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Nitrogen Fertilizer and Herbicide Transport from Tile Drained Fields

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ABSTRACT

Offsite transport of N fertilizers and pesticides through subterranean drainage pipes (tiles) has been linked to surface water contamination in the U.S. Corn Belt. This study was conducted from water years 1995 to 1997 to evaluate N export from two tile systems (Tiles A and B) in adjacent fields [in seed corn-soybean rotation (Zea mays L.-Glycine max (L.) Merr.)] in response to timing and form of N application. In addition, during the 1997 water year, concentrations of two herbicides were determined on grab samples to relate tile herbicide losses with field application rates. During the 1995 and 1996 water years, Tile A exported approximately 20% more N per unit area than Tile B; however, during the 1997 water year, Tile A exported nearly 70% more N. This result was partly caused by the leaching of 142 kg of NH⁺₄-N following a winter application of (NH₄)₂SO₄ fertilizer in the drainage area of Tile A. The fertilizer was applied on top of 10 cm of snow, and within 4 d, a series of afternoon melting events began. We hypothesize that increased tile flow rates were caused by rapid infiltration of melt water through partially frozen soil (Drummer silty clay loam, fine-silty, mixed mesic Typic Haplaquolls) that allowed the NH[‡] ion to bypass the soil matrix (conc. reached 278 mg NH[‡]-N L^{-1}). The incidence of elevated concentrations of N fertilizer and herbicides in tiles during high flow events following agrichemical application indicated rapid water transport via preferential flow paths, thereby limiting the contact of these solutes with the soil.

CRANSPORT of N fertilizers and pesticides from agricultural fields into surface waters has decreased water quality throughout the U.S. Corn Belt. This problem is exacerbated in intensively drained areas of the midwestern USA, such as central Illinois, where conventional farming would not be profitable without artificial drainage (subterranean perforated pipes called tiles) (Fausey et al., 1995). Factors that control leaching losses

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of agrichemicals through soil and into tiles are weather patterns, annual precipitation, soil type, and timing and method of agrichemical application. In the Midwest, NO_3^--N is the most common surface water pollutant linked to tile drainage and agricultural production (e.g., David et al., 1997).

There are many different types and sources of N fertilizer on the market for corn (Zea mays L.) production, which range from granular to liquid under pressure to various combinations of inorganic N. Each type of fertilizer has a distinct set of characteristics pertaining to N form supplied, application method, and application timing (Aldrich, 1980; Hauck, 1984). As the average farm operation in the Midwest increases in size, there are now greater incentives to apply N fertilizer in the late fall or winter. Motivation for this timing of N application is to reduce risk of weather related delays in N application and planting during the spring season. When applying N in the fall, the *Illinois Agronomy Handbook* (1997-1998, p. 93-101) recommends the use of ammoniacal fertilizers after soil temperature decreases below 10°C and suggests the use of a nitrification inhibitor. This practice is intended to maintain fertilizer N in the NH⁺ form longer to minimize potential N loss via NO₃⁻ leaching or denitrification during the winter and early spring.

In recent years, another common practice in central Illinois and Indiana is to spray a solution of ammonium sulfate $(NH_4)_2SO_4$ (6–0–0–6, N–P–K–S), from the Archer Daniels Midland Company (ADM), in the fall when soil temperatures are <10°C or in the winter on frozen soil where the slope is <5% (Illinois Agronomy Handbook, 1997–1998). Fertilizer dealers surveyed in east-central Illinois indicated that the sale of ADM (NH₄)₂SO₄

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Abbreviations: ADM, Archer Daniels Midland Company; DOC, dissolved organic carbon; UAN, urea and ammonium nitrate; BOD, biochemical oxygen demand; TOC, total organic carbon; MSDS, material safety data sheet; MCL, maximum contaminant level.

was 15 to 20% of their total annual sale of N fertilizer for 1997 (Jeff Wessel, 1998, personal communication). Although fall or winter application of N has become common, there is greater chance for N loss (especially in tile-drained fields) because of the extended duration between application time and crop uptake.

Numerous studies conducted in the intensively tiledrained areas of the Midwest have linked agricultural crop production to surface water N concentrations (Drury et al., 1996; Fausey et al., 1995; David et al., 1997; Fenelon and Moore, 1998; Gentry et al., 1998). A consequence of conventional maize production is large soil NO₃ pools, especially after the nitrification of ammoniacal fertilizers, or after a poor growing season with limited crop N uptake (Gentry et al., 1998; Randall et al., 1997). If excessive rainfall occurs when soil NO_3^{-1} pools are high, then tile NO₃⁻ concentrations tend to increase with tile flow rates, and substantial amounts of N may be quickly lost (Logan et al., 1994; Patni et al., 1996). These studies have demonstrated that tile drainage lines serve as conduits for NO₃⁻ transport, as well as other agrichemicals such as herbicides, into surface waters. Several studies in the Midwest have also found high concentrations of herbicides (atrazine and metolachlor) in tile flow during precipitation events immediately following herbicide application (Czapar et al., 1994; Kladivko et al., 1991; Gaynor et al., 1995).

The objective of this study was to evaluate N loss mediated through tile drainage from two adjacent agricultural fields in response to the timing and form of N application. In addition, herbicide loss through tiles was investigated based on a comparison of application rates and leaching losses between the two fields. Tile flow, N export, water chemistry, and tile water temperature during various flow events were examined to evaluate the rapid transport of N fertilizer, atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4 diamine], and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide] through the soil and into the tile systems.

MATERIALS AND METHODS

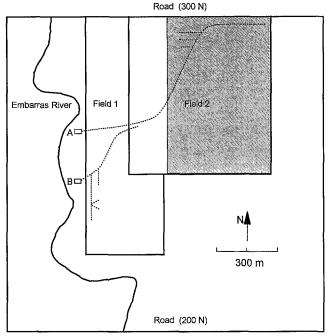
The study site was located along the main branch of the Embarras River in Champaign County, Illinois, and was divided into two adjacent agricultural fields with slopes <1%(Field 1 was 36 ha, Field 2 was 55 ha) owned and operated by two different farmers (Fig. 1). Cultural practices and tile drainage measurements at this site have been previously studied and discussed in David et al. (1997) and Gentry et al. (1998). In this study, agricultural drainage water from two tile systems was evaluated based on the source area drained by each tile. Tiles (perforated plastic pipes) were located primarily in Drummer silty clay loam soil (fine-silty, mixed mesic Typic Haplaquolls) at a depth of 1 to 1.5 m. Tile A was 1660 m in length and drained approximately 15 ha (3 ha of Field 1 and 12 ha of Field 2), and Tile B was 800 m in length and drained 5 ha (4.5 ha in Field 1 and 0.5 ha in Field 2). These drainage areas were estimated by determining each tile length combined with an estimate of the effective area of tile influence (Kurein et al., 1997). The effective area of influence was calculated to be 100 m (50 m on each side of the tile); however, final drainage area estimates were decreased where tile proxFig. 1. Map showing two agricultural fields in seed corn-soybean rotation with tile drainage. Field boundaries (*solid lines*) and drainage tiles (*dashed lines*) are shown. Shaded area of Field 2 represents a 40-ha area fertilized on 27 Jan. 1997.

imity created drainage overlap (either internally or with another tile). In addition, the drainage area estimate for Tile B was further reduced because of its close proximity with the west edge of the field. Areas of overlap between Tiles A and B were considered to have a negligible impact on water chemistry.

Tile flow and N loading were continuously monitored during the 3 water years from 1995 to 1997 (water year begins 1 October of the preceding year and ends 30 September of the named year). Tile flow rates were determined by installing a weir structure fitted with a combination weir plate (a slot and v-notch for low and moderate flow rates and a crest for high rates) at the end of each tile, and tile water was automatically sampled on a flow proportional basis using an ISCO 2900 (Gentry et al., 1998). Water samples from each tile were preserved the same day as collection with pH and conductivity determined on unfiltered samples (APHA, 1995). Subsamples were filtered (Whatman GF/C 1.2-µm glass fiber) and analyzed for NO_3^- – N and $SO_4^2^-$ – S by ion chromatography (APHA, 1995). Ammonium was analyzed by an automated phenate method on a Technicon AutoAnalyzer. The N load exiting the tile system was determined by multiplying the flow rate by the NO_3^- -N and NH_4^+ -N concentrations, assuming the concentration was constant from a time halfway between the previous sample and the present sample to a time halfway between the present sample and the subsequent sample.

Although the study area was managed by two farmers and their cultural practices varied, both fields were in a seed corn and soybean [*Glycine max* L. (Merr.)] rotation where soybean was grown in 1994 and 1996, and seed corn in 1995 and 1997. Also in common between the two fields were: annual crop planting and harvesting dates, seed corn genetics (producing the hybrid 'Northrup King 6822' and 'Northrup King 6432' in 1995 and 1997, respectively), corn planting populations of 69 000 plants ha⁻¹, and corn N fertilization rate (135 kg N ha⁻¹).

Cultural practices that differed between the two fields in-



cluded: tillage, soybean variety, and fertilizer application. Field 1 was in no-till throughout the study period and Field 2 was in a conservation tillage system, where soil was tilled before crop planting (field cultivator) and again after corn harvest (chisel plow). For N application, Field 1 received a sidedress application of anhydrous NH₃ on 3 June 1995 and a preplant application of UAN (urea and ammonium nitrate) solution at 28% N on 28 Apr. 1997. Field 2 received a solution of $(NH_4)_2SO_4$ (6-0-0-6) on frozen ground in the winter of 1995 and 1997. The ADM fertilizer was applied with a floater vehicle (e.g., Ag Chem Terragator 1603) that had a 16.5-m sprayer boom swath, carried 6814 L of fertilizer, and weighed 8.18 Mg when full. To apply 135 kg N ha⁻¹, 1872 L ha⁻¹ were sprayed on top of the soil. Field 2 was entirely fertilized on 9 Feb. 1995; however, because of weather delays in 1997, only the east 40 ha were fertilized on 27 January (cross-hatched section of Field 2) and the remaining 15 ha were fertilized on 13 February (Fig. 1).

Crop grain was machine harvested in September of each year with grain weight and percent moisture determined. Grain yields were recorded based on a standard moisture content of 15.5 and 13% for corn and soybean, respectively. All grain yields represented are based on dry weight.

The $(NH_4)_2SO_4$ fertilizer was produced by ADM and is a by-product of food processing during lysine amino acid synthesis. We obtained a raw sample of the ADM (NH₄)₂SO₄ fertilizer from two independent fertilizer distributors and analyzed them for pH, conductivity, NH4-N, NO3-N, total N, orthophosphate (ortho-P), total P, K, Cl⁻, SO₄²-S, and dissolved organic C (DOC). Unfiltered aliquots were used for pH, conductivity, total N, and total P determinations. For total N, aliquots underwent persulfate digestion and were analyzed for NO₃-N by Cd reduction on a Technicon AutoAnalyzer (APHA, 1995). For total P, aliquots were digested with sulfuric acid and NH₄ persulfate and analyzed by ascorbic acid colorimetric technique (APHA, 1995). Organic P was calculated as the difference between total and ortho-P. All other analysis was conducted on aliquots filtered as previously described. Using the same analytical methods for the tile water samples, NH₄⁺-N was analyzed by an automated phenate method on a Technicon AutoAnalyzer, and NO3-N, Cl-, and SO4- were analyzed by ion chromatography. Potassium was analyzed by atomic absorption, ortho-P by ascorbic acid colorimetric technique, and DOC using a Dohrmann Xertex DC-80 analyzer (APHA, 1995).

To evaluate the potential for chemical interaction or analytical masking between the NO₃⁻ ion and the ADM (NH₄)₂SO₄, a laboratory test was conducted. The ADM (NH₄)₂SO₄ was diluted to 30 and 300 mg L⁻¹ of NH₄⁺-N and spiked with 10 mg L⁻¹ NO₃⁻-N in the form of KNO₃. Nitrate and SO₄²⁻ were then analyzed by ion chromatography.

A biochemical O_2 demand (BOD₅) test was conducted to measure the 5-d O_2 requirement (BOD₅) of microorganisms in the raw ADM fertilizer (APHA, 1995). Dissolved O_2 was measured with an Orion O_2 electrode Model 97-08. A separate comparison was conducted by seeding the samples with Polyseed from Fisher Scientific (a standard bacterial culture). All samples were analyzed for NO₃⁻-N and NO₂⁻-N concentrations before and after incubation to determine the nitrogenous O₂ demand.

Tile water herbicide analysis was conducted during the 1997 water year. To avoid potential sample contamination caused by sorption-desorption of herbicides from the polyethylene bottles used in the automatic water samplers, glass bottles were used to collect grab samples. This technique did not allow for flow proportional sampling; however, an attempt was made to obtain samples during peak flow of major events.

On 26 Mar. 1997, tile water samples were analyzed for atrazine, deethylatrazine [6-chloro-N'-(1-methylethyl)-1,3,5triazine-2,4 diamine], and metolachlor by gas chromatography and mass spectrophotometry (GC/MS) for background determinations before application. On 15 Apr. 1997, Field 1 received Dual 2 at a rate of 2.80 kg ha⁻¹ of metolachlor and Field 2 received Bicep 2 at a rate of 2.24 kg ha⁻¹ of atrazine and 2.80 kg ha⁻¹ metolachlor. On 21 May, both fields received an application of Ladock at a rate of 0.84 kg ha⁻¹ bentazon [3-(1-methylethyl)-(1H)-2,1,3-benzothiadiazin-4(3H)-one 2,2dioxide] and 0.28 kg ha⁻¹ of atrazine. Tile water samples were initially analyzed by ELISA to screen samples for the presence of herbicides. Samples containing 5 μ g L⁻¹ were further evaluated using GC/MS for a more definitive analysis. Both tiles were sampled for atrazine and metolachlor 19 times during the 1997 water year, with four samples from each tile analyzed by GC/MS.

RESULTS AND DISCUSSION

Nitrogen Fertilizers

The three sources of N fertilizer applied on the two fields during this study were anhydrous NH_3 , a UAN solution (28% N), and the ADM (NH_4)₂SO₄. A general understanding of the fate of anhydrous NH_3 and 28% N solution in the soil is well known. The fate of the ADM (NH_4)₂SO₄ fertilizer is not well documented and raises new questions that do not pertain to these other fertilizer sources.

The ADM $(NH_4)_2SO_4$ fertilizer was a dark brown solution with a pH of 5.7 and conductivity of 632 000 μ S cm⁻¹ at 25°C. In general, this product was rated for fertility as 6-0-0-6 (N-P-K-S) with a Material Safety Data Sheet (MSDS) reporting between 4 and 8% total N. The two samples of ADM fertilizer contained 6.4 and 5.9% total N and SO_4^{2-} -S, respectively, with all the N as NH_{4}^{+} . Although not indicated in the MSDS, this product contained 0.15 and 0.07% total P and ortho-P, respectively, and 0.5% K. Also found in the fertilizer was 1.2% Cl⁻ and 7.4% total organic C (TOC). It is the C that gives the product a dark brown color. Based on 6.2% N in the $(NH_4)_2SO_4$ fertilizer and an application rate of 1872 L ha⁻¹, the actual rate of N applied to Field 2 was 143 kg N ha⁻¹. At this rate the fertilizer also provided 3.4 kg total P, 11 kg of K, and 166 kg of TOC ha⁻¹. The presence of the other macronutrients may be beneficial and add to overall soil fertility status.

Although the ADM product supplied some additional plant nutrients, the effect of adding 166 kg of organic C on soil fertility is not known. If the C is in a readily degradable form, it may be an immediate food source for soil microorganisms. Results from the BOD₅ test showed that the O₂ demand was 94 000 mg O₂ L⁻¹. The microbial seeding had no effect on BOD and there was no nitrogenous demand. The Drummer soil overlying the tile systems contained approximately 100 000 kg ha⁻¹ of C in the upper 1 m, with most of this C associated with humus and only slowly available to soil microorganisms. Although the ADM fertilizer added <0.2% of total soil C, its readily degradable form may stimulate denitrification or immobilization of residual soil NO₃⁻-N, and therefore further study is needed.

Table 1. Annual precipitation, tile flow, and NO₃⁻ and NH⁴ export for 3 water years (1995–1997).

Water year†	Precipitation	Tile flow		NO ₃ –N export		NH‡−N export	
		Tile A	Tile B	Tile A	Tile B	Tile A	Tile B
		— mm yr ^{- 1} —			kg	yr ¹	
1995	790	194	254	374	105	3.4	0.7
1996	930	385	380	861	238	0.3	0.4
1997	931	364	308	635	149	142	4.0

* Water year refers to the period from 1 October of the previous year to 30 September of the identified water year.

Tile Flow

The study site received 790, 930, and 931 mm of precipitation during the 1995, 1996, and 1997 water years, respectively (Table 1). In general, tile flow began in late fall or early winter, continued through July, and ended in August; however, flow continued through the end of the 1997 water year. Annual flow for Tiles A and B ranged from 29 100 to 57 700 m³ (25–41% of annual precipitation) and 12 700 to 19 000 m³ (32–41% of annual precipitation), respectively, with the highest annual flow during the 1996 water year. The highest flow rates for both tiles (35 and 17 L s⁻¹ for Tiles A and B, respectively) occurred when there was 105 mm of precipitation during a 5-d period in May 1995 after a winter and early spring with below average precipitation.

Tile A drained approximately three times as much area as Tile B; however, only for the 1996 water year were annual flow volumes consistent with the 3:1 ratio of source area drained. The comparison of annual flow volumes was less than 3:1 for the 1995 water year and greater for the 1997 water year. Because Tile B is deeper than Tile A in the soil profile as dictated by topography, and during a dry year, Tile B may have carried proportionally more water than did Tile A. In contrast, during the 1997 water year, heavy rain events may have induced funneling of overland water into large sub-basins within the drainage area of Tile A and produced proportionally more flow than Tile B. These data suggest that tile flow was a function of source area drained in addition to timing, distribution, and intensity of precipitation.

Tile Nitrogen Export

Annual total N (NO₃⁻–N and NH₄⁺–N) export for Tiles A and B ranged from 378 to 861 kg, and 106 to 238 kg, respectively, with the highest annual N export during the 1996 water year (Table 1). The highest daily export of total N (5 and 3.7 kg N ha⁻¹ for Tiles A and B, respectively) during the study occurred on 17 May 1995 (Fig. 2). Many studies have shown that flow rate is the dominant factor in determining annual N export from tile drained agricultural fields (Lowrance, 1992; Logan et al., 1994; Randall and Iragavarapu, 1995; Patni et al., 1996). For both tiles, this event produced the highest flow rates measured; however, Tile A also had high NO₃⁻ concentrations during peak flow early in the event.

Our data suggested that leaching of NO_3^- was linked to factors such as soil inorganic N pools, timing of N application, crop N accumulation, and tile flow rate. For example, before this high tile flow period in May 1995, only Field 2 had received N fertilization. During peak flow on 16 May 1995, the NO_3^- concentration was 49 mg N L^{-1} in Tile A, but Tile B was only 12 mg N L^{-1} . The highest tile NO_3^- concentrations during the study were observed for both tiles (Tile A and Tile B contained 52 and 26 mg N L^{-1} , respectively) during a precipitation event on 6 June 1997, which occurred after both fields were fertilized. Furthermore, following a poor corn growing season in 1995, Tiles A and B exported proportionally more N (127 and 125%) during the 1996 water year than could be accounted for by the increase in tile flow (98 and 46%) (Table 1). The 1996 water year produced the greatest loss of NO_3^--N per unit area and the highest flow weighted mean concentrations of NO_3^- -N for both tiles (Table 2). Collectively, these data demonstrated that heavy precipitation events during periods of high soil NO_3^- pools can quickly flush high concentrations of NO₃⁻ through the soil and into the tiles.

During the 1995 and 1996 water years. Tile A exported approximately 20% more N per unit area than

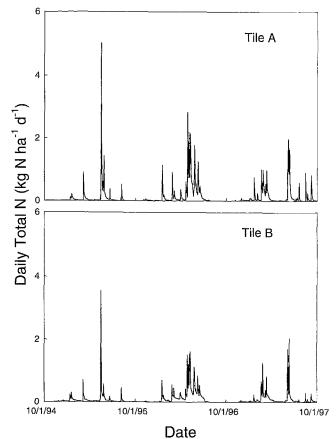


Fig. 2. Daily total N export from Tiles A and B during the 1995 through 1997 water years.

Water year	NO ₃ -N export		NH [‡] -N export		Flow weighted mean NO ₃ -N		Flow weighted mean NH‡-N		
	Tile A	Tile B	Tile A	Tile B	Tile A	Tile B	Tile A	Tile B	
		kg	ha-1		mg L ⁻¹				
1995 1996 1997	24.9 57.3 42.3	21.0 47.4 29.8	0.23 0.02 9.5	0.14 0.08 0.74	12.8 14.9 11.6	8.3 12.5 9.7	0.12 0.01 2.6	0.06 0.02 0.24	

Table 2. Annual NO₃⁻ and NH⁺ loss per unit area and flow weighted means for 3 water years (1995–1997).

Tile B; however, during the 1997 water year, Tile A exported nearly 70% more (Table 2). This result was partly caused by leaching of 142 kg of NH_4^+ –N after a winter (NH_4)₂SO₄ fertilizer application in the Tile A drainage area. Based on the difference of total N export by Tiles A and B during the 1997 water year, there was greater N loss associated with the winter (NH_4)₂SO₄ fertilizer application applied at planting.

Crop Yields

Overall crop growing conditions were good in 1996 and 1997, while high temperatures and low rainfall in July 1995 severely limited seed corn yields. In each year for each crop, grain yields were similar between Fields 1 and 2. Seed corn yields were 0.92 and 2.32 Mg ha⁻¹ in 1995 and 1997, respectively, and soybean yield was 2.73 Mg ha⁻¹ in 1996. In general, the seed corn crop accumulates less N and produces lower yields than hy-

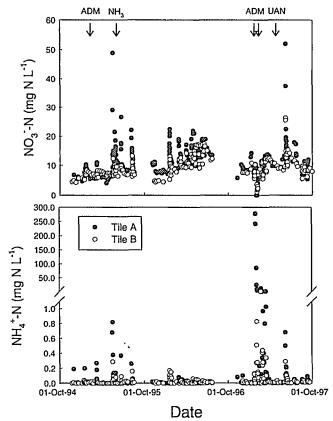


Fig. 3. Nitrate N and NH⁺-N concentrations in Tiles A and B during the 1995 through 1997 water years. Arrows indicate when N fertilizer application occurred.

brid corn (Beauchamp et al., 1976), and therefore a lower N fertilization rate is used. Although the seed corn N rate is lower than for hybrids, the recommended application rate of 135 kg N ha⁻¹ was in excess of crop needs. This is a common scenario caused by the high value of hybrid seed vs. the low cost of N fertilization (Balko and Russel, 1980).

Archer Daniels Midland Ammonium Sulfate Application

In the 1995 and 1997 winters, the ADM (NH₄)₂SO₄ fertilizer was applied only to Field 2. Tile NH⁺ concentrations were typically $< 0.2 \text{ mg N L}^{-1}$ during the study period except for a few water sample concentrations $(0.5-0.8 \text{ mg N L}^{-1} \text{ for Tile A})$ during the spring of 1995. However, at 1815 h on 31 Jan. 1997, the NH⁺ concentration in drainage water from Tile A was 278 mg N L^{-1} and the NO_3^- concentration decreased below the 0.1 mg $N L^{-1}$ detection limit (Fig. 3). This sample also contained 2.3 mg L^{-1} ortho-P, 4.1 mg L^{-1} organic P, 336 mg L^{-1} SO_4^{2-} -S, and 309 mg L⁻¹ TOC. By 830 h on 1 February, concentrations decreased to 86 mg L⁻¹ NH₄⁺-N, 0.4 mg L^{-1} ortho-P, 1.1 mg L^{-1} organic P, 185 mg L^{-1} SO₄²⁻⁻S, and 129 mg N L^{-1} TOC, while the NO₃⁻ concentration remained below the detection limit. The NO₃⁻ concentration in Tile A was below detection limits at least until 1700 h on 2 February, at which time the NH⁺ and TOC concentrations had decreased to 25 and 32 mg L^{-1} , respectively.

Before this subsurface flow event, the ADM fertilizer had not been applied on any portion of the source area for Tile B, and at 2015 h on 31 January, concentrations in Tile B were $0.3 \text{ mg } \text{L}^{-1} \text{ NH}_4^+-\text{N}$, 0.07 mg L⁻¹ ortho-P, 0.1 mg L⁻¹ organic P, 8.6 mg L⁻¹ SO₄²⁻-S, and 10.0 mg L⁻¹ TOC. At this time NO₃⁻ concentration in Tile B was 3.6 mg N L⁻¹, and concentrations of selected samples for the following 5 d ranged from 1.2 to 3.0 mg N L⁻¹. Although NO₃⁻ concentrations in Tile B were three to five times lower than before the tile flow event on 31 January, the concentration never decreased below detection limits.

In 1997, the ADM fertilizer was applied to the east 40 ha of Field 2 on 27 January when approximately 10 cm of snow covered the ground (Fig. 1). On 29 January during subzero temperatures and baseline flow, water from Tile A contained 9.3 mg NO₃⁻-N L⁻¹ and the NH₄⁺ concentration was below detection limits (<0.02 mg N L⁻¹). Between 31 Jan. and 3 Feb. 1997, air temperatures increased above freezing during the day and declined below freezing each night. Daily thawing and freezing resulted in diurnal tile flow cycling for several

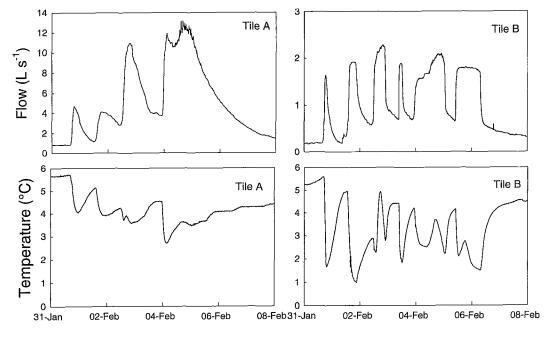
days until 10 mm of rainfall occurred on 4 Feb. 1997 (Fig. 4). The tile nutrient concentration data showed the ADM fertilizer entered Tile A during this thawing and freezing period.

Tiles A and B do not contain surface drains, and therefore, the fertilizer traveled through approximately 1 m of soil within 4 h after air temperatures increased above freezing. Other NO_3^- leaching studies show that tile flow rates respond quickly to heavy rainfall events (Gast et al., 1978; Levanon et al., 1993). In general, maximum flow rates for Tiles A and B occurred within 1 to 3 h of rainfall cessation. This fast movement of water through tile drained Drummer soil indicated that infiltration and water velocity through the soil is controlled by preferential flow paths. Richard and Steenhuis (1988) and Stamm et al. (1998) demonstrated the prevalence of preferential flow paths in various soils, and Flury et al. (1994) discussed the susceptibility of soils to develop preferential flow paths. We hypothesize that preferential flow during snowmelt is enhanced by flow channels developed through partially frozen soils. In addition, we speculate that during a thawing and freezing event when soils were frozen, tile flow rates and water chemistry may be dominated by drainage waters entering tiles at specific points (low-lying areas) in the fields. These data suggest the ADM fertilizer was transported with melt water via preferential flow paths; and the high nutrient concentrations resulted from minimal contact between the ammoniacal fertilizer and the soil.

Researchers have observed that ponds formed during snowmelt sometimes drain rapidly before the soil profile has completely thawed (Kane and Stein, 1983; Johnsson and Lundin, 1991). Stähli et al. (1996) had success predicting snowmelt infiltration through a sandy loam soil by simulating preferential flow through frozen soil layers. They used a one-dimensional, physically based soil, water, and heat model (SOIL) complemented by a twodomain approach option based on the diameter of airfilled pores that exist in partially frozen soils. Recently, Baker and Nieber (1998) proposed a possible mechanism for rapid infiltration of melt water through frozen soil. They found well-defined pockets of unfrozen soil (approx. 1 m in diam.) in an otherwise frozen layer, which presumably served as conduits for rapid meltwater transport following ponding. We contend that the conceptual model put forth by Baker and Nieber (1998) may explain the rapid transport of ammoniacal fertilizer to the tile system.

To address the possibility of direct surface water input through tile blowouts in the fields (blowouts are holes leading from the tile to the soil surface that are created by back pressure from a partially clogged tile), low lying source areas above the tiles were investigated. After inspecting the fields and querying the machinery operators and landowners, no tile blowouts were found. Although the possibility of blowouts cannot be completely disregarded, Tiles A and B showed similar trends in tile water temperature, water chemistry, and flow rates during thawing and freezing events.

Both tiles showed decreases in tile water temperature and NO_3^- concentration when melt waters were responsible for tile flow rate increases. During the thawing and freezing event, Tile A water temperature decreased with increased tile flow and vice versa; it then stabilized after tile flow increased from rainfall on 4 February (Fig. 4). Tile B water temperature and flow during this period showed more overall variation and lower temperature extremes (Fig. 4). The greater temperature change and lower extremes in Tile B compared with Tile A can be explained by Tile B's smaller drainage area and shorter distance between drainage source and monitoring site.



Date

Fig. 4. Tile flow rate and tile water temperature (recorded at 15-min intervals) during a thawing and freezing cycle from 31 Jan. to 8 Feb. 1997.

Unless both tiles systems had blowouts, it appears that preferential flow through partially frozen soil allows rapid movement of melt waters without extensive soil contact.

Because of low NO₃⁻ concentrations in snow, melt waters that bypassed the bulk of the soil matrix would dilute tile NO₃⁻ concentrations. Tile water dilution is consistent with both tiles; NO₃⁻ concentrations declined as melt waters increased flow rates. However, the reason that NO₃⁻ was not detected in Tile A for more than 3 d is not certain. A laboratory experiment was conducted to investigate the possibility of an analytical interference between the ADM (NH₄)₂SO₄ fertilizer and performance of the ion chromatograph. We recreated the concentration of (NH₄)₂SO₄ fertilizer found in the tile water on 1 February and spiked in 10 mg N L⁻¹ as KNO₃. The spike recovery was 100%, so the possibility of an analytical error was dismissed.

When the $(NH_4)_2SO_4$ fertilizer was applied to the remainder of Field 2 (15 ha) on 13 February, a small portion (0.5 ha) of the source area for Tile B was also fertilized (Fig. 1). Although no snow cover remained, the soil had frozen again. On 18 February, ambient temperatures increased to 15°C; however, there was no increase in tile flow rates until 29 mm of rain occurred on 20 and 21 February. Before the rain event at approximately 900 h on 20 February, the NH⁺₄-N concentration was 0.12 mg L^{-1} in Tile A and below detection limits $(<0.05 \text{ mg } \text{L}^{-1})$ in Tile B. The rainfall began later in the day on 20 February and quickly caused increases in tile flow rates as well as NH_4^+ –N concentrations in both tiles (13.2 mg L^{-1} in Tile A and 2.1 mg L^{-1} in Tile B). In addition, there were slight increases in concentrations of ortho-P, organic P, SO_4^2 -S, and TOC for both tiles. However, unlike during the thawing and freezing event, NO_3^- concentrations did not decrease for either tile. We speculate that NO_3^- did not decrease because of the overall water contribution from tile source areas outside the area fertilized on 13 February. These data suggest the ADM fertilizer again entered the tile lines with the quick movement of rainwater through the soil.

In contrast, in 1995 the NH₄⁺ concentration did not exceed 1 mg N L⁻¹ for either tile. Although the air temperature was above freezing the day after fertilizer application in the winter of 1995, below average precipitation (11 mm) in February did not produce any melt water driven tile flow increases. There were nine tile water samples that contained concentrations of NH₄⁺ >0.2 mg N L⁻¹ during the winter and spring of 1995. However, there were no increases in other nutrients associated with the ADM fertilizer during this time. Therefore, in 1995 soil conditions were favorable for allowing sufficient contact of the NH₄⁺ ion with the soil to prevent movement.

Herbicide Preferential Flow

To further evaluate the prevalence of preferential flow through Drummer soils, tile water samples were also analyzed for herbicide concentrations during the spring and summer months of 1997. Recent studies

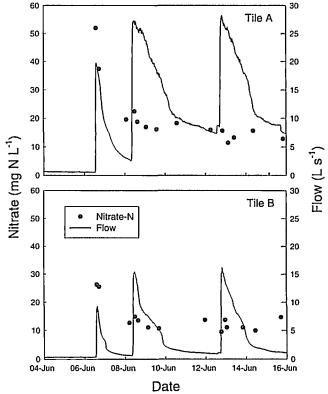


Fig. 5. Tile flow rate (15-min intervals) and NO₃-N concentrations sampled during three rain events between 4 June and 16 June 1997.

(Gaynor et al., 1995; Czapar et al., 1994; Logan et al., 1994; Masse et al., 1996) as well as a review by Flury (1996) have investigated the movement and tile transport of atrazine and metolachlor in various soil types. However, data are lacking on herbicide leaching in the predominant soil type of the intensively tile-drained region of Illinois. Before herbicide application, tile concentrations of atrazine, deethylatrazine (DEA), and metolachlor were found to be below detection limits $(0.5 \ \mu g \ L^{-1})$. Following a period of below average precipitation in April and May of 1997 and no tile flow events, three intense rain events occurred within 7 d in early June, which produced three separate tile flow pulses. Although the first event was the smallest, both tiles carried drainage water containing the highest concentrations of NO₃, atrazine, DEA, and metolachlor for the three events (Fig. 5 and 6). These results support the findings of Gaynor et al. (1995) in which tile herbicide concentrations were highest during the first leaching event following application. In addition, the concentration data suggested that the first event flushed these solutes through the soil, thereby depleting the leachable pool, which is indicated by lower concentrations for each successive event.

Herbicide concentrations varied with tile flow rates by increasing as flow increased (i.e., beginning of each new event) and vice versa (Fig. 6). Field 2 received nine times more atrazine per unit area than Field 1, and Tile A consistently had higher concentrations of atrazine $(6.0-28.0 \ \mu g \ L^{-1})$ than Tile B (<0.5-7.9 \ \mu g \ L^{-1}) during the three flow events (Fig. 6). The USEPA maximum

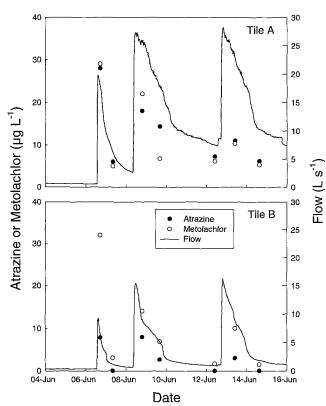


Fig. 6. Tile flow rate (15-min intervals) and herbicide concentrations sampled during three rain events between 4 June and 16 June 1997.

contaminant level (MCL) for atrazine in drinking water is 3 μ g L⁻¹, whereas the USEPA has not set an MCL for DEA. The highest concentration of DEA (3.0 μ g L⁻¹) for either tile occurred in Tile A during peak flow on 6 June 1997. The highest concentration of DEA in Tile B during this period was 0.9 μ g L⁻¹. Although DEA is more soluble than its parent compound (Roy and Krapac, 1994), the low tile concentrations suggest that the 8 wk of dry weather following application may have prevented significant degradation of atrazine.

The USEPA health advisory for metolachlor is 100 μ g L⁻¹ and there were no samples from either tile above this level. An identical rate of metolachlor was used on both fields, which lead to similar concentrations in the drainage water of both tiles. During the three precipitation events, tile metolachlor concentrations ranged from 5.3 to 29 μ g L⁻¹ and 1.7 to 32 μ g L⁻¹ for Tiles A and B, respectively (Fig. 6). Differences in tillage practices between the two fields did not appear to influence metolachlor leachlor.

Based on this limited number of grab samples, we estimated that during 1997 Tile A transported 139 and 126 g of atrazine and metolachlor, and Tile B transported 13 and 35 g of atrazine and metolachlor, respectively. These leaching loads represented 0.50 and 0.30% of the atrazine and metolachlor applied in the drainage area of Tile A and 0.54 and 0.25% of the atrazine and metolachlor applied in the case of atrazine leaching, tile concentration of 6 June exceeded drinking water MCL by 10 times. Overall, these data

show that rapid infiltration of rain water through the soil via preferential flow paths can quickly transport solutes to tiles lines causing high concentrations of agrichemicals to enter surface waters.

CONCLUSION

Although timing and form of N application influenced annual tile N export, weather was the dominant controlling factor. Low rainfall was responsible for a poor corn crop in 1995 and produced the least tile flow and N export by either tile during the study. Tile data suggested that limited crop uptake of N during the poor growing season may have contributed to increased NO_3^- leaching for both tiles during the 1996 water year. The melt water event immediately following the application of the ADM (NH₄)₂SO₄ fertilizer in the winter of 1997, transported approximately 142 kg NH₄⁺–N (\approx 11 kg NH_4^+ –N ha⁻¹ based on the drainage area of Tile A located in Field 2), which was apparently from direct movement into the tile drainage water. Based on the difference of NO_3^- export by Tiles A and B during the 1997 water year, the winter application of $(NH_4)_2SO_4$ fertilizer also produced greater NO_3^- loss than the UAN solution applied at planting; however, corn yields were the same for both fields. Greater N loss from Field 2 did not depress seed corn yields because the N fertilization rate was apparently in excess of crop needs.

Nitrogen fertilizer and herbicides can be quickly flushed through preferential flow paths that limit the contact of agrichemicals with the soil. Furthermore, rapid movement of melt waters through partially frozen soils may have enhanced preferential flow, thereby allowing for the $(NH_4)_2SO_4$ fertilizer to bypass the soil matrix and enter the tile lines. Although artificial drainage is necessary to facilitate farming of poorly drained soils, tiles can rapidly transport agrichemicals offsite, which may adversely impact surface water quality.

Use of this form of $(NH_4)_2SO_4$ fertilizer adds new questions about application timing and its influence on soil fertility and salinity (material contains 1.2% Cl⁻). The presence of snow on frozen soil and the short-term weather forecast are important considerations when applying this fertilizer type in the winter. More research is needed to investigate potential effects from C in the ADM fertilizer on microbial processes such as denitrification and immobilization of residual soil NO_3^- .

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