FIELD ESTIMATES OF AMMONIA VOLATILIZATION FROM SWINE MANURE BY A SIMPLE MICROMETEOROLOGICAL TECHNIQUE

by

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Master of Science

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ABSTRACT:

Recalculation of an existing numerical model for particle diffusion into air from ground-based sources for circular source plots of 7 m diameter show that a satisfactory relationship between horizontal flux of the diffusing gas at a single measuring height above the center of the plot and flux density from the plot can be defined. This provides a simple technique for comparing volatilization rates of NH_3 from treated and untreated manure in the field, under outdoor conditions.

The technique has been applied to the study of effects on swine manure (sus scrofa domesticus) by addition of monocalcium phosphate (MCP) prior to spreading. Mean NH_3 flux densities during peak volatilization periods of the first three days after spreading were lower for MCP-treated plots by an average of 17%, with a maximum reduction of 30%. Variability of results from short-term sampling intervals (1 to 2 h) was high. This makes short-term detection of differences of < 20% difficult by analysis of variance under the adopted experimental procedures. Observations for volatilization from source plots of equal source strength, source plots with different degrees of dilution of applied manure, wetted manure plots as well as separated manure permit a further definition of the sensitivity of the technique. Suggestions are given about possible reductions

in variability from improved experimental procedure.

Résumé

Recalculation d'un modèle numérique de diffusion de gaz vers l'atmosphère à partir de sources terrestres pour des parcelles sources circulaires d'un diamètre de 7 m donne une relation quantitative entre le flux horizontal du gaz à un seul niveau au-dessus du centre de la parcelle source et le débit de gaz venant de la parcelle. Ceci a permis la mise-au-point d'une technique simple pour la comparaison directe de la volatilisation au champ de l'ammoniac à partir du lisier épandu, traité ou non, sous des conditions naturelles.

Cette technique a été appliquée à l'étude de l'effet du traitement du lisier de porc (sus scrofa domesticus) avec du phosphate monocalcique. Les débits d'ammoniac à partir du lisier traité, durant la période de haute volatilisation des trois premiers jours après l'épandage, étaient en moyenne de 17% inférieurs à ceux du lisier non-traité, avec une réduction maximum de 30%. La variabilité dans les observations lors d'échantillonnages à fréquence courte (1 à 2 h) s'avère très élevée, rendant difficile la détection de différences inférieures à 20%. Des observations supplémentaires sont présentées pour démontrer davantage la variabilité des résultats (pour la volatilisation à partir de parcelles sources identiques) et la sensibilité de la technique pour la détection de différences significatives

(pour le lisier dilué à différents degrés). On suggère des moyens pour réduire la variabilité par l'amélioration du protocole expérimental.

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1. INTRODUCTION

Animal manure was at one time the main source of nutrients for crop production. The philosophy of livestock waste management was based on the concept of applying the manure to the land so that the nutrients could be recycled through the plants. Amounts applied usually did not exceed those favourable for crop production, with minimum risk of pollution. But as the cost of labor increased and farm size expanded, manure began to be looked upon more as an agricultural waste than a nutrient resource. Recently, however, the cost of commercial fertilizers has significantly increased to the point where manure is being regarded as an economically feasible alternative source of nitrogen.

Enough total nitrogen (N) from manure is produced annually in the province of Quebec to meet a large percentage of crop requirements, although a significant portion of this N is usually lost before it is utilized by the plants in the field.

Approximately one-half of the N in manure is found in the liquid portion in the form of ammonium (NH_4^+). Although soluble and therefore readily available for crop use, it is quite susceptible to loss through volatilization as ammonia (NH_3), particularly during the first few days after field application (Adriano et al., 1974; Lauer et al., 1976; Hoff et al., 1981; and Beauchamp et al.,1982).

It has become the responsibility of the agrometeorologist, soil scientist, crop specialist and agricultural engineer to develop successful management strategies which can be easily adapted to conventional manuring techniques on the farm in order to minimize nutrient losses.

Apart from the nutrient losses, studies have shown that high atmospheric NH_3 concentrations cause the formation of complex sulfates of NH_3 which are components of smog and acid rain (Dawson, 1977). Another problem associated with high concentrations of NH_3 in the atmosphere is that it contributes to the N enrichment of nearby surface water (Hutchinson and Viets, 1969).

The potential for NH_3 volatilization has been studied since the early part of the last century (Sprengel, 1839; Boussingault, 1844). Salter and Schollenberger (1938) indicated that up to 50% of the total N in manure at the time of spreading could be lost through volatilization. Subsequent investigations in the laboratory and on partially-closed atmospheric chambers over field microplots have demonstrated volatilization losses from manure ranging typically from 20 to 80% of the NH_3-N during the first 3 to 5 days after application (e.g. Stewart, 1970; Mathers and Stewart, 1970; Adriano et al., 1971; Hoff et al., 1981). It must be emphasized, however, that these experiments are not truly representative of field situations since their flow structure, which in turn controls the rate of transport, is substantially different from that of the natural environment.

It is only recently that micrometeorological techniques have become available to measure surface volatilization of gases out-of-doors, without interference in the dynamics of the airflow. With the help of these techniques a greater interest has been placed on the investigation of factors governing the rate of NH_3 volatilization.

The study reported here explores the use of a simple micrometeorological technique originally developed by Beauchamp et al. (1978) in such a way as to make it better suited to replicated studies of effects of physical, biological or chemical treatments of manure on NH_3 volatilization out-of-doors. It then applies this technique to the investigation of:

i) the sensitivity of replicated studies under identical soil-crop-climatic-manure conditions,

ii) the differences in volatilization losses between manure chemically treated with mono-calcium phosphate (MCP) and untreated manure,

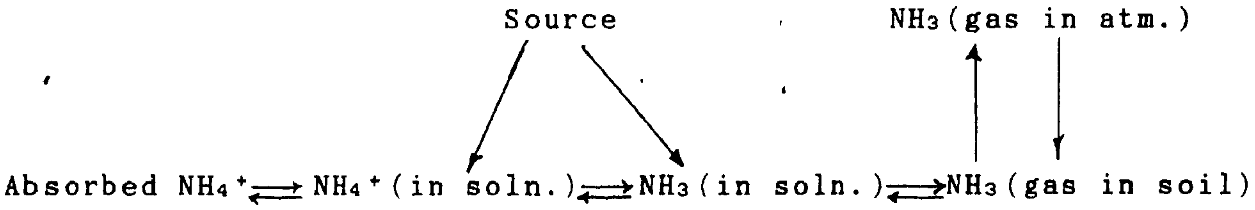
iii) the differences in volatilization losses from various concentrations of surface applied manure,

iv) the differences in volatilization losses from liquid manure (separated) and solid manure (unseparated) and

v) the effect of rainfall on NH_3 volatilization.

2. LITERATURE REVIEW

Ammoniacal nitrogen generally comprises one-half to two-thirds of the total N in livestock manure (Bouldin and Klausner, 1981). Immediately following excretion, conversion of ammoniacal-N to NH_3 begins. Since NH_3 is a gas at atmospheric temperatures and pressures, rapid loss through volatilization from surface applied manure would be expected. The volatilization phenomenon, however, is somewhat slowed down by the fact that compounds of varying degrees of stability are produced in the aqueous and solid forms of manure. Studies reported by Simpson (1981) and Vlek et al. (1981) explained the various reactions which govern NH_3 volatilization losses as shown below:



Adriano et al. (1974) examined the effect of soil moisture and temperature on N losses from manure under greenhouse conditions from measurement of N concentrations in the soil. At 10°C and a moisture content of 60%, the total loss represented 26% of applied N over a 16 week period. At a temperature of 25°C and a 90% moisture content the loss was estimated as being 45% of applied N. Even though NH_3-N measurements were not taken, the authors hypothesized that the loss of N occured mainly through the volatilization of NH_3.

A number of relevant studies invoved NH_3 losses from sewage sludge in a laboratory or greenhouse setting. King and Morris (1974) observed that 36% of the ammoniacal-N was lost from bare soil plots and 24% from grass stubble plots. They concluded that the lower losses from the grass stubble plots were due to the fact that air movement over and through the grass was lower due to the additional boundary-layer resistance introduced by the grass. In a similar study, Ryan and Keeney (1975) found losses between 11 and 60% of the ammoniacal-N applied in the sewage sludge. Losses depended mainly on soil type, decreasing as the clay content of the soil increased from 5 to 30%. Donovan and Logan (1983) concluded that the NH_3 loss increased as the soil temperature and pH increased. They found that a vegetative cover increased the NH_3 loss from sludge with large particles but had no effect on well homogenized sludge. Recently, Adamsen and Sabey (1987) noted that surface applied sludge lost 40% of the ammoniacal-N in the two weeks proceeding application while only 0.4% was lost from sludge placed 25 mm below the surface over the same period of time.

Hoff et al. (1981) used a partially closed system to measure the NH_3-N volatilized from microplots of liquid swine manure in a greenhouse and field experiment. They found that NH_3-N losses varied quite considerably with temperature, soil and manure pH and wind speed. Nearly 65% of the NH_3-N applied to the greenhouse plots was lost in 3.5 days, while only 14% of the NH_3-N was volatilized from the field plots. The difference in the measurements was attributed to a higher pH of the soil (7.0 to 6.5) and manure (7.8 to 6.4) in the greenhouse as compared to the field. Their volatilization sampling procedure was similar to that described by Kissel et al. (1977) which consisted of a volatilization chamber through which air was drawn to acid traps that retained the NH_3 lost from the chamber. Liss (1975) and Lemon (1978) had already pointed out such field measurements to be unrealistic due to the fact that this type of system interfered with turbulent eddies that are essential for volatilization estimates; also, the method was subject to variability due to the non-homogeneous soil conditions which were found by Robston (1978) to produce a variability of ±55%.

Lauer et al. (1976) tried to circumvent this difficulty by determining volatilization losses in the field indirectly from NH_3-content measurements of manure samples and the underlying soil collected at intervals after spreading. Corrections were made for increases in the NH_3-N content of the soil. In experiments of 5 to 25 days duration, total estimated losses of NH_3 represented 61 to 99% of the total initial NH_3-N content, most of which was lost in the first week. Quantities of N volatilized as NH_3 ranged from 17 to 316 kg(N) ha^{-1}, depending on application rate and total NH_3-N content of the manure. They hypothesized NH_3 loss was affected by factors such as the relative partial pressure of the NH_3 in the manure and the ambient atmosphere, the wetting and drying of the manure, the air temperature and the diffusion rates of NH_3 (and NH_4^+). Three general stages of NH_3 volatilization were observed, beginning immediately after application to the land. Initially, the NH_3 concentration was assumed to increase due to a slight increase in the NH_3 partial pressure gradient. As NH_3 was lost, the composition of the manure changed so that a lower pH occured, lowering the partial pressure of NH_3 to that of the ambient atmosphere. They found highest volatilization losses during periods of continuous drying. In the winter their measurements found losses to be quite low due to snow cover, low temperatures and freeze/thaw cycles which in turn increased leaching losses.

Beauchamp et al. (1978) developed a non-interfering diffusion model to predict surface flux of NH_3 from observed windspeed and NH_3 concentration at several levels above the surface. A correction for atmospheric stability was subsequently incorporated into the model by Wilson et al.

(1981 and 1982). The resulting <u>trajectory simulation model (TSM)</u> relates surface flux to horizontal flux profiles in a vertical plane above the surface. It simulates emission of fluid elements (or particles) from the source (i.e. sewage sludge in this particular study) by tracking individual trajectories. The trajectory dynamics are determined by an exponentially-decaying memory term, with a time-constant equal to the Lagrangian time scale, and a random input term for momentum change during a given time step. A simple application of the model consists of predicting the horizontal flux profile above the center of a circular plot. Only plot diameter, surface roughness (micrometeorologically defined roughness length) and a general idea of atmospheric stability must be specified. The advantage of the technique lies in the fact that it summarizes a realistic level of understanding of turbulence statistics (in the form of the Lagrangian time scale and velocity scales), and the dependence of effective turbulent diffusivity on distance from the source, into a statistically predictive model which needs very few input measurements.

The numerical simulations of the TSM showed that horizontal flux profiles over the center of a circular plot, for different cases of atmospheric stability, tend to intersect at a height (ZINST) (Wilson et al., 1983). This permits source strength estimates with very simple instrument requirements, based on mean wind and concentration measurements at this single height, regardless of wind direction and atmospheric stability. ZINST is a weak function of surface roughness, assumed to be homogeneous throughout the test area. By comparison, Eulerian diffusion models require input data at various points in space to define the vertical and horizontal flux components of the mass balance. It may have to be pointed out that the TSM defines the horizontal mass flux at ZINST as a measure of source strength but does not equate the two; the latter corresponds to the vertically-integrated horizontal flux profile.

In their study, Beauchamp et al. (1978) estimated NH_3 losses from anaerobically digested sewage sludge applied in the field. At an application rate of 150 kg ha^{-1}, with 40% of the total-N occuring as NH_3-N they found that 60% of the total-N was lost in 5 days. In subsequent experiments 56% of the total-N was volatilized over a 7 day period. They attributed the difference to lower ambient air temperatures which they found to be directly related to the NH_3 volatilization. As well as stating that air temperature had a significant effect on the NH_3 volatilization they also observed that the volatilization flux densities followed a diurnal pattern, consistent with the observations of McGarity and Rajaratnam (1973), Denmead et al. (1974) and Hoff et al. (1981). They noticed that the largest loss occured at midday and that this diurnal pattern was most significant on the first two days after application. They also found that rainfall slightly depressed the NH_3 lossses but found no evidence of a relationship between NH_3 loss and the atmospheric water vapour deficit.

Beauchamp et al. (1982) used the TSM to determine the NH_3 volatilization from liquid dairy cattle manure applied to a field for 6-7 day periods during four successive yearly studies in the month of May. Estimated losses ranged between 24 and 33% of the NH_3-N in the manure through volatilization in 6 or 7 days after application. They also observed a strong diurnal pattern in the magnitude of the fluxes throughout the day similar to their 1978 findings. Rainfall again tended to decrease NH_3 losses but they found that temperature appeared to play a larger role in the volatilization phenomenon. Their results show lower volatilization losses than those observed by Lauer et al. (1976) but it should be kept in mind that a different experimental method was employed.

Brunke et al. (1988) used the TSM to correlate NH_3 losses from swine and dairy manure with measured meteorological parameters. They found strong correlations on the first day (i.e. the day the manure is applied) with net radiation and windspeed. They concluded that NH_3 volatilization to a large degree depends on the drying of manure as well as the concentration applied. Swine manure exhibited a near linear relationship ($r^2=0.99$) between the NH_3 loss and the ammoniacal-N applied, as well as the total N applied. This relationship did not exist for surface applied dairy manure. Their results also showed that the soil appeared to have a NH_3 binding threshold since the y-intercepts extrapolated from the regression lines were less than zero. This information would be helpful in situations of low N requirements. They also demonstrated, similar to Adamsen and Sabey (1987), that losses from surface applied manure were at least ten times greater than losses found with manure incorporated immediately after application.

Efforts to reduce volatilization losses of NH_3 by chemical treatment have a long and intermittent history. During the early part of the twentieth century the common practice was to add gypsum (land-plaster), kainite, phosphoric acid, sulphuric acid or acid phosphate to freshly excreted manure during storage. Application of these chemical additives to the manure was also practiced at the time of spreading (Agee, 1913 and Thorne, 1930). The advantages were quite apparent, increased conservation of NH_3 was attained as well as the fertilizing effects of the added phosphorus and potassium.

Due to varying and questionable scientific procedures many early studies yielded contradictory results. Lemmerman and Wiessman (1918) and Nolte (1922) found that the addition of gypsum to manure was ineffective at controlling NH_3 volatilization. Earlier studies by Dietzell (1897), Severin (1904) and Vivien (1905) though, observed that gypsum significantly decreased NH_3 losses. Mixed results were also reported for superphosphate, lime and sulphuric acid. Blank (1919) and Wissenlink (1921) noticed that sulfuric acid was successful in the reduction of NH_3 losses. The latter mentioned that the advantages inherent in the addition of sulfuric acid were offset by the fact that it was harmful to livestock and also that it seemed to destroy the carboneous material in the manure. Bjorn-andersen (1905) found that 2% superphosphate significantly decreased NH_3 losses and Lemmerman and Wiesmann (1918) went on to show that 10% and 15% superphosphate reduced NH_3 losses by 27.5% and 70.2% respectively over 62 days.

Salter and Schollenberger (1938) stated that strong acids, such as sulfuric and phosphoric acid, are effective in the reduction of NH_3 losses since they tend to reduce the pH, resulting in more ammoniacal-N occurring as NH_4^+. Midgley and Wiser (1937) ascribed a similar effect to mono-calcium phosphate (MCP) or superphosphate (MCP and gypsum). Both studies discussed in detail the chemistry involved with the addition of these chemicals to manure. They mention that phosphoric acid forms a stable end product when reacting with NH_3 - ammonium phosphate as in the reaction given below:

$$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The reaction of sulfuric acid and NH_3 is essentially the same, as ammonium sulphate is produced as a final product.

When superphosphate is added to manure the following reaction is developed:

$$Ca(H_2PO_4)_2.H_2O + NH_3 \text{ --- } CaHPO_4 + NH_4H_2PO_4 + H_2O \quad .(2)$$

As gypsum is added to NH_3 the resulting reaction given below ensues:

$$CaSO_4.2H_2O + 2NH_3 \longrightarrow (NH_4)_2SO_4 + Ca(OH)_2 \quad \ldots\ldots \quad (3)$$

The assumption expressed by equations (1) to (3) are subject to debate. NH_3 in manure generally occurs as ammonium carbonate rather than free NH_3. As ammonium carbonate reacts with such chemicals as superphosphate or phosphoric acid stable end products such as H_2O, CO_2 and ammonium salt evolve. When gypsum reacts with ammonium carbonate, however, two chemicals are produced, namely ammonium sulfate and calcium carbonate. As the manure dries these two chemicals react and form free NH_3. Therefore gypsum should not be as effective as either superphosphate or phosphoric acid in reducing NH_3 losses due to volatilization (Salter and Schollenberger, 1938).

Safley et al. (1983) found that 94% of the NH_3 from cattle manure was lost after 28 days in the absence of chemical treatment, while 70% and 53% of the NH_3 were lost with treatment of superphosphate and phosphoric acid respectively. Both of these treatments were observed to conserve N better than gypsum.

Significant reductions in NH_3 losses from hog manure were found in the laboratory simulations of Tomar and Mackenzie (1987). Observed losses over 15 days were 23.5 g kg^{-1} for untreated liquid hog manure while they were 4.39 g kg^{-1} and 1.04 g kg^{-1} respectively for treatment rates of 2 and 4 g of added superphosphate per 100 g of manure.

Studies conducted by Fenlon and Mills (1980) and Muck and Herndon (1985) examined the addition of lime to manure to reduce N losses. The theory behind these methods was to add a sufficient amount of lime in order to stabilize the manure and thus prevent the breakdown of urea into NH_3. Their studies showed mixed results; when lime was applied at low rates, N losses were greater than those from unlimed manure. When lime was added at a sufficient amount to bring the pH above 10, no appreciable loss of total N, was observed.

3. MATERIALS AND METHODS

3.1 Modification and application of the TSM model

Considering the desirability of repeated NH_3 volatilization studies under identical soil and wind conditions the numerical simulations of the Trajectory Simulation Model (TSM) were repeated (by Dr. M. Leclerc) for source plots of 3.5 m radius with a roughness length of 1 cm, appropriate for cut grass. The original simulations were based on characteristics of a two-dimensional wind-field. Since turbulence intensities become large close to solid surfaces (Monin and Yaglom, 1971), and since smaller plots are less likely to assure sufficient averaging of crosswind components, the determination of the sampling height (ZINST) was repeated for characteristics of a three-dimensional turbulent wind field.

Results summarized in Figures 3.1 and 3.2 show significant differences between two- and three-dimensional simulation for the higher surface roughnesses. A satisfactory definition of ZINST (of approximately 12.5 cm) can be obtained even for these small source radii, permitting formulation of a quantitative relationship between the observations at the ZINST-level and mean NH_3 flux density of the plot ($F_z(0)$) as:

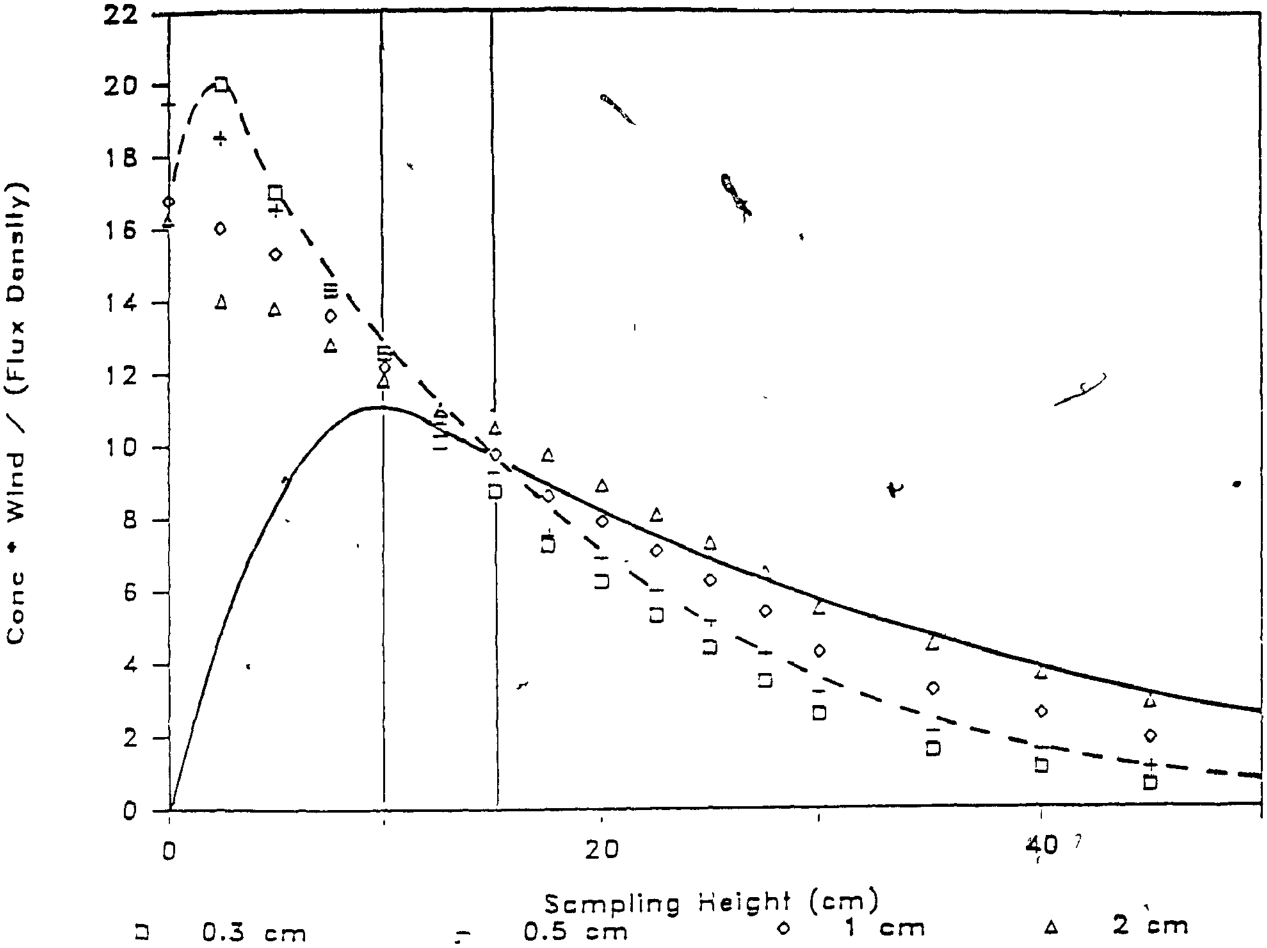


Figure 3.1 Dimensionless normalized horizontal flux SC/Fz(0) versus height for a circular source of radius 3.5 m and various z_o values at neutral atmospheric stability, using a three-dimensional windfield. Solid and dashed lines indicate results of numerical simulations using a two-dimensional windfield, for z_o values of 2 cm and 0.3 cm respectively. Vertical lines define range of possible random shifts of 2.5 cm in position of the sampling orifice from its ideal (12.5 cm) level.

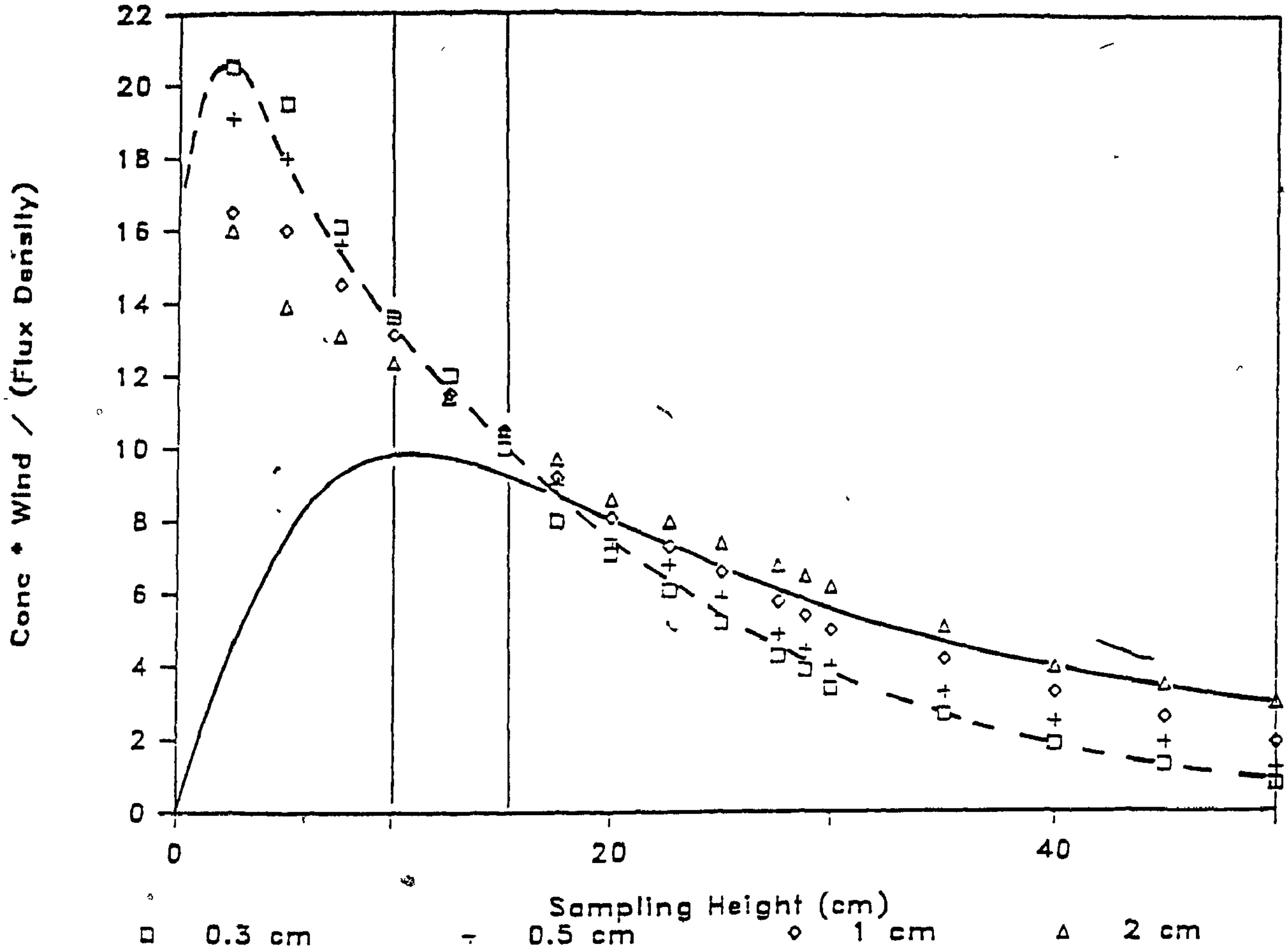


Figure 3.2 Dimensionless normalized horizontal flux SC/Fz(0) versus height for a circular source of radius 3.5 m and various z_0 values under unstable conditions, using a three-dimensional windfield. Solid and dashed lines indicate results of simulations using a two-dimensional windfield, for z_0 values of 2 cm and 0.3 cm respectively.

$$F_z(o) = \frac{\bar{s}\;\bar{c}}{\left[\dfrac{\overline{sc}}{F_z(o)}\right]_{\text{model}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where $\bar{s}$ and $\bar{c}$ are mean cup windspeed and mean ammonia concentration at 12.5 cm above the surface. The numerically-determined constant $\overline{sc}/F_z(o)$, whose value depends on source plot radius and roughness length (z_o), has a value of 12 for the given experimental parameters. The model is normalized to a surface flux $F_z(o)$ of unity.

3.2 Measured Climatic Data

In order to document general climatic conditions various meteorological parameters were recorded at the downwind side of the test circles throughout the experiments, Figure 3.3 displaying the field equipment setup and wiring diagram.

Windspeed was measured over the entire sampling period by a cup anemometer (Climet Co., model 14-102) at the sampling height of the central mast. In addition, air temperature at 1 m above the ground (copper constantan thermocouples), soil temperature at 10 cm depth (thermocouples), soil heat flux at 10 cm depth (Thermonetics flux plate, mod. H11-18-3), net radiation (Fritschen, R-800

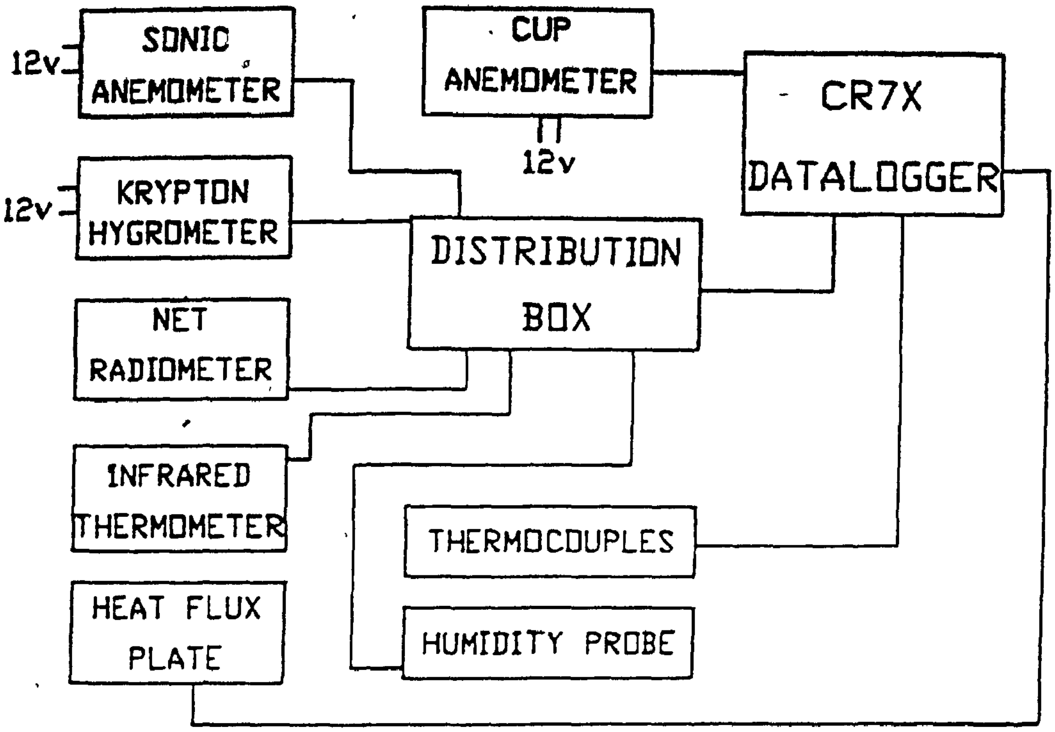


Figure 3.3 Field equipment setup and wiring diagram

miniature net radiometer), relative humidity (Cole Palmer humidity probe) and surface temperature of the ground (Barnes IT3 IR thermometer) were also recorded for each sampling period.

For some of the experiments, latent heat flux was determined by the eddy correlation technique, using a Campbell Scientific sonic anemometer (CA27) and fast-response Krypton hygrometer (KH20). Only a relative measure of the sensible heat flux was used, based on the measured temperature difference between surface and ambient air and a transfer coefficient proportional to the mean horizontal wind speed.

The data collection and manipulation was done by a (Campbell Scientific CR7-X) datalogger which calculated ten minute averages for the above-mentioned parameters. Data were transfered from the datalogger to a cassette tape at the end of each sampling day. From the cassette the data were dumped through a cassette interface (Campbell Scientific C-20) and loaded onto a microcomputer where they were stored on a standard floppy disk. The stored data were averaged over each test period to get a relative measure of the climatic factors encountered during the volatilization sampling.

3.3 Experimental approach

For each experiment, excluding tests 4 and 13 (see Table 4.1), four circular test plots of 7 m diameter were used. The plots were separated from each other by 5 m, and were arranged along a straight line perpendicular to the direction of prevailing wind (south-west) and 1-2 h sampling intervals were conducted simultaneously on all of the plots during daylight hours. The test site was attended at all times during sampling operations and sampling stopped when wind direction shifted by more than ±40° from the prevailing direction to avoid lateral contamination between plots. The site was a level sandy loam field, with soil physical and chemical parameters reported by Lajoie and Baril (1956), located on the McGill (Macdonald College) Experimental Farm, 30 km west of Montreal. It had an upwind fetch of at least 400 m, with short grass up to 150 m and growing corn beyond.

(a) Untreated Swine Manure Tests

Liquid swine manure (LSM) obtained from the Experimental Farm was dumped into four separate 200 L-drums at the test site along each selected plot. The manure was mixed thoroughly by a sump pump and then spread onto the plots with the same sump pump. The volatilization sampling began immediately thereafter.

(b) Mono-calcium Phosphate Tests

LSM was placed to volume into four separate 200 L-drums and mono-calcium phosphate (MCP) added to two of the drums in a completely randomized design, while the remaining two drums were left untreated. Data on the chemistry of MCP are given in Table 3.1. After the addition of MCP the manure mixture was almalgamated thoroughly with a sump pump. The drums were then covered with plastic and left for six days, being mixed again every second day. On day six the manure was once again thoroughly mixed and then applied to the plots and the NH_3 volatilization measurement immediately followed.

Table 3.1 Chemical characteristics of monocalcium phosphate (MCP) (as specified by the manufacturer)

$Ca(H_2PO_4)_2 \cdot H_2O$	91.2%
$Ca(H_2PO_4)_2$	6.7%
Free Acid (H_3PO_4)	0.1%
Moisture (H_2O)	6.5%
Acid Insoluble	0.2%
Arsenic (As)	0.2 ppm
Fluorine (F)	9 ppm
Neutralizing Value	84.5

(c) Manure Dilution Rates Tests

LSM was placed into the four 200 L-drums at different volumes according to a predetermined water to manure ratio. Drums 1 to 4 obtained 50 L, 100 L, 150 L, and 200 L, respectively of manure and were filled to volume with water. The manure-water mixtures were then thoroughly mixed and applied to their respective plots at which time sampling began.

(d) Separated Manure Tests

The manure collection and application procedure for these tests is similar to that of the untreated manure tests stated above. Only two plots are used for these tests with one of the plots receiving separated manure while the other plot received untreated manure. Separation of the liquid fraction was obtained by a 100 μm screen. Immediately following separation the manure was spread onto the plots and sampling began.

(e) Wetted Manure Tests

The manure collection and application procedure for these tests is essentially the same as for the above mentioned untreated manure tests. Once the manure has been applied to each plot, two plots are randomly selected to be wetted by approximately 2 mm of water every 2 h of sampling. This appeared to keep the manure on the surface moist at all times during sampling.

(f) Soil and Manure Samples

For selected tests, soil profile samples were periodically taken for subsequent determination of their ammoniacal-N concentration. Using a soil sampler, samples at depths of 0-2.5 cm and 2.5-7.5 cm were obtained.

Prior to the application of manure to each of the test plots, manure samples were taken from each well mixed drum for the determination of total N according to Bremner and Mulvaney (1982) and ammoniacal-N. Due to financial constraints only selected tests were analyzed for the above mentioned concentrations.

(g) Silica Gel Tubes

Sampling tubes for ammonia with silica gel absorbers (Supelco ORBO-52; 4 mm internal diameter and 70 mm length) were attached to a mast at the center of each plot at a height of 12.5 cm above the zero-plane displacement of the grass surface. Figure 3.4 shows a tube divided into two sections. Section 'a' which is twice the size of section 'b' is the measured section. Section 'b' is measured periodically to see if the probability of sampling loss exists. This is true when the concentration in section 'b'

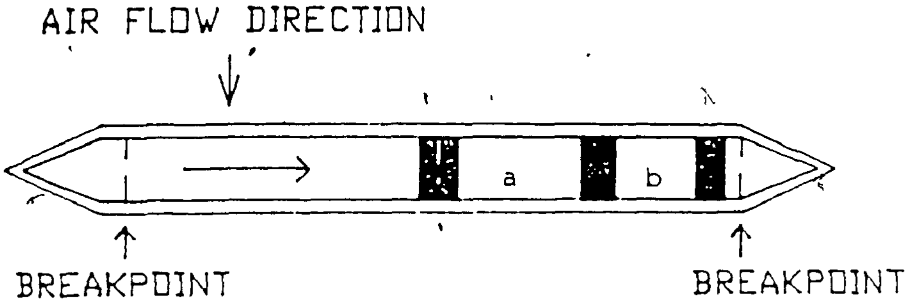


Figure 3.4 Sketch of silica gel tube

is greater than 25% of that in section 'a'. Such a situation was never found to exist for any sampling periods.

The silica gel tubes have been designed to absorb amines and alcohols over a range of concentrations from 16.9 to 67.6 mg m^{-3} which was maintained throughout all tests. Flow rates through the tubes were maintained at 3 ±0.5 L min^{-1}, differences are attributable to varying degrees of resistance introduced into the sampling line from varying dimensions of orifice of the sampling tubes after breaking their previously sealed ends. Flow rates through the tubes were monitored in each sampling line at the beginning and end of each sampling period and found to have remained constant to within 2% during runs. Unless otherwise specified, sampling periods were 1 to 2 h, covering most of the daylight hours of days 1 through 3 after the application of manure.

(h) Ammonia Detection Technique

The ammonia (NH_3) concentration of the soil, manure and silica gel adsorption tubes was performed by an Orion model 95-10 ammonia electrode as seen in Figure 3.5. This electrode allowed us to obtain fast, economical and accurate measurements of dissolved ammonia.

The electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the internal ammonium

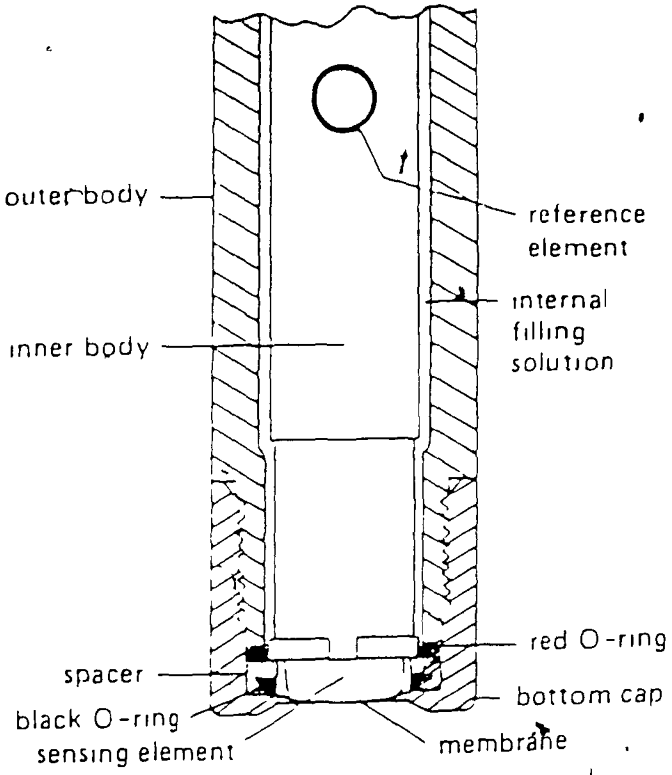


Figure 3.5 Ammonia electrode construction.

salt (NH_4Cl) solution. Dissolved NH_3 in the sample solution diffuses through the gas-permeable membrane with a mean pore size of 0.2 mm, until the partial pressure of the NH_3 is the same on both sides of the membrane. Since the partial pressure of ammonia is proportional to its concentration, the concentration of NH_3 can be calculated.

In order to operate the NH_3 electrode for concentration measurements the following materials had to be used:

- Corning 125 digital pH/mV meter,
- magnetic stirrer,
- 10 M NaOH,
- internal filling solution,
- distilled, deionized water and
- standard solution

To adjust the pH of the sample solution to approximately 13, which is the operating range of the electrode shown in Figure 3.6, laboratory-prepared 10 M NaOH was used.

The water used to dilute the samples had to be NH_3 free in order to obtain accurate measurements. For this we used distilled water which had passed through an anion-cation exchange column.

Ammonium chloride (NH_4Cl) standard solutions 10^{-2} M, 10^{-3} M, 10^{-4} M and $5x10^{-2}$ M concentrations were prepared for calibration of the ammonia electrode. The milli-voltage

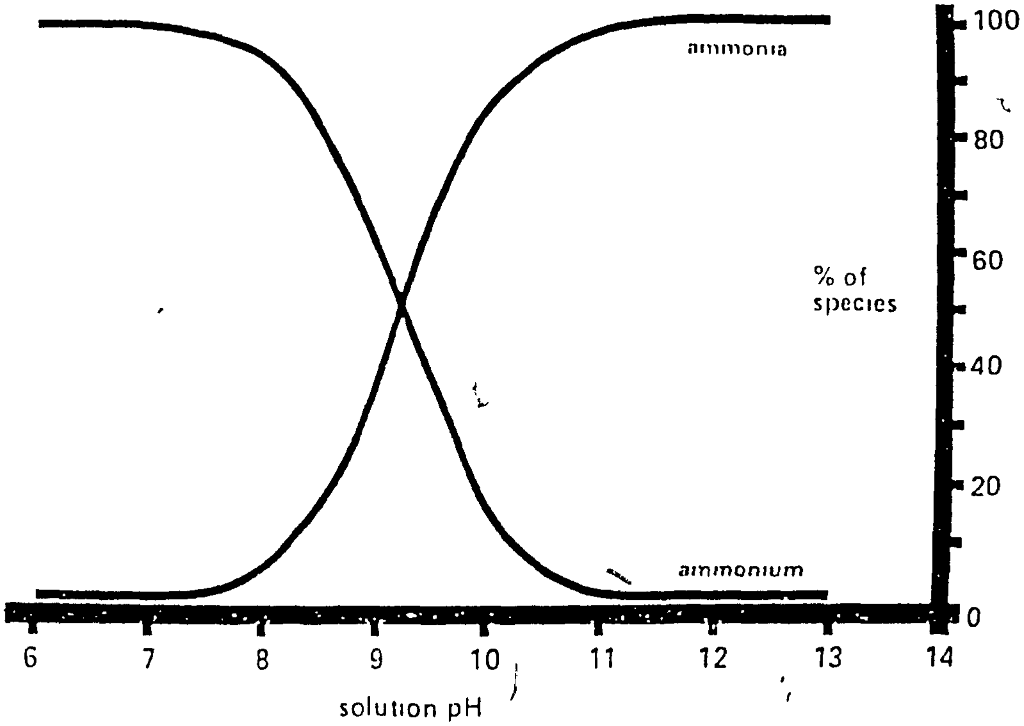


Figure 3.6 Influence of solution pH on ratios of NH_4: NH_3.

potential from the digital pH meter was plotted against the standard concentrations on 4-cycle semi-logarithmic paper. For calibration purposes the 10^{-3} M millivoltage potential reading was adjusted to zero. When plotted, the points produced a straight line slope of approximately 58 mV/decade (as seen in Figure 3.7).

The calibration curve begins to drift at approximately 9×10^{-6} M, outside the operating range of the instrument. In this range the rate of NH_3 diffusion through the membrane and the rate of equilibrium between NH_3 and NH_4^+ in the internal filling solution are slow. NH_3 absorption from the air then may become a source of error.

Figure 3.8 shows the response time of the electrode with respect to step changes in the concentration. For most of our readings (10^{-3} to 10^{-6}) the response time appears to be approximately 1-2 minutes.

The advantages of this type of ammonia electrode over other methods of analysis is that it:

i) allows small sample volumes (2.5 mL) to be measured,

ii) allows quick, accurate and simple measurements,

iii) does not destroy the sample and

iv) functions in coloured or turbid solutions where photometric methods fail.

The disadvantages are that:

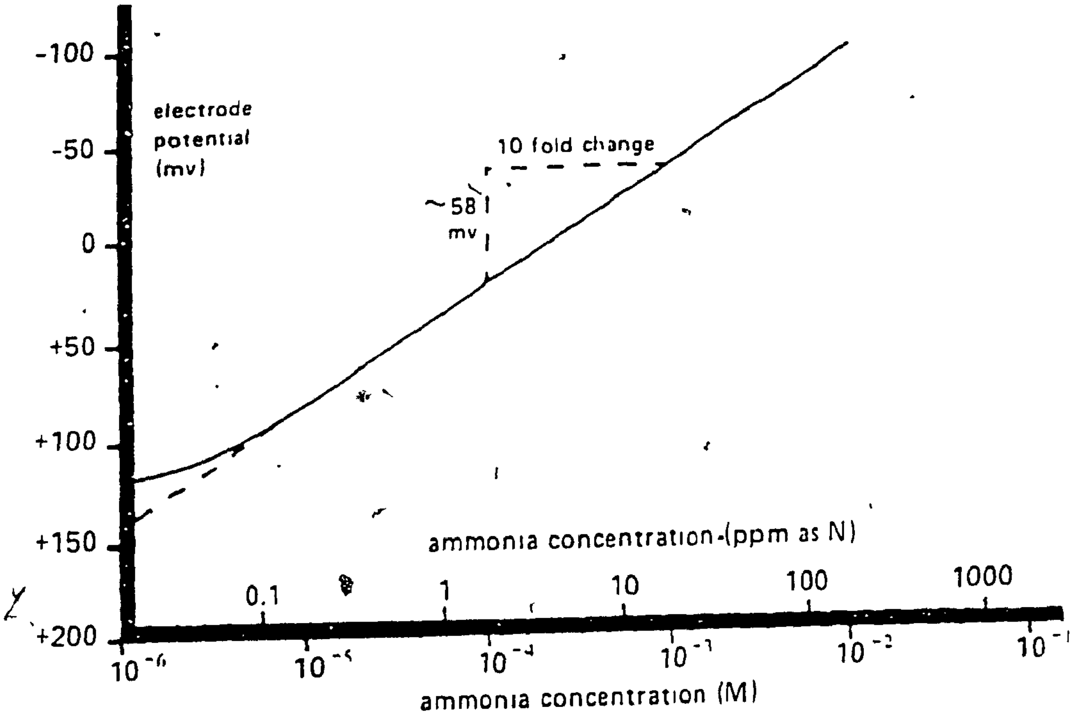


Figure 3.7 Ammonia electrode calibration curve

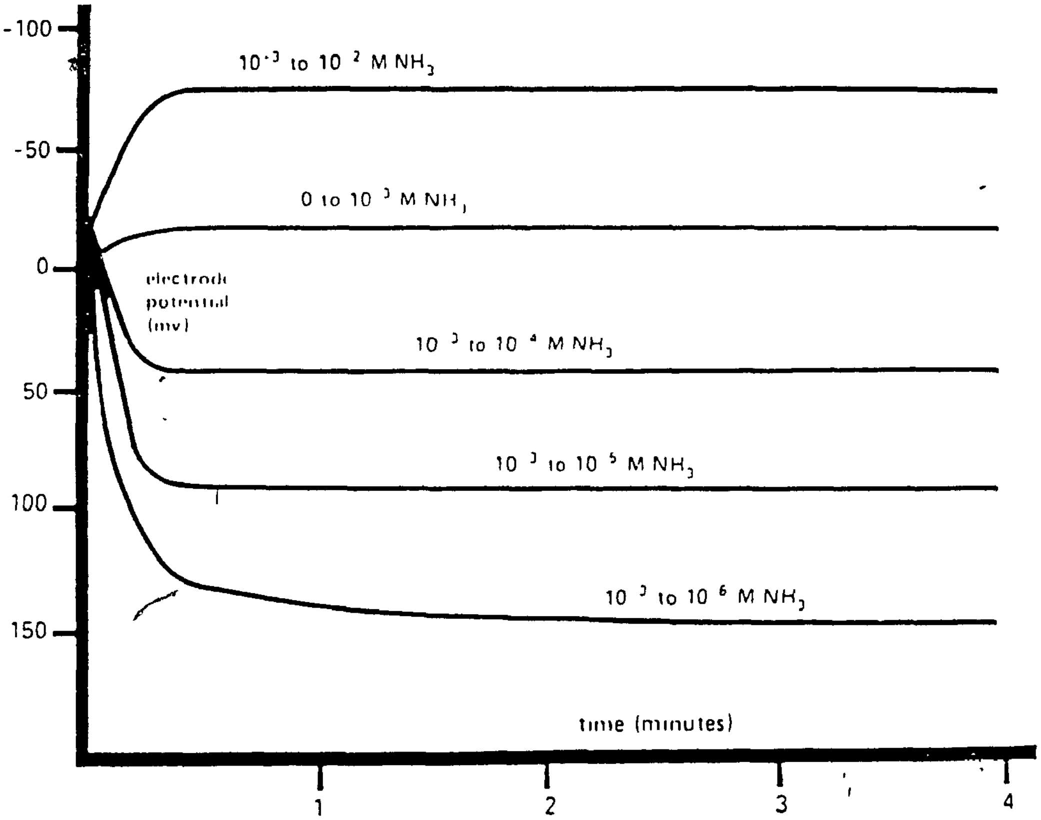


Figure 3.8 Ammonia electrode response to stop changes in ammonia concentrations.

i) frequent calibration (every 60 minutes) is necessary,

ii) it is not specific but selective, so that volatile amines may interfere with measurements and

iii) reproducibility is threatened due to temperature fluctuations, noise and drift.

4. RESULTS AND DISCUSSION

4.1 Summary of Experiments

Thirteen field experiments were carried out on NH_3 volatilization during daylight hours on rainfall-free days of June, 1985 through November, 1987, excluding winter months. Table 4.1 shows the dates and the description of each test conducted. Meteorological conditions averaged over the test periods are summarized in Table 4.2 as a basis for interpretation of differences in estimated NH_3 flux densities. They indicate typical Quebec summer and fall weather conditions. Missing data for some of the tests are generally due to equipment breakdowns and technical problems.

Some "background" levels of atmospheric NH_3 were measured on July 9-10, 1987 at the test site in order to see if upwind contamination of plots should be considered. The measurements were made at the ZINST (12.5 cm) sampling height for the 3.5 m radius plots. The measured concentrations tend to agree with those reported by Denmead et al. (1976) and Beauchamp et al. (1978) for the atmosphere above a grass clover pasture. Our results, given in Table 4.3, were at least three orders of magnitude smaller than observed peak experimental values. Therefore

Table 4.1 Field Experiments

Test #	Date	Description
1	July 4-6/85	MCP
2	July 15-18/85	MCP
3	Aug 22-24/85	MCP
4	Oct 29-31/85	Separated
5	June 25-26/86	Dilutions
6	July 8-10/86	Dilutions
7	July 21-23/86	MCP
8	Aug 19-20/86	Untreated
9	Sept 16-18/86	Wetted
10	July 23-25/87	Untreated
11	Aug 19-21/87	Untreated
12	Oct 8-10/87	Wetted
13	Nov 6-8/87	Separated

Table 4.2 Mean meteorological conditions during test periods: Cumulative precipitation during the preceeding 2 weeks (CP), air temperature at 1 m (Ta), net radiation (Rn), soil heat flux (SF), soil temperature (Ts), mean wind speed (U) and relative humidity (RH).

Test no.	CP (mm)	Ta (deg.C)	Rn (Wm^{-2})	SF (Wm^{-2})	Ts ($^\circ C$)	U ($m\ s^{-1}$)	RH (%)
1	41.3	26.5	n.a.	26.2	27.8	1.7[1]	58.9
2	32.3	23.5	350.5	25.0	22.1	2.6[1]	60.4
3	16.6	24.2	n.a.	n.a.	15.5	1.6[2]	58.0
4	25.2	10.4	193.0	15.0	6.3	2.3[2]	41.0
5	68.8	16.8	413.0	31.0	17.9	0.9[2]	53.0
6	65.7	21.0	517.0	38.0	19.8	1.7[2]	56.0
7	61.6	23.8	501.7	62.3	25.7	1.1[2]	45.1
8	50.4	26.6	450.7	33.4	18.3	1.3[2]	25.2
9	74.6	13.6	350.0	23.0	12.8	0.6[2]	45.0
10	73.8	27.9	473.0	n.a.	25.0	1.1[2]	60.7
11	13.4	25.1	445.0	n.a.	n.a.	1.8[2]	51.3
12	19.0	8.4	185.0	n.a.	n.a.	1.7[2]	58.0
13	50.1	3.2	158.0	n.a.	n.a.	2.8[2]	27.6

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[1]) measured at 1 m height; [2]) measured at 12.5 cm height.

Table 4.3 Background concentrations of atmospheric NH_3 measured at the ZINST sampling height on July 9-10,1987.

Date	Time period	Atm. NH_3 conc. ($\mu g\ m^{-3}$)
July 9/87	1030-1230	.706
	1240-1440	.417
	1440-1640	.357
July 10/87	1030-1230	.429
	1230-1430	.343
	1430-1630	.332

any correction for background sources was deemed unnecessary.

For all of the tests where windspeed was measured close to the ground (ZINST= 12.5 cm), the 0.25 m s^{-1} cup anemometer stalling speed must have introduced underestimation of average windspeed, leading to underestimation of estimated fluxes of up to 10%. These systematic errors would not affect relative comparisons between plots.

4.2 UNTREATED SWINE MANURE

In order to examine the relative variability of data from the 7 m diameter circles for plots of equal expected source strength, four untreated manure plots were simultaneously observed. Mean NH_3 flux density results from tests 8, 10 and 11 conducted in July and August of 1986 and 1987 are presented in Table 4.4. Mean values were estimated for all sampling periods of a given test (16 to 32 h over 2 to 4 days). The fact that longer tests tend to result in lower overall means is not important here since variability between replicates within tests is being examined.

Table 4.4 Mean NH_3 flux densities (kg ha^{-1} h^{-1}) for 4 replications of untreated swine manure.

	Plot #				
Test	1.	2	3	4	F-test
8	1.64	1.62	1.88	1.76	ns
10	0.88	0.82	0.92	0.87	ns
11	7.54	8.48	7.11	8.19	ns

ns = not significant at the 0.05 level of confidence

Analysis of data from these tests show that the advantage of economy of land inherent with small test plots is offset to some degree by high variability of observations, as shown in Figures 4.1 and 4.2. Since the variability appears random in nature among the four simultaneous plots it is not likely attributable to meteorological variables. Differences in applied total N between plots would lead to systematic errors; they are precluded by the fact that N analysis of 50 cm^3 samples between replicated plots showed only one significant difference (35% - attributable to non-representativeness of the small sample) in 8 cases, with 6 samples agreeing within 1%. The uniformity of terrain and length of sampling period (> 1 h) make significant variations in aerodynamic characteristics of adjacent plots equally unlikely. The most likely source of variability lies (a) in random error in ammonia detection and (b) in random errors in adjustment height of silica gel tubes during replacement between sampling periods. Their relative contributions will be further discussed below. Variations in flow rates through sampling lines (of up to 16%) are not considered as a potential source of random error since they were known and corrected for.

Examination of Figures 4.1 and 4.2 show a diurnal pattern of flux magnitude with peak losses generally occuring around noon as the soil surface temperature is increasing and the soil-water content is decreasing. A general reduction in flux magnitude with time can also be

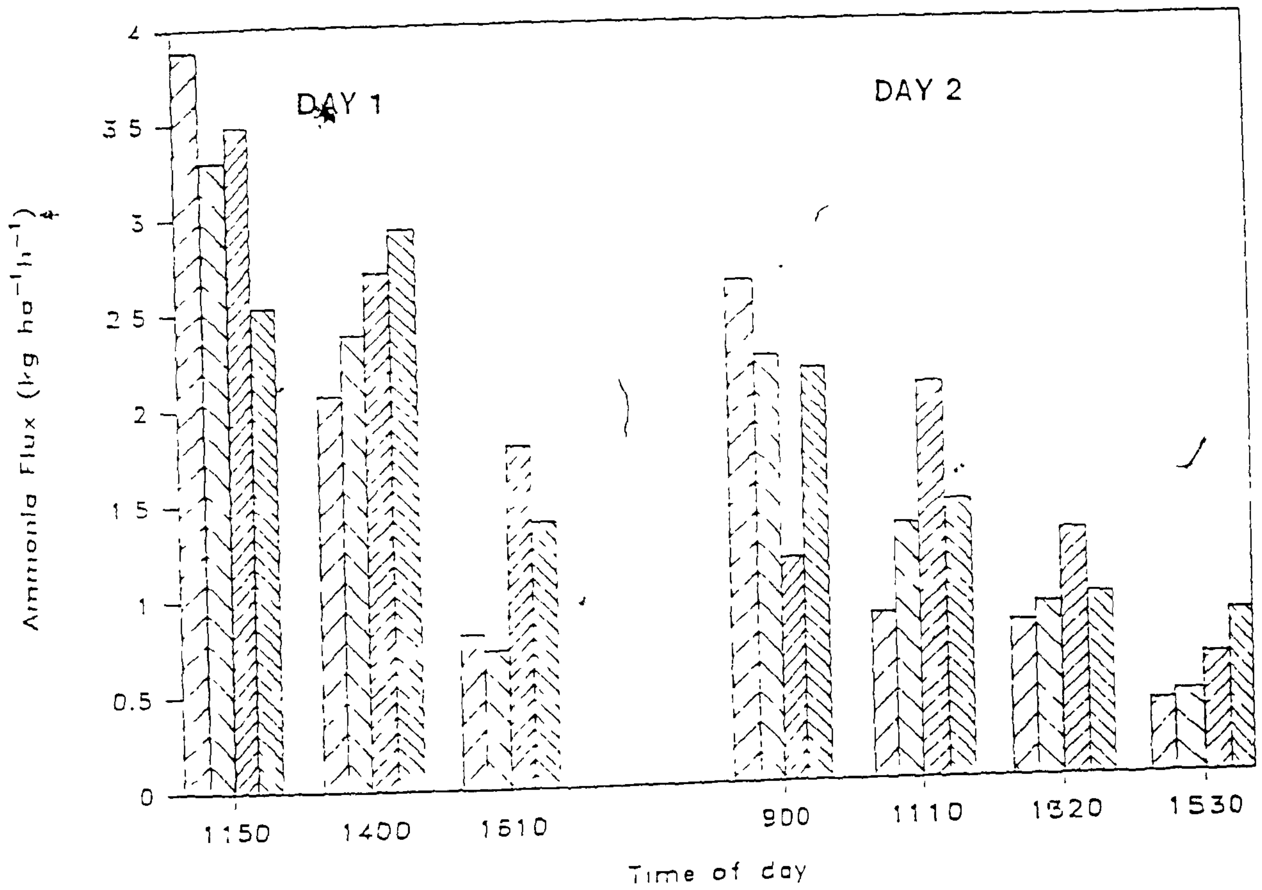

Figure 4.1 Ammonia Flux density for 4 untreated plots of Test 8 (August 19-20, 1986).

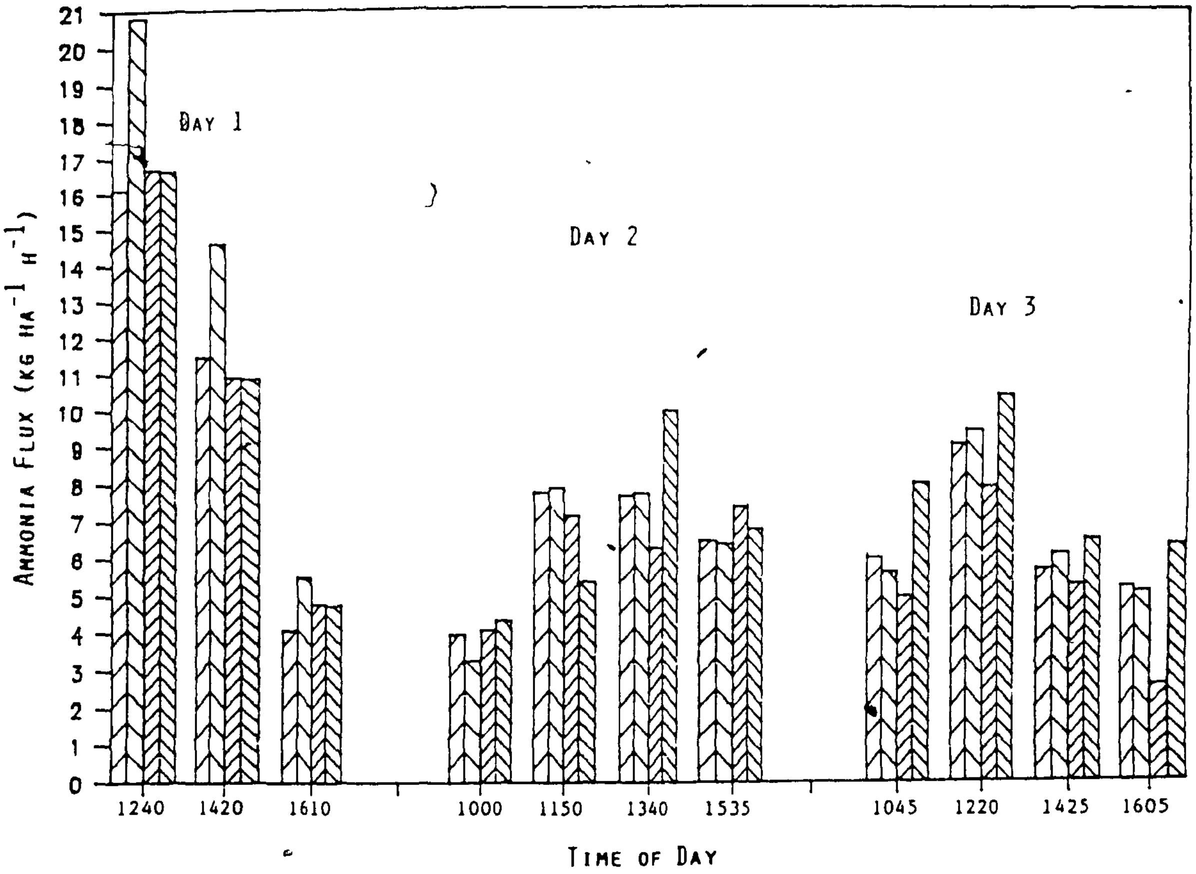

Figure 4.2 Ammonia Flux density for 4 untreated plots of test 11 (August 19-21, 1987).

seen from the above mentioned results. Similar findings have been reported by McGarity and Rajaratnam (1973), Denmead et al. (1974), Beauchamp et al. (1978 and 1982), McInnes et al. (1986) and Brunke et al. (1988).

Even though plot variabilty appears to be rather strong in nature, no statistically significant differences were found to exist between plots. The results of Table 4.1 may be taken to indicate the relative variability expected from the modified technique under the experimental conditions of this study.

Test 11, which was conducted in August of 1987, produced uncharacteristically high flux values. The average NH_3 flux over the entire test of the four plots ranged from 7.11 to 8.48 kg ha^{-1} h^{-1}, which is significantly higher than the mean flux densities for all untreated measurements from the thirteen tests conducted during this study, which was 2.37 $\pm$2.28 kg $ha^{-1}h^{-1}$. Comparatively, test 10 which was conducted only three weeks prior to test 11 generated mean fluxes of between 0.82 and 0.92 kg ha^{-1} h^{-1}. The ammoniacal-N concentration of the manure applied to the plots for test 10 and 11 was 0.46% and 0.60% respectively. This would lead to expectation of a greater NH_3 loss for test 11 but some other veriables must have come into play to produce the actually observed differences. Hoff et al. (1981) pointed out that manure and soil pH were a possible explanation for large differences in their calculated NH_3 losses. The differences in tests 10 and 11 are probably not attributable to dissimilarities in soil or manure pH since the test plots were within 20 m of one another for the two tests, thus any differences in soil pH would be considered negligible. Analysis of manure pH found a standard deviation of only ±0.142, which would not contribute to any noticable differences. Upon examination of Table 4.2, it can be seen that there are only slight differences in most of the measured meteorological parameters. Mean windspeed showed a noticeable difference (1.8 m s^{-1} to 1.1 m s^{-1}) which again might explain some, but not all, of the observed enhancement. Most likely the discrepancy resulted from differences in manure handling and storage procedures which were beyond the scope of our observations.

Figure 4.3 shows that after three days, excluding overnight losses, test 10 lost approximately 10.1% of the initially applied ammoniacal-N content. The corresponding curve for test 11 shows that 63.8% of the ammoniacal-N was lost within three days of field application. Past studies with manure have produced similar results. Lauer et al. (1976) observed up to 99% losses of NH_3 from dairy manure after 25 days and Adriano et al. (1974) reported losses of up to 50% of the total-N applied within a few weeks. Beauchamp et al. (1978) in their sewage sludge experiments lost approximately 60% of the applied ammoniacal-N after 7

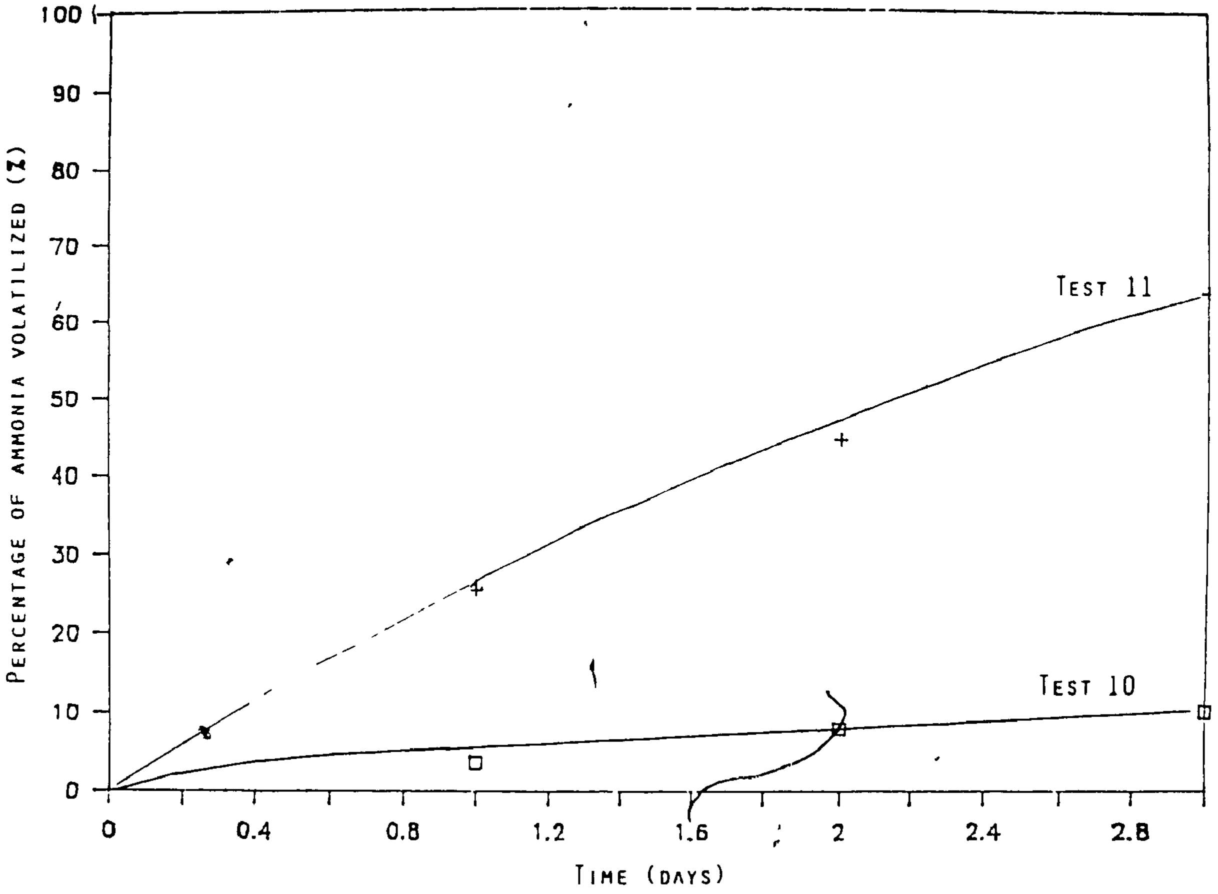

Figure 4.3 Percentage of ammonia volatilized from test 10 and test 11 based on the ammoniacal-N applied.

days.

Most previous studies have also shown similar observations in short-term flux magnitude measurements. McGarity and Rajaratnam (1973) observed first day peak flux values of approximately 0.32 kg ha^{-1} h^{-1} from the application of 118 kg urea-N ha^{-1} to the soil which were one order of magnitude lower than the flux values reported by Denmead et al. (1974), Beauchamp et al. (1978 and 1982) and Brunke et al. (1988). The McGarity and Rajaratnam (1973) study used a semi-closed NH_3 measuring technique and therefore it could be assumed that underestimation of losses may have occured since a disturbance of the natural environment could have eliminated some atmospheric processes that critically influence volatilization of NH_3 (Liss, 1975). Even considering the above mentioned variability in estimating general NH_3 flux magnitudes from 7 m diameter plots, it appears that our observations are well within the accepted range cited in the literature for open systems.

An attempt was made during sampling of test 10 to compare the amount of NH_3 volatilized to the measurements of ammoniacal-N in the soil at depths of 0-2.5 cm and 2.5-7.5 cm as a function of time. Results are given in Table 4.5. Measurements were made prior to field application of the manure and at the end of each of the three sampling days of the test. Some ammoniacal-N moved from the manure into the 0-2.5 cm layer and very little reached the 2.5-7.5 cm layer. The increase in the ammoniacal-N content in the 0-2.5 cm soil layer was relatively insignificant considering the concentration applied with the swine manure. Such a comparison, however, does not permit the definition of an effective N balance due to the fact that no measurements of NO_3-N in the soil were made. Rather it indicates the short term change in ammoniacal-N concentration that can be expected from the application of manure to turfgrass.

Table 4.5 NH_3 volatilized and ammonium content of the 0-2.5 and 2.5-7.5 cm soil layer following application of liquid swine manure from test 10 on July 23-25,1987.

Day	Time	Cum. NH_3 volatilized ($mg\ NH_3\ kg^{-1}$)	Ammonium conc. ($mg\ kg^{-1}$)	
			0-2.5	2.5-7.5
1	0	0	1.10	1.20
1	8h	161.1	84.40	1.40
2	32h	380.7	155.90	1.80
3	56h	450.7	103.70	1.90

4.3 Mono-calcium Phosphate Tests

Four field experiments were carried out on NH_3-volatilization from MCP-treated and untreated manure in July and August of 1985 and 1986. Table 4.6 shows the amount of MCP added to each storage drum approximately six days prior to field application.

There is some uncertainty in the absolute magnitude of the calculated fluxes. For tests 1 and 2 the mean cup windspeed was measured at 1 m and extrapolated to the 12.5 cm level on the basis of an assumed logarithmic wind profile whose determinant parameters (particularly the friction velocity) were not known precisely.

Table 4.6 Experiments and amount of mono-calcium phosphate (MCP) used in tests on MCP-treatment of manure.

Test no.	Date	Amount of MCP added (kg)			
		Plot no.			
		1	2	3	4
1	July 4- 6, 1985	0	1.0	0	1.0
2	July 15-18, 1985	1.0	0	1.0	0
3	Aug. 22-24, 1985	1.0	1.0	0	0
7	July 21-23, 1986	1.0	1.0	0	0

Examples of mean observed rates of NH_3 volatilization are shown in Figures 4.4 to 4.6; in general, they show a diurnal pattern and the expected decrease in relative magnitude with time, consistent with the observations mentioned earlier. This pattern is also evident in the period-by-period mesuremnets of the four test plots (2-treated and 2-untreated) given in Figure 4.7.

Analysis of variance on period-by-period measurements of NH_3 flux of the completely randomized MCP tests showed no significant difference at the 0.05 confidence level between treated and untreated plots. When the mean NH_3 flux densites were examined from the treated and untreated measurements and grouped with tests as an additional variable a significant difference at $p < 0.025$ was found to exist. The results in Table 4.7 show quite well the difference in average fluxes ,which cannot easily be noticed from the period-by-period measurements, with reductions of volatilization from treated plots between 5 and 30%.

Total N measurements showed values between 0.3 and 1% based on liquid weight of the sample and volatilization losses can be expressed in percentage of initial or remaining total N. These values are relative; they do not include NH_3 volatilization during evening or nighttime when sampling did not take place or any losses of N through leaching. The results from test 7 in Table 4.8, indicate

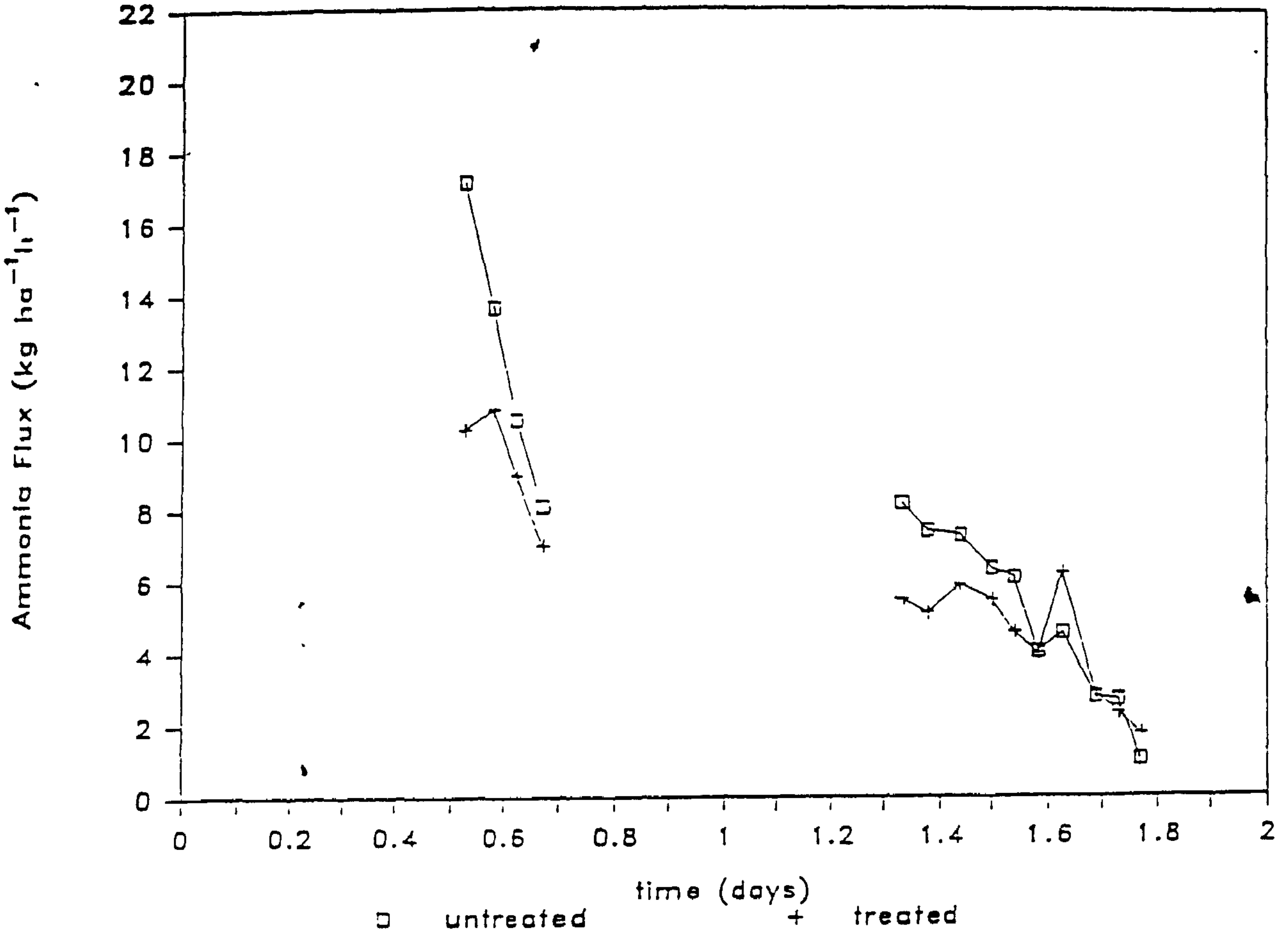

Figure 4.4 Mean Ammonia Flux density results from MCP treated and untreated plots, for days 1-2 of test 2 (July 15-16, 1995).

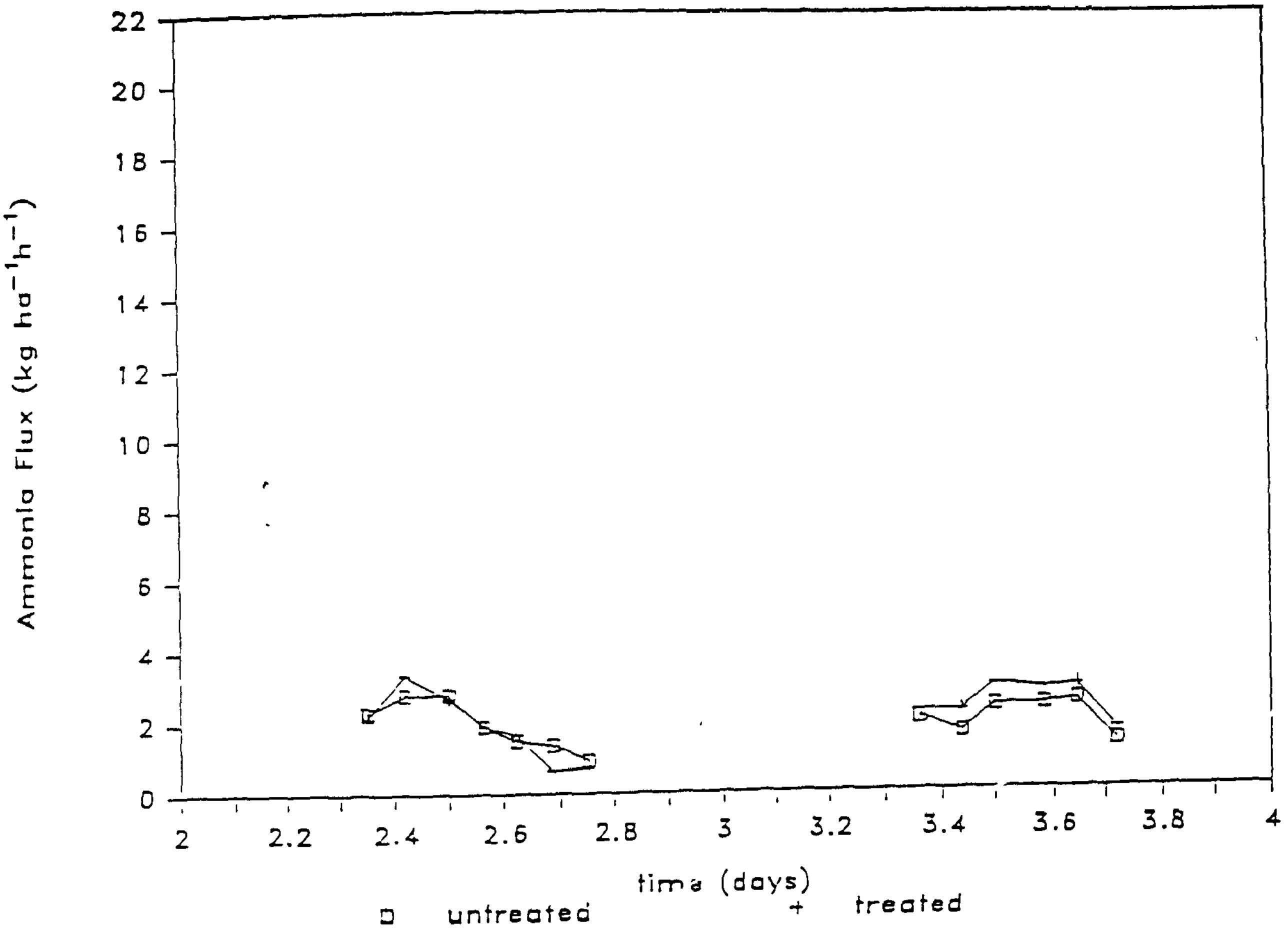

Figure 4.5 Mean Ammonia Flux density results for MCP treated and untreated plots, for days 3-4 of test 2 (July 17-18, 1985).

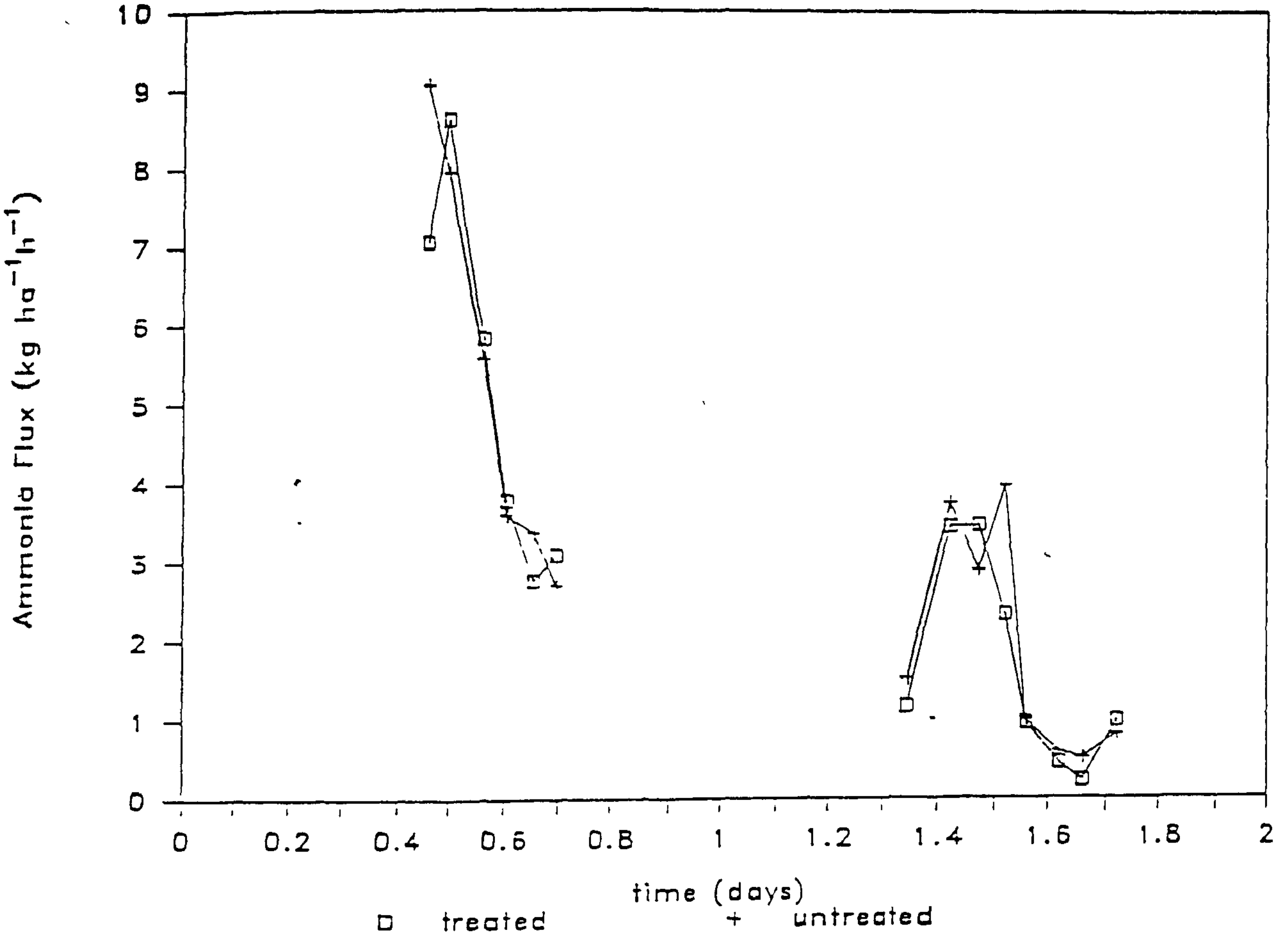

Figure 4.6 Mean Ammonia Flux density results for MCP treated and untreated plots for test 7 (July 21-23, 1986).

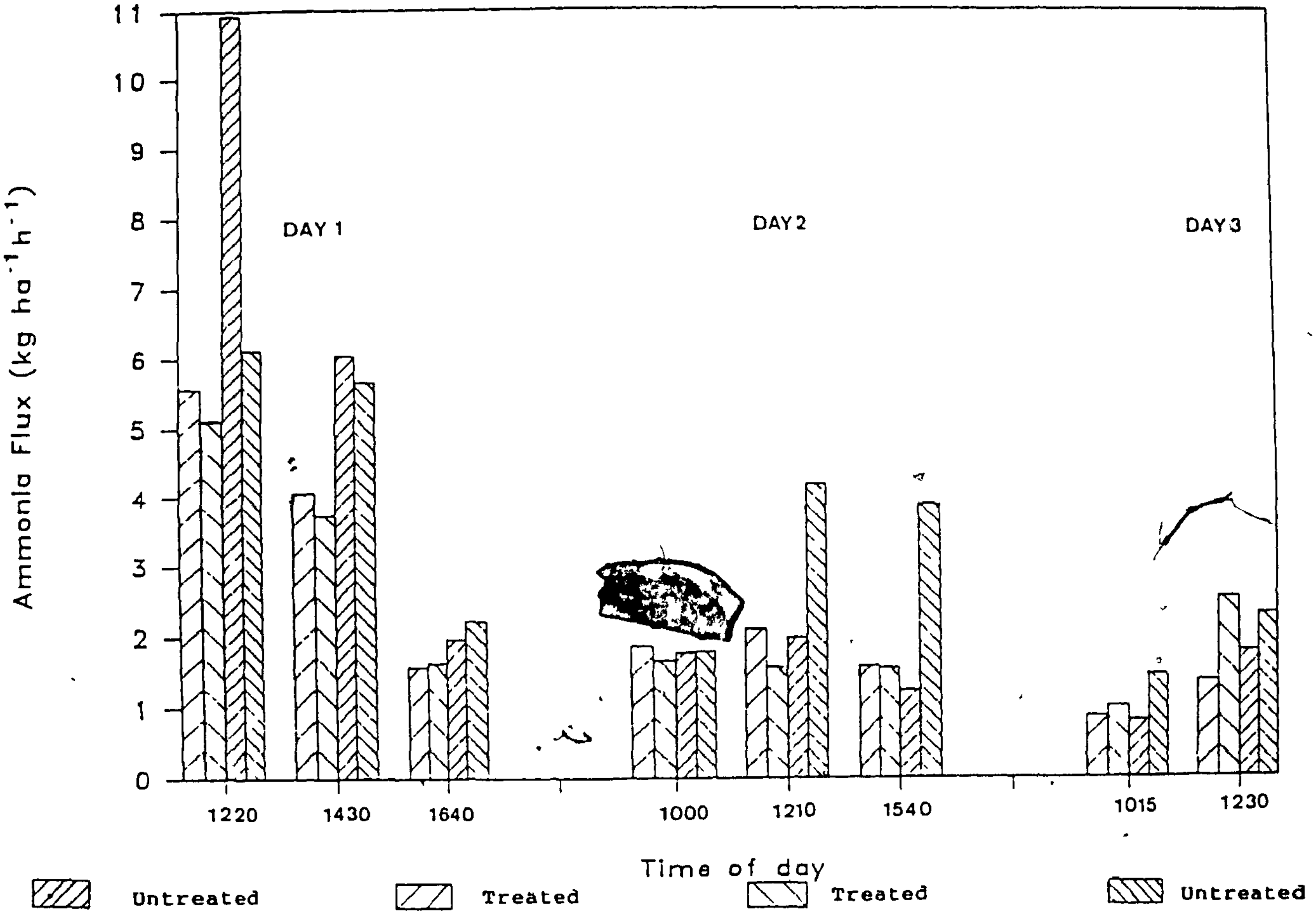

Figure 4.7 Ammonia Flux density for MCP treated and untreated plots, for test 7 (July 21-23, 1986).

that after 8 sampling runs, covering the peak volatilization periods of the first three days after spreading, about 12.5% of the total N from the manure had volatilized from the treated plots while 22.4% of the total N had been lost from the untreated plots.

Table 4.7 Average NH_3 flux densities (kg ha^{-1} h^{-1}) for treated (MCP) and untreated plots.

	Test 1	Test 2	Test 3	Test 7
Treated Plots	4.46	4.26	2.62	2.37
Untreated Plots	5.54	4.94	2.76	3.39
% Difference	19.5	13.8	5.1	30.1

Table 4.8 Volatilization losses as percentage of remaining total N in manure and cumulative loss in terms of initial total N.

Time (h)*)	Average Loss Per Run Treated (MCP)	Untreated
1	3.52%	7.06%
3.5	2.67%	5.22%
5.5	1.13%	1.97%
23	1.25%	1.71%
25	1.32%	2.98%
28.5	1.14%	2.56%
47	0.70%	1.19%
50	1.46%	2.15%
Cumulative loss during the 8 runs	12.5%	22.4%

*) mid-point of sampling run, measured from moment of inital sampling after spreading.

4.4 Dilution Tests

The ability of the 7 m plots to detect significant differences in volatilization rates was examined on dilutions of swine manure with relative proportions of manure (on a per-volume basis) of 100%,75%,50% and 25%. Two tests were conducted in June and July of 1986 based on the above mentioned criteria. The mean NH_3 flux densities over the entire observation period (indicated in Table 4.1) from the dilution tests given in Table 4.9 clearly indicate the expected reduction of NH_3 volatilization from dilute manure, due to reduction in partial pressure of NH_3 (Beauchamp et al., 1982 and Harper et al., 1983). They show, as does Figure 4.8 that an inverse relationship between flux magnitude and dilution of manure exists which is statistically significant with $p < 0.05$.

For both tests a strong correlation was found to exist ($r^2 = 0.95$) between the mean NH_3 flux of the first sampling day and its corresponding dilution rate. This shows that NH_3 volatilization to a large degree depends on the concentration of total N and NH_3 applied; particularly on the first day after spreading. This is similar to the findings of Chao and Kroontje (1964) and Brunke et al. (1988) who observed an almost perfectly linear relationship between applied ammoniacal-N and the NH_3 volatilized.

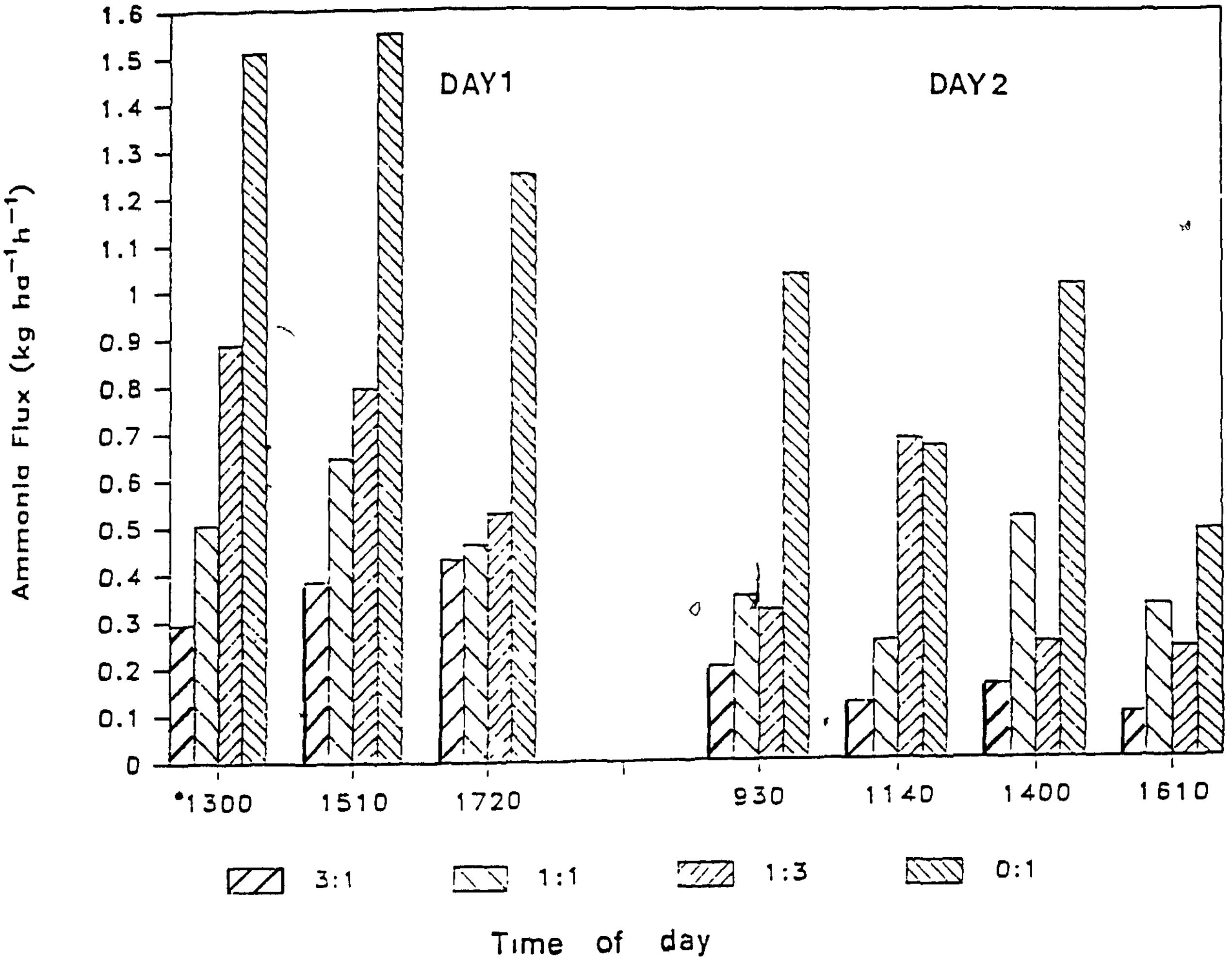

Figure 4.8 Ammonia Flux density for plots with various dilutions of manure, for test 5 (June 25-26, 1986). Ratios represent relative proportions of water added to manure on a per volume basis.

Beauchamp et al. (1982) however, found no apparent correlation between the above mentioned parameters in their study.

Table 4.9 Mean NH_3 flux densities (kg ha^{-1} h^{-1}) for dilutions of swine manure.

	Test 5	Test 6
25%	0.244	0.201
50%	0.438	0.264
75%	0.529	0.514
100%	1.074	0.823
F-test	**	*

*) significant at the 0.05 level of confidence
**) significant at the 0.01 level of confidence

It is also quite interesting to note that the regression line from test 5 presented in Figure 4.9 has a y-intercept that is less than zero. This may indicate an NH_3 deficiency or binding threshold of the soil, similar to the findings of Brunke et al. (1988).

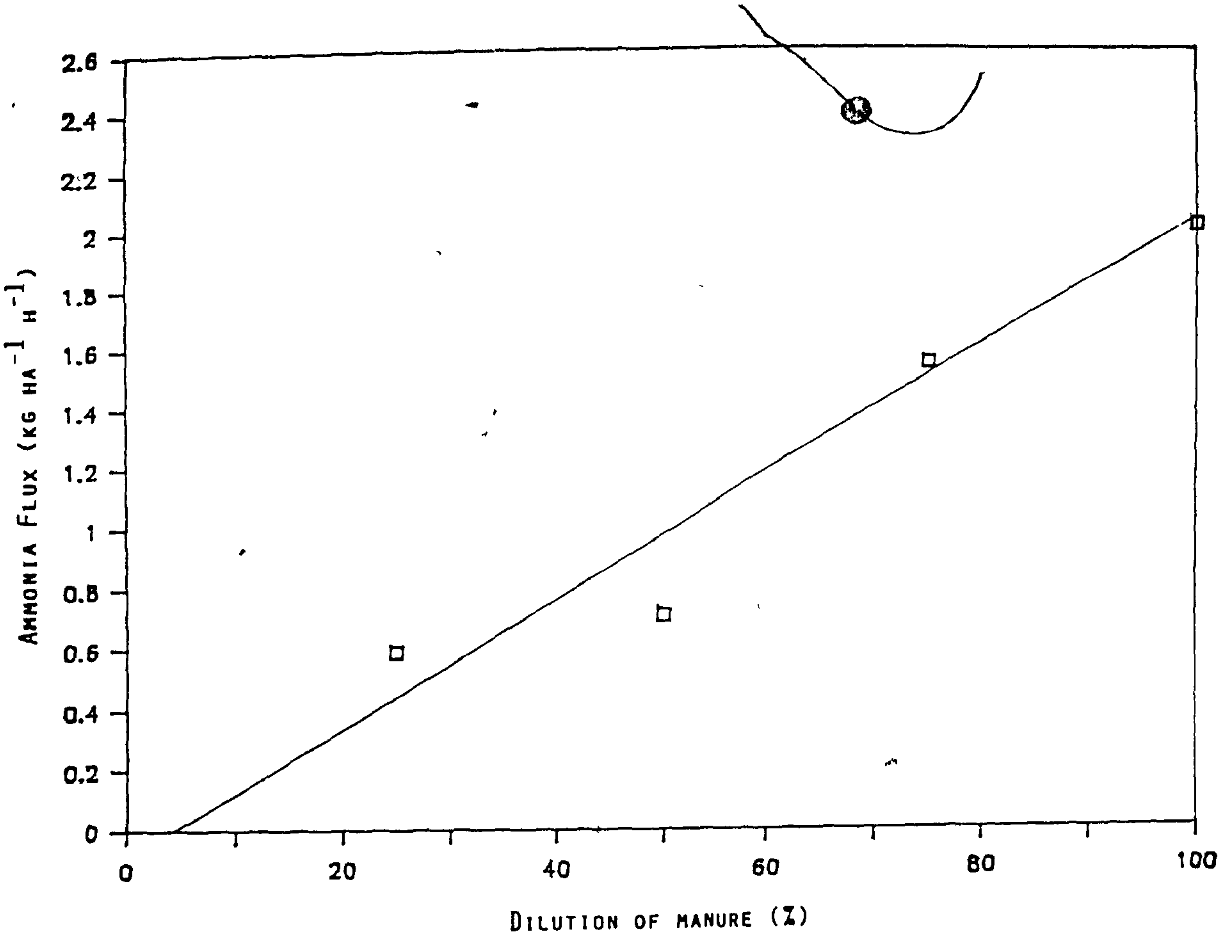

Figure 4.9 Average ammonia flux of first sampling day versus dilution of applied manure for test 5 (June 25-26, 1986).

4.5 Separated Manure Tests

Manure separation tests were conducted in the fall of 1985 and 1987. After field application it was observed that the unseparated manure remained wet for a much longer period of time than the separated manure plot (receiving only the liquid fraction). For both test 4 and 13 the initial NH_3 loss was found to be higher for the separated manure. On subsequent days (i.e. 2nd and 3rd), this pattern reversed and the separated manure was noticed to be significantly lower flux than the unseparated manure with $p<0.005$. These results as seen in Table 4.10 and Figure 4.10 would seem to indicate that initially the separated manure has a higher volatilization potential due to the fact that a greater percentage of its N is in the volatile liquid form. Since the manure is spread on an aerodynamically rough surface (turf grass) the more aqueous solution (i.e. separated manure) tends to attach itself to the surface for a short time where it may in turn, result in a greater initial NH_3 loss through volatilization. The unseparated manure, meanwhile, remains wet for a much longer period of time since its volatile liquid fraction seems to adhere to the solids in the manure before they are eventually drawn out; it therefore has low initial NH_3 losses.

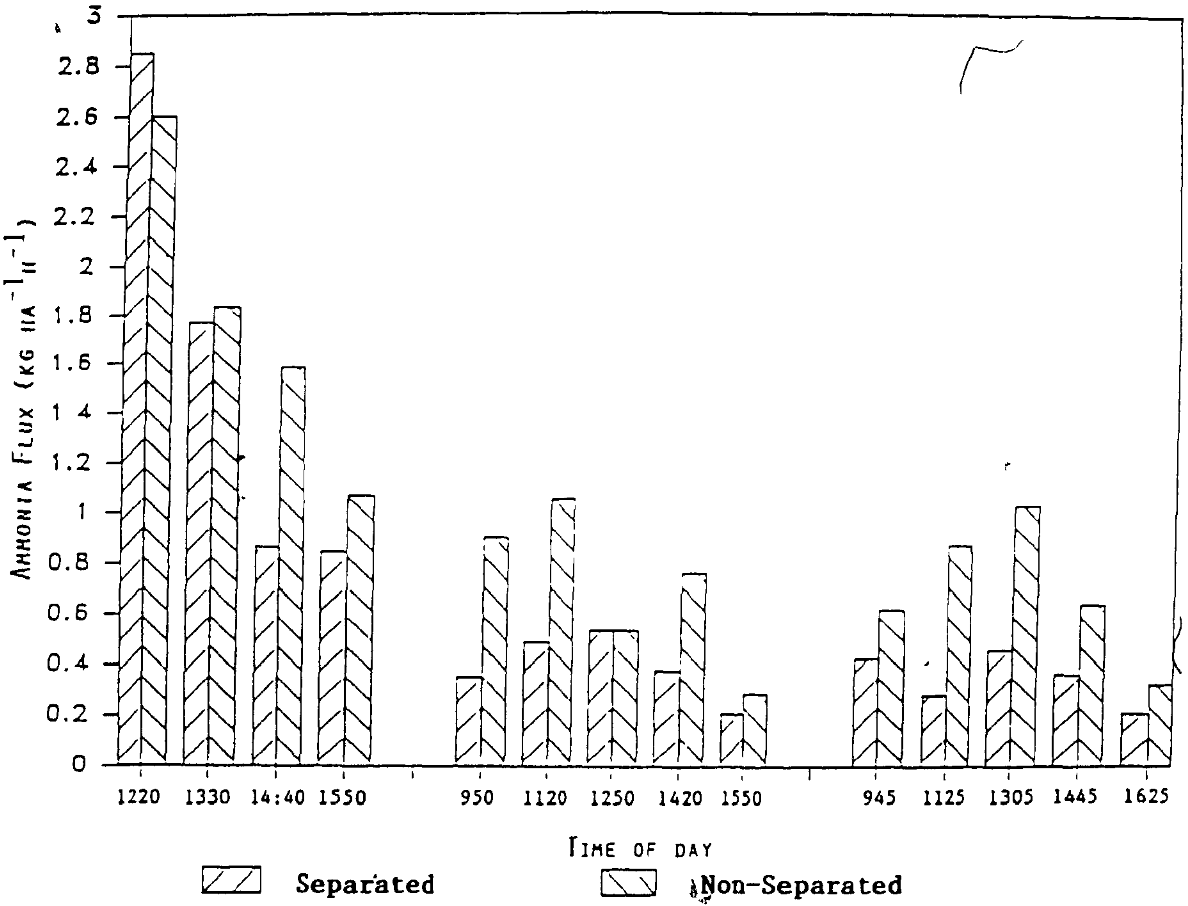

Figure 4.10 Ammonia Flux density for plots with separated and unseparated manure, for test 4 (October 29-31, 1985).

Table 4.10 Mean NH_3 flux densities (kg $ha^{-1}h^{-1}$) for days 2 and 3 for separated manure and unseparated manure tests.

Date	Separated	Unseparated	F-test
Oct 29-31/85	0.371	0.733	**
Nov 6-8/87	0.304	0.350	**

** significant at the 0.01 level

On later days (i.e. 2nd and 3rd) the separated manure may have moved into the soil and as a result the NH_4^+ may have been adsorbed by cation exchange while the unseparated manure may have been trapped on the surface of the turf grass and thus have been exposed to the natural environment for greater NH_3 losses. These findings are similar to those reported by Donovan and Logan (1983) who examined factors affecting NH_3 volatilization from sewage sludge applied in a laboratory study. They observed that volatilization from large sludge particles was generally greater than that encountered with homogenized sludge over a period of time. Their findings, however, were not determined as being statistically significantly different.

For test 13 the NH_3 fluxes for the separated manure were higher for every sampling run of the first day while for test 4 only the initial sampling run of the first day had a greater flux density. These differences in the first day observations of the two different tests may be due to the fact that for test 13 the average ambient air temperature was approximately -1.5 °C for the first day as compared to 7.2 °C for the first day of test 4. This lower air temperature may have inhibited the separated manure from moving into the soil as quickly for test 13 as test 4, thus resulting in a larger NH_3 loss over the first day.

4.6 Rainfall Simulation Experiments

In order to examine the relative effect of rainfall on the magnitude of NH_3 volatilization losses, two tests were conducted in September and October of 1986 and 1987. Considering the fact that all testing was conducted on rainfall free days, rainfall simulation had to be carried out. This was performed by wetting the selected plots with a conventional watering can. Prior to each sampling run (approximately every 2 h) water at a depth of precisely 2 mm was applied to the plots. This amount of water seemed to keep the manure at the soil surface quite wet during the entire sampling period while the unwetted plots appeared to be quite dry on the surface a few hours after spreading.

The mean flux density values are shown in Table 4.11. The initial sampling runs for each test were neglected in the calculation of the mean flux densities, since freshly spread manure was wet for both the wetted and unwetted plots. Therefore we waited for the manure to dry before any water was applied to the wetted plots. In both tests, watering was not performed until prior to the second sampling run of the first day. It can be seen from the results that the simulated rainfall slightly depressed the volatilization of NH_3, similar to the findings of Beauchamp et al. (1978 and 1982). The latter study found that NH_3 flux densities were lowered by rainfall but the diurnal air temperature cycle appeared to dictate the volatilization loss to a larger degree. Harper et al. (1983) and McInnes et al. (1986) reported minimum rainfall amounts in order to reduce NH_3 losses from surface applied urea. Harper et al. (1983) estimated that 5 mm of rainfall was required to prevent NH_3 losses from a tropical pasture while McInnes et al. (1986) stated that a rainfall event of at least 10 mm must occur in order for any reduction in NH_3 losses. Bouwmeester et al. (1985) remarked that interaction between NH_3 loss and rainfall is complex since rainfall may increase the loss potential, because it adds water to the topsoil, while at the same time reducing losses due to transport of ammoniacal-N into the soil.

Table 4.11 Mean NH_3 flux densities for wetted and unwetted manure plots (kg ha^{-1} h^{-1}).

Test	Date	Wetted	Unwetted	F-test
9	Sept. 15-18/86	0.441	0.467	ns
12	Oct. 8-10/87	0.329	0.405	ns

ns= not significant at the 0.05 level

Tests 9 and 12 showed differences between treated and untreated plots ranging from 5% to 18%. However, these differences are not statistically significant from either period-by-period measurements or by taking tests as an added variable. The possibility exists that if greater amounts of simulated rainfall had been applied to test plots (similar to those reported above), effects may have been more pronounced. Figure 4.11 shows the period-by-period measurements of the wetted and unwetted plots from test 9. In general, the diurnal pattern of flux magnitude is apparent and similar to the findings reported earlier in this study.

A possible explanation for the significantly low NH_3 flux values from the first day of sampling could be due to the fact that the average cup windspeed on that day was only 0.10 m s^{-1}. The mean cup windspeed on subsequent days was

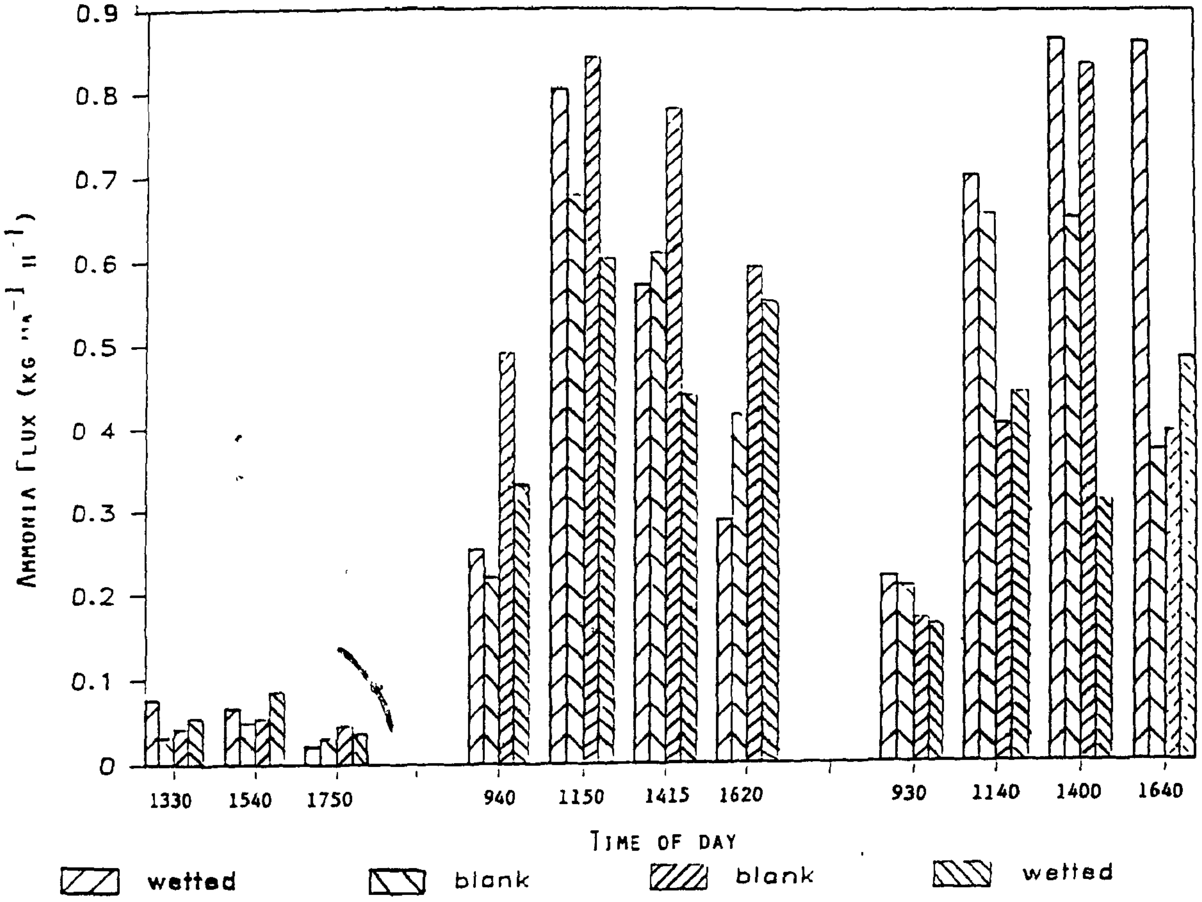

Figure 4.11 Ammonia Flux density for manure plots wetted and unwetted, from test 9 (Sept. 16-18, 1986).

>1.0 m s^{-1} which would account for the greater magnitude of losses due to the fact that NH_3 flux as observed by Brunke et al. (1988) is highly and positively correlated with windspeed.

4.7 Sensitivity Analysis

In order to examine the relative accuracy of results from the 7 m diameter circles, the possible contributions towards random sampling errors from experimental test procedures will be examined:

We estimate uncertainties in the vertical placement of sampling orifice during sampling periods and during replacement of silica gel tubes to have been as large as ±2.5 cm from the required sampling height of 12.5 cm above zero-displacement and roughness length. As seen in Figures 3.1 and 3.2, where the corresponding range of displacement has been indicated by vertical bars, this could lead to errors in flux estimates of 10 to 15%.

Generally the silica gel tubes were refrigerated and stored at 3 to 5 °C. Sample tubes were capped and sealed before storage and storage period was no longer than two weeks before chemical analysis. Thus, storage time was commensurate with the period (of at least 7 days) where NH_3 samples trapped by silica gel tubes are considered stable (NIOSH Manual, 1979).

Error in determination of absorbed NH_3 is suspected as a major source of random variation between plots of similar treatment. The calibration curve for the ammonia electrode has a slope (in the log-linear plot of concentration vs. electrode potential) of approximately a decade (10) per 50 mV. Using best-fit linear regression on measured points, deviations of up to 5 mV were observed between actual points and best-fit curve, corresponding to potential errors of up to 33%. Samples and standards must be kept at the same temperature since a 2% error may result from a one-degree difference in temperature.

The longer response time of the NH_3 electrode at lower concentrations may favor absorption of NH_3 from air; this is expected to be a minor error, however, and we could not quantify it.

It appears likely that the errors outlined above account for the observed variability in the volatilization estimates. As a consequence, analysis and calibration procedures are more crucial to data quality than they are for the larger circles where sampling height and absorbed concentrations are higher. Replicate standards should be used for recalibration every hour of reading. In this way it may well be possible to reduce considerably the fluctuations of the technique. The desirability of anemometers with low stalling speed for measurements close to the ground has already been pointed out if precise flux estimates are to be obtained in conditions of low wind.

5. CONCLUSIONS

The TSM model can be used on small (7 m diameter) test plots, making it attractive for comparative studies on effects of treatments on volatilization of NH_3 from manure under field conditions, as well as for other agriculturally important volatilization processes, such as the revolatilization of deposited pesticide. However, the potential is increased for systematic error (due to non-uniformity of applied dose or loss of wind data due to stalling of anemometers in low near-ground windspeeds) and for random error (in detection of NH_3 at low concentrations and due to incorrect placing of sampling orifice). With the experimental procedures followed in the present study, differences in volatilization rates of < 30% are difficult to detect from short-term sampling periods by statistical analysis, although they will still be observable in longer-term (several days) mean fluxes. Where absolute values of volatilization rates of NH_3 are to be compared at different times of year, uniformity of chemical, physical, and probably microbiological properties of manure prior to spreading should be assured to a higher degree than was done in the present study.

Application of the modified TSM-technique to the NH_3 volatilization from manure spread on sandy-loam under summer and fall field conditions with high soil moisture in Quebec showed reduction in mean volatilization rates between 5% and 30% resulting from the addition of mono-calcium phosphate (MCP) when MCP was added 6 days prior to spreading. Given the fact that this reduction seems low compared to comparative reported laboratory studies, further work on the effect of MCP under field conditions, under different climatic conditions, may be advisable before general conclusions about its effectiveness can be drawn.

NH_3 flux densities were found to be significantly different ($p < 0.05$) when 25%, 50%, 75% and 100% solutions of manure (on a per-volume basis) where applied to source plots. An approximate linear relationship ($r^2 = 0.95$) was observed to exist between mean first day NH_3 flux density and the corresponding applied dilution rate. This supports the assertion that NH_3 losses are dependent upon the amount of ammoniacal-N or total-N applied, particularily on the first day after spreading.

First day volatilization losses from separated manure were greater than those observed from unseparated manure. On subsequent days this pattern reversed and losses from unseparated manure were significantly higher ($p < 0.01$) probably due to the fact that solid manure particles prevented the rapid movement of the volatile liquid fraction into the soil.

Simulated rainfall plots (2 mm prior to each 2 h sampling run) appeared to reduce NH_3 losses by between 5% to 18% as compared to unwetted plots. Significant differences in their respective losses however, were not apparent ($p > 0.05$). A more extensive investigation into the amount of rainfall required to suppress volatilization of NH_3 to a significant degree must be conducted.

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