**Atmospheric
Measurement
Techniques
Discussions**

Eddy covariance flux measurements of ammonia by electron transfer reaction-mass spectrometry

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Eddy covariance flux measurements of ammonia

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Abstract

A system for fast ammonia (NH_3) measurements based on a commercial Proton Transfer Reaction-Mass Spectrometer is presented. It uses electron transfer reaction (eTR) as ionisation pathway and features a drift tube of polyetheretherketone (PEEK) and silica-coated steel. Heating the instrumental inlet and the drift tube to $180°C$ enabled an effective time resolution of ~1 s and made it possible to apply the eTR-MS for eddy covariance (EC) measurements. EC fluxes of NH_3 were measured over two agricultural fields in Oensingen, Switzerland, following fertilisations with cattle slurry. Air was aspirated close to a sonic anemometer at a flow of 100 STP L min^{-1} and was directed through a 23 m long 1/2" PFA tube heated to $150°C$ to an air-conditioned trailer where the eTR-MS sub-sampled from the large bypass stream. This setup minimised damping of fast NH_3 concentration changes between the sampling point and the actual measurement. High-frequency attenuation loss of the NH_3 fluxes of 20 to 40% was quantified and corrected for using an empirical ogive method. The instrumental NH_3 background signal showed a minor interference with H_2O which was characterised in the laboratory. The resulting correction of the NH_3 flux after slurry spreading was less than 1‰. The flux detection limit of the EC system was about 5 ng m^{-2} s^{-1} while the accuracy of individual flux measurements was estimated 16% for the high-flux regime during these experiments. The NH_3 emissions after broad spreading of the slurry showed an initial maximum of 150 µg m^2 s^{-1} with a fast decline in the following hours.

1 Introduction

Ammonia (NH_3) is the least understood of quantitatively important compounds in today's terrestrial nitrogen cycle and accounts for a major proportion of environmentally harmful effects of high nitrogen loads (Erisman et al., 2007). It is the most abundant alkaline trace gas and thus very important for neutralising atmospheric acids like sulphuric or nitric acid. In such, it forms particulate matter (Baek et al., 2004; Smith et

al., 2005; Seinfeld and Pandis, 2006; Ortega et al., 2008; Nemitz et al., 2009), therefore contributing to radiative forcing (IPCC, 2007; Shindell et al., 2009) and impacting human health (Pope et al., 2002; Gutierrez, 2010). Populated areas, mainly in Europe, North- and South America and also in parts of Asia experience a large excess of NH_3, primarily for reasons of intensified agricultural production (Sutton et al., 2008). The excessive nitrogen input in sensitive ecosystems can result in eutrophication, loss of biodiversity and soil acidification (Galloway et al., 2003). On a global scale, NH_3 emissions will most likely increase in future and large uncertainties remain both in the sources and the fate of atmospheric NH_3 (Erisman et al., 2007). Agriculture is by far the most dominant contributor to anthropogenic NH_3 emissions. In central Europe it is responsible for about 90% of the NH_3 release (Erisman et al., 2008), the same holds for Switzerland (Reidy et al., 2008).

Ambient NH_3 mixing ratios range from less than one ppb in remote areas (Sutton et al., 1993b) to levels close to, or exceeding one ppm near strong sources (Flechard et al., 2010). Accurate measurements of NH_3 concentrations with a high time resolution (in the order of one minute or faster) are generally difficult due to the stickiness of the polar NH_3 molecule to all surfaces (Parrish and Fehsenfeld, 2000). Additionally, the partitioning between gaseous NH_3 and particulate NH_4^+ often complicates the interpretation of the measurements (Parrish and Fehsenfeld, 2000; Nemitz et al., 2004b; Wolff et al., 2010b). One consequence of these measurement challenges is that considerable uncertainties persist in the understanding of the processes controlling emissions and distribution of NH_3. For example, knowing the mechanisms controlling NH_3 volatilisation after application of organic fertiliser is important to quantify emission strengths and to optimise mitigation strategies. It remains vital to improve the methodology for precise NH_3 measurements with a high time resolution for better assessing highly dynamic NH_3 fluxes on the field scale (10^3 to $10^5\,m^2$) (Sutton et al., 2007; Fowler et al., 2009).

To date, reported field scale assessments of NH_3 fluxes rely on the aerodynamic gradient method (Baldocchi et al., 1988; Sutton et al., 1993a), mostly by means of

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NH$_3$ analysers that are based on wet chemical analysis which is very labour intensive (Flechard and Fowler, 1998; Erisman et al., 2001; Mosquera et al., 2001; Nemitz et al., 2004a; Wichink Kruit et al., 2007; Flechard et al., 2010; Spirig et al., 2010; Wolff et al., 2010a). The challenging nature of the NH$_3$ flux measurements is also reflected in the
5 results of a recent intercomparison exercise where considerable differences were found (Milford et al., 2009). In order to overcome some of the uncertainties inherent in these measurements, direct flux measurements using the eddy covariance (EC) technique are highly desirable (Sutton et al., 2007; Fowler et al., 2009). It is considered to be the most direct and least error-prone approach (Ammann, 1999; Sutton et al., 2007;
10 Denmead, 2008), but requires the trace gas analyser to resolve the major part of the turbulent spectrum, ranging from frequencies of about 10 to 0.001 Hz (Businger and Delany, 1990).

Only recently several sensitive and fast responding instruments for NH$_3$ became available that theoretically opened the possibility to perform EC flux measurements.
15 These are mostly based on principles of chemical ionisation (Shaw et al., 1998; Španěl and Smith, 1998; Fehsenfeld et al., 2002; de Gouw and Warneke, 2006; Nowak et al., 2006; Norman et al., 2007) and absorption of light in the mid-infrared (Edwards et al., 1994; Berden et al., 2000; McManus et al., 2008). Shaw et al. (1998) presented first trials to employ Chemical Ionisation Mass Spectrometry (CIMS) for EC fluxes of NH$_3$.
20 Famulari et al. (2004) performed NH$_3$ EC measurements by means of Tunable Diode Laser Absorption Spectrometry (TDLAS). In the following, Whitehead et al. (2008) intercompared two fast optical systems (TDLAS and Quantum Cascade Laser Absorption Spectrometer, QCLAS) in EC configuration to determine NH$_3$ fluxes associated with slurry spreading and tested these against the AMANDA wet chemistry gradient
25 system. They found a systematic underestimation of the EC fluxes of 47%, which they could not correct for nor explain.

The difficulties in NH$_3$ measurements primarily have to be attributed to adsorption and re-evaporation of NH$_3$ in filters, inlet tubes and instruments themselves (Parrish and Fehsenfeld, 2000; Fehsenfeld et al., 2002; Schwab et al., 2007). This leads to

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attenuation of concentration changes and thus most severely limits the application of the EC technique for NH_3. Brodeur et al. (2008) evaluated a TDLAS, including inlet lines for NH_3 EC measurements. In the laboratory, they proved the setup to highly underestimate fluxes in most potential measurement situations due to attenuation of fast NH_3 fluctuations in the inlet tube. In field applications, the majority of instruments require an inlet tube of several metres length. This attenuates fast concentration changes (Lenschow and Raupach, 1991; Brodeur et al., 2008; Massmann and Ibrom, 2008; Whitehead et al., 2008) and may even introduce severe NH_3 concentration alteration in special situations, e.g. during periods of condensation inside the tube (Norman et al., 2009) and NH_3 evaporation from the tube walls induced by drying of the inner surface (Hensen et al., 2009; Ellis et al., 2010).

Among the CIMS techniques, Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is fast enough to be applied with EC (Karl et al., 2001; Jost et al., 2003; Mikoviny et al., 2010), as documented by EC flux measurements of volatile organic compounds (VOCs) (Rinne et al., 2001; Karl et al., 2002, 2004; Spirig et al., 2005; Yokelson et al., 2007; Bamberger et al., 2010). Norman et al. (2007) published an approach to measure NH_3 with a modified commercial PTR-MS from Ionicon Analytik GmbH (Innsbruck, Austria), using ionisation of the analyte via electron transfer instead of proton transfer. This so-called "electron Transfer Reaction-Mass Spectrometer" (eTR-MS) reliably measured NH_3 concentrations (Norman et al., 2009), but had a response time too slow for EC measurements. To a major part, adsorption and desorption of NH_3 on surfaces inside the instrument restricted the time resolution.

In the mean time a new smaller drift tube made of inert materials became available that can be heated up to 200 °C.

In this study, we explore whether the new materials and heating enhance the instrumental time resolution and report on the application of eTR-MS for EC flux measurements of NH_3 after organic fertiliser application. The conditions in the field are best suited to test the applicability of the system for EC measurements as they provide the entire range of turbulent structures in the atmospheric surface layer with corresponding

concentration changes that could be simulated only with a very complex laboratory experiment (e.g. Brodeur et al., 2008). The performance of our setup was tested during two slurry applications on an arable and a grassland field.

2 Methods

2.1 Instrumental

2.1.1 Detection of NH_3

PTR-MS (Hansel et al., 1995; Lindinger et al., 1998) is a widely used state-of-the-art CIMS technique, primarily applied to detect VOCs on-line with a high sensitivity and time resolution (de Gouw and Warneke, 2006; Blake et al., 2009). A source gas (water vapour) is protonated inside a hollow cathode and subsequently interacts with the sample gas and transfers protons to components with sufficient proton affinity. The resulting product ions are separated by a quadrupole and afterwards detected with an electron multiplier pulse counter. In recent studies, PTR-MS has been employed to quantify EC fluxes of selected biogenic VOCs (Rinne et al., 2001; Karl et al., 2002, 2004; Spirig et al., 2005; Yokelson et al., 2007). Expanding the field of applications, the PTR-MS instrument has been adopted for measurements of ambient NH_3 concentrations (Norman et al., 2007, 2009). For this purpose, it is operated with pure oxygen as source gas. The main primary ion resulting from the hollow cathode discharge is charged oxygen (O_2^+). Correspondingly, the main reactions in the drift tube are no longer proton, but electron transfers. In the case of NH_3, the resulting product ion is NH_3^+ (Eq. 1), detected as m/z 17 (Španěl and Smith, 1998).

$$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2. \tag{1}$$

In the following, we will refer to the instrument operated in this electron transfer mode as eTR-MS. A detailed description of the sensitivity and selectivity of the eTR-MS is given

in Norman et al. (2007). In particular, they found a sensitivity for NH_3 of more than 40 cps (counts per second) per ppb of NH_3, which is comparable to values typically obtained for PTR-MS measurements of VOCs (Karl et al., 2002; Ammann et al., 2004; Spirig et al., 2005). In contrast to VOC measurements, where time resolutions in the order of a few Hz are possible, the response time was much slower with NH_3 (Norman et al., 2007). The most probable reason for the slow time constants was a strong damping at the inner surfaces of the instrument due to the high affinity of NH_3 to almost any kind of material.

2.1.2 Instrumental modifications

In the meantime a new prototype drift tube has been developed by the manufacturer of PTR-MS (Ionicon Analytik GmBH, Innsbruck, Austria). The new design features a smaller volume resulting in a faster gas exchange time and allows heating up to 200 °C. In addition, the fraction of metal at the inner surface was significantly reduced compared to the conventional drift tube. Table 1 summarises the differences between the new prototype and the conventional drift tube.

The new eTR-MS sample inlet consists of PEEK capillaries (Fig. 1) and was optimised for minimum residence time of the air to be analysed. The drift tube samples $\sim$0.022 STP L min^{-1} through a critical orifice whereas the inlet tubes can be purged with up to 1.1 STP L min^{-1}. The inlet manifold and the drift tube are placed inside an aluminium block equipped with a heater ensuring equal temperatures of all elements. We operated the eTR-MS drift tube at a voltage of 400 V and a pressure of 2.13 mbar resulting in a ratio of the electrical field to the gas number density $E/N \approx 120$ Td $(1\,\text{Td} = 10^{-17}\,\text{V cm}^2)$. According to Norman et al. (2007) this prevents secondary reactions of NH_3^+ with H_2O which become relevant only at a ratios $E/N > 120$ Td.

2.1.3 Characterisation and calibration

Norman et al. (2007) demonstrated the linearity of the eTR-MS over a wide range of NH_3 concentrations. They found the instrumental sensitivity for NH_3 to be independent from sample humidity, but identified a minor offset linearly depending on water vapour concentration. We performed laboratory experiments to determine the water vapour interference in our instrument. Humid zero air was produced by using compressed synthetic air and guiding it sequentially through two impingers controlled by a mass flow controller: the first impinger contained HCl solution ($0.1\,ML^{-1}$) to eliminate residues of NH_3, the second was filled with demineralised water. Both were placed inside a water bath allowing to regulate air humidity via changing the bath temperature. The water was cooled down with ice cubes and subsequently warmed up to room temperature creating a wide range of humidities. Entirely dry zero air was achieved by directing the same synthetic air without impingers through a citric acid coated dry denuder. The eTR-MS sampled out of an overflow. The overflow air humidity was monitored by a dew point mirror. Experiments with this setup allowed to analyse influences of varying humidity on the instrumental background and also revealed that eTR-MS can measure water vapour, detected as *m/z* 37 (clustered water molecules $H_2O \cdot H_3O^+$), equally to the operation of the instrument in PTR-MS configuration (Blake et al., 2009).

In order to analyse the time response of the instrument, the setup was modified to generate fast switches between NH_3-free and NH_3 containing air. For this purpose, a small amount of a gaseous NH_3 standard (50 ppm, purity grade 5.0), regulated by a mass flow controller could be injected into the respective zero air stream. A 3-way solenoid PTFE (polytetrafluorethylen) valve (1/8", Teqcom, Santa Ana, CA, USA) was used to sub-sample either from the zero air or from the NH_3 containing air stream (150 ppb). Concentration steps were easily achieved by switching the valve. To avoid memory effects on surfaces of the setup, the tubes – 1/4" and 1/8" OD, PFA (perfluoroalkoxy) – and the valve were heated to about $150\,^{\circ}C$ and both, zero and NH_3 air lines were continuously flushed. For the same reason, the tubes between valve and

eTR-MS were kept as short as possible. During all these experiments, the system was run for several hours before conducting the test to provide enough equilibration time to create a stable NH_3 concentration and zero air, respectively.

The laboratory experiments did not reveal a dependence of the instrument's sensitivity on the concentration of water vapour. However, a non-linear relationship between water vapour concentration and instrumental NH_3 background signal was found. It was examined over a humidity range of 0 to 30 mmol mol^{-1} of H_2O and could be described as:

$$c NH_{3_{bckgr}} = -0.681 \cdot (cH_2O)^2 + 38.725 \cdot cH_2O, \ R^2 = 0.99, \tag{2}$$

with cNH_3 in units of ppt and cH_2O in mmol mol^{-1}.

The magnitude of the variation in instrumental background was in reasonable accordance with results reported by Norman et al. (2007). In contrast to their findings, no significant humidity related change in the detection limit was encountered. The 2 σ limit of detection corresponded to 460 ppt NH_3 for a one-second time resolution (within the considered humidity range). When integrating the eTR-MS signal over 1 min, the detection limit decreased to 90 ppt.

At the field site, the eTR-MS was calibrated using a permeation oven manufactured by LN Industries (Geneva, Switzerland) equipped with a NH_3 permeation tube (VICI, Metronics Inc., Poulsbo, WA, USA). In this system the permeation tube is constantly kept at 40 °C and continuously flushed with dry zero air (obtained from a cylinder of compressed air) at a flow rate of 0.05 STP L min^{-1}. By dilution with the same zero air, a defined NH_3 concentration is achieved. In case of the zero air calibration, a citric acid coated dry denuder was added in front of the outlet of the device to strip away potential rests of NH_3 to ensure the quality of this calibration. The permeation system was calibrated by directing the gas mixture through an impinger containing acidic solution (H_2SO_4, 0.01 ML^{-1}) and subsequent analysis by ion chromatography.

Calibrations were performed at the field site shortly before the slurry applications at an effective mixing ratio of 68 ppb NH_3 and one additional zero air measurement after

the second fertilisation event. Prior to recording the signal of NH_3 concentrations, an equilibration time of at least half an hour was allowed to exclude any potential errors due to adsorption effects of the tube manifolds. The calibrations showed a stable sensitivity of the eTR-MS of 5.73 ncps (cps normalised to 10^6 cps of O_2^+) per ppb of NH_3

5 with an instrumental zero air offset of about 300 ppt NH_3 in dry conditions.

2.2 Flux measurements in the field

2.2.1 Experimental site and design

The capability of eTR-MS for EC measurements of high NH_3 emission fluxes was tested on the occasion of two cattle slurry applications at Oensingen, Switzerland in

10 August 2009 (for a detailed site description see Spirig et al., 2010). The first fertilisation was on an arable field (4 August 2009) and the second on an adjacent grassland field (6 August 2009). The arable site (wheat) had been harvested days earlier with stubbles of ∼20 cm height remaining in low density, and the grassland had been previously cut as well leaving a vegetation cover of only 5 cm height. The slurry was spread using a

15 tank trailer with splash plate. Table 2 summarises key properties of the applied slurry.
   The sonic anemometer was placed onto the freshly fertilised surface at a height of 1.25 m above ground, whereas the upwind fetch was about 100 and 75 m in the case of the crop and the grassland field, respectively. The eTR-MS was installed in an air conditioned container 15–20 m away from the sonic anemometer at the field

20 border. The sample inlet was placed 25 cm below the centre of the sonic sensors at 1 m a.g.l. (above ground level).

2.2.2 Inlet line

Since the flux measurement system was situated on the fertilised field and the eTR-MS was housed in the container adjacent to the site, an inlet tube of 23 m length was

25 necessary. In order to facilitate fast NH_3 measurements despite the long inlet tube, a

custom-made tube heating was constructed. The 1/2" (OD) PFA Teflon tube was insulated with silicone foam hose (22 mm ID, 8 mm wall thickness; Castan, Freiberg, Germany). The heating consisted of four heating wires (Type KTeS, Wisag, Zürich, Switzerland) with a heat production of 22.5 Wm^{-1} each, evenly distributed parallel along the
5 tube. The tube was completely wrapped with heat resistant aluminium-covered glasfiber tape (Scotch$^{®}$, 3 m, St. Paul, MN, USA). The inlet temperature profile was monitored by K-type thermocouples, fixed at the tube's outer surface inside the wrapping at 5 different locations (0.05, 6.5, 12, 18 and 23 m away from the sample inlet), carefully arranged not to be in direct contact with the heaters. Temperature was regulated and
10 kept at 150 °C by a proportional-integral-derivative (PID) temperature controller using the thermocouple close to the eTR-MS creating an increasing temperature gradient over the entire inlet line as shown in Fig. 2.

The sample tube was flushed with ~100 STP L min^{-1} by a rotary pump (VTE8, Thomas, Memmingen, Germany) installed downstream of the eTR-MS inlet. The
15 Reynolds number (*Re*) inside the tube was $Re \approx 4.4 \times 10^{4}$. The cooling effect of the 100 STP L min^{-1} sample flow outweighed the heating at the first metres of the inlet line. Nevertheless, temperatures above 100 °C were achieved at about 2.5 m from the inlet (Fig. 2). Near the end of the 23 m sample line, a subsample (1.1 STP L min^{-1}) of the air stream was aspirated towards the eTR-MS through a 17 cm long 1/8" (OD) PFA
20 tube heated separately to 150 °C.

2.2.3 Eddy covariance flux calculation

Following the EC method (Baldocchi et al., 1988; Dabberdt et al., 1993), the vertical flux of a trace gas at the sampling point is calculated as the covariance of the discrete time series (average product of the instantaneous deviations from the mean values) of
25 the vertical wind $w(t)$ and concentration $c(t)$ over an averaging period T_a of typically 10 to 30 min. The two time series have to be adjusted to each other by the time lag

(τ_{del}) in order to account for the delayed detection of the trace gas, mainly due to the tube transit time:

$$F_{ECraw} = \text{cov}_{wc}(\tau_{del}) = \left(\frac{\Delta t}{T_a}\right) \cdot \sum_{t=0}^{T_a} \left(w(t) - \overline{w}\right) \cdot \left(c(t - \tau_{del}) - \overline{c}\right), \tag{3}$$

where Δt = time difference between two recordings.

⁵ The EC flux is denoted as "raw" here because it needs some additional corrections due to non-ideal measurement conditions (see below). For the concentration time series $c(t)$ the specific characteristics of the eTR-MS data acquisition have to be considered: within one measurement cycle, the eTR-MS sequentially scans for selected ion masses with differing dwell times (Fig. 3). In the present field experiment one full ¹⁰ measurement cycle of the eTR-MS was completed within 0.93 s.

In order to derive the EC fluxes, the approach presented by Spirig et al. (2005) was applied. The measurement of an individual ion mass is regarded to be representative for one whole measurement cycle and the respective eTR-MS data point is replicated at 20 Hz time resolution until the following cycle is finished, producing a data record with ¹⁵ identical time resolution as that of the sonic anemometer (HS Research Anemometer, Gill Instruments Ltd, Lymington, UK). Such gap-filling introduces additional low-pass filtering of the fluxes that can be corrected for as long as the measurements cycle is relatively short (Hörtnagl et al., 2010). As closed path sampling of sticky compounds produces a considerable amount of high-frequency attenuation (Ammann et al., 2006; ²⁰ Ibrom et al., 2007), the low-pass filter effect due to the gap-filling does not significantly influence the flux calculation since it is included in the applied high-frequency correction (Spirig et al., 2005) (see below).

The sonic anemometer data were recorded by a Labview (National Instruments, Austin, Texas, USA) program whilst eTR-MS data were registered on the same com-²⁵ puter by a modified version of Ionicon's software "PTR-MS control 2.5". The latter externally buffered the data in real-time, so that the sonic anemometer program could record both datastreams with a common rate of 20 Hz.

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In case a turbulent flux is present, the cross covariance function given by Eq. (3) unambiguously peaks at the characteristic time lag of the system (McMillen, 1988). In theory, the time lag corresponds to the residence time of the air in the sampling tube that is determined by the flow rate and the tube volume. For eTR-MS measurements, the gas residence time in the instrument itself, the length of the measurement cycle and the signal integration time (Fig. 3) add to the expected delay (Spirig et al., 2005). In practice, deviations from the expected time lag can occur due to various reasons such as variations of the pump speed or the wind direction, non-negligible data acquisition and processing time (Leuning and Judd, 1996), or humidity dependent sorption effects on the tube walls (Ibrom et al., 2007). Consequently, we chose to derive τ_{del} with a peak detection routine in the covariance function within a given range of plausible lag times. The precision of F_{ECraw} was calculated according to Wienhold et al. (1994) as the standard deviation σ_{cov} of the covariance function within windows shifted -120 to -70 s and $+70$ to $+120$ s from the expected lag. A reliable identification of the covariance peak and thus of the lag time is possible only if the corresponding flux clearly exceeds $2\sigma_{\text{cov}}$. For situations when a peak identification was not possible, a fixed lag τ_{fix} was derived as the mean of τ_{del} obtained from detectable peaks and was used for the calculation of the respective flux F_{ECraw} (τ_{fix}) $\pm 2\sigma_{\text{cov}}$. The dilution effect of water vapour on the NH_3 flux was accounted for by routinely applying the so-called WPL correction (Webb et al., 1980). This altered the slurry emission fluxes by two per mille at maximum (and by about 0.5 to 1 ng m^{-2} s^{-1}, hence a few percent during small fluxes on 15 August 2009, see Sect. 3.2.3).

Ogives (Og_{wc}) (e.g. Desjardins et al., 1989; Oncley et al., 1989) provide information about the contribution of different turbulent frequencies to the flux. They are cumulated co-spectra integrating over all frequencies of the finite co-spectrum of the covariance function:

$$Og_{wc}(f_m) = \sum_{i=1}^{m} Co_{wc}(f_i), \qquad (4)$$

$$f_i = \frac{i}{T_a}; \; m = 1, 2, \ldots, \left[\frac{T_a}{2 \times \Delta t}\right].$$

The value of the function at a certain frequency (f_m) represents the integrated co-spectral contribution to F_{ECraw}. Ammann et al. (2006) presented an ogive-based empirical correction that accounts for signal loss due to insufficient time resolution of the analytical system. Implying co-spectral similarity, the attenuation factor is derived by comparison with the ogive of the sensible heat flux that is assumed to be undamped.

As a consequence of the humidity interference on the NH_3 measurement of the eTR-MS (Eq. 2), variations in ambient water vapour concentration due to turbulent H_2O flux provoke fluctuations in the NH_3 signal appearing as an artificial contribution to the EC NH_3 flux. Therefore, concentrations and EC fluxes of water vapour were monitored in parallel by a conventional open path infrared gas analyser (IRGA; Li-7500, LI-COR Biosciences, Lincoln, USA) operated together with a second ultrasonic anemometer (Ammann et al., 2007). The eTR-MS m/z 37 signal was calibrated against the water vapour concentration of the IRGA to calculate EC H_2O fluxes by eTR-MS as outlined above.

The water correction (Eq. 2) was performed on the high resolution NH_3 time series before it was processed to derive EC fluxes, employing the H_2O concentrations also recorded by the eTR-MS. The amount of flux interference was then quantified as the difference between the EC NH_3 fluxes calculated with and without this correction. A potential error source could be the fact that strictly speaking the eTR-MS measures NH_3 and H_2O not simultaneously (Fig. 3). However, the corresponding time delay of 0.2 s is definitely smaller than the response time limitation due to the high-frequency damping in the EC measurement of both, H_2O and NH_3 fluxes. Therefore, we neglected the influence of non-synchronous mass scans on the water vapour correction.

3 Results

3.1 Improvement of time response with the new drift tube

The reduced residence time and altered materials in the new prototype drift tube had no significant enhancing effect on the instrumental time response. In contrast, heating of the drift tube from $100\,°C$ to $180\,°C$ significantly improved the time response to step changes of the NH_3 concentration as observed in laboratory experiments (Fig. 4). Following the mathematical description given by Whitehead et al. (2008) and Ellis et al. (2010), the decay was characterised by a bi-exponential function:

$$cNH_3(t) = A_1 \cdot \exp\left(-\frac{(t - t_0)}{\tau_1}\right) + A_2 \cdot \exp\left(-\frac{(t - t_0)}{\tau_2}\right), \tag{5}$$

with t_0 = time of concentration step, time constants τ_1 and τ_2 and coefficients A_1 and A_2, where $A_1 + A_2 = cNH_3\,(t_0)$.

The two exponential terms describe the superposition of a fast and a slow reaction of the system to a concentration change (Ellis et al., 2010). The experiment revealed response times $\tau_1 = 2.82\,s$ and $\tau_2 = 56.73\,s$ with the PEEK drift tube at $100\,°C$. According to the relative magnitude of the coefficients A_1 and A_2, the faster exponential function was responsible for 74% of the decrease. With the drift tube heated to $180\,°C$, τ_1 and τ_2 were reduced to $0.82\,s$ and $26.55\,s$, respectively. In this case, the fast exponential decay accounted for 80% of the overall step change.

3.2 Field measurements

3.2.1 Detection of turbulent fluctuations and covariances

In order to illustrate the fast response measurements in the field and the detection of turbulent fluctuations, Fig. 5 shows some exemplary high-resolution time series of the raw data of vertical wind speed (w), air temperature (T), NH_3 and H_2O concentration.

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The data on the left panel were recorded at noon, shortly after the spreading of slurry on the cropland. The temperature time series revealed typical flux signatures, evident as tooth-saw shaped structures that are known to be characteristic for convective elements participating in the vertical transport (Kaimal and Businger, 1971), as well as up- and downdrafts emerging as cyclic features. Similar patterns were also present in the course of the H_2O and NH_3 time series. Changes occurred primarily on timescales ranging from one second to a few tenths of seconds. The NH_3 time series is characterised by high temporal dynamics with a range of minimum to maximum values of about 80 ppb to 3100 ppb. Qualitatively this suggests that the field setup was fast enough to capture the turbulent NH_3 fluctuations.

The data in the right-hand panel in Fig. 5 were recorded above the grassland, 9 days after the fertilisation of that site when the NH_3 fluxes were expected to be much smaller and in a potentially bi-directional exchange regime again (Flechard et al., 2010). As a contrasting instance, they illustrate a situation when positive correlations of temperature and H_2O were observed, but no (positive or negative) relation for NH_3 was apparent. In this case there was either no prevailing flux of NH_3 or it was not detectable by the system.

The covariance functions in Fig. 6 support the qualitative picture of the time series given above. It was possible to identify distinct maxima in all covariance functions for 4 August 2009 (upper panels). The peak value in the function corresponds to the raw vertical flux of the respective scalar quantity. For NH_3, the associated lag time was -2.85 s. Mean empirically derived lag times during both fertilisation events were -2.98 ± 0.14 s in case of NH_3 and -2.44 ± 0.12 s for H_2O, respectively. On average, the NH_3 lag deviated from that of the water vapour flux by -0.54 s. However, since H_2O (m/z 37) was scanned 0.2 s after NH_3 (m/z 17) in the eTR-MS measurement cycle (see Fig. 3), the actual lag difference amounted to -0.74 s. These lag times thus exceeded the calculated theoretical residence times in the measurement system of about 1.75 s for NH_3 and 1.64 s for H_2O, which account for the duration of gas transport in the inlet line and the instrument itself and for the delay due to the sequential mass scanning

(Fig. 3). Comparing the covariance functions of NH_3 and H_2O to that of temperature reveals similar shapes with slightly broader peaks. Overall, the observed covariance functions indicate the suitability of the system for EC flux measurements.

The second set of covariance functions shown in the lower Segment of Fig. 6 demon-
strates the limitations of the NH_3 flux identification. Still, distinct fluxes of sensible heat and water vapour appear as peak covariances, but in case of NH_3 it was not possible to unambiguously determine a peak value in the covariance function corresponding to the NH_3 flux.

The precision and detection limit of a flux measurement do not necessarily corre-
spond to each other and should be treated separately. The noise in the baseline of the covariance function used as a measure for the precision (Sect. 2.2.3) was about pro-
portional to the magnitude of the flux and therefore the large fertiliser emissions had a larger absolute uncertainty than smaller fluxes. In order to obtain a flux detection limit (against a zero flux), the standard deviation of the covariance function was averaged
during a phase (15 August 2009) when no significant covariance function peaks could be detected. The analysis yielded a $2\,\sigma$-flux detection limit of $4.5 \pm 1.5\,\mathrm{ng\,m^{-2}\,s^{-1}}$ for half hourly averaging intervals.

3.2.2 High-frequency attenuation

Figure 7 shows median ogives of NH_3, H_2O and sensible heat fluxes during the period
after the spreading of the slurry on the grassland field. The ogive values are normalised to the respective F_{ECraw} so that they range from 0 to 100% of the flux. The relatively uniform wind speed and unstable stratification on that day allowed a direct statistical evaluation of the individual ogives without conversion to dimensionless frequency. Con-
trasting the ogive of the NH_3 flux with that of the undamped sensible heat flux revealed
a clear attenuation of the NH_3 flux at higher frequencies. The dashed lines in Fig. 7 dis-
play the ogives of the NH_3 and H_2O fluxes after adjusting to the reference sensible heat flux ogive at a threshold frequency of 0.065 Hz. At frequencies above 0.065 Hz the NH_3 ogive slowly begins to deviate from the reference. However, substantial differences of

more than 5% occur at frequencies larger than 0.18 Hz. The ogive of the H_2O flux follows the sensible heat flux ogive somewhat longer, experiencing deviation larger than 5% only around 0.47 Hz. The NH_3 flux was attenuated by about 30% compared to the flux of sensible heat, the H_2O flux only by about 20%. Between the threshold and the low frequency end, the curves agreed considerably well.

As demonstrated in Fig. 8, the damping of the flux was parameterised as a function of horizontal wind speed in order to decrease the scatter of the single values (Ammann et al., 2006). Damping factors of the NH_3 flux showed more attenuation than those for the H_2O flux with decreasing values for both quantities at higher wind speeds.

3.2.3 Concentrations and fluxes following slurry application

Figure 9 gives a picture of the predominant meteorological conditions for the two days of fertilisation investigated here. The temperatures (about 15 to 24 °C and 15 to 27 °C, respectively, during daytime) and solar radiation intensities were quite high, whilst relative humidity was below 50% in the afternoon and highest in the early morning hours. There was no rain; winds prevailed from easterly directions with wind speeds of up to 4 and 2.5 ms^{-1}, respectively.

The series of data highlighted in the following reflect periods of well defined turbulence, selected due to criteria of the integral turbulence characteristics (Foken and Wichura, 1996). Figure 10 demonstrates the course of NH_3 concentrations during daytime on both sites. Failures of the combined sonic and eTR-MS data acquisition system on the first day of operation resulted in some data gaps on 4 August 2009. During slurry spreading, the 10 min moving average NH_3 concentrations recorded by the eTR-MS at 1 m a.g.l. quickly rose to around 1.2 ppm on 4 August 2009 and to more than 2.3 ppm on 6 August 2009. The peak was followed by a fast decay of the concentrations down to around 80 ppb and 40 ppb in the evening. The maximum NH_3 concentration on 4 August 2009 was most probably higher than measured, since the first minutes of the slurry spreading could not be captured. The data revealed enormous concentration fluctuations. Within the first hour, rapid concentration changes of more

than 2 ppm were monitored, even when averaging over 1 min. On 6 August 2009, the one minute averaged concentrations covered a range of more than 5 ppm NH_3 within several minutes.

The course of measured NH_3 fluxes strongly resembled that of the concentrations (Fig. 10). On 6 August 2009 the maximum recorded emission flux of about 150 $\mu g\, m^{-2}\, s^{-1}$ occurred almost immediately after the spreading of the slurry. The emission declined very fast, so that the majority of the time-integrated emission happened within the first and second hour after fertilisation. The same holds for 4 August 2009. Unfortunately, the data gap at the very beginning of this experiment also affected the first half hour of the slurry spreading. Here, the highest measured flux was about 107 $\mu g\, m^{-2}\, s^{-1}$. In the evening, the emissions decreased to roughly 1 $\mu g\, m^{-2}\, s^{-1}$ on both days.

3.2.4 Water vapour fluxes and their interference

Water vapour EC fluxes derived from eTR-MS measurements were compared with corresponding fluxes from the nearby EC system using a common IRGA analyser. Figure 11 shows good agreement between H_2O fluxes observed by both systems during two exemplary days. This demonstrates that, like in the proton transfer configuration (Ammann et al., 2006), the instrument was capable to capture EC H_2O fluxes in its electron transfer mode as well.

As outlined in Sect. 2.2.3, variations in water vapour concentration due to turbulent H_2O flux provoke fluctuations in the raw NH_3 signal inside the instrument appearing as EC NH_3 flux if not corrected for by Eq. (2). In order to check and illustrate the quantitative effect of the H_2O interference, we additionally analysed flux measurements in a situation of background surface-atmosphere NH_3 exchange, i.e. with low concentrations and fluxes unaffected by slurry related emissions (see Flechard et al., 2010). Figure 12 shows such an exemplary day. The diurnal course of NH_3 fluxes shows a depositional pattern in the morning and mainly zero or very small emission fluxes at noon. The interference effect of the H_2O fluxes did not substantially superimpose on the uncorrected

NH$_3$ fluxes ($< 2.1 \, \text{ng m}^{-2} \, \text{s}^{-1}$, see Fig. 12, upper panel). The NH$_3$ interference fluxes scaled with the H$_2$O fluxes by a ratio of $0.17 \pm 0.08 \, \text{ng NH}_3/\text{mmol H}_2\text{O}$. During the fertilisation related emissions this translated into a relative flux interference in the sub-‰ range. Even in the example of background exchange conditions on 15 August 2009 (Fig. 12), the H$_2$O correction was smaller than the precision of the flux determination.

4 Discussion

4.1 Time response

NH$_3$ is known to be among the stickiest trace gases due to its strong dipole (Appl, 1999) causing a high affinity towards surfaces. A conceptual picture of NH$_3$ adsorption emanates from the assumption that the surfaces provide a finite number of sorption sites: the less exchange sites exist and the more molecules are present, the faster the sites are saturated, hence the faster performs the instrument or tube. In addition, heating decreases the amount of H$_2$O molecules adsorbed at walls and hence lowers the impact on NH$_3$ molecules (Ellis et al., 2010) since both species undergo strong hydrogen bonding with each other.

In order to facilitate a fast time response it seems vital to provide inert materials (i.e. low surface energy, permeability) which can be heated. The eTR-MS instrument presented in our study is provided with components made exclusively of PEEK (inert, can be heated $> 200 \, ^\circ\text{C}$) and Siltek-coated steel. The results from the laboratory tests (Sect. 3.1) indeed revealed that especially heating promotes a fast time constant. The modified eTR-MS resolved NH$_3$ concentration steps much better than in the configuration by Norman et al. (2007). Recently, Mikoviny et al. (2010) explored the time resolution for NH$_3$ with a modified high temperature PTR-MS (glass drift tube, altered ion source geometry), operated at $200 \, ^\circ\text{C}$. They found a very fast instrumental response time of 0.3 s, confirming the positive impact of high temperatures.

Although there is not a completely consistent picture in the few studies looking at the performance of various tubing materials with NH_3, it becomes evident that PFA is probably the best suited material which still resists high temperatures (Mukthar et al., 2003; Shah et al., 2006). Additionally, Silcosteel performs slightly better than stainless steel (Whitehead et al., 2008). Ellis et al. (2010) demonstrated how NH_3 tends to be adsorbed more severely on inner walls of PFA tubes with smaller concentration steps and increasing sample air humidity. They confirmed that heating (to 40 °C) improves the time response to NH_3 concentration changes.

The inlet line used for the EC field measurements operated close to ambient pressure and had a large surface in contact with the sample gas. It was therefore equally or even more important to reduce damping effects in the tube as much as possible. Considering the findings mentioned above, the gas inlet line was made of inert PFA which can be heated to more than 100 °C. In this way, the adsorption of NH_3 on walls and thus the attenuation of NH_3 variations in the EC flux system were expected to be reduced. Massmann and Ibrom (2008) presented a mathematical framework to describe the attenuation of H_2O fluctuations in a closed path EC system. Based on the Hertz-Knudsen-Schrage Equation (e.g. Marek and Straub, 2001), their model described the net surface adsorption/desorption mass flux of H_2O to and from tube walls being dependent on the square root of gas (and surface) temperature. However, they found that a purely analytical description of the attenuation in tubes for sticky molecules like H_2O (and consequently NH_3) was not yet possible. In their review Davidovits et al. (2006) summarised that the mass accommodation of H_2O and also of NH_3 on H_2O layers decreases non-linearly (near exponentially) with increasing temperature. There is no empirically verified physical model of NH_3 sorption for materials present in instruments and inlet tubes and so far there seems to be a lack of comprehensive mechanistic understanding of such processes. Nevertheless, it is evident that temperature plays a central role in the mechanisms involved with sorption of NH_3 and H_2O on interfaces. We speculate that the existence of liquid and molecular H_2O layers inside the eTR-MS and the inlet tube can be suppressed (to a large degree) by heating the surfaces

considerably above 100 °C which in turn significantly reduces the stickiness of NH_3 on the involved walls.

Furthermore, the use of a strongly heated inlet line also prevented from condensation of H_2O that might trap NH_3 (Norman et al., 2009), which can re-evaporate from the inner inlet surfaces when these are drying (Hensen et al., 2009; Ellis et al., 2010). The tube temperature (Fig. 2) rose to above 100 °C shortly after the sample inlet and was much higher than in previous studies addressing NH_3 measurements (e.g. Shaw et al., 1998; Famulari et al., 2004; Whitehead et al., 2008; Benson et al., 2010; Ellis et al., 2010; von Bobrutzki et al., 2010). Heating the inlet is constrained not only by the choice of material but also by the requirement that the inlet must not become a source of heat interfering with the ultrasonic anemometer measurement. In the present study, the sensible heat flux did not indicate any alteration by the tube heating fixed in direct proximity to the anemometer.

4.2 High-frequency attenuation

Slurry spreading over an agricultural field offers a unique test for the time behaviour of the setup as it provides high emissions and the turbulent nature of the vertical fluxes produces flux contributions over a large frequency range.

In closed-path systems, the turbulence related concentration fluctuations of different compounds can be retarded with varying time constants dependent on their stickiness. The fact that the maxima in the covariance functions for NH_3 and H_2O were considerably delayed to each other (Sect. 3.2.1) demonstrates that NH_3 was subjected to memory effects in the inlet line even more than H_2O. Like in our measurements, it has been observed earlier that water vapour does not behave like a passive tracer, either (Ammann et al., 2006; Ibrom et al., 2007). The applied high-frequency correction as a function of horizontal wind speed showed a 10% larger damping of the NH_3 flux compared to the H_2O flux. The significant high-frequency losses were promoted by the low measurement height of only 1 m a.g.l. (with a short vegetation cover) leading to a considerable weight of higher-frequent flux contributions (Kaimal and Finnigan, 1994).

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This height was chosen to minimise the extension of the footprint given the relatively small field sizes. It has to be noted that this situation is particularly challenging for EC measurements of sticky compounds. Measuring at higher levels will diminish the effect of high-frequency damping considerably and thus improve the performance of the EC system.

Our high-frequency loss correction implies that below a frequency of 0.065 Hz turbulent variations of NH_3 passed the inlet line undamped. This is perhaps an oversimplification as the response of NH_3 step changes could be described by the superposition two exponential decays (Eq. 5) with the slower decay time constant being in the order of tens of seconds and more. Compared to the ogive of the sensible heat flux, the damping-adjusted ogive of the NH_3 flux showed a very good agreement from 0.065 Hz down to the lowest frequency (Fig. 7), suggesting no attenuation in this range. However, if the slow decay function involved a nearly uniform damping over all frequencies, there is potential risk for a systematic underestimation of the damping that would not become obvious in the ogives, but we did not find any other indication for such an effect.

The observed attenuation is likely to increase with the usage time of the tube as the inner surfaces are getting dirty and the sorption effects might become stronger (Leuning and Judd, 1996; Ibrom et al., 2007). In light of the complexity of the processes involved with sorption related attenuation we applied the empirical high-frequency attenuation correction. As long as easily identifiable NH_3 fluxes are present this could, for instance, be done on a day by day approach allowing to detect systematic changes in the response function e.g. by an increasing damping due to tube ageing.

Ellis et al. (2010) showed that the magnitude of NH_3 concentration steps influences the sorption related time response in tubes with high concentration steps in heated tubes being resolved best. This suggests that the attenuation of NH_3 could be dependent on the magnitude of the flux. However, we are not able to address this issue with the limited dataset presented here.

4.3 Water vapour interference

The amount of H_2O molecules in the sampled air exceeds those of NH_3 by typically three to six orders of magnitudes. The same holds for the associated fluxes. Well known and routinely corrected for is the dilution of the concentration due to increasing water vapour, the WPL correction (Webb et al., 1980). In addition, depending on the type of instrument, various complex water vapour interferences are possible. For instance, high resolution spectroscopy such as QCLAS or cavity ring down spectroscopy show a weak pressure broadening of absorption lines that especially influences small fluxes (Neftel et al., 2010; Tuzson et al., 2010). CIMS systems can suffer from large interferences associated with the ion source. In this respect, a closer analysis of the fluxes presented by Shaw et al. (1998) suggests an artefact related to the interference of water molecules. They reported NH_3 emission fluxes of $145\,\mu g\,m^{-2}\,s^{-1}$ and concentrations of $1340\,\mu g\,m^{-3}$ from a field that was not under cultivation at that time. Such high fluxes and concentrations normally only exist directly after application of organic fertiliser. Even though the EC analyses were technically correct, it is easily possible that water vapour induced some of the reported fluxes.

Most probably, traces of N_2 and H_2O intrinsically create NH_3 inside the eTR-MS ion source (Norman et al., 2007). Our laboratory investigations as well as the studies by Norman et al. (2007, 2009) revealed that the expected water vapour interference for the eTR-MS were small. This is nicely illustrated by comparing the typical absolute water interference effect (Fig. 12, upper panel) with the NH_3 fluxes recorded on slurry application days (Fig. 10) and one and a half week later (Fig. 12, lower panel), when much smaller exchange fluxes fluctuating around zero were observed. Figure 12 indicates no significant coupling between the fluxes of NH_3 and H_2O. It is fully evident that the high slurry NH_3 emissions cannot have been a consequence of any H_2O interference. The flux correction due to the water dependent eTR-MS background signal was $2.1\,ng\,NH_3\,m^{-2}\,s^{-1}$ at most, i.e. below the flux detection limit (see following Sect.). Correcting the raw data for the H_2O interference instead of an integral correction

(e.g. Neftel et al., 2010) eliminates possible interferences on the covariance peak detection of NH_3 and thus facilitates the correct detection of NH_3 fluxes under background exchange conditions.

4.4 Contributions of ammonium aerosol

Heating the sample gas to 150°C and more will cause dissociation of semi-volatile aerosol compounds, such as ammonium-nitrate, as well as partly evaporation of non-volatile species, such as ammonium-sulphate (conditions comparable to processes within thermodenuders, e.g. Huffman et al., 2008). Therefore, the eTR-MS setup was most probably prone to measure the sum of the concentrations of NH_3 and its semi-volatile particulate counterpart NH_4^+ ($NH_x = NH_3 + NH_4^+$). The partitioning in ambient air and hence the importance of aerosol NH_4^+ on the NH_3 measurement depends on relative humidity, temperature and the concentrations of other gaseous reaction partners (Seinfeld and Pandis, 2006). For conditions of small concentrations and fluxes the relative interference on the NH_3 measurement could be significant. For the Swiss central plateau, characterised by intensive agriculture, more than enough NH_3 for neutralising acidic gases is generally available (Spirig and Neftel, 2006), so that we can expect that NH_3 exceeds NH_4^+ under such circumstances. For example, in summer 2006 total aerosol NH_4^+ concentrations at the grassland site have been found to be roughly 10–30% of the gas phase NH_3 content with only short episodes of higher ratios (Wolff et al., 2010a). Partial evaporation of this NH_4^+ in the inlet tube or eTR-MS might interfere with the NH_3 concentration measurement. After the spreading of slurry, however, the gaseous fraction dominates the NH_x concentrations by far. Therefore, aerosol NH_4^+ does not significantly affect the NH_3 concentration measurement.

Regarding the EC flux measurements, the partitioning between NH_3 and NH_4^+ will affect the measured fluxes only when there are distinct NH_4^+ aerosol fluxes. Nemitz et al. (2009) evaluated fluxes of both species after ammonium-nitrate fertiliser application on grassland. They found the aerosol NH_4^+ fluxes to be orders of magnitudes smaller compared to the gaseous NH_3 fluxes. NH_3 emissions following slurry spreading are

even larger than those after mineral fertiliser application. Hence the interference for the eTR-MS derived NH_3 flux is regarded to be negligibly small ($< 1\%$) here.

4.5 Flux accuracy

The accuracy of the eTR-MS flux measurements is influenced by different sources of uncertainty in the process of the flux determination. In principle, errors acting randomly and systematically should be distinguished (Moncrieff et al., 1996; Kroon et al., 2010). Table 3 summarises our estimates of the main error types and contributions.

The calibration was finally based on wet chemical impinger measurements and subsequent analysis by means of ion chromatography with an estimated accuracy of about 5%. The eTR-MS instrumental sensitivity was constant between both fertilisations with a drift of less than 1%. Therefore, we assume the accuracy of the calibration to be 5%.

During the slurry emissions the peak covariance detection was generally not problematic (Fig. 6). Under such circumstances the resulting mean flux precision (as defined in Sect. 2.2.3) was $11 \pm 3\%$ of the measured fluxes.

The correction for high-frequency attenuation exhibits a stochastic source of uncertainty: the standard error of the linear regression that parameterises the damping (Fig. 8) gives an accuracy of the damping factors of about 10%.

The absolute accuracy of the correction for the H_2O interference on the NH_3 flux (Fig. 12) has been estimated to be $< 1\,\mathrm{ng\,m^{-2}\,s^{-1}}$. Considering the extremely small relative contribution to the fluxes during slurry spreading ($< 1\permil$), the influence of the H_2O flux on the overall accuracy of the EC NH_3 assessment could be neglected.

Finally, taking these aspects into consideration, the accuracy of a single EC flux measurement during the slurry dominated NH_3 emissions was estimated to be about 16% using Gaussian error propagation.

4.6 Plausibility of measured fluxes

The dynamics of the measured fluxes after slurry spreading can be described by a combined exponential decay in analogy to Eq. (5) with a fast time constant in the order of 30 min and a slower decrease with a time constant in the order of two to three hours. As the meteorological conditions and especially the wind direction were rather constant in the hours after slurry application (Fig. 9), changes in footprint contributions were of minor importance. Both, the initial fluxes as well as the temporal decrease were in the similar range as in slurry events previously investigated at the same site employing the aerodynamic gradient approach (Spirig et al., 2010). Since the applied slurry exhibited a relatively low dry matter content and consequently a rather low viscosity, highest emission fluxes are expected immediately after spreading of the slurry. Such thin slurry can easily infiltrate into the soil and absorption of NH_4^+ on soil particles decreases emissions (Braschkat et al., 1997). Due to instrumental restrictions, Spirig et al. (2010) had to estimate the first 30 to 200 min of emissions after the spreading of the slurry. With the EC approach at hand, there is now the possibility to measure these fluxes with a high time resolution and to gain a more comprehensive picture of the emissions, especially of the dominating initial phase.

5 Conclusions and outlook

With the aim to perform EC measurements of NH_3 fluxes, we have presented a modified version of the eTR-MS as described by Norman et al. (2007), optimised for fast time response. The system was altered to decrease the residence time of the sample gas, to reduce the metal fraction of interior surfaces, and to be able to run the eTR-MS at temperatures well above 100 °C. This was accomplished by replacing the materials of the central analytical part and the inlet of the instrument with components made of inert and very heat resistive PEEK and silica-coated stainless steel. Significant

advancement in instrumental time resolution for NH_3 was mainly achieved by heating all parts to 180 °C which minimised wall interactions with NH_3.

Using a 23 m long inlet tube heated to 150 °C, it was possible to detect EC fluxes after slurry spreading and to empirically correct the raw NH_3 fluxes for the system's high-frequency attenuation with the sensible heat flux serving as reference. The corrections were between 20% and 40% and turned out to be larger than those for the simultaneously measured H_2O fluxes. A thorough analysis of the potential of H_2O influencing the NH_3 measurements revealed a negligible interference on the observed NH_3 emission fluxes following fertilisations. Even under low flux conditions, the H_2O interference effect remained relatively small. Another source of interference with negligible effect on the high emission fluxes but of potential importance at low fluxes is the dissociation of semi-volatile aerosol NH_4^+ inside the heated tube and instrument.

More work will be required to better characterise the behaviour of the system under low flux conditions. Essentially, it must be further investigated whether deposition fluxes can be measured with sufficient accuracy, since it is possible that the degree of high-frequency damping is inversely correlated with the magnitude of concentration changes (Ellis et al., 2010). In addition, the long-term performance of the inlet line has to be evaluated in order to quantify the impact of tube ageing on memory effects with potential alterations in delay time and high-frequency attenuation (Leuning and Judd, 1996).

A forthcoming publication will include the quantification of NH_3 field emission losses after slurry spreading and compare the presented EC technique with an independently applied horizontal mass flux approach.

We are now confident that under conditions of high NH_3 emission, the eTR-MS setup provides robust EC flux measurements, which represents a substantial improvement in such investigations and will help to reduce the uncertainties associated with the quantification of agricultural NH_3 emissions.

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Table 1. Comparison of the eTR-MS equipped with conventional (PTR-MS HS2 of Ionicon Analytik) and new prototype drift tube and inlet design.

	conventional	new prototype
drift tube volume	$18\,cm^3$	$7\,cm^3$
drifted tube residence time	80 ms	30 ms
drift tube materials	stainless steel, Teflon® (PTFE)	stainless steel coated with Siltek® (Restek, Inc., Bellefonte, PA, USA), PEEK (polyetheretherketone)
drift tube operating temperature	40˚–120 ˚C	40˚–200 ˚C
instrumental inlet design	Silcosteel® (Restek, Inc., Bellefonte, PA, USA); capillaries: 0.25 & 1 mm ID inlet residence time: 120 ms	PEEK; capillaries: 0.2 mm ID, inlet residence time: 90 ms

Table 2. Slurry properties; A_{fert} = fertilized area, V_{slurry} = volume of applied slurry, DM = dry matter content.

	A_{fert} [ha]	V_{slurry} [m^3]	pH	DM [%]	NH$_4^+$-N [g l^{-1}]
4 August 2009	1.23	41.0	7.82 ± 0.10	0.99 ± 0.09	0.87 ± 0.01
6 August 2009	0.77	22.5	7.49 ± 0.19	2.03 ± 0.35	1.18 ± 0.05

Table 3. Estimated individual errors and error types potentially influencing the flux accuracy.

	error	type
calibration	5%	systematic
peak covariance detection	11%	random
H_2O interference correction	< 1‰	random
high frequ. damping correction	10%	systematic
NH_4^+ aerosol interference	< 1%	systematic
flux accuracy	16%	

Fig. 1. Scheme of the eTR-MS including instrumental sample inlet.

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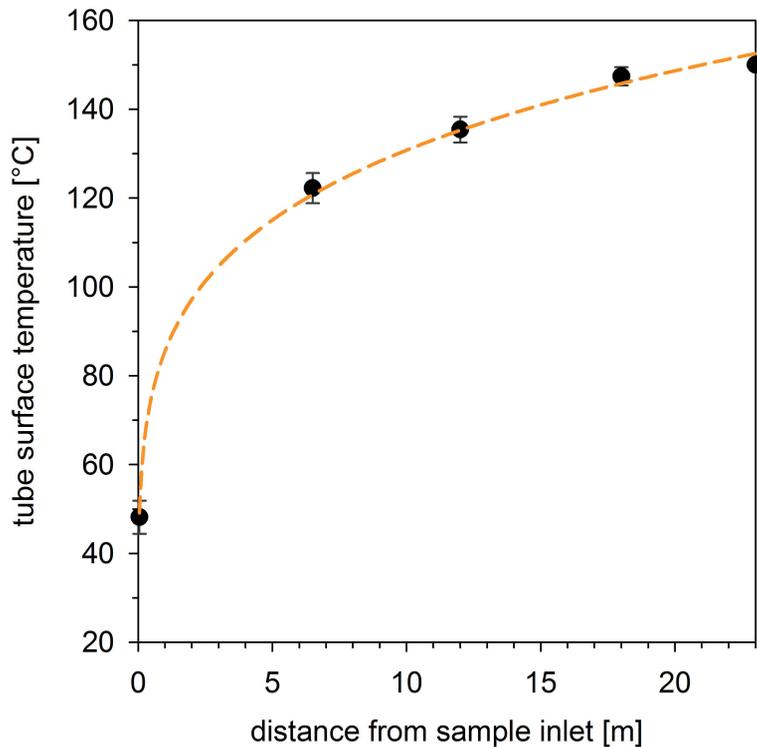
Fig. 2. Average profile of surface temperatures of the 1/2" inlet tube on both days of fertilisation; mean values ± standard deviation.
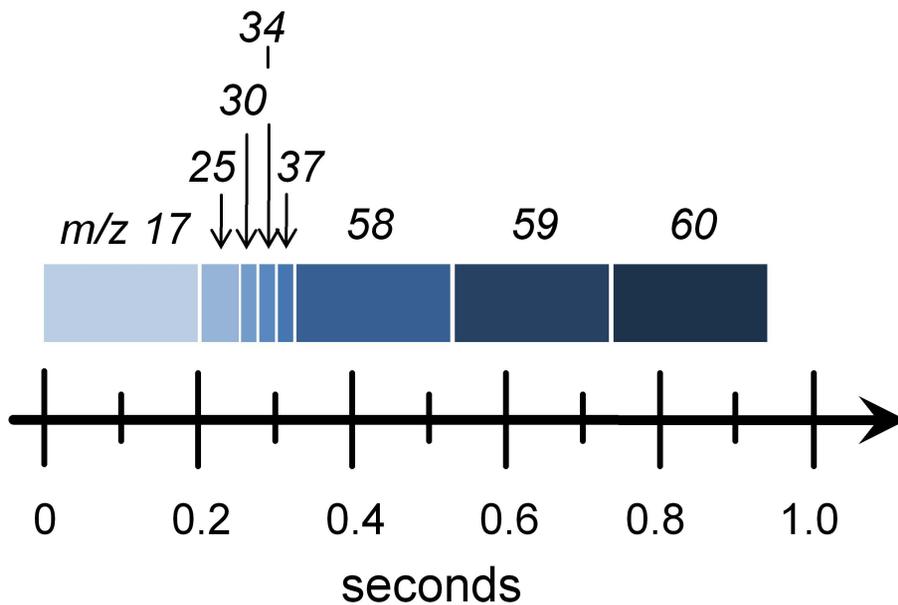
Fig. 3. eTR-MS measurement cycle with several molecular masses and associated dwell times of 0.2, 0.05 and 0.02 s, respectively.

Fig. 4. Improvement of eTR-MS time response by heating of the new prototype PEEK drift tube; switch from 150 ppb to 0 ppb NH_3.

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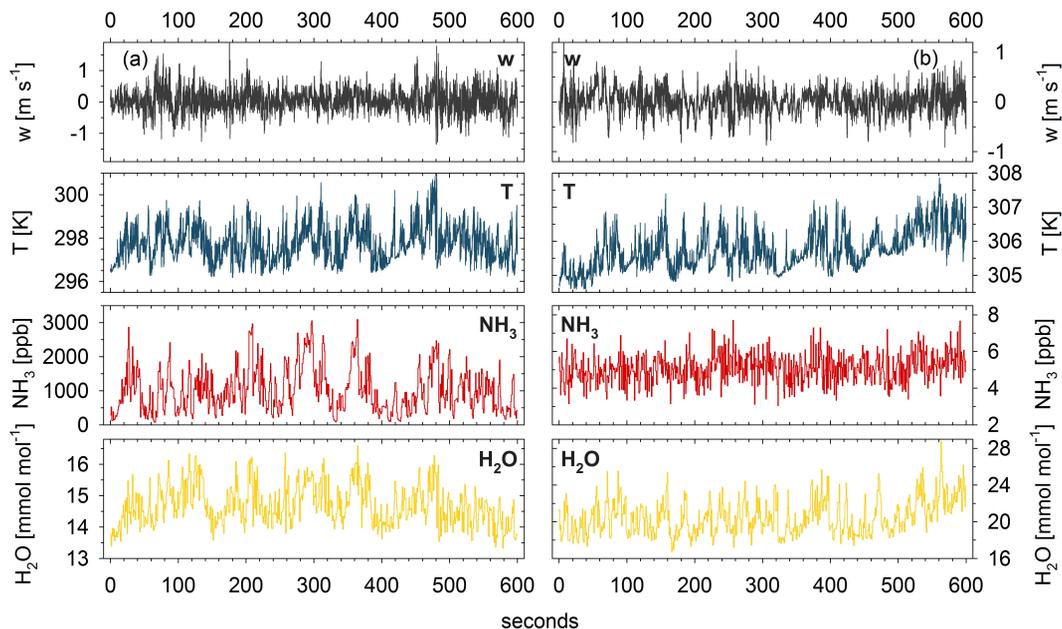
Fig. 5. 20 Hz time series of w, T, NH_3 and H_2O of one measurement interval on **(a)** 4 August 2009, 13:20–13:30 and **(b)** 15 August 2009, 13:30–13:40.
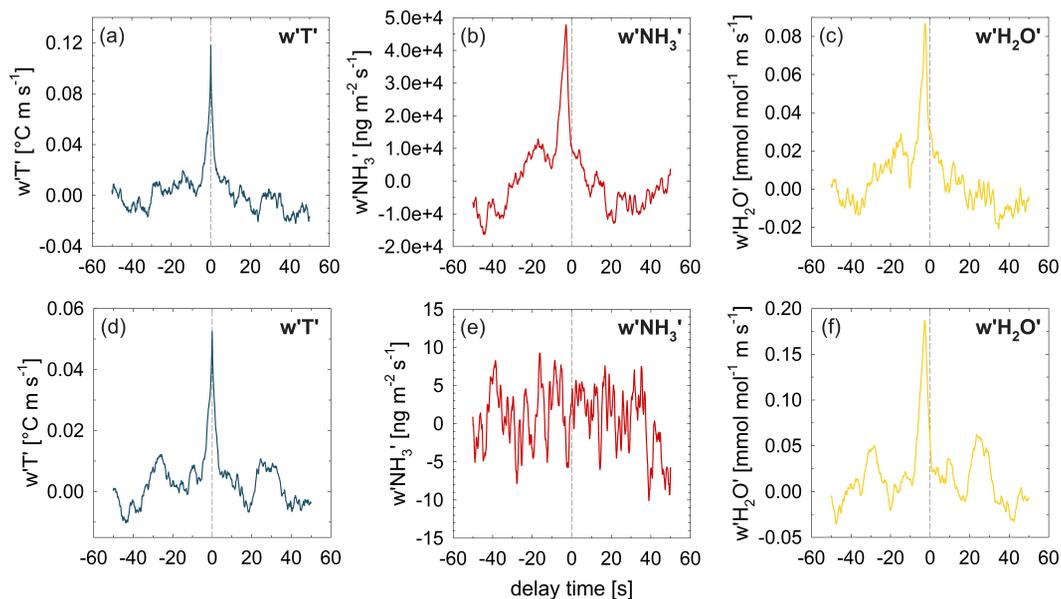
Fig. 6. Two examples of a set of covariances as a function of time shift between the scalar time series and vertical wind time series: **(a–c)** 4 August 2009, 13:20–13:30 and **(d–f)** 15 August 2009, 13:30–13:40.
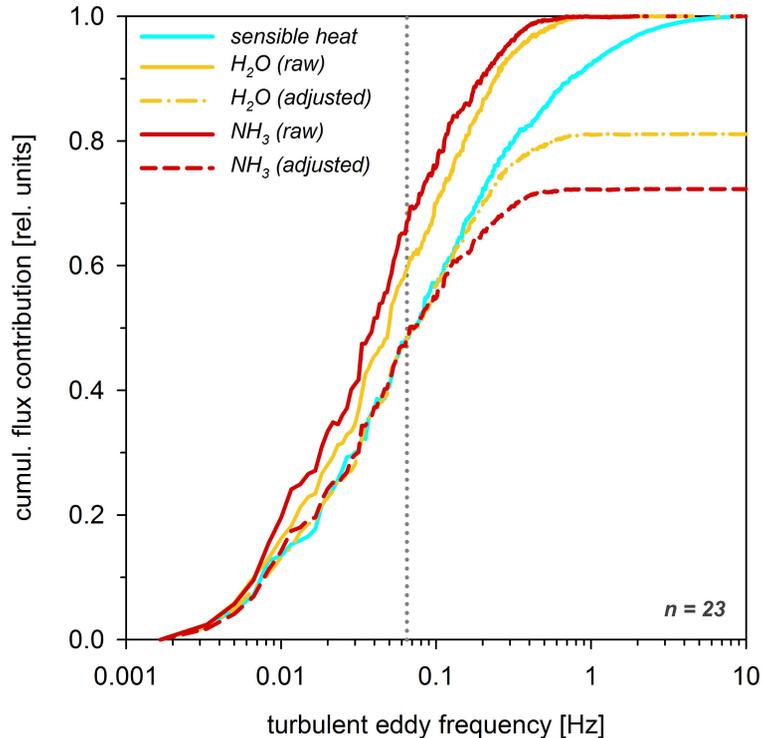
Fig. 7. Normalised median ogives of sensible heat, H_2O and NH_3 flux on 6 August 2009, 11:10–15:00; $U = 1.47 \pm 0.5\,\mathrm{ms^{-1}}$, $(z-d)/L = -0.47 \pm 0.3$; illustrating the effect of high-frequency damping on NH_3 and H_2O flux: dashed lines represent the ogives of the dampened fluxes adjusted to the ogive of the sensible heat fluxes at a threshold frequency of 0.065 Hz (dotted line).
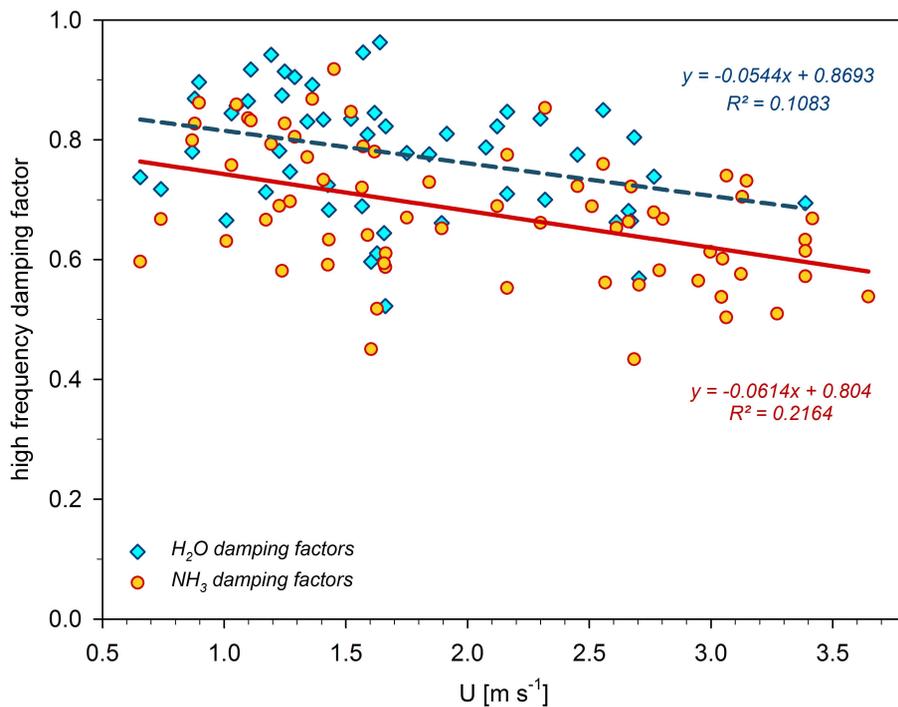
Fig. 8. NH_3 and H_2O damping factors vs. horizontal wind speed (U) on 4 August 2009 and 6 August 2009.

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Fig. 9. Air temperature (T_{air}), relative humidity (RH), global radiation (gR), horizontal wind speed (U) and wind direction (W_{dir}) measured at 3 m a.g.l. at the Oensingen site on **(a)** 4 August 2009 and **(b)** 6 August 2009.
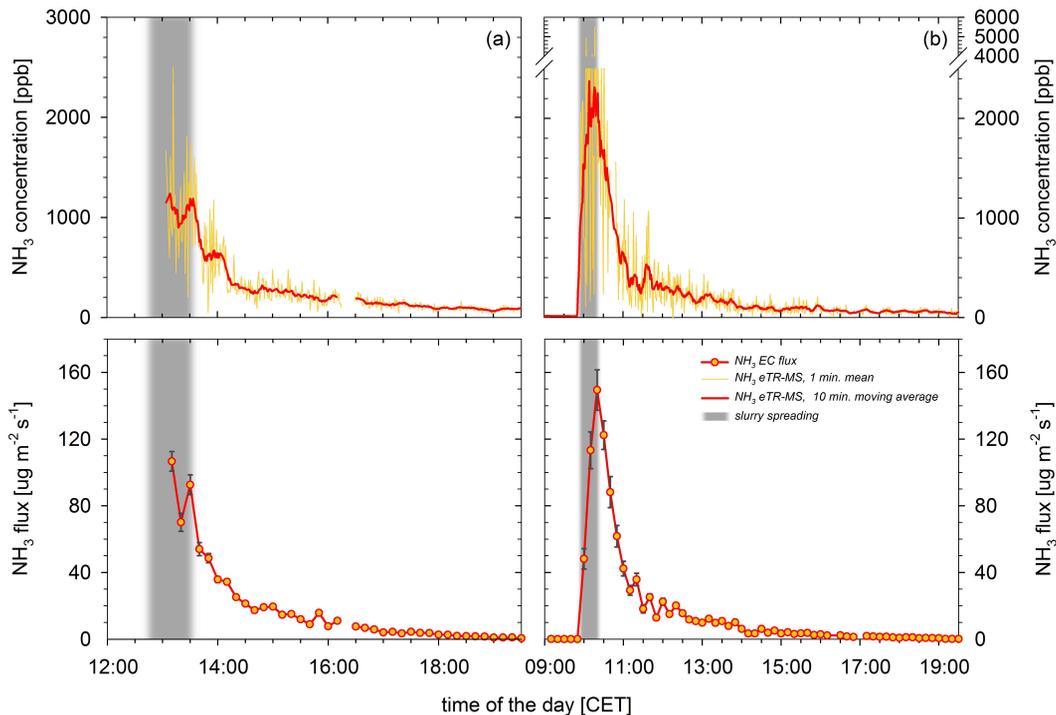
Fig. 10. NH$_3$ concentrations and EC fluxes measured at 1 m a.g.l. during and after the spreading of slurry on **(a)** 4 August 2009 (crop stubble field) and **(b)** 6 August 2009 (cut grassland); vertical error bars of NH$_3$ fluxes represent the precision of the flux, shaded areas indicate the period of slurry spreading affecting the fetch of the measurement.

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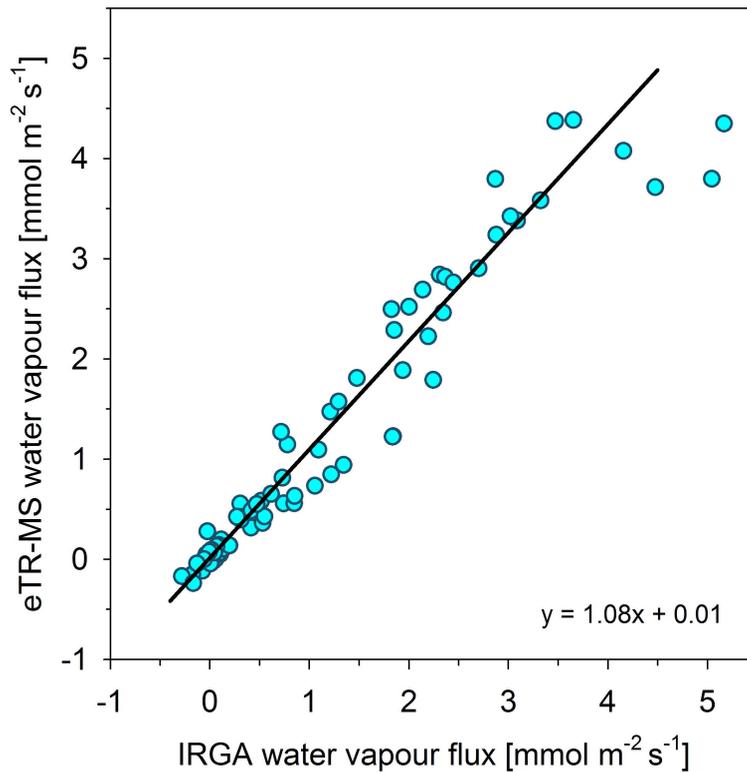
Fig. 11. Fluxes of water vapour measured by IRGA and eTR-MS; Williamson-York bivariate fit (Cantrell, 2008).

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Interactive Discussion
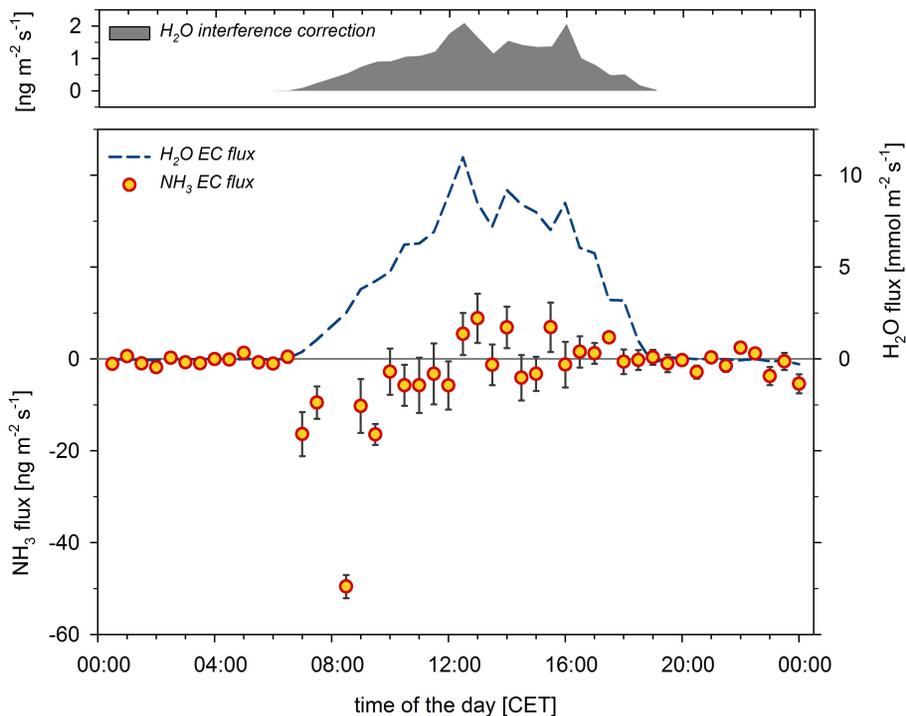
Fig. 12. Lower panel: EC fluxes of NH_3 (evaluated at constant delay time τ_{fix}, raw NH_3 data are corrected for H_2O interference) and of H_2O during conditions of small NH_3 exchange fluxes 9 days after the grassland fertilisation on 15 August 2009; upper panel: amount of NH_3 flux due to H_2O interference.