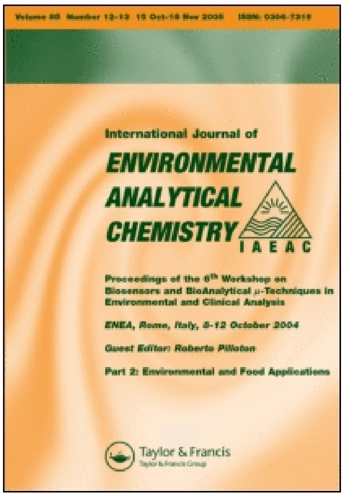

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A Comparison of Methods for use in the Measurement of Ammonia Emissions Following the Application of Livestock Wastes to Land

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A COMPARISON OF METHODS FOR USE IN THE MEASUREMENT OF AMMONIA EMISSIONS FOLLOWING THE APPLICATION OF LIVESTOCK WASTES TO LAND

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During a three week period, comparisons were made between different methods for measuring ammonia emissions following the spreading of cattle slurry on grassland. Micrometeorological and wind tunnel methods were compared, the former including a range of techniques for determining ammonia concentration in air. Agreement between the basic micrometeorological and wind tunnel methods was good, with a maximum difference of 25%. Technical problems with some of the novel techniques (Opsis method and Ferm tubes) limited the period during which a complete set of data was obtained. Nevertheless, the preliminary results reported in this paper indicate good agreement between these methods over a seven hour period and they deserve further investigation.

KEY WORDS: Ammonia emissions, land spreading, livestock wastes, cattle slurry, measurement techniques.

INTRODUCTION

Experiments carried out by van Breemen *et al.*[1] indicated that ammonia deposition is one of the factors influencing soil acidification. It was this finding that generated most of the present research focused on measuring ammonia emissions in Europe.

As far as the sources are concerned, calculations made by Erisman and Heij[2] clearly show that in 1989 62% of all aerial ammonia in The Netherlands originated from animal husbandry. Data presented by Heij *et al.*[3] point to land spreading of animal wastes as the major source within this sector. Since emissions during spreading represent less than 1% of the total emission observed[4], in The Netherlands great effort has been made over the past years to establish emission levels of ammonia emanating *after* land spreading animal wastes.

Although the situation in other European countries is not fully compatible with the Dutch case, the general conclusion remains the same. For this reason much of the emphasis has been on measuring ammonia emissions after land spreading of animal wastes[5,6,7,8,9]. In most cases, emissions have been measured using wind tunnel techniques[10] or micrometeorological methods[11]. The latter have the advantage of not influencing the volatilisation process. Furthermore they enable the use of larger areas of land than is the case with enclosure techniques. This permits the use of farm machinery in studies related to emission reduction on the farm scale (eg incorporation of slurry by ploughing or tillage).

Mass balance methods have been used by a number of previous authors[4,12,13]. The method involves the measurement of wind speed and NH_3-concentrations at the upwind boundary of the experimental area as well as in the centre of a circular plot. Ammonia concentrations in air are generally established by methods of active sampling. Since concentrations are measured at various heights and samples have to be changed at regular time intervals, the micrometeorological mass balance method requires a substantial amount of labour as well as specialized experimental equipment.

The alternative method, in which emissions are calculated from the measurement of wind speed and gas concentration at a single height[14], saves considerably on labour and equipment use. Labour requirements can be even further reduced by in-situ gas analyzing techniques instead of wet chemical sampling techniques.

Other alternatives are based upon passive sampling. Since passive sampling does not rely upon flow control, the equipment needed is relatively cheap. Methods using filterpacks or coated absorption tubes usually require no more than a few masts and sometimes additional wind speed measurement. Because some of the passive sampling methods are robust and straightforward, they may be suitable for use under harsh field conditions occurring after application of animal wastes to land.

Within the framework of a COST 681 workshop on odour and ammonia emissions from livestock farming organised by EC-DG XII in spring 1990 at Silsoe, recommendations were made on comparison of methods for measuring ammonia emissions following application of manure and slurries[15]. In pursuance of the recommendations a research program on the topic was carried out in the late summer of 1990. The experiments were conducted under the auspices of the Anglo-Dutch Agreement on Farm Wastes 1980 by British and Dutch institutes of agricultural research. The aim of the work was focused on evaluation of methods for use in practical studies on ammonia emissions following application of animal slurries to land.

METHODOLOGIES

In the present experiments, the performance of different methods for measuring ammonia emission following slurry application to land was investigated and the results compared. Some of the methods were included because of proven applicability in the current type of research, whilst others were selected for their potential to economize on labour or equipment needed. In summary, the following methods were used.

Micrometeorological Mass Balance Method

The theory underlying micrometeorological methods for measuring ammonia concentrations in the field is discussed by Denmead[11]. The mass balance method assumes the vertically integrated product of wind speed and ammonia concentration divided by the fetch to be equal to the ammonia flux F (mg NH_3-N·s^{-1}.m^{-2}) from the soil surface:

$$F = \frac{1}{x}\int_{Z_0}^{Z_p} \bar{u}\cdot\bar{c}\cdot dz$$

where $\bar{u}$ and $\bar{c}$ are the mean wind speed (m·s^{-1}) and ammonia concentration (NH_3-N·m^{-3} air) respectively over a particular sampling period and x is the fetch (m). The integration limit Z_p is the height (m) at which ammonia concentration is at normal background level, and Z_o is the height at which the wind speed falls to zero. A mass balance is determined from the difference in amount of ammonia driven by the wind across the upwind and downwind boundaries of the experimental area. This involves measurement of wind speed and ammonia concentration at various heights.

In conventional mass balance experiments, ammonia concentrations are measured by active sampling methods. Equipment needed comprises absorption flasks filled with acid, air pumps with flow control and sampling lines between flasks and pumps. Since control and recording of air flows through the absorption flasks is crucial to the final results of the experiment, reliable specialized sampling equipment is of utmost importance. This prerequisite is a dominant factor in the total capital investment involved. Sampling costs however, can be significantly reduced by application of passive sampling methods. Replacement of absorption flasks by diffusion badges, eg Willems badges[16], makes sophisticated sampling equipment redundant. As a result of the potential reduction in cost, Willems badges were used in the present experiments as an alternative to the absorption flasks.

Single height method

Experiments carried out by Wilson *et al.* indicated that, as long as certain conditions relating to size and uniformity of the area surrounding the experimental plot are met, the emission can be inferred from measurements at a single height[17]. The height, termed Z_{INST}, depends upon Z_0 as well as on the fetch.

The rate of emission can be calculated from:

$$F = \bar{s}\cdot\bar{c} \Big/ \left(\frac{\overline{sc}}{F}\right)$$

where F is the rate of ammonia emission per unit area of land (mg NH_3-N·s^{-1}·m^{-2}), $\bar{s}$ and $\bar{c}$ are mean wind speed (m·s^{-1}) and ammonia concentration (NH_3-N·m^{-3} air) respectively, measured at height Z_{INST}. The term $\left(\frac{\overline{sc}}{F}\right)$ is a dimensionless ratio, values of which are given by Wilson *et al.*[17]. It is known from experience by a number of experiments that the height of Z_{INST} is generally between 0.90 and 1.50 m.

In previous experiments, ammonia concentrations at height Z_{INST} were measured using active sampling techniques, changing samples at regular intervals[4,18]. Although sampling is performed at one height only, the labour demanded by the experimental setup remains considerable. Continuous monitoring of ammonia concentrations at height Z_{INST} may reduce labour demands significantly. However, in the case of traditional monitoring using NH_3/NO_x analyzers, considerable care has to be taken to prevent absorption of NH_3 in sampling lines.

Since Differential Optical Absorbion Spectroscopy (DOAS) does not require any special precautions to be taken, it may be a suitable technique for continuous measurement of ammonia concentrations at a single height. The DOAS technique as developed by Platt *et al.*[19] and Platt and Perner[20] is an in situ optical analyzing technique. Over a pathlength to several kilometers the absorption of specific atmospheric gases can be measured. In the case of ammonia, absorption lines are found[21] at 190–230 nm.

A DOAS technique for monitoring gas concentrations in ambient air has become commercially available from Opsis AB in Sweden. The technique used by Opsis differs from other, more conventional, optical methods in that it uses an high pressure xenon lamp as light source with broad band emission characteristics combined with high rate scanning of spectral bands of about 40 nm. Scanning is performed by an on-line computer system. The measured spectrum is fitted to calibration spectra stored in memory. These reference spectra have been measured earlier under laboratory conditions. Until recently ammonia concentrations in air could not measured by Opsis as a result of the light absorption in the optical fibre transporting the captured light from the receiver to the spectral analyzer. However, recent advances in optical fibre technology have cut down light absorption considerably thus enabling successful application of the Opsis-DOAS in measuring ammonia concentrations in ambient air. In order to compare the Opsis technique with traditional active sampling at height Z_{INST}, both methods were included in the present experiments.

Ferm method

Work carried out by Ferm has resulted in a novel concept for measuring ammonia emission following spreading of animal wastes[22,23]. The method defines four rectangular flux frames bordering a circular plot. Each frame represents a wind direction. Four sampling masts, one per frame, placed at the perimeter of the experimental area, are used for measuring ammonia emissions. Ammonia measurements are achieved by passive sampling using small tubes coated internally with oxalic acid. Samplers comprising a pair of glass tubes (10 × 1.5 mm, 100 mm long) with a small orifice at one end were attached to a sampling mast at different heights. The orifices on each pair were placed in opposing directions (Figure 1). Samples were changed at regular intervals. Since wind speeds inside the tubes are proportional to those outside the tubes, no measurement of wind speed in needed. The ammonia loss from the experimental area is calculated by simply subtracting the incoming flux from the outgoing flux. Sampling strategies and calculation methods are described by Ferm *et al.*[24]. Because of the low capital investments involved, the Ferm method was included in the present experiments.

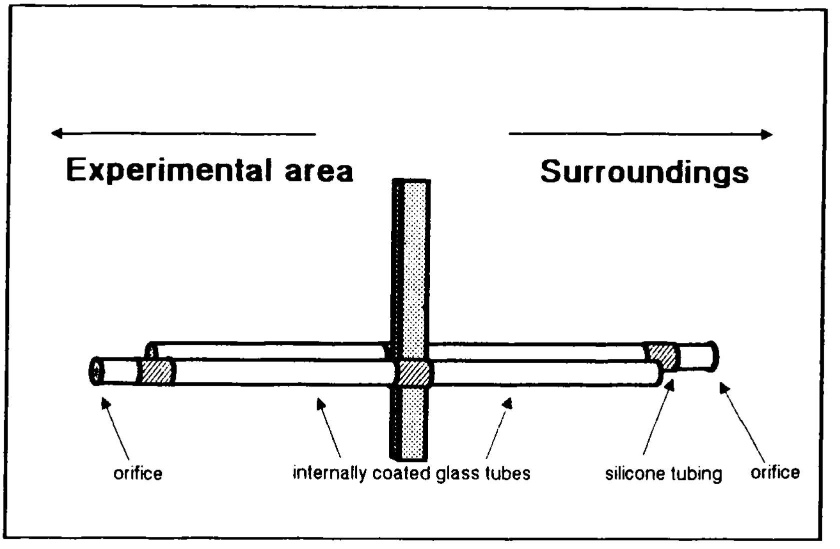

Figure 1 Ferm tube sampler

Wind tunnels

Enclosure, or wind tunnel, techniques are particularly useful for comparative studies on small plots, and allow some parameters, such as wind speed and rainfall, to be controlled. The system used in the present experiments was described in detail by Lockyer[10] and its use in determining ammonia emissions following application of slurries to land by Lockyer *et al.*[25].

Briefly, each tunnel comprised two parts. The first was a transparent canopy (2 m long, 0.5 m wide and 0.45 m high) designed to be pinned into position over an experimental plot measuring 2 m × 0.5 m. A second part comprised a circular cross-section metal housing containing a variable speed fan and an anemometer to control the wind speed through the canopy. The ammonia concentration in air entering and leaving the tunnel was measured using absorption flasks containing acid, in a similar way to that described for the micrometeorological experiments. These data, together with the volume of air passing through the tunnel, enable the ammonia emission from the area covered by the canopy to be calculated. Air pumps, flow meters, fan speed controllers and data loggers were housed in a box trailer. The ammonia emission from the experimental area is equal to:

$$F = (\overline{c_0} - \overline{c_i})\,\overline{u}$$

where $\overline{c_0}$ and $\overline{c_i}$ are the average concentration of outgoing and incoming ammonia respectively over a particular period and $\overline{u}$ the average wind speed in the tunnel over the same period.

EXPERIMENTAL

Site

The experiments were conducted at the experimental husbandry station at Zegveld in The Netherlands during three consecutive weeks in September 1990. Each experiment lasted approx. 96 hours. Three fields of 1–2 ha each were assigned to the experiments. The fields were flat and sown predominantly to perennial ryegrass (*Lolium perenne*). Prior to experimentation, the grass at the experimental area was mown to a height of approx. 3 cm. The soil at the experimental station is classified as peat with a high (-0.30 m) to intermediate (-0.70 m) ground water table. Further soil characteristics are; pH: 4.7–5.2, Organic matter: 36.1–53.1%, Silt: 26–30%.

Application of slurry for micrometeorological experiments

Slurry accumulated beneath the slatted floor of the farm building housing dairy cattle was used in all experiments. Analyses of representative samples are presented in Table 1 and application rates, for both these and the wind tunnel experiments in Table 2.

Slurry was applied to circular areas of diameter in the range 36–41 m, using a trajectory slurry spreader equipped with a traditional splash plate. Spreading was performed over pre-marked circles in parallel passes, the first pass being made along the centre line of the circle. The slurry outlet at the rear of the tanker was opened or closed as soon as the perimeter of the circle was reached. Figure 2 shows the layout of the experimental area.

Measurement procedures used in micrometeorological experiments

Immediately after completion of the first pass, a mast 3.50 m high with cross bars supporting absorption flasks filled with 20 ml HNO_3 (0.002 M) and Willems badges at heights of 0.25, 0.50, 0.75, 1.25, 2.0 and 3.0 m was erected. The inlets to the flasks and badges were located at the centre of the circle. A separate cross bar supporting three absorption flasks was attached to the central sampling mast for ammonia measurement at height Z_{INST}, which, under

Table 1 Slurry analyses.

		Experiment		
		1	*2*	*3*
NH_4^+-N	[mg·kg^{-1}]	2013	2503	2057
Total N	[mg·kg^{-1}]	3943	4650	4223
Total P	[mg·kg^{-1}]	560	880	590
Total K	[mg·kg^{-1}]	4260	4450	4640
Dry Matter	[g·kg^{-1}]	79.2	77.1	73.0
pH	[-]	8.5	7.5	7.3

Table 2 Application rates of cattle slurry to grassland.

		Micro meteo.	*Wind tunnels*
Experiment 1 (week 35,1990)			
slurry	[kg·ha^{-1}]	12,700	15,000
NH_4^+-N	[kg·ha^{-1}]	25.6	30.2
Experimental period	[h]	94	94
Experiment 2 (week 36, 1990)			
slurry [kg·ha^{-1}]		9,700	10,000
NH_4^+-N [kg·ha^{-1}]		24.3	25.0
Experimental period	[h]	93	97
Experiment 3 (week 37, 1990)			
slurry	[kg·ha^{-1}]	8,700	10,000
NH_4^+-N	[kg·ha^{-1}]	17.9	20.6
Experimental period	[h]	93	96

the crop and wind conditions prevailing was calculated to be 1.10 m. Background ammonia concentrations were measured at a mast positioned close to the upward boundary of the circle with absorption flasks and Willems badges at three heights.

Air was drawn through the absorption flasks using small rotary vane pumps (Brey G12/045, Memmingen, D) with flow rates set at 2.5 l·min^{-1}. The actual flows were measured at regular intervals using a 0.5–5.0 l·min^{-1} air flow meter (Platon, Basingstoke, UK). Absorption flasks and badges were changed after pre-determined periods, normally 1, 3, 6,

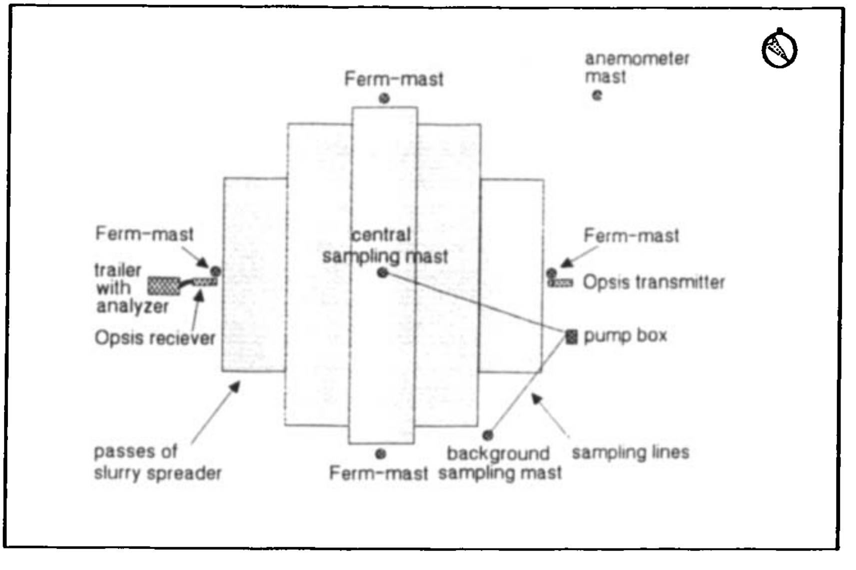

Figure 2 Layout of experimental plot for measuring ammonia emissions following application of animal slurry

12, 24, 36, and 48 hours after slurry application and were finally removed at 96 hours, to determine the cumulative losses and rates of loss of ammonia. In all three experiments slurry was applied during the morning hours.

Immediately after completion of spreading of slurry, four masts were erected supporting pairs of Ferm tube samplers at heights of 0.25, 0.40, 0.80, 1.30, 2.30 and 4.00 m. Positioning of masts at the boundary of the experimental area was at 90° intervals. Tubes pre-coated with oxalic acid were changed at regular intervals.

Approximately 18 hours prior to slurry application, the Opsis equipment was put into operation. Both transmitter and receiver were mounted on light, cubical structures made of mild steel tubing, 25 × 3 mm. The structures were fixed at the perimeter of the experimental area by using four retractable bars which were forced into the soil for at least 0.50 m. Positioning was across the centre line of the circle. After adjustment to 1.10 m height followed by careful alignment, the receiver was connected to the opto-analyzing unit by means of an appropriate optical fibre. After starting the measurement, the system was operated during the entire experimental period without manually changing the alignment. Storage of data recorded as well as optimization of alignment via servo-control on the receiver was carried out by a dedicated personal computer with hard disc facilities.

Meteorological data and wind speeds were measured using a separate mast placed in the vicinity of the experimental area. The digital output from each of the six anemometers (Vector A101M) as well as the analogue output from a wind direction meter (Vector W200P, Vector Instruments Ltd, Rhyl, UK) were recorded on a battery-operated portable data logger fitted with data cards (Meuleman Automation, Wageningen, NL). Further meteorological data recorded included air temperature and relative humidity which were measured by a combined °C/RH sensor (Rotronic MP-100 Meteor., Rotronic AG, Zürich, CH). Rainfall was measured by a tipping bucket system (Casella W5720) and global solar radiation by a solarimeter (Casella W6500, Casella London Ltd., Bedford, UK). All meteorological data recorded were temporarily stored on data cards (Star Card 128 Kb, ITT-Canon) which at the end of the experimental period were transferred to a personal computer (Atari Mega ST2). Final data processing and calculation of results were performed using a Lotus compatible spreadsheet (LDW Power).

A mobile electricity generator (Petter-Lister 8 kVA) was used for power supply to pumps, meteorological datalogger and Opsis.

Ammonia concentrations from the absorption flasks and tubes were determined through ion chromatography following procedure #C-202 of the Waters Ion Chromatography Cookbook[26]. The analyses were performed at the environmental laboratory of IMAG-DLO. Ammonia concentrations from the Willems badges were obtained using spectrophotometry according to Dutch Standard NEN 6472[27]. Analyses were performed by the Department of Air Pollution of the Agricultural University at Wageningen.

Procedures used in wind tunnel experiments

The wind tunnel experiments were conducted on grassland adjacent to that used for the micrometeorological experiments. Cattle slurry was spread on the surface of pre-marked plots with a watering can, and the tunnel canopy immediately pinned into position over the treated area. There were two treatments, each replicated with two tunnels. For the first treatment, the canopy was left in the same position for the duration of the experiment. For the second treatment, slurry was applied to larger areas and the canopy moved to a previously uncovered area every 24 hours, to examine the influence of rainfall. Wind speed was controlled at 1 $m \cdot s^{-1}$ in all tunnels.

RESULTS AND DISCUSSION

Comparison between ammonia emissions over the entire experimental period from micrometeorological and wind tunnel experiments

Although technical problems and priorities prevented continuous operation of all the methods throughout the experimental campaign, some micrometeorological and wind tunnel experiments were conducted simultaneously over 96 hour periods. The results from these comparisons are summarized in Table 3.

During the first experimental period, both wind tunnel methods and most of the micrometeorological methods performed as expected. In the second period, Willems badges were omitted for reasons of priorities in the research programmes. During the third experimental period, the flasks at Z_{INST}, did not perform well. Approximately 10 hours after starting the experiment, the flow control of the air samplers ceased to function. As a result of this, measurements obtained at height Z_{INST} in the third experimental period are not taken into account for comparison over the experimental period.

In general, results from the wind tunnel experiments were of the same order as those from micrometeorological experiments. Differences in the results from the mass balance and wind tunnel measurements are most likely explained by variations in weather conditions over the three week period. Rainfall and especially wind speed are important factors. There is evidence that rates of emission increase with increasing wind speed[28,29]. Close agreement between micrometeorological mass balance and wind tunnel methods was obtained by Ryden and Lockyer[30]. In studies on ammonia volatilisation from urea fertiliser, they demonstrated the importance of matching the wind speed through the tunnel to the wind speed recorded of ambient air. In the current experiments however, this was not achieved. The difference in wind speed between the wind tunnels and ambient air may account for the higher emission from wind tunnels at fixed position. During the first hours of the experimental period in which most of the ammonia volatilisation takes place, the average wind speed in the tunnel was 20% higher than in ambient air.

In earlier experiments, no difference was established between the results of calculations based on measurements from a single height (Z_{INST}) above the experimental area and those based on full profile measurements[4]. In the present experiments, results of Z_{INST} measurement obtained in the second period tend to underestimate total emission. The difference however, is within the ranges reported.

The differences between the results from the two methods of operating the wind tunnel system were not consistent. It is not surprising that moving the tunnel every twenty-four

Table 3 Comparison of micrometeorological and wind tunnel methods for determining loss of ammonia after spreading cattle slurry on grassland.

	Ammonia (NH_3-N) loss over experimental period								
Experiment No.	*1*			*2*			*3*		
Method	*$kg \cdot m^{-3}$ slurry*	*%NH_4^+-N*	*$kg \cdot ha^{-1} \cdot 24\ h^{-1}$*	*$kg \cdot m^{-3}$ slurry*	*%NH_4^+-N*	*$kg \cdot ha^{-1} \cdot 24\ h^{-1}$*	*$kg \cdot m^{-3}$ slurry*	*%NH_4^+-N*	*$kg \cdot ha^{-1} \cdot 24\ h^{-1}$*
Micro meteo.									
Mass balance	1.05	52.2	3.40	1.39	55.6	3.48	1.13	54.8	2.54
ZINST (flasks)	1.09	54.1	3.53	1.18	46.6	2.73	[1])	[1])	[1])
Badges	1.05	52.0	3.40	[1])	[1])	[1])	0.88	42.9	1.98
Wind tunnel									
Fixed position	1.11	55.1	4.25	0.83	33.2	2.05	1.06	51.4	2.65
Moved every 24 h	0.98	48.7	3.75	1.15	47.3	2.85	1.30	63.1	3.25

[1]) no data available.

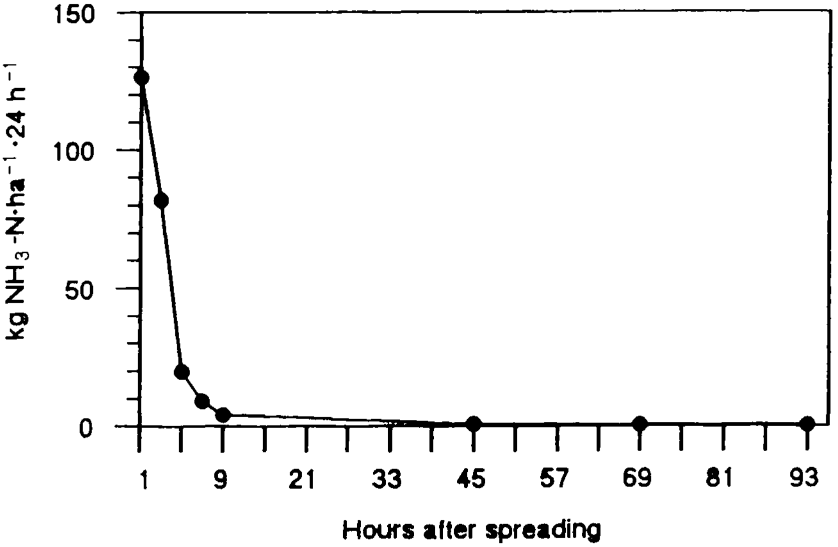

Figure 3 Decay of ammonia flux according to the mass balance method as observed in experiment 3

hours had little effect since the major part of the total emission normally occurs during the first 24 hours after spreading the slurry.

With reference to the fluxes [kg NH_3-N·ha^{-1}·24 h^{-1}] reported in Table 3, the following should be taken into account. The data presented in this table refer to emissions observed over the entire experimental period. Therefore the fluxes reported denote average values. However, the decay of ammonia fluxes observed after land spreading of animal wastes is known to be fast[4,12,31]. Approx. 80% of the total emission occurs within 24 hours. An example which based upon data from the present experiment is given in Figure 3. For this reason the fluxes reported in Table 3 should be considered as approximate only.

Measurements over a period of up to 20 hours

At the start of the first experimental period, the Opsis equipment was configured as a transmitter-receiver on one side of the experimental area with a retro-reflector on the opposite boundary. As a result of substantial absorption of light caused by four passes through quartz glass protecting the parabolic mirrors, no valuable data were obtained during this period. In the second experimental period the retro-reflector was replaced by a transmitter while the combined transmitter-receiver unit was operated as receiver only. As a result of these changes, light absorption was halved thus curing the problem. At the start of the third experimental period the Opsis equipment functioned as expected producing data every 3 to 5 minutes. Unfortunately, the cubical structures supporting the Opsis equipment were not secured rigidly enough to the ground. The Opsis therefore drifted out of focus after approximately 7 hours of operation. Since it was impossible to restore proper functioning of the apparatus within the time left before terminating the experiment, the Opsis measure-

Table 4 Ammonia emissions following application of slurry measured by different methods.

Cumulative ammonia loss (kg NH_3-N·ha^{-1})					
Time after	*Methods*				
spreading	*Mass Balance*		*Single height*		*Ferm tubes*
[h:min]	*flasks*	*badges*	*flasks*	*Opsis*	
0:25′	2.63	2.12	1.75	2.07	
1:00′	6.04	4.96	4.30	5.45	7.17
2:24′	7.24	6.14	5.98	7.17	
4:48′	8.36	6.76	7.09	8.59	10.44
7:29′	8.82	6.96	7.52	9.21	
14:40′	8.93	6.86			9.82

ments were then abandoned. However, over 500 readings were obtained during a period in which most of the ammonia volatilisation occurred. Therefore the Opsis data are considered to be useful and taken into account.

As far as the Ferm method is concerned, properly-coated tubes were not available until the start of the third experimental period. This was due to problems encountered with the equipment for coating of tubes. Unfortunately heavy dew and foggy weather conditions occurring throughout the experimental period in early evening hours and during the night, adversely affecting the coating on the tubes. For this reason reliable measurements were only produced during a period of approximately 20 hours starting from spreading of slurry. As is the case with Opsis, data obtained during this period are still considered to be valuable.

Since most of the methods involved were operating properly for a certain period of time, data obtained during this period are evaluated in this paper. The results obtained are presented in Table 4.

Taking the ammonia losses as measured by the micrometeorological mass balance method combined with absorption flasks as a standard, the following can be concluded. Although the methods used differ in many respects, the results obtained are of a similar order. The difference observed in ammonia losses measured by Ferm tubes as compared to the standard method is in agreement with similar experiments performed by Ferm *et al.*[24]. The drop in cumulative ammonia loss during the last sampling period with Ferm tubes is explained by the adverse effect of fog and dew.

CONCLUSIONS

The total ammonia emission during 96 hours after application of cattle slurry to grassland ranged from 0.70 to 1.51 kg NH_3-N.m^{-3} slurry applied representing 52.2 to 55.6% of the NH_4^+-N applied. These values are of the same order as reported elsewhere[4,25]. Although the results from different methods were of similar order, there were wide variations, for a number of different reasons. Much closer agreement between micrometeorological methods was obtained over a shorter time.

Closer agreement between results from micrometeorological and wind tunnel methods is likely to depend on carefully matching wind speeds, but this is technically difficult to achieve.

Some methods proved easier and less costly than others. The ease of use of Willems badges in the field makes this an attractive method but the subsequent analytical work in the laboratory is more complex than for other methods. Similarly, measurement at a single height using absorption flasks offers significant savings in equipment and manpower required. The same applies to Opsis equipment which has the added benefit of providing instantaneous measurements of ammonia concentration. However, the cost is high and the technical problems relating to alignment are still to be resolved.

Although not fully successful in the present experiments, the sampling strategies developed by Ferm offer many advantages over other methods and are worthy of further investigation.

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References

1. N. van Breemen, P.A. Burrough, E.J. Velthorst, H.F. van Dobben, T. de Wit, T.B. de Ridder and H.F.R. Reijinders, *Nature*, **229**, 548–550 (1982).
2. J.W. Erisman and G.J. Heij, in: *Acidification Research in The Netherlands* (G.J. Heij and T. Schneider eds. Elsevier Science Publishers, Amsterdam, NL, 1991) pp. 51–96.
3. G.J. Heij, J.W. Erisman and J.H. Voorburg, in: *Acidification Research in The Netherlands* (G.J. Heij and T. Schneider eds. Elsevier Science Publishers, Amsterdam, NL, 1991) pp. 37–50.
4. B.F. Pain and J.V. Klarenbeek, *Research Report* 88–2 (IMAG-DLO, Wageningen, NL, 1988), 36pp.
5. V.R. Phillips, B.F. Pain and J.V. Klarenbeek, in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 198–106.
6. K. Vlassak, H. Bomans and R. van den Abbeel in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 116–125.
7. A. Amberger in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 126–131.
8. H. Döhler in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 132–140).

9. S.G. Sommer and B.T. Christensen in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 141–147.
10. D.R. Lockyer, *J. Sci. Food Agric.*, **35**, 837–848 (1984).
11. O.T. Denmead, in: *Gaseous Loss of Nitrogen from Plant-Soil Systems* (J.R. Freney and J.R. Simpson eds. Martinus Nijhoff, The Hague, NL, 1982).
12. J.V. Klarenbeek and M.A. Bruins, in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 107–155.
13. B.F. Pain, V.R. Phillips, J.F.M. Huijsmans and J.V. Klarenbeek, *Report 91–9* (IMAG-DLO, Wageningen, NL, 1991, ISBN 90–5406–002–6) 28pp.
14. J.D. Wilson, V.R. Catchpoole, O.T. Denmead and G.W. Thurtell, *Agric. Meteorol.*, **29**, 183–189 (1983).
15. V.C. Nielsen and B.F. Pain, in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 214–217.
16. J.J.H. Willems and P. Hofschreuder, in: *Field Intercomparison Exercise on Ammonia and Ammonia Measurement* (I. Allegrini, A. Febo and C. Perrino eds. Air Pollution Research Report No 37, CEC Brussels, B, 1992) in press.
17. J.D. Wilson, G.W. Thurtell, G.E. Kidd and E.G. Beauchamp, *Atmospheric Environment*, **16**, 1861–1867 (1982).
18. B.F. Pain, V.R. Phillips, C.R. Clarkson and J.V. Klarenbeek, *J. Sci. Food Agric.*, **47**, 1–12 (1989).
19. U. Platt, D. Perner and H.W. Plätz, *J. Geoph. Res.*, **84**, 6329–6335 (1979).
20. U. Platt and D. Perner, *J. Geoph. Res.*, **85**, 7453–7458 (1983).
21. H. Erdner, R. Amer, P. Ragnarson, M. Rudin and S. Svanberg. Paper presented at the international congress on optical science and engineering, The Hague, NL. (1990).
22. M. Ferm, *Ph.D-thesis* (Department of Inorganic Chemistry, Chalmers Tekniska Högskola, Götenborg, S. ISBN 91–7900–006–1, 1986).
23. M. Ferm and B.T. Christensen, in: *Ammonia and acidification* (W.A.H. Asman and S.M.A. van Diederen, eds. National Institute of Public Health and Environmental Hygiene, Bilthoven, NL. 1987) pp. 28–41.
24. M. Ferm, J.K. Schørring, S.G. Sommer and S.B. Nielsen, in: *Odour and Ammonia Emissions from Livestock Farming* (V.C. Nielsen, J.H. Voorburg and P. l'Hermite eds. Elsevier Applied Science, Barking, Essex, UK, 1991) pp. 148–155.
25. D.R. Lockyer, B.F. Pain and J.V. Klarenbeek, *Environ. Poll.*, **56**, 19–30 (1989).
26. *Waters Ion Chromatography Cookbook*, Millipore Corp., Waters Chromatography Div., Ion Chromatography Group, Milford, Massachusetts, USA. 1989.
27. *NEN 6472*, National Institute for Standards, Delft, NL. 1983.
28. R.B. Thompson, B.F. Pain and Y.J. Rees, *Plant and Soil*, **125**, 119–128 (1990).
29. J. van der Molen, D.W. Bussink, N. Vertregt, H.G. van Faassen and D.J. den Boer, in: *Nitrogen in organic wastes applied to soils* (J.A. Hansen and K. Henriksen eds. Academic Press, London, 1989) pp. 185–201.
30. J.C. Ryden and D.R. Lockyer, *J. Sci. Food Agric.*, **36**, 781–788 (1985).
31. V.R. Phillips, B.F. Pain, C.R. Clarkson and J.V. Klarenbeek, *Farm Buildings and Engineering*, **7**, 2, pp. 17–23 (1990).