ABSTRACT

It is important to know the fate of nitrogen (N) fertilizers to ensure crop production and avoid pollution, but frequent measurement of soil N is difficult. Therefore, we developed a digital model to calculate the occurrence, movement, and dissipation of nitrate-nitrogen (NO$_3^-$-N) within the soil profile of fertilized agricultural lands. Daily NO$_3^-$-N amounts and distributions within a 1.8-m soil profile were calculated by representing the major processes influencing NO$_3^-$-N for the entire year. Daily soil moisture amounts and movement were predicted by a previously developed soil moisture-evapotranspiration model.

Profiles of NO$_3^-$-N measured periodically on two research watersheds in western Iowa, one normally fertilized (168 kg/ha per year) and the other excessively fertilized (448 kg/ha per year) with N were used for model verification. The daily calculations for the fertilized cornfields (Zea mays L.) with moderately permeable soils included NO$_3^-$-N movement, dissipation, and profile leaching. The predicted NO$_3^-$-N profiles closely represented those measured.

Additional Index Words: nitrogen, leaching, uptake, mineralization, pollution, solute transport.

The movement of water and chemicals within the soil profile is quite complex, but highly important to agricultural production and the environment. Nitrogen fertilizers are usually required for optimum nonleguminous crop yields, but the high solubility of the nitrate ion (NO$_3^-$) allows it to leach and become a potential environmental contaminant. To understand how to maintain optimum NO$_3^-$-N in the soil for crop use while minimizing the pollution potential, we must understand the several sources and sinks of soil NO$_3^-$ and the space-time interaction of the controlling processes.

Most major processes of the N cycle within aerated agricultural soils are known and can be quantified. Many other processes usually play a minor role and often are less understood (Allison, 1965). The same can be said of water movement in soils. Frere (1973) described how NO$_3^-$ and water interact on the agricultural landscape, but accurate and comprehensive prediction methods of NO$_3^-$ movement and dissipation are not readily available.

Our objectives were to quantify the dissipation of N fertilizers applied to agricultural watersheds with permeable soils and high-yielding corn (Zea mays L.) Nitrogen transport by rainfall, runoff, and erosion was measured (Schuman et al., 1973; Schuman and Burwell, 1974) but to understand the movement and dissipation of N within the soil profile required an analytical approach because the required number of measurements was impractical. A digital model was developed to compute daily NO$_3^-$-N movement and distribution within a 1.8-m, well-aerated, soil profile. Major processes influencing soil NO$_3^-$-N were represented to allow full-year computations. Soil water movement and dissipation were computed with a model previously developed and described (Saxton et al., 1974). In this paper, we briefly describe the NO$_3^-$-N model representations and operation, show the model verification, and discuss the results and applications.

MODEL DESCRIPTION

A model to adequately describe NO$_3^-$ quantities and movement within agricultural soils must include additions, subtractions, storage, and biological conversions, each represented as a time distribution. In contrast with some chemicals, NO$_3^-$ is not significantly adsorbed by the soil and readily moves with the soil water. Therefore, both NO$_3^-$ and soil water processes must be carefully considered.
Several other researchers have modeled soluble chemical transport in soils. Their models vary considerably in format and purpose. The one by Dutt et al. (1972) is complex and considers many items as mineralization and plant uptake required to represent field conditions with a growing crop. These models either did not include all of the important processes or were too complex for several years of daily calculations.

The occurrence and movement of soil water was calculated with a previously developed soil moisture-evapotranspiration (SM-ET) model (Saxton et al., 1974). Input to that model was: (i) measured daily precipitation and runoff, (ii) daily pan evaporation, (iii) plant canopy development, (iv) plant phenological status, (v) root distributions, and (vi) plant moisture stress characteristics. Soil moisture-tension-conductivity relationships representative of each 15-cm layer were used to calculate moisture redistribution and percolation. Daily calculations with the SM-ET model provided input values for the NO$_3^-$ model. These were: (i) soil evaporation, (ii) plant absorption from each layer (dependent on root and soil water distributions), (iii) infiltration, (iv) soil moisture redistribution between layers, (v) profile percolation, and (vi) soil moisture quantity in each layer.

The NO$_3^-$ model, which is essentially a NO$_3^-$ budget within the system boundaries of Fig. 1, was used to compute NO$_3^-$ amounts and distributions on a daily basis for the entire year. Each known process that influences NO$_3^-$ movement was evaluated for significance in the case of a well-aerated soil with growing corn. Those processes included in the model were:

1) Nitrate transport by
   a) infiltration

2) Plant uptake
3) Fertilizer addition
4) Rainfall addition
5) Mineralization and nitrification

These are shown schematically in Fig. 1 and the model representations are described in the following sections.

Those processes assumed negligible and not included in the model were: (i) denitrification (ii) fixation (iii) losses by runoff and erosion. Denitrification is usually considered small in well-aerated soils although this is not readily documented or verified. We assumed denitrification to be negligible for our study site as a first approximation with the view that if this assumption was invalid, the model would fail to be verified. Leguminous crops were not considered, thus no significant N fixation would be expected. Nitrate-N losses by runoff and erosion were measured and shown to be quite small for these watersheds (Schuman et al., 1973). Several other processes occur within the N cycle on agricultural land, but also were considered negligible.

Water Movement of Nitrates

Nitrate ions largely exist in the soil solution, and their negative charge causes anion exclusion (Thomas and Swoboda, 1970) so that higher concentrations form toward the exterior of the water films. Although a gradient exists, the NO$_3^-$ was assumed uniformly distributed within the water held at tensions of <15 bar. For drier soils, the NO$_3^-$ was considered to be within the 3% of water held at the lowest tension.

Anions in the soil solution are moved and dispersed by mass transport, mechanical diffusion, and molecular diffusion—processes summarized by Gardner (1965). Several others have developed and presented mathematical representations of solute transport in both saturated and unsaturated conditions (Warrick et al., 1971; Fried and Combramous, 1971; Kirkham and Powers, 1972; Davidson and Chang, 1972; Bresler, 1973). Most represent these simultaneous processes in differential equation form with corresponding coefficients. Bresler (1973) showed good comparisons of measured and calculated solute transport when applying a finite difference solution.

The following numerical procedure of solute transport was applied in our model to conform to the space-time incrementation. Each 15-cm soil layer was considered to have uniform solute concentrations. Nitrate quantities leaving or entering a layer were calculated as the product of the computed water movement and the existing NO$_3^-$ concentrations. New concentrations were computed for each time increment and layer by the equation:

$$CON_i(t+\Delta t) = CON_i(t) + q_i(t) \Delta t CON_i(t) - q_i(t) CON_i(t)$$

where

- $CON$ = NO$_3^-$ concentration, kg kg$^{-1}$
- $QN$ = nitrate quantity in 15-cm layer, kg ha$^{-1}$
- $q$ = water flow rate during time increment, kg ha$^{-1}$ hour$^{-1}$
- $QW$ = water quantity in 15-cm layer, kg ha$^{-1}$
- $QWWP$ = water quantity at $> 15$ bar tension, kg ha$^{-1}$
- $\Delta t$ = delta time, hour
- $i$ = layer of soil profile, and
- $t$ = time increment.

These new concentrations were considered uniform throughout each soil layer and different from adjacent layers. Like most numerical methods, some numerical dispersion was introduced by this technique, but the effects did not appear significant for the field conditions of this study. For soil moisture conditions significantly wetter than field capacity, subsequent model testing has shown that this procedure of solute transport computation predicts
excess nutrient movement and leaching efficiency must be considered, but these conditions were not present in this study.

Water and NO$_3$- movement caused by infiltration, redistribution, and percolation were calculated by this solute transport procedure. A constant NO$_3$- concentration of 0.75 ppm was applied to the infiltrating rainfall (Schuman and Burwell, 1974). Redistribution between soil layers was allowed to be either up or down at each layer interface, depending on relative soil water tensions and gravity. Similarly, vertical movement through the lower profile boundary ($P_e$) could be either up or down. For upward movement, the boundary concentration was assumed equal to the concentration of the lowest soil layer, although these situations were infrequent and never of significant quantity.

### Plant Uptake

Average annual N uptake ($U$) by the corn crop on the research watersheds was determined by analyzing whole plant samples removed at the soil surface. Total $U$ (stalks and grain) during the 3-year study for the excessively fertilized corn averaged 202 kg/ha per year of N, and 157 kg/ha per year for the normally fertilized corn. The seasonal $U$ distribution was estimated from previous observations of corn growth; therefore, it was based essentially on dry matter accumulation. The accumulative results of this distribution are shown in Fig. 3.

Several studies have shown that the uptake of water and nutrients by the root system is complex and not well understood.
(Olsen and Kemper, 1968; Barley, 1970; Terman and Noggle, 1973; Liao and Bartholomew, 1974). For our calculations, we assumed that the nutrient uptake from each soil layer was proportional to the water uptake (which already contains root distribution effects) multiplied by the NO$_3$-N concentration of the water in the layer. The accumulative daily amount from all soil layers was made equal to the daily plant uptake (previously established by the annual amount and time distribution) by a single proportionality coefficient applied to all layers which was usually much <1.0 but quite variable among days. The coefficient was determined by the relationship:

$$U = C \sum T_i (T_i \cdot CON_i)$$

where

- $U$ = plant uptake defined by annual distribution, kg ha$^{-1}$ day$^{-1}$
- $C$ = daily proportionality coefficient, $T$ = plant water uptake for 15-cm soil layer, kg ha$^{-1}$ day$^{-1}$
- $CON_i$ = NO$_3$-N concentration, kg kg$^{-1}$, and
- $i$ = layer of soil profile.

**Fertilizer Addition**

Fertilizers of the ammonia (NH$_4^+$) form bond readily with the soil matrix and are converted to the NO$_3$~ form by biological action. The conversion rate is largely dependent on soil temperature (which governs biological activity) and on the quantity of NH$_4^+$ present. Only slight biological oxidation of ammonia to nitrate (nitrification) occurs below 10°C (50°F) (Saber et al., 1956; McIntosh and Frederick, 1958).

The production of NO$_3$~ from applied NH$_4^+$ fertilizer was considered uniform in the upper 15-cm layer and was assigned an exponentially declining rate distribution of the form:

$$N(t) = K'N_0 e^{-t/\tau}$$

where

- $N(t)$ = remaining applied N, kg ha$^{-1}$
- $t$ = time from beginning day, days
- $K'$ = coefficient, and
- $N_0$ = amount of applied N, kg ha$^{-1}$

The beginning date of NH$_4^+$ conversion was the date on which the 15-cm soil temperature reached 10°C if fertilizer was applied before that date; or, if the soil temperature reached 10°C before fertilizer was applied, the date of application was the beginning date. A 10% application loss was assumed based on visible vaporization behind the applicator and lack of measured data. A 60-day conversion duration was selected for our Iowa location according to information by McIntosh and Frederick (1958). A $K$ value of 0.9622 provided a 90% conversion in 60 days of the total N applied.

**Mineralization**

Organic matter decay by biological activity provides a source of NO$_3$-N. Harmens and Kolenbrander (1965) review this process, and Stanford and Epstein (1974) showed that the potential quantity was related to soil moisture; however, actual quantities and time distributions must yet be estimated. We reasoned that the total soil organic matter does not change significantly from year to year; therefore, the annual amount of decay must approximate the annual amount of residue returned. Although the mineralized material is not all recent residue, the annual amounts still would be comparable under continuous cropping.

Analyses of the excessively fertilized corn showed that 78 kg/ha per year of N remained in the residue. Not all of this N would be mineralized to the NO$_3$~ form, and some losses would probably occur; thus, we estimated that two-thirds of the residue N, 52 kg/ha per year, would be converted to NO$_3$~ during the year. We used this estimate for both the normal and excessive fertility rates. Plant roots were not included in plant uptake or in mineralization, but they should be included when quantifying values are available.

**FIELD DATA**

Nitrogen data were obtained on two agricultural watersheds in western Iowa near Treynor. These adjacent watersheds, W-1 (30 ha) and W-2 (34 ha), were instrumented for hydrologic, erosion, and water quality studies, entirely cropped with continuous corn, and contour farmed. The deep loess topography has 6-12% slopes with deep, moderately permeable soils. The silt loam loess is 5-25 m deep with no horizon restrictions, and is underlaid by very slowly permeable glacial till that causes a saturated zone and seepage flow to local streams. The principal soil types are Typic Hapludolls, Typic Haploorthents, and Cumulic Hapludolls (Marshall-Monona-Ida Series). A more complete watershed description is given by Saxton et al. (1971).

The watersheds were fertilized at constant, but different rates from 1969 to 1974. A N rate of 168 kg/ha per year, was recommended as normal rate for optimum corn yields at this location, was applied annually to W-2. An excessive N rate of 448 kg/ha per year was applied annually to W-1 to allow us to measure N movement and dissipation. Most of the N was applied as anhydrous ammonia knifed 20-30 cm deep in the soil, but about 50-100 kg/ha of the excessive rate was surface applied as granular ammonium nitrate. Phosphorus and potassium were applied at recommended rates of 39 and 29 kg/ha per year, respectively, to both watersheds. The fertilizer was usually applied in April before any preplant tillage. The entire area of each watershed was uniformly treated to correspond with hydrology and erosion data.

Soil coring was begun in 1971 to measure NO$_3$-N concentrations to a 6.1-m depth. A middleslope location was chosen on each watershed for a 4 x 4 grid of coring sites spaced 12.5 m apart (Schuman et al., 1975). Cores were drilled at some or all of these sites six times between 1971 and 1974 (Table 1). Each 7.6-cm length of the 2.5-cm diameter core was separated as an individual sample and extracted with 1 M KCl. The NO$_3$-N concentration of the extract was determined by a continuous-flow, colorimetric technique (Henriksen and Selmer-Olsen, 1970). Results from adjacent samples were averaged to provide concentrations for 15 cm (6-in) depth increments. Then, we averaged the several profiles of NO$_3$-N concentration for each date for each depth increment to provide a mean NO$_3$-N concentration profile and amount to a 6.1-m depth below the soil surface. A standard error of the mean ($\sigma$) was computed for each depth increment.

The total mean profile quantities and standard errors of the mean are given in Table 1. The NO$_3$-N distributions and quantities in the upper 1.8 m were used for model verification, and the measured quantity changes in the 1.8-6.1 m soil depth were compared with predicted leaching amounts from the 1.8-m soil profile.

**MODEL OPERATIONS**

Initial soil water and NO$_3$-N profiles were specified as averages for each 15-cm soil layer of the 1.8-m soil profile. Then each process was considered on a daily basis. The daily calculation sequence was fertilizer addition, mineralization addition, plant uptake, infiltration addition and transport, and transport by redistribution and percolation. A
revised water and NO$_3$-N profile was calculated after each process and the profiles at the end of the daily calculation sequence became input for the succeeding day.

The model was operated to represent the normally (W-2) and excessively (W-1) fertilized areas. Initial NO$_3$-N profiles were set equal to the measured profiles on the first sampling date (Table 1), then calculations proceeded independently of all other field measurements of NO$_3$-N. Three years of calculations were made for the excessively fertilized area (W-1) during which five other field-sample sequences became input for the succeeding day. The NO$_3$-N profile was calculated after each $^3$.

Three years of calculations were made for the excessively fertilized area (W-2) was modeled for nearly two years with two verification sample sets.

Example time distributions of water and NO$_3$-N quantities are shown in Fig. 2 and 3. Daily infiltration and evapotranspiration primarily determine the soil moisture regime. In Fig. 2, observed soil moisture were compared with predicted soil moisture calculated with the SM-ET model. This model also was used to estimate the percolation from the 1.8-m soil profile.

The accumulative NO$_3$-N amounts for the major processes considered, shown in the lower part of Fig. 3, reflect the assigned model representations and their interactions; the total profile NO$_3$-N quantities, in the upper part of Fig. 3, show the combined effect. Some processes, like fertilizer addition and mineralization, repeat each year; but others, like leaching, vary considerably depending on water movement, NO$_3$-N profiles, or other variables.

**MODEL VERIFICATION**

Model verification requires an assessment of the model's prediction accuracy for achieving the intended purpose. For our study, the NO$_3$-N quantities and distributions within the 1.8-m soil profile, quantities leached below the 1.8-m soil profile, and the change in these values throughout the year were of primary importance.

Observed and predicted NO$_3$-N quantities are given in Table 1. Variation is present as expected; thus, the significance in terms of future predictions must be assessed. Differences occur because of both prediction and measurement accuracy. Spatial sampling error also is involved because the model represented mean watershed conditions by applying watershed averages of the hydrologic, crop, and soil inputs.

The standard errors of the means shown in Table 1 help to define the sampling accuracy. Further statistical comparisons of measured and predicted values cannot be made meaningfully. Largely, the verification becomes a judgment of the differences when considering the model's usefulness for the study objectives and interpretations. All predicted values were essentially within one standard error of the mean, except the last sample date of W-2. For many applications, the differences in Table 1 are well within acceptable tolerances.

Measured changes of NO$_3$-N quantities in the 1.8-6.1 m depth should compare with the amount of NO$_3$-N leached out of the upper 1.8-m profile if we assume insignificant leaching at the 6.1-m depth. (Measured NO$_3$-N concentrations near the 6.1-m depth always were relatively low.) The accumulative measured NO$_3$-N changes and predicted leached NO$_3$-N shown in Table 1 contain some differences in both quantities and time distributions. The model's accuracy and some leaching at the 6.1-m depth may account for a portion of the discrepancies, and the predicted percolation at the 1.8-m depth is a sensitive calculation not easily verified under field conditions. However, the total predicted leached NO$_3$-N and measured NO$_3$-N changes for the 3-year W-1 study period are reasonably close (869 vs. 723 kg/ha).

The predicted and measured NO$_3$-N amounts for W-2 differed considerably, and the reasons are not evident. Measurement and predictions for low concentrations both are more subject to bias and error. The measured loss of 150 kg/ha between 13 June 1972 and 23 April 1973 appears unreasonable based on the observed concentrations and percolation. With only two sample dates after the initial date and these apparent discrepancies, the W-2 data are of less value for model verification than the W-1 data.

Selected NO$_3$-N profiles for the excessively fertilized watershed (W-1) are shown in Fig. 4, and for the normally fertilized watershed (W-2) in Fig. 5. Although NO$_3$-N profiles were computed for each day of the study period, only those on the dates of measured profiles and others at about 1-month intervals are shown. The predicted and measured NO$_3$-N profiles showed the distribution of the total amounts given in Table 1. For the five dates of measured vs. predicted NO$_3$-N profiles shown in Fig. 4, the first comparison on 10 Nov. 1971 is the poorest. For the four other dates, the observed and calculated profiles and quantities are quite close even though the profile shapes and magnitudes differ greatly among the dates, particularly the profile change before and after the 1972 fertilizer addition. The good comparisons after many months of daily calculations verify that the model and assumptions reasonably represent the field situation.

The predicted and observed profiles for the normally fertilized watershed (W-2) shown in Fig. 5 have similar shapes. All concentrations, however, are much lower than those for the excessively fertilized watershed (W-1, Fig. 4). The W-2 predicted and observed total profile amounts for 8 April 1974 (Table 1) were quite different. This difference is the result of integrating the small concentration bias shown in Fig. 5 between the two NO$_3$-N profiles throughout the soil profile depth. The reason for the bias is not obvious, however, it is undoubtedly related to the accuracy of the model representations at low NO$_3$-N concentrations.

<table>
<thead>
<tr>
<th>Watershed†</th>
<th>Date sampled</th>
<th>Soil cores sampled</th>
<th>Measured ± 2σ</th>
<th>Predicted Leaching‡</th>
<th>Measured NO$_3$-N changes, 1.8-6.1 m</th>
<th>Predicted NO$_3$-N leaching at 1.8 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>13 April 1971</td>
<td>16</td>
<td>277 ±40</td>
<td>277§</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10 Nov. 1971</td>
<td>8</td>
<td>681 ±96</td>
<td>480</td>
<td>158</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>27 Mar. 1972</td>
<td>7</td>
<td>421 ±63</td>
<td>454</td>
<td>232</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>13 June 1972</td>
<td>16</td>
<td>788 ±109</td>
<td>748</td>
<td>340</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>23 April 1973</td>
<td>17</td>
<td>209 ±61</td>
<td>183</td>
<td>622</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>9 April 1974</td>
<td>7</td>
<td>159 ±33</td>
<td>183</td>
<td>723</td>
<td>869</td>
</tr>
<tr>
<td>W-2</td>
<td>13 June 1972</td>
<td>7</td>
<td>278 ±45</td>
<td>278§</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>23 April 1973</td>
<td>7</td>
<td>68 ±16</td>
<td>68</td>
<td>-150</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>8 April 1974</td>
<td>7</td>
<td>143 ±13</td>
<td>40</td>
<td>-34</td>
<td>174</td>
</tr>
</tbody>
</table>

† Nitrogen application rates were 448 kg/ha per year on W-1, 168 kg/ha per year on W-2.
‡ Accumulative differences of mean NO$_3$-N profiles between sampling dates. Negative values indicate a net loss.
§ Predicted made equal to measured on the initial date.
Fig. 4—Predicted (circles) and measured (triangles) NO$_3$-N concentration (dry soil basis) profiles for the excessively fertilized watershed (W-1), 1971-1974.

and Hanks (1969) reported similar results and introduced a buffering term not included in our model. The sequence of profiles, particularly those in Fig. 4, demonstrate the dynamic development, movement, and dissipation of NO$_3$-N profiles. These profiles, of course, reflect the combined result of those processes demonstrated in Fig.
1, 2, and 3. High NO$_3$-N concentrations appear soon after fertilizer application in the upper soil layers, and subsequent leaching causes the formation of a concentration bulge. Where fertilization was excessive, this bulge was only partly dissipated by crop uptake during the growing season, but it was almost entirely depleted for the normally fertilized watershed. During and after the creation of the concentration bulge, it was moved and diffused by water transport. The downward movement of three such bulges, one in each year, is particularly evident in Fig. 4.

**SUMMARY AND CONCLUSIONS**

A model to compute the movement, distribution, and dissipation of NO$_3$-N was developed from relationships that describe the major influencing processes within the vertical soil-plant-atmosphere system. Beginning with measured initial soil moisture and NO$_3$-N profile distributions and daily input data, NO$_3$-N quantities and distributions in a 1.8-m soil profile were calculated for each day of a 3-year study period for corn excessively fertilized with N (448 kg/ha per year) and a 2-year period for corn normally fertilized with N (168 kg/ha per year). Measured NO$_3$-N profiles verified that the model represented the NO$_3$-N amount and movement so that results could be useful for understanding NO$_3$-N movement and dissipation. The effect of soil water movement on NO$_3$-N movement and dissipation was particularly evident.

The model is applicable to well-aerated agricultural soils, but not to those soils or situations in which the assumptions are violated. The model was verified with corn crops, but it could be valid for other nonlegume crops with proper descriptions of rates and distributions of water and NO$_3$-N uptake. Like most prediction methods, this one was developed to a state of utility, but revisions, improvements, and additions are always possible and desirable. Many of the model representations could be improved by including additional details and refinements. And some assumptions, like negligible denitrification, could be eliminated if proper representations were available.

The model is an analytical procedure that should be useful for deriving management guidelines and for future research. The simultaneous consideration of the many processes which influence NO$_3$-N within the soil profile reveals their relative magnitudes and interactions and defines where additional research is most needed. Decisions, like fertilizer application rates and time of application, can be analyzed with the model to assess management consequences on NO$_3$-N crop availability and potential environmental hazards.

**LITERATURE CITED**


