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Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland)

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Abstract. As part of a field campaign in the framework of the NitroEurope project, three different instruments for atmospheric ammonia (NH_3) measurements were operated side-by-side on a managed grassland site in Switzerland: a modified Proton Transfer Reaction Mass Spectrometer (PTR-MS), a GRadient of AErosol and Gases Online Registrator (GRAEGOR), and an Automated Ammonia Analyzer (AiRRmonia). The modified PTR-MS approach is based on chemical ionization of NH_3 using O_2^+ instead of H_3O^+ as ionizing agent, GRAEGOR and AiRRmonia measure NH_4^+ in liquids after absorption of gaseous NH_3 in a rotating wet-annular denuder and through a gas permeable membrane, respectively. Bivariate regression slopes using uncorrected data from all three instruments ranged from 0.78 to 0.97 while measuring ambient NH_3 levels between 2 and 25 ppbv during a 5 days intercomparison period. Correlation coefficients r^2 were in the range of 0.79 to 0.94 for hourly average mixing ratios. Observed discrepancies could be partly attributed to temperature effects on the GRAEGOR calibration. Bivariate regression slopes using corrected data were >0.92 with offsets ranging from 0.22 to 0.58 ppbv. The intercomparison demonstrated the potential of PTR-MS to resolve short-time NH_3 fluctuations which could not be measured by the two other slow-response instruments. During conditions favoring condensation in inlet lines, the PTR-MS underestimated NH_3 mixing ratios, underlining the importance of careful inlet designs as an essential component for any inlet-based instrument.

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1 Introduction

As the most dominant gas phase base in the atmosphere ammonia (NH_3) plays a key role for the neutralization of acidic gases and aerosol particles (Asman et al., 1998). The uptake of NH_3 on aerosol particles influences the aerosol chemical composition (Wells et al., 1998) and controls the acidity and nitrification of precipitation (Charlson and Rodhe, 1982; Dentener and Crutzen, 1994). NH_3 is emitted in large quantities both from natural and anthropogenic sources (Bouwman et al., 1997). The natural sources include emission from soils, oceans, vegetation and living organisms. NH_3 is known to be both emitted from and deposited to vegetation and it has positive effects on plants at low concentration, while it is harmful at higher concentrations (Fangmeier et al., 1994). However, large uncertainties still exist about the concentrations, surface-atmosphere exchange fluxes and cycling of atmospheric NH_3. One major uncertainty is the uptake and/or emission rate from plants and soils. Much of this uncertainty is due to the relative scarcity of direct flux measurements, which in turn mainly has been due to the lack of reliable measurement techniques that can be operated automatically and with high time-resolution in the field.

One major difficulty for the development of measuring techniques for atmospheric NH_3 is the simultaneous presence of NH_x in the gaseous, the particulate (e.g., ammonium nitrate) and the liquid phase (NH_4^+(aq) in clouds and fog). The partitioning between these phases strongly depends on environmental factors, such as temperature and relative humidity (Mozurkewich, 1993). Another difficulty is the interaction of NH_3 with the surface of many materials as well as its high water-solubility, thus making measurements

with any kind of inlet a challenge (Parrish and Fehsenfeld, 2000; Yokelson et al., 2003). These problems have caused the progress in the development of NH_3 measurement techniques to be slower than for many other atmospheric compounds. The denuder technique is nowadays the most widely applied sampling technique for NH_3 (Ferm, 1979). However, major limitations of the denuder technique are a relatively low time-resolution (minutes to hours) and the need for subsequent wet-chemical analysis, which may introduce errors due to sample storage and/or contamination problems when applied for in-situ measurements. Until the last decade most automatic atmospheric NH_3 measurements with sufficiently low detection limits were based on wet chemistry, like for example the AMANDA technique (Ammonia Measurement by Annular Denuder sampling with on-line Analysis; Wyers et al., 1993; Erisman et al., 2001), and the DS-FIA (diffusion scrubber flow injection analyzer; Genfa et al., 1989; Dasgupta 1993). More recent developments of fast response techniques with low detection limits include for example Differential Optical Absorption Spectroscopy (DOAS, Gall et al., 1991), Photoacoustic Spectroscopy (Pushkarsky et al., 2002), Tuneable Diode Laser Absorption Spectroscopy (TDLAS, Warland et al., 2001) and Chemical Ionization Mass Spectrometry (CIMS, Nowak et al., 2007).

Several attempts have been made to compare different NH_3 measurement techniques. An intercomparison by Wiebe et al. (1990) tested four measurements techniques for NH_3 by filter packs, transition-flow reactors, simple and annular denuders and Fourier-Transform Infrared-Spectroscopy. Williams et al. (1992) compared five different NH_3 measurement techniques including a photofragmentation/laser-induced fluorescence instrument (PF/LIF), a molybdenum oxide annular denuder sampling/chemiluminescence detection technique (MOADS), a tungsten oxide denuder sampling/chemiluminescence detection system (DARE), a citric acid coated denuder sampling/ion chromatographic analysis method (CAD/IC) and an oxalic acid coated filter pack sampling/colorimetric analysis method (FP/COL). A detailed study for determining the suitability of measuring techniques for air quality monitoring in the Netherlands is presented by Mennen et al. (1996). The study included seven methods, a wet-annular rotating denuder (WRD or WAD), a WO_3-coated thermodenuder, a V_2O_5-coated thermodenuder, a DOAS system, a photoacoustic monitor and a chemiluminescence NO_x monitor with NH_3 converter. A field intercomparison was performed by Milford et al. (2000) during the ACE-2 experiment in Tenerife and included the AMANDA and the DS-FIA. The informal intercomparison reported by Fehsenfeld et al. (2002) compared a first version of the CIMS for NH_3 measurements with conventional methods like the citric acid denuder and the Molybdenum oxide (MoO_x) converter difference method. CIMS techniques for NH_3 measurements were further tested by Nowak et al. (2006) who compared two different CIMS instruments, the NOAA Chemical Science Division (NOAA-CSD) apparatus and the Georgia Tech (GT) low pressure tube flow reactor, in the field. An ambitious laboratory test of six different techniques is presented in the study by Schwab et al. (2007). The study included the TDLAS, the wet-scrubbing long-path absorption photometer (LOPAP), the wet effusive diffusion denuder (WEDD), the ion mobility spectrometer (IMS), the Nitrolux laser acousto-optical absorption analyzer as well as a modified chemiluminescence analyzer. A recent study compared the performance of a quantum cascade laser spectrometer (QCLAS), a TDLAS and an AMANDA system both for concentration and flux measurements of ammonia (Whitehead et al., 2008).

The intercomparison presented here was performed within the framework of NitroEurope (NEU, www.nitroeurope.eu). One of the main NEU objectives is to establish robust datasets of land/atmosphere exchange fluxes of nitrogen and to study their impact on greenhouse gas budgets for representative European ecosystems. In line with this objective, NH_3 was measured over an intensively managed grassland site at Oensingen, Switzerland, during July and August 2006. One of the main goals was to determine the drivers of surface-atmosphere exchange fluxes of NH_3 in grassland in relation to meteorological conditions and management practices, including fertilization and cutting. Three different instruments were compared for measurements of atmospheric NH_3: (a) an Automated Ammonia Analyzer AiRRmonia^{TM} instrument (Mechatronics BV, Hoorn, The Netherlands) (Erisman et al., 2001), (b) the GRadient of AErosol and Gases On-line Registrator (GRAEGOR) (Thomas et al., 2009) and (c) a modified proton transfer reaction mass spectrometer (PTR-MS) (Norman et al., 2007). As far as we know, this is the first study to include these three systems. It describes results from the intercomparison, potential sources of error and the suitability of the different methods for in-situ measurements with a high temporal resolution.

2 Experimental

2.1 Site description

The field site was established in 2001 and is situated near the village of Oensingen in central Switzerland ($47°17'$ N, $07°44'$ E) at about 450 m a.s.l. The site consists of two 50 x 150 m plots of grassland. One plot undergoes extensive management with no fertilizer application and 2–3 cuts per year and the second one is intensively managed with four fertilizer applications (150–200 kg N ha^{-1} y^{-1} as ammonium nitrate and slurry) and 4–5 cuts per year (Ammann et al., 2004). The surrounding area is characterised by intensive agriculture, dominated by grasslands and arable crops. The prevailing climate at the site is temperate continental, with an average annual rainfall of about 1100 mm and a mean annual air temperature of 9°C.

The measurement site has been used for studies of carbon and greenhouse gas budgets within the EU-funded GREEN-GRASS and CarboEurope-IP programmes (Ammann et al., 2004; Flechard et al., 2005) and in ozone studies (Jäggi et al., 2006) as well as in nitrogen studies (Ammann et al., 2007; Neftel et al., 2007).

A trailer was placed on the border between the intensively managed plot and the extensive managed plot. The measurements in this paper were performed above the intensively managed plot. The PTR-MS instrument was placed inside the trailer. A 17 m long inlet tube extended out onto the field and was placed on a tripod. Both the AiRRmonia analyzer and the GRAEGOR were placed in the centre of the field. The maximum distance between the AiRRmonia instrument, the GRAEGOR and the tripod with the PTR-MS inlet was 5 m. Furthermore, the prevailing wind directions parallel to the field orientation (Ammann et al., 2007) favoured minimal footprint differences for the three instruments.

The measurements presented in this paper were performed between the afternoon of 26th and midday on 31st of July 2006. This was the only period of the 2006 summer campaign when all three instruments were operated simultaneously. The latest fertilisation of the field prior to the measurement phase occurred on 13th of July by application of liquid cattle slurry.

2.2 Measurements techniques

2.2.1 AiRRmonia

The AiRRmonia analyzer was designed for long-term monitoring of gas-phase atmospheric NH_3 and it is a further development of the AMANDA technique (Wyers et al., 1993; Erisman et al., 2001). The AiRRmonia has been employed in national NH_3 monitoring networks e.g., in the Netherlands and in Denmark. Air is sampled via a 5 cm long PE (Polyethylene) tubing with d_i=0.17 cm (inner diameter) at a flow of 1 SLPM (Table 2). In the sample block (SB), absorption of NH_3 from the air flow takes place via a gas-permeable PTFE (polytetrafluoroethylene) membrane into an acid buffer (or "stripping") solution, with a scrubbing efficiency of close to 100%. Ammonium-containing aerosols are not retained by the sampling membrane. This was verified by laboratory experiments where less than 1% and 3% of $(NH_4)_2SO_4$ and NH_4NO_3 particles, respectively, were captured (Otjes et al., 1999). The pH of the stripping solution is subsequently raised by addition of sodium hydroxide, which triggers the release and transfer of the captured NH_3 through a second PTFE membrane in the detector block (DB), into a stream of pure deionized water in counter-flow on the other side of the membrane. The NH_3 transfer efficiency of the AM-FIA detector block is 90%. The NH_4^+ concentration in the solution is determined by a conductivity measurement, and calibration is made using aqueous NH_4^+ standard solutions (cf. Slanina et al., 2001). As with similar instruments based

Table 1. Characteristics of the NH_3 instruments compared in this study.

	Institute	Detection limit (2σ)	Sampling time
AiRRmonia	ART, Zürich, Switzerland	120 pptv	15 min
GRAEGOR	MPIC, Mainz, Germany	94 pptv	30 min
PTR-MS	University of Innsbruck, Austria	90–270 pptv[1]	1 min[2]

[1] The background and hence the detection limit for the PTR-MS varies with absolute humidity, see text. [2] The sampling time for the PTR-MS is variable (seconds to minutes), but in this paper we only present 1-min sampling time data.

Table 2. Description of the different inlets for the NH_3 instruments in this study.

	AiRRmonia	GRAEGOR	PTR-MS
Type	PE	PFA	PFA
Length	5 cm	30 cm	17 m
Inner diameter, cm	0.17	0.8	0.95
Flow, SLPM	1	16.7	15
Air speed, m s^{-1}	7.3	5.5	3.5
Reynolds number	860	3880	2470
Surface to volume ratio, m^{-1}	2350	500	420
Residence time, s	0.007	0.054	4.8

on quantitative sampling of gaseous compounds into liquids and subsequent analysis in the liquid phase, the establishment of constant and precise liquid flows for all solutions is critical. The AiRRmonia applies syringe pumps for this purpose; their performance was verified by equipping the instrument with a liquid flow meter (Liquiflow L1, Bronkhorst NL) and continuously monitoring the total liquid flow.

The response time of the analyzer is of the order of 10–15 min and depends on the liquid flow rate, and thus on syringe pump speed. Detection limit and accuracy of the AiRRmonia have previously been determined as 0.1 $\mu g/m^3$ and 3%, respectively (Erismann et al., 2001). For an estimate representative of the measurement period presented here, we used the 2σ (twice the observed standard deviation) from conductivity measurements in the field without air flow in sampling block as an estimate for the detection limit and twice the observed standard deviation from calibrations in the field as an estimate for the accuracy. The resulting values were 0.08 $\mu g/m^3$ or 120 pptv for detection limit and 10% accuracy at NH_3 mixing ratios of 5 ppbv, c.f. Table 1. The detector block was placed 1.25 m above the grass field. The AiRRmonia was operated by personnel from Agroscope Reckenholz-Tänikon Research Station (ART) in Zürich, Switzerland.
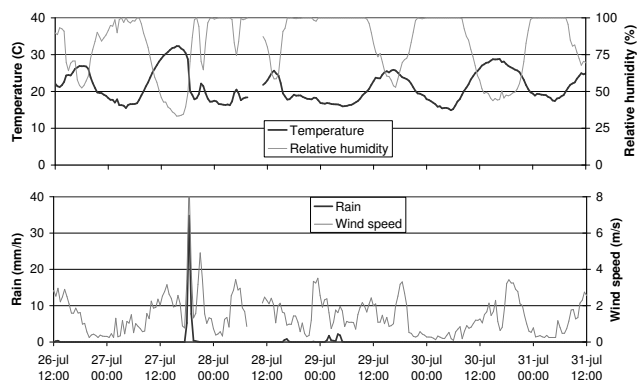
2.2.2 GRAEGOR

The recently developed GRadient of AErosol and Gases Online Registrator (GRAEGOR) measures mixing ratios of water-soluble gases, such as NH_3, HNO_2, HNO_3, HCl, SO_2 and their related aerosol compounds NH_4^+, NO_3^-, Cl^-, SO_4^{2-} (Thomas et al., 2009). The instrument consists of two sampling units, an analytical part, and a vacuum pump (Becker VT 4.16). The sampled air is drawn through two PFA (perflouroalkoxy) Teflon tubing connections (d_i=0.8 cm, l=30 cm, Table 2) to two sampling units that can be placed at two different heights to measure gradients. Water-soluble gases and aerosol species are collected simultaneously by two horizontally aligned rotating wet-annular denuders (WAD or WRD) and two Steam-Jet Aerosol Collectors (SJAC), respectively (Slanina et al., 2001; Trebs et al., 2004). A critical orifice provides controlled sample airflows of approx. 16.7 l min^{-1} (293.15 K and 1013.25 hPa) through each of the WRD/SJAC sampling lines. The airflow was regularly checked with a Gilibrator Air Flow Calibration System. To minimize wall losses of sticky gases such as HNO_3 (Neuman et al., 1999), no preimpactor or cyclone was connected in front of the inlet. In contrast to previous studies that have employed similar instrumentation (e.g., Trebs et al., 2004), one major improvement of the GRAEGOR is the application of syringe pumps for the precise transport of liquids which is crucial for accurate analyses (cf. section above). The sample flow through the system is constant at 0.333 ml min^{-1} and is controlled with a Bronkhorst liquid flow meter. The sample solutions are analyzed on-line using ion chromatography (IC) for anions (results are not included in this study). Ammonium (NH_4^+) is analyzed using the same method as applied in the AiRRmonia (ammonium flow injection analysis, AMFIA). However, the AMFIA detector in GRAEGOR only has a NH_3 transfer efficiency of 30% (Slanina et al., 2001). The detector was calibrated in the same way as that of the AiRRmonia using standard solutions of NH_4^+. The accuracy is 12% as determined by Gaussian error propagation, including uncertainties of the sampled air volume, the liquid flow and conductivity detection. The detection limit for NH_3 was estimated from field blanks (2σ-definition) to 94 pptv (Table 1). The air samples that the GRAEGOR analyzes represent an average of the second half of each hour. This is the fastest sampling time achievable when GRAEGOR is operated as gradient monitor since two gas samples and two aerosol samples need to be analyzed subsequently and each analytical cycle takes 15 min. The response time of GRAEGOR, i.e. the time it takes for the signal to drop to 1/e of the starting value (ambient NH_3 mixing ratio) after switching off the air pump, was shown to be 58±2 min (cf. Thomas et al., 2009). For gradient measurements, the lower measurement height was 0.37 m and the upper measurement height was 1.23 m. In this paper we only present data from the upper level measurements. The GRAEGOR was oper-

ated by personnel from Max Planck Institute for Chemistry (MPIC) in Mainz, Germany.

2.2.3 PTR-MS

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is a state-of-the-art chemical ionization mass spectrometry (CIMS) technique for highly sensitive on-line measurements of volatile organic compounds (VOC) as described in Hansel et al. (1995) and Lindinger et al. (1998). A new technique for fast measurements of gas phase NH_3 using the PTR-MS instrument has recently been presented by Norman et al. (2007). Oxygen (O_2) is used as a source gas to produce O_2^+ as chemical ionization (CI) reagent instead of H_3O^+. The O_2^+ ions react with the NH_3 molecules via the electron transfer reaction $O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$ which occurs at collision rate. Primary (O_2^+) and product ions (NH_3^+) are separated by a quadrupole mass spectrometer and detected using an electron multiplier SEM pulse counting system. The correct terminology of the instrument would be ETR-MS (Electron Transfer Reaction Mass Spectrometer), since it uses electron transfer instead of proton transfer as in the conventional PTR-MS. However the instrument itself is not changed and we will through the paper use the well-established terminology PTR-MS when referring to the instrument. A detailed description of the instrument settings, sensitivity and selectivity can be found in Norman et al. (2007). During laboratory tests the detection limit (2σ) was found to be 90 pptv for a 1 s signal integration time at dry conditions, increasing to 270 pptv for humid conditions (Table 1). The instrumental time response, defined by $1/e^2$ decay in the calibration signal was around 30 s. The instrument used for these measurements was a conventional PTR-MS instrument built at the University of Innsbruck. The PTR-MS inlet consisted of a 17 m long d_i=0.95 cm PFA tubing with a flow of 15 SLPM (Table 2). The inlet was not heated, but covered with aluminum foil to minimize effects from direct solar radiation on the tube. The inlet was mounted 1.25 m above the grass field on a tripod in close vicinity to the other two instruments on the intensively managed plot. The sample inlet to the PTR-MS drift tube consisted of a 15 cm silica coated stainless steel tube (Sulfinert®, Restek Corp., Bellefonte, PA, USA) which was pressure and temperature controlled. The passivated stainless steel tube sampled air from the centre of the main inlet tubing. The air flow into the PTR-MS instrument was ∼30 sccm. The sampling time for the PTR-MS instrument used in this study varied between 0.5 s to 30 s, but we only present 1 min averages (Table 1).

The PTR-MS instrument was calibrated using a permeation device manufactured by Real Sensors Inc. (Hayward, California, USA). Given the high uncertainty in the specified permeation rate, the permeation rate was re-calibrated using denuders coated with 5% citric acid solution as in Sutton et al. (2001). The estimated accuracy using this calibration approach is ±10%. The permeation tube was kept
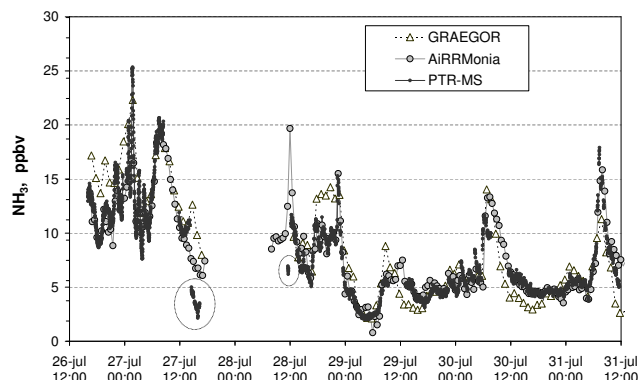
Fig. 1. Observed meteorological parameters for the 5-day intercomparison period.


Fig. 2. NH$_3$ mixing ratios measured 1.25 m above the intensively managed grass field. The data are presented in 1 min, 30 min and 1 h sampling time for the PTR-MS, AiRRmonia and GRAEGOR, respectively. PTR-MS data within the circles are discussed separately.

in a temperature controlled oven at 30°C and was continuously flushed with NH$_3$ free air. NH$_3$ free air was generated using a platinum and palladium (Pt/Pd) catalyst operated at 350°C (Parker-Balston, Haverhill, MA, USA). NH$_3$ free air was also generated using oxalic acid coated filters. Using one or two stage dilution with NH$_3$ free air from the Pt/Pd catalyst and/or the oxalic acid NH$_3$ scrubber, the instrument was calibrated in the field for mixing ratios between 8 and 150 ppbv. Details about the calibration system can be found in Norman et al. (2007). The PTR-MS was operated by personnel from the Institute for Ion and Applied Physics at the University of Innsbruck, Austria.

3 Results

3.1 Time series analysis

The field site was equipped with a meteorological station providing half-hour averages of air temperature, relative humidity, precipitation, wind speed and wind direction. The meteorological conditions during the measurement period are presented in Fig. 1. The period was dominated by relatively high daytime temperatures between 20° and 30°C. There was a heavy thunderstorm on the 27th July with almost 40 mm/h rain and heavy winds and a sharp drop in temperature. A longer rain period occurred in the morning of the 29th with mostly light rain. The relative humidity was close to 100% during nighttime and mostly dropped to below 50% during daytime. Figure 2 shows the time-series of measured NH$_3$ mixing ratios during the intercomparison period for all three instruments. The thunderstorm in the evening of 27th July caused a power failure and the measurements started again in the morning of 28th July. The time series analysis shows an overall good agreement between the three different instruments. The time course of NH$_3$ shows large variations, with mixing ratios around 10–15 ppbv on 26th July and in the morning of 27th July. NH$_3$ levels dropped in the morning of 27th July and continued falling until the power fail-

ure in the evening. The mixing ratios were lower following the heavy thunderstorm rainfall. The PTR-MS data showed a sudden drop in mixing ratio during the rainfall as well as during the start up in the morning after (data within the circles in Fig. 2). As discussed later in the paper, this drop was most likely caused by water condensation in the main inlet line. On 28th July highly variable mixing ratios were observed with a sharp drop in the late evening before the onset of rainfall. The period from 29th to 31st July was characterized by a sharp NH$_3$ peak every morning around 09:00 a.m. Similar increases during morning hours have been observed over grassland sites elsewhere, e.g., by Trebs et al. (2005). The mixing ratio typically decreased throughout the afternoon.

The different sampling times of the three instruments result in slightly different features of the temporal NH$_3$ structure. The 1-min PTR-MS data indicate fast NH$_3$ variations on 26th July and early morning of 27th July. A detailed version of the NH$_3$ levels observed by the PTR-MS and the AiRRmonia instruments during this period is shown in Fig. 3. While both instruments found a very similar mixing ratio pattern at half-hour sampling time, the PTR-MS was able to capture additional changes of NH$_3$ occurring at the time scale of minutes. These fast variations may be caused by small scale changes in the advection of air masses close to the ground, as supported by the concurrent variation of the wind speed.

The absolute levels agree reasonably well between the instruments on average throughout the period, with some periods with significant differences. The AiRRmonia measured lower mixing ratios than the other two instruments before the thunderstorm on 27th July, but most of the time, the PTR-MS and the AiRRmonia followed each other overall rather closely, while the GRAEGOR occasionally showed some divergence from the other two instruments. The GRAEGOR mixing ratios were 20–30% higher than both the PTR-MS
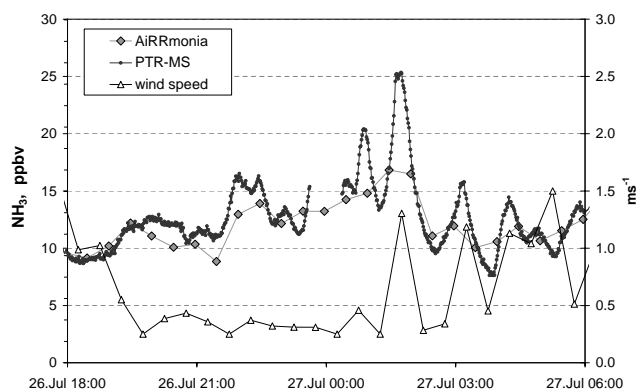
Fig. 3. The AiRRmonia and the PTR-MS data for a 12 h period on the 26th and 27th July when fast NH_3 variations were observed.

and the AiRRmonia levels in the afternoon of 26th July and in the afternoon of 28th July following rain events with associated high relative humidities (Fig. 1), but they were 20–40% lower in the early mornings of 29th and 30th July as well as during midday on 29th, 30th and 31st July.

3.2 Regression analyses

Hourly averaged values were calculated from the data presented in Fig. 2 (the PTR-MS data in the circles excluded). Bivariate regression analyses of the calculated hourly averages are presented in Fig. 4. As for the time series analysis an overall good agreement was found between all three instruments. The correlation between the PTR-MS and the AiRRmonia (Fig. 4a) was found to be excellent (r^2=0.94). The AiRRmonia shows marginally lower mixing ratios than the PTR-MS, reflected in a slope of 0.97. A brief laboratory intercomparison between the AiRRmonia analyzer and the PTR-MS instrument presented in Norman et al. (2007) also showed an r^2>0.95 and difference of mixing ratios <5%. The regression also shows that the AiRRmonia and the PTR-MS depict a linear correlation throughout the whole measured mixing ratio range with an offset of less than 0.25 ppbv.

The comparison between the GRAEGOR and the AiRRmonia (Fig. 4b) shows the poorest correlation with an r^2=0.79. The GRAEGOR showed on average higher mixing ratios than the AiRRmonia at mixing ratios above 10 ppbv but also slightly lower at mixing ratios below 5 ppbv. This resulted in a slope of 0.78 and an offset of 1.25 ppbv.

The comparison between the GRAEGOR and the PTR-MS (Fig. 4d) resulted in a correlation coefficient r^2=0.85. As for the comparison with the AiRRmonia, the GRAEGOR showed higher mixing ratios above 10 ppbv and slightly lower mixing ratios below 5 ppbv. This resulted in a slope of 0.80 and an offset of 0.96 ppbv.

The GRAEGOR data shown in Fig. 4b and d were derived using a calibration made on the 26th of July before the power failure when (liquid) temperatures were >30°C. In contrast,

Fig. 4c and e show regressions of the GRAEGOR data with AiRRmonia and PTR-MS, respectively using a calibration made on 1st of August (at the end of the intercomparison period) when (liquid) temperatures were <28°C. While r^2 does not change much using the latter calibration made at lower temperatures, the other regression parameters improve substantially (slopes of 0.92 and 0.95 and offsets of 0.58 and 0.27 ppbv, respectively).

4 Discussion

The difficulty of measuring atmospheric NH_3 is demonstrated in the wide variety of results from NH_3 intercomparison exercises found in literature.
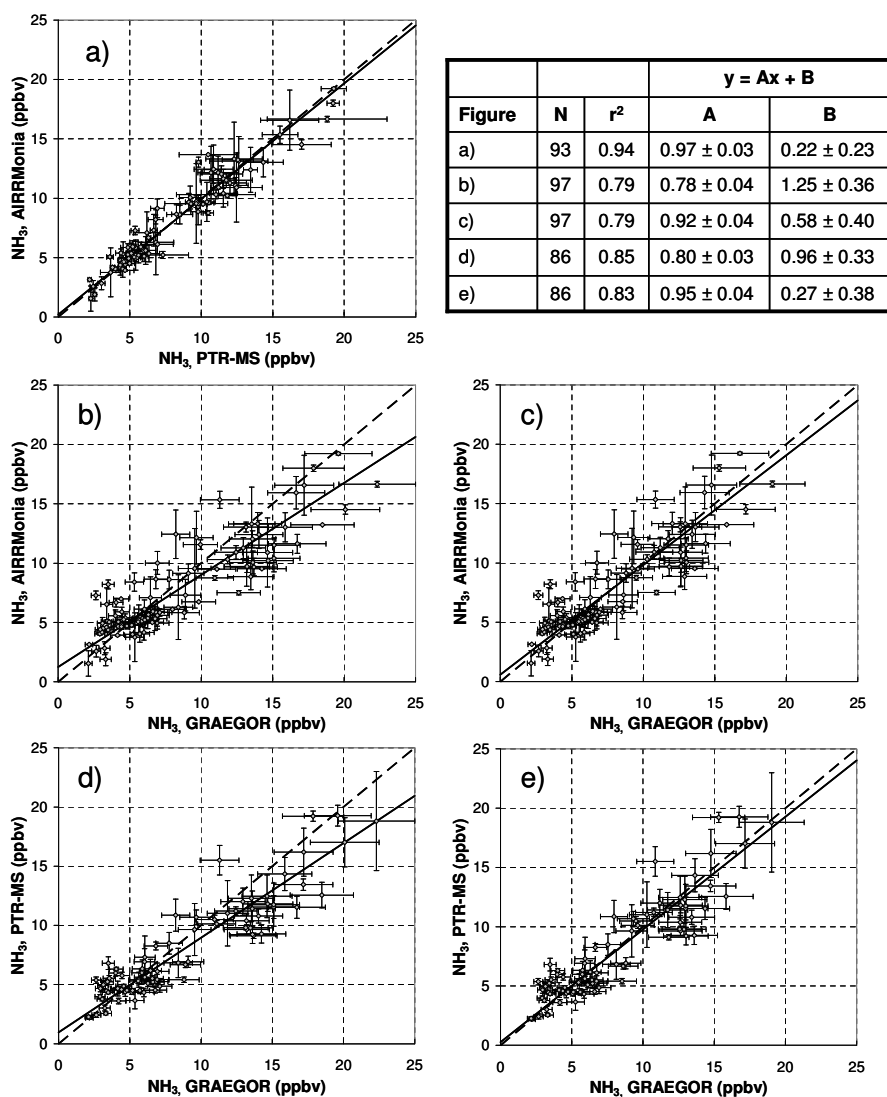
The study by Wiebe et al. (1990) showed that the measurements including filter packs and annular denuders agreed to within ±30% for NH_3 levels higher than 1.5 ppbv, but with a relatively coarse sampling time (minimum 4 h). The five different NH_3 measurement techniques tested by Williams et al. (1992) all agreed within a factor of two for NH_3 levels above 0.5 ppbv. The photofragment instrument (PF/LIF) and the citric acid coated denuders (CAD/IC) however agreed within 15% for all measured ambient mixing ratios (0.2–5 ppbv) for a sampling time of 2–8 h.

The detailed study by Mennen et al. (1996) showed that the wet-annular rotating denuder (WRD) met all the requirements for air quality monitoring on one hour sampling. The study also showed that both the DOAS and the NO_x converter instruments showed correlations of r^2>0.9 with the WRD, but were found not to be accurate enough for low concentrations. The photoacoustic monitor was rejected because it could not be operated without frequent attention and the thermodenuders were rejected due to their low sampling time.

The field intercomparison by Milford et al. (2000) showed that the AMANDA and the DS-FIA had an overall difference of 35% for 30 min sampling times, but also with a substantial scatter of the data. The intercomparison reported by Fehsenfeld et al. (2002) showed that the CIMS and the MoO_x converter method correlated with the citric acid denuder with an r^2>0.91 for sampling times of at least 2 h. However, the averaged concentration ratio for the CIMS and the MoO_x converter difference method compared to the denuder was 0.8 and 1.75, respectively.

The two different CIMS instruments, tested in the field by Nowak et al. (2006) with ambient levels ranging 0.4 to 13 ppbv showed a difference of 17% and an r^2=0.71 for a sampling time of one minute. The r^2 would be higher if averages over longer periods were calculated.

Among the six different techniques tested in the laboratory by Schwab et al. (2007), all except the modified chemiluminescence analyzer were able to measure mixing ratios within 25% of the expected values under stable conditions between 0 and 20 ppbv. However the TDLAS and the LOPAP showed on average the best agreement with the expected values. The

Figure	N	r^2	A	B
			y = Ax + B
a)	93	0.94	0.97 ± 0.03	0.22 ± 0.23
b)	97	0.79	0.78 ± 0.04	1.25 ± 0.36
c)	97	0.79	0.92 ± 0.04	0.58 ± 0.40
d)	86	0.85	0.80 ± 0.03	0.96 ± 0.33
e)	86	0.83	0.95 ± 0.04	0.27 ± 0.38

Fig. 4. Bivariate regression plots of hourly averaged data from all three instruments. Data in **(a)**, **(c)** and **(e)** represent hourly averaged data from Fig. 2. (c) and (e) are the same as **(b)** and **(d)** respectively, but with a different calibration for the GRAEGOR (see text). The error bars represent the observed variability ($\pm\sigma$, standard deviation) within the respective hour (the GRAEGOR only produces one value every hour and in this case error bars present the instrument accuracy of $\pm12\%$). The dashed line gives the 1:1 relationship and the solid line gives the result of a reduced major axis regression. N is the number of data points.

TDLAS was also found to have shortest time response during spiking tests.

The intercomparison of a QCLAS, a TDLAS and an AMANDA system by Whitehead et al. (2008) found correlations (r^2) to be good, ranging between 0.74 and 0.98 for concentration measurements during and after slurry application, with better correlations during the high concentration period. Despite the high correlations, the averaged concentration ratio between individual systems varied significantly (between 0.44 and 1.3).

The three instruments tested in this study showed a good correlation with $r^2 > 0.79$ for 1 h averaged values. Uncorrected mixing ratios levels agreed to within 22% with offsets

ranging from 0.22 to 1.25 ppbv. The PTR-MS and the AiR-Rmonia agreed to 3% with an $r^2 = 0.94$. The results in this study are well in line with the intercomparison studies mentioned above and the agreement between these very different measurement concepts is encouraging.

There exist several possibilities for the deviations from a 1:1 correlation. The departures from the 1:1 ratio shown in Fig. 4a to e were not found to be correlated to one particular meteorological parameter (e.g., wind speed and temperature). Most likely the observed differences were largely attributable to a combination of different effects, which are discussed below.

4.1 Calibration procedures and temperature influence

The PTR-MS method is not reported to be temperature dependent (Norman et al., 2007). Furthermore, the instrument was placed inside a temperature-controlled trailer. The GRAEGOR and the AiRRmonia instruments were placed outside and were therefore exposed to temperature fluctuations at the field site. The AiRRmonia and the GRAEGOR use identical analytical procedures (AMFIA, see above) and were calibrated with liquid standards, while the PTR-MS was calibrated with a gaseous standard. Any dependence of the scrubbing- or collection efficiency on the mixing ratios for the GRAEGOR and the AiRRmonia could therefore lead to differences over the observed mixing ratio range. The PTR-MS has a linear response to the gaseous NH_3 standard (Norman et al., 2007). In contrast, the conductivity measurements in the AiRRmonia and the GRAEGOR feature a quadratic response to the introduced liquid standards. Moreover, the transfer of NH_3 through the semi-permeable PTFE membrane in the detector block and the conductivity response are a function of temperature (Decuq et al., 2008), which is corrected for using an empirically derived relationship (see e.g., Trebs et al., 2004).

In case of the GRAEGOR, substantial differences between calibrations made at different temperatures were observed (as mentioned above). While the AiRRmonia detector was calibrated in the early morning when temperatures were around 15–20°C (Fig. 1) the first GRAEGOR calibration was performed on 26th of July when (liquid) temperatures >30°C were measured. The calibration on 1st of August (at the end of the intercomparison period) was made at (liquid) temperatures <28°C (cf. Fig. 4b and d) and results in NH_3 values that were on average about 15-20% lower than the mixing ratios based on the calibration on the 26th of July. Hence, the slope and offset of the regression between GRAEGOR and the other instruments improves using the calibration from 1st of August as observed in Fig. 4c and e (cf. Sect. 3.2). The following GRAEGOR calibrations at the field site with liquid temperatures around 25°C agreed within 5% with that on the 1st of August, suggesting that it is critical to perform calibrations at temperatures higher than 30°C. It is important to note, that the lower NH_3 transfer efficiency of the AMFIA in GRAEGOR (30% compared to 90% of the AiRRmonia) would generally promote the temperature effects. Decuq et al. (2008) propose that the empirically derived relationship for the AMFIA detector does not give accurate results (particularly for high temperatures) and a more suitable correction for temperature effects may be required.

Figure 5 shows a combined graph of the time series for both calibrations of the GRAEGOR data. The difference between the two calibrations was larger before the power failure on the 27th of July. The power failure caused a loss of the AMFIA deionized water background conductivity signal, which mainly serves to monitor the water quality and is used in the calculation of the NH_3 mixing ratio. The calibration
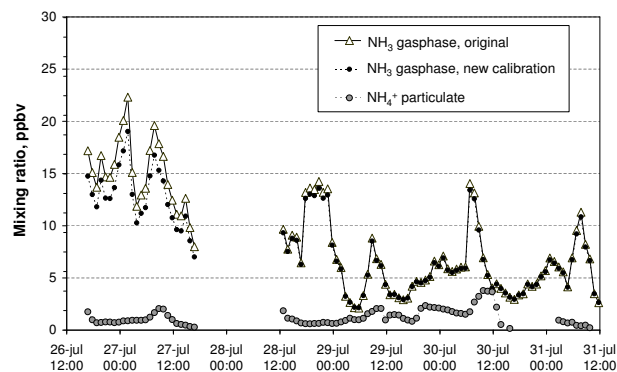
Fig. 5. Gas phase NH_3 mixing ratios and particulate NH_4^+ mixing ratios measured 1.25 m above the grass field from the GRAEGOR instrument. The NH_3 data is presented for two different calibrations of the GRAEGOR (see text).

made on 1st of August includes this signal loss (i.e., the AMFIA signal is derived only from the sample conductivity). Thus the data before the power failure, which still contained the background conductivity, are probably overcorrected using the calibration from the 1st of August.

4.2 Particle interference

One major complication for NH_3 sampling described e.g., by Parrish and Fehsenfeld (2000) is the simultaneous presence of NH_x in the gaseous, particulate and liquid phases. For accurate sampling of gaseous NH_3 the particulate and gas phase should be separated before sampling in order to avoid positive artifacts by sampling of particles. The GRAEGOR separates the gas phase from the particulate phase and its measured NH_3 mixing ratios are therefore not expected to be affected by particles. The AiRRmonia samples through a gas-permeable membrane with particle interference below 3% (Otjes and Erisman, 1999). The PTR-MS has no separation of gas and particulate phase in front of the inlet and it has not yet been tested for any particle interference. Thus, it is not known what happens to particulate NH_4^+ in the low pressure system of the instrument. However, large inlet cross sectional area in combination with high flow rates largely reduces the interference of larger particles. The aerosol NH_4^+ measured with the GRAEGOR during the intercomparison period ranged from 0.3 to 3.8 ppbv (Fig. 5), which was between 5 and 70% of the NH_3 mixing ratio. We expect that particle interferences only had a minor contribution to the observed NH_3 differences. Potentially this might have been the case when GRAEGOR measured lower NH_3 mixing ratios than the AiRRmonia and the PTR-MS during midday on the 29th, 30th of July when aerosol NH_4^+ was on average 50% of the measured NH_3 mixing ratio. During these periods the sharp drop of relative humidity potentially promoted evaporation of NH_3 from aerosol and ground surfaces, a dynamic feature that was most likely not captured to the same extent by all instruments.

4.3 Inlets and humidity dependence

Several studies have reported difficulties measuring NH_3 due to its interaction with the surface material of the inlets (e.g., Whitehead et al., 2008; Yokelson et al., 2003; Parrish and Fehsenfeld, 2000). Teflon (PFA and PFTE) and Polyethylene (PE) have been found to be well suited materials (Yokelson et al., 2003; Shah et al., 2006; Whitehead et al., 2008), but it is still recommended to choose the inlet length as short as possible to avoid losses (Fehsenfeld et al., 2002). The instruments in this study used a wide variety of inlet lengths and flow regimes as presented in Table 2. The PTR-MS used a 17 m long PFA with d_i=0.95 cm, the inlet of the GRAEGOR consisted of 30 cm long PFA tubing with d_i=0.8 cm and the AiRRmonia inlet was made of PE and had a length of only 5 cm and d_i=0.17 cm.

We observed losses in the PTR-MS inlet during and directly after the thunderstorm on the 27th July. During the rainfall the inlet tubing was cooled by water on the outside of the inlet apparently causing condensation in the inlet and uptake of NH_3 on the tubing walls. This was clearly seen in the data with a sudden drop of more than 50% of the mixing ratios in comparison to the other instruments (data shown within the circles in Fig. 2). No loss of NH_3 in the PTR-MS inlet compared to the other instruments was observed during the other periods without rainfall although the relative humidity was close to 100% during several nights. The AiRRmonia has similar if not less potential than GRAEGOR for adsorption of NH_3 on inlet walls. Most likely, adsorption-desorption in the AiRRmonia and the PTR-MS were not important, since largest differences occurred between GRAEGOR and PTR-MS/AiRRmonia. These results suggest that no losses of NH_3 on the PFA tubing surface to the PTR-MS instrument were observed when compared to the AiRRmonia and the GRAEGOR inlet as long as the tubing was not cooled causing condensation. An optimal design of an inlet might therefore be thermal insulation and if possible heating to a few degrees above the ambient temperature, keeping in mind that large temperature differences between outside and the inlet air cause aerosol ammonium nitrate to evaporate forming artifact NH_3.

The PTR-MS has a background signal that is observed to increase from 70 to 400 pptv with increasing humidity associated with also an increase in detection limit (cf. Table 1; Norman et al., 2007). A correction for the observed absolute humidity was therefore applied to the data. The departures from the 1:1 ratio observed in Fig. 4 for any of the correlations were not found to be correlated to the prevailing humidity.

5 Summary and conclusions

This paper compares measurements of atmospheric NH_3 by three different instruments performed at the Oensingen in-

tensively managed grassland site during 5 days in July and August 2006 within the framework of NitroEurope.

During the intercomparison period ambient temperatures were relatively high (18–32°C) and relative humidities ranged from 30 to 100%.

The instruments included in the experiment were the AiRRmonia, the GRAEGOR, and a modified PTR-MS instrument. The GRAEGOR collects air samples using wet-annular denuders combined with steam-jet aerosol collectors, analysis is performed on-line using ammonium flow injection. The AiRRmonia analyzer samples air through a gas-permeable membrane and analysis is performed in the same way as with the GRAEGOR. The modified PTR-MS approach is based on chemical ionization mass spectrometry using O_2^+ primary reagent ions.

All three instruments measured simultaneously at the site for a period of 5 days. During the intercomparison period the gas phase NH_3 mixing ratios varied between 2 and 25 ppbv. Correlation analyses between the instruments for 1-h averages showed correlation coefficients r^2>0.79 with the highest grade of correlation between the AiRRmonia and the PTR-MS (r^2=0.94). According to the regression analysis the GRAEGOR measured on average about 20% higher mixing ratios than both the AiRRmonia and the PTR-MS instruments. One potential cause for this deviation was unusually high temperatures during the period the GRAEGOR was calibrated in the 5-day intercomparison phase. An analysis of all calibrations performed during the multi-week deployment of the GRAEGOR revealed that this particular calibration stood out with a significantly different sensitivity curve, whereas the all other calibration agreed within 5%. Using these other GRAEGOR calibrations for data analysis, the average difference decreased to <7% and the offset was <0.6 ppbv. If obvious condensation events in the PTR-MS sampling line were excluded, AiRRmonia and PTR-MS measurements agreed to within 3% with an offset <0.25 ppbv.

During conditions favoring condensation in inlet lines, the PTR-MS measured significantly less NH_3 than the wet chemical systems, which had much shorter inlets. This underlines the importance of a careful inlet design and needs to be considered for any instrument measuring NH_3 directly in the gas phase.

The three instruments included in this study have different fields of application. The AiRRmonia is developed for time-extended NH_3 monitoring in the field without intensive maintenance in contrast to both the GRAEGOR and the PTR-MS. The GRAEGOR instrument allows to selectively and simultaneously measure several gas and particulate components and to sample simultaneously at two different levels for aerodynamic gradient studies. The PTR-MS measures NH_3 at a sampling time of seconds, although the effective response time is somewhat slower probably because of adsorption effects within the instrument (Norman et al., 2007). Still, it is considerably faster than the other instruments which have a sampling time of 30 min to one hour. The PTR-MS

is therefore suitable for process based studies or for measurements on moving platforms where fast changes of mixing ratios occur, provided that inlet lines cause no significant damping of rapidly changing mixing ratio signals.

The results from these measurements are well in line with previously reported intercomparisons proving that these three instruments are suitable for atmospheric NH_3 measurements under the tested conditions.

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