COMPARISON OF FOUR METHODS OF MEASURING VOLATILIZATION LOSSES OF NITROGEN FOLLOWING UREA FERTILIZATION OF FOREST SOILS

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Four methods were compared for measuring ammonia volatilization losses following urea application (220 kg N/ha) to a forest soil from Vancouver Island: (i) closed-static, (ii) semi-open, (iii) 15N-balance, and (iv) closed-dynamic. The first three methods were used in the field; the fourth in the laboratory. In addition, the effects of two levels of simulated rainfall were assessed with methods ii, iii and iv. Significantly greater (P≤0.05) amounts of volatile ammonia were measured by each of the following three methods in the order: closed-static (13%) < semi-open (17%) < closed-dynamic (22–26%). The 15N-balance method measured 35–42%, but these values could not be compared directly with the other three methods, because it measures losses from gases other than ammonia alone. The simulated 12-mm rainfall significantly (P≤0.05) decreased ammonia losses, but did not change the relationship among methods: semi-open < closed-dynamic < 15N-balance for 9, 12 and 22%, respectively. Since estimated ammonia losses (i.e. total minus other gases) in open microplots with 15N-urea approximated that obtained by the closed-dynamic method, the latter gives a more representative estimate of ammonia losses than the semi-open or closed-static systems. Losses from nitrogen oxides (NO and NO₂), measured by the closed-dynamic method, were less than 1% of the applied fertilizer, while unaccountable losses by the 15N-balance method approached 23%. This suggests that losses as di-nitrogen (N₂) and nitrous oxide (N₂O), following urea application to forests, might be more important than is usually recognized. Significant differences in ammonia recovery by the closed-dynamic method from non-tracer (standard) granules and 15N-enriched granules (26 vs. 22%) was unexpected. Further research is warranted to determine the effects of re-processing techniques used to enrich the 15N content of urea.

On a comparé quatre méthodes pour mesurer les déperditions d’ammoniac par volatilisation suite à l’application d’urée (220 kg/N/ha) à un sol forestier sur l’île Vancouver: (i) fermée-statique, (ii) semi-ouverte, (iii) 15N-équilibrée, et (iv) fermée-dynamique. Les trois premières méthodes ont été employées sur le terrain et la quatrième en laboratoire. En plus, on a évalué avec les méthodes ii, iii et iv les effets de deux niveaux de précipitation simulée. Des quantités significativement plus grandes (P≤0.05) d’ammoniac volatil ont été mesurées au moyen des trois méthodes suivantes dans l’ordre: fermée-statique (13%) semi-ouverte (17%) fermée-dynamique (22–26%). La méthode 15N-équilibrée a accusé une mesure de 35–42%, mais ces valeurs ne pouvaient se comparer directement aux trois autres, vu qu’elle mesure les déperditions de gaz autres que l’ammoniac seul. La précipitation simulée de 12 mm de pluie a diminué sensiblement (P≤0.05) les déperditions d’ammoniac, sans modifier le rapport entre les méthodes: semi-ouverte < fermée-dynamique < 15N-équilibrée.

When urea fertilizer is added to forest soil, it is usually hydrolyzed to ammonium carbonate by soil urease. The rapid accumulation of ammonium and ammonia and a corresponding rise in pH lead to gaseous loss of fertilizer nitrogen as ammonia. There is some agreement concerning the qualitative effect of certain climatic and soil factors on volatile ammonia losses from urea fertilizer (Wollum and Davey 1975), but estimates of the magnitude of ammonia loss vary widely. Losses from forest soils have commonly been reported as being less than 5% (Overrein 1968, 1969, 1972; Volk 1970; Mahendrappa and Ogden 1973; Marshall and McMullan 1976) to more than 20% and as high as 40% (Bhure 1970; Watkins et al. 1972; Nömmik 1973a).

Much less is known with respect to factors affecting, or the magnitude of, losses for other nitrogenous gases. Recently, there have been reports and considerable speculation regarding gaseous losses of di-nitrogen (N₂), nitrous oxide (N₂O), and various nitrogen oxides (NOₓ) from fertilized soils (Knowles 1975; Focht and Stolzy 1978; Ryden et al. 1979).

Methods used by workers to detect gaseous ammonia losses are of four main types. Three of these contain acid sorbers for trapping ammonia but differ in the extent and mechanisms by which ammonia and other gases may move from the soil to the atmosphere: (i) closed-static systems (Volk 1970; Crane 1972) which restrict exchange with the atmosphere, thereby creating a closed ammonia sink; (ii) semi-open systems which permit exchange with the atmosphere via diffusion (Carrier and Bernier 1971; Nömmik 1973b), and (iii) closed-dynamic systems in which ammonia and other gases are removed from the soil surface by sweep air bubbled through an ammonia trap (Watkins et al. 1972). The fourth type involves use of ¹⁵N-enriched urea to assess fertilizer nitrogen balances; amounts that cannot be accounted for in known pools are attributed to gaseous losses, presumed to be mainly ammonia (Nömmik 1973a). In general, methods involving diffusion in closed-static systems have led to lower estimates of ammonia loss than have methods using semi-open systems, closed-dynamic or ¹⁵N-balances. This suggests that differences in results may be due partly to differences in research methodology.

The present study compares gaseous losses detected in the field by closed-static (Volk 1970), semi-open (Nömmik 1973b), ¹⁵N-balance methods, and in the laboratory by the closed-dynamic method (Watkins et al. 1972). Secondary objectives of the study were: (i) to determine the proportion of ammonia loss coming from the fertilizer as opposed to native soil nitrogen; (ii) to examine the effect of rainfall on gaseous losses, and (iii) to assess the possibility that nitrogen gases other than ammonia may be important components of volatilization losses.
MATERIALS AND METHODS

Characteristics of Study Area

The field experiment was conducted in a 50-yr-old Douglas fir (Pseudotsuga menziesii (Mirb.) Franco) stand with dominant tree height of 26 m. The site was situated near Sooke on Southern Vancouver Island (48°23'N, 123°43'W). Experimental plots were on a gently sloping terrace with a northerly aspect, west of De Mamiel Creek. The vegetation was typical of the Strait of Georgia Section (C1) of the Coastal Forest Region (Rowe 1972). Douglas fir had naturally regenerated, with a current stocking of 1531 stems/ha, including minor amounts of alder (Alnus rubra Bong.), western hemlock (Tsuga heterophylla (Raf.) Sarg.) and western red cedar (Thuja plicata Donn). Ground vegetation was composed mainly of swordfern (Polystichum munitum (Kaulf.) Presl.) and salal (Gaultheria shallon Pursh.).

Soils of the site are classified as an Orthic Dystric Brunisol derived from marine clay underlain by till. They are of the Fair Bridge complex with an Fe:Al ratio of 0.53:0.41 in the Bm1 horizon and a disrupted litter layer caused by earthworm activity. Some data on the chemical analysis of the soil are given in Table 1.

The climate is Cool Mediterranean (Köppen Csb) with about 1950 sunshine h/yr. Mean annual precipitation is 1000 mm, 78% of which falls between October and April. Mean daily temperatures are 4.3°C for January and 14.4°C for July.

Other environmental data are given in Fig. 1. The minimal wind speed for operation of the recording anemometer was 5 km/h and this was not exceeded during the observation period.

Plot Installation

The field techniques were similar to those of Nömmik (1973a,b). Microplots (186 cm²) were laterally isolated by steel-walled cylinders of 154 mm i.d. and of two depths (305 and 457 mm). The cylinders were driven into the soil by a pile driver, taking care not to disturb the natural stratification of the soil within the cylinders. Cylinders were installed 8 days before fertilization to permit equilibration of soil conditions. Plants within microplots were clipped at the soil surface. The cylinders protruded 2 cm above the soil surface for fitting the gas sorbers. Figure 1 gives some environmental data for the site during the observation period. Prior to plot establishment, weather conditions were drier.

<table>
<thead>
<tr>
<th>Soil horizon</th>
<th>Depth (cm)</th>
<th>C</th>
<th>N</th>
<th>C/N</th>
<th>OM</th>
<th>pH</th>
<th>Clay (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-H</td>
<td>0-14</td>
<td>10</td>
<td>36</td>
<td>3.8</td>
<td>0.22</td>
<td>18</td>
<td>38</td>
</tr>
<tr>
<td>Bm1</td>
<td>14-23</td>
<td>10</td>
<td>49</td>
<td>2.1</td>
<td>0.9</td>
<td>1.2</td>
<td>42</td>
</tr>
<tr>
<td>Bm2</td>
<td>23-40</td>
<td>5</td>
<td>49</td>
<td>0.5</td>
<td>0.4</td>
<td>0.0</td>
<td>47</td>
</tr>
<tr>
<td>BC1</td>
<td>40-60</td>
<td>4</td>
<td>38</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>47</td>
</tr>
<tr>
<td>BC2</td>
<td>60-70</td>
<td>3</td>
<td>38</td>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
<td>47</td>
</tr>
<tr>
<td>Till</td>
<td>70+</td>
<td>2</td>
<td>57</td>
<td>0.8</td>
<td>0.0</td>
<td>0.0</td>
<td>47</td>
</tr>
</tbody>
</table>

The soil: CaCl₂: 6 H₂O solution (0.01 M) ratio used for determining pH was 1:5 for the L-H horizons and 1:12 for mineral soil horizons.
than indicated by Fig. 1; therefore, the soils in the microplots were brought to field capacity by watering 24 h before fertilization.

### Experimental Design and Treatment

The experiment was laid out in two blocks within a 50 x 50-m area with microplots at least 45 cm apart. The first block of 20 microplots employed cylinders 305 mm deep and received no simulated rainfall. Four treatments were randomly assigned to five replicate microplots:

1. Control (unfertilized) with semi-open sorbers (modified from Nõmnik 1973b).
2. Fertilized (220 kg N/ha as standard Cominco forestry grade urea); closed-static sorbers (modified from Volk 1970).
3. Fertilized (220 kg N/ha as ^15N-enriched urea); semi-open sorbers.
4. Fertilized (220 kg N/ha as ^15N-enriched urea); no sorbers (open microplots).

The second block of 10 microplots, 10 m away, employed cylinders 457 mm deep and received 12 mm of simulated rainfall 96 h after fertilization. Two treatments, in five replications, were randomly assigned to the microplots:

1. Control (unfertilized) without sorbers.
2. Fertilized (220 kg N/ha as ^15N-enriched urea); semi-open sorbers.

Approximately seven urea fertilizer granules (410 mg of N) were uniformly placed on the surface of fertilized microplots in late October. All granules were 6 mm diam and contained 45.5% nitrogen: Unlabelled ones were Cominco forestry grade granules with formaldehyde (0.025% by weight) and coated with a kaolinite conditioner. Singly tagged ^15N-urea granules (2.826 atom percent) were prepared by combining appropriate proportions of labelled and unlabelled urea in a small beaker. The beaker was placed on a hot plate and granules were slowly heated to melting point (about 133°C). When melting was complete, the mixture was stirred thoroughly and immediately poured into 6-mm molds. The molds were coated with PAM® (a vegetable oil spray) to facilitate removal of the granules after cooling.

### Sorber Techniques

The two types of sorbers used in the field were modified from Nõmnik (1973b) (semi-open) and Volk (1970) (closed-static). The semi-open sorbers (Fig. 2) were made of a single plexiglas tube, 140 mm i.d. and 152 mm high. Polyfoam sorption pads were 26 mm thick and 140 mm diam and were held in place by a single 5 mm diam aluminum pin driven through the center of the plexiglas tube 47.5 and 115 cm from the bottom of the tube. This provided a sorption air-space of 770 mL. A 1-cm strip polyfoam gasket provided a tight fit between the sorbers and the steel cylinders. The closed-static sorbers (Fig. 2) were made of materials similar to the semi-open ones, but were 83 mm high and sealed, above a single sorption pad, by a sheet of plexiglas 7 mm thick. The sorption air-space was also 770 mL. Each microplot was protected from rain by an umbrella of polyvinyl sheeting, 47 cm diam, supported 35 cm above the ground. The umbrellas were tilted about 15° to deflect rain. Ammonia was sampled at 24-h intervals for the first 15 days, at day 17 (one 48-h interval), and then at 72-h intervals until the 41st day after fertilization. Sorption pads were thoroughly cleaned with three rinses of 150 mL of distilled water and were prepared for ammonia sorption as follows. They were placed in 150-mm Buchner funnels attached to 0.5 atmosphere vacuum, saturated with a...
Fig. 2. Apparatus used in the field for trapping ammonia volatilized from urea fertilizer: (a) semi-open sorber, (b) closed-static sorber, (c) umbrella over sorber.

50-mL solution of 2.2 N H₃PO₄ and 25 mL of glycerine, and allowed to drain until they contained about 25 mL of the acid-glycerine solution. The pads were then placed in airtight containers for transport to the field, where they were removed from the containers and quickly inserted into the plexiglas holders, which were then placed into the cylinders of the microplots. At prescribed intervals, ammonia-free pads were quickly exchanged with the exposed pads, which were returned in the airtight containers to the laboratory for ammonia extraction.

**Analytical Procedures**

**GASEOUS AMMONIA.** Exposed sorption pads were alternately rinsed and squeezed dry three times with approximately 150 mL of distilled water and the extract was made up to a volume of 500 mL with more distilled water. Duplicate 25-mL aliquots of this solution were used to determine ammonia-N. The extract was distilled with 20 mL of 60 g/L N-free NaOH, collected in saturated boric acid and back-titrated with 0.05 N H₂SO₄ to calculate the milligrams of ammonia-N; ¹⁵N samples were condensed for N-isotope-ratio analysis by mass spectrometry.

**SOIL SAMPLES.** The cylinders were removed from the field on the 42nd day following fertilization. In the laboratory, the soil columns from 0-mm rainfall plots were divided into organic (L, F, H)
and 0–5, 5–10, 10–20 and 20–25 cm of the mineral horizons. The microplots that received the 12-mm simulated precipitation (cylinders 457 mm deep) were similarly sectioned, but the deeper layers were divided at 20–30 and 30–35 cm of the mineral horizons. Sections were air-dried at 20°C and 40% relative humidity for 10 days. The organic layers were ground to pass a 0.08-mm sieve; the mineral soil was screened by a 2-mm sieve. Roots greater than 2 mm were ground, screened by a 0.08-mm sieve and thoroughly mixed with the screened soil for nitrogen analysis. Representative samples of each section were oven-dried (105°C) to calculate moisture content. The nitrogen was determined by the Kjeldahl method (McMullan 1971), but with increased sample size (0.5 g for organic layers and 5 g for mineral soil) and with certain modifications to prevent contamination of the samples prior to 15N analysis and to increase the amount of nitrogen available for analysis (Bremner 1965; Bremner and Edwards 1965).

15N-ANALYSIS. The 15N content of duplicate samples was determined with a Varian GD 150 double collector mass spectrometer, using dry air as a standard.

Laboratory Experiment (Closed-Dynamic Method)

APPARATUS AND GAS TRAPS. Twenty-five undis­turbed soil cores (153 mm diam × 305 mm deep) were collected from the area of the field study (Sooke site) with a cylindrical soil sampling unit. Each soil core was contained in a plexiglas cylinder having an air space, 152 mm in height, above the soil surface. After transport to the laboratory, the soil cylinders were placed in the apparatus described by Watkins et al. (1972), but with the following changes. Sweep air leaving the soil chambers was divided into two streams. A relatively small portion (about 150 mL/min) was passed through a series of traps: (1) an acid trap containing 0.1 N H2SO4 for collection of ammonia (some nitrogen dioxide, and nitric oxide was also captured), (2) a subsequent trap containing 0.1 N NaOH and 3% H2O2 for collection of the remaining nitrogen dioxide and nitric oxide, and (3) a third trap containing water which scrubbed acids and bases from the air stream prior to passage through the valves and vacuum manifold. The remainder of the air was directed through the vacuum manifold.

TREATMENTS. Three fertilizer-rainfall treat-
mements, each replicated five times, were imposed upon the soil cores: (i) 15N-enriched urea with no rainfall, (ii) standard Cominco forestry grade urea with no rainfall, and (iii) 15N-enriched urea with 12-mm simulated rainfall 96 h after fertilization. The dosage level was common to all fertilizer treatments and was equivalent to 220 kg N/ha. Unfertilized soil cores, with and without simulated rainfall, served as controls.

Other conditions were similar for all cores and were adjusted to approximate conditions in the field. Soil and air temperature was maintained at 5°C; relative humidity at 90%, and air flow rate at 3 L/min (<0.1 km/h).

GAS SAMPLING AND ANALYSIS. Trapping solutions were changed daily and analyzed for ammonia (Berthelot reaction) and nitrates plus nitrites (hydrazine reduction) by a Technicon Auto-analyzer. Total amounts of ammonia-N and nitrogen oxide-N (NO plus NO2) evolved were calculated from the amounts trapped (mg in trap × mL/min total air flow) divided by the portion of total air (mL/min) that passed through the trap. Daily values were expressed as a percentage of fertilizer nitrogen applied.

Statistical Analysis

An analysis of variance, using a completely random design, was carried out separately on data from the field and from the laboratory experiments. For a comparison of methods for measuring volatilized ammonia (closed-static, semi-open and closed-dynamic), data from the field and laboratory were also analyzed together as a completely random design. The 15N-balance method was omitted from the latter analysis, because it gives losses of other gases in addition to ammonia. Significance of each mean difference was determined by Student-Newman-Keuls’ multiple range test (Steel and Torrie 1960). Except where otherwise stated, significance is for \( P \leq 0.01 \).

RESULTS

Field Experiments

AMMONIA LOSSES VIA CLOSED-STATIC AND SEMI-OPEN METHODS. Daily losses of volatilized ammonia as determined by closed-static and semi-open sorption methods are shown in Fig. 3. The background level of ammonia, as measured in unfertilized plots with semi-open sorbers,
never exceeded 0.2 mg N per plot per day and totalled only 1.3 mg N per plot for the 41-day observation period. Differences in daily amounts of ammonia from control microplots with and without simulated rainfall were insignificant. Daily values were therefore averaged for Fig. 3. More than 80% of ammonia losses from fertilized plots occurred during the first 15 days. Peak loss for plots, with semi-open sorbers and receiving 12-mm simulated rainfall, was evident on the 5th day, whereas peak loss for plots with closed-static and semi-open sorbers having no rainfall occurred near the 7th day. Losses were minimal after the 15th day and continued to decrease gradually, almost reaching background level by the 41st day. Although similar patterns of ammonia evolution were detected in both closed-static and semi-open sorbers, the magnitude of losses differed significantly. For plots receiving no rainfall, semi-open sorbers trapped 18% of the applied nitrogen, whereas only 14% was captured as ammonia.
by the closed-static method (Fig. 4). Simulated rainfall (12 mm) applied 96 h after urea application significantly reduced ammonia loss to one-half (9%) of that detected by semi-open sorbers without rainfall.

**AMMONIA FROM FERTILIZER.** Isotope ratio analysis of ammonia captured by semi-open sorbers provided the percentage of nitrogen that came from the fertilizer as opposed to that from native soil nitrogen (Fig. 5). The proportion of daily nitrogen losses derived from fertilizer showed a similar trend for plots with and without simulated rainfall. Between the 2nd and 10th days after urea application, when most of the gaseous losses occurred, more than 80% of the volatilized ammonia came from fertilizer. The proportion gradually decreased thereafter, and was 66 and 56% on the 41st day for no rain and rainfall treatments, respectively. Application of percentage relationships shown in Fig. 5 to daily loss data for the 41-day period revealed that 88% of the ammonia volatilized from plots receiving no rainfall came from the fertilizer. A slightly lower proportion (82%) was derived from fertilizer in the plots receiving rainfall.

**GASEOUS LOSSES VIA 15N-BALANCE METHOD.** Results of isotope ratio analysis of soil components and trapped ammonia are presented in Table 2. There was a trend for increased retention of applied nitrogen in the soil as follows: open microplots with 0-mm rainfall < microplots with semi-open sorbers and 0-mm rainfall < microplots with semi-open sorbers and 12-mm rainfall. However, all means were not separated statistically. Only 57.7% of the fertilizer nitrogen applied to open microplots remained in the soil profile after 41 days. Eighty-seven percent of this (57.7% of applied N) is contained in the organic horizons (L, F, H), and nearly 8% is found in the 0–10 cm layer of the mineral horizons.

Amounts of fertilizer nitrogen detected below 20 cm were insignificant (less than 0.01%). Placement of semi-open sorbers over the plots resulted in retention of somewhat higher amounts of fertilizer nitrogen in the organic and 0–5 cm mineral layer; the soil contained 64.7% of the applied nitrogen and another 15.8% was detected as ammonia loss. Nearly 20% of fertilizer applied to plots covered by semi-open sorbers remained unaccounted for. Microplots with semi-open sorbers receiving rainfall showed a somewhat greater downward movement of applied nitrogen into the soil profile. Only 7.4% was captured as ammonia; thus approximately 14% was unaccounted for.

**Laboratory Experiment (Closed-Dynamic Method)**

**AMMONIA LOSSES.** Daily losses of volatile ammonia are shown in Fig. 6. Background levels of ammonia detected in control cores showed minor changes during the 24-day observation period, but never exceeded 0.7 mg N per core per day. Since differences in daily amounts of ammonia volatilized from control microplots with and without rainfall were insignificant, values were averaged for Fig. 6. As in the field experiment, most (88–95%) of the ammonia losses occurred during the first 15 days. Rainfall simulated
Fig. 5. Volatile ammonia originating from $^{15}$N-enriched urea applied in the field and measured with semi-open sorbers.

96 h after urea application again significantly reduced volatility losses to about half of the no-rainfall treatment (Fig. 7). Rather surprisingly, total losses from standard Cominco forestry grade urea were significantly higher than losses from reprocessed $^{15}$N-enriched urea granules.

NITROGEN OXIDE LOSSES. The cumulated total of nitrogen oxide gases (NO plus NO$_2$) was less than 1% of the applied nitrogen in all three treatments (Fig. 8). Although curves for standard Cominco granules and $^{15}$N-enriched granules with rainfall are closely associated and separated from the

<table>
<thead>
<tr>
<th>Component</th>
<th>Open (0 rain)</th>
<th>Semi-open (0 rain)</th>
<th>Semi-open (12 mm rain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>50.1</td>
<td>54.3</td>
<td>65.7</td>
</tr>
<tr>
<td>Organic (L-H)</td>
<td>7.3</td>
<td>10.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Mineral</td>
<td>0.2</td>
<td>0.2</td>
<td>4.7</td>
</tr>
<tr>
<td>0-5 cm</td>
<td>0.1</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>5-10 cm</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>10-20 cm</td>
<td>$^\dagger$</td>
<td>$-$</td>
<td>0.1</td>
</tr>
<tr>
<td>20-25 cm</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>25-30 cm</td>
<td>57.7 $^a$</td>
<td>64.7 $^{ab}$</td>
<td>78.5 $^b$</td>
</tr>
<tr>
<td>Total soil</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Ammonia loss</td>
<td>$-$</td>
<td>15.8</td>
<td>7.4</td>
</tr>
<tr>
<td>Unaccounted for losses</td>
<td>$-$</td>
<td>19.6</td>
<td>14.1</td>
</tr>
<tr>
<td>Total losses</td>
<td>42.3</td>
<td>35.3</td>
<td>21.5</td>
</tr>
</tbody>
</table>

$^\dagger$Indicates that no measurement was made for component.

$^a,b$ Total soil values followed by the same letter are not significantly different (P<0.01).
Fig. 7. Cumulative net volatile ammonia in the laboratory, measured by the closed-dynamic method with non-tracer and $^{15}\text{N}$-enriched urea.

Fig. 8. Cumulative net volatile NO$_x$ gases (NO plus NO$_2$) in the laboratory, measured by the closed-dynamic method with non-tracer and $^{15}\text{N}$-enriched urea.

$^{15}\text{N}$-enriched granules receiving no rainfall, differences among the treatments in total NO$_x$ volatilized are not significant.

**Comparison of Methods**

Total gaseous losses for the four basic methods (including $^{15}\text{N}$-balance method with sorbers and closed-dynamic method
Table 3. Comparison of gaseous loss detected by the four methods; values expressed as percent of applied N volatilized (%ANV) and coefficient of variation (CV%)

<table>
<thead>
<tr>
<th>Method and type of granule</th>
<th>Days after urea application</th>
<th>0 mm</th>
<th>12 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Closed-static, standard granule</td>
<td>24</td>
<td>13.1</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>10.4</td>
<td>12.6</td>
</tr>
<tr>
<td>II. Semi-open, reprocessed 15N-enriched granule</td>
<td>24</td>
<td>16.7</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>15.7</td>
<td>13.9</td>
</tr>
<tr>
<td>III. Closed-dynamic, standard granule</td>
<td>24</td>
<td>26.0</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>11.5</td>
<td>10.0</td>
</tr>
<tr>
<td>IV. Nitrogen (15N) balance with semi-open sorber</td>
<td>41</td>
<td>35.3</td>
<td>42.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.2</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.1</td>
<td>21.5</td>
</tr>
</tbody>
</table>

†Closed-static, semi-open and closed-dynamic methods as reported here measure only gaseous ammonia loss; 15N-balance method is presumed to estimate all gaseous losses.
‡Indicates that no measurement was taken in that treatment.

with standard granules) are listed in Table 3. Analysis of variance for methods that measured ammonia losses for 24 days, with 0-mm simulated rainfall, showed that significantly (P≤0.05) greater amounts of volatile ammonia were measured in the order: closed-static < semi-open < closed-dynamic method. In the closed-dynamic method, ammonia losses from reprocessed, 15N-enriched granules were about 16% (21.9% vs. 26.0%) lower than losses from standard urea granules. Fertilizer unaccounted for by the 15N-balance method and presumed to represent gaseous losses was substantially higher than ammonia losses detected by any other method. Presence of a semi-open sorber on the 15N-balance plots reduced such losses from 42.3 to 35.3% of the applied nitrogen fertilizer, but this difference was not statistically significant. Although addition of rainfall in selected methods decreased losses markedly, the same general trend prevailed (semi-open < closed-dynamic < 15N-balance). However, the 24-day values of 8.5 and 12.4% for the semi-open and closed-dynamic methods, respectively, were not significantly different.

The coefficient of variation (CV) was generally higher with the simulated rainfall treatments, but it was very similar for all methods receiving 0-mm rainfall. The latter data suggest that none of the methods was clearly superior in precision for measuring volatilized ammonia.

DISCUSSION

Effect of Urea Reprocessing for 15N Enrichment

The significant difference in ammonia recovery by the closed-dynamic method for standard (14N) Cominco granules and reprocessed 15N-enriched granules was unanticipated and is inexplicable. Although differences could be associated with labelling per se (i.e. 15N material volatizing at a slower rate), the melting and molding needed to accomplish 15N-enriched forestry grade granules may also be involved. Since standard granules were used with the closed-static sorbers in our field experiment, differences in NH3 losses estimated by the
closed-static and semi-open methods are probably less than would have been the case had the same type of granules been used with both methods. Other workers may also be faced with this problem; thus research is needed to explain the effects and determine the significance of re-processing techniques used to enrich the $^{15}$N-content of urea granules.

**Effect of Simulated Rainfall**

The large reduction in ammonia loss associated with application of 12 mm simulated rainfall, as opposed to 0 mm rainfall, was similar for the semi-open, closed-dynamic, and $^{15}$N-balance methods. This finding corroborates earlier reports of substantial reductions in volatility losses if minimal rainfall occurs soon after fertilizer is applied (Crane 1972; Carrier and Bernier 1976). These reduced losses are associated with movement of urea (and products of its hydrolysis) from the ground surface into the forest floor and upper mineral soil horizons. Such movement would decrease ammonia concentration and thereby lessen the initial rise in soil pH that accompanies urea application. Moreover, a wide and more uniform distribution of soil-forest floor matrix should enhance adsorption on exchange sites.

Most of the volatilized ammonia came directly from the fertilizer, as opposed to native soil nitrogen, irrespective of the rainfall treatment. Nevertheless, the high evolution of ammonia during the first 7 days after urea application and the 50% reduction of such losses with 12-mm simulated rainfall give support to the current practice of applying urea in the Douglas Fir Region only during the rainy season (late fall and early spring).

**Efficiency of Methods**

Previous experiments on volatilization from urea fertilizer applied in Douglas fir forests have estimated gaseous losses ranging from below 5% (Crane 1972) to 25% or more (Watkins et al. 1972). It has been established that gaseous loss can be affected by many factors, including air movement, temperature, soil acidity (Watkins et al. 1972), form and rate of nitrogen application (Volk 1970; Carrier and Bernier 1976; Musa 1968; Overrein 1972), and previous history of soil fertilization (unpublished data on file at Forestry Sciences Laboratory, Olympia, Washington).

Such factors undoubtedly account for some of the variance in estimated losses, but Watkins and his co-workers (1972) hypothesized that differences in research technique may also be involved. Results of the present experiment, conducted under identical (or nearly so) soil, fertilizer application and climate conditions support the suggestion that discrepancies in estimated gaseous losses are indeed due in part to experimental methods.

Lowest ammonia losses were estimated in the field experiments by two similar methods (closed-static and semi-open) which restricted air flow. Movement of ammonia from the soil surface to sorbers in these methods was solely dependent upon diffusion. Losses estimated by the semi-open technique (18.0%) were 25% greater than those measured by the closed-static method (14.3%). Significant differences in amounts of ammonia trapped by these two methods may have been due to the capacity for water vapor to diffuse to the atmosphere from the semi-open sorber. Such movement probably would have increased drying rate and therefore volatilization loss; also, the acid sorbers would have scrubbed the hydrophilic ammonia from water vapor passing through them. Ammonia losses estimated by the closed-dynamic method (21.9%) were significantly ($P \leq 0.05$) higher than losses determined in the field by semi-open sorbers (16.7%) with the same fertilizer (reprocessed $^{15}$N-enriched granules) and no rainfall. The slightly higher losses probably result from mass movement of air and also perhaps from increased efficiency of ammonia trapping methods.
In open microplots of the $^{15}$N-balance method, only about 58% of the added nitrogen was recovered from the soil after 41 days. Thus, 42% of the fertilizer nitrogen was unaccounted for. Microplots covered with semi-open sorbers (with and without simulated rainfall) had somewhat higher amounts of fertilizer nitrogen retained in the soil, but 22–35% was lost in some way. Sorbers in the latter microplots, however, trapped 7–16% of the applied nitrogen. If a similar ratio of ammonia loss to unaccounted-for loss is assumed for the open microplots, ammonia loss from fertilizer would be estimated at 19% and other unaccounted for losses at about 23%.

The failure of the $^{15}$N-balance sheet to approach 100% is not likely due to plant uptake, leaching, soil sampling, sorption, or isotopic interchange. All aboveground vegetation in the microplots was clipped before fertilizer was applied and remaining roots were ground and analyzed with forest floor and mineral soil samples. Leaching losses must also be discounted because microplots were protected from rain and even in simulated rainfall treatments less than 1% of applied nitrogen reached the 20–30 cm layer. Neither does soil sampling appear to be a major source of error. The litter was milled and the screened soil was thoroughly mixed for aliquot sampling, a method that has proven successful under other conditions (Carter et al. 1967). Small ammonia gains during air drying of the soil samples would not have affected the results (Nelson and Bremner 1972). Losses from nitrate, which was not included in the soil analysis, are usually an insignificant amount of the total soil nitrogen (Roberge and Knowles 1966; Allen et al. 1973; Heilman 1974). The capacity of the sorbers was adequate because less than 3% of their capacity was utilized by the maximum ammonia evolution for a given collection period. Also, the top pad (sorber I, Fig. 2) did not exceed the background level of nitrogen, indicating that the ammonia-collecting pad nearest to the soil (sorber II) was never saturated. However, little is known about the equilibrium that is established between the phosphoric acid in the sorption pads and the humid air trapped between the pad and the soil surface. If the humid air contained appreciable amounts of ammonia, this ammonia would be lost during the frequent switching of exposed pads for fresh ammonia-free pads. Under our conditions, major biological interchange seemed unlikely. The difference between background nitrogen of the check plots (1.3 mg per plot for 41 days) and that from native nitrogen of the fertilized plots (8.5 mg) could have resulted from cation exchange or isotope exchange. Assuming that the 7.2 mg was all due to isotope exchange, it would account for less than 2% of the 410 mg applied and would not significantly affect the balance sheet. If this is taken as a measure of direct isotope exchange, the underestimate in the gaseous losses as ammonia should be over-compensated for by a higher $^{15}$N-content in the soil.

Conversely, it seems most plausible that volatilization loss of nitrogen in forms other than ammonia is an important factor. Although Hüser (1969) and Kundler (1970) suggested that nitrogen oxide losses may exceed ammonia losses in certain instances, low recovery of NO$_x$ gases in the laboratory lysimeter (less than 1% of applied N) indicated that such loss was not in the form of NO or NO$_2$. Significant gaseous loss as dinitrogen (N$_2$) or nitrous oxide (N$_2$O) is more probable (Stevenson et al. 1970; Cho and Sakdinan 1978; Christianson et al. 1979). Overrein (1972) could not account for 20% of the urea (250 kg N/ha) applied to the soil. Since this was applied as a solution, it is unlikely that much would be volatilized as ammonia; Overrein theorized that N$_2$ gas was important in such losses and the processes were probably related to spontaneously occurring chemical reactions between urea (or intermediate products from urea hydrolysis) and specific groups in the humic structure. Since we did account for NH$_3$ loss in two of three balance sheet treatments (Table 2), the indirect evidence
for significant N\(_2\) and/or N\(_2\)O losses appears rather cogent.

The open system is theoretically the technique that most closely approximates conditions under which gaseous losses occur in forest fertilizing operations. Because losses of other gases in addition to ammonia appear to be important and are included in estimates by this method, it cannot be compared directly with other methods which assess only ammonia losses. Let us, however, assume: (i) a ratio of ammonia loss to total loss (via balance sheet) similar to that obtained with the semi-open sorber with no rainfall, and (ii) a similar proportion of fertilizer nitrogen to total nitrogen (0.88) volatilizing as ammonia. Given such assumptions, ammonia volatilization loss in the open system is estimated at 21.6% of the applied nitrogen. This is nearly identical to the ammonia loss estimated in the laboratory by the closed-dynamic method (21.9%) and is higher than that determined by the semi-open sorber (18.0%). It therefore appears that ammonia losses estimated by the closed-dynamic method are more representative of ammonia losses under field conditions than those estimated by the other methods tested here.

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