



report

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Comparison of different techniques to measure ammonia emission after manure application

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Sammanfattning/Summary Manure application leads to a number of different environmental problems, as ammonia emission, leaching and nitrous oxide emission. The environmental aspects are on local, regional and global scales. New methods for manure applications have to be developed in order to mitigate the problems. During the developing of these methods, measurements of the nitrogen exchange with the atmosphere has to be performed. For this purpose suitable and reliable measuring techniques are needed. A number of methods to measure the NH ₃ exchange were therefore tested in parallel. Ammonia emission after band spreading of pig slurry on a young wheat crop was measured using five different techniques. Three variants of the gradient technique were used. The techniques were: i) concentration gradients measured over short periods using FTIR spectroscopy were multiplied with the diffusivity determined by an aerodynamic method, ii) FTIR gradient with the diffusivity estimated using a trace gas release, iii) integrating gradient technique in which the wind speed weighted average concentration profile was multiplied with the average diffusivity, iv) A mass balance technique in which the horizontal flux of ammonia entering and leaving the field was measured, v) a chamber technique in which the emission was calculated from the mass transfer coefficient, ambient, and equilibrium concentrations. The results agreed within ca 25 % with one exception for the chamber technique.	
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Introduction

Animal breathing is the dominant source of atmospheric ammonia. Manure and urine (urine after decomposition of organic nitrogen compounds) contain 1 - 4 ‰ ammonium which is in equilibrium with volatile gaseous ammonia. When the manure is stored, brought in contact with soil or a large volume of air (e.g. exposed to wind after surface application to soil), the equilibrium will be displaced to the ammonium form. Ammonia is highly water soluble and will therefore to a substantial degree be deposited near the source. The fraction that is not deposited is diluted in the mixing layer and reacts with acidic gases. Particle-bound ammonium salts are formed which then can be transported over long distances (Ferm, 1998). Since nitrogen is essential for life, the deposited ammonium will be taken up into the ecosystems. The number of animals per unit land area in the industrialised world is, however, far higher than nature would allow. High deposition of N is not a problem for agriculture itself as the high yielding crops selected require a high nitrogen input. In contrast, the high N deposition on natural ecosystems like coniferous forests and lakes results in loss in biodiversity, favouring a more nitrogen-demanding community. In the past, economic constraints have held back any significant action to reduce ammonia emissions. With the general increase in environmental awareness, however, efforts to reduce ammonia emissions have been initiated. These focus on displacing the ammonia/ammonium equilibrium by reducing the contact with air (roof on open manure containers, band spreading etc.), increasing the contact between manure and soil (injection, mulching etc.), decreasing the pH of the manure (additives), and production of less ammonium. In the latter case, enzymes are added to low nitrogen content fodder which reduce the ammonium content in the manure, or by simply reducing the animal density.

Manure application leads to a number of different environmental problems, as ammonia emission, leaching and nitrous oxide emissions (IPCC, 1997). The environmental aspects are on local, regional and global scales. New methods for manure applications have to be developed in order to mitigate the problems. During the developing of these methods all the aspects have to be simultaneously investigated. This puts a large demand on the experimental design and method selection. The overall aim of this project was to investigate and compare available methods for estimating the emission of NH_3 in agricultural applications e.g. after spreading of liquid manure. The experiments were conducted as part of a joint effort between different research disciplines where more recent developments are described elsewhere in the literature; dual beam FTIR techniques (Griffith & Galle, 2000) and direct measurement of fluxes by trace gas release (Galle *et al.*, 2000). Five different techniques were used to measure the NH_3

emission, i) gradient aerodynamic technique, ii) gradient tracer release technique, iii)) integrating gradient technique, iv) mass balance technique (horizontal fluxes) and v) chamber technique.

Materials and Methods

The comparisons were performed at Lanna experimental farm, which is located in southwest Sweden (58°21'N, 13°08'E). The clay content of the soil varies from 40% (topsoil) to 60 % (subsoil) and the organic content between 3 to 6 %. The subsoil is well structured and contains fine angular aggregates formed from winter frost action. Additional soil characteristics are described in Bergström & Brink, (1986). At time of spreading and measurements the wheat crop was about 0.40 m high. Pig slurry was spread on the field at a rate corresponding to 60 kg NH₄-N/ha.

1. Gradient aerodynamic technique

In the gradient technique (Pasquille & Smith, 1983), the emission is determined using the fact that under favourable meteorological condition there is a linear relationship between the vertical flux of a gas and its vertical concentration gradient.

$$E_g = -K_z \frac{dC_g}{dz} \quad (1)$$

The diffusivity K_z is depending on the atmospheric turbulence and the height (z) and can be derived from micrometeorological measurements. The following formula was used to calculate the NH₃ emission:

$$E_{NH_3} = \frac{k^2}{\varnothing_M \cdot \varnothing_H} \cdot \frac{\Delta u}{\Delta \ln(z-d)} \cdot \frac{\Delta C_{NH_3}}{\Delta \ln(z-d)} \quad (2)$$

The stability factors for heat \varnothing_H and momentum \varnothing_M are close to unity during neutral or unstable conditions and was set to 1.0 here. von Karmans constant, $k = 0.41$. u is the wind speed. The zero plane, d was set to 70% of the crop height, which was 40 cm. The emission obtained in this way assumes an infinitely large source area.

In this application of the gradient technique the concentration measurements were conducted by means of a medium resolution FTIR spectrometer coupled to two identical multipass cells with 25 litres volume each and an optical path of 96 m. Air was continuously pumped through the two cells via Teflon tubing connected to inlets at the gradient mast. A computer controlled valve system switched the inlets to 0.6, 1.2 and 1.8 m respectively in a sequence ensuring near-simultaneous measurements of the concentrations every 20 minutes (Griffith & Galle, 2000). The absorption spectra were evaluated for NH_3 , SF_6 and H_2O using classic least squares multiregression techniques. Calibration spectra were generated from the database HITRAN using the software MALT (Griffith, 1996).

2. Gradient tracer release technique

To convert the measured gradients to flux knowledge of the diffusivity K_z is necessary. In method 1 above K_z was obtained by calculations from standard micrometeorological measurements at the site using an aerodynamic method. In the tracer gas method, K_z is determined experimentally by measurement of the gradient obtained from a known area release of a tracer gas (Galle *et al.*, 2000). The controlled area emission of SF_6 upwind the mast was obtained by means of a permeation system comprising 1 km silicon tubing (diameter 16 mm) covering an area of 50 x 40 m. From simultaneous measurements of the gradients of SF_6 and NH_3 , and from knowledge of the SF_6 emission rate, the NH_3 emission could be calculated according to equation 3.

$$E_{\text{NH}_3} = E_{\text{SF}_6} \frac{\Delta C_{\text{NH}_3} / \Delta \ln(z-d)}{\Delta C_{\text{SF}_6} / \Delta \ln(z-d)} A_{\text{fetch}} \quad (3)$$

Here A_{fetch} is a correction factor taking into account that the tracer emission does not cover the total fetch area of the ammonia emission. This factor was calculated using a gaussian plume spreading model (Galle *et al.*, 2000) and for the actual conditions it was calculated to 0.47.

3. Integrating gradient technique

In this variant of the gradient technique the wind speed weighted average concentration profile was multiplied with the average diffusivity. The wind speed weighted concentrations ($\overline{C_{ww}}$) were obtained by dividing the total horizontal flux at a certain height, with the average wind speed (\overline{u}) at the same height as described by Schjørring *et al.*, (1992). The NH₃ flux was measured using passive samplers, consisting of glass tubes internally coated with oxalic acid. A plate with a small hole that reduces the wind speed inside the tubes and makes this velocity proportional to the wind speed component along the tube (Ferm, 1986, Schjørring *et al.*, 1992) was attached to one of the ends, at three heights ($z=0.6, 1.2$ and 1.8 m) while wind speeds were measured at three other heights ($1.5, 4.0$ and 9.0 m). The wind speeds at the heights where flux measurements were made were calculated using a logarithmic wind profile. Only one 8h sample was taken. The emission was calculated from:

$$E = \frac{\overline{du}}{d\{\ln(z-d)\}} \cdot \frac{d\overline{C_{ww}}}{d\{\ln(z-d)\}} \cdot \frac{k^2}{\varnothing_M \cdot \varnothing_H} \quad (4)$$

4. Mass balance technique

The horizontal incoming and outgoing ammonia fluxes at the edges of a 12 x 20 m plot were measured using similar passive samplers as in the integrating gradient technique. Manure was applied to this plot, which was situated upwind of the main field in order to decrease the background flux of ammonia. Four masts were mounted 0.5 m outside the middle of the sides surrounding the plot. Incoming and outgoing fluxes were measured at five heights on each mast (0.6, 1.2, 1.8, 2.5 and 3.5 m).

The emission was calculated by adding all the outgoing fluxes ($F_{z, out}$) at all heights ($z=1-5$) at one mast, multiplied with the height intervals (Δz_z) that the samplers at a certain height represent and the width of the field at a certain mast (W_m). The corresponding incoming fluxes are subtracted ($F_{z, in}$). This was repeated for all four masts ($m=1-4$) according to:

$$E = \sum_{m=1}^{m=4} \sum_{z=1}^{z=5} W_m \cdot \Delta z_z (F_{z, out} - F_{z, in}) \quad (5)$$

One sample integrated over 29 h was taken.

5. Chamber technique

The chamber technique has been the most widely used in earlier studies. The air movements and thereby ammonia emissions are, however, changed when a chamber is placed on the soil surface. The NH_3 emission from the covered plot is therefore not equal to the emission from an open plot (Ferm, 1983). The technique was here used to measure the equilibrium concentration of NH_3 at the soil surface (Ferm, 1983). The emission is then obtained from the equilibrium concentration (C_{eq}), the ambient concentration (C_a) and the mass transfer concentration between air and soil (M_z). The ambient NH_3 concentrations and the mass transfer coefficient for NH_3 between the soil surface and the air was measured using two set of diffusive (passive) samplers (Kirchner *et al.*, 1999). They were placed under a rain shield ca 2 cm above the soil surface. The equilibrium concentration of NH_3 between the soil surface and the air was measured with another diffusive sampler mounted inside a battery operated stirred and ventilated chamber (Svensson & Ferm, 1993). The NH_3 emission (E) was calculated from equation 6. ($C_{\text{eq}} - C_a$) represent the driving force for the emission. M_z represent the inverted value of the transport resistance i.e. the diffusion coefficient for NH_3 in air divided by the thickness of the laminar boundary layer, through which NH_3 is mainly transported by molecular diffusion.

$$E = (C_{\text{eq}} - C_a) * M_z \quad (6)$$

Measurements of all three parameters were made with duplicate diffusive samplers at two places. The sampling period was 1 - 2 hs during the first day. One sample was taken during the night and one the following day. Sometimes too low or even negative ammonia emissions have been obtained with the chamber technique when crops have been present inside the chamber. In order to check this effect in the present study, an extra sample on a 2 x 2 m plot where the crops had been removed was taken during the last 2h period.

Results and Discussion

Due to unfavourable meteorological conditions reliable gradients were not obtained until morning May 29 and the trace gas release was stopped on the evening of May 29. The two FTIR gradient techniques measured continuously and the results are given in Fig. 1. The average emissions are shown in Table 1. During the overlapping time period the two methods show very good agreement. The advantage with the FTIR gradient techniques are that they give continuous real time measurements of the emission with high sensitivity and accuracy. A disadvantage is that the equipment is relatively expensive and complicated, however after installation the measurements can be conducted with only minor attention. The restricting requirement of good micrometeorological fetch can to some degree be relaxed using the tracer method, provided the tracer can be released over the ammonia emitting area within the footprint of the gradient measurement.

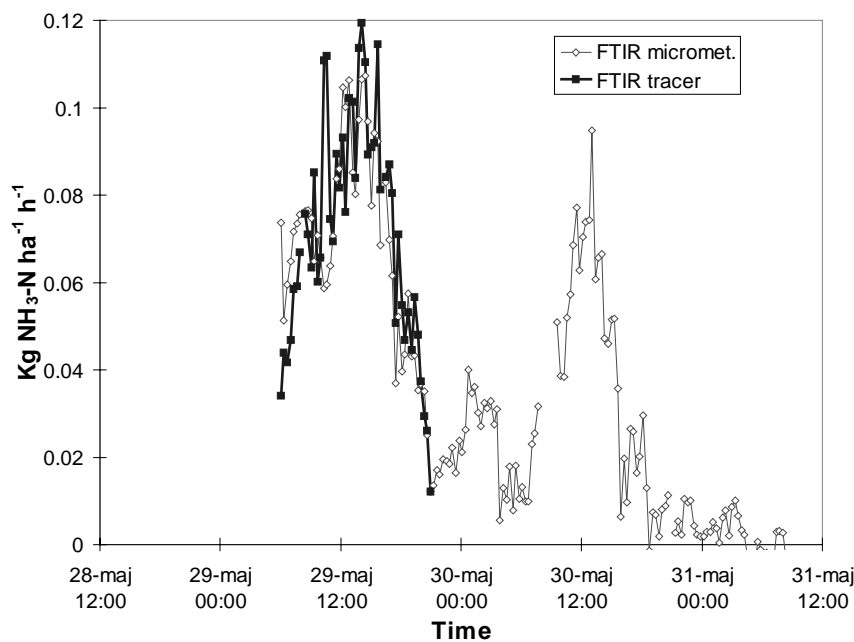


Fig. 1. Ammonia emissions measured with the two FTIR methods, starting at noon May 28.

Table 1. Comparison between ammonia flux obtained with different methods ($\text{kg NH}_3\text{-N ha}^{-1} \text{ h}^{-1}$).

Interval (hours after spreading)	0 - 8	8-20	20 - 29	0 - 29
Gradient aerodynamic (FTIR).			0.08	
Gradient trace release (FTIR)			0.09	
Integrating gradient	0.15			
Mass balance				0.19
Chamber	0.18	0.12	0.55*	0.25*

As can be seen in Table 1 the agreement between the different methods is fairly good, about 25 %, except for two emissions obtained with the chamber technique (marked with asterixes).

Advantages with the chemical measuring techniques (integrating gradient, mass balance and the chamber techniques) are low costs for the equipment, neither gas phase calibration nor mains power is needed.

In the integrating gradient technique the concentration is integrated over longer periods (several hours to several days) using passive flux samplers. Wind speed weighted average concentrations are then used instead of time weighted averages. The integration interval can then be increased because a variation in diffusivity has a smaller effect on the result (Schjørring *et al.*, 1992). The vertical gradient was rather strong and simple to measure (the friction velocity was 0.13 m s^{-1} and the roughness length 0.011 m), see Fig. 2. The NH_3 concentration versus $\ln(z-d)$ should make a straight line, but the fit was not so good. As mentioned earlier the meteorological conditions were not favourable and the flux tubes don't work perfectly at very low wind speeds.

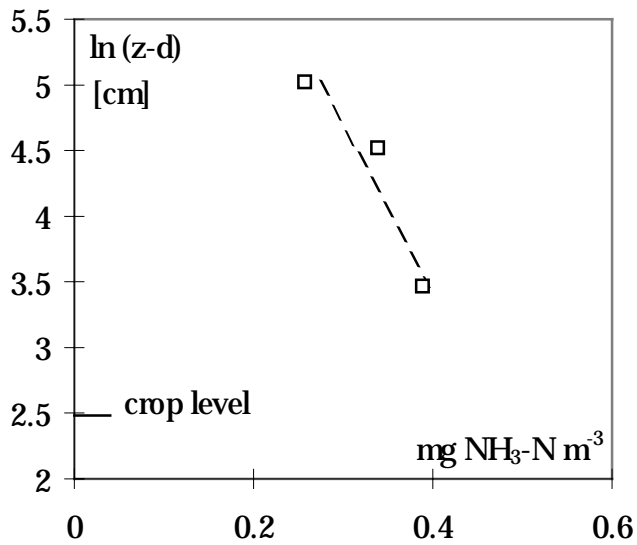


Fig. 2. Wind speed weighted average NH_3 concentration ($\overline{C_{\text{ww}}}$) profile.

The integrating gradient technique has been used for weekly measurements of NH_3 emission from fertilised crop (e.g. Ferm, 1993). The whole growing season can thus be covered. As for all gradient techniques, large homogenous fields are needed.

The outgoing and incoming NH_3 fluxes for the five height intervals used in the mass balance technique are shown in Fig. 3. The difference between them was simple to measure, because the outgoing fluxes were much larger than the incoming. This is, however, not always the case. The net fluxes for all intervals are added according to equation 5. Most of the ammonia escaped the border of the plot (12x20 m) below 2 m even though some NH_3 escaped above the highest interval, see Figure 3. The mass balance technique can not be used on large fields, but on plots with a length of ca 5-25 m. This technique neither requires stable wind nor homogeneous surroundings. It can therefore be used to measure the NH_3 emission from dung heaps or slurry tanks. A drawback is that the accuracy becomes unsatisfactory when the outgoing flux is similar to the background (incoming) flux of NH_3 .

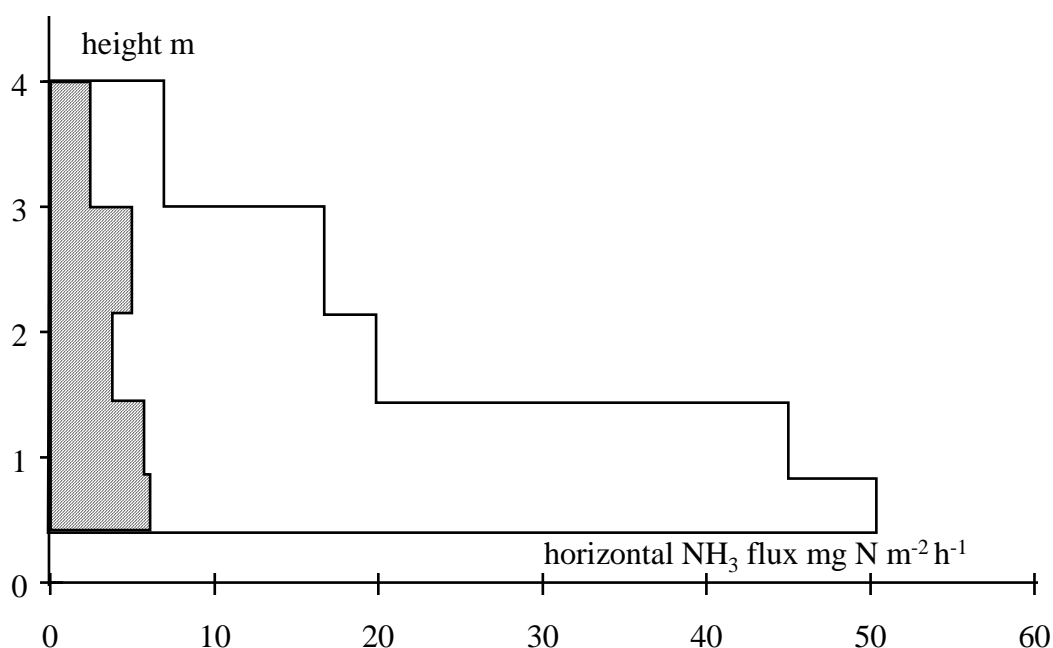


Fig. 3 Average horizontal NH₃ fluxes as a function of height intervals obtained by the mass balance technique. The incoming (background) flux is shaded. The flux below the crop (~0.4 m) is assumed to be zero.

The emissions measured with the chamber technique as a function of time interval is shown in Fig. 4. The last emission was very high and the two chambers gave very different results. As the reproducibility between the duplicates of the samples was also poor, contamination can not be excluded. It has earlier been found that the chamber and mass balance techniques agree when no growing crop, only very little and old barley stubble was present (Ferm & Svensson 1992). When crop that absorbs NH₃ is present the chamber technique can under-estimate the emission because the mass transfer inside the stirred chamber is higher than outside the chamber. This has earlier been observed (Ferm *et al.*, 1998). In order to see if the crop absorbed NH₃ in this case the crop was cut off at one place and C_a and C_{eq} was measured. The equilibrium concentration (0 cm above ground) as well as the ambient concentrations as a function of height is shown in Figure 5 both with and without crop. The lowest level of the ambient concentration was measured by digging down the sampler so that the inlet had the same level as the soil. These samplers measured the concentration at a height equal to the thickness of the laminar boundary layer, which was 0.31 cm with crop and 0.19 cm without. As can be seen from the Figure the crop had very little influence on the NH₃ concentration. Figure 5 further shows that the difference between ambient and equilibrium NH₃

concentrations (the driving force and thus the atmospheric resistance) is largest across the laminar boundary layer.

The chamber technique can be used to measure emission from very small plots as well as huge fields. It can therefore for instance be used to measure edge effects in plots or fields. A high background concentration is not a big problem.

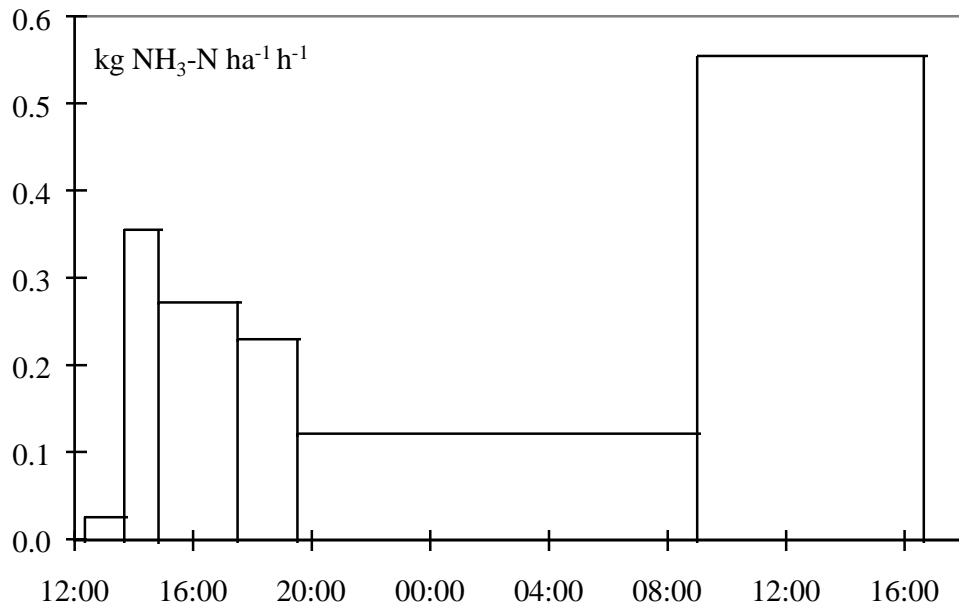


Fig. 4. Ammonia emission obtained with the chamber technique as a function of time, starting at noon May 28.

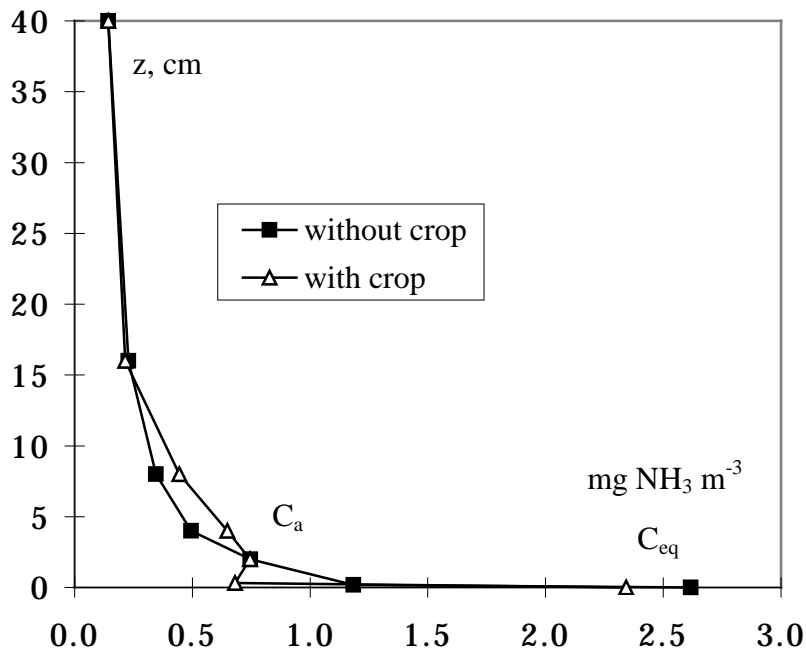


Fig. 5. Equilibrium and ambient NH_3 concentrations as a function of height 5-7 h after spreading.

Conclusion

The atmospheric ammonia losses were very small, only 8% during the first 29 h after spreading. All five techniques agreed in most cases within 25%, which is very good considering the difficulties involved with measuring fluxes and the unfavourable meteorological conditions during this campaign. The different techniques have different advantages and shortcomings. Different techniques therefore have to be used at different occasions. It is therefore satisfactory that the techniques give comparable results.

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