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DIVISION S-8—FERTILIZER TECHNOLOGY AND USE

A Direct Field Measurement of Ammonia Emission After Injection of Anhydrous Ammonia[1]

O. T. DENMEAD, J. R. SIMPSON, AND J. R. FRENEY[2]

ABSTRACT

Studies of the efficiency of applications of anhydrous ammonia fertilizer require a measurement of ammonia retention or loss at the time of application. Because of sampling problems, conventional measurements based on soil analysis are difficult to make in the field. A new method is described, based on calculating the aerial transport of ammonia across the downwind edge of the treated field from measurements of wind speed, wind direction, and atmospheric ammonia concentration. Ammonia losses as small as 1 kg N/ha can be easily detected. Maximum errors are reckoned at no more than 20%. In a field experiment in which anhydrous ammonia was applied at 107 kg N/ha, aerial sampling gave a loss of 1 kg N/ha. Soil sampling detected no loss because of a large sampling error (SE 15 kg N/ha).

Additional Index Words: nitrogen loss, fertilizer efficiency, atmospheric pollution.

LOSSES OF AMMONIA to the atmosphere during application of anhydrous ammonia are of concern not only from the economic viewpoint, but also because of their possible involvement in eutrophication of nearby water bodies (3) and in atmospheric chemistry (6). While there have been numerous laboratory and greenhouse studies on the retention of anhydrous ammonia by soils (5), there have been few field measurements of ammonia losses during anhydrous ammonia application. So far as we know, there has been only one previous attempt at direct field determination (1). Usually, retention, and by inference, loss, are measured by total nitrogen analysis of the soil. The method is tedious and subject to large errors because of sampling problems.

This paper describes an aerial sampling technique and its use for the direct determination of ammonia loss to the atmosphere during injection of anhydrous ammonia in the field. The method is based on measuring the aerial transport of emitted ammonia across the downwind edge of the treated area. In a field experiment, the loss calculated by this method was compared with the loss calculated by a conventional soil sampling technique. The experiment also provided information on the kinetics of ammonia emission.

METHODS

Micrometeorological

Ammonia escaping from the soil after injection is spread vertically by turbulent diffusion and convected horizontally by the wind. Consequently, the concentration of ammonia in the air downwind of the treated area is increased. For a steady wind direction, the net flux of ammonia convected from the treated area can be calculated, in the manner described below, from measurements of ammonia concentrations and wind speeds at the downwind edge of the field. Since reabsorption of the emitted ammonia is likely to be negligibly small, this flux of ammonia from the field can be equated with the loss from the soil surface.

The basis of the aerial flux calculation can be understood by considering a perpendicular plane normal to the wind at the downwind edge of the field. The rate of transport of ammonia across a unit area of the plane at height z, due to emission from the soil, will be the product $u(z)c(z)$, where u is horizontal wind speed and c is the ammonia concentration in excess of the background level. The mean rate of transport over a period of time will be $\overline{uc}$.

The instantaneous wind speeds and concentrations, u and c, can be represented as sums of means, $\bar{u}$ and $\bar{c}$, averaged over the same time period, and deviations from the means, u' and c', so that

$$\overline{uc} = \bar{u}\,\bar{c} + \overline{u'c'}. \qquad [1]$$

The first term on the right hand side of Eq. [1] represents the transport due to advection; the second, that due to horizontal diffusion. In micrometeorological treatments of this kind, it is usual to neglect the diffusion term because of its relative smallness (e.g., 7). Then $\overline{Q}$, the total mean flux of ammonia across a face of unit width in the plane, will be given by

$$\overline{Q} = \int_0^Z \bar{u}(z)\bar{c}(z)\,dz, \qquad [2]$$

where Z is the height of the air layer affected by the emission. Note that $\overline{Q}$ is also the net rate of emission per unit width of soil surface upwind of the edge.

Experimental

The experimental site was in a field of 160 ha near Narrabri, New South Wales. The soil is a heavy clay, of pH 8.2, low in organic matter (0.07% N) and at the time of injection it was very moist so that the disturbed soil did not fall back readily to cover the injection slit. These factors could be conducive to large losses of ammonia (5).

The injector bar, pulled by a tractor, held six tool shanks at 1-m spaces. Each shank carried a delta-wing foot which lifted the soil and allowed ammonia to be injected horizontally under it. The injection tube bifurcated at the shank, resulting in the placement of two bands of ammonia per delta-wing and an effective band spacing of 0.5 m. The mean injection depth was 12.4 cm. Ammonia was metered on at the rate of 107 kg N/ha.

The layout of the experiment is shown in Fig. 1. Cup-anemometers (Casella) and ammonia traps (2) were mounted on masts at heights of 0.31, 0.74, 1.24, and 2.24 m above the ground at the downwind edge of the field, midway along the track of the injection rig. Wind direction was also recorded by a wind vane. The rig was drawn up and down the field in traverses parallel to the downwind edge, working progressively away from the masts. The first injection band was 0.5 m upwind.

During each traverse, $\bar{u}$ and $\bar{c}$ were measured from the instant the rig passed the masts to the moment it returned to the same point, i.e., over the period for the rig to travel to the end of the field (500 m away) and back. The average time for such a traverse was 17 min. After four traverses, the rig was stopped, but the measurements were continued in 17-min sampling periods for the equivalent of three more traverse times.

To measure ammonia concentration, $\bar{c}$, air was drawn at approx-

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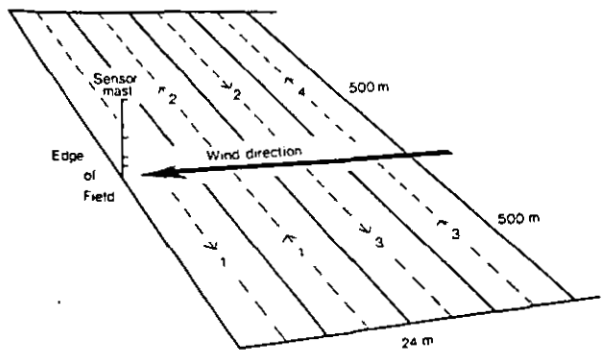

Fig. 1—Layout of experiment (not to scale). Dashed lines and arrows indicate direction of travel of injection rig. Numbers are traverse numbers.

imately 15 liters/min through acidified traps (2) via humidifiers containing 40 ml of 0.1*N* NaOH. At the end of the sampling period, the trapped ammonia was eluted with water and measured (2). [Experience has shown that humidifiers are necessary to reduce water loss (and consequent loss of efficiency) from the acid traps on warm, dry days.]

Previous tests showed that all the ammonia in an air sample was collected in one trap. The reproducibility of the measurements was examined by comparing ammonia concentrations measured with duplicate traps mounted at the same height. For 20 pairs of readings at an atmospheric ammonia concentration of 3.6 μg N/m^3, the mean difference between duplicates was 0.39 μg N/m^3, which indicates an uncertainty of approximately 10%.

Soil Sampling

The slits opened by the ammonia injection were marked on the soil surface and two steel plates, 30 by 40 cm, 5-cm apart, were driven into the ground, directly over and perpendicular to the direction of the slit. The isolated soil block was excavated and the center of the injection band was located using a pH indicator and a dusting of calcium sulphate (gypsum) on the soil surface. Four sampling rings of diameter 3.4, 7.3, 12.5, and 16.1 cm, were placed concentrically over the band center to give soil samples at known distances from it. Samples obtained in this way from 25 different positions across the field were dried, crushed, and analysed for total nitrogen by a micro-Kjeldahl method. Bulk density and soil water content were obtained on separate samples. The average volumetric soil moisture content was 0.34.

RESULTS

Micrometeorological

Table 1 lists the micrometeorological data for each sampling period, and Fig. 2 shows their general character. Notable features are the increased vertical dispersion of ammonia as the width of the treated area increased (compare, for instance, sampling periods 1 and 3 where *Z*, the height of the affected air layer, increased from approximately 1.6 to 2.5 m), and the fact that ammonia continued to be emitted for some time after injection was stopped (sampling periods 5 to 7).

To calculate the mean emission rates, $\bar{Q}$, plots of $\bar{u}\,\bar{c}$ vs. height, similar to those in Fig. 2, were drawn for each sampling period and the integrals in Eq. [2] determined by planimetry. This involved some extrapolation above and below the highest and lowest sampling positions, but the consequent errors are small because of the rapid decline in $\bar{c}$ at the higher levels and $\bar{u}$ at the lower. The integrated fluxes

Table 1—Micrometeorological data during the experiment.

Sampling period	Upwind distance treated	Mean wind direction†	Height, m: 0.31	0.74	1.24	2.24	0.31	0.74	1.24	2.24
			Mean wind speed				Mean NH_3-N concentration‡			
	m	degrees	m/sec				μg/m^3			
1	6	174	2.55	3.13	3.41	3.80	139	30	6	0
2	12	192	2.24	2.79	3.02	3.48	160	83	54	7
3	18	204	2.08	2.58	2.77	3.16	175	125	77	14
4	24	223	2.32	2.84	3.08	3.49	98	86	51	11
5	24	180	2.26	2.50	3.03	3.45	42	41	38	18
6	24	225	2.17	2.67	2.83	3.19	39	25	23	0
7	24	195	2.07	2.29	2.44	2.79	35	12	7	0

† A direction of 180° is normal to the edge of the field.
‡ The background concentration (during the experiment) of 3 μg/m^3 has been subtracted from these values.

were then corrected for variations in wind direction by dividing each by the cosine of the deviation of the mean wind direction in that sampling period from 180°. The corrected emission rates are shown in Fig. 3.

That emission continued for a time period longer than each traverse of the injection rig is evidenced by the increase in emission rate as the treated area increased (compare, for instance, the rate for sampling periods 2, 3, and 4 with that for the first period), and the continued emission in sampling periods 5 to 7, after injection had ceased. Thus the ammonia fluxes calculated for sampling periods after the first contained residuals from previous traverses, and it was necessary to calculate the time dependence of the emission in order to arrive at the total ammonia loss.

The character of the data in Fig. 3 and consideration of the probable dynamics of ammonia evolution following injection suggest a rate of emission which depends on the concentration of ammonia in the soil air spaces, and which consequently decreases exponentially with time. Accordingly, we have adopted a relationship of the type

$$\dot{q}(t) = q(o) \exp(-\lambda t) \qquad [3]$$

to describe the instantaneous emission rate from each injected band. In Eq. [3], q is the rate of emission per unit length of band, $q(o)$ being the initial rate, t is time, and λ is a rate constant. The mean emission rate $\bar{q}$ over the time τ of one complete traverse of the injection rig is then given by

$$\bar{q} = (1/\tau) \int_0^\tau q(t)\, dt = q(o)[1 - \exp(-\lambda\tau)]/\lambda\tau. \qquad [4]$$

If we designate the traverse number m and the sampling period n, so that $\bar{q}_{m,n}$ is the mean emission rate from each band injected in the mth traverse, in the nth sampling period, it follows that

$$\bar{q}_{1,1} = q(o)[1 - \exp(-\lambda\tau)]/\lambda\tau, \qquad [5]$$
$$\bar{q}_{1,7} = \bar{q}_{1,1} \exp(-6\lambda\tau)$$
$$\bar{q}_{2,2} = \bar{q}_{1,1}$$
$$\bar{q}_{2,7} = \bar{q}_{1,1} \exp(-5\lambda\tau)$$
$$\bar{q}_{m,n} = \bar{q}_{1,1} \exp[(m-n)\lambda\tau], \quad (m = 1, 4; n = 1, 7). \qquad [6]$$

Recalling that twelve bands are injected in each traverse, the mean emission from all bands in the nth sampling period, $\bar{Q}_n$, is then obtained by summing the appropriate $\bar{q}_{m,n}$, so that

$$\bar{Q}_n = 12\bar{q}_{1,1} \sum_{m=1}^{n} \exp[(m-n)\lambda\tau], \qquad (n \le 4): \quad [7]$$

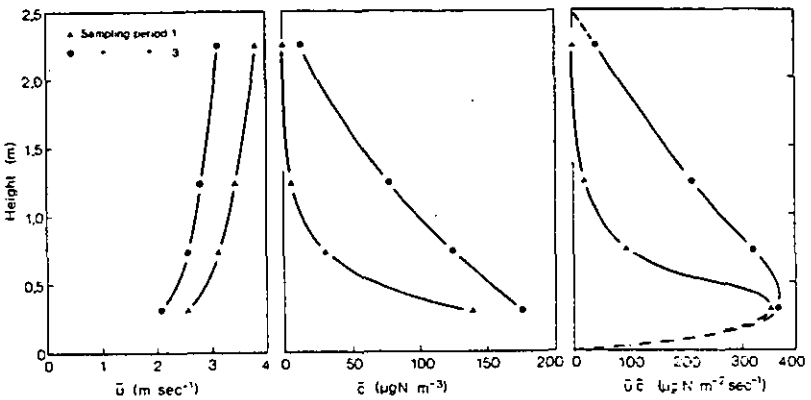

Fig. 2—Profiles of mean wind speed $\bar{u}$, mean atmospheric ammonia concentration $\bar{c}$, and horizontal flux density of ammonia $\overline{uc}$ in two periods.

and

$$\bar{Q}_n = 12\bar{q}_{1..3} \sum_{m=1}^{4} \exp[(m-n)\lambda\tau], \qquad (n \geq 5). \quad [7a]$$

Using Eq. [5], [6], and [7], we obtained those values of $q(o)$ and λ which gave the best least-squares fit to the data in Fig. 3. They were

$$\hat{q}(o) = 30.5\ \mu g\ m^{-1}\ sec^{-1},$$

and

$$\hat{\lambda} = 6.3 \times 10^{-4}\ sec^{-1}.$$

The curve in Fig. 3 is the emission calculated from these figures. The estimated time constant of the decay is 26 min. Ninety-nine percent of the ammonia emission from one band would occur in 122 min.

To complete the analysis, the total emission from each injected band, E, was obtained by integrating Eq. [3] with respect to time:

$$E = \int_0^\infty q(o)\exp(-\lambda t)\,dt = q(o)/\lambda. \qquad [8]$$

For the $\hat{q}(o)$ and $\hat{\lambda}$ above, the estimated total emission per band is 0.048 g/m, which represents a loss of 0.96 kg N/ha. Thus the estimated retention of nitrogen was 106 kg N/ha from an application of 107 kg N/ha.

Soil Sampling

The amount of ammonia retained per unit length of injection band was also determined from soil sampling and total N analysis. The ammonia remained in distinct bands even after 4 days. Of the applied nitrogen, 48% of the application remained within a ring of 7.3 cm diam, 86% remained within a 12.5-cm diam ring, and 100% within a 16.1-cm diam ring.

From soil analysis the recovery of ammonia was 106 kg N/ha (SE 15 kg N), which agrees extremely well with the result obtained by the aerial sampling technique, but because of the large SE, this good agreement can only be regarded as fortuitous.

DISCUSSION

For investigations of ammonia losses, and possibly other gaseous emissions, the aerial sampling technique described here has distinct advantages in terms of labor and accuracy over methods based on soil sampling. In this experiment, for instance, the aerial sampling and chemical analysis were completed in 2 hours, whereas the soil sampling alone required almost 2 days.

Some indication of the comparative sensitivities of the two methods can be obtained from sampling period 7 (Fig. 3), in which the mean rate of transport of ammonia across the edge of the field was 55 μg N m^{-1} sec^{-1} or approximately 0.02 kg N/ha over the whole period. The main errors in the aerial method are associated with the atmospheric ammonia concentrations and the graphical integration procedure. For the former, we estimate an uncertainty of approximately 10% (see Methods). The errors in the latter depend on how well the profiles of wind speed and ammonia concentration are defined: particularly, on how well they encompass the full height of the affected air layer. Allowing for an error of up to 10% in the procedure, the toal error is believed to lie between 10 and 20%. Thus in this example,

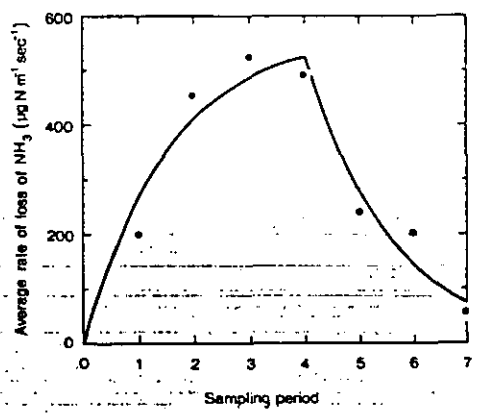

Fig. 3—Measured *(dots)* and calculated *(curve)* ammonia emission rates.

the uncertainty would be 0.004 kg N/ha. For the soil sampling, however, the uncertainty of ± 15 kg N/ha attached to the estimated loss, which is not inordinately large for the technique [c.f., 4, Table 1], indicates that such a sensitivity would be quite unattainable.

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Micronutrient Concentrations in Soil Solution After Ammonium Phosphate Applications[1]

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ABSTRACT

Two fluid ammonium polyphosphates, 11-17-0 (11-37-0 oxide basis), a commercial 10-15-0 (10-34-0), and an equimolar mixture of mono- and diammonium phosphate (MAP-DAP), each with a solution pH of about 6.2, were well mixed with 1-kg lots of several soils to supply 2,000 ppm of P, which approximates the P concentration in soil near a fertilizer band at a P rate of 50 kg/ha. Each soil was then moistened to 0.2 or 0.3 atm and stored in plastic bags. After periods up to 28 days, soil samples were placed in a lucite cell and a portion of the soil solution was expressed by N_2 gas. These solutions were analyzed for Cu, Fe, Mn, Zn, organic C, and total and orthophosphate P.

Micronutrient concentrations in solutions of acid soils were temporarily increased by both ortho- and polyphosphates. Increases were related in part to the amount of soil organic matter solubilized by these fertilizers. Organic C in solutions of treated soils increased in the order: MAP-DAP, 10-15-0, and 11-17-0, which was related to the original percentage of the total P in polyphosphate form (0, 50, and 78, respectively). Micronutrient concentrations in solutions of acid soils were highest during the first week and decreased to those in untreated soil by 28 days. Soluble micronutrient concentrations in neutral and calcareous soils were not affected by phosphate applications even after 1 day. Thus, solubilization of soil micronutrients by polyphosphates does not appear to play an important role in micronutrient nutrition of crops, especially in calcareous soils.

Phosphorus concentrations in soil solution generally were higher in soils treated with ortho- than with polyphosphates. Decreasing polyphosphate concentrations in solutions of polyphosphate-treated soils with time indicated hydrolysis and precipitation of water-soluble polyphosphates; less than 25% of the soluble P was in polyphosphate form after 2 weeks, with higher polyphosphate concentrations found in 11-17-0 than in 10-15-0 treated soils during the first 2 weeks after application.

Additional Index Words: polyphosphates, hydrolysis, sequestration, soil organic matter.

AMMONIUM polyphosphate (APP) fertilizers have rapidly gained in popularity in the past 15 years. They usually contain about one-half of their P in the orthophosphate form, and the remainder as pyrophosphates or longer chain molecules. Recent advances in pipe reactor technology have resulted in increased polyphosphate contents, but triammonium pyrophosphate, $(NH_4)_3HP_2O_7$, still remains the major nonorthophosphate compound in both solid and fluid ammonium polyphosphates. Polyphosphate fertilizers are water soluble and generally are used in clear liquids or suspensions.

Polyphosphates generally are considered equal to monoammonium phosphate (MAP) for early growth response (Terman and Engelstad, 1966). Rates of polyphosphate hydrolysis to orthophosphates are quite rapid in most agricultural soils. Gilliam and Sample (1968) reported 50% hydrolysis of applied pyrophosphates within 28 days after soil application; highest hydrolysis rates were on acid soils. Hashimoto and Wakefield (1974) reported hydrolysis half-lives of 4 to 13 days in three soils incubated at 25°C. Terman (1975) concluded that APP fertilizers were usually equal to comparable orthophosphates as sources of N for crops and of P after hydrolysis.

Miner and Kamprath (1971) reported equal effectiveness of granular superphosphate and APP for supplying P to field corn (*Zea mays* L.) on an acid soil in North Carolina. Adriano and Murphy (1970) reported that MAP and APP were equally effective for irrigated field corn on noncalcareous soils in Kansas adequate in available Zn. However, row-applied MAP was more effective than APP if Zn was limiting; greater P uptake from APP antagonized Zn uptake of corn under these soil conditions and resulted in poorer growth. Subbarao and Ellis (1975) reported equal effectiveness of granular APP and diammonium phosphate (DAP) for corn on a neutral (pH 6.8) and calcareous (pH 8.2) soil in a growth chamber study.

Differential effectiveness of ortho- and polyphosphate fertilizers in some calcareous soils has been attributed by some workers to the effects of polyphosphates on micronutrient availability. Singh and Dartigues (1970) stated that

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