JOURNAL OF
ENVIRONMENTAL HYDROLOGY
The Electronic Journal of the International Association for Environmental Hydrology
On the World Wide Web at http://www.hydroweb.com
VOLUME 8 2000

USE OF ISOTOPICALLY LABELED FERTILIZER TO TRACE NITROGEN FERTILIZER CONTRIBUTIONS TO SURFACE, SOIL, AND GROUND WATER

Donald H. Wilkison
Dale W. Blevins
U.S. Geological Survey, Independence, Missouri, U.S.A.

Steven R. Silva
U.S. Geological Survey, Menlo Park, California, U.S.A.

The fate and transport of a single N fertilizer application through plants, soil, runoff, and the unsaturated and saturated zones was determined for four years at a field site under continuous corn (Zea mays L.) management. Claypan soils, which underlie the site, were hypothesized to restrict the movement of agrichemicals from the soil surface to ground water. However, N fertilizer moved rapidly through preferential flow paths in the soil and into the underlying glacial till aquifer. Most N transport occurred during the fall and winter when crops were not available to use excess N. Forty months after application, 33 percent of the fertilizer had been removed by grain harvests, 30 percent had been transpired to the atmosphere, and 33 percent had migrated to ground water. Although runoff volumes were 50 percent greater than infiltration, less than 2 percent of the fertilizer was lost to runoff. Small measured denitrification rates and large measured dissolved oxygen concentrations in ground water favor the long-term stability of NO_3^{-1} *in ground water. Successive fertilizer applications, in areas that lack the ability to moderate N concentrations through consumptive N reactions, risk the potential of N-saturated ecosystems.*

INTRODUCTION

Nitrogen accounts for the largest input of agrichemicals to croplands, and its use in commercial fertilizers has increased twenty-fold since 1945 (Puckett, 1995; Kitchen et al., 1997). Ground water in the Midwestern United States is especially vulnerable to nitrate (NO_3^{-1}) contamination (Kellogg et al., 1994) because intensive row-crop farming and heavy reliance on inorganic fertilizers is commonplace (Mueller et al., 1995). Once applied, N fertilizer is subject to soil biogeochemical processes that can redistribute N through fixation, mineralization, nitrification, and immobilization (Foth, 1990). A variety of chemical species are produced, some of which [NO_3^{-1}, nitrite (NO_2^{-1}), and ammonium (NH_4^{+1})] are highly soluble and mobile in soil and water. Other species are gases at temperatures and pressures commonly found near the earth's surface [elemental nitrogen (N_2), nitrous oxide (N_2O), and ammonia (NH_3)]. The numerous N processes and species that are present in most soils and which combine to allow N fertilizer to be lost to surface runoff, grain harvest, volatilization from soils and plants, and leachates makes the monitoring of fertilizer through the hydrologic cycle difficult.

Problems with tracing ground-water contamination from N fertilizer using isotopic signatures of N have been well documented (Fogg, 1998). This is because the $\delta^{15}N$ signature (ratio of ^{15}N to ^{14}N, relative to atmospheric N, expressed in per mil) of fertilizer is often indistinguishable from natural soil organic matter. Also, the resultant $\delta^{15}N$ signature is often the product of multiple source mixing which further complicates source identification (Kendall et al., 1998). Once in the soil N cycle, fertilizer is subject to the aforementioned biogeochemical processes, each of which can further mask the original $\delta^{15}N$ signature. Even in cases where signatures are discrete enough to indicate contamination sources, the time frame of the contamination is generally unclear without additional hydrologic evidence, such as age dating. However, the use of a labeled N fertilizer overcomes the problem of blurred isotopic signatures and additionally allows for the tracing of a single fertilizer application through the hydrologic cycle for many years (Olson and Swallow, 1984). Because labeled N is costly and isotopic analyses expensive, most labeled N studies are carried out on small microplots (generally 1m^2 or less) or on soil cores in laboratory experiments (Berecz et al., 1997; Glendining et al., 1997; Pilbeam et al., 1997). We coupled an integrated sampling approach at a comparatively large (432 m^2) field site with less expensive, safer, and more efficient onsite and laboratory methods for N isotope analyses. This allowed us to trace the movement of a single fertilizer application through plants, soil, runoff, and the unsaturated and saturated zone for a period of 4 years.

APPROACH AND METHODS

Sampling protocol

A tracer plot was installed at the Missouri Management Systems Evaluation Area (MSEA) site (Figure 1). The plot covered 0.04 ha (432 m^2) and was instrumented to sample surface runoff, soil water, and ground water for $\delta^{15}N$, $\delta^{15}N\text{-}NO_3^{-1}$ ($\delta^{15}N$ in NO_3^{-1}), bromide (Br), and concentrations of various N species. Methods of laboratory analysis of $\delta^{15}N$ (refers to all N in a sample), $\delta^{15}N\text{-}NO_3^{-1}$ (refers to all NO_3^{-1} in a sample), Br, N species, and other constituents in this study are described in Fishman and Friedman (1989), Kendall and Grim (1990), and Silva et al. (1996).

The plot instrumentation included a continuous-recording flume, an automatic runoff sampler, an interflow collector, 2 neutron probe access tubes, 10 gravity lysimeters, 16 suction lysimeters, and 14 monitoring wells (Figure 1). Interflow is defined as water in a saturated layer on top of the claypan (B soil horizon) that can move down a hillslope. Interflow and gravity lysimeters were constructed

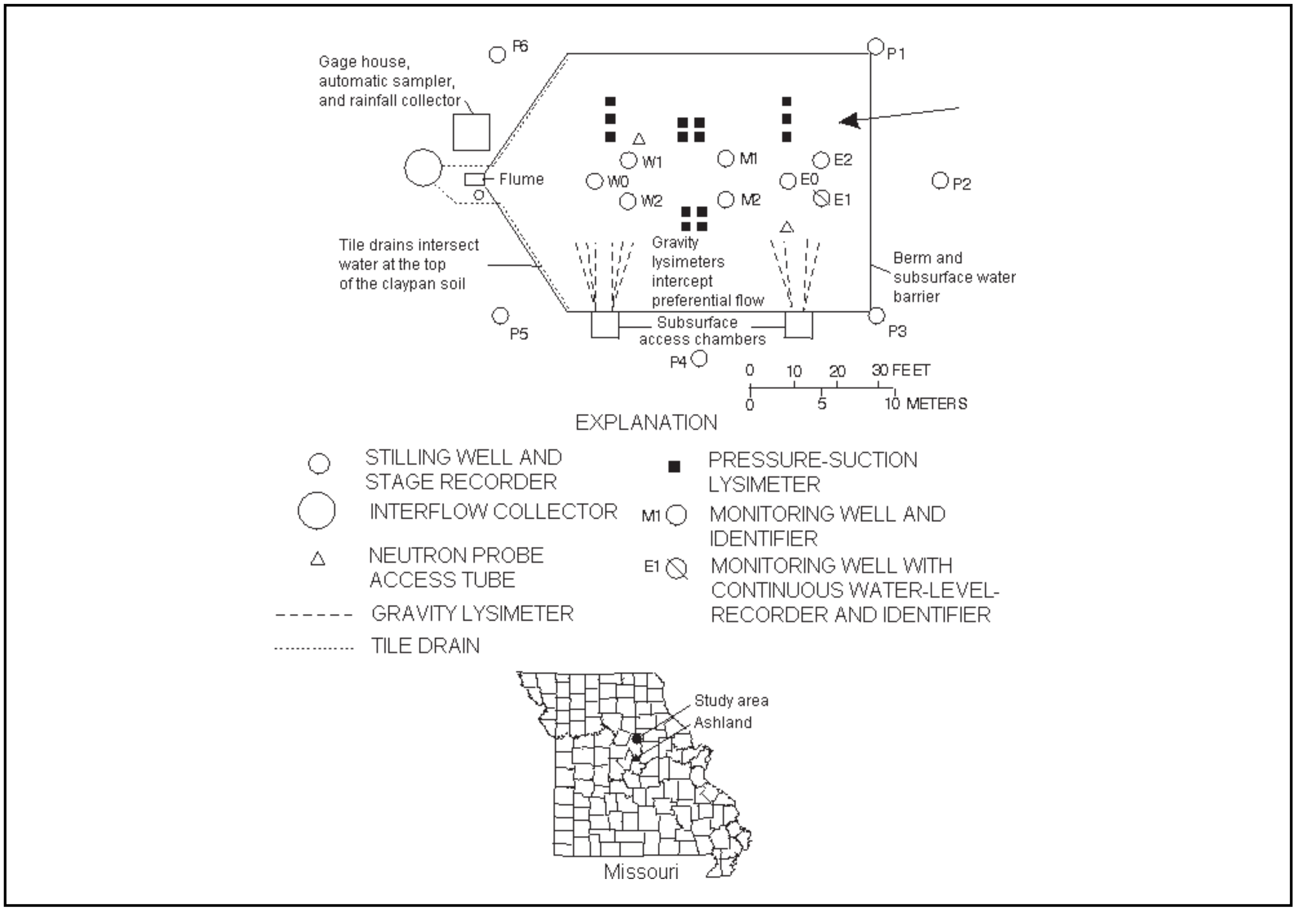

Figure 1. Instrumentation at and location of the study plot. (Arrow indicates general direction of ground-water flow).

with 5-cm diameter polyvinyl chloride (PVC) pipe, slotted on top and installed horizontally to collect water not held by capillary forces in the soil. Soil matrix water was sampled using pressure-suction lysimeters.

The gravity and suction lysimeters were installed at three depths: immediately above the claypan (46 cm), within the claypan (71 to 90 cm), and in the glacial till immediately beneath the claypan (114 to 120 cm). Monitoring wells were screened at depth intervals that ranged from 1.2 to 8.5 m below land surface. Water levels at one well were continuously monitored with an automatic recorder and were measured weekly in the remainder. A 30-cm high berm was maintained around the plot to prevent off-site runoff from entering the plot. Soil water was prevented from moving onto the plot by the presence of a subsurface water barrier, which extended through the claypan to a depth of 112 cm beneath the berm. Soil moisture in two 1.8-m deep access tubes was measured weekly with a neutron probe at 15-cm depth intervals using methods described in Gardner (1986). Continuous precipitation (data on file at the Agricultural Research Service, Columbia, MO), runoff, interflow, and ground-water level data were used to calculate a hydrologic budget for the plot (Table 1).

Site treatment

Conventional tillage practices were used to produce an annual corn crop from May 1991 to September 1995. The crop was planted between mid-May and early June of each year dependent upon weather and soil conditions. Plant stover (the part of the plant above ground, excepting the grain) was left on the plot to decompose after each crop harvest that occurred in late September or early October.

Table 1. Hydrologic Budget and Effective Porosity Calculations for Three Time Intervals at the Tracer Plot [--, not determined]

Time period	Measured precipitation volume, in cubic meters	Measured runoff volume, in cubic meters	Measured interflow volume, in cubic meters	Measured soil moisture volume, in cubic meters	Computed ground-water recharge volume, in cubic meters	Measured ground-water rise, in meters	Computed change in saturated aquifer volume, in cubic meters	Computed percent effective porosity
11/23/92 to 03/31/93	93.4	23.3	22.4	14.6	33.2	2.72	1,177	2.8
09/23/93 to 03/31/94	136.0	49.9	4.21	18.1	63.7	2.99	1,293	4.9
11/01/94 to 01/31/95	103.6	29.0	4.80	41.5	28.3	2.87	1,240	2.2
Average	--	--	--	--	--	--	--	3.3

Random samples of grain and stover were collected at harvest and analyzed for moisture content, Br, N, and $\delta^{15}N$. Just prior to planting each spring, the fertilizer and any remaining stover was incorporated into the upper 10 cm of the soil horizon using a rear-tine tiller.

In May 1992, a ^{15}N-labeled fertilizer (hereafter referred to in this report as labeled N) and Br spike was applied to trace N fertilizer movement. The application was enriched with $\delta^{15}N\text{-}NO_3^{-1}$ to 3,080 per mil and spiked with 4.67 kg of Br. Smaller amounts of fertilizer were applied during 1993 and 1994 to diminish dilution effects on the 1992 labeled N application. Fertilizer application rates are listed in Table 2 and were consistent with local application rates.

Table 2. Fertilizer Application Rates and Recovery Efficiencies at the Tracer Plot, 1991-95 [--, no data]

Year	Fertilizer application rate, as nitrogen, in kilograms per hectare	Fertilizer nitrogen recovery efficiency, in percent of fertilizer applied in May 1992	Cumulative fertilizer nitrogen recovery efficiency, in percent of fertilizer applied in May 1992	Available soil nitrogen, in kilograms per hectare
1991	161	--	--	354
1992	94	37.8	37.8	319
1993	74	7.1	44.9	--
1994	74	6.2	51.1	204
1995	124	1.2	52.3	184

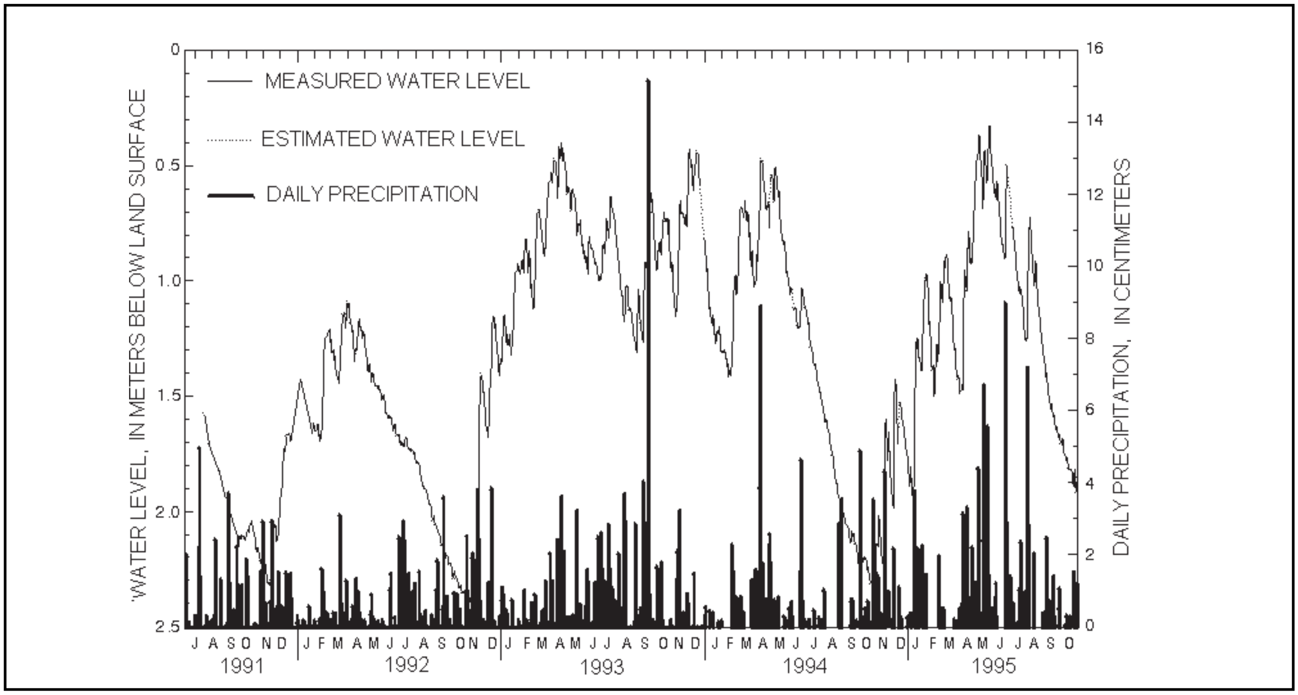

Figure 2. Ground-water levels and daily precipitation at the trace plot.

Labeled-N determinations

The formula used to calculate the mass or concentration of labeled N in a sample was:

$$C_{LN} = C_{NO3} \times [(\delta^{15}N\text{-}NO_3) - 10] / 3070,$$

where C_{LN} is the concentration of labeled NO_3^{-1} in the sample in mg L^{-1}as N, C_{NO3} is the concentration of NO_3^{-1} in the sample in mg L^{-1} as N, and $\delta^{15}N\text{-}NO_3^{-1}$ is the measured N isotopic value of the sample. The value of 10 represents the average background permil value of $\delta^{15}N\text{-}NO_3^{-1}$. The value 3070 represents the $\delta^{15}N\text{-}NO_3^{-1}$ value of the fertilizer corrected for the background value. The heavy enrichment of the applied fertilizer allows for sufficient precision in calculation of the mass or concentration of the labeled N in samples.

Quality assurance

Ten percent of all samples were quality assurance samples. All ground-water samples for $\delta^{15}N\text{-}NO_3^{-1}$ analysis were collected in replicate to provide a backup sample in case reanalysis was needed. Field spikes (20 mg L^{-1} solution of KNO_3 with a $\delta^{15}N\text{-}NO_3^{-1}$ of +3.49 per mil) and field blanks (inorganic free water) were processed in the field between collection of environmental samples to assess potential cross contamination. The average deviation of the $\delta^{15}N\text{-}NO_3^{-1}$ analysis based on analysis of 42 replicates was 0.31± 0.01 per mil. The average deviation of the NO_3^{-1} analysis based on analysis of 20 replicates was 0.02 ± 0.03 mg L^{-1}. The average deviation of the Br analysis based on analysis of 17 replicates was 0.02 ± 0.05 mg L^{-1}. The accuracy of 6 field spikes was 0.07 ± 0.03 per mil. Six field equipment blanks were all below the analytical detection limit. Results of quality assurance samples indicate that field collection procedures and laboratory variability were inconsequential sources of error.

Hydrogeology of the site

The site is located on deposits of loess and glacial till that overlie Mississippian and Pennsylvanian bedrock composed of interbedded limestones and shales. The glacial till serves as a source of domestic water in the area. The soil is an Albaquic Halpludalf of the Adco series, a principal feature of which is a claypan at 41 to 46 cm depth (Alberts et al., 1993). Such soils cover about 41,000 km^2 of the Midwestern United States. The mineralogical composition of the argillic horizon often exceeds 50 percent smectites so consequently, rapid or prolonged infiltration events allow water and dissolved solutes to perch on the claypan for brief periods. However, a well-developed network of preferential flow paths quickly diverts water and solutes through the claypan and into the underlying glacial till aquifer (Wilkison et al., 1999).

Continuous water-level data was collected at the site, located near a ground-water divide and recharge area for the glacial till, between July, 1991 and October, 1995 (Figure 2). Most recharge occurs between October and April; during the mid-May through September growing season, water levels generally decline. The average annual precipitation at the site is 93.3 cm (National Oceanic and Atmospheric Administration, 1995). Water level declines were dampened during the 1993 growing season because precipitation that year was 144% of normal. Horizontal gradients of both the soil surface and claypan at the plot are small (<2). Water-level increases in response to precipitation are brief and rapid, which indicates effective porosity is extremely low.

Ground-water recharge was estimated by summing water-level increases over the study period and multiplying these increases by the average effective porosity of the upper till. Effective porosity was calculated for three wintertime periods when evapotranspiration from ground water was considered negligible (Table 1). During these periods, the total of water-level increases was equal to precipitation minus runoff, interflow, and soil saturation volumes. Although some evapotranspiration probably occurred during the measurement period, the average value of 3.3% determined for this study is very near the 2.2% value previously reported by Kelly and Pomes (1998) and determined over a much shorter time interval when evapotranspiration was known to be negligible.

RESULTS AND DISCUSSION

Samples of runoff, soil and soil water, interflow, gravity lysimeter, ground water, and grain and stover were analyzed to track the labeled N and Br between the application in May 1992 and October 1995. Background distribution of $\delta^{15}N$, $\delta^{15}N\text{-}NO_3^{-1}$, N species, and Br in runoff, soil, and ground water at the tracer plot was established using data collected between May 1991 and May 1992 (Wilkison et al., 1994). At the end of the study, in October 1995, labeled-N losses from the plot could be attributed to the following pathways: runoff (1.6%), interflow (1.4%), ground water (33.3%), grain (33.2%), and gaseous losses (30.5%). From 12 July 1991 to 30 September 1995, precipitation totaled 442.5 cm. Of this amount, 17.7 cm (4%) left the plot as interflow, 99.4 cm (22.5%) left as runoff, 67.6 cm (15.3%) infiltrated the ground surface, and 257.8 cm (58.3%) left the plot as evapotranspiration. A conceptual model of N transport through the hydrologic system is shown in Figure 3. If N inputs continuously exceed N outputs, then the potential exists for the development of an N saturated ecosystem. Where this occurs, substantial quantities of N will be leached to ground water or transpired to the atmosphere.

Rainfall and runoff

The N content of rainfall was measured at Ashland, Missouri (Figure 1), 48 km south of the study area (National Atmospheric Deposition Program/National Trends Network, 1991-1995). The N contribution from rainfall NO_3^{-1} and ammonium averaged 5.0 kg ha^{-1} between 1991 and 1994, which was small as compared to the amount of N applied as fertilizer and the amount of N resident in the soil (Table 2). Most N in runoff occurred as organic N, although increased NO_3^{-1} concentrations were

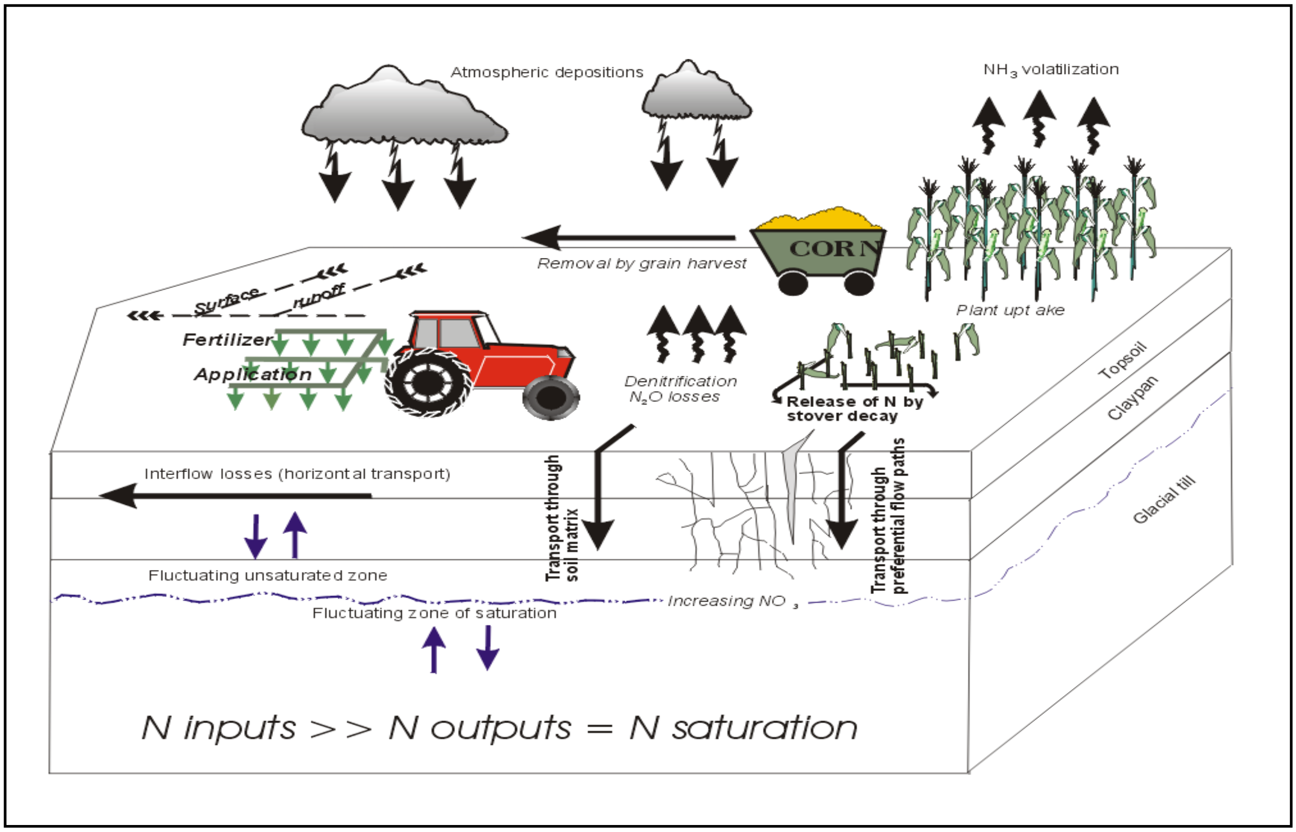

Figure 3. Conceptual model of N transport through the hydrologic system. When N inputs greatly exceed N outputs, N saturation can occur, and leach NO_3 to ground water.

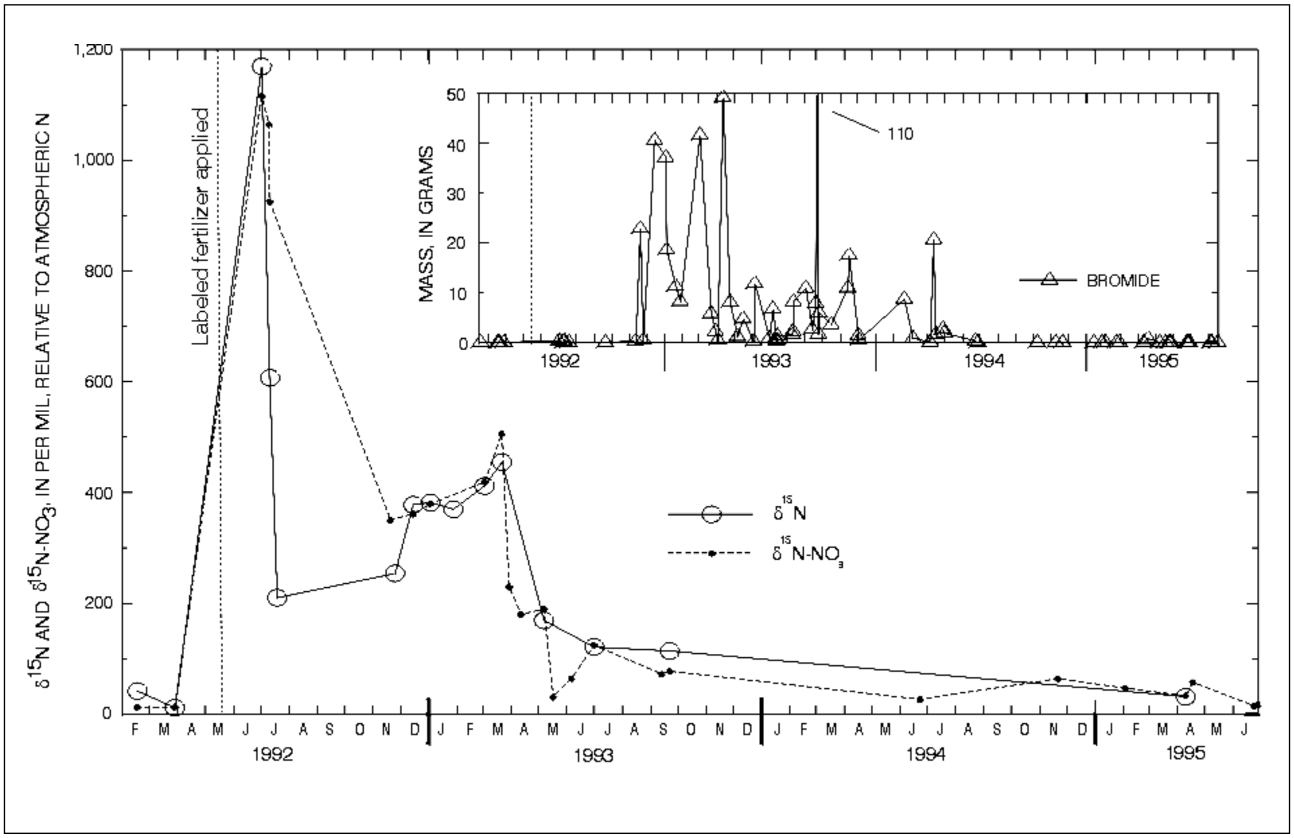

Figure 4. $\delta^{15}N$ and $\delta^{15}N\text{-}NO_3^{-1}$ values and bromide mass in runoff from the tracer plot.

detected in samples collected immediately after fertilizer applications in most years. Elevated labeled-N concentrations were also detected in runoff (Figure 4) as stover decayed during the winter and spring.

Composite runoff samples from the tracer plot were analyzed for $\delta^{15}N$, $\delta^{15}N\text{-}NO_3^{-1}$. Values of $\delta^{15}N$ for unsampled runoff were estimated by interpolation between the points on the graph (Figure 4). A regression relation between the log normal of total N load and runoff volume (coefficient of determination = 0.86) was used to estimate N loads from unsampled storms.

Labeled N accounted for 35% of the NO_3^{-1} in runoff samples from the first storm after application. But runoff, while constituting a substantial part of the overall hydrologic budget (22.5%), removed only minor amounts (1.6%) of labeled N over four growing seasons. This is due to several factors. The tracers were initially incorporated into the upper topsoil and the first storm event served to move the tracers even deeper into the soil profile. Because of that, they are not as easily mobilized into runoff. Also, as plant growth begins, a portion of the tracers are taken up as nutrients and removed (at least temporarily) from the runoff pathway.

The labeled N and Br breakpoint [time at which one-half of the runoff mass was lost ($t_{1/2}$)] in runoff occurred 355 and 358 days after application. The coincidence of these breakpoints indicates the usefulness of Br as a surrogate tracer for timing N movement in runoff, at least through the first year. While small amounts of labeled N were still detected in runoff samples as long as 3 years after application, 90% of the labeled-N losses to runoff occurred within 715 days (30 April 1994) of application. These data indicate that incorporated N fertilizer contributes only minor amounts of N to runoff, but may do so for several years after the initial application.

Interflow

Nitrate was the predominant interflow N species. Although initial concentrations were high, only 1.4% of the labeled N was removed by interflow. The mean labeled N concentration in the first 10 samples collected after application was 2.3 mg L^{-1} with a standard deviation of 0.7 mg L^{-1}. The labeled N breakpoint in interflow samples occurred 270 days after the fertilizer was applied (Figure 5A) and 90% of the loss had occurred after 336 days. Although water frequently perched on the claypan, only minor quantities of fertilizer N were transported horizontally via interflow, primarily because the claypan gradient was shallow (< 2%) and flow was quickly redirected downward through preferential flow paths (Wilkison et al., 1999).

Recharge and soil water

Nitrogen in recharge and soil water also was dominated by NO_3^{-1}. As soil N leached to the top of the claypan, NO_3^{-1} concentrated there through evaporation or ion exclusion (Blevins et al., 1996). The mass of labeled N and Br in gravity lysimeter samples was determined by summing the ground-water level change from each recharge event and multiplying this value times the effective porosity and the measured concentrations of labeled N and Br in the samples (Figures 5B, 5C, and 5D). As discussed in Kelly and Pomes (1998) these data provide estimates of the mass of labeled N and Br moving through preferential flow paths at different depths.

Breakpoint values from the different gravity lysimeters were then used to determine transport rates of the tracers through the claypan. The calculated rate of transport ranged from 2.1 to 2.8 x 10^{-5} cm s^{-1} with an average value of 2.4 x 10^{-5} cm s^{-1}. These values represent transport rates rather than hydraulic conductivity because of the intermittent nature of gravity flow. Kelly and Pomes (1998) determined that transport rates during periods when soil saturation continuously exceeded 80% were

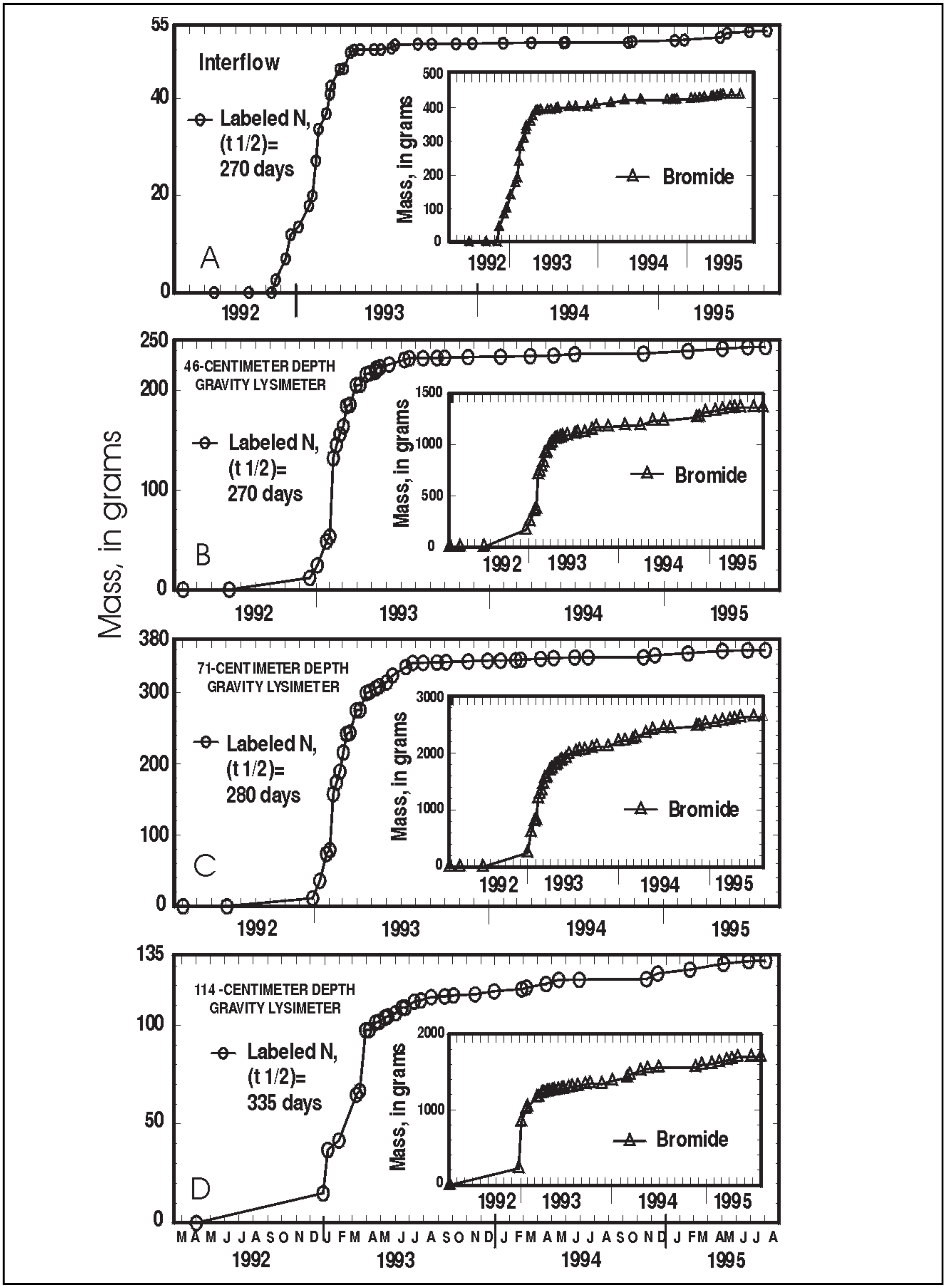

Figure 5. Cumulative mass of labeled N and bromide in interflow and gravity lysimeter samples from the tracer plot.

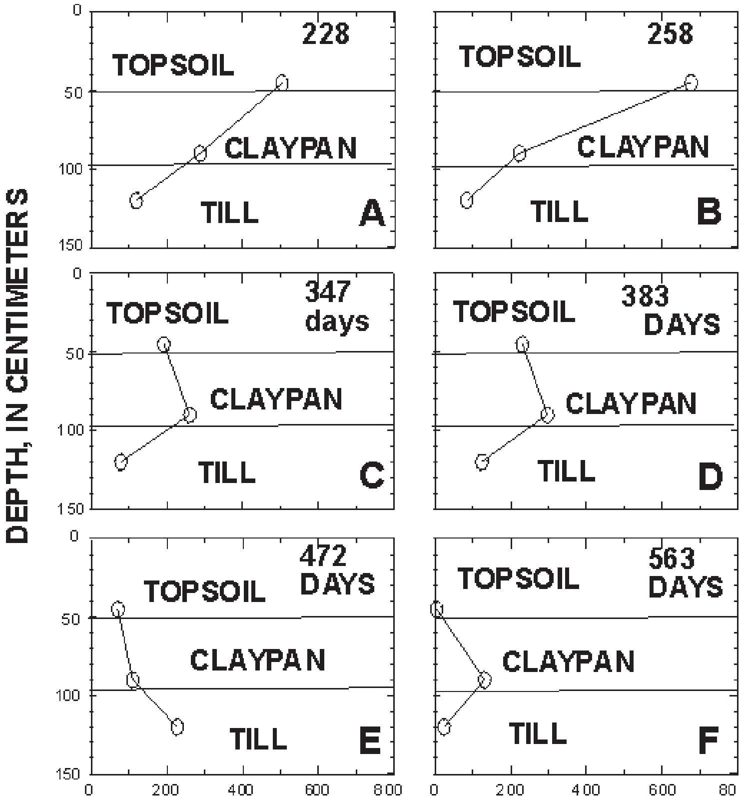

Figure 6. Mass of labeled N, as nitrogen, in soil water, time in days after application.

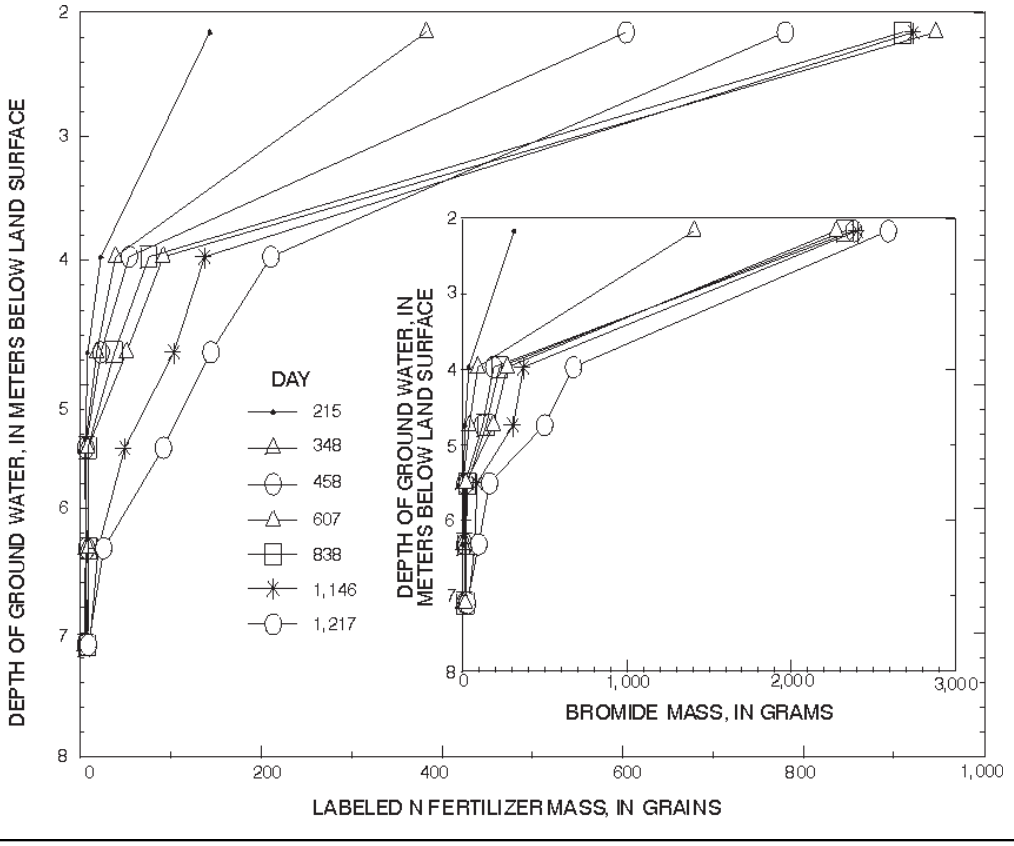

Figure 7. Time series of mass of labeled N and bromide in ground water beneath the tracer plot.

an order of magnitude faster than our transport rates. During dry periods, most soil water was contained within the soil matrix. As soil saturation increased above 80% and preferential flow began, NO_3^{-1} in the soil matrix water was mobilized into preferential soil water and then transported downward.

Concentrations of labeled N from suction lysimeters and soil moisture data were used to calculate the mass of labeled N in three soil horizons: topsoil, claypan, and glacial till immediately beneath the claypan (Figure 6). The travel time between peak mass of labeled N at each horizon was then used to determine unsaturated zone transport times. Values ranged between 2.0 and 4.4×10^{-6} cm s^{-1} with an average value of 3.3×10^{-6} cm s^{-1}. These rates are an order of magnitude slower than the rates through preferential flow paths because unsaturated flow is highly dependent on periods of soil saturation (Hillel, 1982). Above 80% soil saturation, water can essentially by-pass the soil matrix as it moves through preferential flow paths.

Ground Water

Masses of tracers in ground water were determined for various times after application (Figure 7). Masses were determined by first dividing the plot into 6 layers. Tracer concentrations from each well were then multiplied by the saturated thickness of each layer times a weighted factor determined from the portion of the screened interval that crossed each layer and the well's zone of influence (data not shown) times the aquifer porosity. The depths shown in Figure 7 represent the midpoint depth of each layer. The porosity of the saturated zone was estimated, from the average of neutron probe readings taken below the water table, to be 42.5%.

Small amounts of labeled N reached the saturated zone within several days of the first major recharge event after application of labeled N. This occurred in November 1992 (Wilkison et al., 1994). By 13 September 1995 (1,217 days, or 40 months, after the application of the labeled N), one-third of the labeled N had reached ground water. Most of this mass was confined to a layer of ground water less than 4 m below land surface and, in fact, more than 60% was confined to shallow ground water [less than 2.1 m below land surface]. Because flume, interflow, gravity, and suction-lysimeter data indicated that little of the labeled N remained in the unsaturated zone at this time, the mass of labeled N in ground water is not expected to increase measurably, beyond the amount measured in September 1995. Neither of the tracers were detected in ground water at depths below 7.4 m. The total mass of labeled N and Br increased in ground water throughout this study, which indicates saturated horizontal flow rates are very slow. Small amounts of labeled N and Br were detected in two monitoring wells outside of the plot boundaries, but these amounts accounted for less than 0.3% of the labeled-N loads in ground water and probably represent the effects of diffusion and dispersion. Blevins et al. (1996) previously reported an average saturated hydraulic conductivity of 1×10^{-5} cm s^{-1}. From that rate, it would take about 35 years for the center of mass of the tracers to move off the boundaries of the plot.

Large concentrations of dissolved oxygen, large quantities of oxidized N (average NO_3^{-1} concentration was 24 mg L^{-1}), and small quantities of reduced-N species in ground water beneath the plot indicate that oxidizing conditions limit N loss due to denitrification. Thus, once NO_3^{-1} reached ground water it would be expected to remain stable for long periods (Blevins et al., 1996).

Grain and stover

Plants took up a little more than one-half (52%) of the labeled N during four growing seasons (Table 2). However, only the labeled N incorporated into the grain was actually removed from the system because the remaining stover was left on the plot. As the stover decomposed, the N was mobilized and became available to leave the plot through runoff, leach to ground water, or be taken up by succeeding crops. Grain harvest removed 33.2% of the labeled N from the plot - more than 90% of which was removed during the first two growing seasons.

Plants took up an almost equal percentage (49%) of Br as labeled N; however, Br was incorporated almost exclusively into plant stover. Because this stover was left on the plot to decompose, most Br was eventually released back into the soil and little was removed from the plot. This non-parallel behavior limits the effectiveness of Br as a surrogate tracer for N after one growing season.

Gaseous N losses

Gaseous N losses represent a potential loss of N from the tracer plot. Primary processes producing gaseous N losses include soil denitrification and soil and plant volatilization of NH_3. These processes have been indicated to be substantial sources of fertilizer losses. Baker and Timmons (1994) estimated fertilizer N losses from denitrification and NH_3 volatilization at 23 to 36% from no-till corn. Francis et al. (1993) determined post-anthesis NH_3 volatilization from corn accounted for 10 to 20% of the applied fertilizer.

The effect of soil denitrification was measured using both qualitative and quantitative methods. The ratios of N_2 to argon and $\delta^{15}N$ of N_2 in soil gases were used as qualitative measures of denitrification (Boelke and Denver, 1995). These values were near atmospheric indicating that little denitrification occurred near the time of sample collection. Because these samples represented only two short periods, a quantitative determination of N_2O fluxes was conducted during the 1995 growing season (Pomes et al., 1998). Nitrous oxide fluxes accounted for only 3% of the applied fertilizer, even though soil conditions were conducive for denitrification during the entire growing season. Also, experimentally derived N_2O fluxes from soil cores collected at the MSEA site were determined to be less than 1% (Tindall et al., 1995). The low soil organic carbon content (1.2% in the topsoil) probably limits denitrification losses. However, N_2O fluxes may increase in the fall because plant stover decomposition contributes to soil organic matter.

Ammonia volatilization from corn plants and soils at the MSEA site was measured at 2-week intervals during the 1995 growing season. However, the observed losses were estimated to be less than 1% of the applied fertilizer (M.L. Pomes, U.S. Geological Survey, written commun., 1996). Soil pH ranged from 4.6 to 5.9 at the site, which should limit soil NH_3 volatilization. Volatilization of NH_3 from corn plants occurs in rapid spurts late in the growth cycle as soil and plant N is assimilated into grain (Francis et al., 1993). Because of this, a 2-week sampling frequency may have missed a large part of NH_3 plant volatilization. Schjoerring et al. (1993) suggested that NH_3 emissions varied from year to year and were dependent on weather and crop N economy. Measurements of NH_3 in 1995 may not accurately reflect meteorological conditions and plant N economy that existed between 1992 and 1994 and, therefore, probably do not accurately estimate these losses.

Unaccounted labeled N (30.5%) represents the combination of gaseous N losses and net measurement error. A conservative tracer, Br, was applied simultaneously with the labeled N. Because Br is not expected to volatilize, this provides some check on net measurement error. A Br balance showed that at the end of the study 107% of the Br was accounted for in the following proportions: runoff (11%), interflow (9%), grain (1%), and ground water (86%). If the 7% error were applied entirely to gaseous transport, then the gaseous N losses resulting from both denitrification and NH_3 would range from 23.5 to 37.5%. Most of this loss is expected to have resulted from NH_3

volatilization because denitrification rates were demonstrated to be no greater than 4%. Our combined gaseous loss value was consistent with those of previous studies (Baker and Timmons, 1994).

Fertilizer nitrogen recovery efficiency

The fraction of fertilizer N in the aboveground crop can be used to determine the efficiency of the crop to use the applied fertilizer. Kitchen et al. (1993) reported fertilizer N recovery efficiency (FNRE) values at the Missouri MSEA site ranged from 32 to 67%. Fertilizer N not used during the growing season remains behind in the soil N pool. As residual stover decomposes, it also releases assimilated fertilizer N back into the soil. If this excess N is not removed from the system, then it is available for future crops. Crop management practices that limit this excess N, or that prevent its movement beyond the root zone, have the potential to improve the efficiency of fertilizers and thereby limit losses (Angle, 1993; Menelik, 1994).

Annual and cumulative FNRE of labeled N from the plot are reported in Table 2. During the first year, the crop used 37.8% of the applied fertilizer. As N was recycled within the soil N pool, the FNRE had increased to 52.3% by the end of the study. Most of this N was used within the first 3 years, and 1995 left little of the labeled N in the available pool of soil N.

CONCLUSIONS AND IMPLICATIONS

Nitrogen fertilizer contributions to surface, soil, and ground water can be monitored for many years using labeled N fertilizer. This is important because shorter time-scale studies cannot adequately address the effects of farming practices on water quality. Fertilization rates generally exceed a crop’s ability to assimilate N. This leaves excess soil N available for succeeding crops, or to leave the system as either runoff or interflow, or ultimately to leach to ground water. We found that at a site underlain by a claypan soil and glacial till, most excess N was leached to ground water.

Several factors made NO_3 leaching to ground water inevitable. First, the corn crops were inefficient users of N. whereas one-half of the fertilizer was assimilated during crop growth, only 33% was removed in grain harvest and removed from the soil N pool. Second, mobile N was released at times when crops were not available to use it. Fall and winter recharge quickly moved mobile N into shallow ground water. Finally, measured denitrification rates were small (<3%), and oxidizing conditions were prevalent; thus, NO_3^{-1} was stable in soil and ground water. The fertilizer N contribution to NO_3^{-1} concentrations in ground water continued to increase 40 months after application. However, because only small amounts of labeled N remained in the upper 1.2 m of soil, fertilizer inputs to ground water are not expected to increase.

Nitrogen leached below the root zone represents a fundamental shift in soil N dynamics with adverse implications for water quality (Kahl et al., 1993). This phenomenon of a “nitrogen saturated” ecosystem has been observed in northeastern United States forested basins where surface water NO_3^{-1} concentrations are increasing in response to increased atmospheric N deposition. Elevated NO_3^{-1} concentrations in ground water may represent a similar response to N fertilizer applications in excess of the ability of a crop to assimilate N.

Substantial quantities of N are available to leach to ground water from conventional farming practices. Unless measures are taken to either increase the efficiency of N uptake or to remove some of the N from the system, most excess N from fertilizer application eventually moves to shallow ground water in glacial till. Crop rotations that require yearly N inputs can lead to N-saturated ecosystems with subsequent degradation of water quality. Ground-water quality is particularly vulnerable to this degradation because pathways to remove N can be limited. Farming techniques that optimize N fertilization rates and thus limit N excess, cover-crop techniques that tie up mobile N during the fall-winter recharge period, or crop rotations that decrease overall N application rates may help to minimize N leaching. Wagger (1989) found that the winter annual legumes hairy vetch (*Vicia villosa* Roth) and crimson clover (*Trifolium incarnatum* L.) provided approximately 30 and 36% of the corn N requirements for the following year. By fixing atmospheric N during the fall and winter, the use of legume cover crops might actually contribute excess N available to leach to ground water. Non-leguminous cover crops such as rye (*Secale cereale* L.), wheat (*Triticum aestivum* L.), oat (*Avena sativa* L.), and barley (*Hordeum vulgare* L.) may offer better opportunities to immobilize N. However, timely management of cover crops is essential to prevent deleterious effects to both the water and N requirements of the succeeding principal crop (Wagger and Mengel, 1988).

REFERENCES

Alberts, E.E., T. Prato, N.R. Kitchen, and D.W. Blevins; 1993. Research and education to improve surface and ground water quality of a claypan soil. p. 21-38. In Proceedings of the Conference on Agricultural Research to Protect Water Quality. Minneapolis, MN. February 21-24, 1993. Soil and Water Conservation Society. Ankeny, IA.

Angle, J.S.; 1993. Soil nitrate concentrations under corn as affected by tillage, manure, and fertilizer applications. Journal of Environmental Quality. v. 22, pp. 141-147.

Baker, J.L., and D.R. Timmons; 1994. Fertilizer management effects on leaching of labeled nitrogen from no-till corn in field lysimeters. Journal of Environmental Quality. v. 23, pp. 305-310.

Boelke, J.K., and J.M. Denver; 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. Water Resources Research. V. 31, pp. 2319-2339.

Berecz, K., K. Debreczeni, and I. Ragasits; 1997. Incorporation of 15N-labelled fertilizer nitrogen into wheat grain proteins during grain development. Acta Agronomica Hungarica. V. 45, pp. 35-45.

Blevins, D.W., D.H. Wilkison, B.P. Kelly, and S.R. Silva; 1996. Movement of nitrate fertilizer to glacial till and runoff from a claypan soil. Journal of Environmental Quality. v. 25, pp. 584-592.

Fogg, G.E., D.E. Rolston, D.L. Decker, D.T. Louie, and M.E. Grismer; 1998. Spatial variation in nitrogen isotope values beneath nitrate contamination sources. Ground Water. V. 36, pp. 418-426.

Fishman, M.J., and L.C. Friedman; 1989. Methods for determination of inorganic substances in water and fluvial sediments. U. S. Geological Survey Techniques of Water-Resources Investigations. Book 5. Chapter A1.

Foth, H.D. 1990. Fundamentals of soil science. John Wiley and Sons. New York.

Francis, D.D., J.S. Schepers, and M.F. Vigil; 1993. Post-anthesis nitrogen loss from corn. Agronomy Journal. v. 85, pp. 659-663.

Gardner, W.H.; 1986. Chapter 21. Physical and mineralogical methods. p. 528-544. In A. Klute (ed.) Methods of Soil Analysis. Part 1. 2nd ed. Agronomy Monogram 9. Agronomy Society of America and Soil Science Society of America, Madison, WI.

Glending. M.J., P.R. Poulton, D.S. Powlson, and D.S. Jenkinson; 1997. Fate of 15N-labelled fertilizer applied to spring barley grown on soils of contrasting nutrient status. Plant and Soil. V. 195, pp. 83-98.

Hillel, D.; 1982. Introduction to soil physics. Academic Press. San Diego, CA.

Kahl, J.S., S.A. Norton, I.J. Fernandez, K.J. Nadelhoffer, C.T. Driscoll, and J.D. Aber; 1993. Experimental inducement of nitrogen saturation at the watershed scale. Environmental and Science Technology. v. 27, pp. 565-568.

Kellogg, R.L., M.S. Maizel, and D.W. Goss; 1994. The potential for leaching of agrichemicals used in crop production: A national perspective. Journal of Soil and Water Conservation, v. 49, pp. 294-298.

Kelly, B.P., and M.L. Pomes; 1998. Field-based measures of hydraulic conductivity and transport of Br and NO3 tracers through a claypan soil, near Centralia, Missouri. Ground Water. v. 36, pp. 484-494.

Kendall, Carol, and E. Grim; 1990. Combustion tube method for measurement of nitrogen isotope ratios using calcium oxide for total removal of carbon dioxide and water. Analytical Chemistry. v. 62, pp. 526-529.

Kitchen, N.R., P.E. Blanchard, D.F. Hughes, and R.N. Lerch; 1997. Impact of historical and current farming systems on groundwater nitrate in northern Missouri. Journal of Soil and Water Conservation, v. 52, pp. 272-277.

Kitchen, N.R., D.F. Hughes, K.A. Sudduth, and K.S. McGinty; 1993. Missouri MSEA farming systems and landscape position effects on nitrogen fertilizer use and crop production. In Proceedings of the Conference on Agricultural Research to Protect Water Quality. Minneapolis, MN. February 21-24, 1993. Soil and Water Conservation Society. Ankeny, IA.

Menelik, G.; 1994. Corn yield and nitrogen uptake as influenced by tillage and applied nitrogen. Journal of Plant Nutrition. v. 17, pp. 911-913.

Mueller, D. K., P.A. Hamilton, D.R. Hesel, K.J. Hitt, and B.C. Ruddy; 1995. Nutrients in ground and surface water of the United States - An analysis of data through 1992. U.S. Geological Survey Water-Resources Investigations Report 95-4031, 74 p.

National Atmospheric Deposition Program/National Trends Network; 1991-1995. NADP/NTN Coordination Office. Natural Resources Ecology Laboratory. Colorado State University. Fort Collins.

National Oceanic and Atmospheric Administration; 1995. Climatological data, annual summary, Missouri. National Climatic Data Center. Asheville, NC.

Olson, R.V., and C.W. Swallow. 1984; Fate of labeled nitrogen fertilizer applied to winter wheat for five years. Soil Science Society of America Journal. V. 48, pp. 583-586.

Pilbeam, C.J., A.M. McNeill, H.C. Harris, and R.S. Swift; 1997. Effects of fertilizer rate and form on the recovery of 15N-labelled fertilizer applied to wheat in Syria. Journal of Agricultural Science. V. 128, pp. 415-424.

Pomes, M.L., D.H. Wilkison, and P.B. McMahon; 1998. Nitrous oxide fluxes from a claypan soil overlying nitrate-enriched glacial drift. Journal of Environmental Hydrology. v. 6., no. 8, pp. 1-14.

Puckett, L.J. 1995. Identifying the major sources of nutrient water pollution. Environmental Science and Technology. v. 25., no. 9, pp. 408-414.

Schjoerring, J.K., A. Kyllingsbaek, J.V. Mortensen, and S. Byskov-Nielsen; 1993. Field investigations of ammonia exchange between barley plants and the atmosphere. I. Concentration profiles and flux densities of ammonia. Plant Cell and Environment. v. 16, pp. 161-167.

Sievers, D.M., and C.D. Fulhage; 1992. Survey of rural wells in Missouri for pesticides and nitrate. Ground Water Monitoring Review. v. 12, pp. 142-150.

Silva, S.R., C.C. Chang, C. Kendall, P.B. Ging, and D.H. Wilkison; 1996. A new technique for collection and preparation of dissolved NO_3 for $d^{15}N$ and $d^{18}O$ analyses and preliminary applications, *in* Puckett, L.J., and Triska, F.J., eds., U.S.Geological Survey Nitrogen-Cycling Workshop: U.S.Geological Survey Open-File Report 96-477, p. 35.

Tindall, J.A., R.L. Petrusak, and P.B. McMahon; 1995. Nitrate transport and transformation processes in unsaturated porous media. Journal of Hydrology. v. 169, pp. 51-94.

Wagger, M.G.;1989. Cover crop management and nitrogen rate in relation to growth and yield of no-till corn. Agronomy Journal. v. 81, pp. 533-538.

Wagger, M.G., and D.B. Mengel; 1988. The role of nonleguminous cover crops in the efficient use of water and nitrogen. p. 115- 127. In W.L. Hargrove (ed.) Cropping Strategies for Efficient Use of Water and Nitrogen. Special Publications 51. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Madison, WI.

Wilkison, D.H., D.W. Blevins, and S.R. Silva; 1999. Observations on preferential flow and transport of nitrogen fertilizer in the unsaturated zone. Journal of Environmental Quality. v. 28, pp. 1568-1580.

Wilkison, D.H., D.W. Blevins, B.P. Kelly, and W.C. Wallace; 1994. Hydrology and water quality in claypan soil and glacial till at the Missouri Management Systems Evaluation Area near Centralia, Missouri-May 1991 to September 1993. U.S. Geological Survey Open-File Report 94-705.

Wilkison, D.H., and R.D. Maley; 1994. Occurrence of herbicides, nitrite plus nitrate, and selected trace elements in ground water from northwestern and northeastern Missouri, July 1991 and 1992. U.S. Geological Survey Open-File Report 93-332.

Wilkison, D.H., and R.D. Maley; 1996. Occurrence and distribution of nitrate and selected pesticides in ground water in Missouri, 1986-94. U.S. Geological Survey Water-Resources Investigations Report 96-4183.

ADDRESS FOR CORRESPONDENCE
Donald H. Wilkison
U.S. Geological Survey
301 W. Lexington
Independence, MO 64050
U.S.A.

E-mail: wilkison@usgs.gov