0.69	1.11	0.95	0.65	–
	Slope									

Table 5. Inter-comparison of correlation coefficients and biases between each instrument for the entire data range. Biases are given in the bottom half and correlation coefficients are indicated by the top (grey) of the matrix. Bold numbers indicate high biases (>20%), mainly of the Dual-QCLAS.

	RBD	AMANDA	AiRRmonia	CIMS	c-QCLAS	DUAL-QCLAS	WaSul-Flux	Nitrolux	CRDS	IMS
	R^2									
RBD	–	0.93	0.93	0.82	0.87	0.95	0.95	0.84	0.86	0.80
AMANDA	–11.1	–	0.99	0.76	0.92	0.97	0.98	0.98	0.98	0.90
AiRRmonia	–1.77	9.41	–	0.74	0.91	0.98	0.98	0.96	0.97	0.82
CIMS	–18.8	–15.6	–26.8	–	0.89	0.94	0.79	0.75	0.71	0.58
c-QCLAS	–11.7	–5.91	–15.8	1.96	–	0.97	0.93	0.93	0.93	0.70
DUAL-QCLAS	–43.4	–29.8	–38.9	–37.7	–33.0	–	0.98	0.97	0.91	0.66
WaSul-Flux	–8.85	–0.3	–9.50	3.19	1.80	48.3	–	0.95	0.95	0.82
Nitrolux-100	–12.4	0.33	–9.83	8.00	2.62	65.0	–1.40	–	0.99	0.57
CRDS	–10.7	–0.2	–10.6	14.7	13.8	86.4	–0.12	0.37	–	0.20
IMS	14.3	–10.9	10.9	–60.8	–5.58	–19.9	15.2	–51.1	–60.5	–
	Bias [%]									

for the RBD. The AiRRmonia seemed to have the least time delays in the system: τ_{95} of 14.4 ± 4.0 min closely matched the internal measurement cycle of 10 min.

The IMS derived with $\tau_{95} = 34.9 \pm 6.4$ min the highest delay with reported data of 3 s, but the limited amount of data qualified this statement. The CIMS and DUAL-QCLAS have similar time responses as the c-QCLAS and this approach is therefore not suitable to characterise them further. They are therefore not listed in Table 9.

4 Discussion

4.1 Overall measurement agreement

The instruments tested in the present study revealed good correlation with $R^2 > 0.84$ for one hour averages compared with NH₃–ens. It should be pointed out, that the regressions show relative performance of the instruments against NH₃–ens (Fig. 4a–j) or against each other (Tables 4, 6, 8). They do not demonstrate a functional relationship of a dependent to an independent variable. Thus, a consideration

Table 6. Inter-comparison of linear correlations between each instrument of data less than 10 ppbv. Slopes are given in the bottom half and intercepts are indicated by the top (grey) of the matrix. Bold numbers indicate noticeable non-zero intercepts (> 1.5 ppbv).

	RBD	AMANDA	AiRRmonia	CIMS	c-QCLAS	DUAL-QCLAS	WaSul-Flux	Nitrolux	CRDS	IMS
	Intercept [ppbv]									
RBD	–	0.37	0.48	3.08	1.22	0.48	0.28	3.92	3.82	0.02
AMANDA	1.15	–	0.20	2.95	1.02	0.34	–0.06	3.75	3.42	–0.09
AiRRmonia	0.85	0.73	–	2.64	0.84	0.05	0.01	3.26	3.58	–0.14
CIMS	0.71	0.68	0.89	–	–0.62	0.28	–0.81	2.51	1.22	–0.88
c-QCLAS	0.79	0.64	0.86	0.81	–	0.16	–0.68	3.47	3.46	–0.64
DUAL-QCLAS	0.86	0.70	1.03	0.35	0.78	–	0.09	3.90	3.91	0.30
WaSul-Flux	0.85	0.77	0.94	0.56	1.03	0.79	–	3.47	3.75	0.10
Nitrolux-100	0.40	0.40	0.51	0.52	0.53	0.43	0.52	–	–0.05	–2.22
CRDS	0.25	0.46	0.44	0.69	0.46	0.24	0.58	1.02	–	–1.13
IMS	1.14	0.93	1.17	0.68	1.15	0.75	1.13	0.95	0.65	–

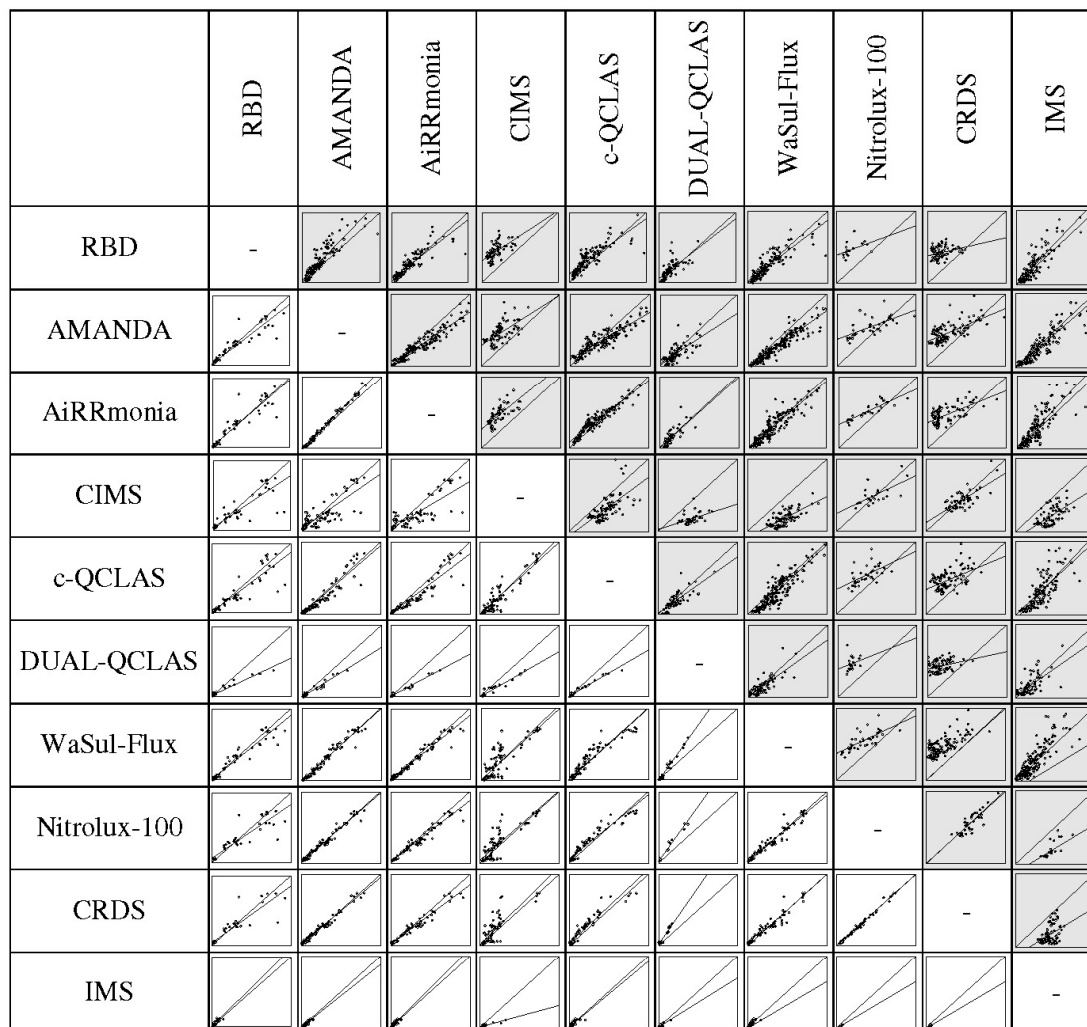
Table 7. Inter-comparison of correlation coefficients and biases between each instrument of data less than 10 ppbv. Biases are given in the bottom half and correlation coefficients are indicated by the top (grey) of the matrix. Bold numbers indicate high biases (> 20%).

	RBD	AMANDA	AiRRmonia	CIMS	c-QCLAS	DUAL-QCLAS	WaSul-Flux	Nitrolux	CRDS	IMS
	R^2									
RBD	–	0.81	0.79	0.37	0.72	0.51	0.77	0.21	0.09	0.79
AMANDA	26.8	–	0.91	0.40	0.81	0.52	0.90	0.45	0.46	0.83
AiRRmonia	–0.46	–22.7	–	0.55	0.91	0.62	0.85	0.79	0.43	0.73
CIMS	105	66.7	91.6	–	0.43	0.20	0.54	0.44	0.55	0.40
c-QCLAS	12.6	–14.9	6.66	–31.6	–	0.63	0.82	0.33	0.27	0.66
DUAL-QCLAS	10.5	–16.8	5.40	–58.5	–16.2	–	0.62	0.06	0.11	0.46
WaSul-Flux	–6.87	–23.7	–5.45	–59.9	–12.3	–17.5	–	0.62	0.50	0.78
Nitrolux-100	101	12.3	16.6	–1.96	35.7	146	41.8	–	0.72	0.57
CRDS	107	32.8	46.0	–6.32	45.5	96.3	68.4	1.21	–	0.20
IMS	14.8	–49.45	12.5	–50.7	–2.33	–12.2	16.0	–51.1	–60.5	–

of an a priori uncertainty would not be appropriate for this analysis. Nevertheless, a possible approach of performing regression analysis by using a least-squares fitting with uncertainties of the data can be found in Cantrell (2008).

The CIMS, CRDS and Nitrolux-100 revealed elevated intercepts compared with the other instruments pointing at a possible contamination of the inlet filters (CRDS and Nitrolux-100), inlets or both. The detected results during this campaign are in line with the studies listed below. Measurements of RBD, AMANDA, AiRRmonia, WaSul-Flux and c-QCLAS were within $\pm 25\%$ for NH₃ concentrations of 10 to 120 ppbv.

It should be noted that, although an attempt was made to eliminate the effect of spatial heterogeneity, emissions from grazed and fertilised grassland are expected to show some variability. It was neither possible (though desirable) for all instrument to sample from a common point (e.g. the wet chemistry instruments do not use an inlet tube, while the OP-FTIR provides a line average), nor was the use of a common inlet in the spirit of this experiment, in which we wanted to test independent systems with the respective inlets as they would have been operated by the different groups in the field. There is some indication that at times, instruments that were located more closely to

Table 8. Linear regression between each instrument for the entire data range (bottom left) and less than 10 ppbv (shaded top right).

each other (e.g. WaSul-Flux/AMANDA/RBD/AiRRmonia and CIMS/DUAL-QCLAS/c-QCLAS/Nitrolux-100/CRDS) agreed more closely with each other, but this observation was not consistent.

Previous comparison campaigns have already illustrated the challenges involved in measuring ambient NH₃ concentrations accurately, especially at low concentrations. The results in the study of Wiebe et al. (1990) showed an agreement within $\pm 30\%$ for NH₃ concentration >1.5 ppbv with time resolution of minimum four hours for the filter packs and the annular denuders. The five instruments compared

by William et al. (1992) yielded an agreement of within a factor of two for NH₃ concentration >0.5 ppbv. In detail the CAD/IC and PF/LIF agreed within 15% for NH₃ concentration of 0.2 to 5.0 ppbv for a time resolution of 2 to 8 h. The framework of the NAQMN study by Mennen et al. (1996) determined a general applicability for all requirements for air quality monitoring on one hour sampling. Further, the DOAS and the NO_x converter instruments reached $R^2 > 0.9$ compared with the wet-annular rotating denuder, but both were only useful during high NH₃ concentration near stacks or stables. In the study by Mennen et al. (1996)

Table 9. Analysis of the response time of AMANDA, RBD, WaSul-Flux, AiRRmonia, Nitrolux-100, CRDS and IMS in comparison to c-QCLAS with corresponding statistical parameters.

	$\tau_{1/e}$ (min)	τ_{50} (min)	τ_{95} (min)
AMANDA	10.7±1.3	7.4±0.9	32.2±3.7
RBD	28.7±4.2	19.9±2.9	85.9±12.5
WaSul-Flux	19.1±5.4	13.3±3.7	57.3±16.1
AiRRmonia	4.8±1.4	3.4±0.9	14.4±4.0
Nitrolux-100	3.6±0.8	2.5±0.6	10.9±2.5
CRDS	4.5±1.7	3.1±1.2	13.4±5.0
IMS	11.6±2.1	8.1±1.5	34.9±6.4

the photoacoustic monitor was eliminated due to high maintenance demands and because of leaving only 1% useful data. During the campaign of Milford et al. (2000) AMANDA and DS-FIA showed an overall difference of 35% for a sampling time of 30 min, but with substantial scatter. Fehsenfeld et al. (2002) reported for CIMS and MoO_x converter method $R^2 > 0.9$ compared with the citric acid denuder (sampling time minimum two hours). The average concentration difference compared with the denuder was 0.8 for the CIMS and 1.75 for the MoO_x converter method. Two CIMS instruments tested during the field study in Nowak et al. (2006) measured $R^2 = 0.71$ and concentration difference of 17% (time resolution one minute) with NH₃ concentrations from 0.4 to 0.13 ppbv. Milford et al. (2009) compared measurements with three AMANDA systems and a mini-WEDD system. The NH₃ measurements showed good agreement between the instruments (<20% difference) for some periods, but with poorer agreement on some individual days, due to variable performance of the automatic wet chemistry detection systems.

Of particular interest here are the results of the recent laboratory inter-comparison study of Schwab et al. (2007), because it followed a complementary approach (being laboratory based), while including some of the same instrument models tested here. The seven instruments tested during the laboratory comparison agreed within 25% of the expected calibration value. The IMS and Nitrolux-100 yielded biases of $\pm 25\%$ with slower time response than the TDLAS (similar to the QCLAS used here). Further, the wet chemical instruments LOPAP and WEDD worked well in the calibration tests in view of absolute accuracy of measured concentrations, but a disadvantage was the slower time response of the WEDD.

In the recent field inter-comparison of Norman et al. (2009) the slopes of hourly uncorrected data of PTR-MS (an alternative CIMS technique using a different ionisation scheme), GRAEGOR (based on the same collection and analytical technique as the AMANDA, but with lower

flow rates) and AiRRmonia ranged between 0.78 to 0.97 for NH₃ concentrations from 2 to 25 ppbv. During atmospheric conditions favouring condensation in inlet lines, the PTR-MS underestimated NH₃ concentrations. The authors point out the need to put more emphasis on the inlet designs for future campaigns. Whitehead et al. (2008) reported that their concentration measurements from the QCLAS and the AMANDA instrument correlated well, with $R^2 = 0.84$. However, the QCLAS underestimated fluxes by 64% compared with the AMANDA instrument.

4.2 Instrument specific issues

While providing a good response to the concentrations, the Nitrolux-100 and CRDS measurements in the present study were subject to a similar high intercept compared with the other instruments. There were two aspects common to these instruments: they shared the same sampling line, which may have been contaminated, but they also both use inlet filters, exchanged infrequently (up to 3 months, according to manufacturers), which may collect NH₄NO₃ which then could dissociate at low concentrations, providing a (temperature dependent) offset. This process clearly affected the Nitrolux-100 data at the start of the experiment, taken with an old filter, which were discarded from the analysis. This inlet / filter issue may also have affected the regressions of these instruments, especially over the low concentration range, as the intercept may not be stable in time. Apart from this issue, both instruments are convenient to operate as they are both manufacturer calibrated with long service intervals.

The only other instrument using an inlet filter is the WaSul-Flux, which operates on a similar principle as the Nitrolux-100. However, its filter was changed weekly, minimising the effect of NH₄NO₃ volatilisation. An attempt was made to investigate the potential of NH₄NO₃ interference on those instruments that do not remove the aerosol phase. In the c-QCLAS inlet a virtual impactor removes the coarse aerosol fraction. The CIMS does not use a filter and the residence within the heated inlet is 0.1 s and thus, the interference from NH₄NO₃ volatilisation is expected to be negligible, as noted by Fehsenfeld et al. (2002). Indeed, laboratory tests have shown that NH₄NO₃ volatilisation only becomes an issue for $T > 325$ K. Filters were not used on the IMS and the DUAL-QCLAS systems either, but the residence time in the analysis cell of the DUAL-QCLAS is of the order of 0.2 s and laboratory tests have found NH₄NO₃ interference to be negligible. In the wet chemistry systems aerosols are thought to pass the inlet uncollected. Unfortunately, the regional NH₄⁺ concentration was fairly constant during the campaign (Fig. 2), except for a period which coincided with the fertiliser emission peak of NH₃, during which NH₄⁺ still made a minor contribution to total NH_x. As a consequence, the effect of inlet heating (to 50 °C) on NH₄NO₃ volatilisation in the WaSul-Flux inlet could not be investigated.

The WaSul-Flux performed well against the other instruments, but has a relatively slow time response (45 min) at the background concentrations. It can achieve a detection limit of 0.25 ppbv at 45 min time resolution (Table 1), which may still not be sufficient for all applications. Work is underway to improve the sensitivity further.

By contrast, the IMS is highly sensitive, but less specific and affected by competing ion chemistries, which makes it applicable only to situations of low NH₃ and where no interfering compounds are to be expected. Its comparatively poor performance over the entire concentration range is misleading as concentrations >20 ppbv had to be removed due to saturation. It shows one of the best correlations with the average at the sub-10 ppbv comparison ($R^2=0.87$, Table 2).

Three instruments deployed here (DUAL-QCLAS, c-QCLAS and CIMS) have the potential to provide a fast NH₃ spot measurement, of particular interest for aircraft applications and eddy-covariance flux measurements. Although their time response was not characterised here, they clearly provide faster response than the other instruments and previous characterisations has shown response times to be better than 1 s, depending on inlet design (e.g. Whitehead et al., 2008).

The QCLAS technique (like OP-FTIR) in principle provides an absolute measurement of the concentration. However, without calibration, the instruments turned out to significantly underestimate the concentration. The c-QCLAS was calibrated at regular intervals in the field with a permeation tube calibration source, while a regular zero calibration but a one-off span calibration were applied to the DUAL-QCLAS, with average span calibration factors in the region of 1.3 and 1.2, for the two instruments respectively. This difference in the calibration approach is likely to be responsible for the poorer performance of the DUAL-QCLAS during this campaign. In addition, the DUAL-QCLAS was set up for eddy-covariance flux measurements, with a relatively long inlet, which may have added further uncertainty. The DUAL-QCLAS sampled air through a 2 m length of 6.4 mm PFA tubing. Owing to the “sticky” nature of NH₃, this can have an impact on NH₃ measurements (Shaw et al., 1998; Whitehead et al., 2008). This may therefore partly explain the under-estimate in the NH₃ concentration at the peak concentrations. Against this possible argument, it should be noted that the DUAL-QCLAS showed one of the highest R^2 values (0.98 for the full dataset), with a small intercept compared with other instruments (Fig. 4d and Table 6), indicating a significant but rather constant slope of ~ 1.2 . By contrast, the c-QCLAS was one the better performing instruments tested here.

The CIMS provides a fast, highly sensitive technique and this was the first field deployment of this particular instrument, which showed more scatter than most instruments. Although, it should be noted that it is uncertain how much of this scatter is natural variability and how much is represented by instrumental noise. The instrument was calibrated

hourly and the sensitivity of the instrument was (2.5 ± 0.5) Hz ppt⁻¹ 1σ and the 1σ background noise corresponded to 45 pptv. In a subsequent deployment of this instrument (C. J. Percival, personal communication, 2009), which employed a similar inlet design and throughput, large variability in NH₃ signal was observed on a second by second basis, such variability was not present in the background and calibration cycles, indicating that the inlet is able to respond to rapid changes in the NH₃ concentration associated with different plumes and is therefore capturing real, rather than artificial variability. It appears that, as with the c-QCLAS approach, stability in the instrument response coupled with the need for a reliable zero and span gas-phase calibration source is the limiting factor in improving performance. This is consistent with the observations of Nowak et al. (2007), who reported the need for very frequent background determinations for an airborne CIMS instrument, especially when targeting background concentrations.

The OP-FTIR instrument averages over a path-length of 100 m which possibly limits comparability with the other point measurement techniques. Furthermore, measurements were made over a more limited concentration range. Yet, the comparison with the other fast-response techniques is encouraging (Fig. 5). Like the c-QCLAS, the OP-FTIR should also provide an absolute measurement but reports some of the lowest concentrations. At very low concentrations, instrument noise may exceed the signal from NH₃, which may explain the high intercept (>3.74 ppbv) in comparison with other detection methods. Interestingly, both c-QCLAS and OP-FTIR underestimate the concentration when used in absolute (uncalibrated) mode and both rely on the accuracy of the same absorption line information of the HITRAN database.

All three wet chemistry systems used here are based on flow injection analysis using a selective ion membrane, which is known to have some cross sensitivity for some amines (Husted et al., 2000). Although probably unimportant here, they may make a more significant contribution in other situations, e.g. of organic animal manure emissions. Using batch sampling and off-line analysis, the RBD is the most “manual” technique included here. It is surprising that the RBD performed better (compared with the average) at small concentrations than over the entire concentration range (Table 2). This is possibly due to sample carry-over in situations of highly variable concentrations. AMANDA and AiR-Rmonia compared well with each other and, together with WaSul-Flux and IMS (and closely followed by c-QCLAS), achieved the best agreement with each other over the low concentration range. AMANDA and IMS read somewhat higher than the other instruments. The excellent agreement on the common liquid standard within $\pm 3\%$ (Table 2) indicates that the wet chemistry instruments are stable and easy to calibrate, as long as the collection efficiency can be assumed to be 100% and the flow rates are well established. The wet chemistry instruments have the implicit advantage

that they do not rely on an accurate gas-phase standard or any absorption cross sections. Further, they provide a more robust approach to separating gas and aerosol phase. However, they could potentially suffer artefacts from interfering gas-phase compounds in certain situations.

The WaSul-Flux instrument was compared against an AMANDA in previous measurement campaigns (Pogány et al., 2009), where a correlation coefficient of 0.98 was found between the photoacoustic signal and the concentration readings of AMANDA for concentrations 0 to 120 ppbv, which agrees with the correlation coefficients for NH_3 -ens in this campaign (0.98, Fig. 4f), and the correlation coefficients between WaSul-Flux and the wet-chemistry instruments (0.98 for AMANDA and AiRRmonia and 0.95 for the RBD; Table 5). However, the limit of detection of the WaSul-Flux instrument (0.25 ppbv) is currently higher than that stated for the AMANDA (0.02 ppbv) or AiRRmonia (0.04 ppbv).

4.3 Time responses

The additional capture of NH_3 variations of instruments with higher time resolution, shown in Sect. 3.1, is consistent with the observations of Norman et al. (2009). The calculated time response for the instruments in Sect. 3.3 showed higher values than stated by the manufacturers (Table 1). This is particularly true for the AMANDA system for which the actual response time was estimated to be 37 min. A similar observation was made for the GRAEGOR analyser, based on the same horizontal annular denuder design, but using a lower liquid flow rate (Thomas et al., 2009). Faster response could be achieved by further minimising the liquid pool in the denuders, or by increasing the liquid flow rate (thereby sacrificing sensitivity). For the AiRRmonia, the calculated time response of 14.4 ± 4.0 min time to obtain 95% of the signal is only slightly slower than the 10 min measurement cycle (Table 1). The same is true for CRDS and Nitrolux-100 with 13.4 ± 5.0 min and 10.9 ± 2.5 min to obtain 95% of the signal, respectively, as compared with instrument recording every 6 s (Table 1). During the study of Schwab et al. (2007), a TDLAS reached a value near 35 ppbv within 6 min, whereas IMS and Nitrolux-100 had the slowest time response of all the instruments investigated in their experiment. The same observations were made during this inter-comparison, where the IMS presented the slowest time response, probably due to the use of internal materials which are not optimised for NH_3 measurements.

5 Conclusions

This paper reports an inter-comparison of eleven instruments for measuring atmospheric NH_3 at ambient concentrations, representing the largest NH_3 inter-comparison under typical field conditions to date. The approaches deployed included automated wet chemistry techniques, optical, photo-acoustic

and mass spectrometric techniques. There were differences in the concentrations reported, but overall the high correlation with $R^2 > 0.84$ compared with the average of all instruments used, is very encouraging. The correlation worsens if only concentrations < 10 ppbv are considered. Concentrations of RBD, AMANDA, AiRRmonia, WaSul-Flux and c-QCLAS agreed within $\pm 25\%$ for concentrations > 10 ppbv. Some reasons for variability were identified: inlet length greatly affects measurement precision and time-response. Where used, inlet filters need to be changed very frequently (e.g. daily to weekly), at much shorter intervals than stated by some manufacturers. Instruments based on chemical ionisation mass spectroscopy and quantum cascade laser absorption spectroscopy need to be calibrated or at least zeroed frequently, and the provision of a reliable gas-phase calibration source in the field determines their measurement accuracy. Wet chemistry instruments show good long-term stability, are housed to operate with very short inlets and the liquid part of the system is easier to calibrate. They provide a reliable differentiation between gas-phase NH_3 and aerosol NH_4^+ , which could not be validated for the other instruments during this study. For future inter-comparisons using all inlets at a single sampling point should be attempted, bearing in mind the logistic constraints when working with a large number of sizeable instruments. Not all instruments tested here are suitable for accurate measurements at concentrations < 1 ppbv, while the application of ion mobility spectroscopy is limited to low concentrations (< 20 ppbv) and conditions with no competing pollutants. Despite, recent advances in technologies, the continuous measurement of NH_3 remains a challenging and costly enterprise, in terms of capital investment or running costs or both.

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Appendix B:

Paper II Factors affecting the ammonia content in the air surrounding a broiler farm

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Research Paper

Factors affecting the ammonia content in the air surrounding a broiler farm

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The emission and dispersion of ammonia (NH₃) in the atmosphere near a large livestock facility was investigated for its direct impact on the environment. Ammonia emission and dispersion are influenced by various local factors. The major factors affecting the NH₃ concentrations in the air around the broiler farm over an entire growing cycle were monitored. Both internal and external factors in connection with the broiler barns were considered. Ten factors-of-influence (FOI) that strongly influence the dispersion of NH₃ were selected. The FOI employed included: NH₃-mass-flow, internal and external temperatures, mean and turbulent wind components in horizontal and vertical directions, atmospheric stability, day-of-growing cycle, and exhaust air height. Multiple linear regressions (MLR) were implemented to analyse the relationship between FOI and the NH₃ measured in the air. Different approaches of MLR were applied, considering the entire data range and subsets of data to determine a general model and other more restrictive models that can be used. Overall, the precision of the predictive models of atmospheric NH₃ dispersion, based on different datasets, was satisfactory (coefficient of determination R² > 0.83). Irrespective of the models applied, the mean vertical wind component proved to have significant influence on the concentration of NH₃ in the air. The results of this study show that the monitoring of specific FOI can be used to predict the concentration of NH₃ in the air surrounding a broiler farm. This particular monitoring practice enables investigators to assess the possible negative impact of NH₃ on the environment.

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1. Introduction

Emissions from livestock production are a major source of ammonia (NH₃) in the atmosphere (Ferm, 1998). Ammonia is at the same time an important component of nitrogen. Ammonia emissions are likely to increase due to the pressure on the food production industry to keep pace with the growing

world population. As a result, animal production in modern livestock facilities will intensify (Aneja et al., 2008). Furthermore, NH₃ plays an essential role in atmospheric chemistry, because it is the one gas among the alkaline group it is the most prolific (Duyzer, Verhagen, Weststrate, Bosveld, & Vermetten, 1994; Moeller, 2003). Ammonia affects gas-to-particle conversion by its reaction with atmospheric acids that

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Nomenclature*Symbols*

c_{in}	Inside NH_3 concentration, $mg\ m^{-3}$
c_{out}	Outside NH_3 concentration, $\mu g\ m^{-3}$
day_{gc}	Days of the growing cycle, d
dH	Exhaust air height, m
d_s	Rooftop stacks diameter, m
h	Height of the broiler barns, m
H	Sensible heat flux, $W\ m^2$
L	Monin–Obukhov length, m
m	NH_3 -mass-flow, $kg\ h^{-1}$
P	Precipitation, mm
q	Air-volumetric flow rate, $m^3\ h^{-1}$
T	Acoustic temperature at $z/h = 1.4$, $^{\circ}C$
T_{out}	Acoustic temperature at $z/h = 2.3$, $^{\circ}C$
T_{in}	Inside temperature, $^{\circ}C$

T_{2m}	Outside temperature in 2 m above ground, $^{\circ}C$
u_*	Friction velocity, $m\ s^{-1}$
u	Wind component with the wind, $m\ s^{-1}$
v	Lateral wind component, $m\ s^{-1}$
w	Vertical wind component, $m\ s^{-1}$
ws	Wind speed, $m\ s^{-1}$
wd	Wind direction, $^{\circ}$
z	Measurement height, m
σ_{ws}	Horizontal turbulent components of wind, $m\ s^{-1}$
σ_w	Vertical turbulent components of wind, $m\ s^{-1}$

Abbreviations

DWD	German meteorological service
FOI	Factors-of-influence
MLR	Multiple linear regression
MP1	Monitoring tower
PTFE	Polytetrafluoroethylene
TA-Luft	Technical instruction on air quality control

in turn produces ammonium salts (NH_4^+). The atmospheric lifetime of gaseous NH_3 is relatively short compared to particle-phase NH_4^+ , which can be transported over much greater distances (Aneja et al., 2001; Warneck, 1988). Ammonia is removed from the atmosphere via wet and dry deposition and by particle formation. Dry deposition is the most important means of removal near sources of NH_3 emission (Asman, 1998). With respect to air pollution, atmospheric NH_3 is responsible for causing various negative environmental effects. It produces a sickening odour and if deposited in amounts above critical levels it negatively affects plants and ecosystems. Depending on the environmental setting, an over-enrichment of nitrogen in an ecosystem can lead to acidification of soils, enhanced eutrophication of water bodies, forest decline or decreasing biological diversity (Fangmeier, Hadwiger-Fangmeier, van der Eerden, & Jäger, 1994; Ferm, 1998; Sutton, Fowler, Burkhardt, & Milford, 1995). Ammonium is also a significant component in the formation of particulate matter (Erisman, Bleeker, Hensen, & Vermeulen, 2008; Wu, Hu, Zhang, & Aneja, 2008).

Ammonia emissions from intensively operated poultry enterprises accounted for up to 7% of the overall agricultural livestock emissions in Germany (UBA, 2002). According to the targets set by the European National Emission Ceilings Directive (NECD) 2001/81/EG, Germany has to reduce its NH_3 emissions from $764\ kt\ yr^{-1}$ in 1990 to $550\ kt\ yr^{-1}$ in 2010. This equates to a decrease of 28%. The National Inventory Report revealed that Germany's Greenhouse Gas Inventory (1990–2008) exceeded the allowable limit by 11% (UBA, 2010).

Concerning the quantification of NH_3 emissions from housed livestock, a wide range of scientific results have been published (Aneja et al., 2001; Blunden, Aneja, & Westerman, 2008; Gates, Casey, Wheeler, Xin, & Pescatore, 2008; Misselbrook, Webb, & Gilhespy, 2006; Welch, Colls, Demmers, & Wathes, 2005). Different measurement techniques have been developed for monitoring atmospheric NH_3 in agricultural areas as summarised by von Bobrutski et al. (2010), Erisman et al. (2001) and Kirchner et al. (1999).

These measurement techniques are strongly affected by the variations in the meteorological factors that influence the emission and dispersion of atmospheric NH_3 . Furthermore, the complex local topography and the diversity of livestock buildings, which vary in size and in the number of animals they house, complicates matters further when attempts are made to make accurate estimations of the emission and dispersion of NH_3 in the air (Erisman, Hensen, Mosquera, Sutton, & Fowler, 2005). During the first Workshop on Agricultural Air Quality (Maryland, USA), the authors stated that the current monitoring methodologies needed to be improved in order to get better and more reliable data on atmospheric NH_3 as an agricultural air emission. Further, by implementing best management practices (BMPs), it is possible to assess the effects and minimise the negative environmental impact of agricultural emissions (Aneja et al., 2008).

The processes involved in measuring NH_3 emissions, and the variability of dispersion of the emission behaviour, are complex. Therefore, various computer models have been used for simulated measurements. Regarding NH_3 dispersion, an accurate EU-wide quantitative assessment is still difficult to make, because the models used on the regional level are still under development (Loubet et al., 2009). For modelling on a local-scale, a precise description of all processes and input data involved are required. Hill (1998) and Sutton et al. (1998) described a suitable and widely-used atmospheric transport model LADD (local area dispersion and deposition) with which has $50 \times 50\ m$ resolution. For atmospheric transport modelling, it is also crucial to understand the main environmental variables and processes that cause emission change (Cellier et al., 2009; Dragosits et al., 2002).

The work presented here focused on an adequate selection of factors that are known to exert a strong influence on the emission and dispersion of NH_3 in the air. Prior studies have been attempted to identify the main aspects responsible for the dispersion of NH_3 in the air. Kaimal and Finnigan (1994) stated that horizontal and vertical wind components have to be taken into account. Another factor involved in the transport process is the combination of mean and turbulent-mixing of

air in both horizontally and vertically. Another factor is the atmospheric stability that affects the dispersion of NH_3 in the air. An unstable atmosphere creates conditions for an optimal dispersion of air and NH_3 emissions. In contrast, a stable atmosphere restricts dispersion processes (Oke, 1987).

The design and operational parameters of the broiler barns and their ventilation systems are important considerations when identifying factors which affect the emission and dispersion of NH_3 in the air (Demmers et al., 1999; Mosquera, Monteny, & Erisman, 2005). Redwine, Lacey, Mukhtar, and Carey (2002) reported increasing internal NH_3 concentrations in broiler barns as the growing cycle progressed. Thus, the concentration of NH_3 correlates to the age of the birds and the corresponding higher rates of excretion.

This paper explores the differences between the time-series of the build-up of NH_3 concentrations inside and outside a large broiler barn facility over an entire growing cycle. Both time-series showed a weak correlation. This fact implied that other factors affected the dispersion of NH_3 in the air. Thus, we selected ten factors-of-influence (FOI) to find out how each factor influenced each other and the dispersion of NH_3 in the air. These factors represent the atmospheric and meteorological conditions as well as the operational parameters of the broiler barns. In order to make a proper evaluation of these FOI, extensive measurements of internal and external data were taken. By implementing multiple linear regression (MLR) analyses, the relationship between FOI and the measured atmospheric NH_3 was analysed. The aim was to obtain predictive models that relate the observed atmospheric NH_3 to the FOI. This was accomplished by applying the entire data range and data subsets, which were measured during the growing cycle.

2. Materials and methods

2.1. Study site

Measurements were carried out at a broiler farm located to the southeast of Berlin, Germany. The farm covers an area of about 6 ha. It is surrounded mostly by pine woodland, with trees of approximately 8–10 m in height. There is open space to the northeast, where the road leading to the farm entrance lies (Fig. 1a).

The broiler installation consists of nine small barns (length: 88 m, width: 12 m and height: 3.5 m), each containing 21,800 broilers. There are also three big barns (length: 93 m, width: 29 m and height: 4.5 m) with 62,000 broilers each (Figs. 1a, b). In total, around 382,200 broilers are raised during a growing cycle. The nine small broiler barns are equipped with side-forced ventilation. In contrast, the three big barns have 18 rooftop stacks with controlled fans. Each of these rooftop stacks has a diameter (d_s) of 0.65 m and a height of 1 m above the roof. The operation of the fans is controlled by the internal temperature of the broiler barns; the temperatures ranged from 22 to 34 °C during the growing cycle.

In each of the seven to eight annual growing cycles, the broilers were kept in the barns for 36 days with a market mass of approximately 1.5–1.8 kg. The broilers shared a common genetic pool and therefore produced the same type of NH_3 . Thus, the measurements taken in one barn would be comparable in the concentration of NH_3 to those taken in any other barn on the farm. Each growing cycle starts simultaneously in all of the barns. The bedding material was sawdust.

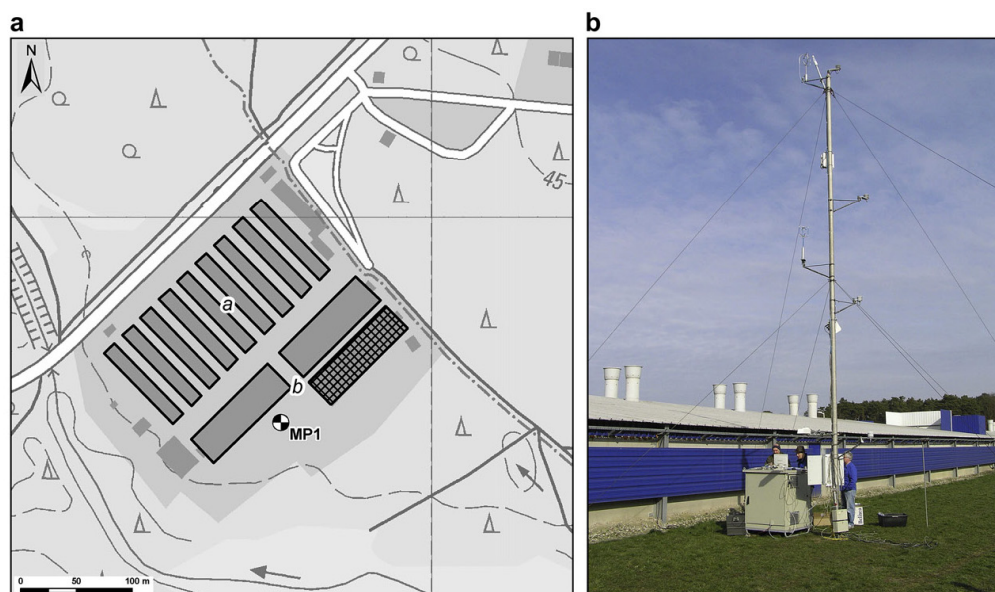


Fig. 1 – (a) Location of the monitoring tower on the broiler farm grounds (MP1). The subject broiler barn is highlighted, whereas “a” and “b” represent the smaller and the bigger broiler barns, respectively. (b) MP1 (monitoring tower) for measuring NH_3 in the air and wind with speed and direction.

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The barns were cleaned and sterilised during the 7-day periods between the growing cycles.

2.2. Environmental conditions during the study

The study was carried out during a growing cycle that ran from 21 February to 27 March 2007. There were no other farms in the surrounding area of the study site that could have produced false ammonia readings. Fig. 2 shows the time-series of local daily data of precipitation (P) and outside air temperature (T_{2m}) during the observed growing cycle.

In the upper half of Fig. 2, meteorological data of Central Europe at 12 UTC was recorded by the German Meteorological Service (Deutscher Wetterdienst – DWD). The origin of wind movements is represented by the direction of the arrows and the humidity is given by “w” = wet and “d” = dry periods. The DWD definition of humidity was arrived at by measuring the vertical integration of the water-vapour content in the atmosphere from ground-level to 300 hPa. In a second step, the humidity was compared with a long-term daily mean for the 20-year period 1981–2000 (DWD, 2010). The information provided by the DWD is included to show the influence of large-scale weather on local conditions.

During the growing cycle, large-scale wind movements over Central Europe blew from the west and changed to an easterly direction during the last seven days. The first half of the growing cycle was influenced by wet weather conditions over Central Europe. Locally, rain occurred several times, yielding the maximum amounts of $>10 \text{ mm d}^{-1}$ between days 28 and 30 of the growing cycle. Overall, dry weather conditions prevailed over Central Europe from day 28 to 30. Thus, this shows that local meteorological conditions were only marginally influenced by large-scale weather patterns. Furthermore, the

surrounding woodland provides shelter to the immediate farm area from large-scale weather conditions.

The predominant outside air temperature was above 5°C . Only on days two and three of the growing cycle did the daily outside air temperature drop below 0°C .

During the study, the prevailing wind direction (wd; Fig. 3a) was of NNE/ENE and SSW/WSW (Fig. 7). The wind very rarely blew from the S and E. However, winds from all directions were observed during the experiment. The mean wind speed (ws; Fig. 3b) was approximately 2 m s^{-1} . At the beginning and the end of the study, ws was higher for a few days and it reached a maximum of 5.6 m s^{-1} on day 25.

2.3. Measurements

The monitoring tower (MP1), marked in Fig. 1a and shown in Fig. 1b, was erected on the farm site. It was placed in the best position possible, considering the spatial restrictions imposed on us by the layout of the barns on the farm. For exact analysis of meteorological conditions, a non-dimensional factor z/h was defined, where z was the measurement height and h the height of the broiler barns (4.5 m). An ultrasonic anemometer (VDI 3786, 1994) at the monitoring tower measured the three-dimensional components of the wind. These included the component with the wind (u), the lateral component (v), the vertical wind component (w), and the acoustic temperature at $z/h = 1.4$ (T) and $z/h = 2.3$ (T_{out}). From these datasets, hourly mean values of \bar{u} , \bar{v} , \bar{w} , \bar{T} as well as horizontal wind speed (\bar{ws}) and wind direction (wd) were calculated.

Atmospheric NH_3 concentrations (c_{out}) were measured with a chemiluminescence NH_3 analyser (Breitenbach & Shelef, 1973) at $z/h = 2.3$ by sampling the air via a PTFE-hose, attached to the ultrasonic anemometer.

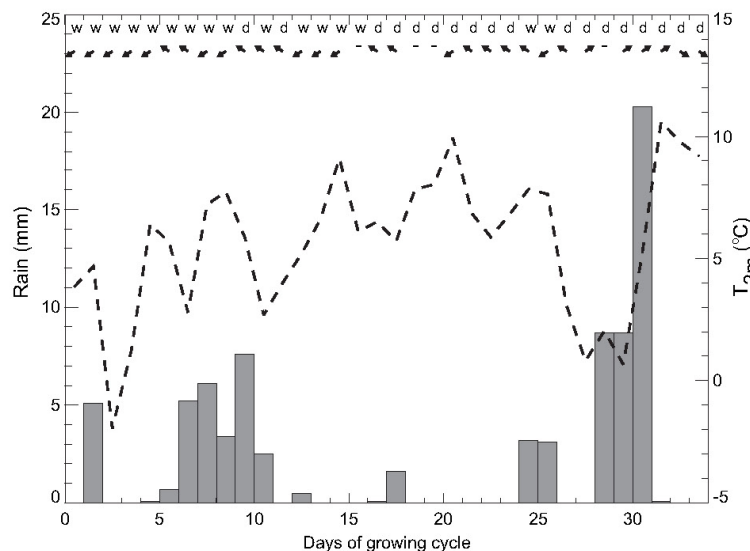


Fig. 2 – Mean local outside air temperature (dotted line) in 2 m height and rain (bars). The general Central Europe wind direction is indicated by arrows (horizontal bar represents calm days) and the weather situation is marked by “w” = wet, “d” = dry.

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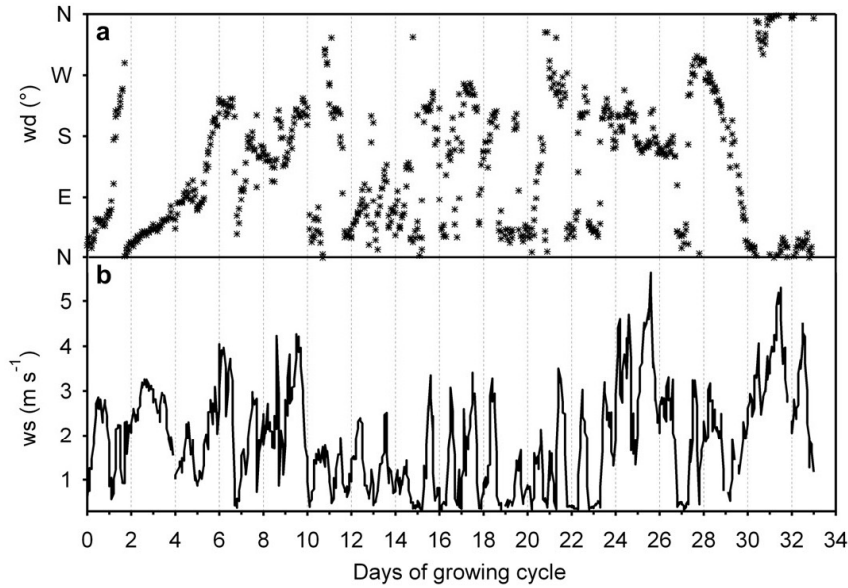


Fig. 3 – (a) Wind direction (wd) and (b) horizontal wind speed (ws) measured at $z/h = 2.3$ of the monitoring tower during the growing cycle.

Inside of the subject broiler barn (Fig. 1a), the NH_3 concentration (c_{in}), air-volumetric flow rate (q) and air temperature (T_{in}) were recorded close to the exhaust air outlets. In this case, the NH_3 concentration was sampled by a gas monitor via PTFE-hoses.

The NH_3 -mass-flow (kg h^{-1}) was calculated (Eq. (1)) as:

$$m = c_{\text{in}} * q \quad (1)$$

Because of logistical set-up restrictions, measurements were taken over 32 instead of all 35 days of the growing cycle (day_{gc}) (i. e. from day 3 to 35). The reason for using complete days of data rather partial days was to ensure a consistent evaluation of the NH_3 -mass-flow. This was necessary because the NH_3 output fluctuated on a daily basis, depending on the air temperature. All the variables used, along with the specifications of the techniques applied, are listed in Table 1.

2.4. Eddy-covariance analyses

Atmospheric transport processes are defined based on turbulent fluxes, called “eddy-fluxes”. The “Reynolds averaging” approach is used to quantify these turbulent processes by separating the mean and turbulent component of a variable as follows (Kaimal & Finnigan, 1994):

$$x(t) = \bar{x} + x'(t) \quad (2)$$

where $x(t)$ represents the sum of \bar{x} as the means over an interval of time (1 h in this study) and $x'(t)$ the turbulent component.

Eddy-covariance defines the flux as the average product of the instantaneous deviations of vertical wind velocity (w') and the deviations of a scalar x' from its mean value ($\overline{w'x'}$). This

technique has already been extensively described in the literature of this field (Foken, 2008; Stull, 1988).

For this study, vertical (σ_w) and horizontal (σ_{ws}) turbulent components of wind, friction velocity (u^* in m s^{-1}) and sensible heat fluxes (H in W m^{-2}) were derived directly from the eddy-covariance measurements at $z/h = 2.3$:

$$\sigma_w = \sqrt{w'w'} \quad (3)$$

$$\sigma_{ws} = \sqrt{u'u' + v'v'} \quad (4)$$

$$u^* = (\overline{u'u'^2} + \overline{v'v'^2})^{1/4} \quad (5)$$

$$H = -c_p \rho (\overline{w'T'}) \quad (6)$$

where H is positive in the downward direction, ρ is the density of air (kg m^{-3}) and c_p is the heat capacity of air ($\text{J g}^{-1} \text{K}^{-1}$). The turbulent wind components (σ_w , σ_{ws}) are expressed as standard deviations. These can be used to interpret the extent of the deviation from the average mean. Therefore, these were used to quantify the intensity of turbulence (Stull, 1988).

Atmospheric stability was parameterised through the Monin–Obukhov length (L in m):

$$L = -\frac{c_p \rho u^*{}^3 T}{g k H} \quad (7)$$

where g is the acceleration due to gravity (m s^{-2}) and k is von Karman's constant (0.41).

A negative L represents a more unstable behaviour of the atmosphere and a positive L indicates a more stable atmospheric condition. Very rarely was the atmosphere neutral where $L \sim 0$ (Oke, 1987).

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Table 1 – Summary of the variables and the characteristics of used instruments.

Variable	Manufacturer	Units	Height [m]	Temporal resolution	Accuracy	Detection limit	Range
Wind speed (ws)	Metek USA 1,	m s^{-1}	10.5	10 Hz	± 0.01	0.01	0 to 50
Wind direction (wd)	Metek GmbH,	$^{\circ}$			± 0.4	0.4	0 to 359.9
Acoustic temperature (T_{out})	Elmshorn, Germany	$^{\circ}\text{C}$			± 0.01	0.01	–30 to +50
Wind speed (ws)	Gill Windmaster Pro,	m s^{-1}	6.2	10 Hz	12 m s^{-1}	0.01	0 to 65
Wind direction (wd)	Gill Instruments Ltd,	$^{\circ}$			$<1.5\%$	0.1	0 to 359.9
Acoustic temperature (T)	Lymington, UK	$^{\circ}\text{C}$			12 m s^{-1}	–	–40 to +70
					$<2^{\circ}$		
Precipitation (P)	Young 52202,	mm	1.5	0.1 mm	25 mm $<2\%$	0.1	–
	RM Young Company,						
	Traverse City,						
	Michigan, USA						
Outside temperature (T_{2m})	Temperature probe,	$^{\circ}\text{C}$	2	1 min	$<0.4^{\circ}\text{C}$	–	–40 to +70
	CS 215,				(5–40 $^{\circ}\text{C}$)		
	Campbell Scientific Ltd,						
	Shepshed, UK						
Inside concentration of NH_3 (c_{in})	Photoacoustic field gas monitor	mg m^{-3}	4	1 min at each of 12 points	$<1\%$	0.2	–
	Type: 1312,						
	UA 0973 filter,						
	INNOVA AirTech						
	Instruments,						
	Ballerup, Denmark						
Air-volumetric flow rate (q)	Measurement ventilators,	$\text{m}^3 \text{h}^{-1}$	4	Every 10 min at 18 points	–	–	–
	Type: MVP63,						
	Hotraco Group,						
	Hegelsom, The						
	Netherlands						
Inside temperature (T_{in})	Temperature probe,	$^{\circ}\text{C}$	4	Every 10 min at 2 points			
	Type: N2000,						
	Comark Instruments,						
	Hitchin, UK						
Outside concentration of NH_3 (c_{out})	NOx converter	$\mu\text{g m}^{-3}$	10.5	15 s	$<1\%$	10	0 to 1000
	HORIBA Apna 360,						
	HORIBA Ltd.,						
	Kyoto, Japan						

2.5. Exhaust air height calculation

The broiler buildings were equipped with forced ventilation systems that were operated through the mechanical energy created by the vacuum existing inside the barn. Additionally, air transported out of the barns acted as a buoyancy force for the emissions. For calculating the exhaust air height (dH) out of the stacks (of the broiler barns), the plume rise calculation (Briggs, 1972) was applied (Eqs. (8)–(10)):

$$B = \frac{0.25 \times g \times v_s \times d_s^2 \times (T_{\text{in}} - T)}{T_{\text{in}}} \quad (8)$$

for $B < 55$,

$$dH = h_s + \frac{21.31311057 \times B^{0.75}}{U} \quad (9)$$

for $B > 55$,

$$dH = h_s + \frac{38.87776061 \times B^{0.60}}{U} \quad (10)$$

where B represents the buoyancy flux ($\text{m}^4 \text{s}^{-3}$), v_s is the exit velocity out of the stacks (m s^{-1}), T is the acoustic air

temperature at $z/h = 1.4$ (K), h_s is the physical stack height (5.5 m) and U defines a default ws of 2 m s^{-1} .

2.6. Statistical analysis

Before carrying out the statistical analysis, data of c_{out} were pre-processed by a natural logarithmic transformation (\log_e). Multiple regression analyses were performed to generate linear regression models. These related the natural logarithms of c_{out} to ten FOI, without applying an intercept. The following FOI were selected: m , T_{out} , T_{in} , \overline{ws} , \overline{w} , σ_{ws} , σ_w , dH , L and day_{gc} . These factors characterise the atmospheric and meteorological conditions as well as the operational parameters of the broiler barns. The aim of the analysis presented here was to comprehensively evaluate the relationship between measured c_{out} and FOI.

This led to the following formula:

$$\log_e(c_{\text{out}})_i = a_1 x_{i1} + a_2 x_{i2} + a_3 x_{i3} + a_4 x_{i4} + a_5 x_{i5} + a_6 x_{i6} + a_7 x_{i7} + a_8 x_{i8} + a_9 x_{i9} + a_{10} x_{i10} \quad (11)$$

Following the computer-generated MLRs, all values where the probability was greater than $p > 0.05$ were deleted manually.

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All statistical analyses were carried out using SAS v.9.2 (SAS Institute, Cary, NC, USA).

3. Results

3.1. Emissions of NH_3 and measured c_{out}

The NH_3 -mass-flow (m ; Eq. (1)) out of the twelve broiler barns rose during the growing cycle (Fig. 4). This rise was attributed to the increased output of the ventilation system. More and more ventilation became necessary as the cycle progressed, since a certain internal air temperature had to be maintained to keep pace with the broilers' physical growth and because NH_3 concentrations rose as the birds grew in size.

Calculated from sum of m over the growing cycle (Fig. 4), the unit emission was $2.4 \text{ g NH}_3 \text{ broiler}^{-1}$ per growing cycle $^{-1}$. Assuming eight growing cycles per year and considering the lower emission rates in winter, this corresponds to $0.02 \text{ kg NH}_3 \text{ broiler}^{-1} \text{ a}^{-1}$.

Concerning the variations of m and atmospheric NH_3 concentrations (c_{out}) at $z/h = 2.3$, five different phases could be identified; these are indicated in the upper part of Fig. 4. During the first eleven days (phase 1) m and c_{out} increased to the values $<1 \text{ kg h}^{-1}$ and $<60 \mu\text{g m}^{-3}$, respectively. Within phases 2, 3 and 4, a near stagnation of m occurred, resulting in less NH_3 being transported into the atmosphere (at the monitoring tower).

During an earlier stage (day 11–15), and at the end (day 25–28) of the growing cycle, comparatively low c_{out} ($<5 \mu\text{g m}^{-3}$) occurred. During phase 5, m and c_{out} increased up to a maximum of $4 \text{ kg NH}_3 \text{ h}^{-1}$ and $202 \mu\text{g m}^{-3}$, respectively.

Fig. 5 depicts the correlation and result of the linear regression analysis. The weak correlation ($R^2 = 0.18$) between m and measured c_{out} , implies that 18% of the variance of c_{out} can be interpreted by the variance of m . Using a linear regression curve-fitting, a slope of 15.3 was calculated. The intercept of $2.9 \mu\text{g m}^{-3}$ was interpreted as background concentration of atmospheric NH_3 . This value corresponds to the basic atmospheric concentration of NH_3 in European agricultural areas.

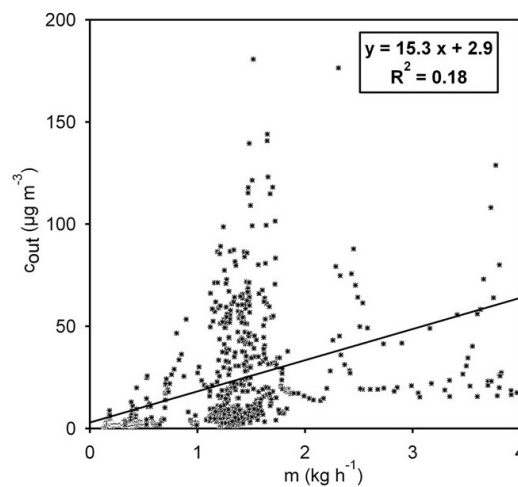


Fig. 5 – Scatter plot of NH_3 -mass-flow (m) out of twelve broiler barns vs. measured NH_3 in the air (c_{out}) at $z/h = 2.3$. The solid line gives the result of the axis regression.

A high correlation was achieved between m and day_{gc} ($R^2 = 0.95$) using the relationship:

$$\log_e(m) = 3.39 + 0.44 \text{ day}_{\text{gc}} - 0.02 \text{ day}_{\text{gc}}^2 + 0.0003 \text{ day}_{\text{gc}}^3 \quad (12)$$

confirming that including day_{gc} in the analysis of the relationship between FOI and measured c_{out} , was a useful approach.

As described in Eqs. (8)–(10), dH was calculated using buoyancy forces and the mechanical impulse that was created by the forced ventilation (Fig. 6). Within the first 14 days, dH ranged up to 12 m. During this period, high ground-level internal air temperatures ($\sim 30^\circ\text{C}$) are required for optimal growth of young broilers.

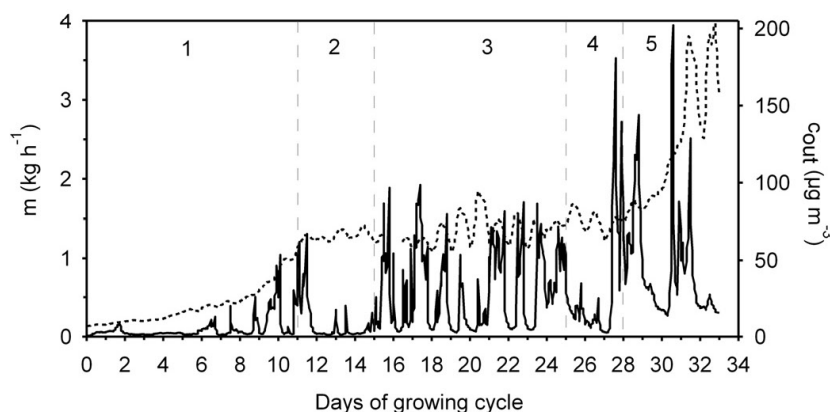


Fig. 4 – Ammonia-mass-flow (m) out of twelve broiler barns with 382,200 broilers in total (dashed line) and measured NH_3 concentration in the air (c_{out}) at $z/h = 2.3$ (solid line) during the growing cycle. The numbers 1–5 mark phases during which different patterns of NH_3 -mass-flow and atmospheric NH_3 occurred.

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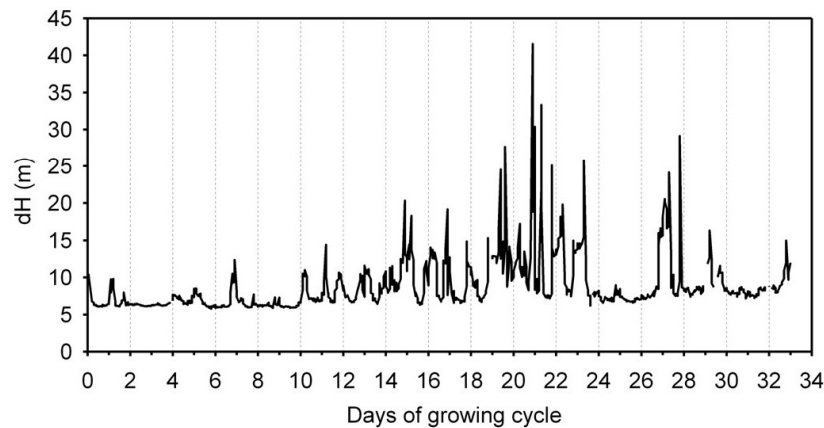


Fig. 6 – Exhaust air height (dH) out of one stack of the subject broiler barn during the growing cycle.

Hence, the air-volumetric flow rate (q) increased only slowly because the internal air temperature itself rose slowly. The same slow-rising behaviour was observed in the case of m . After the first 14 days of the growing cycle, the internal air temperature was reduced, since the broilers are older and do not need the same relatively high internal air temperature. In order to reach the necessary lower internal air temperatures, the ventilation rate was increased. This in turn, caused dH to rise to its maximum of 42 m.

The wind blew most frequently from the SSW and WSW. When this was the case (34% of the time; Fig. 7), low c_{out} ($<10 \mu\text{g m}^{-3}$) was measured at the monitoring tower, because the surrounding woodland area (over which these winds blew) possesses no other source of NH_3 .

When the wind blew from the NNE and ENE (22% of the time), it encompassed the entire farm; this led to high accumulations of NH_3 . Consequently, higher c_{out} ($>10 \mu\text{g m}^{-3}$) was measured at the monitoring tower. Changes in wind direction caused different atmospheric NH_3 dispersion patterns. The location of the monitoring tower affects these patterns. Thus, an investigation of FOI of the various wind directions was necessary. In the following analyses, the winds from E to WSW and W to ENE are referred to as leeward side and windward side, respectively.

3.2. Multiple linear regression (MLR) analyses of FOI on measured c_{out}

3.2.1. MLR of FOI on the entire data set of the growing cycle
A MLR analysis on the entire data set showed that six out of the 10 FOI had a significant effect on measured c_{out} ($p < 0.05$) (Table 2). The model describes the relationship between FOI and measured c_{out} as follows:

$$\log_e(c_{out}) = 0.03T_{out} + 0.05T_{in} - 5.11w - 0.22ws + 0.11\text{day}_{gc} - 0.05dH \quad (13)$$

According to Table 2, the model could explain 89% of the total variance of measured c_{out} by applying six FOI. Thereby, the mean component of vertical (\bar{w}) and horizontal (\bar{ws}) wind

(see Eq. (2)) exerted the main influence; both were negative in sign. Further, day_{gc} presented the highest impact of all FOI in this model and it was positive in sign.

3.3.2. MLR of FOI on subsets of data for separate time phases
Table 3 shows MLR on five subsets of data concerning different patterns of m and c_{out} observed during the growing cycle, as indicated in Fig. 4. During phases 1, 2 and 4, the $-\bar{w}$ was most prominent. In phase 3, $+T_{in}$, had the most influence. For phase 5, $+ws$ indicated the highest estimated parameters. However, concerning the maximum values of m up to $202 \mu\text{g m}^{-3}$ (Fig. 4), the estimated parameters of -0.31 was assumed to be the greatest FOI.

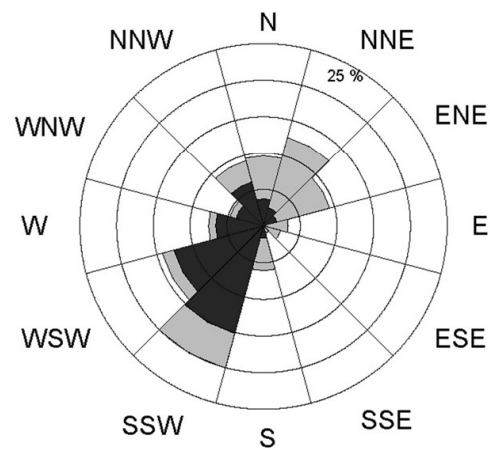


Fig. 7 – Wind frequency distribution ($z/h = 2.3$) with 12 wind sectors of 30° (letters label name of sectors): Each circle presents 5% of occurrence; light grey = atmospheric NH_3 concentration $<10 \mu\text{g m}^{-3}$, dark grey = atmospheric NH_3 concentration $>10 \mu\text{g m}^{-3}$. E to WSW and W to ENE are referred to as leeward side and windward side, respectively.

Table 2 – Estimated parameters and coefficient of determination (R^2) for a multiple regression model on the entire data range; including factors-of-influence (FOI) as independent variables; and \log_e of NH_3 concentration in the air (c_{out}) as dependent variable.

m^a (kg h^{-1})	T_{out}^a ($^{\circ}\text{C}$)	T_{in}^a ($^{\circ}\text{C}$)	\bar{w}^a (m s^{-1})	\bar{ws}^a (m s^{-1})	σ_w^a ($\text{m}^2 \text{s}^{-2}$)	σ_{ws}^a ($\text{m}^2 \text{s}^{-2}$)	L^a (m)	day_{gc}^a	dH^a (m)	R^2
	0.03	0.05	–5.11	–0.22				0.11	–0.05	0.89

a Empty cells indicate no significant relationship ($p > 0.05$).

3.3.3. MLR of FOI on subsets of data for separate wind directions (leeward and windward)

For an investigation of FOI on measured c_{out} , it was necessary to take into account the location of the monitoring point and analyse the wind sectors separately. The following models used subsets of data. These considered the difference between the leeward and windward sides; taking into account the relationship between FOI and measured c_{out} (Fig. 7). The model for the leeward side yielded five FOI for describing the variance of measured c_{out} ($R^2 = 0.9$). The corresponding model for the windward side showed three FOI that had a significant effect (Table 4).

Both models show $-\bar{w}$ and $+\text{day}_{\text{gc}}$ as main influences. Further, $-\bar{ws}$ and $-dH$ (from the leeward side model) are the most significant estimated parameters used to explain the measured c_{out} .

3.3.4. MLR of FOI on subsets of data for separate wind directions and atmospheric conditions

Table 5 depicts four models of MLR on subsets of data that represent a combination of Table 4 along with additional information on atmospheric stability (Eq. (7)). In all investigated models, $+\text{day}_{\text{gc}}$ acted as the main estimated parameter, except for the combination windward/unstable. The estimated parameters $-\bar{w}$ and $-\bar{ws}$ were the most influential factors during both stable and unstable atmospheric conditions on the leeward side of the monitoring tower. Only $-\bar{w}$ proved to have a significant influence during stable atmospheric conditions on the windward side.

ventilation system guaranteed the desired internal air temperature inside the barns.

The mean annual emission rate, estimated from the data of this study ($0.02 \text{ NH}_3 \text{ kg broiler}^{-1} \text{ a}^{-1}$), was consistent with the data reported by the German Technical Instruction on Air Quality Control (TA-Luft, 2002). In this TA-Luft (2002) document, the factor $0.05 \text{ kg NH}_3 \text{ a}^{-1} \text{ broiler}^{-1}$ represents a mean value, taking both winter and summer emission rates into consideration. Ventilation rates are higher during the summer and this in turn produces higher emission rates. Therefore, the mean factor reported here was lower than the one given in TA-Luft (2002), because this study was conducted during the winter.

Fig. 5 indicated only a slight influence of NH_3 -mass-flow out of the broiler barn in relation to the NH_3 concentration measured at the monitoring tower. The weak correlation of $R^2 = 0.18$ between both points indicated that external factors (FOI) were strongly influential and had to be taken into consideration. Thus, by applying an MLR, the relationship between FOI and the measured atmospheric NH_3 was described.

The general non-restrictive model used allowed for the inputting of data without having to filter that data according to any special criteria. The model shown in Eq. (13) represents the data recorded over the whole growing cycle. This model could interpret 89% of the total variance of c_{out} by using six FOI. This appears to justify the choice of this model. The estimated parameter with the high negative value ($-$) of \bar{w} was surprising. In general, \bar{w} ranges from 0.001 to 0.01 (Stull, 1988), in contrast to values of -0.4 and 1.3 m s^{-1} that were measured during the growing cycle.

This fact suggested a strong influence of dH when considering the mechanical and buoyancy forces exerted by ventilation system (Fig. 6). It can be assumed that the rising NH_3 emissions continued their physical upward rise above the stacks, which means that the plumes rose above the measuring device (monitoring point), fixed at $z/h = 2.3$, without being measured. A seemingly contradictory relationship was thereby observed, since it was possible to detect an increased

4. Discussion

The results indicated that the increasing NH_3 -mass-flow out of twelve broiler barns during the growing cycle resulted from increasing ventilation rates during the same period. The

Table 3 – Estimated parameters and coefficient of determination (R^2) for a multiple regression model for subsets of time-limited data; including factors-of-influence (FOI) as independent variables; and \log_e of NH_3 concentration in the air (c_{out}) as dependent variable.

Time period	m^a (kg h^{-1})	T_{out}^a ($^{\circ}\text{C}$)	T_{in}^a ($^{\circ}\text{C}$)	\bar{w}^a (m s^{-1})	\bar{ws}^a (m s^{-1})	σ_w^a ($\text{m}^2 \text{s}^{-2}$)	σ_{ws}^a ($\text{m}^2 \text{s}^{-2}$)	L^a (m)	day_{gc}^a	dH^a (m)	R^2
1			0.14	–5.85	–0.41					–0.21	0.86
2	–0.89		–0.26	–5.66					0.31		0.85
3			0.13				1.01 E ^{16}		0.05	0.04	0.92
4				–5.82				0.002			0.94
5	–0.31		0.24		0.36					0.12	0.98

a Empty cells indicate no significant relationship ($p > 0.05$).

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Table 4 – Estimated parameters and coefficient of determination (R^2) for a multiple regression model on subsets of leeward and windward sides data; including factors-of-influence (FOI) as independent variables; and \log_e of NH_3 concentration in the air (c_{out}) as dependent variable.

	m^a (kg h^{-1})	T_{out}^a ($^{\circ}\text{C}$)	T_{in}^a ($^{\circ}\text{C}$)	\bar{w}^a (m s^{-1})	\bar{ws}^a (m s^{-1})	σ_w^a ($\text{m}^2 \text{s}^{-2}$)	σ_{ws}^a ($\text{m}^2 \text{s}^{-2}$)	L^a	day_{gc}^a	dH^a (m)	R^2
Leeward			0.05	–5.22	–0.3				0.11	–0.04	0.90
Windward		0.06		–5.49					0.10		0.86

a Empty cells indicate no significant relationship ($p > 0.05$).

concentration of atmospheric NH_3 during a downward flow of \bar{w} . This meant that while the NH_3 concentrations rose (positive values), the three estimated parameters of \bar{w} , \bar{ws} and dH (Table 2) sank (i.e. had negative values).

Within this general non-restrictive model, it was found that the $+\text{day}_{gc}$ had the highest effect. An increase of day_{gc} showed an increase of m because they are mutually dependent (Eq. (12)). This fact was attributed to the higher ventilation rates and an increase of internal NH_3 concentrations that resulted from the birds growing older. These results were consistent with the study of Redwine et al. (2002).

In order to understand better the relationship between FOI and measured c_{out} , subsets of data were considered separately. The results of these different MLR on subsets of data (Tables 3–5) demonstrated a good correlation ($R^2 > 0.83$). This evidence suggested that the decision to use these FOI in the models was justified. In all the models in Tables 3–5, an estimated parameter with a high negative value (–) of \bar{w} was observed, which further supported the assumption of a strong influence of dH , as already mentioned above in the reference to the general non-restrictive model (Eq. (13)).

An exception to this observation was seen in periods 3 and 5 (Table 3). In this model, the internal conditions, indicated by T_{in} as the highest significant estimated parameter, may have affected the NH_3 in the air. In period 5 the highest NH_3 emissions were recorded ($202 \mu\text{g m}^{-3}$). In order to explain this result, the main influencing factor, dH , was taken into consideration. It was, however, only 16 m high, which was comparatively low. Therefore, it could be assumed that the monitoring device could capture only a part of the NH_3 plume. When the NH_3 plume was comparatively low, the \bar{w} was also low.

In contrast, \bar{ws} of up to 5.3 m s^{-1} pointed to a mainly horizontal transport of NH_3 through the air. When the winds

blew from the sector between the NNE and NNW, they blew over the whole area of the broiler farm. This led to an enrichment of NH_3 in the air (Fig. 3a, b). This may explain the high peaks of NH_3 in the air during period 5. It seems, then, that the interaction of the various significant estimated parameters of the models could explain the NH_3 concentrations that were measured. Because of the location of the monitoring tower, relative to the NH_3 sources (the surrounding broiler barns), an investigation of FOI within the leeward and windward side was the proper approach (Table 4). The model of the leeward side explained the atmospheric NH_3 with five estimated parameters, while it was showed that the $-\bar{w}$ exerted the main influence. It should be noted that the air blowing from the leeward direction reached the monitoring tower after sweeping over the surrounding woodland area, without picking up any traces of NH_3 . Nevertheless, the sensor detected NH_3 in the air. The reason for this was that wind from the windward side transported NH_3 -laden air to the sensor. Obviously, a complex interaction of FOI took place during the transportation of NH_3 through the air. Both of the significant mean-transport processes, vertical and horizontal (\bar{w}, \bar{ws}), transported the NH_3 in the air from the windward side back to the sensor. These estimated parameters with negative values (–), seen in Table 4, illustrated a fast-sweeping transport of NH_3 past the sensor. Therefore, it is probable that only fractions of the airborne NH_3 were measured.

The atmospheric stability affects the dispersion of NH_3 (Oke, 1987). Therefore, we included this information when considering the leeward and windward side-winds (Table 5). The calculated models for the leeward side (Tables 4 and 5) coincided well with respect to their significant FOI. When comparing the atmospheric conditions there was a more extensive exchange of NH_3 in the air during unstable

Table 5 – Estimated parameters and coefficient of determination (R^2) for a multiple regression model on subsets of leeward and windward sides and atmospheric stability data; including factors-of-influence (FOI) as independent variables; and \log_e of NH_3 concentration in the air (c_{out}) as dependent variable.

	m^a (kg h^{-1})	T_{out}^a ($^{\circ}\text{C}$)	T_{in}^a ($^{\circ}\text{C}$)	\bar{w}^a (m s^{-1})	\bar{ws}^a (m s^{-1})	σ_w^a ($\text{m}^2 \text{s}^{-2}$)	σ_{ws}^a ($\text{m}^2 \text{s}^{-2}$)	L^a (m)	day_{gc}^a	dH^a (m)	R^2
Leeward/ unstable			0.06	–6.3	–0.36				0.13	–0.05	0.90
Windward/ unstable										0.08	0.83
Leeward/ stable			0.06	–4.04	–0.22				0.10		0.92
Windward/ stable		0.08		–8.24					0.11		0.90

a Empty cells indicate no significant relationship ($p > 0.05$).

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situations. This was verified by the higher values of $-\bar{w}$ and $-\bar{ws}$ (Table 5). Nevertheless, the sensor measured some NH_3 while the wind blew from the leeward side, although there were no sources of NH_3 on that side. This fact confirmed the complex interaction of FOI for transporting NH_3 through the air to the sensor. Therefore, it must be assumed that NH_3 was transported back to the sensor from the windward side by two mechanisms; by reverse winds and by winds blowing downwards from NH_3 -laden air above the monitoring device.

Wind from the windward side passed over the whole area of the broiler barns and accumulated NH_3 on the way. This shows that m , although it is not a significant estimated parameter, did have an indirect effect on the c_{out} because of the interrelationship of m and day_{gc} . For that reason, day_{gc} was included in all windward side investigating models (Tables 4 and 5). During unstable atmospheric conditions, day_{gc} was the only significant estimated parameter. Under optimal atmospheric dispersion conditions (unstable), a direct flow of emitted NH_3 out of the broiler barns towards the monitoring device could be assumed.

In contrast, a stable atmosphere restricts dispersion. This may therefore explain why $-\bar{w}$ was the highest factor under stable atmospheric conditions (Table 5).

The predictive ability of the various models in Tables 2–5 was effective and this suggests that they could be used to estimate NH_3 in the air under the experimental conditions described in this paper. It is important to note that the models presented here used data that was based on one particular growing cycle. Future work will be required to further enhance the models. By upgrading the data records, the accuracy of predicting the concentrations of NH_3 in the air will be improved. However, when information about FOI is available, specific models, in principle, should be able to improve the accuracy in predicting the presence of NH_3 in the air. Appropriate atmospheric local-scale models (e.g. LADD) could be used to evaluate the potential of FOI-impact on a given broiler farm; in relation to the concentration of atmospheric NH_3 . It should be noted, however, that the conditions would have been similar to those listed in Tables 2–5.

5. Conclusions

This study reports an observation of the time-series of NH_3 emissions from a broiler farm during one growing cycle. It also measured the amounts of NH_3 in the air using a device mounted on a monitoring tower located on the farm grounds. In order to describe the variance in the measurements of NH_3 in the air, certain FOI were defined. Multiple linear regressions (MLRs) were implemented to analyse the relationship between the FOI and the NH_3 in the air. Overall, the precision of the predictive models was good ($R^2 > 0.83$). In nearly all models, the mean vertical wind component played a role and proved to be the most influential factor. This fact suggested that the height of the air coming out of the stacks of the broiler barns strongly influenced the elevation of the exhaust fumes. Considering the effects of the ventilation system, it can be assumed that emitted NH_3 plumes rose above the height of the monitoring tower. The sensor at the monitoring tower detected NH_3 in the air even when the wind blew over an area

without sources of NH_3 (i.e. the wooded area surrounding the farm). This observation implied that NH_3 -enriched reverse winds blew back in the direction of the monitoring tower. It also implied that a downward flow of NH_3 -enriched air reached the measuring device and was detected. These partially unexpected processes should be considered in any future study focussing on the spatial dispersion of NH_3 in the air. Local-scale atmospheric models can be evaluated and improved by applying sufficient input data. However, by monitoring specific FOI, it is possible to apply models for predicting atmospheric NH_3 concentrations. Future improvements of the MLR models should focus on an upgrade of the data records in order to further improve the accuracy of predicting the presence of NH_3 in the air.

In order to determine the best monitoring methods, it is important to consider the location of the monitoring tower. The optimal location can be found by assessing the environmental impact of NH_3 in the air at one particular location. Thus, pinpointing the proper location for the tower is essential for a successful and accurate outcome. Measuring at various spatial points simultaneously (e.g., by employing passive-samplers) should be attempted in future studies in order to gain more accurate information about the spatial dispersion patterns of NH_3 in the air. However, a possible disadvantage of doing this is that the high time resolution could be reduced. Further, logistical and set-up constraints have to be considered when working with numerous instruments in closely packed farm surroundings. Bearing this in mind, a compromise in the form of a combination of both measuring methods has to be found.

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Appendix C:

Paper III Ammonia emissions from a broiler farm: spatial variability of concentrations in the vicinity and impacts on adjacent woodland

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H.-J. Müller, D. Scherer and B. Strohbach**

Ammonia emissions from a broiler farm: spatial variability of concentrations in the vicinity and impacts on adjacent woodland

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Abstract

Agricultural NH₃ emissions affect air quality and influence the nitrogen cycle. In the present study, NH₃ emissions from a broiler farm and resulting atmospheric concentrations in the immediate vicinity during three growing cycles have been quantified. Additionally, vegetation along a transect through an adjacent woodland were analysed. The resulting emissions amounted to up to 10 kg NH₃ h⁻¹ and atmospheric concentrations ranged between 33 and 124 µg NH₃ m⁻³ week⁻¹ in the immediate vicinity. Measurements of atmospheric concentrations over seven weeks showed a substantial decline of mean concentrations (three weekly mean) from ~13 to <3 µg NH₃ m⁻³, at 45 and 415 m distance from the farm. Vegetation surveys showed an increase of nitrophilous species with decreasing distance from the farm. Clearly visible damage of pines was observed within 200 m distance from the farm, illustrated the significant impacts of NH₃ emission from agricultural sources on sensible ecosystem.

Keywords: ammonia; broiler; emission; spatial dispersion; woodland flora

Introduction

Ammonia (NH_3) as a nitrogen compound emission has a profound effect on air quality. The need for food in a world of growing numbers of people leads to increased agricultural emissions of atmospheric NH_3 (Aneja et al. 2001). In Europe, more than 90% of atmospheric NH_3 is related to agriculture emissions which further enhance the current perturbation of the nitrogen cycle (Erisman et al. 2008). Livestock industry represents the largest source of NH_3 and creates significant hot spots of atmospheric NH_3 concentration (Theobald et al. 2004). The distribution of these sources in the countryside and their variability in magnitude and time is responsible for the spatial occurrence of high NH_3 concentrations (Fowler et al. 1998). As the dominant gaseous base present in the atmosphere, NH_3 is important for neutralising acid products and for particulate ammonium formation (NH_4^+) (Warneck 1988; Sutton et al. 1993). Ammonia is very reactive and, therefore, its lifetime is relatively short. However, the atmospheric residence time could be extended to up to one week when converted into particulate NH_4^+ . Hence, it can be transported across much longer distances (Aneja et al. 2001; Erisman et al. 2007). Deposition of both, gaseous NH_3 and particulate NH_4^+ , result in a major perturbation to ecosystems.

Deposition rates depend on type of land use and surface roughness (Skiba et al. 2006). Deposition rates can be two to three times larger in a forest than over low vegetation (Fowler et al. 2004). Fowler et al. (1998) found that concentrations of emitted NH_3 from a poultry farm to the woodland, declined to background levels within 300 m distance. Deposition of gaseous NH_3 and particulate NH_4^+ may cause effects such as acidification of soils, enhanced eutrophication of water bodies, forest decline or decreasing biological diversity (Sutton et al. 1993; Fangmeier et al. 1994; Sutton et al. 1995; Ferm 1998; Krupa 2003). Transect studies at intensive livestock farms in the UK showed the impact of atmospheric NH_3 on woodland ground flora (Pitcairn et al. 1998, 2002). It is important to quantify the spatial scale of near-source variability and to know where environmental impacts are expected to assess the effects of NH_3 emissions and to minimize their influence on the environment (Sutton et al. 1998; Aneja et al. 2008). The emission of NH_3 and the occurrence of atmospheric NH_3 are strongly influenced by various local factors (Erisman et al. 2005). Owing to the relevance of gaseous NH_3 , it is included in different agreements: UNECE (UNECE 1999), the European Union National Emissions Ceilings Directive (2001/81/EC) and the EU Directive on Integrated Pollution Prevention and Control (IPPC, 2008/1/EC).

The assessment of impacts of atmospheric NH_3 requires its reliable quantifying. Monitoring of atmospheric NH_3 concentrations is challenging due to their spatial and temporal variations. A variety of different NH_3 measurement techniques exist which use different methodologies, summarised and compared in Erisman et al. (2001), Clemmshaw (2004), von Bobrozki et al.

(2010). Concerning its simplicity and cost effectiveness, passive sampling is a widely used practical technique (Namiesnik et al. 2005; Seethapathy et al. 2008). The theoretical basis of passive sampling was described in detail by Fowler (1982) and Brown (1993).

The objectives of this study have been to quantify NH₃ emissions from a large broiler farm and to evaluate the spatial occurrence of atmospheric NH₃ concentration in the vicinity as well as along a transect through the woodland adjacent to the farm. Additionally, the influence of atmospheric NH₃ to surrounding woodland vegetation with increasing distance from the farm was analysed.

Ammonia concentrations and air flow rate in a large broiler house (62000 broilers) were measured during three growing cycles. At the same time, atmospheric NH₃ concentrations close to the large farm were documented using passive samplers. Furthermore, the composition of plant communities was compared at three sites with increasing distances from the farm. A detailed evaluation of local impacts of NH₃ emissions of an intensive livestock farm (within ~400 m distance) on the surrounding mixed woodland vegetation was conducted.

Materials and Methods

Study site

Measurements took place in and around a broiler farm which covers an area of about six hectares. The farm is surrounded by a forest (dominated by pines). Details of the location, livestock and surrounding vegetation are summarised in Table 1. The arrangement and location of the twelve broiler houses within the forest can be taken from Fig. 1.

Table 1 Site description and surrounding vegetation.

Location	Livestock	Housing and ventilation system	Main Vegetation
Broiler farm: SE of Berlin / Germany	382200 broilers ^a	9 smaller houses ^b (each 21800 broilers) with side forced ventilation	Mature mixed woodland of pines and black locust, Scattered with sessile and common oaks with some birches. Ground flora of <i>Avenella flexuosa</i> and <i>Calamagrostis epigejos</i>
Weather station: SW of the broiler farm	(farmed on a 36-day cycle 7-8 times per year)	3 bigger houses ^c (each 62000 broilers) with controlled fans and 18 rooftop stacks ^d	

^a 1.5 - 1.8 kg slaughter mass

^b length 88 m, width 12 m, height 3.5 m, see *a* in Fig. 1

^c length 93 m, width 29 m, height 4.5 m, see *b* in Fig. 1

^d additional working gable fans during summertime

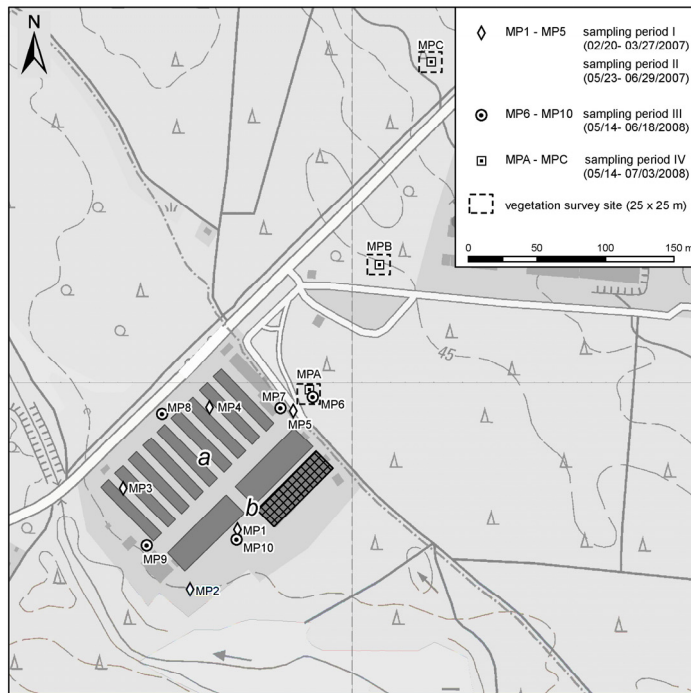


Fig. 1 Site plan with all monitoring points (MP) for sampling period I-IV; the hatched house represents the investigated broiler house; a and b mark the smaller and bigger broiler houses, respectively.

The operation of the ventilation system was controlled by the internal temperature of the broiler houses, which differs between 22-34°C depending on the age of the broilers.

All broiler houses were operated by an all-in/all-out management. Owing to the large number of broilers in all houses, it was not possible to bring all broilers to slaughter at the same time. This fact caused a few day shift of the period of the growing cycle between single broiler houses. Between growing cycles, all broiler houses were cleaned and sanitized during the service period which lasts about seven days. Sawdust was used as bedding material.

The weather conditions are documented by wind direction (*wd*), air temperature (*T*) and relative humidity (*RH*), provided as hourly values by a weather station of the German weather service (DWD), situated 20 km away from the farm (Table 1). Generally, the climate at the location can be described as continental with a mean annual precipitation of 500 to 560 mm and a mean annual temperature from 18.5-20°C. The prevailing *wd* of the study site is SW and NE.

Measurements

The emissions were analysed during three growing cycles (I: 02/19/2007-03/27/2007, II: 05/20/2007-06/27/2007, III: 05/14/2008-06/19/2008). According to Eq. 1, the emissions were calculated as the NH₃-mass-flow (m). The NH₃ concentration (c_{in}) and the air flow rate (q) were measured in one of the larger broiler houses with 62000 broilers (hatched broiler house in Fig. 1) close to the exhaust air outlets. Air flow rate was accumulated per hour, while the NH₃ concentration was averaged per hour. These values were used to extrapolate the total farm NH₃ emission. First, the NH₃-mass-flow was calculated for a single broiler. The resulting value m was then multiplied by the total number of 382200 broilers which were raised during a growing cycle.

$$m = c_{in} * q \quad (1)$$

Higher temperatures during summer time caused an operation of additional gable fans. This fact resulted in strong fluctuations of the ventilation rate and the NH₃-mass-flow. Therefore, the hourly data of the investigated growing cycles were plotted as a moving average across 25 values.

All used devices are listed in Table 2.

Table 2 Summary of used variables and characteristics of techniques.

Variable	Manufacturer	Measuring height	Units	Sampling rate	Accuracy	Detection limit
Internal concentration of NH ₃ (c_{in})	Photoacoustic field gas monitor INNOVA 1312 UA 0973 filter	4 m	mg m ⁻³	1 min at each of 12 points	<1%	0.2
Air flow rate (q)	Measurement ventilators	4 m	m ³ h ⁻¹	every 10 min at 18 points	-	-

Atmospheric NH₃ concentration was measured around the farm at five monitoring points (MP) with badge-type A samplers. More details are given in Table 3. Along a transect through the forest adjacent to the farm samplers of badge-type B were installed at three points (MPA-MPC) at different distances from the farm (45, 205, and 415 m). Sampler mechanics rely on diffusion through an air-gap ('tubes' e.g. Campbell 1988; Brown and Wright 1994; Cocheo et al. 2008) and on permeation through a membrane ('badges' e.g. Ferm 1991; Löflund et al. 2002). More details, concerning design and functionality of used passive samplers are described by Ferm (1991), Kasper and Puxbaum (1994).

The MPC at 415 m distance from the farm could be interpreted as a 'background' site (Fig. 1). The sampling measurement height was 2 m above ground and the samplers were

protected by a rain shield against environmental impact. According to the EU recommendation (DIN-EN 13528-3), samplers can be applied as an indicative method.

Table 3 Summary of the implemented passive samplers for sampling periods I: 02/20/2007-03/27/2007, II: 05/23/2007-06/29/2007, III: 05/14/2008-06/18/2008 for badge-type sampler A and IV: 05/14/2008-07/03/2008 for badge-type sampler B.

Label	Type	Collecting medium	Analytical method	Exposure Time (weeks)	Detection limit ($\mu\text{g m}^{-3} \text{ week}^{-1}$)	Number of monitoring points	Number of replications
A	Badge	Impregnated filter (citric acid)	Indophenol segment flow analyser	1	0.3	5	4
B	Badge	Impregnated filter (citric acid)	Flow Injection Analysis (FIA)	3	0.8	3	1

Vegetation surveys

At three sites (255 m²; 25 m x 25 m) at three different distances (45, 205 and 415 m) from the broiler farm vegetation surveys were performed during the sampling period IV (Fig. 1). In the following, these three sites are referred to as site A-C, respectively. The surveys along this transect focused on quantifying the frequency and degree of cover of the major plant species. Thereby, flora species were graded into tree layer, shrubs, herbs and mosses.

Defoliation and needle yellowing were observed on six representative pines (*Pinus sylvestris*) sample at each investigated site. Forest vitality was assessed according to damage classes (Table 4) used for rating of forests in German lowlands (Kallweit and Böttinger 2001).

Table 4 Damage classes according to Kallweit and Böttinger (2001).

Defoliation class		Discoloration class / Yellowing (%)				Damage class
Defoliation class	Defoliation (%)	1	2	3	4	
		0-10	11-25	26-60	61-100	
1	0-10	1	1	2	3	
2	11-25	2	2	3	3	
3	26-60	3	3	4	4	
4	61-99	4	4	4	4	
5	100	4	4	5 (dead)		

The damage classes can be characterized as followed: 1 to 2 assign to vital growing and barely damaged stock, whereas 4 and 5 show significant damages due to pollutants.

Results and discussion

Ammonia emissions

Owing to the same processes of broiler rearing over all periods, the NH_3 -mass-flow (m ; Eq. 1) out of the twelve broiler houses increased to the same degree throughout the three growing cycles (Fig. 2a). This rise resulted from the growth of the broilers and their increased activity. As a consequence, higher ventilation rates were required to guarantee the desired internal temperatures, whereby the NH_3 -mass-flow increased. These facts were consistent with the observations of Blanes-Vidal et al. (2008) which stated that animal activity and ventilation flow are the major factors influencing the variability of NH_3 emissions.

At the beginning of all growing cycles, high internal temperatures of 30-34°C in the broiler houses were required. This fact resulted in low ventilation rates to keep the default temperature. During the first ten days in all investigated growing cycles similar pattern of m occurred. Owing to the low excretion levels of the young animals, less than 2 kg $\text{NH}_3 \text{ h}^{-1}$ were measured within this time. In contrast, the external temperatures obviously did not affect m (Fig. 2b). Afterwards, the external temperatures and increasing excretion rates of growing broilers had a higher influence on m during all three observed growing cycles.

Higher temperatures and ventilation rates caused NH_3 mass flow of maximum 10 kg $\text{NH}_3 \text{ h}^{-1}$ at the end of growing cycle III. The direct correlation between increasing internal NH_3 concentration and increasing broiler age has been confirmed by other studies (Redwine et al. 2002). Bessei (2006) reported thermal discomfort of the animals inside the broiler houses at the end of the growing cycle due to increasing stocking density. Therefore, he recommended considering the physical conditions of broilers in addition to environmental factors.

Ammonia emissions varied between 0.02 and 0.03 kg $\text{NH}_3 \text{ broiler}^{-1} \text{ a}^{-1}$, assuming eight growing cycles per year. For comparison, in the German technical instruction on air quality control (TA-Luft 2002) a factor of 0.05 kg $\text{NH}_3 \text{ a}^{-1} \text{ broiler}^{-1}$ is assumed. This factor (TA-Luft 2002) represents a mean of winter and summer emission rates with forced ventilated broiler houses and is therefore higher than 0.03 kg $\text{NH}_3 \text{ broiler}^{-1} \text{ a}^{-1}$, observed in this study. Gates et al. (2008) calculated 0.09 kg $\text{NH}_3 \text{ a}^{-1} \text{ broiler}^{-1}$ during five 40-day growing cycles per year in a forced ventilated broiler houses with a slaughter mass per broiler of 2.1 kg. This implies that the NH_3 emissions, measured here over the three growing cycles, were relatively low.

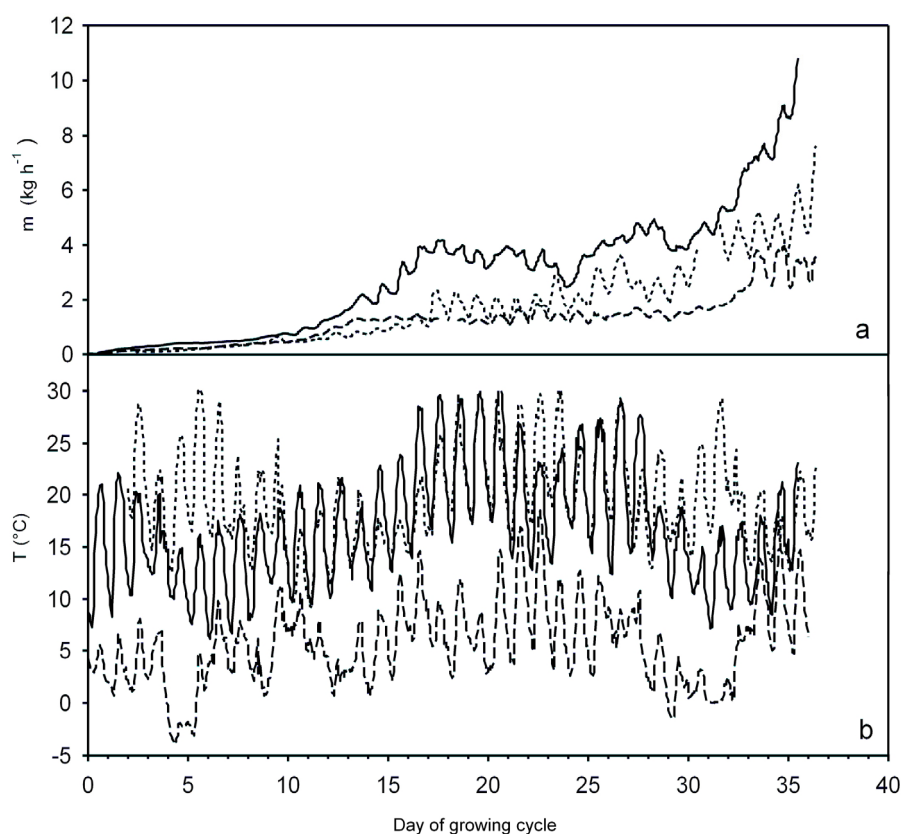


Fig. 2 Time series of (a) external temperatures (T) at DWD weather station, (b) NH_3 -mass-flow (m) out of twelve broiler houses for growing cycle I: 02/20/2007-03/27/2007 (dashed line), II: 05/23/2007-06/29/2007 (dotted line) and III: 05/14/2008-06/18/2008 (solid line).

Atmospheric NH_3 concentrations

Figure 1 shows an overview of the location of the passive samplers at the MP during the three observed sampling periods. Related weekly averages of atmospheric NH_3 concentrations and meteorological conditions (wd , RH , T) are summarised in Tables 5-7.

Prevailing wind directions in growing cycle I, II and III were from W to SW, E to SE and NE to SE, respectively. During sampling periods I-III, measured atmospheric NH_3 concentrations increased over time due to rising NH_3 emissions out of the broiler houses (Fig. 2a). The measured concentrations were higher in summer ($123.9 \pm 4.4 \mu\text{g m}^{-3}$; sampling period II, week 5, MP4) than in winter ($33.0 \pm 2.3 \mu\text{g m}^{-3}$; sampling period I, week 5, MP1). This observation agreed well with studies of Buijsman et al. (1998) and Thöni et al. (2004). The lower atmospheric NH_3 concentration in winter is attributed to the reduced volatility of NH_3 at lower temperatures and the generally higher relative humidity during this season (Seethapathy et al. 2008).






High atmospheric NH₃ concentrations occurred in sampling period I, week 5 at MP3 and in sampling period II, week 5 at MP5. This might be caused by starting the collection of broilers for slaughtering in the broiler house near MP5. In this case, the broiler houses were opened when the growing cycle ended and high NH₃ concentration were emitted. In further analyses, results of MP5 were omitted.

Relative standard deviations (RSD) in Tables 5-7 were in the range of 0.1-11.2%. This agreed well with results of Kirchner et al. (1999) which reported RSD = 15.2%, valid for the same badge-type samplers with one week exposure. Further, Kirchner et al. (1999) obtained smaller RSD at longer exposure time. In the same study, an overall uncertainty of 75% for one week exposure was detected. For each MP during sampling period I-III four replicates of the badge-type A samplers were used. Zimmerling (2000) and Hinz et al. (2008) reported a RSD of 10-20% of measured atmospheric NH₃ concentration between each replicate. These numbers indicate the range of measured variation of atmospheric NH₃ concentrations and should be considered when the results of passive samplers were interpreted and evaluated.

The observed atmospheric NH₃ concentrations showed varying concentration patterns due to the different spatial positions of the MPs relative to the surrounding broiler houses and the prevailing *wd*. Thereby, atmospheric NH₃ concentrations were highest when a MP was located within the prevailing wind direction.

In case of MP4 and MP5 (sampling period I and II) and MP6 and MP7 (sampling period III) atmospheric NH₃ concentrations were higher than those of other MP. This fact was caused by wind originated from SW which transported air enriched with NH₃ from the whole area of the farm. For NE wind similar observations for MP 9 (sampling period III) were carried out.






Table 5 Weekly averages of wind direction (*wd*), relative humidity (RH), temperature (T) and atmospheric NH₃ concentration for sampling period I: 02/20/2007-03/27/2007.

Week	1		2		3		4		5	
<i>wd</i>										
<i>RH</i> (%)	83.8		87.2		77.5		78.1		75.9	
<i>T</i> (°C)	3.0		5.1		8.2		6.7		5.8	
	NH ₃		RSD ^b		NH ₃		RSD ^b		NH ₃	
MP1 ^a	4.2	0.9	9.5	0.6	13.9	1.4	27.4	1.8	33.0	2.3
MP2 ^a	4.2	1.0	3.5	0.2	4.4	0.6	7.6	1.3	10.9	1.9
MP3 ^a	4.3	0.1	8.9	0.3	17.2	2.6	19.1	0.9	130.1	3.8
MP4 ^a	2.7	0.3	16.1	0.7	21.1	2.1	28.3	5.2	26.5	4.0
MP5 ^a	5.6	0.8	13.5	3.0	20.2	2.5	29.7	3.2	26.5	3.8

^a MP: monitoring point

^b RSD (%): relative standard deviation






Table 6 Weekly averages of wind direction (*wd*), relative humidity (*RH*), temperature (*T*) and atmospheric NH₃ concentration for sampling period II: 05/23/2007-06/29/2007.

Week	1		2		3		4		5	
<i>wd</i>										
<i>RH</i> (%)	78.4		80.8		59.1		67.3		79.0	
<i>T</i> (°C)	19.1		16.3		20.1		20.7		16.4	
	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b
MP1 ^a	9.0	4.4	16.9	1.1	28.1	5.2	43.5	3.8	46.9	3.6
MP2 ^a	5.51	1.3	12.7	1.5	15.7	2.4	18.2	1.2	10.5	1.4
MP3 ^a	15.9	9.8	17.0	5.5	54.6	9.5	64.7	4.7	41.6	1.1
MP4 ^a	8.3	0.7	15.1	0.5	45.1	4.3	115.2	11.2	123.9	4.4
MP5 ^a	7.8	0.4	6.4	0.7	17.2	1.7	79.5	4.4	231.7	45.0

^a MP: monitoring point

^b RSD (%): relative standard deviation

Table 7 Weekly averages of wind direction (*wd*), relative humidity (*RH*), temperature (*T*) and atmospheric NH₃ concentration for sampling period III: 05/14/2008-06/18/2008.

Week	1		2		3		4		5	
<i>wd</i>										
<i>RH</i> (%)	69.5		66.2		45.6		49.1		68.9	
<i>T</i> (°C)	13.8		15.1		21.9		20.6		14.0	
	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b	NH ₃	RSD ^b
MP6 ^a	5.4	0.7	4.4	0.2	5.8	0.5	7.1	0.9	29.1	2.7
MP7 ^a	5.2	0.5	5.0	0.9	6.2	0.3	6.8	0.2	30.8	1.7
MP8 ^a	6.2	0.7	9.9	1.0	20.8	0.6	13.3	0.7	33.4	4.8
MP9 ^a	8.2	0.5	16.6	1.0	28.5	1.2	37.0	2.3	72.6	1.1
MP10 ^a	7.5	1.2	8.6	0.3	7.8	1.0	11.4	1.5	26.4	0.9

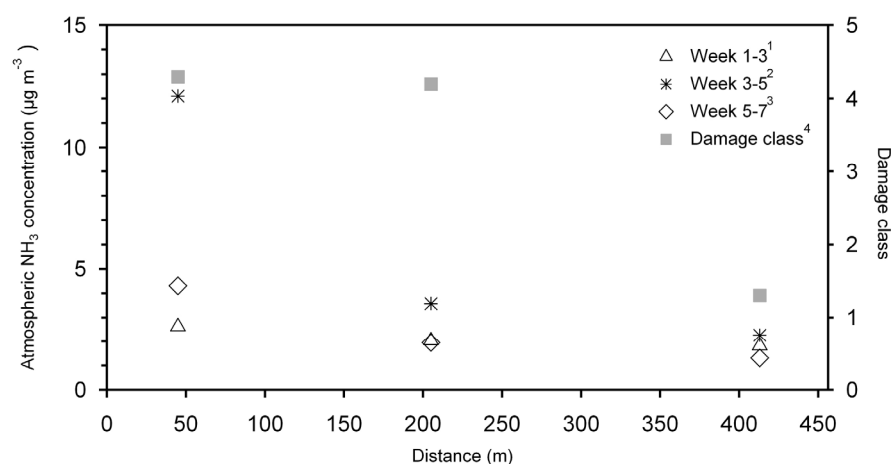
^a MP: monitoring point

^b RSD (%): relative standard deviation

Relationship between atmospheric NH₃ concentration and distance

Three-week means of atmospheric NH₃ concentrations along the selected woodland transect (squared markers in Fig. 1) substantial declined with increasing distance from the farm. Average atmospheric NH₃ concentrations close to the farm were highest with 12 µg NH₃ m⁻³ in 45 m, and declined to <3 µg NH₃ m⁻³ in 415 m (Fig. 3). Kirchner et al. (1999) reported a

comparison of different passive samplers, observed over 1, 2 and 4 week exposure. For badge-type B samplers, the overall uncertainty varied between 25 and 16% for 2 and 4 week exposure, respectively. By using an overall uncertainty of 20% as an average of both exposure values, the difference to the average concentration of the three sites at 45, 205 and 415 m distance were ± 1.2 , ± 0.5 and $\pm 0.4 \mu\text{g NH}_3 \text{ m}^{-3}$, respectively. However, the trend of decreasing atmospheric NH_3 concentrations with increasing distance from the source is consistent with observations of Fowler et al. (1998) and Skiba et al. (1998, 2006).



¹ Beginning of growing cycle

² Centre of growing cycle

³ End of growing cycle including service period

⁴ According to Kallweit and Böttinger (2001)

Fig. 3 Atmospheric NH_3 concentration and damage class at corresponding distance from the broiler farm at MPA (45 m), MPB (205 m) and MPC (415 m) for sampling period IV: 05/14/2008-07/03/2008. Prevailing wind direction: week 1-3: SE, week 3-5: NW and E, week 5-7: NW.

Measured atmospheric NH_3 concentrations at the three sites along the transect were influenced by the current status of the growing cycle and the prevailing *wd*. In the following explanations, wind from NE and SW is referred to as downwind and upwind, respectively (Fig. 1).

Sampling period IV was overlapping growing cycle III (Table 3), and therefore largest NH_3 emissions out of the broiler houses occurred in week 3-5 when broilers nearly reached their slaughter mass. During week 1-3 of sampling period IV, atmospheric NH_3 concentrations were mainly sampled under upwind conditions. As a consequence, lower atmospheric NH_3 concentrations were detected compared to downwind condition and corresponding higher NH_3 emissions from the source.

Results in the study of Fowler et al. (1998) showed annual mean atmospheric NH_3 concentrations of $<2 \mu\text{g m}^{-3}$ (NH_3 emission = 4800 kg N a^{-1}) at a distance of 280 m from a

broiler farm. Skiba et al. (2006) reported concentrations of $<2 \mu\text{g NH}_3 \text{ m}^{-3}$ at a distance of 270 m from a broiler farm. The lower atmospheric NH_3 concentrations can be explained by a smaller farm with 160000 broilers per 40-day growing cycle. Thus, the atmospheric concentrations of $<3 \mu\text{g NH}_3 \text{ m}^{-3}$ at a distance of 415 m from the broiler farm, measured during the present study, were the same range. Nevertheless, Pitcairn et al. (2009) observed an adversely affect toward the species composition of ground flora with atmospheric concentrations of $>2 \mu\text{g NH}_3 \text{ m}^{-3}$. Thus, it could be assumed that a negative impact of the broiler farm on the occurring species existed.

Concerning an estimate of the forest vitality, six representative samples of pine trees were evaluated at different distances from the farm. Site A is located close to the farm (45 m) and the discoloration and defoliation on the trees was highest with a mean damage class of 4.3 (Fig. 3). The trees showed significant damages with defoliation $>60\%$ and discoloration of needles $<60\%$ (Table 4). A high portion of the needles was already brown and withered. Subsequently, a needle necrosis can occur with brown discoloration and finally result in death of needles. This process was partly detected on trees at site A. The observed pines at site B yielded a mean damage class of 4.2 which was only slightly smaller, compared with results of site A. Again, the needle loss was $>60\%$. Lots of needles were brown and withered with progressed tendency to needle necrosis. For the representative trees at site C at 415 m distance from the farm (Fig. 3) a damage class of 1.3 was calculated which corresponded to a decline of 70% comparing with 4.3 at 45 m distance from the farm. With an average defoliation and discoloration of needles of up to 10%, this result of site C was in good agreement with the official forest condition report 2008 (Waldzustandsbericht 2008) valid for the investigated region. This report assigned an average crown defoliation of 18% for *Pinus sylvestris*, as the dominant species in the region. Forest vitality at site C could be characterized as a vital growing and barely damaged (Table 4).

The plant canopy can be expected to be a consistent sink for NH_3 (Pryor et al. 2001). Fowler et al. (1998) reported that the efficiency of the foliar surface for NH_3 uptake declines with increasing NH_3 concentration. This fact explains the higher vitality of the investigated species at site C, at increased distance (~ 400 m) from the farm. This finding of a decline of elevated atmospheric NH_3 concentrations over a relative short distance to background concentrations ($<3 \mu\text{g NH}_3 \text{ m}^{-3}$) confirmed the results of Tyndall et al. (2007) and Adrizal et al. (2008). These authors proposed the use of vegetative shelter belts with modest heights (3 to 9 m) near agricultural sources to capture farm emissions. Such shelter belts create a biological filter restricting the pollution to a small local area. The effect of the fast decrease of NH_3 concentrations over a short distance through the adjacent forest is not directly verifiable in the present study, and how high would be the concentration levels without the influence of

the forest still unidentified. Therefore, further investigations are necessary to verify this effect by physically modeling the surroundings in a wind tunnel.

Vegetation surveys

Along the three sites at 45, 205 and 415 m distance from the broiler farm, species diversity of the shrub and moss layer declined. Nitrophilous species such as *Pinus sylvestris*, *Avenella flexuosa* and *Calamagrostis epigejos* dominated all three sites. According to van der Eerden (1982), Fangmeier et al. (1994) and Krupa (2003), these species represent an intermediate to low susceptibility to acute NH₃ injury. Moss community mainly consisted of *Pleurozium schreberi* and *Scleropodium purum*. This vegetation is common to woodlands, but is also associated with nutrient species. The same mosses were detected in studies of Pitcairn et al. (1998, 2002) where woodland flora in the vicinity of livestock farms in the UK was investigated.

The composition of the three sites is shown in Table 8. Site A was dominated by *Avenella flexuosa* and *Calamagrostis epigejos* as herbaceous species. Additionally, the nitrophilous *Pinus sylvestris* and two moos species occurred pointing to an elevated NH₃ input. This is consistent with the observations of Pitcairn et al. (2009), who reported an abundance of *Avenella flexuosa* and *Urtica dioica* close to farms in the UK.

The high occurrence of *Robinia pseudoacacia* at site B led to a largely reduced irradiation at lower vegetation layers and may have contributed to the absence of *Calamagrostis epigejos*. Nevertheless, *Avenella flexuosa* was still dominant within the herbaceous layer. The increasing number of *Pinus sylvestris* was eye-catching and, in contrast the decrease of *Scleropodium purum* within the 200 m distance between site A and B. Fangmeier et al. (1994) detected a low susceptibility of *Scleropodium purum* to NH₃ injury. This fact may therefore partly explain the abundance close to the farm at site A.

Neither the forest vitality diagnosis, nor the vegetation survey could explain the sparse occurrence of *Pinus sylvestris* at site A. An intermediate susceptibility to NH₃ injury of *Pinus sylvestris* (van der Eerden 1982) may explain this observation. Other factors than the high NH₃ impact may also have influenced the vegetation cover at the investigated site.

Species with sensitive susceptibility to acute NH₃ injury, such as *Vaccinium myrtillus* and *Pleurozium schreberi* became more abundant at increased distance from the farm (site C). Many species considered as nitrogen indicators still existed at site C, but their fraction declined. This observation agreed with the study of Pitcairn et al. (2009), who reported that *Pleurocarpus* mosses became more abundant with increasing distance from the farm. Site C was dominated by *Avenella flexuosa* and *Pinus sylvestris*, and could be considered as a more or less undisturbed location. According to Skiba et al. (2004) enhanced nitrogen

deposition may increase the soil mineral nitrogen content; it may also intensify a change in biodiversity. Therefore, it may be possible that the variation in *Avenella flexuosa* abundance is more a response to soil acidification rather than to increased nitrogen supply, as also assumed by Pitcairn et al. (2002).

Table 8 Vegetation survey with cover percentage of species in 25x25 m plot at three sites along the transect of the broiler farm.

Species	Site A (45 m) Cover (%)	Site B (205 m) Cover (%)	Site C (415 m) Cover (%)
Tree layer			
<i>Pinus sylvestris</i>	20	70	70
<i>Robinia pseudoacacia</i>		20	
Shrub layer			
<i>Robinia pseudoacacia</i>	3	20	
<i>Betula pendula</i>	1		
<i>Quercus robur</i>	1		
<i>Quercus petraea</i>	1		
<i>Padus serotina</i>		30	1
<i>Sambucus nigra</i>	0.5		
<i>Sorbus aucuparia</i>		2	1
Herb layer			
<i>Acer pseudoplatanus</i>		1	
<i>Acillea millefolium</i>	1		
<i>Avenella flexuosa</i>	40	40	80
<i>Calamagrostis epigejos</i>	40		0.50
<i>Dactylis glomerata</i>	0.50		
<i>Dryopteris cathusiana</i>		0.50	0.50
<i>Moehringia trinervia</i>	0.50	0.25	0.25
<i>Padus serotina</i>		2	2
<i>Poa nemoralis</i>		5	
<i>Quercus robur</i>		2	1
<i>Quercus petraea</i>	1		
<i>Sorbus aucuparia</i>		1	2
<i>Urtica dioica</i>	1		
<i>Vaccinium myrtillus</i>			15
Moss layer			
<i>Pleurozium schreberi</i>	20	20	30
<i>Scleropodium purum</i>	20		

Conclusions

Ammonia emission from a large broiler farm and the spatial occurrence of atmospheric NH_3 concentrations in the immediate vicinity of the farm were simultaneously monitored during three growing cycles. Additionally, measurements of atmospheric NH_3 concentrations and vegetation surveys along a transect in the woodland, adjacent to the farm were conducted. The NH_3 emitted by the three observed growing cycles increased over time due to the rising excretion rates of growing broilers. Higher ventilation rates were required to guarantee the desired internal temperature level, whereby the NH_3 -mass-flow increased.

Furthermore, the present study focused on the local scale variability and the impacts of atmospheric NH_3 on plant species in the close surrounding of the farm. The farm as a source of NH_3 emission caused a significant increase in atmospheric NH_3 concentrations in the immediate vicinity. The total effect was strongly influenced by the prevailing wind direction. The measured atmospheric NH_3 concentrations were four times higher during summer than in winter. Relative standard deviations up to 11.2% were observed due to the passive samplers used. Within ~400 m distance from the farm, atmospheric NH_3 concentrations rapidly declined, from ~12 $\mu\text{g NH}_3 \text{ m}^{-3}$ in 45 m to <3 $\mu\text{g NH}_3 \text{ m}^{-3}$ in 415 m. It can be concluded that the air pollution was restrained to a small local area by the tree belt and the adjacent woodland. Thus, the long range transport of NH_3 was reduced. The conclusion, rapid reduction of NH_3 concentrations had been occurred due to the effect of the adjacent forest, cannot be proved. Consequently, further studies are indispensable to demonstrate this positive effect by simulating the adjacent environment in a wind tunnel. Atmospheric NH_3 concentrations affected the actual species composition within the 45 to 415 m transect. On *Pinus sylvestris* trees visible injury with defoliation (>60%) and needle discoloration (<60%) was observed, within 200 m distance from the farm. Species number and diversity increased with distance from the farm which was consistent with observations in previous studies. Close to the farm, a prevalence of nitrophilous species and a lack of nitrogen sensitive species were observed. At a distance of 415 m from the farm, still many species existed which were considered as nitrogen indicators, but with decreasing abundance. This observation illustrated the significant spatial impacts of NH_3 emission from agricultural sources on sensible ecosystem, considering the risk of loss and change in biodiversity.

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Appendix D:

Contribution of author to included papers

Paper I

K. von Bobruzki^{1,2}, C.F. Braban¹, D. Famulari¹, S.K. Jones¹, T. Blackall³, T.E.L. Smith³, M. Blom⁴, H. Coe⁵, M. Gallagher⁵, M. Ghalaieny⁵, M.R. McGillen⁵, C.J. Percival⁵, J.D. Whitehead⁵, R. Ellis⁶, J. Murphy⁶, A. Mohacsi⁷, A. Pogany⁸, H. Junninen⁹, S. Rantanen⁹, M.A. Sutton¹ and E. Nemitz¹, (2010): Field inter-comparison of eleven atmospheric ammonia measurement techniques. *Atmospheric Measurement Techniques* 3, 91-112.

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² Leibniz Institute for Agricultural Engineering, Potsdam, Germany

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⁶ Department of Chemistry, University of Toronto, Toronto, Canada

⁷ Research Group on Laser Physics of the Hungarian Academy of Sciences, Budapest, Hungary

⁸ Department of Optics and Quantum Electronics, University of Szeged, Szeged, Hungary

⁹ Department of Physics, University of Helsinki, Helsinki, Finland

Own Contribution:

Preprocessing

- Preparing of the experiment site (intensively managed agricultural field) including setup of barriers and scaffolding
- Consideration about the arrangement of the involved instruments
- Preparing the measurement and conducting a function test of the Annular Rotating Batch Denuder (RBD)
- Literature review about former NH₃ inter-comparisons

During the field experiment

- Running the RBD during the experiment (20.08.-04.09.2008)
- Owing to the offline analysis of the RBD, a daily change of test tubes was necessary
- Lab analyses of the samples with a NH₃ Flow Injection Analyser (AMFIA)
- Presentation of the first results of measured NH₃ concentrations of the RBD, for a first comparison with other instruments

Postprocessing

- Finishing the lab analyses of the samples with a NH₃ Flow Injection Analyser (AMFIA)
- Compilation and preparation of selected meteorological variables from existing data (Fig.2)
- Extensive literature review about former NH₃ inter-comparisons, about the characteristics of the involved instruments and about useful statistical analyses
- Compilation of provided information of the co-authors about measurement techniques in Section 2.3
- Handling of amalgamation of the data of all involved instruments
- Statistical analyses for the instruments inter-comparison, including time-series (Figs. 3a, b), scatter plots of linear regressions (Figs. 4a-j; Tables 4-7), time resolution (Figs. 5, 6) and response time (Table 9)
- Various drafts of the manuscript with all Figures and Tables and subsequently revision of the manuscript after comments and improvements of co-authors
- Handling of all related steps from submission to publication of the manuscript in the Journal "Atmospheric Measurement Techniques" including the earlier online discussion forum "Atmospheric Measurement Techniques Discussion"

Contribution of co-authors:

C.F. Braban

- Preparing of the experiment site (intensively managed agricultural field) including setup of barriers and scaffolding
- Consideration about the arrangement of the involved instrument
- Running the CRDS and the Nitrolux-100 during the experiment
- Providing of the data of the CRDS and the Nitrolux-100 for analyses
- Providing the information and the text about the CRDS and the Nitrolux-100 within the Section 2.3 “Measurement techniques”
- Support of the lab analyses
- Support of the decision of suitable statistical analyses
- Revision of the first draft of the manuscript

D. Famulari

- Preparing of the experiment site (intensively managed agricultural field) including setup of barriers and scaffolding
- Consideration about the arrangement of the involved instrument

S.K. Jones

- Preparing of the experiment site (intensively managed agricultural field) including setup of barriers and scaffolding
- Organising the fertilisation event on 28.08.2008
- Running the AMANDA during the experiment
- Providing of the data of the AMANDA for analyses
- Providing the information and the text about the AMANDA within the Section 2.3 “Measurement techniques”

T. Blackall

- Running the OP-FTIR during the experiment
- Providing of the data of the OP-FTIR for analyses

T.E.L. Smith

- Supporting T. Blackall by providing the data of the OP-FTIR for analyses

M. Blom

- Running the AiRRmonia during the experiment
- Providing of the data of the AiRRmonia for analyses
- Providing the information and the text about the AiRRmonia within the Section 2.3 “Measurement techniques”

H. Coe

- Supporting C.J. Percival by providing the data of the CIMS for analyses

M. Gallagher

- Temporally running the DUAL-QCLAS during the experiment
- Providing the information and the text about the DUAL-QCLAS within the Section 2.3 “Measurement techniques”

M. Ghalaiey

- Running the CIMS during the experiment
- Supporting C.J. Percival by providing the data of the CIMS for analyses

M.R. McGillen

- Running the CIMS during the experiment
- Supporting C.J. Percival by providing the data of the CIMS for analyses

C.J. Percival

- Running the CIMS during the experiment
- Providing of the data of the CIMS for analyses
- Providing the information and the text about the CIMS within the Section 2.3 “Measurement techniques”

J.D. Whitehead

- Temporally running the DUAL-QCLAS during the experiment
- Providing of the data of the DUAL-QCLAS for analyses

R. Ellis

- Running the c-QCLAS during the experiment
- Providing the information and the text about the c-QCLAS within the Section 2.3 “Measurement techniques”

J. Murphy

- Temporally running the c-QCLAS during the experiment
- Supporting R. Ellis by providing the data of the c-QCLAS for analyses

A. Mohacsi

- Temporally running the WaSul-Flux during the experiment
- Supporting A. Pogany by providing the data of WaSul-Flux for analyses

A. Pogany

- Running of the WaSul-Flux during the experiment
- Providing the information and the text about the WaSul-Flux within the Section 2.3 “Measurement techniques”
- Providing of the data of the WaSul-Flux for analyses

H. Junninen

- Temporally running of the IMS during the experiment
- Providing of the data of the IMS for analyses
- Providing the information and the text about the IMS within the Section 2.3 “Measurement techniques”

S. Rantanen

- Running of the IMS during the experiment

M.A. Sutton

- Initiator of this inter-comparison of atmospheric NH₃ measurement techniques within the framework of the European Commission Integrated Project NitroEurope

E. Nemitz

- Initiator of this inter-comparison of atmospheric NH₃ measurement techniques within the framework of the European Commission Integrated Project NitroEurope
- Supervisor of this inter-comparison of atmospheric NH₃ measurement techniques
- Preparing of the experiment site (intensively managed agricultural field) including setup of barriers and scaffolding
- Consideration about the arrangement of the involved instrument
- Support of the decision of suitable statistical analyses and their presentation in the paper
- Support of the preparation of Figs. 2, 3a, b and the scatter plots in Fig. 4a-j
- Revision of the various drafts of the manuscript up to the final version of the published paper

Paper II

K. von Bobrutzki¹, H.-J. Müller¹ and D. Scherer² (2011): Factors affecting the ammonia content in the air surrounding a broiler farm. Biosystems Engineering (in press), doi: 10.1016/j.biosystemseng.2011.01.005

¹ Leibniz Institute for Agricultural Engineering, Potsdam, Germany

² Chair of Climatology, Technische Universität Berlin, Berlin, Germany

Own Contribution:

Preprocessing

- Preparing the setup of the experiment including consultations with the farmer of the broiler farm about the performance of the experiment
- Consideration about the arrangement of the involved measurement techniques and the monitoring tower
- Introductory literature review about former monitoring campaigns of atmospheric NH₃ concentrations

During the field experiment

- Collecting the meteorological data of the monitoring tower and the NO_x converter during the experiment (21.02.-27.03.2007) with support of the team of the Department of Engineering for Livestock Management (Leibniz Institute for Agricultural Engineering Potsdam-Bornim)

Postprocessing

- Extensive literature review about former monitoring campaigns of atmospheric NH₃ concentration, about possible influencing factors of it and about useful statistical analyses
- Compilation and preparation of measured data inside the broiler barn and external at the monitoring tower (meteorological data and atmospheric NH₃ concentrations)
- Statistical analyses toward the relationship between factors-of-influence and measured atmospheric NH₃ concentrations

- Various drafts of the manuscript with all Figures and Tables and subsequently revision of the manuscript after comments and improvements of co-authors
- Handling of all related steps from submission to acceptance of the manuscript in the Journal “Biosystems Engineering”

Contribution of co-authors:

H.-J. Müller

- Providing the contact to the farmer of the broiler farm for realising the experiment
- Setup and conducting of the measurements inside the broiler barn with support of the team of the Department of Engineering for Livestock Management
- Revision of Section 2.1 of the manuscript

D. Scherer

- Supervising the field experiment
- Setup of the monitoring tower with support of the team of the Chair of Climatology, Technische Universität Berlin
- Support of the data editing and processing
- Support of the decision of suitable statistical analyses and their presentation in the paper
- Support of the preparation of Figs. 2, 7
- Revision of the various drafts of the manuscript up to the final version of the published paper

Paper III

K. von Bobrutzki¹, C. Ammon¹, W. Berg¹, P. Einert², M. Fiedler¹, H.-J. Müller¹, D. Scherer³, B. Strohbach² (2010): Ammonia emissions from a broiler farm: spatial variability of concentrations in the vicinity and impacts on adjacent woodland. Environmental Monitoring and Assessment (submitted).

Manuscript number: EMAS7115

¹ Leibniz Institute for Agricultural Engineering, Potsdam, Germany

² Eberswalde Forestry competence centre, Research Institute of the public enterprise Forst Brandenburg

³ Chair of Climatology, Technische Universität Berlin, Berlin, Germany

Own Contribution:

Preprocessing

- Preparing the setup of the experiment including consultations with the farmer of the broiler farm about the performance of the experiment
- Consideration about the arrangement of the involved measurement techniques and passive samplers
- Introductory literature review about former monitoring campaigns of atmospheric NH₃ concentrations

During the field experiment

- Collecting the data of passive samplers during the experiment within sampling period I and II in 2007 with support of the team of the Department of Engineering for Livestock Management (Leibniz Institute for Agricultural Engineering Potsdam-Bornim)

Postprocessing

- Extensive literature review about former monitoring campaigns of atmospheric NH₃ concentration, about passive sampling and about useful statistical analyses
- Compilation and preparation of measured data inside the broiler barn and external from the passive samplers of sampling period I-IV

- Analysing the relationship between the NH₃ emissions from the broiler farm, the spatial dispersion patterns and along a transect the sampled atmospheric NH₃ concentrations and vegetation abundance
- Various drafts of the manuscript with all Figures and Tables and subsequently revision of the manuscript after comments and improvements of co-authors
- Handling of all related steps submitting the manuscript to the Journal "Environmental Monitoring and Assessment"

Contribution of co-authors:

C. Ammon

- Support of the preparation of Tables 5-7
- Revision of the various drafts of the manuscript up to the final version of the submitted paper

W. Berg

- Support of preparing the setup of the experiment
- Revision of the first draft of the manuscript

P. Einert

- Collecting and providing the data of passive samplers during the experiment within sampling period IV in 2008

M. Fiedler

- Collecting the data of passive samplers during the experiment within sampling period III in 2008 with support of the team of the Department of Engineering for Livestock Management

H.-J. Müller

- Providing the contact to the farmer of the broiler farm for realising the experiment
- Setup and conducting the inside measurements of the broiler house with support of the team of the Department of Engineering for Livestock Management

D. Scherer

- Support of the organisation and the setup of the experiment during the initial period
- Revision of latest draft of the manuscript before submitting the paper

B. Strohbach

- Collecting the data of passive samplers and vegetation surveys during the experiment within sampling period IV in 2008
- Providing information to Section “Vegetation Surveys” and Table 8

Appendix E:

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