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Field evaluation of the equilibrium concentration technique (JTI method) for measuring ammonia emission from land spread manure or fertiliser

T.H. Misselbrook^{a,*}, M.N. Hansen^b

^a *Institute of Grassland and Environmental Research, North Wyke, Okehampton, Devon EX20 2SB, UK*

^b *Danish Institute of Agricultural Sciences, Research Centre Bygholm, PO Box 536, 8700 Horsens, Denmark*

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Abstract

Three experiments were conducted in which intercomparisons were made between the equilibrium concentration technique, developed at JTI, Sweden, and the integrated horizontal flux technique for measuring ammonia emissions following applications of urea fertiliser, cattle slurry and solid pig manure to land. Mean square prediction error analysis was used to compare the emission rates measured by the two techniques. There were no significant differences between the measurement techniques, although there was some evidence that emission rates were overestimated by the equilibrium concentration method relative to the integrated horizontal flux technique at higher emission rates ($> 400 \text{ g N ha}^{-1} \text{ h}^{-1}$). The equilibrium concentration method provides a practical and relatively inexpensive technique for measuring emissions under ambient conditions from small plots but good sampler preparation, adequate replication of emission measurements and appropriate choice of duration of sampling periods are necessities for obtaining reliable results. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In Europe, land application of livestock manures and, to a lesser extent, fertilisers are two important sources of ammonia (NH_3) emission to the atmosphere (Pain et al., 1998). With increasing concern about the potential environmental damage caused by atmospheric transport and subsequent deposition of NH_3 , it is important to have reliable measurements of emission sources both for development and evaluation of potential abatement strategies and compiling national emission inventories.

Various techniques have been developed for the measurement of NH_3 emissions from land amended

with livestock manure or fertilisers, with those most commonly used being described by McGinn and Janzen (1998). Measurements may be conducted on a field or large plot scale, using micrometeorological techniques, or on a small plot scale using techniques such as small wind tunnels or chambers (ventilated or closed). For absolute measurements of emission, micrometeorological methods are to be preferred, as the measurement technique does not interfere with the emitting surface. However, the main disadvantage of these methods are that large uniform areas of land are required (minimum fetch lengths of 20 m), with resultant difficulties in achieving replication or studying multiple treatments at the same time.

A method has been developed more recently by Svensson (1994) at JTI, Sweden, which is essentially a micrometeorological approach but suitable for use on small plots. Other advantages of the method are that it relies on inexpensive equipment and does not require

*Corresponding author. Tel.: 44-1837-883500, fax: 44-1837-82139.

E-mail address: tom.misselbrook@bbsrc.ac.uk (T.H. Misselbrook).

electric power. The method relies on the measurement of the equilibrium concentration of NH_3 in the air at the emitting surface and the mass transfer coefficient for NH_3 from the air at the emitting surface to the free atmosphere (Svensson and Ferm, 1993). This method will be referred to as the JTI method throughout this paper.

1.1. JTI method

The JTI method uses the micrometeorological law of resistance to determine the flux of NH_3 (Φ_{NH_3} , $\mu\text{g m}^{-2} \text{s}^{-1}$) from an NH_3 emitting surface by estimation of the equilibrium concentration of NH_3 in the air at the emitting surface (C_{eq} , $\mu\text{g m}^{-3}$), the NH_3 concentration in the air above the emitting surface (C_a , $\mu\text{g m}^{-3}$) and the mass transfer coefficient for NH_3 (K_a , m s^{-1})

$$\Phi_{\text{NH}_3} = (C_{\text{eq}} - C_a)K_a. \quad (1)$$

The method is described in detail by Svensson and Ferm (1993) and Svensson (1994) but is summarised briefly here for clarity and to aid discussion later in the paper. Passive diffusion samplers (PDS) are used to measure NH_3 concentration in the air. Two types of PDS are used which differ in the length of the diffusion path. For the L-type, the NH_3 absorbing filter is directly exposed to the ambient air. The C-type has the NH_3 absorbing filter placed 10 mm below a Teflon membrane filter. The amount of NH_3 collected by the PDS-C type (X , μg) and PDS-L type (Y , μg) is given by

$$X = DCt \frac{A}{(L_R + L_{\text{LBL}})} \quad (2)$$

and

$$Y = DCt \frac{A}{L_{\text{LBL}}} \quad (3)$$

respectively, where D is the diffusion coefficient for NH_3 in air ($\text{m}^2 \text{s}^{-1}$), C the concentration of NH_3 in the air ($\mu\text{g m}^{-3}$), t the exposure time for the PDS (s), A the exposed area of the filter (m^2), L_R the distance between the Teflon membrane filter and the NH_3 absorbing filter for PDS-C type (m) and L_{LBL} the laminar boundary layer above the top of the PDS (m). By combining Eqs. (2) and (3) an expression for L_{LBL} can be derived:

$$L_{\text{LBL}} = \frac{XL_R}{(Y - X)}. \quad (4)$$

The mass transfer coefficient can then be derived from the relationship

$$K = \frac{D}{L_{\text{LBL}}}. \quad (5)$$

Concentration of NH_3 in the air can be determined by combining Eqs. (3) and (4)

$$C = \frac{XYL_R}{DtA(Y - X)}. \quad (6)$$

By using the two types of PDS close to the surface of a treated plot (ca. 2 cm above the soil surface), both the concentration of NH_3 in the air just above the emitting surface (C_a , $\mu\text{g m}^{-3}$) and the mass transfer coefficient (K_a , m s^{-1}) can be determined from Eqs. (4)–(6). The other parameter required in Eq. (1), C_{eq} , is determined by use of a ventilated chamber. The chamber is ventilated by a fan via small inlet and outlet openings ensuring that condensation does not form on the internal walls. Inlet air is assumed to have an NH_3 concentration C_a , as measured by the PDS outside the chamber. NH_3 flux from the area covered by the chamber can be calculated according to Eq. (1) as

$$\Phi_{\text{NH}_{3\text{ch}}} = (C_{\text{eq}} - C_{\text{ch}})K_{\text{ch}} \quad (7)$$

where C_{ch} is the NH_3 concentration of air inside the chamber and K_{ch} the mass transfer coefficient for NH_3 inside the chamber (which should be constant for a given flow rate and surface conditions). Flux from the chamber can also be calculated by mass balance

$$\Phi_{\text{NH}_{3\text{ch}}} = (C_{\text{ch}} - C_a)F/A \quad (8)$$

where F is the air flow rate through the chamber ($\text{m}^3 \text{s}^{-1}$) and A the area of emitting surface covered by the chamber (m^2). Combining Eqs. (7) and (8) gives an expression for the equilibrium concentration at the emitting surface:

$$C_{\text{eq}} = C_{\text{ch}} \left(1 + \frac{F/A}{K_{\text{ch}}} \right) - C_a \left(\frac{F/A}{K_{\text{ch}}} \right). \quad (9)$$

By exposing both types of PDS within the chamber, values can be derived for C_{ch} and K_{ch} , as they were for C_a and K_a , using Eqs. (4)–(6), enabling derivation of C_{eq} from Eq. (9). This value can then be used in Eq. (1) together with the determined values for C_a and K_a , to derive the flux from the treated area for the measurement period.

1.2. Integrated horizontal flux (IHF)—mass balance method

The mass balance method equates the vertical flux of NH_3 from a treated area of limited upwind extent with the net integrated horizontal flux at a known downwind distance (Wilson et al., 1983). The horizontal NH_3 flux for a given height can be measured using passive flux samplers (Leuning et al., 1985). The mean horizontal flux \overline{uc} ($\mu\text{g m}^{-2} \text{s}^{-1}$) is derived from

$$\overline{uc} = M/At \quad (10)$$

where M is the mass of NH_3 collected (μg) in the sampler during sampling period t (s) and A is the effective cross-sectional area of the sampler (m^2) as determined in wind-tunnel calibrations. Using passive flux samplers mounted at several positions to a height z (m), on masts placed at the upwind edge of an emitting

surface and at a known distance x (m), downwind of that edge, the net horizontal flux (F , $\mu\text{g m}^{-2}\text{s}^{-1}$) is derived from

$$F = \frac{1}{x} \left[\int_0^z (\overline{u})_{\text{dw}} dz - \int_0^z (\overline{u})_{\text{uw}} dz \right], \quad (11)$$

where \overline{u} is the mean horizontal flux measured by each sampler at the downwind (dw) or upwind (uw) edge of the treated area.

The aims of the study reported in this paper were to compare the JTI method and the integrated horizontal flux (IHF) mass balance approach and to investigate the constraints of the JTI method when used for measuring NH_3 emission from field applied fertiliser and manure.

2. Materials and methods

Three experiments were conducted in which NH_3 emission measurements were made using the JTI and IHF mass balance methods simultaneously. Experiment 1 was conducted in the UK at IGER, North Wyke, and Experiments 2 and 3 were conducted in Denmark at Research Centre Bygholm.

2.1. Experimental

In Experiment 1, granular urea fertiliser was applied uniformly, using a calibrated small-plot applicator, to a $40\text{ m} \times 40\text{ m}$ grassland plot at a rate of 300 kg ha^{-1} (138 kg N ha^{-1}) in October 1999. The grass had been cut the previous day to approximately 6 cm sward height. For the IHF method, a mast supporting five passive flux samplers (Leuning et al., 1985) at heights 0.25, 0.65, 1.20, 2.00 and 3.05 m was positioned at the centre of the treated area and a second mast supporting three samplers at 0.25, 1.25 and 3.05 m was positioned at the upwind edge. For the JTI method, six dynamic chambers and six ambient samplers, each having two replicate C-type and L-type PDS, were positioned randomly across the plot. Sampling periods were identical for both methods, with samplers being changed morning and evening each day for the first 3 days; then measurements were made during the daytime only for days 4–6, giving nine sampling periods. Chambers were moved to new positions between sampling periods.

In Experiment 2, cattle slurry was band spread to a $36\text{ m} \times 36\text{ m}$ recently cut grassland plot at a rate of $38\text{ m}^3\text{ ha}^{-1}$ ($50\text{ kg NH}_4^+\text{-N ha}^{-1}$) in June 1999. Measurements using the IHF and JTI method were as for Experiment 1 with the exception that four dynamic chambers and two ambient samplers were used. Measurements continued for 6 days after application. Measurements were only conducted during the daytime using the JTI method whereas measurements of emission

both during daytime and overnight were made using the IHF method.

In Experiment 3, solid pig manure was applied to a circular plot of bare soil of 20 m radius at a rate of 9.6 t ha^{-1} ($4.3\text{ kg NH}_4^+\text{-N ha}^{-1}$). Measurements using the IHF and JTI method were as for Experiment 1 with the exception that five dynamic chambers and two ambient samplers were used. Measurements continued for 6 days after application, with five sampling periods for both methods.

For all three experiments, continuous measurements were made of air temperature (T , K) close to the soil surface (at the same height as the PDS were situated), so that the diffusion coefficient required for the JTI method calculations could be determined from

$$D = T^{1.5} \times 4.59 \times 10^{-9}. \quad (12)$$

Differences in D due to variations in atmospheric pressure were not accounted for, as air pressure was not measured, but would have had very small influence on the overall calculation. Wind direction was measured continuously on-site for each experiment, so that the mean fetch length for each sampling period, as required in the IHF method (Eq. (11)) could be determined.

The passive flux samplers of the IHF method were prepared by shaking with a 3% solution of oxalic acid in methanol and discharged after exposure with deionised water as described by Sherlock et al. (1989). Two unexposed samplers were analysed each time to provide a blank value. Ammoniacal-N content of the sample was determined by automated colorimetry (Searle, 1984).

For the PDS of the JTI method, thorough washing of the paper filters was found to be very important to obtain low blank values. Paper filters (Whatman Grade 40) were washed in hot, deionised water for 2 min and then rinsed twice in methanol (pre-shaken with ion exchange resin). (Alternatively, for Experiments 2 and 3, filters were washed in deionised water in an ultrasonic bath for three 15 min periods, followed by three further rinses in deionised water). These were then allowed to dry in a ventilated NH_3 -free chamber. Filters were then soaked for 2 min in a 3% (w/v) solution of tartaric (Experiment 1) or oxalic (Experiments 2 and 3) acid in methanol and allowed to dry again in the NH_3 -free chamber. Following exposure, filters were leached with 4 ml deionised water for analysis. Unexposed filters were also analysed to provide a blank value. Ammoniacal-N content of the leachate was determined as for the passive flux samplers.

2.2. Ammonia flux calculation

For the IHF method, ammonia flux from the treated area was calculated according to Eqs. (10) and (11). For the JTI method, the mean C_a value for the plot was derived from the ambient samplers. This mean value was

used in Eq. (9) together with chamber-specific C_{ch} and K_{ch} values to give a C_{eq} value for each chamber position. These were then used in Eq. (1), together with mean plot values for C_a and K_a , to derive a flux value for each chamber position. The flux values for each chamber position were averaged to derive the flux for the plot. A mean blank value was derived for the PDS, and filter concentrations not significantly greater than the mean blank value ($P > 0.05$) were excluded from the calculation.

2.3. PDS saturation tests

A knowledge of the absorption capacity of the PDS used in the JTI method is important in determining exposure times, particularly of the L-type samplers situated in the dynamic chamber which may quickly become supersaturated at high emission rates. Two studies were conducted to determine the absorption capacity. In the first, performed at Research Centre Bygholm, 64 L-type filters (impregnated with oxalic acid) were prepared and exposed within a chamber which was ventilated with air containing 12 mg m^{-3} NH_3 . The NH_3 concentration in the chamber was monitored continuously (Bryl & Kjaer Multipoint sampler type 1303). Four replicate filters were removed for analysis every 15 min for 3 h, then every 30 min for a further 2 h. In the second study, performed at IGER North Wyke, eight C-type and eight L-type filters (impregnated with tartaric acid) were exposed in a closed chamber to which NH_3 gas was introduced. Six exposure experiments were made with NH_3 concentrations (as measured using absorption flasks containing orthophosphoric acid) between 0.8 and 6 mg m^{-3} NH_3 -N and exposure times of between 60 and 320 min.

2.4. Statistical analyses

Data from the three field experiments were pooled and the two methods for measuring NH_3 compared using mean square prediction error (MSPE) analysis (Theil, 1966; Dhanoa et al., 1999) together with the application of concordance correlation coefficient to measure reproducibility (Lin, 1989). This combination of analyses provides a more powerful means of comparing the two methods than simple linear regression analysis, yielding information on departures from equality in addition to correlation. In particular, MSPE quantifies the proportion of the variation accounted for by line bias (i.e. one method consistently giving higher results than the other), systematic bias (i.e. the slope of the regression line being other than unity) and unaccounted for error. Ordinary (Pearson) correlation provides a measure of the precision of a fitted regression line. Concordance correlation provides a measure of reproducibility, or the deviations from a fitted line with

slope of one and intercept of zero. A useful discussion on analysis of method comparison studies is given by Altman and Bland (1983).

3. Results

In the first of the absorption test studies, increase in concentration measured by the PDS filters was approximately linear to 50 mg N l^{-1} in 5 ml leachate (Fig. 1), i.e. $250 \text{ } \mu\text{g N}$ per filter. In the second study the combination of exposure times and NH_3 concentrations resulted in collection of 20–240 $\mu\text{g N}$ on the L-type filters, and the amount collected increased linearly with increase in product of concentration and time over that range.

Ammonia emission rates as measured by the two methods for Experiments 1–3 are given in Tables 1–3, respectively. Emission rates from applied urea reached a maximum rate 46–53 h after application as measured by the IHF technique (Table 1). For sampling periods 4 and 6 in the JTI method, the exposure times for the samplers within the chambers were too long, and this resulted in saturation of the L-type samplers (values in excess of 80 mg N l^{-1} in the 4 ml leached extract). Although results from the IHF method indicate that emission rate during sampling period 5 was actually greater than for sampling periods 4 and 6, the sampling period was of shorter duration (7 h as compared to 17 h) and there was no saturation of samplers. Cumulative emission for the measurement periods where data were available for both measurement methods (i.e. excluding sampling periods 4 and 6) was 15.13 and $15.42 \text{ kg N ha}^{-1}$ for IHF and JTI methods, respectively. Emission rates from slurry applied to grassland declined rapidly after the first sampling period (Table 2). In this experiment, the blank values for the PDS were rather high and variable, reducing the overall sensitivity of the method. Exposure times were insufficient to obtain a valid measurement for sampling periods 5 and 6. Cumulative emission over the first 4 sampling periods was 5.65 and $4.64 \text{ kg N ha}^{-1}$ for IHF and JTI methods, respectively. Emission rates from the solid manure (Table 3) were much lower, reflecting the much lower application of NH_4^+ -N to the plot and low temperatures during the experiment, and declined over the measurement period. Cumulative emission over the measurement period was 1.38 and $1.80 \text{ kg N ha}^{-1}$ for IHF and JTI methods, respectively.

MSPE analysis of the pooled data from the three experiments showed that there was good correlation between the two methods, the fitted regression line accounting for 87% of the variation. There was no significant difference between the fitted regression line and a line of equality (i.e. slope of one and intercept of zero) (Fig. 2a), with line bias accounting for <1% of the variation and systematic bias for 7%. Plotting the difference (IHF–JTI) in measured emission rate against

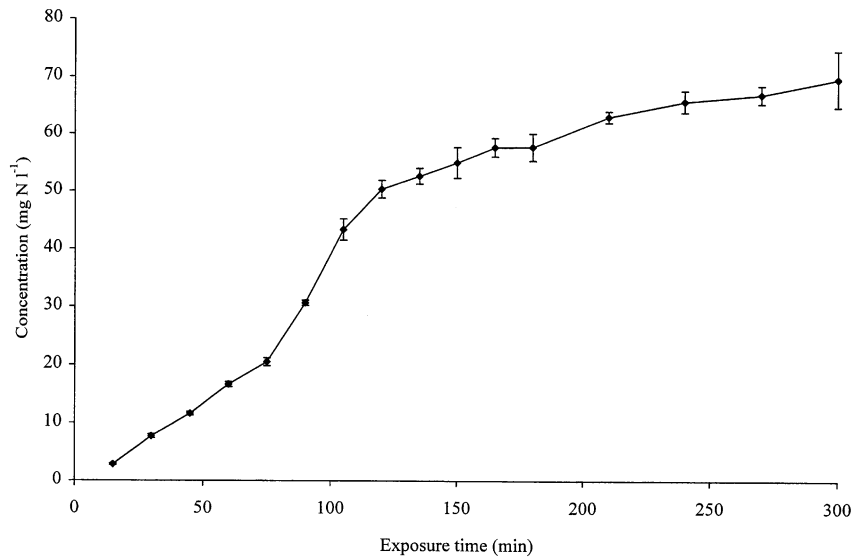


Fig. 1. PDS saturation curve. Concentration of $\text{NH}_4^+\text{-N}$ (mg l^{-1}) in 5 ml leachate from filters coated in 2% oxalic acid vs. time of exposure to air containing $12 \text{ mg m}^{-3} \text{ NH}_3$.

Table 1

Ammonia emission rates ($\text{g N ha}^{-1} \text{ h}^{-1}$) following urea application to grassland (Experiment 1) as measured by IHF and JTI methods

Sampling period	1	2	3	4	5	6	7	8	9
Hours after application	0–6.5	6.5–22	22–30	30–46	46–53	53–70	70–77	93–101	119–125
IHF	127	132	429	484	736	458	351	120	81
JTI	32	88	537	^a	898	^a	356	121	44
	(3) ^b	(13)	(189)		(203)		(100)	(39)	(49)

^a Saturation of PDS.

^b Standard errors in parenthesis.

Table 2

Ammonia emission rates ($\text{g N ha}^{-1} \text{ h}^{-1}$) following band application of cattle slurry to grassland (Experiment 2) as measured by IHF and JTI methods (results given for matching sampling periods only)

Sampling period	1	2	3	4	5	6
Hours after application	0–2	2–6	25–30	49–53	72–77	118–126
IHF	1242	487	25	37	24	14
JTI	905	679	3	14	^a	^a
	(393) ^b	(336)	(6)	(4)		

^a Below detection limit.

^b Standard errors in parenthesis.

the mean for each sampling period showed a mean difference of zero (Fig. 2b). It should be noted, however, that the data point to the top right corner of Figs. 2a and b exerts high leverage on the regression line and omitting this point would result in a significant

systematic bias (59% variance), with the JTI method giving higher values than IHF at high emission rates. A greater number of mid-to-high emissions data would have been desirable to increase the stability of the systematic bias.

Table 3

Ammonia emission rates ($\text{g N ha}^{-1} \text{h}^{-1}$) following band application of solid pig manure to arable soil (Experiment 3) as measured by IHF and JTI methods^a

Sampling period	1	2	3	4	5
Hours after application	0–1.5	1.5–5.5	5.5–28	28–72	72–144
IHF	60	29	14	10	6
JTI	98	17	15	27	1
	(76)	(8)	(8)	(8)	(1)

^aStandard errors in parenthesis.

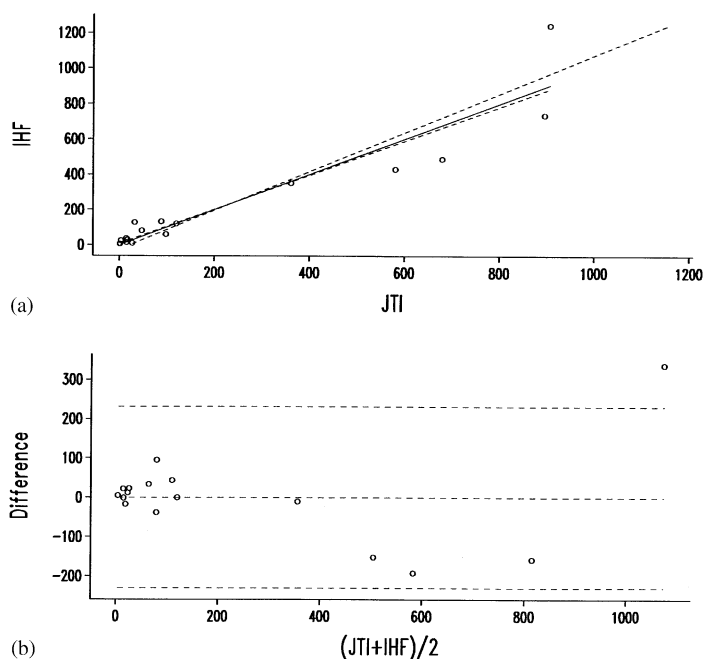


Fig. 2. IHF vs. JTI measured ammonia emission rates ($\text{g N ha}^{-1} \text{h}^{-1}$) for Experiments 1–3. (a) IHF and JTI values with reference to line of equality (solid line). Also shown are fitted lines (regression equations) for IHF on JTI and JTI on IHF (dashed lines). (b) Difference (IHF–JTI) vs. IHF and JTI average plot. The middle horizontal line indicates the mean of the distribution of differences and the other two lines enclose the 95% confidence interval.

4. Discussion

Typical emission rates were observed in the three experiments. Emission rates for applied animal manures are greatest immediately following application (e.g. Pain et al., 1989) but decline rapidly to much lower levels. For urea, a delay in reaching peak emission rate has been noted previously because of the time period necessary for urease activity to develop in response to the addition of urea (Black et al., 1985; Whitehead and Raistrick, 1990).

From the MSPE analysis, the two measurement methods are in agreement. However, there was a suggestion of a systematic bias in the regression if one

data point was omitted, and more data are required, particularly at higher emission rates, to be confident in the agreement between the two methods. Ferm et al. (1999) measured NH_3 emission by the JTI method and mass balance technique where masts supporting passive flux samplers were mounted around the periphery of the treated area (Schjoerring et al., 1992) following application of pig slurry to cereal crops. Emission measured using the chambers was only ca. 30% of that measured using the mass balance technique. The authors argued that this large difference was due to direct crop uptake of NH_3 within the JTI chambers being greater than that outside the chambers. They gave no indication of crop

height, but it may be that such an effect is more evident on a taller crop than for short grass swards, such as used in our comparisons. Further intercomparison/validation studies are required to confirm whether the JTI method is appropriate on taller crops. Ferm et al. (1999) also measured emissions following application of pig slurry to bare soil, but no results are given for the mass balance technique.

In the present study, between 4 and 6 chambers and 2–6 ambient samplers were used per plot for the JTI method. As the chambers only cover a small area of the plot, variability in emission rates between chambers can be high (hence high standard errors in Tables 1–3). Variability was less for Experiment 1 because urea fertiliser provided a more uniform NH_3 source than slurry or, particularly, solid manure, in Experiments 2 and 3. Generally, variation was less for C_a than C_{ch} , therefore a smaller number of ambient samplers than chambers are required. An example of the increased uncertainty introduced by using fewer chambers per plot is given in Fig. 3, using data from Experiment 1 (sampling period 8). Emission rates, together with 95% confidence intervals, were recalculated for each of the possible combinations of 5, 4, 3 and 2 chambers. Mean values for the upper and lower 95% confidence limits were derived, together with the maximum upper limit and minimum lower limit, for each set. The uncertainty in the mean emission rate increases more rapidly as chamber numbers become fewer. The ideal number of chambers per plot would depend on the inherent variation in the emission rate and the desired maximum allowable error level. Obviously there will always be a compromise between the number of replicate chambers used per plot and the number of replicate plots, but this high variability between chambers needs to be considered when designing experiments.

For a given chamber design and surface conditions, K_{ch} will have a constant value, being dependant on wind speed and surface roughness. Establishing the K_{ch} value for different surfaces would negate the requirement to expose L-type PDS in the chambers, thereby reducing the number of filters for preparation and analysis by at least 25%. Mean K_{ch} values for Experiments 1–3 were 0.0119 (short grass), 0.0093 (short grass) and 0.0124 m s^{-1} (bare soil), respectively. Svensson (1994) gives a value of 0.0160 m s^{-1} for smooth bare soil and Misselbrook (unpublished data) has measured mean values of 0.0104 m s^{-1} (range 0.0048 – 0.0148) and 0.0083 (range 0.0058 – 0.0093) m s^{-1} for manure coated concrete and short grass surfaces, respectively. The range in these reported values means that the use of a common mean K_{ch} for measurements on a particular surface may lead to inaccuracies. For example, using the mean value of 0.0083 m s^{-1} from previous measurements on short grass to calculate emission rates in Experiment 1 gave a cumulative total loss for the measured periods of $20.3 \text{ kg N ha}^{-1}$, compared with $16.5 \text{ kg N ha}^{-1}$ when the mean value for the experiment (0.0119 m s^{-1}) was used and $14.5 \text{ kg N ha}^{-1}$ when Svensson's value of 0.0160 m s^{-1} for bare soil was used. For accurate results, therefore, K_{ch} should always be measured. A compromise might be to measure K_{ch} for the first sampling period only, using the mean value for later sampling periods.

The sensitivity and accuracy of the JTI method are dependant on the preparation of PDS filters with consistently low blank values ($<0.5 \mu\text{g N}$ per filter). The minimum detection level for exposed filters will depend on both the mean and the variability in blank values. An important requirement of the method is the availability of an NH_3 -free laboratory or chamber for preparation and analysis of the PDS. Minimum emission rates which can be measured will depend on both

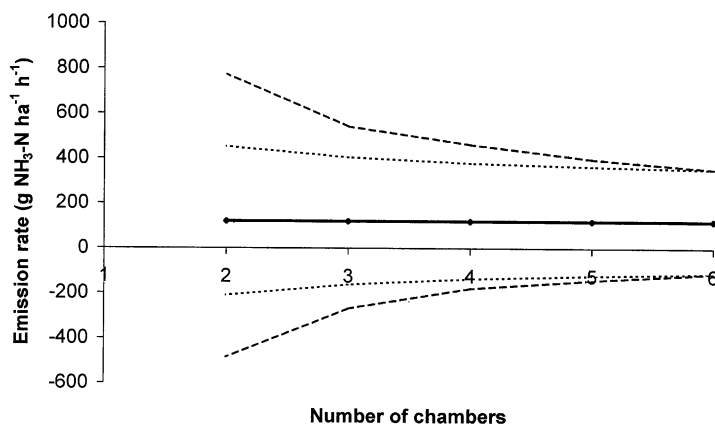


Fig. 3. The effect of reducing the number of chambers per plot on the uncertainty of the estimate of emission rate (data from Experiment 1 sampling period 8). Shown are mean emission rate, $\text{g N ha}^{-1} \text{ h}^{-1}$ (bold line), mean 95% confidence interval (dotted line) and maximum 95% confidence interval for combinations of fewer chambers per plot.

the minimum detection levels of the PDS filters and the duration of exposure. A combination of low blank value and long exposure time enabled an emission rate of $1 \text{ g N ha}^{-1} \text{ h}^{-1}$ to be measured in Experiment 3. Calculation of appropriate exposure times depends on the NH_3 concentration, but should be such that C-type ambient PDS reach detectable levels while L-type chamber PDS do not become saturated. Generally, for measurements following manure applications, exposure periods will be short (e.g. 1–2 h) immediately following application and longer (4, 8 or >24 h) on subsequent days. However, prediction of suitable exposure times for measurement of emission following fertiliser application is more difficult. Example curves for exposure time vs. NH_3 concentration are given by Svensson and Ferm (1993).

The equilibrium concentration technique for measuring emissions of NH_3 following fertiliser or manure applications to land is a practical, relatively inexpensive method which can be used on small plots and which, in this set of comparisons, gave results not significantly different from those measured by a standard mass balance technique. However, to ensure reliable results from the technique, care is required in the preparation of PDS, replication of chambers and ambient samplers is required and consideration needs to be given to the choice of exposure times.

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