Spatial Variability and Transport of Nitrate in a Deep Alluvial Vadose Zone

Yuksel S. Onsoy, Thomas Harter,* Timothy R. Ginn, and William R. Horwath

ABSTRACT

Little empirical evidence exists about the spatial distribution of NO$_3$–N in deep vadose zones and about the associated fate and transport of NO$_3$–N between the root zone and the water table. We investigated NO$_3$–N occurrence in a deep alluvial vadose zone and its relation to geologic site characteristics, hydraulic properties, and fertilizer application rates via an intensive three-dimensional core-sampling campaign beneath an irrigated orchard in semiarid Fresno County, California. Statistical and geostatistical analyses were used to determine spatial variability of NO$_3$–N and water content, to estimate total NO$_3$–N mass in the vadose zone beneath each of three fertilizer treatments, and to compare NO$_3$–N occurrence with that predicted from standard agronomic analysis of N and water mass balances. Vadose zone NO$_3$ was highly variable and lognormally distributed. Fertilizer treatment had a significant effect on NO$_3$–N levels in the vadose zone. In all cases, deep vadose zone N mass estimated by kriging measured data totaled only one-sixth to one-third of the mass predicted by the N and water mass balance approach. Vadose zone denitrification estimates could not account for this discrepancy. Instead, the discrepancy was attributed to highly heterogeneous flux conditions that were not accounted for by the mass-balance approach. The results suggest that spatially variable vadose zone flow conditions must be accounted for to better estimate the potential for groundwater NO$_3$ loading.

Intensive use of agrochemicals such as fertilizers and pesticides has been recognized as a major source of nonpoint source pollution. Subsurface NO$_3$ transport is of particular interest because of the widespread application of inorganic and manure based NO$_3$ fertilizers. Highly mobile and persistent, NO$_3$ has become a primary groundwater pollutant (USEPA, 1990; Lunn and Mackay, 1994; Bransby et al., 1998; Ling and El-Kadi, 1998). Between 1945 and 1993, the use of NO$_3$ in commercial fertilizers in the USA increased 20-fold (Puckett, 1995). In semiarid regions with intensive irrigated agricultural production (e.g., in California and the southwestern USA), conflicts between water scarcity and NO$_3$ groundwater pollution have further heightened concerns about soil N management (Owens et al., 1992).

Driven in part by pollution prevention measures that attempt to optimize the use of fertilizers, N budgeting methods for specific crop–fertilizer application scenarios have been widely used in agronomy to determine the fate of N in soils and the potential for N leaching to groundwater (Tanji and Gupta, 1978; Frissel et al., 1981; Legg and Meisinger, 1982; Willigen and Neeteson, 1985). These methods are driven by experimental studies of N cycling processes that have almost exclusively focused on the uppermost soil horizon (0–30 cm, Paustian et al., 1990; Tindall et al., 1995; Watkins and Baraclough, 1996; Simek and Kalck, 1998; Schmasakkar et al., 1999) or on the root zone (0–1.8 m, Lafolie et al., 1997; Trettin et al., 1999; de Vos et al., 2000; Allaire-Leung et al., 2001; Stenger et al., 2002). Some experiments examined the annual N budget with intensive field investigations, but were not of long enough duration for a proper assessment of the effects of land management practices on groundwater quality (e.g., Paustian et al., 1990; Aronsson, 2001).

Critical gaps remain in our understanding of the influence of the vadose zone below the root zone, where it exists, on the estimation of N loading to aquifers (Ling and El-Kadi, 1998). Mechanisms involved in N transfer in the (deep) vadose zone below the root zone are rarely measured. The dearth of information about the deeper vadose zone results partly from the misconception that little chemical and biological activities occur below the root zone (i.e., below 0.3–1.8 m) (Pionke and Lowrance, 1991; Krug and Winstanley, 2002), but the vadose zone of many agricultural regions is considerably deeper and may contain appreciable amounts of organic matter (OM) or NO$_3$ or both (Stevenson, 1986). Nitrate well below 1.8 m may be available to some plants (Smith and Cassel, 1991). Furthermore, denitrification between the root zone and the water table may significantly reduce N loading to groundwater, although this is difficult to quantify (Rees et al., 1995). Our current understanding of NO$_3$ fate and transport below the root zone is further limited by prohibitive experimentation costs (e.g., Rees et al., 1995), by potentially long travel times through deep vadose zones, and perhaps most importantly, by a large degree of spatial variability.

Spatial variability is caused by spatially variable water and N application rates (i.e., external variability) and by spatially variable vadose zone hydraulic and chemical properties (i.e., intrinsic variability). Both may lead to highly nonuniform distribution of NO$_3$ and other agrochemicals (Rao and Wagenet, 1985; Mohanty and Kanwar, 1994). Past studies have quantified spatial variability of NO$_3$ by geostatistical methods, but only within the root zone of agricultural field soils (Dahia et al., 1984; Tabor et al., 1985; White et al., 1987; van Metten and Hofman, 1989; Istok et al., 1993; Cambardella et al., 1994; Hofman et al., 1994; Mohanty and Kanwar, 1994; Schmasakkar et al., 1999; Allaire-Leung et al., 2001; Ilsemann et al., 2001; Stenger et al., 2002).

Equivalent field work on the spatial variability and storage of NO$_3$ in the deep vadose zone (below the root zone) and analysis of its relationship to field-scale N mass balance and NO$_3$ leaching into groundwater has,---
to our knowledge, not yet been attempted. The goal of our work is therefore to provide a detailed field analysis of NO$_3^-$ occurrence in a deep alluvial vadose zone, its relationship to the geologic and hydraulic characteristics of the vadose zone and to fertilizer management, and to discuss the implications of our findings with respect to common interpretations of vadose zone data.

Recognizing that the study is site specific, we do not make a strong claim that our results can be quantitatively transferred to other sites and situations. However, the general site conditions (alluvial soils, semiarid Mediterranean climate, irrigated crops) are representative of many important agricultural regions around the globe. The fundamental conditions at the study site, namely the strong heterogeneity of the NO$_3^-$ distribution, the lack of significant denitrification, and the strong control of the heterogeneous hydraulic and flow conditions on the NO$_3^-$ distribution are therefore not unique to this site and provide universal insight into “real” deep vadose zones. Therefore, findings from this site provide important evidence for the fate and transport of NO$_3^-$ in deep vadose zones in general. In particular, we hope that studies like the one presented here will provide a useful basis for developing guidance on the role of monitoring devices in the deep vadose zone.

In the following, we give a brief description of the site and the experimental methods. We then implement a conventional field-scale root zone water and N mass balance (MB) analysis to estimate NO$_3^-$ leaching from soil and to provide a predictive framework for the assessment of deep vadose zone NO$_3^-$N. A statistical analysis of the measured water content and NO$_3^-$N distribution is used to separate deterministic large-scale spatial variability that can be explained by depth, N treatment, and discrete lithofacies zonation from random smaller-scale spatial variability. For the nondeterministic residuals, we develop appropriate geostatistical models of the deep vadose zone water content and NO$_3^-$N data to estimate the total deep vadose zone NO$_3^-$N mass. In the discussion, we compare this estimate with the total NO$_3^-$N mass predicted from the MB analysis to evaluate the deep vadose zone NO$_3^-$ fate and transport processes and the role of spatial variability in assessing potential NO$_3^-$ leaching to groundwater.

**METHODS**

**Field Site**

The site is a flood-irrigated, 0.8 ha (2 acres) ‘Fantasia’ nectarine [Prunus persica (L.) Batsch var. nucipersica (Suckow)] C.K. Schneid. ‘Fantasia’ orchard at the University of California Kearney Agricultural Center (http://www.ukac.edu), located 20 km southeast of Fresno, CA, on the Kings River alluvial plain (elevation: 103 m above sea level). The site has a semiarid, Mediterranean climate.

**Fertilizer Treatments**

Planted in 1975, the matured orchard was subject to a 12-yr fertilizer trial that began in September 1982. A complete random block design was used (Fig. 1) with application rates of 0, 110, 195, 280, or 365 kg N ha$^{-1}$ yr$^{-1}$ in several replicates. Fertilizer was broadcast in September of each year at a rate of 110 kg N ha$^{-1}$ to all rows except the control treatments (0 kg N ha$^{-1}$ yr$^{-1}$). During the following spring, the 195, 280, and 365 kg N ha$^{-1}$ yr$^{-1}$ treatments received additional applications at a rate of 85 kg N ha$^{-1}$ (or 75 lb ac$^{-1}$) once, twice, and three times, respectively, to achieve the desired annual fertilization rate. In the first year, (NH$_4$)$_2$SO$_4$ was applied. To prevent soil acidification, NH$_4$NO$_3$ (33.5% N content) and Ca(NO$_3$)$_2$ (15.5% N content) were used throughout the remainder of the study. There was no application of fertilizer in 1995. In September 1996, 110 kg N ha$^{-1}$ was applied throughout the entire orchard including the control plots in the usual broadcast application method. Vadose zone water quality analysis was not part of the original project’s scope.

**Irrigation and Climate Measurements**

Flood irrigation dates were obtained from farm records at the Kearney Agricultural Center. Irrigation records indicate
that the approximate amount of applied water was 13.4 cm ha$^{-1}$ (5.3 in ac$^{-1}$) per irrigation. Depending on spring precipitation patterns, 9 to 16 irrigations (average of 13 irrigations) were applied to the orchard each year. Daily reference evapotranspiration and precipitation data were measured at a California Irrigation Management Information System climate field station located within 1 km from the site. Crop evapotranspiration was computed from the product of the daily reference evapotranspiration rates and crop coefficients, $k_c$, for nectarine orchards (California Department of Water Resources, 2000). Over the past 20 yr, annual precipitation ranged from 160 to 490 mm, while groundwater levels during that period fluctuated between 12 and 20 m below ground surface.

**Yield and Plant Nitrogen Uptake**

The nectarine orchard blossoms in mid- to late February immediately before leafing out. Fruit ripening is completed immediately before leafing out. Fruit ripening is completed between July and October 1997, 60 undisturbed continuous soil cores were drilled with a Geoprobe Systems (Salina, KS) direct-push drilling rig to a depth of 15.8 m (52 ft), including 18 cores from each subplot (Fig. 1). Cores were obtained in approximately 1.2-m sections (4 ft), their sedimentologic characteristics were described, and then the cores were sampled. More than 1000 soil samples of 22.5 cm long and 4 cm in diameter were taken at 30- to 60-cm intervals depending on stratification. Subsamples were prepared and preserved for later analysis. During the drilling phase, groundwater was detected at approximately 16 m below the ground surface.

**Vadose Zone Textures**

The entire vadose zone at the site consists of unconsolidated sediments deposited on a stream-dominated alluvial fan. The textural groups range from clay and clayey paleosol hardpans to a wide range of silt and sand, including occasional coarse sand and gravel sediments. Coarse-grained materials are believed to represent channel deposits embedded within finer-grained floodplain and levee deposits. Sandy loam is the most common textural unit in the profile while clay was the least (48 and 8% of the vertical profile length, respectively). Ten major stratigraphic units were identified based on texture, color, and cementation and are referred to as “lithofacies.” They exhibit vertically varying thicknesses, yet are laterally continuous across the experimental site. The measured saturated hydraulic conductivity data, best described by a lognormal distribution, indicate high hydraulic variability at the local scale (10$^{-2}$–10$^{-1}$ cm, for details see Minasny et al., 2004).

**Soil Water Content and Nitrate**

Gravimetric water content $\theta_{gq}$ (g g$^{-1}$) was determined using measured values of oven-dried (105°C for 24 h) 1.25-cm (1/2-in.)-long samples. Bulk density was measured on 119 core samples and varied from 1.3 to 1.9 g cm$^{-3}$, with an average of 1.6 g cm$^{-3}$. However, core samples, particularly finer-textured samples, were subject to variable compression during coring. Therefore, a more representative constant bulk density $\rho_b$ of 1.45 g cm$^{-3}$ (Hausenbuiler, 1985) and the measured values of $\theta_{gq}$ were used to compute volumetric water content $\theta$ (m$^3$ m$^{-3}$). Regardless of the specific number used for bulk density, the potential error introduced is small (<10%) compared with the large range of observed NO$_3$ concentrations (see below).

Nitrates were measured in 0.5 m K$_2$SO$_4$ soil extractions (5/1 ratio, 1-h reciprocal shaking) prepared from 809 core subsamples sieved through a 1-mm screen (Horwath and Paul 1994). Soil extracts were analyzed by automated flow-injection colorimetry following the methods of the USEPA 353.2 (Wendt, 1999). At each subplot, the smallest horizontal sampling interval varied between 1.2 to 3 m (10 and 4 ft, respectively, Fig. 1). The average vertical sampling interval was approximately 0.6 m (2 ft). Two hundred twenty-four sample concentrations were below the limit of detection (LOD = 10$^{-3}$ mg L$^{-1}$ = 10$^{-3}$ g m$^{-3}$) and recorded as zero. Measured values were converted to aqueous concentrations NO$_3$–Naq in units of grams per cubic meter (or equivalently μg mL$^{-1}$), using measured water content data. Both, $\theta$ and NO$_3$–Naq measurements contribute to the N mass estimate and are therefore both included in the statistical analysis. Results of core analyses for $\theta$ and NO$_3$–Naq are summarized in Table 1.

**FIELD-SCALE WATER AND NITROGEN FLUXES: NITROGEN BUDGET**

The principle method for analyzing and predicting the NO$_3$ leaching potential is a field- or plot-scale MB analysis coupled with a simple uniform steady-state flow model. We applied the method to provide a basis of comparison for the amount of NO$_3$–N in the deep vadose zone from the three subplots. The vadose zone was conceptually divided into two compartments: soil root zone and deep vadose zone (Fig. 2). The root zone is considered to be 1.8 m (6 ft) deep. Approximately 90% of the tree roots in the nectarine orchard are contained in this zone, with some roots to depths of 3 m (10 ft). Individual roots are expected to grow as long as 6 to 9 m (20–30 ft) horizontally (Scott Johnson, personal communication, 2004). The deep vadose zone is bounded by the soil root zone at the top and the water table at the 15.8-m depth. A long-term root zone N mass balance yields annual NO$_3$–N leaching, N$_{leaching}$, from the root zone into the deep vadose zone:

$$N_{leaching} = N_{input} - N_{uptake} - N_{transformation} - \Delta N \quad [1]$$

where $N_{input}$ is the total N input to the root zone, $N_{uptake}$ is the N used for plant uptake, $N_{transformation}$ is the N loss through various N transformations in the root zone other than N leaching, and $\Delta N$ is the change in the total amount of N (organic and inorganic) stored in the root zone. N$_{leaching}$ is equivalent to the long-term potentially leachable N (LPLN) described in Meisinger and Randall (1991).

**Nitrogen Storage Changes**

When soil, climate, and management factors are constant for an extended time (5–20 yr), annual mineralization of N from soil OM has been found to be approximately equivalent to organic N returned to the soil in crop residues plus microbial immobilization (Legg and Meisinger, 1982; Stevenson, 1982). Hence, annual changes in N storage reach a quasi-steady state, $\Delta N = 0$ (Meisinger and Randall, 1991). Warm, semiarid climate conditions with irrigation further accelerate the time required for a system to reach quasi-steady-state conditions with respect to annual N storage changes. The 12-yr duration of the fertilizer treatment was considered sufficient to assume that annual N storage changes were negligible ($\Delta N = 0$).
Table 1. Basic statistics of water content \( \theta \), nitrate-nitrogen \( \text{NO}_3^-\text{Na}_q\) and log-transformed \( \text{NO}_3^-\text{Na}_q\). The number of samples measured for water content are: 339 in the control, 391 in the standard, and 310 in the high subplot. During the data quality check, 27 water content samples were removed due to inconsistencies (10 from both the control and standard subplots and 7 from the high subplot), which reduced the number of samples used in geostatistical analysis to 1013. Also shown are basic statistics of \( \text{NO}_3^-\text{Na}_q\) and log-transformed \( \text{NO}_3^-\text{Na}_q\) categorized by subplots.

<table>
<thead>
<tr>
<th>Data Subplot</th>
<th>No. of data</th>
<th>Mean</th>
<th>Min.</th>
<th>Max.</th>
<th>Variance</th>
<th>SD</th>
<th>CV</th>
<th>Mean</th>
<th>Variance</th>
<th>Skewness</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta ), cm(^3) cm(^{-3})</td>
<td>–</td>
<td>1183</td>
<td>0.23</td>
<td>0.004</td>
<td>0.59</td>
<td>0.015</td>
<td>0.12</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \text{NO}_3^-\text{Na}_q ) w/ND, g m(^{-3})†</td>
<td>–</td>
<td>809</td>
<td>3.28</td>
<td>0</td>
<td>129.72</td>
<td>62.74</td>
<td>7.92</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \ln\text{NO}_3^-\text{Na}_q ) w/ND, g m(^{-3})†</td>
<td>–</td>
<td>585</td>
<td>4.54</td>
<td>0.04</td>
<td>129.72</td>
<td>81.10</td>
<td>9.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \ln\text{NO}_3^-\text{Na}_q ) w/o ND, g m(^{-3})‡</td>
<td>–</td>
<td>809</td>
<td>0.70</td>
<td>–</td>
<td>4.61</td>
<td>4.87</td>
<td>1.54</td>
<td>1.24</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \ln\text{NO}_3^-\text{Na}_q ) w/ND, g m(^{-3})†</td>
<td>–</td>
<td>204</td>
<td>3.73</td>
<td>–</td>
<td>8.06</td>
<td>8.98</td>
<td>241%</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \ln\text{NO}_3^-\text{Na}_q ) w/o ND, g m(^{-3})‡</td>
<td>–</td>
<td>204</td>
<td>0.51</td>
<td>–</td>
<td>6.40</td>
<td>2.53</td>
<td>NA§</td>
<td>NA§</td>
<td>NA§</td>
<td>–</td>
</tr>
</tbody>
</table>

† Including nondetects, ND, which are set to zero for \( \text{NO}_3^-\text{Na}_q\) data and to half the limit of detection (4.605) for \( \ln\text{NO}_3^-\text{Na}_q\).
‡ Excluding nondetects.
§ Sample \( \text{NO}_3^-\text{Na}_q\) mean, \( m \), and variance, \( s^2 \), estimated from mean, \( \mu \), and variance, \( \sigma^2 \), of the logtransformed dataset: \( m = \exp(\mu + 0.5 \sigma^2) \) and \( s^2 = m^2[\exp(\sigma^2) - 1] \). Coefficient of variation estimated for \( \text{NO}_3^-\text{Na}_q\) sample mean and variance, NA: No estimates were computed from \( \ln\text{NO}_3^-\text{Na}_q\) data with the nondetects included at 4.605 because the bimodal distribution of that dataset violates the normality assumption.

### Nitrogen Inputs

Annual N inputs included fertilizer applications, and N received from irrigation, precipitation, dry deposition, and nonsymbiotic N\textsubscript{2} fixation. Table 2 lists average annual N inputs and margin of errors (95% confidence intervals) in the N mass balance analysis (e.g., Berthouex and Brown, 1994). Average \( \text{NO}_3^-\text{N} \) concentration in irrigation water was 4 g m\(^{-3}\) (Harter et al., 1999). Long-term average annual irrigation N input is therefore 70 kg N ha\(^{-1}\) yr\(^{-1}\). A margin of error of ±10% primarily accounts for the lack of precise irrigation flow measurements and also for measurement errors of the \( \text{NO}_3^-\text{N} \) concentration.

Wet and dry depositions and biological N fixation at the site are considered secondary N inputs because of their small contribution to the N budget. Wet and dry depositions were estimated as 2 and 14 kg N ha\(^{-1}\) yr\(^{-1}\), respectively, based on data collected by the California Acid Deposition Monitoring Program at the nearest monitoring stations to our site, Lindsay, Tulare County and Bakersfield, Kern (e.g., Blanchard and Tonnesen, 1993; Mutters, 1995). Biological N fixation (BNF) is small due to readily available N, low OM, and the lack of plant growth that supports N-fixing bacteria fertilization. Stevenson (1982) reported BNF inputs to be in the range of 2 to 7 kg N ha\(^{-1}\) yr\(^{-1}\).

### Nitrogen Plant Uptake and Transformations

In the first year of the experiment, there were no significant differences in yield or average fruit weight among the subplots. In the second and third years, the control subplot dropped off in both yield and fruit size, but then remained at about the same level for the duration of the experiment. The 7-yr average yield was 36, 51, and 48 t ha\(^{-1}\) for the control, standard, and high subplots, respectively, indicating a negative response of the high subplot to overfertilization. Nitrogen content in dry fruit measured in 1983 was 0.71, 1.51, and 2.05% for the control, standard, and high subplots, respectively. Nitrogen uptake estimates are based on 7-yr average annual crop yield and the dry matter fruit N content measured in 1983.

![Fig. 2. A schematic representation of the components of the N budget and water mass balance.](image-url)
Table 2. Root zone water balance, root zone N mass balance, and deep vadose zone N storage estimation by the mass balance method. The 95% confidence intervals are given in parentheses. For computed results, confidence intervals were obtained by standard, linear error analysis (Berthouex and Brown, 1994). Confidence intervals for deep vadose zone storage were computed at the lower and upper 95% confidence intervals for the mean travel time through the deep vadose zone, given the confidence intervals of N_leaching and recharge.

<table>
<thead>
<tr>
<th>Control</th>
<th>Standard</th>
<th>High</th>
<th>All 3 subplots</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Root zone water balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irrigation $I$, cm yr$^{-1}$</td>
<td>174 (157/192)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation $P$, cm yr$^{-1}$</td>
<td>33 (32/35)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evapotranspiration ET, cm yr$^{-1}$</td>
<td>98 (93/103)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recharge = $I + P - ET$, cm yr$^{-1}$</td>
<td>110 (91/128)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Root zone N balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary inputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer appl., kg ha$^{-1}$ yr$^{-1}$†</td>
<td>0</td>
<td>110</td>
<td>365</td>
</tr>
<tr>
<td>Irrigation, kg ha$^{-1}$ yr$^{-1}$†</td>
<td>70 (56/84)</td>
<td>70 (56/84)</td>
<td>70 (56/84)</td>
</tr>
<tr>
<td>Secondary inputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation + dry deposit, kg ha$^{-1}$ yr$^{-1}$‡</td>
<td>16 (11/21)</td>
<td>16 (11/21)</td>
<td>16 (11/21)</td>
</tr>
<tr>
<td>Nonsymbiotic N fixing, kg ha$^{-1}$ yr$^{-1}$‡</td>
<td>5 (2/7)</td>
<td>5 (2/7)</td>
<td>5 (2/7)</td>
</tr>
<tr>
<td>Total, kg ha$^{-1}$ yr$^{-1}$</td>
<td>91</td>
<td>201</td>
<td>456</td>
</tr>
<tr>
<td>Primary outputs (transformations)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plant N uptake, kg ha$^{-1}$ yr$^{-1}$</td>
<td>25 (19/37)</td>
<td>77 (65/82)</td>
<td>98 (74/112)</td>
</tr>
<tr>
<td>NH$_3$ losses, kg ha$^{-1}$ yr$^{-1}$‡</td>
<td>–</td>
<td>11 (2/22)</td>
<td>37 (7/73)</td>
</tr>
<tr>
<td>Denitrification, kg ha$^{-1}$ yr$^{-1}$‡</td>
<td>9 (2/7)</td>
<td>20 (4/60)</td>
<td>46 (9/137)</td>
</tr>
<tr>
<td>Secondary outputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil erosion + surface runoff, kg ha$^{-1}$ yr$^{-1}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total, kg ha$^{-1}$ yr$^{-1}$</td>
<td>34</td>
<td>108</td>
<td>181</td>
</tr>
<tr>
<td>$\Delta$N change in organic/inorganic N pool, kg ha$^{-1}$ yr$^{-1}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$N_{leaching} = \Delta N_{inputs} - \Delta N_{outputs} + N_{pot}$</td>
<td>57 (36/78)</td>
<td>93 (59/127)</td>
<td>275 (228/322)</td>
</tr>
<tr>
<td>Potentially leachable N (LPLN) risk</td>
<td>low</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td><strong>Deep vadose zone N storage</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measured, kg ha$^{-1}$</td>
<td>48 (42/62)</td>
<td>36 (33/47)</td>
<td>87 (79/107)</td>
</tr>
<tr>
<td>Predicted for 1997, kg ha$^{-1}$</td>
<td>218 (130/334)</td>
<td>261 (147/427)</td>
<td>478 (271/784)</td>
</tr>
</tbody>
</table>

† Measured.
‡ Estimated from literature reference values.

$N_{uptake} = (\text{annual yield} \times 10\%) \times (\%N_{content}/100)$ [2]

where 10% is the dry matter content in the fresh fruit. In the absence of multyear measurements, fruit N concentrations (but not yield) were assumed to vary proportional to leaf N content (Scott Johnson, personal communication, 2004), which remained practically constant throughout the experiment. Annual yields varied among the 7 yr that N leaf content was measured. The measured range of annual yields provided a conservative basis for estimating the 95% confidence interval of the long-term average annual N uptake (Table 2).

Nitrogen in tree leaves is considered to be completely recycled into the root zone. Losses due to soil erosion and surface runoff are negligible since the ground surface at the orchard is flat and the basin irrigation system (surface flooding) generates no surface water return flow.

Denitrification and NH$_3$ losses were estimated from previous experimental studies (Meisinger and Randall, 1991) that took into account various controlling site conditions (e.g., irrigation, drainage, climate, soil OM, and pH). The observed range of 6 to 20% N loss from denitrification is consistent with the experimental findings of Dowdell and Webster (1984), who reported N loss of 2 to 19% during a long-term N balance study, but lower than the 15 to 30% loss estimates reported by Allison (1966) and Hauck (1981). We adopted an average N loss of 10% of $N_{uptake}$ with the error margins equal to the range of reported loss percentages (2–30%, Table 2). Neutral to slightly acidic soil pH conditions at the site (not shown here) keep NH$_3$ volatilization at a minimum (Paustian et al., 1990). Average volatilization losses are approximately 10% with error margins equivalent to those of denitrification (Table 2) (Meisinger and Randall, 1991).

Water Mass Balance and Deep Vadose Zone Nitrogen

The average annual water budget, as illustrated in Fig. 2, is (Martin et al., 1991)

$$R = I + P - ET$$ [3]

where $R$ (m yr$^{-1}$) is the average annual deep percolation (recharge) from the root zone, and $I$, $P$, and ET (m yr$^{-1}$) are average annual irrigation, precipitation, and (crop) evapotranspiration amounts for the 12 yr from 1984 to 1995. In the deep vadose zone, water flux is typically assumed to be at steady state and equal to the average water leaching rate from the root zone.

For predictive purposes, we applied a commonly used simple one-dimensional uniform steady-state flow concept. Average NO$_3$–N concentration (g m$^{-2}$) in the 14-m-deep vadose zone was obtained by multiplying annual NO$_3$–N leaching loss from the root zone with the recharge rate $R$. The total amount of NO$_3$–N (kg ha$^{-1}$) contained within the deep vadose zone was computed by multiplying the annual NO$_3$–N leaching loss, $N_{leaching}$, with the average time of travel, $\tau$, through the deep vadose zone, where $\tau = 14$ m $\times \theta_{surf}/R$, and $\theta_{surf}$ is the average reported field capacity (25%) for the dominant soil texture (Martin et al., 1991).

**Statistical and Geostatistical Analysis**

**Statistical Analysis**

Statistical analysis was used to determine sample distributions and to identify deterministic factors controlling the spa-
tial variability of water content $\theta$ and NO$_3$--$N_{eq}$. Factors considered included depth, $N$ treatments, and lithofacies distribution. Depth-dependent trends were determined using a separate regression analysis of the log and logtransformed NO$_3$--$N_{eq}$ for each subplot treatment. After removing trends, a Kolmogorov–Smirnov (K–S) test (e.g., Davis, 1986; Olea, 1999) was used to test normality of the log and logtransformed NO$_3$--$N_{eq}$ distribution. The effects of subplot treatment (three groups: control, standard, and high) and lithofacies (10 sample groups, one for each lithofacies), and their interactions (30 groups) on $\theta$ and lnNO$_3$--$N_{eq}$ were measured by a sigma-restricted ANOVA with effective hypothesis decomposition (Hocking, 1985) to account for the unbalanced design (unequal number of samples between groups). Homogeneity of variance was assumed if the ratio of the largest to smallest group standard deviation did not exceed 3. Where significant effects were observed ($p < 0.05$), Newman–Keuls and Duncan’s multiple range tests were performed for post-hoc pair-wise comparison of means. Nitrate-N samples below the LOD were not included in the significance analysis. To check for potential bias from exclusion of nondetects, a nonparametric Kruskal–Wallis ANOVA was performed on the bimodally distributed data with nondetect samples recorded at one-half the LOD concentration (see below). A Kruskal–Wallis test was also performed to test for significant effects of subplot and vertical location on the probability of nondetects (using an indicator variable of 1 for “non-detects” and 0 for “detects”). All statistical analyses were performed with the Statistica software (Statsoft, 2002).

Geostatistical Analysis of Water Content and Nitrate Data

After trends were removed and appropriate variable transformations were done based on the results of the statistical analysis, geostatistical analysis was used (i) to quantify the amount of spatial variability in the $\theta$ and NO$_3$--$N$ distributions unexplained by depth, treatment, and lithofacies location; (ii) to characterize differences in the NO$_3$--$N$ distribution among the three different fertilizer treatments; and (iii) to quantify the field-scale N loading rate to groundwater from those local-scale measurements. The correlation coefficient between NO$_3$--$N_{eq}$ and $\theta$ was $-0.11$; hence, $\theta$ and NO$_3$--$N_{eq}$ were considered uncorrelated for purposes of the geostatistical analysis. Due to a large number of nondetect NO$_3$ concentrations, two sets of experimental NO$_3$--$N_{eq}$ semivariograms were computed for the complete dataset and for the dataset that excluded nondetects.

Directional (horizontal and vertical), nested spherical semivariograms were fitted to the observed semivariograms by initially using a manual calibration followed by a least square optimization process (e.g., Davis, 1986; Olea, 1999). Directional semivariograms were constructed with appropriate lag intervals that were assigned according to average horizontal and vertical sampling scheme (Fig. 1).

Ordinary block kriging (Deutsch and Journel, 1992) was applied to estimate average volumetric block values of lnNO$_3$--$N_{eq}$ and residual (i.e., trend-removed) $\theta$ from their point measurements. The kriging domain size for each subplot was $x = 24.8, y = 3.6$, and $z = 16$ m (80 ft, respectively), discretized into blocks with $\Delta x = 0.75$ m, $\Delta y = 0.3$ m, and $\Delta z = 0.15$ m.

RESULTS

Field-Scale Water and Nitrogen Balance: Long-Term Potentially Leachable Nitrogen

As expected, LPLN increases with N application rates since crop N uptake consumes only part of the increased amount of N fertilizer (Table 2). The LPLN computed for the high subplot represents a potentially high risk for groundwater pollution (Meisinger and Randall, 1991). The net percolating water below the root zone ($R$) is 1.1 (±0.2) m yr$^{-1}$ (Table 2), reflecting the low irrigation efficiency of the flood irrigation. The margin of error stems mostly from the large uncertainty about the mean irrigation rate, which was much larger than that for precipitation or crop evapotranspiration. The estimated net annual mean vertical solute travel distance is 4.4 (±0.8) m ($\theta_{soil} = 25\%$) and the mean travel time to groundwater, $\tau$, is 3.2 (2.8–3.8) yr (Fig. 2). At $\tau = 3.2$ yr, field-scale N concentration in the leachate (and recharge) is predicted to be 5, 9, and 25 g m$^{-3}$ for the control, standard, and high subplots, respectively. Corresponding deep vadose zone N storage is predicted to be 180, 300, and 880 kg N ha$^{-1}$, respectively. For 1997, the deep vadose zone storage can be computed by considering that all subplots were subject to the “control” leaching rate in 1995 (no fertilizer application) and to the “standard” leaching rate in 1996 (uniform standard fertilizer application). Then, the predicted deep vadose zone N storage at the time of drilling in 1997 is 220, 260, and 480 kg N ha$^{-1}$. The wide confidence intervals for the deep vadose zone N storage, summarized in Table 2, reflect potential errors in both the recharge and the LPLN computation.

Statistical Analysis of Water Content and Nitrate Distribution

Water Content

Measured water content data follow an approximately symmetric, normal distribution (Table 1). Within all subplots water content is characterized by a significant linear increase with depth. Separate linear trend models were fit to each subplot dataset, as illustrated in Fig. 3. Trend residuals are shown to be normally distributed and lognormal (significance level, $p = 0.05$) after excluding nondetect samples (Fig. 4b). Resulting sample means ($\mu$) and lognormal ($\sigma$) are 5.2, 3.3, and 7.4 g m$^{-3}$ for the control, standard, and high subplots, respectively. Detectable NO$_3$--$N_{eq}$ concentrations range from 0.04 to 129.72 g m$^{-3}$.
Fig. 3. Scatter plots of water content with depth for each subplot. Line represents linear regression models for the trend defined as a function of depth. Equations for the trends are $\theta_0 = 0.089 + 0.019z$ for the control subplot, $\theta_0 = 0.127 + 0.013z$ for the standard subplot ($r^2 = 0.48$), and $\theta_0 = 0.087 + 0.017z$ for the high subplot ($r^2 = 0.36$).

(21% measure $< 1 \text{ g m}^{-3}$ and 10% exceed the maximum contamination level for drinking water ($10 \text{ g m}^{-3}$)).

Significant differences exist between subplots. In the high subplot, the fraction of low NO$_3$-Naq measurements is less than one-third of the fraction observed in the other two subplots. On the other hand, most of the high concentration samples, exceeding 10 g m$^{-3}$, are found in the high subplot, while only a small fraction (8%) of these are found below the root zone of the control plot.

Figure 5a shows the profiles of lithofacies-specific mean lnNO$_3$-Naq in the three subplots. The lithofacies effect represents the combined influence of depth and sediment texture on NO$_3$-Naq since the lithofacies are sorted in vertical sequence. At all three subplots, the highest average NO$_3$-Naq levels occur in the root zone to approximately 3 m, which is mostly comprised of a fine sandy loam lithofacies (SL). Below SL, NO$_3$-Naq concentrations are lower, but no significant vertical trends or contrasts were observed. The high subplot shows the largest NO$_3$-Naq mean concentrations throughout most of the profile, which is consistent with the higher fertilizer applications. Differences between the control and standard subplot means are not significant. Coefficients of variation for each subplot range from 1.6 to 2.4 (Table 1) and similarly for individual lithofacies and lithofacies X subplot groups.

Almost one-third of the samples (28% of all samples) have nondetectable levels of NO$_3$-Naq (Fig. 5b): 22% of the control, 32% of the standard, and 25% of the high subplot, and from 13% to 50% for individual facies. The fewest nondetects were observed at depths below 12 m (SL2, HP2) (Fig. 5b). The highest fractions of nondetects occurred in the coarse-textured, sandy lithofacies Var1, in the hardpan HP1, and in the sand lithofacies S, where approximately one-half of the samples had nondetectable levels of NO$_3$-Naq.

Because of the large number of nondetects, replacing nondetects with a default value of −4.605 (one-half of the LOD) leads to a bimodal lnNO$_3$-Naq distribution; the LOD for NO$_3$-Naq is significantly lower than the extent of the left tail of the lnNO$_3$-Naq distribution in Fig. 4b. In other words, the number of nondetects (224)

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**Geostatistical Analysis of Water Content and Nitrate Distribution**

Separate water content and NO$_3$ semivariograms were computed for each subplot. Data density was not sufficient to derive well-structured separate semivariogram models for individual lithofacies within each subplot. But by applying a thin vertical bandwidth (<15 cm) in the search window, horizontal semivariograms were computed for data pairs containing only points within the same lithofacies (e.g., Deutsch and Journel, 1992).

**Water Content**

Semivariograms of the water content trend residuals exhibit not only a significant geometric anisotropy (un-
suggest that the deeper portion of the control and high subplots is wetter than that of the standard subplot.

**Nitrate**

Separate semivariograms for the complete dataset and for the detectable level dataset were computed and, for comparison, plotted after normalizing the semivariograms by their respective variances (Fig. 8). The semivariogram of the complete dataset with its strong bimodal distribution and large standard deviation (2.63, see Table 1) reflects the combined effect of two spatial variability structures: (i) the spatial variability structure between measurable \( \ln \NO_3-N_{aq} \) levels (pattern of different colors in Fig. 9) and (ii) the spatial variability of the bimodal pattern of zones with undetectable \( \NO_3-N_{aq} \) and zones with detectable \( \NO_3-N_{aq} \) (pattern of purple/dark vs. other colors in Fig. 9). Separate variograms were computed for the two datasets, to determine whether the pattern created by the bimodality dominated the semivariogram structure because of the large concentration difference between the two modes in the distribution. However, the normalized semivariograms of the two datasets were found to be essentially identical. Only the vertical nugget effect, especially in the high subplot, is notably smaller for the semivariograms of the smaller (detectable levels only) dataset. Hence, vertical spatial continuity is higher within zones of measurable \( \NO_3-N_{aq} \) (triangles) than between zones of measurable and non-detectable \( \NO_3-N_{aq} \) (diamonds). In the horizontal direction, differences between the two sets of semivariograms are not significant.

Kriged concentrations (using the semivariograms of the complete dataset) are found to be highly variable with several “plumes” of high concentration observed near the top and in the upper third of the profile of each subplot (Fig. 9). The total N mass in the vadose zone obtained from kriging is 52 (±9.7), 40 (±7), and 93 (±14.1) kg N ha\(^{-1}\) for the control, standard, and high subplots, respectively. Confidence intervals represent the average kriging error variance. The deep vadose N mass (without the root zone) is 48, 36, and 87 kg N ha\(^{-1}\), respectively. These latter kriged (“measured”) total N masses amount to 24% (15–40%), 15% (9–27%), and 19% (12–34%), respectively, of those predicted from the MB analysis for 1997 (values in parentheses account for estimation errors in the MB analysis).

These observations raise several issues to be discussed in the following section: What are the potential errors contributing to the difference between predicted and measured deep vadose zone N? How representative and significant is the amount of observed spatial variability of water content and \( \NO_3 \)? What does the observed spatial variability of water content and \( \NO_3 \) indicate with respect to the spatial distribution of water flux and the expected fate of transport?

**DISCUSSION**

**Measured vs. Predicted Nitrate Mass in the Deep Vadose Zone**

Several reasons may explain the large discrepancy between the two estimates of deep vadose zone \( \NO_3 \):
estimation errors in the MB method yielding an errone- ous interpretation for LPLN, estimation errors in the geostatistical analysis of vadose zone N mass, significant N losses in the deep vadose zone not accounted for in

the MB method, and nonuniform flow conditions in the vadose zone.

The computed error margins for recharge, LPLN, and the resulting deep vadose zone storage (Table 2) are on the same order as the 30% of actual leaching losses suggested by Meisinger and Randall (1991). Although large, neither these errors nor those from the kriging analysis can explain the observed difference between MB predicted and measured deep vadose zone N.

If the differences were assumed to be primarily caused by denitrification (Bar-Yosef and Kafkafi, 1972; Arons- son, 2001) under predominantly uniform vertical flow conditions, the amount of N loss in the deep vadose zone should be on the order of one hundred to several hundred kilograms per hectare within one leaching cycle (i.e., 3.2 yr) with much higher denitrification rates under the high subplot than the other two subplots. Most of this denitrification would have had to occur in the shal- lowest zone because no significant depth-dependent de- crease in NO₃–N was observed below the root zone and because several relatively high NO₃–N concentrations were measured even at depth. However, denitrification rates of more than 55 to 60 kg ha⁻¹ yr⁻¹ are unlikely, given the low organic C content of the root zone and its relatively coarse texture (e.g., Rolston et al., 1982; Aronsson, 2001; Sanchez et al., 2001; Krug and Winstan- ley, 2002). This is also consistent with the lack of signifi- cant vertical trends in the N isotope fractionation ob- served at the site (Harter et al., 2004).

While the denitrification processes in the deep vadose zone may be locally significant (Harter et al., 2004), other explanations, namely the role of heterogeneity and flow nonuniformity (not considered in the MB model) must be considered to explain the large discrepancy be- tween field measured and MB estimated deep vadose zone N content. The site stratigraphy and hydraulic properties are highly variable both between facies and within facies (Minasny et al., 2004). The significant de- gree of layering observed at the site is typical of the alluvial fan architecture in the region, which contains laterally extensive hardpans and floodplain deposits in- tercalated between higher permeable sediments of varying texture representing channel and overbank deposits (Page and LeBlanc, 1969; Weismann et al., 1999). While

Fig. 6. Experimental and spherical model semivariograms for water content (trend residuals) in the horizontal direction for the (a) control, (b) standard, and (c) high subplot; and in the vertical direction for (d) the control, (e) standard, and (f) high subplot. Diamonds denote experimental values and lines denote spherical semivariogram models.

Fig. 7. Contour maps of the kriged (a) water content at the control, standard, and high fertilizer treatment sites; (b) various depth profiles of water content at each subplot.
flow paths of NO$_3$ are thought to be predominantly vertical within one layer, the stratigraphic layering may contribute to lateral flows (Iqbal, 2000) leading to both, preferential flow pattern and potentially significant NO$_3$ exchange between subplots.

Spatial Variability of Water Content and Nitrate

Water Content

The geometric and zonal anisotropy (Fig. 6) are the result of the highly stratified conditions and strong horizontal layering of water content across the site, which is also evident in the kriged water content map (Fig. 7a, 7b). Such “layering” of moisture content can be the result of either layered strata with significant textural differences and also of transiency in the water flux. The significant contribution of textural layering to the water content distribution suggests that textural differences at the site are the main cause of the water content differences with depth. Similar phenomena have been observed in other field experiments and in numerical studies of vadose flow through heterogeneous media (e.g., Hills et al., 1991; Polmann et al., 1991).

Nitrate

Lognormal NO$_3$-N$_{aq}$ distributions found at this deep vadose zone site are not unlike those reported in other studies focusing on the root zone (e.g., Tabor et al., 1985; SharmaSarkar et al., 1999; Ilsemann et al., 2001). However, CVs for each subplot treatment (Table 1) are significantly higher than those measured elsewhere, where reported CVs typically range from 20 to 50% and in few cases are as high as 70 to 100% (e.g., Mohanty and Kanwar, 1994; SharmaSarkar et al., 1999; Ilsemann et al., 2001). In part, the higher observed variability of NO$_3$-N$_{aq}$ may be attributed to the small sample size (3.5-cm diameter by 7.5-cm length) relative to other typical soil samples (∼3.2-cm diameter by 30-cm length). It may also be a result of the fact that practically all samples are taken at depths well below the mechanical impact zone of agricultural practices. It cannot be attributed to lithofacies control, since no large concentration contrasts were observed between most lithofacies.

The significantly larger mean NO$_3$-N$_{aq}$ of the high subplot indicates that higher than standard fertilizer treatment indeed affects NO$_3$ transport to groundwater. However, the difference must be interpreted carefully in light of the high degree of spatial variability. Some of the key patterns in NO$_3$-N$_{aq}$ distribution are also due to other boundary effects:

- High concentrations of kriged NO$_3$-N$_{aq}$ near the top and in the upper third of the profile of each subplot are attributed to the most recent fertilizer application in 1996 and explain the significant shift in the mean NO$_3$-N$_{aq}$ in the upper 3 m (Fig. 5a). In the control subplot, we suspect that the higher NO$_3$-N$_{aq}$ content is likely the result of poor root uptake. After 12 yr, tree roots of the control subplot were likely unable to capture the additional N of the one-time application because the root system had grown to capture nutrient supply primarily or exclusively from neighboring treatments (Scott Johnson, personal communication, 2004).

- Significant reduction of the number of nondetects below depths of 12 m is likely the result of the fact that the bottom of the vadose zone had been fully saturated (part of the shallow groundwater system) in some high water years before 1989. Shallow groundwater contains elevated levels of NO$_3$ (4 g m$^{-3}$ or more).

Nitrate semivariograms exhibit a statistically significant spatial continuity as postulated in theoretical stochastic models of solute transport through the vadose zone (e.g., Harter and Yeh, 1996). The observed geometric anisotropy may be caused by nonuniform N applications (extrinsic variability). Possibly, such strong geometric anisotropy may also be the result of highly heterogeneous vadose flow processes (see below). While it is difficult to further facilitate the comparison of the results of spatial correlation that we observed for NO$_3$
with results obtained from stochastic models of flow and transport in heterogeneous porous media. Harter and Yeh (1998) and Harter and Zhang (1999) demonstrated that spatially variable soil properties lead to approximately normal distributed moisture distributions while the resulting vadose moisture velocity distribution is highly skewed (lognormal), which then leads to a skewed concentration distribution. Like its marginal probability distribution, the kriged NO$_3$–Na$_q$ distribution pattern at the experimental site is also surprisingly similar to that found in other experimental studies (e.g., Hills et al., 1991; Roth et al., 1991) and to that postulated in numerical models (e.g., Harter and Yeh, 1996; Ünlü et al., 1990; Tompson and Gelhar, 1990) of transport in highly heterogeneous hydraulic conductivity fields. We observed zones with individual plumes apparently moving laterally in some locations and downward in others, high concentration variability, and large zones with negligible NO$_3$ concentrations.

The conceptual framework of lognormally distributed flow rates (e.g., Harter and Yeh, 1996) is in fundamental contrast to the uniform flow conditions assumed in the LPLN estimates of N mass in the deep vadose zone. Under the conditions of lognormal flow rates (i.e., strongly heterogeneous flux rates), quasipreferential flow paths exist (Polmann et al., 1991; Russo et al., 1994; Harter et al., 1996; Harter and Yeh, 1996), creating a flow pattern not unlike that in soils with a relatively low permeable matrix and a highly permeable macropore structure (Roth et al., 1991). Under such heterogeneous flux conditions, the majority of the pore space is occupied by regions with slow velocities (including stagnant zones that do not contribute significantly to active flow). Nitrate in those low flow regions can have tortuous flow paths, long travel times, and be subject to local denitrification, particularly in the shallow vadose zone after storm events (Pionke and Lowrance, 1991; Ryden and Lund, 1980; Xu et al., 1998; MacQuarrie and Sudicky, 2001). Largest flux contrasts between preferential flow paths and stagnant flow zones would be observed in coarse-textured material because of its low capillary potential. This is consistent with the fact that the largest amount of NO$_3$–Na$_q$ nondetects at the site occurred in the sand lithofacies S located in the center of the vadose zone profile.

Theoretical models indicate that the relatively high flow zones are of only limited spatial extent (e.g., Fig. 9 in Harter et al., 1996), but their high flux rates lead to rapid NO$_3$ transfer through the vadose zone. Such effects of textural heterogeneity on flow nonuniformity are further enhanced by potentially unstable infiltration into the sandy loam root zone, which were documented for this site in Wang et al. (2003). Even stronger instabilities and fingering may occur at and below the interface of fine-textured lithofacies overlying coarse-textured lithofacies (Glass et al., 1988), such as in the deeper sand lithofacies S, which had relatively low water content and a high ratio of NO$_3$–Na$_q$ nondetects.

The combined evidence of textural heterogeneity, lithofacies contrasts, hydraulic heterogeneity (Minasny et al., 2004), and spatial variability of water content and

**Fig. 9.** Contour maps of the kriged (a) lnNO$_3$–Na$_q$ (g m$^{-3}$ = µg mL$^{-1}$) at the control, standard, and high fertilizer treatment sites; (b) various depth profiles of lnNO$_3$–Na$_q$ at each subplot.
NO₃⁻Naq strongly suggests three major processes controlling the fate and transport of NO₃ in the vadose zone:

- limited, localized denitrification in the slow flow regions,
- lateral flow and N exchange between subplots, and
- preferential flow and perhaps fingering, which lead to rapid, highly localized N transport toward the water table.

These processes would explain both the large number of nondetects and the overall low N mass remaining in the deep vadose zone. The rapid NO₃⁻Naq transport in localized flux channels significantly reduces the amount of N stored in the deep vadose zone, strongly limiting the role of denitrification. Our results suggest that the lack of N stored below the root zone should not automatically be interpreted as significant N attenuation due to denitrification (or other unquantified losses within the root zone). We point out that the conceptual framework of heterogeneous flow (as opposed to uniform deep vadose zone flow) also suggests the simultaneous occurrence of significantly older water next to very young water within the vadose zone. Hence, the NO₃ distribution at the site (Fig. 9a) represents as much average conditions during the long-term fertilizer treatment (in lower flux regions) as it represents only the most recent two N applications (in 1994, 1996), the latter of which was uniform across all treatments (in the localized high flux regions). This would explain the relative similarity in measured total N levels between subplots.

CONCLUSIONS

An intensive field sampling campaign resulted in a unique snapshot of the vadose zone NO₃⁻N distribution throughout its 16-m depth under three different 12-yr fertilization trials. While results are site specific, the site conditions are typical of many agricultural regions in alluvial basins. Our findings summarized below are therefore relevant to heterogeneous, alluvial vadose zone sites below agricultural production areas in general.

1. Significantly higher NO₃⁻N leaching occurs in overfertilized tree crops, when compared with those fertilized under standard or substandard conditions.
2. The field data reveal significant variability in water content and particularly in the NO₃⁻N distribution throughout the deep vadose zone, with measured NO₃ values varying by several orders of magnitude over relatively short distances. Almost one-third of the core samples had nondetectable levels of NO₃⁻N.
3. Despite the high variability, NO₃⁻N semivariograms discern the presence of a significant short-range spatial structure at the scale of a several decimeters, particularly in the vertical direction, normal to the horizontal layering in the sedimentary structure. The highly heterogeneous NO₃⁻N distribution is consistent with the significant textural and hydraulic heterogeneity observed in the vadose zone at the site.
4. The presence of strongly heterogeneous geologic formations at the site, highly variable hydraulic conductivity and water content, and the strongly log-normal, variable distribution of NO₃ concentrations suggest that highly heterogeneous, skewed or log-normally distributed flux conditions and, in coarse facies, finger-like flow dominate the vadose zone hydrology in these alluvial sediments.
5. The variability of NO₃⁻N concentrations underscores the importance of high spatial sampling frequencies when monitoring field-scale solute leaching with suction lysimeters or other common soil monitoring tools that measure relatively small volumes of soil water.
6. In alluvial sediments, the often used assumption of uniform flow in the deep vadose zone is inadequate to predict NO₃⁻N levels in the deep vadose zone below the root zone. Actual NO₃⁻N levels are potentially much lower due to rapid N transport in preferential flow paths of limited spatial extent.
7. Vice versa, measured NO₃⁻N levels below the root zone should not be used to validate a LPLN analysis or to close the mass balance of the LPLN framework assuming uniform field-scale flow conditions. Doing so would lead to significant underestimation of NO₃ leaching rates to groundwater.
8. Denitrification may locally occur throughout the deep vadose zone, but our data indicate that it is not likely to be a major process and cannot account for the relatively low N mass found in the deep vadose zone.
9. Given that field measurements of NO₃⁻N fluxes below the root zone remain difficult in light of the observed spatial variability, alternative methods for measuring NO₃⁻N leaching will continue to play a significant role. In particular, proper determination of the field-scale water and N mass balance, independent of root zone NO₃⁻N measurements, remains an important option. The results also suggest that groundwater quality measurements at the water table are a viable monitoring tool, as travel times through deep vadose zones may be shorter than previously assumed under uniform flow assumptions.

The results are consistent with, albeit not a direct proof of, theoretical work on the effects of soil and sediment heterogeneity on vadose flow and transport. The extensive deep vadose zone sampling campaign presented here provides the first extensive dataset to confirm the applicability of stochastic concepts of unstable flow to predicting solute flux in the deep vadose zone. Ongoing work to substantiate the role of heterogeneity and denitrification will include a detailed, site-specific modeling analysis.

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