

# Water Quality in Walnut Creek Watershed: Nitrate–Nitrogen in Soils, Subsurface Drainage Water, and Shallow Groundwater

C. A. Cambardella,\* T. B. Moorman, D. B. Jaynes, J. L. Hatfield, T. B. Parkin, W. W. Simpkins, and D. L. Karlen

## ABSTRACT

Nonpoint source contamination of surface and groundwater resources with nitrate–N ( $\text{NO}_3\text{-N}$ ) has been linked to agriculture across the midwestern USA. A 4-yr study was conducted to assess the extent of  $\text{NO}_3\text{-N}$  leaching in a central Iowa field. Water flow rate was monitored continuously and data were stored on an internal datalogger. Water samples for chemical analysis were collected weekly provided there was sufficient flow. Twelve soil cores were collected in spring, early summer, mid-summer, and after harvest for each of the 4 yr. Nitrate–N concentrations in shallow groundwater exhibited temporal trends and were higher under Clarion soil than under Okoboji or Canisteo soil. Denitrification rates were two times higher in Okoboji surface soil than in Clarion surface soil and the highest denitrification potential among subsurface sediments was observed for deep unoxidized loess. Soil profile  $\text{NO}_3\text{-N}$  concentrations decreased with depth and were the same below 30 cm for fertilized corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr.). Nitrate–N concentrations in subsurface drainage water exceeded  $10 \text{ mg L}^{-1}$  for 12 mo and were between 6 and  $9 \text{ mg L}^{-1}$  for 32 mo during the 4-yr study. The temporal pattern of  $\text{NO}_3\text{-N}$  concentrations in subsurface drainage water was not related to the timing of fertilizer N application or the amount of fertilizer N applied. Total  $\text{NO}_3\text{-N}$  losses to subsurface drains were greatest in 1993 ( $51.3 \text{ kg ha}^{-1}$ ) and least in 1994 ( $4.9 \text{ kg ha}^{-1}$ ). Most of the subsurface drainage water  $\text{NO}_3\text{-N}$  was lost when crop plants were not present (November–May), except in 1993. Our results indicate that  $\text{NO}_3\text{-N}$  losses to subsurface drainage water occur primarily as a result of asynchronous production and uptake of  $\text{NO}_3\text{-N}$  in the soil and the presence of large quantities of potentially mineralizable N in the soil organic matter.

NONPOINT SOURCE contamination of surface- and groundwater with  $\text{NO}_3\text{-N}$  has been linked to agricultural production in the midwestern USA. This is especially true for surface waters in the upper Midwest due to extensive subsurface draining of the highly productive but poorly drained soils found in this region (Gast et al., 1978). However, the extent to which agriculture contributes to water-quality deterioration is not fully known. In some geographic regions, surface-water  $\text{NO}_3\text{-N}$  concentrations in excess of the  $10 \text{ mg L}^{-1}$  drinking water standard frequently have been reported (Hallberg, 1986). Keeney and DeLuca (1993) found that  $\text{NO}_3\text{-N}$  concentrations in Des Moines river water in central Iowa were above  $10 \text{ mg L}^{-1}$  for an average of 14 d per year, generally in the spring.

Subsurface drainage water  $\text{NO}_3\text{-N}$  concentrations exhibit yearly and seasonal variability (Kladivko et al., 1991). Nitrogen flux to subsurface drains appears to be primarily a function of precipitation amounts and distribution, and is only slightly affected by crop N up-

take patterns. The concentration of  $\text{NO}_3\text{-N}$  in subsurface drainage water is especially dependent on growing season precipitation through the effect of precipitation on subsurface drain flux (Jaynes et al., 1999). When the soil is dry and precipitation is low, infiltration and percolation are negligible and plant uptake is limited. However, mineralization of soil organic N continues to occur and results in an accumulation of inorganic N. When precipitation finally exceeds evapotranspiration,  $\text{NO}_3\text{-N}$  concentrations in subsurface drain water can increase very rapidly and result in large  $\text{NO}_3\text{-N}$  loading losses to the subsurface drains, which subsequently empty into surface waters. Randall and Iragavarapu (1995) report annual subsurface drain  $\text{NO}_3\text{-N}$  loads ranging from 1.4 to  $139 \text{ kg ha}^{-1}$ , with the lower loading losses occurring during years with less than average growing season precipitation. Annual losses of  $\text{NO}_3\text{-N}$  in subsurface drainage water from corn fields ranged between 11 and  $107 \text{ kg N ha}^{-1}$  in four different tillage systems in Iowa (Bjorneberg et al., 1996). A large portion of the N loss occurred prior to fertilizer application in early April. Subsurface drainage water  $\text{NO}_3\text{-N}$  concentrations, averaged over the growing season, were consistently above  $10 \text{ mg L}^{-1}$ , and were greater from corn than from soybean. Patni et al. (1996) reported 13 to  $30 \text{ kg ha}^{-1}$  loss of  $\text{NO}_3\text{-N}$  through subsurface tile drains in fields cropped to corn in southern Ontario.

Nitrate–N has been detected in groundwater at levels ranging from 0.17 to  $36 \text{ mg L}^{-1}$  in the Midwest Corn Belt (Hallberg, 1986; Burkart and Kolpin, 1993; Spalding and Exner, 1993). Excess concentrations of  $\text{NO}_3\text{-N}$  ( $>3 \text{ mg L}^{-1}$ ) are more frequently found in unconsolidated aquifers than in bedrock aquifers (Burkart and Kolpin, 1993). In Iowa, the distribution of  $\text{NO}_3\text{-N}$  contamination in groundwater is not uniform. Contamination occurs most frequently in southwest, northwest, and south-central portions of the state. North central and central Iowa have the lowest incidence of contamination (Spalding and Exner, 1993). One possible explanation for these differences is higher rates of denitrification in the poorly drained central Iowa soils. In addition, significant amounts of  $\text{NO}_3\text{-N}$  are being intercepted by subsurface drains and discharged to surface waters (Power and Schepers, 1989).

Our experimental objectives were: (i) to quantify  $\text{NO}_3\text{-N}$  concentrations and loadings in subsurface drain water, shallow groundwater beneath the subsurface drains, and in the soil profile over a 4-yr time period, (ii) to quantify denitrification rates in surface soils and subsurface sediments, and (iii) to assess the effect of

USDA-ARS, National Soil Tilth Lab., 2150 Pammel Dr., Ames, IA 50011-4420. Received 23 Jan. 1998. \*Corresponding author (cindyc@nstl.gov).

soil type on the amount of  $\text{NO}_3\text{-N}$  in the soil profile and in subsurface drainage water and shallow groundwater.

## MATERIALS AND METHODS

### Site Description and Sampling

The site covers 38 ha in the western part of the Walnut Creek watershed, near Kelly, IA. The soils are mapped as Clarion (fine-loamy, mixed, mesic Cumulic Hapludoll); Nicollet (fine-loamy, mixed, mesic Aquic Hapludoll); Canisteo (fine-loamy, mixed (calcareous), mesic Typic Haplaquoll); Harps (fine-loamy, mesic Typic Calciaquoll); and Okoboji (fine, montmorillonitic, mesic Cumulic Haplaquoll) (Fig. 1). The southern half of this field (18 ha) contains two closed depressions or potholes mapped as Harps and Okoboji soils. An intensive sampling of 6.25 ha of the southern half of the field in 1992 (Cambardella et al., 1994) described field variability at the site and additional measurements from soil cores are provided in Table 1. The farming practices include a corn-soybean rotation, disk tillage in the spring, fall application of anhydrous ammonia and application of banded herbicides. These practices are fairly representative of the production systems used in this watershed (Hatfield et al., 1999). In 1991, 1993, and 1995 soybean was grown, and the herbicides applied included trifluralin and metribuzin. In 1992 and 1994 corn was grown with a cyanazine-atrazine herbicide mixture applied for weed control. Nitrogen fertilizer was applied following soybean harvest in April 1992 (weather prohibited application in fall of 1991) and in November of 1993 using anhydrous ammonia at a rate of  $134 \text{ kg N ha}^{-1}$ . An additional 44 and  $21 \text{ kg N ha}^{-1}$  of dry N fertilizer was broadcast applied with P and K in late winter in 1992 and 1994, respectively. The farmer-cooperator used a bulk blend mixture of mono- and diammonium phosphate and muriate of potash (KCl).

Two transects of shallow well nests span the large pothole in the southern part of the field. One transect of eight nests was placed along an east-west line across the field and the second is on an intersecting north-south line from a hill-top just north of the large pothole to the south fenceline (Fig. 1). Wells were constructed by augering a 5 cm hole to the proper depth before inserting 5 cm i.d. Tri-Loc tubing. A cavity 15

**Table 1. Properties of soils within the area drained by subsurface tiles.**

Soil	Depth cm	Organic C† g kg <sup>-1</sup>	Sand — % —	Clay — % —	pH
<b>Clarion</b>					
Surface soil	0–25	17.2	52	20	5.6
Oxidized till	40–110	3.7	52	24	7.6
Oxidized till	140–210	0.60	54	20	8.0
Unoxidized till	320–335	0.90	nd	nd	7.5
<b>Canisteo</b>					
Surface soil	0–25	25.4	46	24	5.9
Oxidized till	40–110	4.2	46	26	7.7
Oxidized till	140–210	0.80	54	20	8.2
<b>Okoboji</b>					
Surface soil	0–25	51.6	28	30	6.8
Oxidized till	40–110	12.9	20	36	7.2

† Determined by dry combustion methods using a Carlo-Erba NA1500 NCS analyzer (Haake Buchler Instruments, Paterson, NJ).

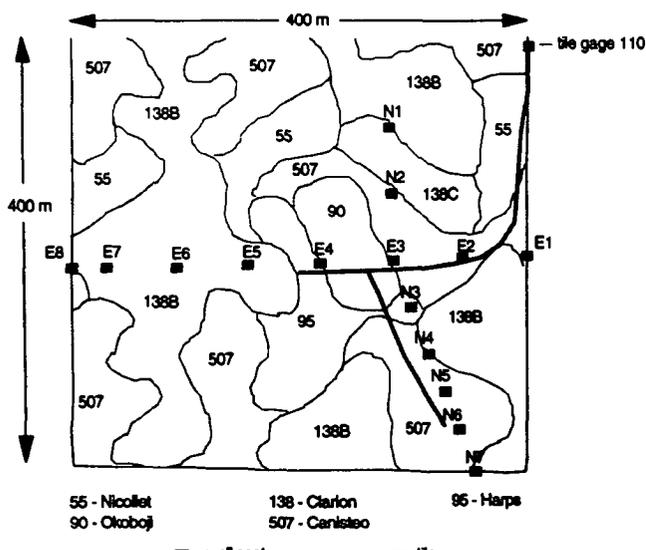
cm deep and 15 cm in diameter was excavated around the top of each well and filled with a sand-cement mortar to prevent water from flowing down the side walls. At each nest, wells with a 0.76 m screen with 0.5 mm slots were installed with the screen centered at 0.6, 1.5, and 2.6 m depths. The wells were sampled beginning in 1991, but some wells were not installed until 1992, nor was there water in all wells at all sampling times (especially the 0.6 m depth wells). The large pothole and surrounding area is drained by a subsurface tile drain running from the pothole northeast to the edge of the field where it joins a larger county tile drain identified as site 110 by Jaynes et al. (1999). At this junction, equipment described by Jaynes et al. (1999) was installed to measure water flow and to sample water in the subsurface tile line draining the large pothole. We determined the drainage area of the subsurface tile drain to be 8.9 ha. Sampling was initiated on Day 344 of 1991. Samples were collected weekly (by hand) and automatically during discharge events (Jaynes et al., 1999).

### Laboratory Methods

#### Soil and Water Inorganic Nitrogen

Soil cores (2.5 cm i.d.) were taken in spring, early summer, mid-summer, and after harvest to a depth of 105 cm with a Giddings truck or high-boy tractor mounted hydraulically-driven soil sampler (Giddings Co., Ft. Collins, CO) at locations throughout the entire 37 ha field to determine the concentrations of  $\text{NO}_3\text{-N}$  in the soil profile. Location of sampling sites was stratified by soil map unit, and at least three replicate cores from each soil type (Table 1) were removed at each sample date. Cores were contained within acetate liners. After transport to the laboratory, cores were frozen until analysis. Prior to extraction and analysis for  $\text{NO}_3\text{-N}$ , cores were cut into depths, mixed, and a 5 g subsample weighed for extraction in 2 M KCl. Nitrate-N was quantified using Lachat flow-injection technology (Lachat Instruments, Milwaukee, WI)<sup>1</sup>. Soil moisture content of additional subsamples was also determined and results are expressed on a dry weight of soil basis. Soil pore water  $\text{NO}_3\text{-N}$  concentrations for each depth increment were calculated using the bulk density, soil water content, and soil  $\text{NO}_3\text{-N}$  concentrations. Water samples were stored at 5°C prior to analysis. The samples were colorimetrically analyzed for  $\text{NO}_3\text{-N}$  using a Lachat Flow Injection autoanalyzer. The detection limit was  $1.0 \text{ mg L}^{-1}$ .

<sup>1</sup> Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.



**Fig. 1. Map of the field site in the Walnut Creek watershed showing soil map units digitized from the county soil survey and location of well nests.**

**Table 2.** Nitrate-N in shallow wells beneath the field site in the Walnut Creek Watershed presented according to well depth or soil map unit.†

Nitrate-N	Category (depth or soil)		
	0.6 m	1.5 m	2.6 m
Mean, SD, mg/L	10.7 ± 8.7	9.2 ± 6.4	5.9 ± 7.0
Median, mg/L	9.95a	9.50a	3.90a
Detection frequency, %	94	91	76
Freq. exceeding MCL, %	50	47	24
Number of observations	266	750	876
	Clarion	Canisteo	Okoboji
Mean, SD, mg/L	10.7 ± 6.5	6.4 ± 8.0	7.5 ± 5.7
Median, mg/L	11.0a	3.9b	7.1c
Detection frequency, %	97	78	88
Freq. exceeding MCL, %	57	23	34
Number of observations	619	794	479

† Concentrations calculated using values of zero for samples below detection limit.

### Denitrification Rates

Denitrification rates were determined on subsoil material collected from six boreholes at three different positions in the field. Soil cores were wrapped in plastic film and transported to the laboratory where they were stored under a N<sub>2</sub> headspace in an anaerobic hood. Within 48 h we shaved the outside surface of the cores with a sterile knife and 200 g sediment material was placed in flasks with 200 mL sterile dH<sub>2</sub>O. The headspace of the flasks was sparged with He. Flasks were shaken for 1 h and 10 mL aliquots of sediment slurry were transferred to sterile 20-mL serum vials, which were then stoppered and flushed with He. Denitrification rates were determined under three treatment regimes; (i) sterile H<sub>2</sub>O, (ii) 2.5 mM NO<sub>3</sub>, and (iii) 2.5 mM NO<sub>3</sub> + 2.5 mM glucose. Acetylene (1 mL) was added to the headspace of each vial and N<sub>2</sub>O concentrations were measured at 24 and 48 h using a gas chromatograph equipped with an electron capture detector operated at 300°C and Porapak Q column (60/80 mesh) operated at 80°C.

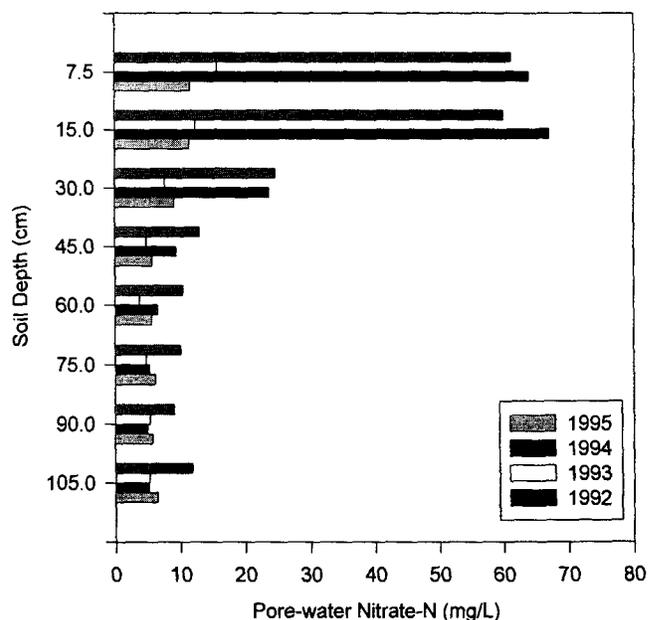
### Long-term Denitrification Potentials

To estimate the long-term potential of subsurface materials to support denitrification, we established microcosms in sterile 1 L glass jars. Each microcosm contained 500 g of subsoil material, 500 mL of sterile dH<sub>2</sub>O, and 10 mL of a 1 M KNO<sub>3</sub> solution. The microcosms, which were incubated under a He headspace at room temperature (24–26°C), in the dark, were sampled at infrequent intervals over a 2-yr period for changes in NO<sub>3</sub> and NH<sub>4</sub> concentrations.

### Data Analysis

Nitrate-N concentrations were reported as average concentrations (mg kg<sup>-1</sup> soil) or calculated as concentrations in the soil solution (mg L<sup>-1</sup>) for comparison to subsurface drainage water concentrations. In addition, the quantities of soil NO<sub>3</sub>-N (kg ha<sup>-1</sup>) are summed for the entire soil profile to a depth of 105 cm based on the NO<sub>3</sub>-N concentration and bulk density for each soil type.

Mean and median concentrations of NO<sub>3</sub>-N in groundwater samples were calculated using values of zero assigned to samples below detection limits (Jaynes et al., 1999). Trends in concentrations were determined using nonparametric one-way ANOVA on ranks, using depth (Friedmans procedure) and soil types (Kruskal-Wallis) as class variables (Gilbert, 1987). Depth comparisons were averaged across soil type and soil type comparisons were averaged across depths (Table 2).



**Fig. 2.** Soil pore-water NO<sub>3</sub>-N concentrations with depth for 1992 to 1995.

In order to conduct a conservative mean separation test (Mann-Whitney Rank Sum Test) for paired comparisons, the analysis of mean separations for paired well depths was constrained to include only those dates when data from the two compared well depths was available (data not shown). In all cases, this conservative test provided the same ranking of depths as when the analysis wasn't constrained (Table 2), even though the absolute mean NO<sub>3</sub>-N concentration at each depth may have been different.

## RESULTS AND DISCUSSION

### Soil Profile Nitrate-Nitrogen

Pore-water NO<sub>3</sub>-N concentrations in the soil profile generally decreased with depth when data for all soil cores for all sampling dates within a single year are averaged (Fig. 2). Expressed as solution concentrations, NO<sub>3</sub>-N below 30 cm depth was <10 mg L<sup>-1</sup>, except for 1992 when average concentrations were between 10 and 12 mg L<sup>-1</sup>. On average, pore-water NO<sub>3</sub>-N concentrations were 4 mg L<sup>-1</sup> less than subsurface drainage water NO<sub>3</sub>-N concentrations for 1992 to 1995, except in November of 1992 (data not shown). In 1992, pore-water NO<sub>3</sub>-N concentration was high relative to all other years for all depths below 30 cm (Fig. 2), an observation that may be related to the previous years' weather patterns. Soil concentrations of NO<sub>3</sub>-N (mg kg<sup>-1</sup>) were higher under corn than under beans only in the top 30 cm of soil and only in the late spring and early summer (Fig. 3). Surface soil NO<sub>3</sub>-N concentrations were greatest in May and June of 1992 and 1994 due to fertilizer application preceding corn planting in those years. Soil NO<sub>3</sub>-N concentrations were equal and relatively constant for all sampling times over all years at depths below 30 cm, and there was no evidence of the NO<sub>3</sub>-N concentration bulge that has been observed in other studies following application of high rates of N fertilizer

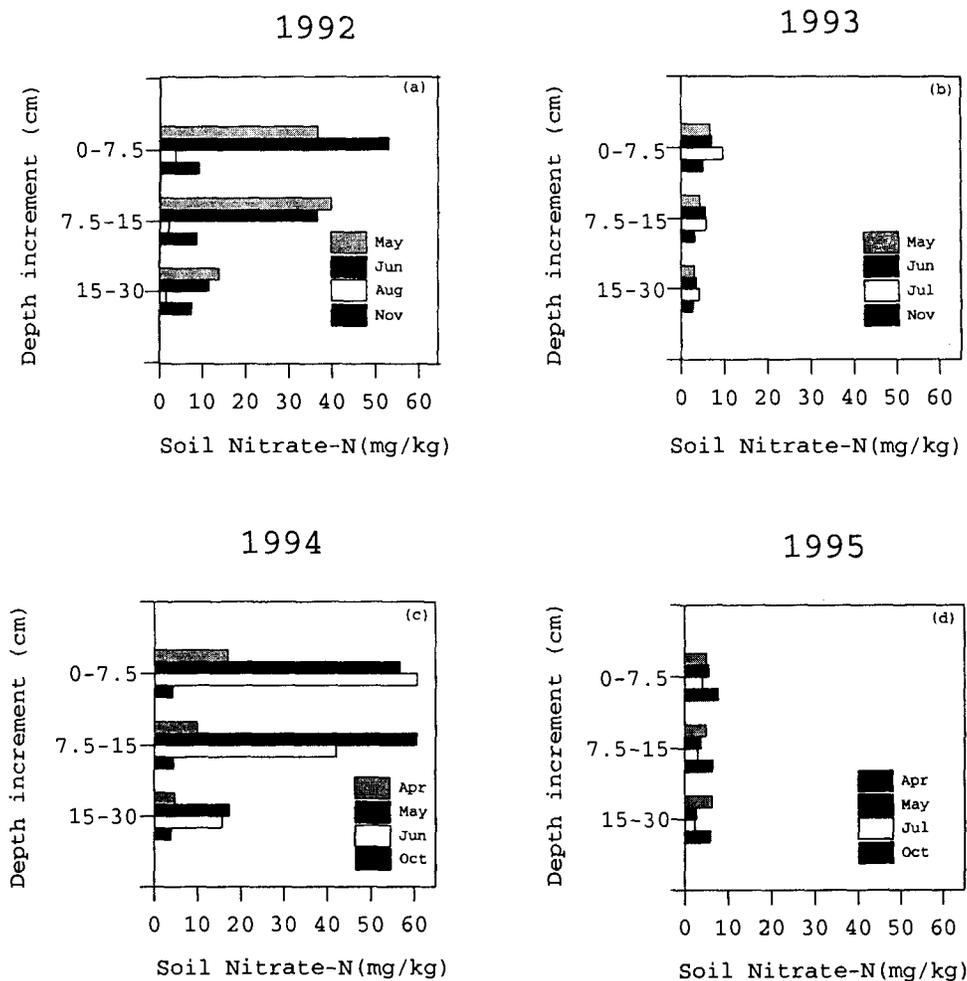


Fig. 3. Soil  $\text{NO}_3\text{-N}$  concentrations with depth for 1992 to 1995.

(e.g., Jolley and Pierre, 1977; Schuman et al., 1975; McMahon and Thomas, 1976).

Some fertilizer applied for corn production was removed in the grain, but most was retained in the soil or lost through various mechanisms. Studies by Sanchez and Blackmer (1988) on similar soils at a nearby site showed that one year after application, 23 to 30% of the applied anhydrous N fertilizer remained in the soil with 22 to 38% removed in the grain. Later studies by Baker and Timmons (1994) at a nearby site showed that fertilizer accounted for 17% of the total  $\text{NO}_3\text{-N}$  leaching loss in the first year following subsurface banding of UAN solution. In the second and third years after fertilizer application, fertilizer N (applied in Year 1 and remineralized in Years 2 and 3) accounted for 25 and 7% of the  $\text{NO}_3\text{-N}$  leaching losses, respectively. These studies demonstrated that substantial quantities of N fertilizer become incorporated in soil organic matter, which can be remineralized in subsequent seasons. We cannot determine what fraction of  $\text{NO}_3\text{-N}$  leached into the subsurface drains came from fertilizer applied to corn, but based on these earlier studies and the distributions of  $\text{NO}_3\text{-N}$  in the soil profiles, it is likely that fertilizer N directly accounted for <25% of the  $\text{NO}_3\text{-N}$  lost to subsurface drainage water in the year it was applied.

The quantities of  $\text{NO}_3\text{-N}$  in soil profiles to a depth of 105 cm showed distinct patterns related to the crop, time of season, and soil type (Fig. 4). Soil profile  $\text{NO}_3\text{-N}$  in soybean years (1993 and 1995) was <50  $\text{kg ha}^{-1}$  in all soils and generally constant during the growing season. Soil profile  $\text{NO}_3\text{-N}$  under corn displayed strong seasonal patterns that were different in 1992 and 1994 and varied in the different soils. The amounts of  $\text{NO}_3\text{-N}$  early in the corn-growing season were relatively low (40–70  $\text{kg ha}^{-1}$ ) and were similar in the Canisteo, Clarion, and Okobojo soils. Nitrate-N in the soil profile subsequently increased and by the middle of May (DOY 138 and 139)  $\text{NO}_3\text{-N}$  contents exceeded 150  $\text{kg ha}^{-1}$ , except in the Okobojo soils, which contained substantially less  $\text{NO}_3\text{-N}$ . These increases were due to nitrification of the anhydrous ammonia fertilizer applied to the fields after soybean harvest and mineralization of organic N in the soil. Canisteo, Clarion, and Okobojo soil profiles had about 180, 180, and 140  $\text{kg ha}^{-1}$  of  $\text{NO}_3\text{-N}$ , respectively, stored to a depth of 105 cm by DOY 150 in 1992. A similar pattern emerged in 1994, where, by DOY 152, the amount of profile  $\text{NO}_3\text{-N}$  was greatest for Canisteo and Clarion soils, and less for Okobojo soil. Plant uptake, leaching, and denitrification resulted in low  $\text{NO}_3\text{-N}$  contents in August of 1992 (DOY 230). Soil

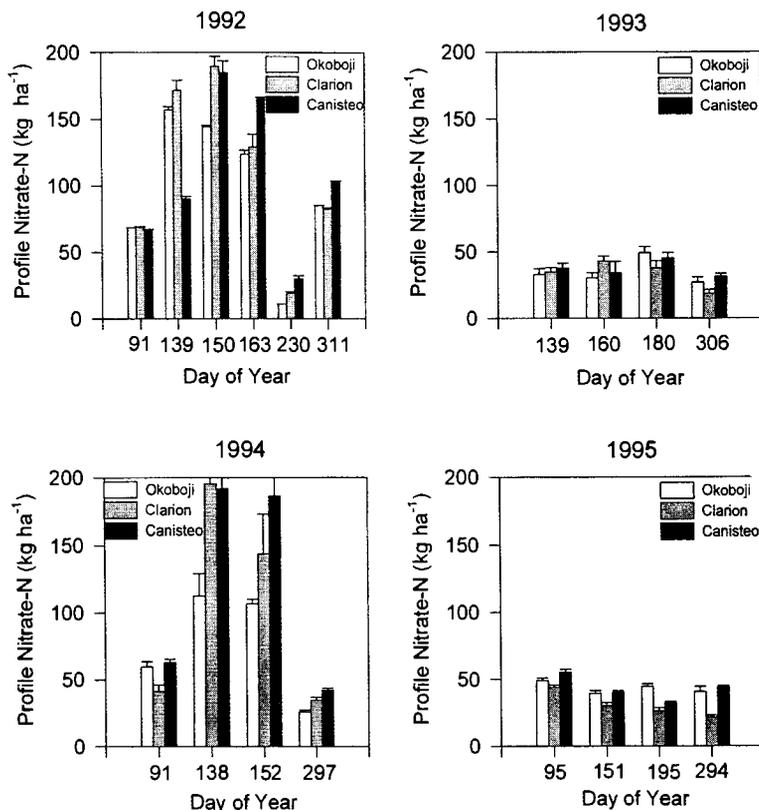


Fig. 4. Soil profile  $\text{NO}_3\text{-N}$  loading summed to a depth of 105 cm. Error bars are 1 SD.

cores were not taken in August of 1994. Decreases in soil  $\text{NO}_3\text{-N}$  were due in part to plant uptake which accounted for 105 to 115  $\text{kg N ha}^{-1}$  at this site. In the fall of 1992, favorable soil temperature and moisture conditions increased N mineralization and  $\text{NO}_3\text{-N}$  production resulting in increased profile  $\text{NO}_3\text{-N}$  contents. If conditions for these processes are unfavorable,  $\text{NO}_3\text{-N}$  concentrations may remain low, as in the fall of 1994.

### Denitrification in Soil and Subsoils

The Wisconsinan age subsoils (12 000–17 000 yr old) underlying Clarion-Okoboji surface soils form three distinct layers. The upper most layer is an oxidized glacial till and is characterized by low organic C levels (0.06–0.2%) and the presence of oxidized iron. Below the oxidized till, at depths of 2 to 7 m below the soil surface, is an unoxidized glacial till that has higher organic C levels (0.15–0.55%). A loess deposit underlies the glacial till at depths >5 m. The loess is unoxidized and has organic C levels in the range of 0.5 to 2.0% (Simpkins and Parkin, 1993).

Denitrification rates for Okoboji surface soil (unamended treatment) were significantly higher than denitrification in the Clarion soil (Table 3). Surface soil denitrification responded positively to  $\text{NO}_3$  and ( $\text{NO}_3$  + glucose) treatments, and these treatments eliminated the difference in denitrification rates between the Okoboji and Clarion soils. Denitrification rates of the subsurface soils incubated without amendments were significantly lower than either Clarion or Okoboji soils for all the treatments. There were no significant differences

in short-term denitrification rates between the oxidized glacial till, unoxidized glacial till, and loess subsoils; although the loess material tended to show an increased denitrification rate in response to added  $\text{NO}_3$ . All of the subsurface materials exhibited stimulated denitrification activity in response to added ( $\text{NO}_3$  + glucose). These data are consistent with observations by McCarty and Bremner (1992) who measured the denitrification response of Iowa surface (0–25 cm) and subsurface (150–200 cm) soils. These investigators reported very low rates of subsoil denitrification in response to added  $\text{NO}_3$ , but addition of both  $\text{NO}_3$  and glucose stimulated denitrification. They concluded that the slow rate of denitrification in Iowa subsoils was not due to a lack of denitrifying organisms, but rather to a lack of available organic C. From the depth information and the organic C contents reported (0.15–0.78%), it is likely that the subsoils investigated by McCarty and Bremner (1992) were from the oxidized glacial till deposit. Our data indicate the deeper unoxidized glacial till and loess subsoils contain higher organic C and may support sustained denitrification activity if exposed to  $\text{NO}_3$ .

Microcosms of subsurface material amended with  $\text{NO}_3$  but with no added C indicate the potential for long-term  $\text{NO}_3$  removal (Fig. 5). The oxidized till showed very low denitrification capacity, and over 1070 d  $\text{NO}_3$  loss ranged from 25 to 95 mg N/kg subsoil. Nitrate loss from the unoxidized till was higher, and averaged 280 mg N/kg subsoil. The highest  $\text{NO}_3$  loss rate was observed with the loess subsoil that showed a marked capacity to remove  $\text{NO}_3$ . Nitrate-N concentrations decreased to

**Table 3. Short-term denitrification potential of surface soils and subsoils.**

Soil/subsoil	Denitrification rate		
	No amendments	+ NO <sub>3</sub>	+ NO <sub>3</sub> + Glucose
		μg-N g <sup>-1</sup> d <sup>-1</sup>	
Clarion silt loam	0.198a* (0.172)†	6.234a (2.13)	12.9a (3.02)
Okoboji	0.529b (0.294)	6.778a (1.38)	15.3a (1.75)
Oxidized glacial till	0.032c (0.029)	0.052b (0.064)	2.72b (1.90)
Unoxidized glacial till	0.019c (0.003)	0.008b (0.008)	3.82b (2.91)
Loess	0.012c (0.002)	0.258b (0.539)	2.57b (2.57)

\* Different letters following denitrification rates indicate significant differences ( $P < 0.05$ ) between soil/subsoil material within a given treatment as determined by Student Newman Keuls Test.

† Values in parentheses are 1 SD.

<38 mg N/kg subsoil over the first 240 d (Fig. 5). When these samples were re-spiked with NO<sub>3</sub>, one microcosm showed complete removal of NO<sub>3</sub> by Day 1070, and in the other loess microcosm, NO<sub>3</sub> loss continued at a rapid rate up to Day 471 and then decreased. Average NO<sub>3</sub> removal by the loess was 530 mg N/kg subsoil over the 1070 d incubation period. These results are consistent with the report of high rates of anaerobic microbial activity in glacial till and loess subsoils driven by buried Pleistocene-aged C substrate (Parkin and Simpkins, 1995).

We suspect that the NO<sub>3</sub> losses observed in our long-term microcosm incubations were due to denitrification. We doubt that other process such as dissimilatory NO<sub>3</sub> reduction to ammonium (Tiedje et al., 1984) or NO<sub>3</sub> immobilization are important mechanisms. Ammonium was undetectable in the microcosms at the termination of the experiment (<0.1 mg N/kg subsoil) and the organic C content of the subsurface subsoil was likely too low to support significant N immobilization. Evidence

that denitrification is the primary mechanism is provided by the short-term denitrification incubations with added NO<sub>3</sub>. The loess denitrification rate of 0.258 mg N kg<sup>-1</sup> d<sup>-1</sup> (Table 3) equates to a loss of 276 mg N if extended over a 1070 d period. This estimate is of the same magnitude of N loss (530 mg N/kg) observed in the loess microcosms.

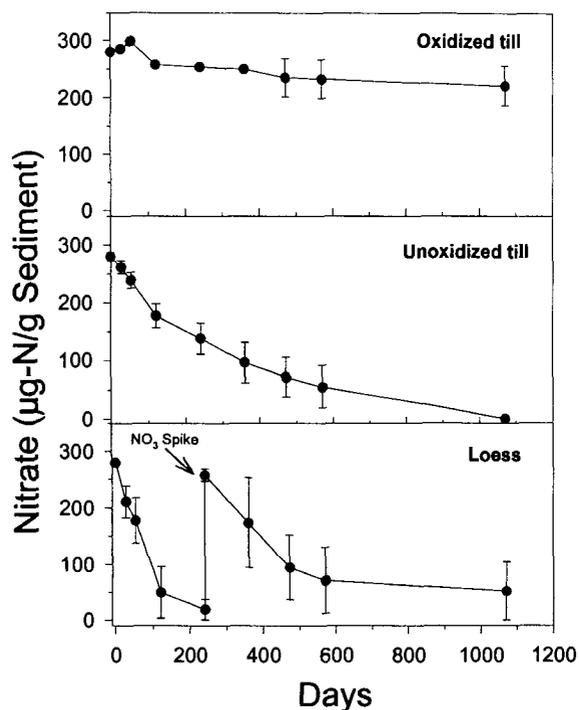
We estimate that the lifetime capacity of the deep subsoils to remove NO<sub>3</sub> is 20 340 kg N/ha. This estimate is based on our long-term microcosm incubations along with the assumptions that the average bulk density of subsurface soils is 1.8 g/cm<sup>3</sup>, and that the thicknesses of the oxidized till, unoxidized till, and loess subsoils average 80, 280, and 530 cm, respectively (Parkin and Simpkins, 1995). To put this estimate of NO<sub>3</sub> removal capacity into context, we calculated that if NO<sub>3</sub>-leaching inputs to the deep subsoils are 36 kg N/ha per year (equivalent to 20% of a typical fertilizer-N application rate of 180 kg N/ha), it would take a minimum of 565 yr to exceed the capacity of the deep subsoils to remove this added NO<sub>3</sub>.

### Soil-Groundwater Relationships

Samples were collected from wells placed in the lower root zone (0.6 m depth), just beneath the root zone (1.5 m depth) and in the oxidized, late-Wisconsinan till (2.6 m depth). Wells screened at the 0.6 m depth yielded fewer samples than were obtained at the other depths due to groundwater dropping beneath this depth during the summer months.

Nitrate-N was found in more than 90% of samples from the root zone (0.6 m) and in 75% of the samples from 2.6 m depth (Table 2). Averaging across soils, the median NO<sub>3</sub>-N concentration was lowest (3.9 mg L<sup>-1</sup>) at the 2.6 m depth, similar to the pattern observed for herbicides (Moorman et al., 1999). The percentage of samples exceeding the 10 mg L<sup>-1</sup> maximum contaminant level (MCL) concentration was greatest in the root zone and declined to 24% at 2.6 m depth.

Nitrate-N concentrations in groundwater under Clarion soil tended to be higher than under the Canisteo and Okoboji soils. Temporal trends were evident in NO<sub>3</sub>-N concentrations at the 1.5 and 2.5 m depth in some wells (Fig. 6). At well nest E3 (Fig. 1) under Okoboji soils, NO<sub>3</sub>-N concentrations exhibited a cyclic temporal pattern that wasn't related to N fertilizer application (Fig. 6). In well nest E5 (Fig. 1) under Clarion soil, the pattern of NO<sub>3</sub>-N concentration in shallow



**Fig. 5. Long-term NO<sub>3</sub>-N removal from subsurface subsoils.** Values for oxidized till and loess represent means of two samples and error bars indicate range. Values for unoxidized till are means of six samples and error bars are 1 SD.

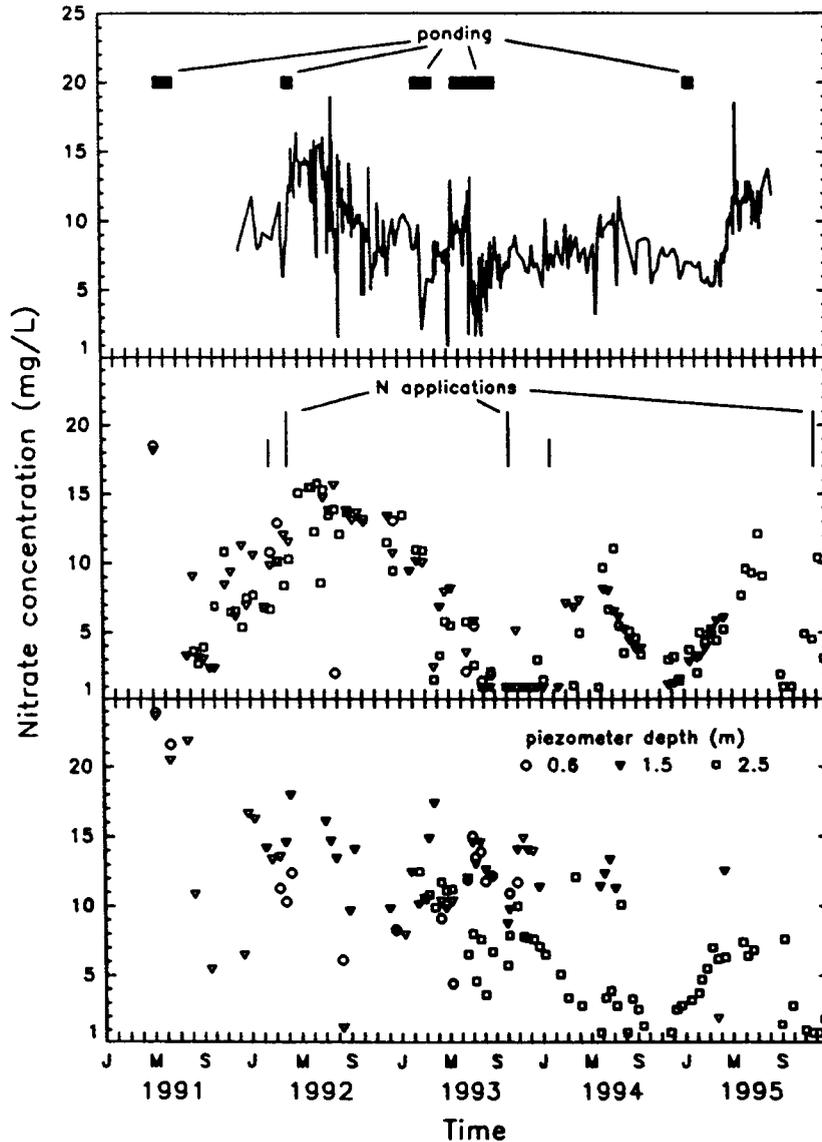


Fig. 6. Nitrate-N concentrations in subsurface drainage (top panel) and in groundwater (bottom two panels) from 1991 to 1995 for well nest E3 (middle panel) under Okoboji soil and E5 (bottom panel), under Clarion soil. Data are grouped by well depth for each nest. Long vertical bars show dates of anhydrous ammonium applications and short vertical bars show dates of dry N fertilizer applications. Ponding periods indicate when the potholes contained standing water.

groundwater was not cyclic (Fig. 6). Nitrate-N concentrations were much more variable than for well nest E3 and decreased consistently from 1992 through 1995. Presumably, denitrification contributed to the temporal patterns in  $\text{NO}_3\text{-N}$  concentration observed for shallow groundwater at this site, but our sampling scheme was not designed to directly address this question. The temporal pattern of  $\text{NO}_3\text{-N}$  concentrations in subsurface drainage water mimics the pattern for well E3 but not for well E5 or other wells placed at the edge of the field.

The data indicate that  $\text{NO}_3\text{-N}$  leaching and denitrification were affected by soil type. Shallow well-water  $\text{NO}_3\text{-N}$  concentrations were found to be significantly higher under Clarion soils than under Canisteo or Okoboji soil profiles for all years and denitrification activity was two times higher in Okoboji surface soils than in Clarion surface soils. These observations support the hypothesis that leaching was the predominant route of

$\text{NO}_3\text{-N}$  loss in Clarion soils and denitrification was the predominant route of  $\text{NO}_3\text{-N}$  loss in Okoboji soils. Denitrification activity in subsoils was highest in the unoxidized loess, which suggests that if  $\text{NO}_3\text{-N}$  were to leach to depths  $>5$  m at this site, complete denitrification would result.

#### Shallow Groundwater Observations throughout Walnut Creek

Observations of  $\text{NO}_3\text{-N}$  were made in wells around fields located throughout Walnut Creek as described by Hatfield et al. (1999). The transect wells located at the pothole field (Jaynes et al., 1999) were not included in this dataset. More than 2090 samples were collected from all the shallow wells within Walnut Creek since 1991. Nitrate-N concentrations generally decreased with increasing depth (Table 4), except for wells at 1.5

**Table 4. Observations of NO<sub>3</sub>-N at various depths in all shallow groundwater wells within Walnut Creek watershed from 1991 through 1996.**

Nitrate-nitrogen	Depth below soil surface				
	0.0-0.9	0.9-1.5	1.5-3.0	3.0-4.6	>4.6
	m				
Total observations	7	80	913	457	640
Mean conc., mg L <sup>-1</sup>	15.8	5.7	10.3	4.3	1.8
Median conc., mg L <sup>-1</sup>	10.6	2.8	8.5	1.8	1.1
Max. conc., mg L <sup>-1</sup>	47.7	45.7	51.8	31.8	23.9
% >1 mg L <sup>-1</sup>	86	79	90	70	59
% >10 mg L <sup>-1</sup>	57	20	44	16	4

to 3.0 m depth. Nitrate-N concentrations had a mean value of 15.8 mg L<sup>-1</sup> in the 0 to 0.9 m depth and 1.8 mg L<sup>-1</sup> at depths >4.6 m (Table 4). High variability complicates the interpretation of observed trends in shallow groundwater NO<sub>3</sub>-N concentration. Only 4% of the observations at depths >4.6 m exceeded the 10 mg L<sup>-1</sup> MCL for drinking water. This fraction of observations that exceeded the MCL is similar to that reported by Burkart and Kolpin (1993). These more general observations agree with the detailed observations from the pothole field and suggest that the patterns throughout Walnut Creek can be generalized to the prairie pothole region.

### Soil-Subsurface Drainage Water Relationships

The quantities of subsurface drainage water from this site, expressed as equivalent depth (mm), were generally similar to drainage amounts from much larger areas within the watershed (Jaynes et al., 1999). The 833 mm of discharge in 1993 resulted from the massive rainfall in spring and summer that lead to widespread flooding throughout the Midwest (Table 5). In contrast, 30-average annual precipitation for the watershed was 818 mm (Hatfield et al., 1999). The subsurface drainage at this site was also affected by surface runoff that accumulates in the potholes. These standing waters were sampled by hand at least once during each ponding event (Fig. 6). Average NO<sub>3</sub>-N concentrations were 1.8 mg L<sup>-1</sup> and the maximum NO<sub>3</sub>-N concentration was 9.7 mg L<sup>-1</sup>. We visually estimated the average depth of standing water in the potholes to be between 5 to 10 cm. Using NO<sub>3</sub>-N concentrations and standing water depth, we calculated the additional N-loads to ponded soils would likely range from 0.8 to 2.1 kg N ha<sup>-1</sup>.

Nitrate-N concentrations in subsurface drainage water showed seasonal patterns. Monthly flow-weighted concentrations exceeded 10 mg L<sup>-1</sup> for 12 mo and were between 6 and 9 mg L<sup>-1</sup> for 32 mo during the 48 mo study

(Fig. 7). The range of monthly flow-weighted NO<sub>3</sub>-N concentrations in subsurface drainage water during 1992 to 1995 was 4.7 to 14.4 mg L<sup>-1</sup>. The periods when NO<sub>3</sub>-N exceeded 10 mg L<sup>-1</sup> were April through July and in September in 1992, and May through October in 1995. The highest NO<sub>3</sub>-N concentration observed for 1992 was in May, and for 1995, during August.

Nitrate-N concentrations in subsurface drainage water were slightly higher than average concentrations in soil pore water at the 105-cm depth increment (Fig. 2). Soil pore water NO<sub>3</sub>-N at 105 cm closely tracked the monthly flow-weighted NO<sub>3</sub>-N concentration in subsurface drainage water in the spring for all 4 yr but not at other times of the year (data not shown). Analysis of individual storm hydrographs showed that NO<sub>3</sub>-N concentrations were relatively constant across time for 4 yr and were not affected by rainfall events (see Jaynes et al., 1999), thus macropore flow was probably not a major mechanism in the transport of NO<sub>3</sub>-N. Average subsurface drain NO<sub>3</sub>-N concentrations for the growing season (May through October) within any given year were not different than concentrations for the off-season (Table 5). However, NO<sub>3</sub>-N loading in subsurface drainage water was different within each year for the growing season and off-season months (Table 5). Subsurface drainage water NO<sub>3</sub>-N loading in this system appeared to be primarily controlled by the amount of subsurface drainage water, which was generally controlled by precipitation (Hatfield et al., 1999).

Average monthly NO<sub>3</sub>-N loads (data not shown) did not always correspond to the periods of greatest NO<sub>3</sub>-N concentration in subsurface drainage water (Fig. 7). In 1993, NO<sub>3</sub>-N losses were high during late spring and early summer, but concentrations never exceeded 10 mg L<sup>-1</sup>. Dilution may have reduced concentrations during late spring and early summer in 1993. Considerable ponding occurred in the potholes in 1993 and NO<sub>3</sub>-N concentrations declined during those periods. In contrast, dry weather in the early spring and summer of

**Table 5. Application rates, concentrations, and losses of NO<sub>3</sub>-N in subsurface drainage from an 8.9 ha drainage area in a 38 ha field cropped to corn in 1992 and 1994 and to soybean in 1993 and 1995.**

Year	Drainage mm	Applied	kg ha <sup>-1</sup>			avg. mg L <sup>-1</sup>		
			Total loss	GS† loss	NGS‡ loss	Total conc.	GS conc.	NGS conc.
1992	240	178	26.3	9.8	16.5	10.6	10.8	10.4
1993	833	0	51.3	35.4	15.9	7.1	6.7	7.5
1994	63	156	4.9	1.1	3.9	8.0	8.5	7.5
1995	140	0	13.3	4.3	9.0	9.4	11.8	7.6

† GS = Growing season (June–October).

‡ NGS = Nongrowing season (November–May).

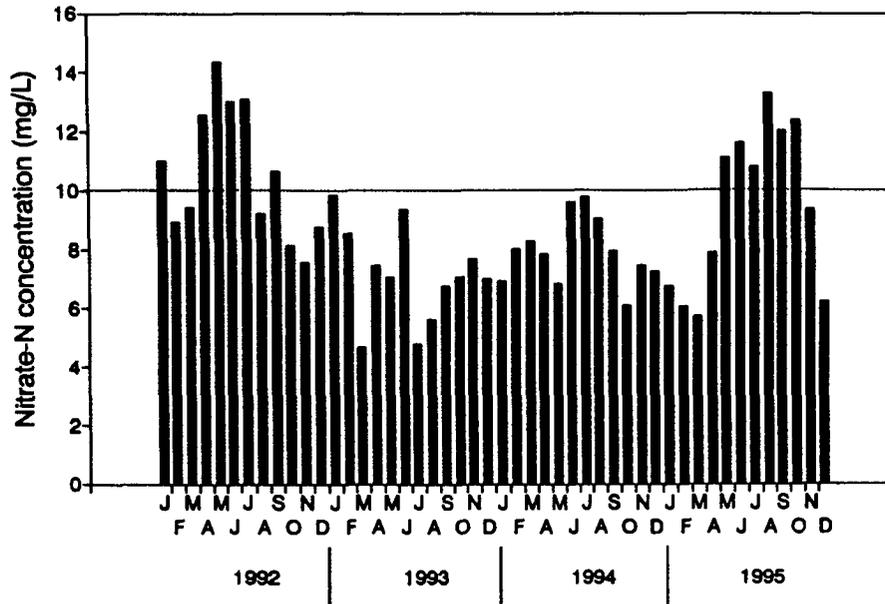


Fig. 7. Monthly flow weighted average NO<sub>3</sub>-N concentrations in subsurface drainage water.

1994 reduced drainage and NO<sub>3</sub>-N losses. The same general yearly pattern of NO<sub>3</sub>-N transport was present in 1993 and 1994, but monthly averaged NO<sub>3</sub>-N concentrations did not exceed the MCL in these years. Annual losses of NO<sub>3</sub>-N ranged from 4.9 kg ha<sup>-1</sup> in 1994 to 51.3 kg ha<sup>-1</sup> in 1993 (Table 5). Most of the subsurface drainage water NO<sub>3</sub>-N was lost when crop plants were not present (November to May), except in 1993 (Table 5). The results indicate that nongrowing season mineralization of soil organic N is greater than expected for these glacial till soils. Similarly, Drury et al. (1996) reported that 88 to 95% of the NO<sub>3</sub>-N loss to subsurface drainage occurred during the noncrop period (November through April) for a corn-production system in southern Ontario.

Both NO<sub>3</sub>-N concentration and total load of NO<sub>3</sub>-N in water exiting the field are the result of complex interactions between production of NO<sub>3</sub>, NO<sub>3</sub> uptake by the crop, and water movement. Nitrification of mineralized N from organic matter and fertilizer N increases as spring temperatures increase. Although corn uptake accounted for approximately 100 to 115 kg N ha<sup>-1</sup>, the majority of N uptake by corn occurred after the middle of June. Nitrate-N production and leaching in the early spring, before significant plant root development, appeared to account for the majority of the NO<sub>3</sub>-N loss in most years. Nitrate-N production in the fall may have also contributed to this process. This pattern was not observed in 1993. Rainfall patterns in this year were very unusual, leading to saturated soil conditions that probably resulted in very little deep root development and increased rates of denitrification. Bauder and Montgomery (1979) found some nitrification of fall-applied ammonium during field studies in North Dakota. We found a significant linear relationship between overwinter subsurface drainage water NO<sub>3</sub>-N concentrations and the NO<sub>3</sub>-N content in soil profiles at the postharvest sampling ( $r^2 = 0.59$ ). A relationship between soil profile

NO<sub>3</sub>-N and overwinter losses was also reported by Jemison and Fox (1994). Total losses of NO<sub>3</sub>-N were variable, but the average loss of 24 kg ha<sup>-1</sup> of NO<sub>3</sub>-N was generally similar to or smaller than losses in southern Ontario (Drury et al, 1996; Patni et al., 1996) and in the northcentral USA (Bjorneberg et al., 1996; Randall and Iragavarapu, 1995) for corn-production cropping systems.

## SUMMARY

We initiated a 4-yr study to assess the extent of NO<sub>3</sub>-N leaching to subsurface drainage water and shallow groundwater in a central Iowa field cropped to corn in 1992 and 1994 and soybean in 1993 and 1995. Nitrate-N concentrations in shallow groundwater were higher under Clarion soil than under Okobojo or Canisteo soil. Shallow groundwater wells placed under Okobojo soil exhibited a cyclic temporal pattern in NO<sub>3</sub>-N concentration that was not related to N fertilizer application. The pattern of NO<sub>3</sub>-N concentration in shallow groundwater under Clarion soil was not cyclic, but rather decreased consistently from 1992 through 1995. Temporal patterns in shallow groundwater NO<sub>3</sub>-N concentration may be related to temporal patterns in denitrification, but corroboration of this hypothesis is not possible since the current study was not designed to answer this question. Denitrification rates were higher in Okobojo surface soil than in Clarion surface soil and the highest potentials for denitrification among subsurface subsoils were observed for deep unoxidized loess. Soil profile NO<sub>3</sub>-N concentrations decreased with depth and concentrations were the same below 30 cm for unfertilized soybean and fertilized corn. Quantities of NO<sub>3</sub>-N in soil profiles to a depth of 105 cm showed distinct patterns related to soil type, crop, and time of season.

Nitrate-N concentrations in subsurface drainage water exceeded 10 mg L<sup>-1</sup> for 12 mo and were between 6

and  $9 \text{ mg L}^{-1}$  for 32 mo during the 4 yr study. The range of  $\text{NO}_3\text{-N}$  concentrations in subsurface drainage water during 1992 to 1995 was  $4.7$  to  $14.4 \text{ mg L}^{-1}$ . The temporal pattern of  $\text{NO}_3\text{-N}$  concentrations in subsurface drainage water was not related to the timing of fertilizer N application or to the amount of fertilizer N applied. Total  $\text{NO}_3\text{-N}$  loading in subsurface drainage water was greatest in 1993 ( $51.3 \text{ kg ha}^{-1}$ ) and least in 1994 ( $4.9 \text{ kg ha}^{-1}$ ). Nitrate-N loads leaving the field in subsurface drainage water were related to the amount of subsurface drainage water and controlled primarily by precipitation patterns. Most of the subsurface drainage water  $\text{NO}_3\text{-N}$  was lost when crop plants were not present (November to May), except in 1993 (Table 5), which suggests that nongrowing season mineralization of soil organic N was greater than expected for these glacial till soils. Our results indicate that  $\text{NO}_3\text{-N}$  losses to subsurface drainage water occur primarily as a result of asynchronous production and uptake of  $\text{NO}_3\text{-N}$  in the soil and presence of large quantities of potentially mineralizable N in the soil organic matter. Nongrowing season mineralization of soil organic N is greater than expected for these glacial till soils. The data also indicate that soil properties may be important factors controlling the spatial and temporal pattern of  $\text{NO}_3\text{-N}$  concentration in shallow groundwater.

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