Eddy covariance measurement of ammonia fluxes: comparison of high frequency correction methodologies

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Key words: transfer function, closed-path analyser, ogive, inductance, QC-TILDAS

Summary

Several methods are available for evaluating and correcting the underestimation of trace gas fluxes measured by eddy covariance (EC) method and due to the design and the setup of the employed equipment. Different frequency correction factors (CF) to apply to the measured EC ammonia (NH\textsubscript{3}) fluxes have been applied using the following approaches: (i) the spectral theoretical transfer function (CF\textsubscript{Theor}) with and without phase shift; (ii) the in-situ ogive method (CF\textsubscript{O}); and (iii) the inductance correction method (CF\textsubscript{L}). The NH\textsubscript{3} fluxes were measured in an experimental field located in south Italy, above a sorghum crop submitted to Mediterranean semi-arid climate and fertilized with urea. A fast analyser based on Tunable

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Infrared Laser Differential Absorption Spectroscopy (TILDAS) coupled with a quantum cascade (QC) laser was used to measure NH$_3$ concentration at high frequency. The results showed that correction of the values of NH$_3$ EC fluxes over natural surfaces are necessary for taking into account the dumping of high frequency contribution due to the coupling of ammonia fast analyser by QC-TILDAS and sonic anemometer. In particular, the calculated flux losses ranged between -23% (inductance method, with the $CF$ threshold selected to 2.5) and -43% (experimental-ogive method); while the two theoretical transfer function approaches gave comparable loss estimates i.e. -30 and -31% for the methods with time lag and phase shift, respectively.
INTRODUCTION

Ammonia (NH₃) is naturally present in the troposphere with ambient concentrations varying from 5 ppt in remote regions (Sutton et al., 2001) to 500 ppb near sources (Krupa, 2003).

Actually, NH₃ plays a key role in the environment as the main base neutralizing atmospheric acids and as a precursor of particulate matter, which causes human health hazards, visibility problems and modifies the radiative forcing of the climate system (Asman et al., 1998; IPCC, 2007). Due to its negative environmental impacts (Galloway et al., 2003; Sutton et al., 2009), NH₃ has become the object of many investigations by the scientific community: in 1999, the UN Convention on Long-range Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground-level Ozone was extended by the Gothenburg Protocol to include NH₃ (http://www.unece.org/env/lrtap/) and its emissions started to be more regulated and monitored.

Ammonia is mainly emitted by anthropogenic sources. It is estimated that the majority of NH₃ emissions arises from agricultural activities: in central Europe agriculture is responsible for about 90% of NH₃ release (Erisman et al., 2008). However, large uncertainty exists on NH₃ dynamics in the soil-plant-atmosphere continuum due to the scarcity of reliable direct flux measurements. This can mainly be attributed to difficulties in measuring fluxes of such a reactive compound (Harper, 2005). In particular, the first issue is the presence of NH₃ in atmosphere in gaseous, particulate (e.g. (NH₄)₂SO₄ and NH₄NO₃) and liquid (i.e. NH₄OH in cloud and fog droplets) forms, where the partition of these three phases is highly variable (Fehsenfeld, 1995). Another difficulty is the tendency of NH₃ to form strong hydrogen bonds with water and thus to be readily adsorbed on any material exposed to ambient air, producing memory effects in the measurements. These troubles – in addition to the contamination due to NH₃ produced by people (Sutton et al., 2000) – have delayed progress in the development of NH₃ measurement techniques with respect to other trace gases.

Considering its reactive nature and the dependence of NH₃ exchanges by environmental factors, the micrometeorological methods are the preferred ones, due to their non intrusive character (Denmead, 1983; Kaimal and Finnigan, 1994). The aerodynamic gradient method coupled to wet chemical analysis is the most widely used (Wyers et al. 1993, Neftel et al. 1998, Erisman et al., 2005, Kruit et al. 2007, Milford et al. 2009, Spirig et al. 2010), but it is very time consuming. Moreover, the lack of fast sensors for NH₃ has delayed the application of the eddy covariance (EC) method which is considered the most direct and least error-prone approach (Denmead, 2008). The evolution of techniques for NH₃ monitoring starts with the
passive filters and denuders developed by Ferm (1979), nowadays the most widely used method for its simplicity and inexpensiveness. However, the drawbacks of this approach are the relatively low time resolution (minute to hours) and the laboratory intensive labour required for preparing them and for manual off-line sample analysis. Coupled to the chemical analytical methods, progress in optical methods have been achieved with the development of spectroscopic devices characterized by high time resolution and sensitivity to NH$_3$, but which are still expensive. Von Bobrutzki et al. (2010) recently provided inter-comparisons for NH$_3$ measurement techniques in field, highlighting that many challenges still have to be faced for measuring NH$_3$ accurately. Nevertheless, Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) using a quantum cascade (QC) laser are now available for monitoring NH$_3$ concentration with a sufficient sensitivity and robustness to be employed in the field. However, the application of the EC method for monitoring NH$_3$ is considered a challenge by the scientific community, as demonstrated by the scarce literature available on this topic (Shaw et al., 1998; Famulari et al., 2005; Whitehead et al., 2008; Brouder et al., 2009; Sintermann et al., 2011) in which are highlighted the difficulties to its routine applicability. In particular, the employment of a setup involving a fast closed-path analyser could introduce considerable damping of high frequency fluctuations and consequent underestimation of the fluxes, that have to be corrected for (e.g. Massman, 2000).

Several methods are available for evaluating and correcting these underestimations when EC equipment is used for trace gas fluxes (Massman and Clement, 2004 for CO$_2$ for example). In particular, Whitehead et al. (2008) evidenced that the correction for EC fluxes of NH$_3$ using TILDAS is fundamental to accurately estimate the real fluxes at different time scales.

However, up to now, no attempt has been made to evaluate, using different methodologies, the correction of the underestimation of EC ammonia fluxes when a QC-TILDAS is used for measuring NH$_3$ fluctuations in the cropped field. Furthermore no EC data of NH$_3$ turbulent fluxes are available for crop grown in arid environments.

In this study, we report EC measurements of NH$_3$ fluxes performed employing a fast closed-path analyser for NH$_3$ concentration, the QC-TILDAS-76 SN002-U developed by Aerodyne Research Inc. (ARI; Billerica, MA, USA) (Zahniser et al., 2005) under custom specifications. The trial was carried out over a field in an intensive agricultural area of south Italy, in a semi-arid to arid Mediterranean climate. The plot was fertilized with urea pellets to stimulate NH$_3$ emission and to test the device over a wide range of concentrations. The aim was to assess the performance of the QC-TILDAS used for the first time in an EC system for measuring NH$_3$ fluxes over an irrigated cropland in Mediterranean environment. The challenge was to verify
the adequacy of the system in terms of setup and quality of the data. In order to reach a robust assessment of the needed correction, three possible methods for correcting the flux losses due to the design and the setup of the employed equipment were considered in this analysis. In particular, we compare different frequency correction factors ($CF$) to apply to the measured EC NH$_3$ fluxes obtained by the following approaches: (i) the spectral theoretical transfer function ($CF_{\text{Theor}}$); (ii) the in-situ ogive method ($CF_{\text{O}}$) (Massman and Clement, 2004); and (iii) the inductance correction model ($CF_L$) developed by Eugster and Senn (1995).

1 MATERIAL AND METHOD

1.1 Field site

The experiment was carried out from 17 to 30 July 2008 (DOYs 199 to 211) in Rutigliano ($41^\circ$N, $17^\circ$54'E, 122 m a.s.l.) near Bari in southern Italy. All experimental activities were performed in a 2 hectares field, dimensions were 200 m x 100 m. The soil type is classified as loamy clay (Clay 41%; Silt 44%; Sand 15%) and the terrain is flat. The climate is semi-arid Mediterranean, with hot and dry summer and short and temperate winter. The mean annual temperature is 15.7 °C with a mean annual precipitation of 600 mm; the main wind direction is north during the summer time. In this study, most of the analysis will focus on the period 22-29 July 2008 (DOYs 204-211) where the NH$_3$ fluxes were the largest.

1.2 Crop and urea spreading

During the experimental campaign the field was cultivated with Sorghum vulgare (cv Hay Day) sowed on 10$^{th}$ June 2008 and irrigated by sprinkler irrigation. A commercial urea product (46% N content) in granular form was applied. The total N supply was around 240 kg N ha$^{-1}$ divided into three applications: 30, 90 and 120 kg N ha$^{-1}$ on 1$^{st}$, 16$^{th}$ and 22$^{nd}$ July 2008, respectively. The first application was carried out at crop emergence. Before the second application the field was irrigated with 7.9 mm water, while further irrigation (9.3 mm) was applied before and after the third application. The amount of urea was slightly higher than current agronomic practices in the area, since the dry conditions (high temperature, no rain and no irrigation applied) between the second and the last urea spreading inhibited NH$_3$ volatilization so that no fluxes were detected. The last urea application combined with irrigation was necessary in order to increase the probability to detect NH$_3$ fluxes.
1.3 NH$_3$ fluxes by the eddy covariance method

The fluxes of NH$_3$ were measured with the eddy covariance method (e.g., Kaimal & Finnigan, 1994; Lee et al., 2004; Mahrt, 2010). The EC method is based on estimating the transport of a scalar by turbulent motions of upward and downward moving air contained in the atmosphere. The vertical flux ($F$) of scalar at the measurement height is given by:

$$ F = w \beta + \bar{w} \cdot \bar{\beta} $$

(1)

where $w$ is the component of the wind speed normal to the surface and $\beta$ is the scalar concentration, and the usual Reynolds decomposition is used where prime denotes fluctuating quantities. $\bar{w} \beta$ is the covariance between $\beta$ and $w$. With the usual assumption of steady state horizontally homogeneous flow, there is no vertical flux of dry air, i.e. $c_d \bar{w} = 0$, where $c_d$ is the dry air concentration. Since the dry air concentration fluctuates due to heat and water vapour fluxes, $\bar{w}$ is not necessarily equal to zero. The Webb, Pearmann, Leuning (WPL) correction (Webb et al., 1980; Leuning, 2007) gives the expression of $\bar{w}$. The impact of this term depends on the concentration of the gas and the typical magnitude of the flux (Denmead, 1983; Liebethal and Foken, 2004): for trace gas with small concentration and large fluxes, such as NH$_3$ over a source, these corrections are negligible.

The turbulent flux $\bar{w} \beta$ as a time-averaged quantity can also be viewed as a frequency averaged quantity, i.e. the integral of the co-spectral density ($Co_{w\beta}$) (Kaimal and Finnigan, 1994; Aubinet et al., 2000; Massman, 2000)

$$ \bar{w} \beta = \int_{0}^{\infty} Co_{w\beta}(f) df $$

(2)

To catch all relevant turbulent fluctuations, $\beta$ and $w$ should be measured with a sampling frequency much larger than the frequency of the eddies carrying the energy of the signal ($f_x$) (Horst, 1997; Massman, 2000). Usually, a sampling frequency of 10 Hz is considered sufficient above a vegetated surface. However, flux loss is inevitable with any EC system, especially employing closed-path analysers to which the air sample is transported into the measuring cell by means of a tube. The mixing effects in the tube and additional possible chemical or micro-physical processes occurring in the system produce low-pass filtering effects on the measured covariances (Ibrom et al., 2007). Nowadays, a variety of methods are available to correct these underestimated measured fluxes by means of frequency response correction factors (e.g. Ammann et al., 2006; Shimizu, 2007; Aubinet et al., 2000; Massman 2000; Eugster and Senn, 1995). However, in this work, since the adopted closed-path analyser
for NH$_3$ concentration measurements is relatively new and it is the first time it is being used under semi-arid climates, we compare a variety of methods to correct the NH$_3$ fluxes measured over an agricultural plot.

### 1.4 NH$_3$ concentration measurements

#### 1.4.1 The QC-TILDAS analyser

##### 1.4.1.1 The instrument

The QC-TILDAS employed during this research is the compact QC-TILDAS-76 SN002-U developed by Aerodyne Research Inc. (ARI, Billerica, MA, USA) (Zahniser et al., 2005). This spectrometer combines QC laser designed for pulsed operation at near room temperature (Alpes Lasers, Neuchâtel, Switzerland), an optical system together with a computer-controlled system that incorporates the electronics for driving the QC laser along with signal generation and a data logger. Molecular transition selection for given laser is achieved by temperature tuning, typically within a small range around 40 °C using a two-stage Peltier element. The laser frequency is swept across the full molecular transition at 967.34 cm$^{-1}$ which means that the scan is done over a narrow range of wave numbers chosen to contain an absorption feature of the trace gas of interest. The optical system collects light from the QC laser and directs it through an astigmatic Herriott type multi-pass absorption cell (76 m effective path length), onto a TE-cooled photovoltaic detector (Vigo Systems). A detailed description of the device can be found in Zahniser et al. (2005).

##### 1.4.1.2 The inlet design and the sampling

Ellis et al. (2010) report the characterization of the QC-TILDAS by laboratory tests. In particular, they reported a detailed analysis on the performance of the QC-TILDAS in function of the inlet design. To achieve accurate atmospheric measurements of NH$_3$, the sampling setup has to reduce gas interactions with surfaces, then it is crucial the configuration of the device’s inlet through which the air is drawn into the optical cell. The inlet used is a short glass tube containing a critical orifice needed to keep the air flow rate constant and to reduce the pressure in the optical cell to approximately 5.40 kPa, a compromise between minimising line broadening and adsorption effects, maximising time response and achieving good sensitivity (Warland et al., 2001). The setup of the inlet is done to remove particles in the air sample relying on inertia to remove more than 50% of particles larger than 300 nm; in
particular, the flow is split into two branches: 90% of the flow makes a sharp turn and is
pulled into the optical cell by a pump (VARIAN TriScroll 600 Series), the other 10% is
pulled by a second air pump (VARIAN, mod SH110). This inlet design is optimized to
eliminate the need of filters and any interference they may cause. The operation of the
spectrometer is fully automated and computer-controlled through a Windows-based
proprietary software (TDL Wintel) developed at ARI. Concentrations are real-time
determined from the light absorption spectra through a non-linear least-squares fitting
algorithm (Levenberg-Marquardt) that uses spectral parameters from the HITRAN (high-
resolution transmission) molecular absorption database (Rothman et al., 2003). The pressure
and temperature in the multi-pass cell are continuously monitored to supply information
needed for spectral fitting. The software calculates absolute concentrations, so no calibration
was performed in the field. However, laboratory tests demonstrate the need to carry out a
post-proceeding calibration in order to overcome the failure of the analyzer to reproduce the
values of the ammonia standard. Moreover, we would justify the calibration factor found for
the QC-TILDAS using ethylene standard, which has absorbing frequency close to ammonia
one, but it is not affected by stickiness. Part of the problem with absolute spectroscopic values
for NH\textsubscript{3} in our instrument was due to using pulsed-QCLs rather than CW-QCLs; with the
laser linewidth considerably greater than the molecular linewidth, the spectral analysis
required much effort to get absolute values. Thus a post-proceeding calibration was done and
zeroing was routinely carried out in order to optimize the calculated spectra following
Whitehead et al. (2008).

1.4.1.3 The response time

The decreasing of the mixing ratio of the ammonia was well represented by two exponential
decay functions, which in Ellis et al., (2010) is written as:

\[ y = y_0 + A_1 \exp\left(-\frac{(t-t_0)}{\tau_1}\right) + A_2 \exp\left(-\frac{(t-t_0)}{\tau_2}\right) \]  

(3)

where \( A_1 \) and \( A_2 \) are constants and their sum is equal to the stable mixing ratio of NH\textsubscript{3} prior to
the calibration flow being switched off; \( y_0 \) is equal to the NH\textsubscript{3} mixing ratio reached at the end
of the decay; \( t \) is time and \( t_0 \) is the time at the start of the fit; \( \tau_1 \) and \( \tau_2 \) are time decay
constants, the first of which is fast and corresponds to the gas exchange time of the system
(0.4 s in our case), and the second being much slower and corresponding to interactions of
NH\textsubscript{3} with surfaces on the interior surfaces of the inlet, sampling lines and absorption cell (15
In this case the response time was checked in laboratory and it is controlled by pumping speed and by adsorption/desorption on the walls. In particular, it is affected by the flow rate, the length and the heating of the sampling tubes. Therefore, acting on these parameters would allow optimizing the instrument for measuring the fluxes by EC technique.

Moreover, for a mixing ratio of 350 ppb, the amount of noise (1σ) in a 10 Hz measurement obtained by Ellis et al. (2010) by an Allan variance analysis was 3.15 ppb (2.2 µg NH₃ m⁻³). Based on statistics obtained for sensible heat, CO₂ and temperature, was estimated to be around 0.23 ± 0.13 (mean ± SE), and taking σₚ~ 2 µg NH₃ m⁻³ and σᵦ~ 1.25 u*, would mean that the flux detection limit of the setup would be around 2.5 u* (in µg NH₃ m⁻² s⁻¹), hence typically around 750 ng NH₃ m⁻² s⁻¹. However, most of the turbulent signal is transported by eddies with a frequency around 0.2 Hz (evaluated as the co-spectral peak frequency for air temperature (Tₐ), CO₂ and water vapour (H₂O)). At this frequency, the Allan variance of the QC-TILDAS found by Ellis et al. (2010) is around 0.2 µg NH₃ m⁻³, and hence the detection limit should be on the order of 0.25 u* (typically 75 ng NH₃ m⁻² s⁻¹). As reported by Ellis et al. (2010), there is an increase in the relative importance of NH₃ surface interactions at mixing ratios lower than 100 ppb, which further increased when sampling humid air as opposed to dry nitrogen. Then, the heating in the sampling line to prevent condensation is crucial to perform accurate NH₃ measurements. There was no line heating used in our study, since we assumed that this was not needed since the air temperature encountered in the field was very high (up to 33°C). On the other hand, under such conditions, it was required the use of an air conditioner for the box containing the QC-TILDAS to limit instrumental drift induced by changes in the optical alignment, as well as in the laser power, beam width and temperature.

1.4.2 The ALPHA badges and ROSAA system

The NH₃ concentration β measured with the QC-TILDAS were compared against passive diffusion samples (ALPHA badges; Tang et al., 2001). These ALPHA badges were positioned at the same height as the QC-TILDAS inlet and changed twice a day to get daily and nightly concentrations. Three replicates were used to evaluate the uncertainty in the measurements. The background concentration βbgd was estimated with three sets of badges put at three locations at more than 100, 100 and 300 m away from the field and changed weekly. The badges were prepared with filters coated with citric acid. The filters were extracted in 3 ml double deionised water and analysed with a FLORRIA analyser (Mechatronics, NL).
addition, during the trial, NH$_3$ concentration was monitored by means of the new device, ROSAA, developed at INRA (Loubet et al., 2010, 2011). It relies on the coupling of NH$_3$ capturing by means of an acid stripping solution (wet-effluent denuders) to convert NH$_3$ in NH$_4^+$, and the analysis of the NH$_4^+$ concentration by means of a detector based on a semi-permeable membrane and a unit to perform temperature controlled conductivity measurements (ECN, Netherlands). In the ROSAA system the three denuders were sampling at three heights (at $z = 0.5; 0.7$ and $1.4$ m) above ground and the averaged concentration was measure every 30 minutes.

1.5 The eddy covariance system: description of the equipment

The EC system was equipped with the QC-TILDAS and a three axis ultrasonic anemometer (Gill R2, Gill Instruments Ltd, UK). The analogue signals from the QC-TILDAS were passed to the sonic anemometer which uses an analogue-to-digital converter to digitise the signal at 10 Hz. The sonic anemometer acquired data at 168 Hz internally and reported average values at 20.8 Hz. The digitised signals from the QC-TILDAS were then combined with the wind velocity information and sent to the serial port of a personal computer. NH$_3$ fluxes were computed offline with a time step of half an hour. The software package EddySoft (Kolle and Rebmann, 2007) was used for the data acquisition. The same software package was used for post processing EC data and to obtain the cospectra useful for applying the TF method, while custom Matlab® and R scripts were used to process and analyse data for the ogive and the inductance methods, respectively. Trace gas and heat fluxes were calculated as well as other micrometeorological parameters. The components of the wind velocity were rotated every 30 minutes to set $\bar{w}$ and $\bar{v}$ to zero. No detrending was applied and block averaging was instead used (Leuning, 2007).

The sonic anemometer was mounted on a 1.5 m tall mast, so that the height of the EC sensors was about 0.7 m above the top of the crop, and adjusted to follow crop development. Ambient air close to the sonic anemometer head was continuously sampled through a 2.5 m long inlet line (PFA, 3/8” outer diameter) leading to the QC-TILDAS. The flow of air through the tube was measured before and after the T connection used for splitting the flow: the flow rate towards the sampling cell was about 9 litres/minute, resulting in a laminar flow regime with a Reynolds number ($Re$) of about 2000, below the turbulence limit (for pipe flow, $Re=2300$, Shimizu, 2007) which was the primary cause of the high frequency loss in the measuring system (Eugster and Senn, 1995). The limits in the power supply lines in our experimental
site have prevented the use of pumps able to provide a turbulent regime into the sampling tube.
The eddy covariance system, together with ROSAA and ALPHA samples equipments were located close to the centre of the field, which provided an acceptable upwind fetch (around 120 m) in the prevalent wind direction during the trial, anyway the footprint of EC measurements was found to be always inside the experimental field.

1.6 Spectral correction methods for low-pass filtering in a closed-path EC system

As mentioned before, all eddy covariance systems tend to underestimate the true atmospheric fluxes due to physical limitations of the flux measurement instrumentation which causes losses of eddy flux contributions at low and high frequencies. These losses can be quantified and corrected for by multiplying the measured covariance (subscript \( m \)) with a frequency response correction factor (\( CF \geq 1 \)):

\[
\overline{w\beta} = CF\overline{w\beta}_m \quad \text{ (4)}
\]

The correction factor can be estimated by means of spectral correction methods that can be divided into two families: the spectral theoretical transfer function (\( TF \)) methods and the in-situ methods (Massman and Clement, 2004). The general approach consists of three steps: 1) the identification of a spectral transfer function (theoretical or experimental), 2) its use to calculate a correction factor, and 3) the parameterisation of the correction factor with meteorological variables, mainly the wind speed, which is directly linked to the turbulence.

Here, three methods have been employed in order to estimate \( CFs \) to apply at our measured EC NH\(_3\) fluxes: (i) Theoretical \( TF \) analysis, \( CF_{\text{theor}} \); (ii) A variant of In situ experimental \( TF \) method, the Ogive method, \( CF_O \); (iii) the inductance method, \( CF_L \). These methodologies are the most analysed in the literature for evaluating the most accurate \( CFs \) for gas trace fluxes over natural surfaces.

Common to all approaches is the requirement of a measured or evaluated reference cospectrum for scalar as well as a measured cospectrum and the estimate of the flux loss as a function of frequency. In any case, an important aspect relative to any EC system is the time delay between the instant open-path \( w \) measurement and the closed-path scalar concentration measurement, \( \beta \). This time lag is due to the transport time in the tubing system and the phase shift due to low-pass filtering (Ibrom \textit{et al.}, 2007). It depends on the tube length and the flow rate: it may change slightly due to changing flow rates in the tube caused by pumping variation or density changes. Usually, this delay can be calculated empirically by determining
the maximum of the covariance function between \( w' \) and \( \beta' \) (Moncrieff et al., 1997) which includes the time lag due to the longitudinal (streamwise) separation distance from the air sample inlet to the sonic anemometer depending on wind speed and direction. The individually determined time delays for each 30 minutes set of data can be used for calculating the cospectra: in this case the phase shift due to low-pass filtering and longitudinal sensor separation has already been corrected for (Ibrom et al., 2007). So, two subcategories can be identified in the theoretical transfer function analysis: with \( CF_{Theor\_time\_lag} \) and without the time lag \( CF_{Theor\_phase\_shift} \) applied to computation of the covariances and cospectra.

### 1.6.1 Theoretical TF analysis

Following Moore (1986), theoretical transfer functions, characterizing the measurement process, have been developed. The correction factor in this case is summarized by Massman and Clement (2004) using the following equation:

\[
CF_{TF} = \frac{\overline{w' \beta'}}{\overline{w' \beta}}_m = \frac{\int_0^\infty \overline{Co_{w' \beta}(f)} df}{\int_0^\infty \left[ 1 - \sin^2(\pi T_b f) \right] H(f) \overline{Co_{w' \beta}(f)} df}
\]  

(5)

where \( \overline{w' \beta'}_m \) is the measured covariance and \( \overline{w' \beta} \) is the true flux, \( H(f) \) is the product of all the appropriate transfer functions associated with HF losses \( H(f) = \prod_{i=1}^n TF_i \), \( \overline{Co_{w' \beta}(f)} \) is the one-side reference cospectrum, \( T_b \) is the block averaging period, \( \left[ 1 - \sin^2(\pi T_b f) / (\pi T_b f)^2 \right] \) is the TF for the low frequency spectral attenuation. The reference cospectrum is either taken from literature (Kaimal and Finnigan, 1994) or a site specific reference cospectrum, usually derived from sensible heat flux measurements. The requirements to apply this method are: the TFs and a model of the cospectra which is the weakness of this approach since smooth cospectra are not typical of the atmospheric surface layer (Massman and Clement, 2004). In particular, in this work we used the reference cospectral models (eq. 6-9) given by Moncrieff et al. (1997), where \( f_k = f(z-d)/u \) is normalized frequency, \( f \) is the natural frequency, \( u \) is horizontal wind speed, \( z-d \) is height above the zero-plane displacement, \( d \). For stable atmospheric condition, the reference cospectrum is:

\[
f \overline{Co_{w' \beta}(f)} = \frac{f_k}{A_{w' \beta} + B_{w' \beta} f_k^2}
\]  

(6)

where
While, for unstable atmospheric conditions, the reference cospectrum is:

\[ fC_{w,\beta}(f) = \frac{12.92 f_k}{[1 + 26.7 f_k]^{3/5}} \quad \text{for} \quad f_k < 0.54 \]

\[ fC_{w,\beta}(f) = \frac{4.378 f_k}{[1 + 3.8 f_k]^{0.5}} \quad \text{for} \quad f_k \geq 0.54 \]

Moore (1986) developed the first theoretical TFs for EC systems taking into account the attenuation due to the dynamic frequency response of the sensors, the scalar path averaging, the sensor separation, the sensor response mismatch, while Moncrieff et al. (1997) gave a complete description of TFs of EC systems with closed-path analysers. Then, considering the wide literature on the used theoretical TFs (see Shimizu 2007 for a review) and the weight of each TF on the total one for our equipment set-up, here we report only details about TFs related to: (i) the lateral separation (i.e., perpendicular to the mean wind direction) between the sonic anemometer and QC-TILDAS inlet (TF\(_s\): Moore, 1986); (ii) the tube damping effect (TF\(_\text{tube}\): Lenschow and Raupach, 1991); (iii) the volume averaging in a measurement cell (TF\(_\text{vol}\): Massman, 2004); (iv) the total phase shift (TF\(_\text{phase\_shift}\): Massman, 2000). In detail:

(i) Following Moore (1986) the effect of lateral/longitudinal separation, \(s\), between two sensors, can be represented by the following cospectral transfer function:

\[ TF_s = 9.9 \exp(-9.9 n^{1.5}) \]

where \(n = fs/u\). As suggested by Massman (2000) the horizontal separation between the two sensors has been set to 0.30 m.

(ii) The function TF\(_\text{tube}\) describing the attenuation of the fluctuation concentrations down the sampling tube in which there is a laminar flow for covariance calculation (Lenschow and Raupach, 1991; Aubinet et al., 2000) is:

\[ TF_{\text{tube}} = \exp\left(-\frac{\pi^2 r_t^2 f_t^2 L}{12 D_s U_t}\right) \]

Here, \(r_t\) is the tube radius and \(D_s\), the molecular diffusivity of the scalar, around 0.2 cm\(^2\)s\(^{-1}\) for NH\(_3\) (Massman, 1998). Moreover, the attenuation may vary with time: Leuning and Judd (1996) showed that the attenuation to water vapour by aged and dirty tubes is much greater than that by new and clear tube. In the case of laminar flow through the tube, the theoretical
cut off frequency, $f_{co,t}$, at which the $TF$ equals $2^{-1/2}$ is given by:

$$f_{co,t} = 0.649 \frac{U D}{r_c L_t}$$

(12)

about 1.4 Hz in our EC system. To minimizing HF losses due to nonuniform velocity profiles, turbulent flow would be preferred (Lenschow and Raupach, 1991). This requires a powerful pump with high power consumption and a tremendous start-up current (13 A at 230 V AC for an Edwards Tri-Scroll pump, for example; pers. comm. W. Eugster) that was unrealistic at our field site. Hence, we had to use a less powerful pump and thus need to account for the extra loss in frequency response due to laminar flow in the intake hose (Moncrieff et al., 1997). The possible tube damping correction does not correct potential absorption/desorption of moisture by hygroscopic dirt particles in the tube: however, a strong pressure drop along the intake hose reduces risk of condensation on the walls of the tube. On the other hand, HF due to wall interaction in the sample tube could be reduced by minimizing length’s tube and maintaining high flow rate. In general, the line loss is a function of tubing type and how dirty the tube is (Sukyer and Verma, 1993).

(iii) As reported by Massman (2004), in a closed-path detector, the flow velocity within the detection chamber can be very different than the wind speed of the ambient atmosphere near the tube inlet, so that the transfer functions need to be expressed in terms of the volume flushing time constant of the detection chamber, $\tau_{vol}$:

$$TF_{vol} = \frac{\sin^2(\omega \tau_{vol}/2)}{(\omega \tau_{vol}/2)}$$

(13)

where $\omega = 2\pi f$ and $\tau_{vol}$ is equal to the time needed to fill the chamber and its minimum value is given by the ratio between the volume of the chamber (0.5 l) and the maximum flow rate.

(iv) However, if covariances and the cospectra are calculated without the time lag, that means without the method of maximum covariance function, or if there is no clear time lag due to lag depending on the frequency of the eddies (sensor separation in the wind direction), or if there are complex adsorption and desorption processes, it is necessary to take into account the phase shift (Massman, 2000). The $TF$ associated with the total phase shift (Massman, 2000) is:

$$TF_{phase\_shift} = \cos \left[ \alpha \left( \frac{l_{lon}}{u} + \frac{L}{U_t} \right) \right] - \omega \tau_{\beta} \sin \left[ \alpha \left( \frac{l_{lon}}{u} + \frac{L}{U_t} \right) \right]$$

(14)

where $l_{lon}$ is the longitudinal sensor separation (function of wind direction) and $\tau_{\beta}$ is the intrinsic time constant of the scalar sensor. This latter was estimated by using the Boyle’s law
applied to the measurement chamber working at 3.3 kPa and using the measured flow rate: it is about 0.1 s and, moreover, it means that the sampling frequency of 10 Hz is adequate for the employed QC-TILDAS in the EC system.

For the theoretical TF approach, cospectra of the vertical wind speed and T and NH$_3$, respectively, were calculated using the post processing EddySpec package of Eddysoft software, using the following setup: number of frequencies 4096 for calculating the cospectra for half-hourly runs, multiplied by frequency, tapering the time series with a Hamming window (Kaimal and Finnigan, 1994) and averaging into 20 logarithmically spaced bins. Either the time lag or the phase shift was used in the functions of the two approaches $CF_{Theor\_time\_lag}$ and $CF_{Theor\_phase\_shift}$, respectively.

1.6.2 **In situ ogive method**

The limitation of the theoretical TF approach is that it could miss additional chemical or micro-physical process occurring in the EC system, a restriction that is expected to be overcome by the in situ experimental methods. Moreover, the experimental approach is based on the assumption of cospectral similarity between scalar fluxes and, unlike the theoretical TF approach, these methods do not require smooth models of atmospheric cospectra (Massman and Clement, 2004). The correction factor can be estimated as the ratio between the attenuated flux and a reference flux (usually the sensible heat flux). Aubinet *et al.* (2000) give the procedure to estimate this experimental frequency transfer function, but since the cospectra derived from sensible heat fluxes are often not well-defined, then, direct application of this approach can produce implausible values.

Starting from the hypothesis of similarity between all scalars cospectra, Ammann *et al.* (2006) developed a method for estimating HF losses. Applied to EC measurement of NH$_3$ fluxes, the method consists in fitting the ogive for NH$_3$ $O_{gwNH3}$ (the ogive is the integrated cospectra $C_{gwNH3}$ from low to high frequencies) against the ogive of air temperature $O_{gwT}$. The fitting was made with an iterative linear least square method in which the points being too far away from the regression line were eliminated progressively (*robustfit* function under Matlab®).

The high-frequency damping correction ($CF_D$) is simply evaluated as the value of the fitted NH$_3$ ogive ($O_{gwNH3}$) at the highest frequency. The frequency band over which the linear regression is performed is determined as the frequency for which $O_{gwT}$ larger than 0.1 and $O_{gwNH3}$ is smaller than 0.8. This choice was arbitrary and may not be appropriate if the damping of the NH$_3$ signal was below the range chosen. The ogives were calculated using detrended signals.
1.6.3 The inductance method

Eugster and Senn (1995) propose a correction model for EC data affected by systematic error introduced by the combination of all sources of damping, which also includes chemical reaction (in the case of NO₂) besides the possible damping due to laminar flow in the sampling tube and sensor separation. This damping loss is described by an analogy to inductance, \( L \), in an alternating current circuit, which can be used for taking into account the reduction of spectral density in the inertial subrange. This model follows the approach of Moore (1986), using electronic components in a current circuit instead of a gain function.

As reported by Eugster and Senn (1995), the covariance of the measured (i.e. damped) scalar flux is given by:

\[
\bar{w} \beta_L = \int_0^\infty C_{w,\beta_L}(f) df = \frac{1}{1 + 4\pi^2 f^2 L^2} \int_0^\infty C_{w,\beta_{L,0}}(f) df \quad (15)
\]

where \( C_{w,\beta_{L,0}}(f) \) is the undamped cospectrum. The value of \( L \) is modified in order to fit the measured cospectrum. The independent variables in this correction model are: the measuring height above zero-plane displacement, \( z-d \), the mean horizontal wind speed, \( u \), the Monin-Obukhov stability parameter, \( \zeta \), the natural frequency, \( f \), and the inductance, \( L \). The value for \( L \) can be derived from spectral and cospectral analysis and is assumed not vary significantly as long as the measuring system is not altered.

The damped cospectra can be derived combining equation (14) with the empirical formula of Kaimal et al. (1972) for stable, unstable and neutral stratification as modified by Eugster and Senn (1995) (equations 29 and 30 in their paper). The approximated solutions of Eugster and Senn (1995) for \( CF \) range between 1.0 (no damping at all) and \( \infty \) (no signal at all), but they suggest to restrict the fit to the range between \( CF=1.0 \) and \( CF=2.5 \): that means all measurements which represent less than 40% of the real fluxes were discarded.
2 RESULTS AND DISCUSSION

2.1 Micrometeorological conditions

During the trial, the air temperature ranged from 16°C to 33.5°C and averaged 24.7°C, while the soil surface temperature reached more than 54.6°C at hourly scale. The sky was clear most of the period apart from the 23-24/07/2008 where there was little rain (8.2 mm). The global solar radiation was following the fair weather diurnal course throughout the period and reached 950 W m\(^{-2}\) at maximum. The daily average relative humidity was around 60%, with variations ranging between 25 and 93%.

The prevalent wind direction during the experimental period (84% of the runs) was NW, the wind speed ranged from 0.5 to 8.9 ms\(^{-1}\) and averaged 3.4 ms\(^{-1}\), while the friction velocity \(u^*\) ranged between 0.01 and 0.99 ms\(^{-1}\), with an average of 0.30 ms\(^{-1}\) (Figure 1a). The energy balance for the period of the trial is reported in Figure 2b at hourly scale. In particular, it is clear the direct impact of the net radiation \((R_n)\) on the sensible heat flux \((H)\) and on the latent heat flux \((LE)\). The pattern of \(LE\) were strongly correlated with the available energy \(R_n\), with distinct peaks immediately following irrigation, which provided water to evaporate from plant and soil.

2.2 Ammonia concentrations

The field NH\(_3\) concentrations measured by the diffusive samplers (ALPHA badges) over several hours ranged from 3 to 118 µg NH\(_3\) m\(^{-3}\), while the 30 minutes ROSAA concentrations varied from around 0 to around 90 µg NH\(_3\) m\(^{-3}\). The ROSAA concentrations averaged over the same intervals as the ALPHA badges slightly underestimated the badges concentration by 8% on average \((\beta_{ROSAA} = 0.92 \beta_{ALPHA}, R^2 = 0.82)\). The uncalibrated QC-TILDAS concentrations strongly underestimated the ALPHA badges concentrations by 67%, but without any offset \((\beta_{QC-TILDAS} = 0.34 \beta_{ALPHA}, R^2 = 0.90)\). This underestimation is larger than what Ellis et al. (2010) found with the same instrument in a laboratory calibration. Since the correlation was very good, the regression against the ALPHA badges was used to calibrate the QC-TILDAS concentration data. The correction factor was found to be 2.86 ± 0.09. The calibrated QC-TILDAS concentration was in quite good agreement with the ROSAA concentrations both in terms of magnitude and dynamics (Figure 2). In Figure 3 a detailed comparison between calibrated values of QC-TILDAS NH\(_3\) concentrations and ROSAA values is shown. Since we did not find a significant offset in the regression of QC-TILDAS
measurements with respect to the ALPHA badges, the same correction factor (2.86 ± 0.09) could be used for EC fluxes for which only the span calibration is relevant.

The background concentration measured with ALPHA badges over several days varied from 1.9 ± 0.3 to 7 ± 1.5 µg NH₃ m⁻³, and averaged 2.7 ± 1.2 µg NH₃ m⁻³ over the whole experimental period. The background was therefore very small compared to the NH₃ concentration in the field during the period 22 to 30 July 2008 (see Figure 2).

2.3 Quality of the eddy covariance signal

2.3.1 Integral Turbulence Test

In order to test the validity of the eddy covariance measurements and to test the development of the turbulent conditions, the integral turbulence characteristic, the so-called flux variance similarity, was analyzed as first proposed by Foken and Wichura (1996). The ratio of the standard deviation of vertical wind component and sonic temperature and their respective turbulent scaling variable (u* and T*, respective) are shown in Figure 4 as a function of the Monin-Obukhov stability parameter ζ (defined by z/L_MO, where L_MO is the Monin-Obukhov length). The experimental data are compared to the theoretical model under unstable and near neutral conditions (Kaimal and Finnigan, 1994):

\[
\frac{\sigma_w}{u} = c_1 \left( \frac{z}{L_{MO}} \right)^{c_2}
\]

(16)

\[
\frac{\sigma_T}{T} = c_1 \left( \frac{z}{L_{MO}} \right)^{c_2}
\]

(17)

where the constant c₁ and c₂ are reported by Foken et al. (2004). Because of the relative large errors on integral turbulence characteristic in near neutral condition, temperature data were discarded when sensible heat flux density was less than 100 W m⁻². The experimental data nicely follow the theoretical behaviour for the vertical wind component whereas values slightly higher than the model are observed for the sonic temperature variance. This additional turbulence was likely due to the high surface heterogeneity of a not completely closed canopy and to the low measurement height.

2.3.2 Cross-correlations w’β’

Before the analysis of the fluxes, we looked at both the time and frequency response of the signal. An example of the cross-correlation functions between w’, β’ (CO₂ and NH₃) is given
in Figure 5. The delay time (or lag time) can clearly be identified by the location of the maximum of the cross-correlation function between \( w' \) and \( \beta' \). It is close to zero for temperature and CO\(_2\) (measured by an open path analyzer, Li-7500, Licor Biosciences, USA). A positive lag is also clearly seen for the QC-TILDAS NH\(_3\) signal. The difficulty for estimating the time delay from the cross-correlation function can be seen from the long tail observed for NH\(_3\). This tail can be interpreted as NH\(_3\) adsorbed and subsequently released from the lines. Nevertheless, the lag times, estimated with the cross-correlation method for CO\(_2\), H\(_2\)O and NH\(_3\) were 0.20 ± 0.04 s, 0.20 ± 0.03 s and 6.90 ± 0.14 s, respectively. In the case of NH\(_3\), however, we have to take into account that this delay is basically the sum of two terms: the time delay of the DAC conversion (6 s) and the gas residence time in the tube and device.

### 2.4 Cospectral density of NH\(_3\) and other scalars

An example of averaged and normalized scalar cospectra for one day of good data is given in Figure 6, for the runs from 8:00 to 16:00 in a clear day. We did not use the dimensionless frequency to average our cospectra because wind speed variation within the selection of runs was small. The cospectrum of sensible heat, \( C_{O_wT} \), compares very well to the theoretical one, while the cospectrum of NH\(_3\), \( C_{O_wNH_3} \), obtained taking in to account the time lag, falls off faster than the theoretical one for frequencies higher than the cut-off frequency of \( f_c \sim 0.3 \) Hz. Moreover, for higher frequencies the NH\(_3\) cospectrum is also more noisy with values sometimes being negative: we, hence, show the absolute values as suggested by Mammarella et al. (2010). This allows inspecting the fall-off in the inertial subrange which is the result of all high frequency losses. In the following we analyse the correction of these HF losses by the considered approaches. Moreover, Figure 7 is a clear example of the data with an underestimation of all the measured scalar cospectra during the trial: in particular, both the cospectra relative to the CO\(_2\) and the sensible heat show a loss at high frequency like the NH\(_3\) cospectra.

#### 2.4.1 High Frequency loss corrections

Figure 8 shows the trends of the theoretical TF due to the dynamic response time reported and all the TF expressed in equations from 9 to 13 \( (T_F, T_{F_{tube}}, T_{F_{vol}}, T_{F_{phase\_shift}}) \); moreover, their product to give the total theoretical transfer function to apply at cospectra is reported. In particular, two total theoretical TFs are plotted: the \( T_F_{tot}=T_F_{dyn\_response}*T_F_{s}*T_F_{tube}*T_F_{vol} \) to apply at data elaborated taking into account the maximum correlation function method for the computation of the time lag and the \( T_F_{tot\_phase\_shift}=T_F_{dyn\_response}*T_F_{s}*T_F_{tube} * \).
where the total phase shift is involved. For the latter, the \( TF_{\text{phase\_shift}} \) is responsible for negative values of the overall transfer function (Massman, 2000). The individual cut-off frequencies can be estimated for the two theoretical approaches, considering the frequency at which the total \( TF \) equals \( 2^{-1/2} \); these values are around 0.6 and 0.2 Hz for \( TF_{\text{tot}} \) and \( TF_{\text{tot\_phase\_shift}} \), respectively (see Figure 8). Then, the resulting \( CF_{\text{Theor\_phase\_shift}} \) are higher than the \( CF_{\text{Theor\_time\_lag}} \) ones (around 1.5), with a wider range between 1.6 and 4.5.

On average the correction factor found by the ogive method was 1.36 ± 0.37. Figure 9 shows an example of temperature, CO\(_2\) and NH\(_3\) ogive as well as the fitted NH\(_3\) ogive and the corresponding estimation of the high-frequency attenuation for NH\(_3\). It shows a typical situation where the CO\(_2\) and H\(_2\)O HF loss was around 15% while the NH\(_3\) HF loss was around 20%. The corresponding HF correction factor for NH\(_3\) for this particular example would be around 1/0.8.

The damping computed using the inductance method, \( CF_L \), has a wide range starting from 1; however, following suggestion by Eugster and Senn (1995) a threshold of 2.5 has been used in order to reject data where we have not measured at least 40% of the expected flux. An example of the application of the method is reported in Figure 10, where measured NH\(_3\) cospectrum is plotted with the idealized empirical one given by Kaimal et al. (1972) and the damped cospectrum obtained using in equation (14) the value of \( L \) which gives the best fit of the measured cospectrum.

For invariant set up of instruments, the frequency correction factors should depend on: (i) the lag time, which affects the shape of the measured spectra, (ii) the atmospheric stability, which affects the shape of the reference cospectra and (iii) the wind speed, which affects the distribution of cospectra density across the frequency range. In order to compare the above-described correction methodologies applied to our set of data, relationships between the correction factors and the wind speed have been searched, separating stable and unstable conditions (Table 1). The relationships for the theoretical \( TF \) have been obtained using all the data, while for the inductance method, because of the relatively large scatter of the individual data, they were grouped in wind speed classes of 1 m s\(^{-1}\) width, for which the median were determined and fitted describing the overall dependence of the damping factor on wind speed under stable and unstable condition, using only damping factor less than 2.5 as suggested by Eugster and Senn (1995). For stable conditions, the relationships in Table 1 show lower \( r^2 \) than the ones under unstable conditions due to the lower number of data. By means of these relationships the EC NH\(_3\) fluxes have been corrected and the ones relative to 5 days of the
second week of the trial (24-29 July) are plotted in Figure 1.

Table 1 Frequency correction factors \((CF)\) in function of wind speed \((u)\) under stable and unstable atmospheric conditions.

<table>
<thead>
<tr>
<th></th>
<th>Unstable</th>
<th>Stable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical TF with</td>
<td>(CF_{\text{theor_time_lag}} = 0.08u + 1.21)</td>
<td>(CF_{\text{theor_time_lag}} = 0.08u + 1.44)</td>
</tr>
<tr>
<td>time lag</td>
<td>(r^2 = 0.95)</td>
<td>(r^2 = 0.32)</td>
</tr>
<tr>
<td>Theoretical TF with</td>
<td>(CF_{\text{theor_phase_shift}} = 0.55u + 1.38)</td>
<td>(CF_{\text{theor_phase_shift}} = 3.30u + 0.30)</td>
</tr>
<tr>
<td>phase shift</td>
<td>(r^2 = 0.96)</td>
<td>(r^2 = 0.85)</td>
</tr>
<tr>
<td>Experimental-Ogive</td>
<td>(CF_O = 0.11u + 1.50)</td>
<td>(CF_O = 0.025u + 1.23)</td>
</tr>
<tr>
<td></td>
<td>(r^2 = 0.99)</td>
<td>(r^2 = 0.47)</td>
</tr>
<tr>
<td>Inductance</td>
<td>(CF_L = 0.30u + 1.17)</td>
<td>(CF_L = 0.21u + 0.81)</td>
</tr>
<tr>
<td></td>
<td>(r^2 = 0.81)</td>
<td>(r^2 = 0.76)</td>
</tr>
</tbody>
</table>

In general, the correction applied following the different approaches agree quite well among them except where the inductance method gives larger correction \((CF_L > 2.5)\) with respect to the theoretical ones.

To evaluate the overall effects of spectral losses on eddy covariance measurements, the cumulated values of the \(\text{NH}_3\) fluxes in the experimental period were calculated, taking into account the correction factors following the methods studied in this work. The results are reported in Table 2 as percentage of the losses estimated by the applied corrections.

Table 2 Flux losses estimated by the four correction methods described in the section 2.6.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical TF with</td>
<td>-31</td>
</tr>
<tr>
<td>time lag</td>
<td></td>
</tr>
<tr>
<td>Theoretical TF with</td>
<td>-30</td>
</tr>
<tr>
<td>phase shift</td>
<td></td>
</tr>
<tr>
<td>Experimental-Ogive</td>
<td>-43</td>
</tr>
<tr>
<td>Inductance</td>
<td>-23</td>
</tr>
</tbody>
</table>

**Calculated flux** losses ranged between -23% (inductance method, with the \(CF_L\) threshold selected to 2.5) and -43% (experimental-ogive method); while the two theoretical \(TF\) approaches gave comparable loss estimates. However, it should be underlined that the inductance method only **corrects** for high-frequency losses, whereas the ogive method also corrects low-frequency differences. There is no doubt that the experimental approach takes into account damping effects due to absorption and desorption of ammonia, which are not considered by the theoretical ones.
It is of interest to compare these results with the other few works where the fluxes are measured with equipment based on EC technique with NH$_3$ fast analysers. Actually, the values of flux underestimation are in agreement with the work of Whitehead et al. (2008), who found -41% using a QCLAS and -37% using a TDLAS, during a specific experimental period and applying the cospectral similarity between the ammonia and heat fluxes. On the other hand, Shaw et al. (1998) found a greater underestimation of -48% using a tandem mass spectrometer and a TF approach; Sintermann et al. (2011) found high frequency attenuation losses from 20 to 40% using a chemical ionisation mass spectrometer.

4. Conclusions

In this work we evaluated the correction to be applied to the NH$_3$ eddy covariance fluxes from a crop for taking into account the damping of the high frequencies contribution, due to the set-up of the equipment, when a Tunable Infrared Laser Differential Absorption Spectrometer with a quantum cascade laser source is used. This instrument has only recently become available for routine measurements of NH$_3$ concentrations at high frequency as is needed for direct eddy covariance flux measurements. Here three methodologies were analysed in detail for determining the correction factor for the NH$_3$ fluxes: (1a) the spectral theoretical transfer function with time lag; (1b) the spectral theoretical transfer function with total phase shift; (2) the ogive method which is a variant of the in-situ spectral experimental transfer function technique and (3) the inductance correction method.

A comparison between passive diffusion samples (ALPHA badges) and QC-TILDAS clearly showed that this last equipment underestimated the NH$_3$ concentration values, therefore they should be corrected before the calculation of EC fluxes (the correction factor was found to be around 3). When this correction factor is applied the concentration values of ammonia measured by the QC-TILDAS are quite similar to that measured by an independent system (ROSAA), based on wet-effluent denuders.

Secondly, the correction factors of the EC fluxes all follow linear functions of the wind speed \( (CF=a \, u+b, \, u \text{ wind speed}) \), for all the methodologies above mentioned. However, for unstable atmospheric conditions, the most common encountered during the experiment, the wind speed dependency of \( CF \) is very low for the spectral theoretical TF with time lag \( (a=0.08 \, \text{ and } \, b=1.21) \) and the ogive method \( (a=0.11 \, \text{ and } \, b=1.50) \), whereas it is similar for the remaining two methodologies \( (a=0.55, \, 0.30; \, b=1.38, \, 1.17 \) for the TF with phase shift and inductance, respectively). Overall, when the calculated \( CFs \) are applied to EC NH$_3$ fluxes measured in our experimental field, the values of the fluxes obtained are comparable and
basically reflect the conceptual differences in assumptions that must be made under absence of an undisputed reference flux measurement.

In conclusion, correction of the values of NH$_3$ concentration and EC fluxes over natural surfaces are necessary for taking into account the dumping of high frequency contribution due to the coupling of ammonia fast analyser by QC-TILDAS and sonic anemometer.

Considering that we made measurements just above the crop, the contribution of the high frequencies to the whole flux of ammonia is comparatively large, therefore the underestimation of the EC fluxes has to be corrected for. Moreover, considering that we lack an undisputed reference NH$_3$ flux against which the methods could be tested, and hence the differences are basically the conceptual differences of the approaches, it would not be possible to firmly establish that one is better than the other, however there are pro and contra for each of them. Hence, at present either method could provide realistic results and, therefore, future research should also focus on the question of how realistic it is to use sensible heat flux for similarity with NH$_3$ fluxes, namely on fields with finite extent where fertilizer was applied, and from which NH$_3$ fluxes can originate, whereas sensible heat flux is also determined by surrounding. However, in case the sensible heat cospectra of the experimental site are not available, the theoretical TF approach or the inductance method could be used to determine the percentage of the flux that is lost by the measurement system.

Acknowledgements

This study has been supported by Italian Projects FISR “CLIMESCO” (DD 285/ric 2/2/2006) and AQUATER (DM n. 209/7303/05). European Project NitroEurope supported the experimental field work. First author has been also funded by NinE - ESF Research Networking Programme “Nitrogen in Europe” and ACCENT - Biaflux (Network of Excellence funded by EC, FP6, PRIORITY 1.1.6.3 Global Change and Ecosystems: subproject Biosphere-Atmosphere Exchange of Pollutants). The authors thank Céline Decuq, Pasquale Introna, Nicola Martinelli and Sylvie Masson for them helping in conducting the experimental work in the field and Dr. Domenico Vitale for artwork.

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32(6), 1111-1127.


**Figure captions**

**Figure 1** Trends of (a) friction velocity, $u^*$, and (b) energy balance components during the trial. Net radiation ($R_n$), latent heat flux ($LE$), sensible heat flux ($H$) and soil heat flux ($G$) are shown. Moments of irrigation are shown with blue triangles.

**Figure 2** Ammonia ($NH_3$) concentration measured with the QC-TILDAS (calibrated), the ROSAA analyser (calibrated) and the ALPHA diffusion samplers. The QC-TILDAS concentrations were calibrated as explained in the section 3.2.

**Figure 3** Ammonia ($NH_3$) concentration measured with the QC-TILDAS (calibrated) against the values measured by the ROSAA analyser. The linear regression gives $Concentration_{QCL} = Concentration_{ROSAA} \times 0.9958 \ [0.9356 -1.0560]$, where the 95% confidence interval is given in brackets.

**Figure 4** Normalized standard deviation for vertical wind speed, $\sigma_w/u^*$, and temperature, $\sigma_T/T^*$, in function of the Monin Obukhov stability parameter ($|z/L_{MO}|$). Continuous lines are relative to the model reported by Foken and Wichura (1996).

**Figure 5** Typical cross-correlation function for ($w^'s, T_a^'$), ($w^' \beta_{CO2}^'$) and ($w^' \beta_{NH3}^'$), for the DOY 207 at 11h30 UT and DOY 2009 at 7h30 UT, determined over 60 minutes. Here $w$ vertical component of the wind speed, $T_a$ the sonic temperature, $\beta_{CO2}$ the CO$_2$ concentration and $\beta_{NH3}$ the NH$_3$ concentration, while a prime denote a fluctuating quantity determined by linear detrending.

**Figure 6** Normalized averaged cospectra (ratio of cospectra over covariance) of NH$_3$ ($Co_{wNH3}$) and sensible heat fluxes ($Co_{wT}$) over a 8 h period (from 8:00 a.m. to 4 p.m., with $U = 2$ m s$^{-1}$ and $z/L_{MO} = -0.02$). The negative values of NH$_3$ cospectrum ($Co_{wNH3}\neg$) have been inverted to be represented on the logarithmic scale.

**Figure 7** Normalized averaged cospectra of NH$_3$, (CoSpwnh3), temperature (CoSpwt), water (CoSpwq) and CO$_2$ (CoSpwc) over a 4 h period (DOY 208 from 8:00 a.m to 12:00 a.m., with $U = 2.1$ m s$^{-1}$ and $z/L_{MO} = -0.02$. A high pass filter has been applied at $f = 0.00139$ Hz (12 min).
Figure 8 Trend of the single theoretical transfer functions ($TF$) and the total ones, $TF_{total}$ and $TF_{total\_phase\_shift}$, to apply to cospectra obtained taking into account the maximum cross-correlation function and the total phase shift, respectively (see the section 2.6.1 for details about each theoretical $TF$). The data are relative to a half an hour with $U=2.1$ ms$^{-1}$ and $z/L_{MO}=-0.04$.

Figure 9 Example ogives for heat, CO$_2$, H$_2$O and NH$_3$ fluxes and corresponding estimation of the high frequency damping by ogive fitting (DOY 208 from 08:00 a.m. to 12:00 a.m.). $T$ stands for temperature ogive, init. is the initial ogive, and corr. is the corrected ogive (fit to the temperature ogive as explained in section 2.6.2). The High Frequency loss damping is simply one minus the value of the corrected ogive at the higher frequency. Here the CO$_2$, H$_2$O, and NH$_3$ high frequency dampings are 0.17 = 1 – 0.83, 0.18 = 1 – 0.82 and 0.37 = 1 – 0.63. A high pass filter has been applied at $f = 0.00139$ Hz (12 min).

Figure 10 An example of the inductance method applied to half an hour dataset (DOY 207 10:00 a.m.). The measured (black dots and lines), the Kaimal et al. (1972) (blue) and the damped (red) cospectra are plotted. The values of inductance $L$, wind speed $u$, flux $F_{NH3}$ and time lag are reported.

Figure 11 Ammonia (NH$_3$) fluxes corrected by means of the correction factors (CF) calculated using the approaches explained in the section 2.6: (i) theoretical transfer function with time lag ($CF_{theor\_time\_lag}$) and total phase shift ($CF_{theor\_phase\_shift}$); (ii) in situ Ogive method ($CF_O$); (iii) inductance method ($CF_L$).
FIGURE 1
FIGURE 2
FIGURE 3

QCL calibrated concentration (µg NH₃ m⁻³) vs. ROSAA concentration (µg NH₃ m⁻³)
FIGURE 4
FIGURE 5
FIGURE 6

Natural frequency (Hz)

$10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $10^{0}$ $10^1$

$f_1$ (Scalar Cospectra)

- $4/3$

- $C_{oWT}$
- $C_{oNH5}$
- $C_{oNH5}\text{neg}$
FIGURE 7
FIGURE 8
FIGURE 9

CO₂

H₂O

NH₃

\[\text{Ogive} \]

\[f (\text{Hz})\]

\[10^{-4} \quad 10^{-2} \quad 10^{0}\]

\[1 \quad 0.8 \quad 0.6 \quad 0.4 \quad 0.2 \quad 0\]

\[1 \quad 0.8 \quad 0.6 \quad 0.4 \quad 0.2 \quad 0\]

\[1 \quad 0.8 \quad 0.6 \quad 0.4 \quad 0.2 \quad 0\]

\[10^{-4} \quad 10^{-2} \quad 10^{0}\]
FIGURE 10

\[ F_{\text{NH}_3} = 1.4626 \text{ ppb ms}^{-1} \]

\[ u = 2.572 \text{ ms}^{-1} \]

\[ \text{Lag} = 6.86 \text{ s} \]

\[ L = 0.2556 \pm 0.0917 \ (p = 0.0066) \]
FIGURE 11

NH₃ flux (ng m⁻² s⁻¹)

○ EC calibrated (2.86)
- CF theor. time lag
- CF theor. phase shift
- CFₐ < 2.5
- CF₀

Date (UT)

23/07/08  24/07/08  25/07/08  26/07/08  27/07/08  28/07/08  29/07/08
Energy fluxes (W m$^{-2}$)

Rn  H  LE  G  Irrigation

Figure
FIGURE 5

Cross correlation functions with \( w \):

- \( T_a \)
- \( CO_2 \)
- \( H_2O \)
- \( NH_3 \)

DOY 209 @ 7h30 UT

DOY 207 @ 11h30 UT

Time lag (s)
Natural frequency (Hz)

$f_{i}$(Scalar Cospectra)

Figure
Natural frequency ($f_{co}$)

$w'_{NH_3}$

$10^{-3}$ $10^{-2}$ $10^{-1}$ $10^{0}$

Natural frequency (Hz)

$L = 0.2556 \pm 0.0917$ ($p = 0.0066$)

$u = 2.572 \text{ ms}^{-1}$

$F_{NH_3} = 1.4626 \text{ ppb ms}^{-1}$

Lag = 6.86 s

$NH_3$

Idealized

Damped

$0.6$ $0.4$ $0.2$ $0.0$ $0.2$ $0.4$ $0.6$

$I_{CO}^{^{\delta}\text{HN,M}}/\langle I_{CO}^{^{\delta}\text{HN,M}} \rangle$

$-0.4$ $-0.2$ $0.0$ $0.2$ $0.4$ $0.6$

$F_{NH_3}$