

# Long-Term Effects of N Fertilizer on Groundwater in Two Small Watersheds

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## Abstract

Changes in agricultural management can minimize leaching of  $\text{NO}_3\text{-N}$ . But then how much time does it take to improve groundwater quality? This study was conducted in two small, first-order watersheds (30 and 34 ha) in southwest Iowa. Both were kept in continuous corn from 1964 through 1995, but one received large fertilizer-N applications, averaging  $446 \text{ kg ha}^{-1} \text{ y}^{-1}$ , between 1969 and 1974. This study's objective was to determine if  $\text{NO}_3\text{-N}$  from these large applications persisted in groundwater. In 1996, transects of piezometer nests were installed, deep cores were collected, then water levels and  $\text{NO}_3\text{-N}$  concentrations were measured each month. In 2001, 33 water samples were collected and analyzed for tritium and stable isotopes. The watershed that received large N applications had greater  $\text{NO}_3\text{-N}$  concentrations in groundwater and stream baseflow, by  $8 \text{ mg L}^{-1}$ . Groundwater time-of-travel estimates and tritium data support persistence of  $\text{NO}_3\text{-N}$  from fertilizer applied 30 years ago. "Bomb-peak" precipitation (1963-1980) most influenced tritium activity in groundwater beneath toeslope positions, and deep groundwater was dominated by pre-1953 precipitation. Data from cores suggest  $\text{NO}_3\text{-N}$  may take 30 years to percolate to groundwater below the watershed's divide. Stable isotope data suggest runoff/infiltration processes contribute greater recharge and mixing of groundwater below the toeslope. Therefore historical and current practices affect  $\text{NO}_3\text{-N}$  concentrations in groundwater near the stream. It may take years to quantify impacts of management systems implemented in 1996 by monitoring groundwater. In many areas, changes in agricultural practices may take decades to fully impact groundwater quality.

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## Introduction

Agricultural land use has been linked with loadings of nutrients to ground and surface waters. Agricultural practices can be modified to reduce these loadings through nutrient management, crop rotation, and other practices (e.g. Kitchen and Goulding 2001). Once a management change is made, the quality of runoff waters may improve rapidly, particularly if erosion is reduced. However, most streamflow is comprised of baseflow that originates from groundwater. The timing of groundwater responses to changes in agricultural management is difficult to predict and depends on many factors. Groundwater quality in the Midwest US has been affected by  $\text{NO}_3\text{-N}$  leaching (Burkart and Stoner 2001). As changes are implemented to address this problem, the time needed to improve groundwater quality must be better understood. If response times are underestimated, research on BMPs may be too short-term, causing groundwater quality benefits to be underestimated. Targeted timelines to achieve improved water quality may also be set too optimistically. This paper demonstrates the time frame that may be required to realize the full benefit of BMPs on groundwater quality.

This study took place in two watersheds (W1 and W2) of the Deep Loess Research Station (DLRS) in southwest Iowa (Figure 1; Karlen et al. 1999). Research at this site, begun in the 1960s, focused on erosion and nutrient balances under corn production (Karlen et al. 1998). Both watersheds were under continuous corn and conventional tillage from 1964 through 1995, and showed similar hydrology (Kramer et al. 1999). But experimental N-fertilizer applications occurred between 1969 and 1974, when W1 received an average  $446 \text{ kg N ha}^{-1} \text{ y}^{-1}$  and W2 received an average  $172 \text{ kg N ha}^{-1} \text{ y}^{-1}$ . This experiment was used to assess  $\text{NO}_3\text{-N}$  movement in deep soils (Schuman et al. 1975, Alberts et al. 1977,

Alberts and Spomer 1985), and in baseflow (Burwell et al. 1976). New crop rotations were established in 1996, when W1 was placed in a corn-soybean rotation, and W2 was placed in a six-year, contour-strip rotation with corn, soybeans, corn, and three years of alfalfa (Figure 1). With both rotations, only corn receives N fertilizer. The difference in current farming practices is hypothesized to cause a difference between the two catchments in groundwater and stream-baseflow  $\text{NO}_3\text{-N}$  concentrations. But if  $\text{NO}_3\text{-N}$  from large N applications from 1969-1974 persist in groundwater, it will be difficult to test this hypothesis directly. This study determined if these large N applications made 30 years ago could persist in groundwater and baseflow.

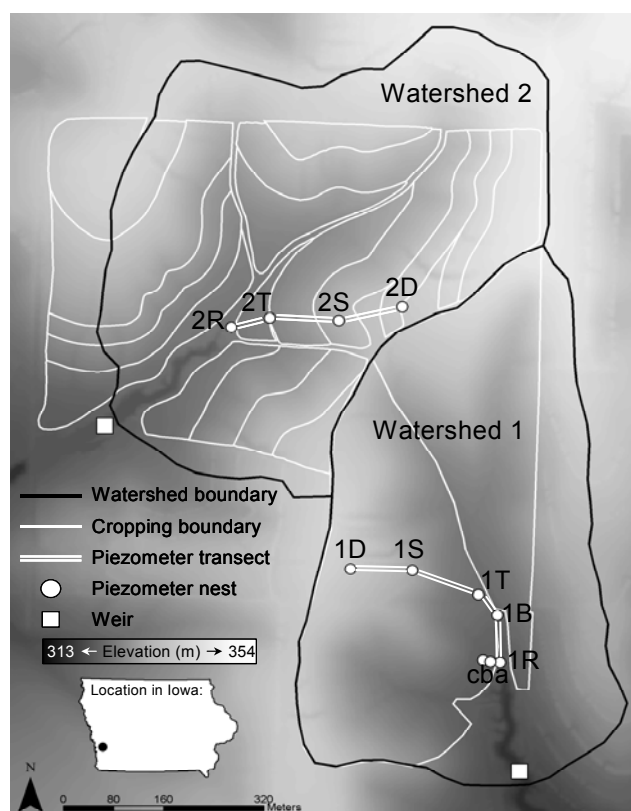


Figure 1. Map of watersheds W1 and W2, showing topography, piezometer-nest transects, weirs, and cropping boundaries.

## Methods

In 1996, piezometer nests were installed in transects, at divide (D), mid-slope (S) toe-slope (T), and riparian valley (R) positions of both watersheds. These nests are identified by watershed number and position (Figure 1). Additional riparian piezometers

were installed in W1 in 1999, and are denoted as 1B, 1Rb and 1Rc (Figure 1). Piezometer-nests comprise three transects, identified by watershed (W1, W2 and W1<sub>rip</sub> for the riparian transect in W1), that each portray an expected path of groundwater flow. During drilling, cores were taken to the depth of glacial till, which is an aquitard limiting the downward flow of groundwater beneath the deep loess. Cores were analyzed for bulk density and  $\text{NO}_3\text{-N}$ . Materials encountered during coring included loess at upland (D and S) positions, and alluvium from reworked loess at lower (T and R) positions. Water levels and groundwater  $\text{NO}_3\text{-N}$  concentrations were measured on a monthly basis. Three lines of evidence helped to determine if past N applications have had a persistent effect on groundwater nitrate. These lines of evidence were based on hydrologic measurements, spatial trends in isotope chemistry, and spatial and temporal trends in  $\text{NO}_3\text{-N}$  concentrations in water and deep sediments.

The hydraulic conductivity ( $K_s$ ) of the saturated zone was measured by conducting slug tests, and a geometric mean  $K_s$  value was calculated for each type of deposit (till, sand at the till interface, loess, and alluvium). Positional survey data, coring descriptions, water levels, and  $K_s$  values were used with the Darcy equation to estimate groundwater travel times along the three transects. Hydraulic gradients were based on water levels for June 2001 and April 2002, when the highest and lowest average water levels were observed. An effective porosity of 0.2 was applied to calculate pore velocities, which were divided into the transect distances to obtain travel time estimates. Total porosities averaged 0.42, and an effective porosity of about half this value was selected to represent the mean (center of mass) movement of a solute plume through the groundwater.

In June 2001, 33 water samples were collected for isotopic analyses of  $\delta^{18}\text{O}$ ,  $\delta^2\text{D}$ , and  $^3\text{T}$ . Samples were taken from 30 piezometers, from stream baseflow passing the weir of each watershed, and an aggregate sample was collected from four, 1.8-m-depth suction lysimeters to represent recent precipitation. A record of annual tritium activities in precipitation was constructed to represent the age distribution of tritium activities (TU) in groundwater recharge at the site. We obtained TU data for annual precipitation from IAEA (1992), IAEA/WMO (2001), and Simpkins (1995). Records from monitoring stations at Lincoln NE, St. Louis MO, and Ottawa ONT were used to compile a continuous tritium input record from 1953 to 1999. Correlations between these stations, and a time-trend of local data provided two methods of

estimation, which gave good agreement. Once these precipitation records were constructed, the expected tritium activity of each year's precipitation in 2001 was calculated, based on a half-life of 12.43 years (Gonfiantini et al. 1998).

## Results and Discussion

Estimated groundwater velocities between piezometer nests averaged  $13.5 \text{ m y}^{-1}$ , and varied from  $5.3$  to  $27.1 \text{ m y}^{-1}$ . Travel time estimates (Table 1) varied according to the length of each transect and changes in hydraulic gradients. Along the W2 transect, larger gradients occurred with higher water levels measured in June 2001. But along W1, larger gradients occurred during April 2002. Between 64 and 82% of the groundwater travel times occurred above the toeslope positions. Travel times are considered conservative because vertical and horizontal gradients are present, causing actual travel distances to be greater than horizontal distances.

Table 1. Transect lengths and estimated groundwater travel times using hydraulic gradients from two sets of measurements.

Transect	Length (m)	Travel time (y) based on water levels from:	
		Jun 01	Apr 02
W2	277	22.7	25.9
W1	337	36.1	31.0
W1 <sub>rip</sub>	28	1.4	2.5

When isotopic decay was applied to constructed tritium-precipitation records, expected residual tritium activities in 2001 indicated that: 1) waters that fell as precipitation within 20 years of sampling cannot be differentiated; 2) water with ages between 20 and 40 years would be indicated by tritium activities exceeding 12 TU; and 3) water at least 45 years old is indicated by small tritium activities (<3 TU). Tritium activities of the 33 water samples ranged from 0.8 to 18.5 TU. Small tritium activities (<3 TU), indicating the oldest water, occurred in six of the 33 samples and were always in the deepest groundwater (Figure 2). Tritium values exceeding 12 TU, showing an influence of 20-40 year old precipitation, occurred in 9 of the 33 samples. In groundwater these larger tritium activities always occurred at midslope (1S, 2S) and at or near toeslope (shallow at 2T, 1Rc) positions (Figure 2). Values of intermediate tritium activity (3-12 TU) were typically found at or below toeslope positions (1T, 1B, 1Ra, 1Rb, deep at 2T, 2R), indicating recent or

mixed-age waters. Samples collected from the weirs had tritium activities of 11.1 and 12.5 TU for Watersheds 1 and 2, respectively, which are considered similar. The baseflow is probably of mixed origin, with a weak influence of 20-40 year-old waters.

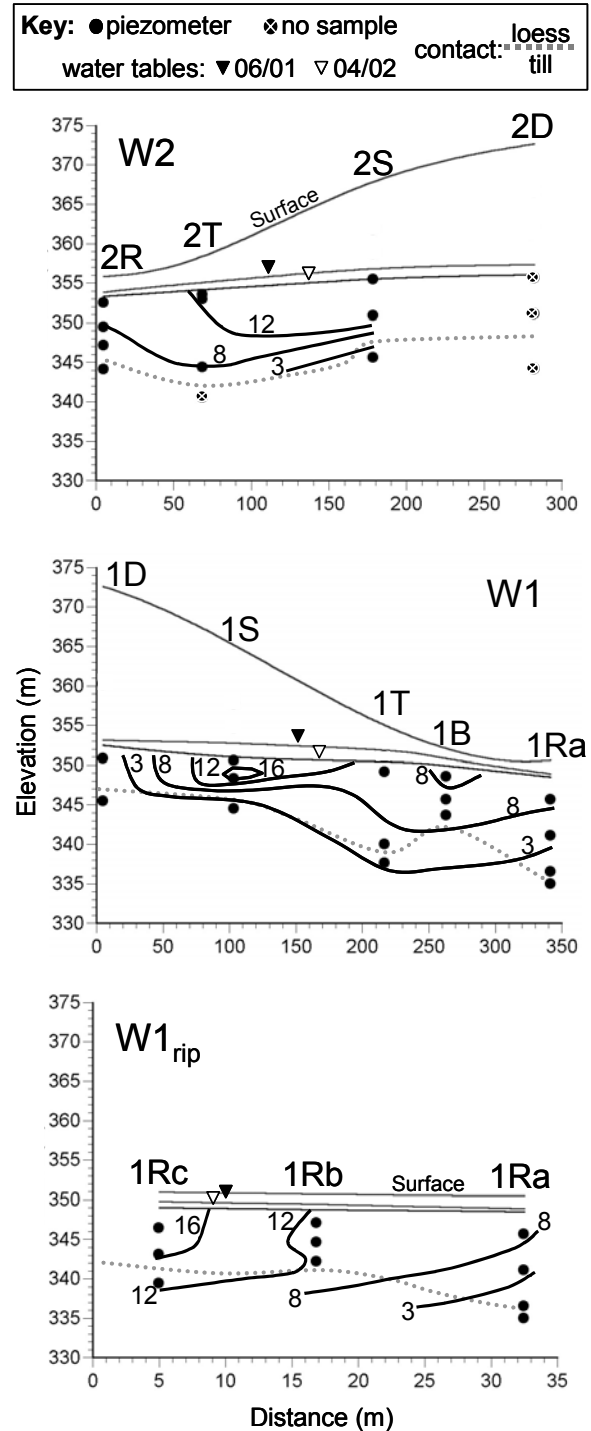


Figure 2. Cross sections showing variations in groundwater tritium activity (TU) along three transects during June 2001.

Stable isotopes also showed noteworthy results. The average  $\delta^{18}\text{O}$  was  $-7.1\text{‰}$  (range  $-5.6$  to  $-8.9\text{‰}$ ) and the average  $\delta^2\text{H}$  was  $-49.2\text{‰}$  (range  $-39.6$  to  $-60.9\text{‰}$ ), similar to other Midwest data (Simpkins 1995, IAEA 1992). Groundwater contains mixed waters with fairly small isotopic variability. But despite their limited variation, the isotope data did follow a distinct spatial pattern. Groundwater beneath the upper landscape positions (D and S) was isotopically enriched compared to toeslope (T) or riparian valley (R) positions ( $p < 0.01$ , based on a t-test). This indicates differences in processes or sources affecting groundwater according to landscape position. Probably, seasonal changes in runoff and infiltration act to segregate recharge waters according to landscape position. Snowmelt and cold spring rains are isotopically depleted, and occur when there is little plant cover. These depleted waters would be most prone to runoff from upper slopes and then infiltrate near the toeslope. This means that riparian valley groundwater is affected by recent precipitation, as well as groundwater being contributed from upslope.

A large increase in sediment  $\text{NO}_3\text{-N}$  concentrations ( $\text{ug}^{-1}$ ) was observed in the deep cores obtained during 1996 at position 1D (Figure 3), centered near 17.5 m depth. This pattern was not observed in any of the other deep profiles, and only 25 out of 323 samples collected at the other positions showed  $\text{NO}_3\text{-N}$  concentrations exceeding  $4 \text{ ug g}^{-1}$ . This 17.5 m depth, when plotted with depths of peak  $\text{NO}_3\text{-N}$  concentrations from cores collected from Watershed 1 during 1972, 1974-76, 1978, and 1984 (Schuman et al. 1975, Alberts et al. 1977, Alberts and Spomer 1985), shows a strong linear relationship ( $r^2 = 0.98$ ) with cumulative baseflow since 1969, when the large N applications in Watershed 1 began. (Figure 3). This relationship suggests that  $\text{NO}_3\text{-N}$  from these large applications moved through the unsaturated zone in response to hydrologic fluxes through the watershed's subsurface. Given the inferred movement of this  $\text{NO}_3\text{-N}$  pulse to depth, one would anticipate that, at lower-elevation landscape positions, this  $\text{NO}_3\text{-N}$  would have percolated into the saturated zone before this 1996 core sampling. This would explain why large sediment concentrations were not observed at depth at lower W1 positions. Also, at position 1D, one would expect increases in groundwater  $\text{NO}_3\text{-N}$  as this  $\text{NO}_3\text{-N}$  pulse moved from the sediment into groundwater (Figure 3). Such an increase was observed and its timing was consistent with baseflow volumes measured during the late 1990s.

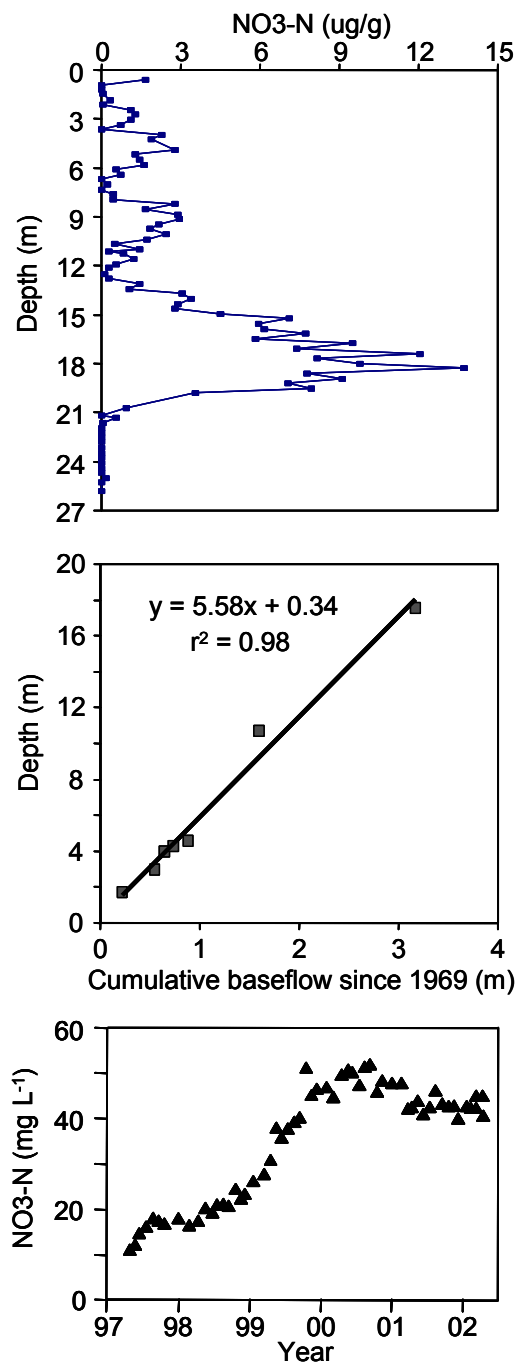


Figure 3. Top: Concentrations of  $\text{NO}_3\text{-N}$  in sediment with depth at position 1D measured in cores taken in 1996 (top). Middle: Depths of maximum  $\text{NO}_3\text{-N}$  concentrations, as measured in 1972, 1974-1976, 1978, 1984 (Alberts et al. 1975; Schuman et al. 1985), and 1996, are related to stream baseflow since large fertilizer N applications. Bottom: Increases in  $\text{NO}_3\text{-N}$  in the underlying water table were consistent with continued percolation of this pulse.

Concentrations of  $\text{NO}_3\text{-N}$  in baseflow were greater at the outlet of W1 ( $p < 0.01$ , based on a paired t-test), where an average of  $20 \text{ mg L}^{-1}$  contrasted  $12 \text{ mg L}^{-1}$  from W2. Three independent lines of evidence (groundwater travel, tritium, and N in sediment)

suggest this difference could, at least in part, be due to large N applications from 1969 to 1974.

## Conclusion

Groundwater time-of-travel estimates and tritium data both suggest that groundwater remains resident in these watersheds for more than 30 years. Furthermore, analyses of sediments from deep cores show that soil NO<sub>3</sub>-N may take 30 years to reach groundwater in upper parts of these watersheds. Concentrations of NO<sub>3</sub>-N in groundwater beneath upslope positions in Watershed 1 are still influenced by N applications made from 1969 to 1974. Stable isotope data suggest that in lower landscape positions, historical and recent land use practices affect current NO<sub>3</sub>-N concentrations. It will be difficult to discern impacts of recent cropping changes between W1 and W2 by simply monitoring groundwater or baseflow. Monitoring of shallow unsaturated-zone waters may be the most reliable means to do this. Multiple lines of evidence suggest it takes at least several decades for subsurface water to travel from the divide to the stream. In many locations, changes in agricultural practices may take decades to fully affect improvements in groundwater quality.

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