Nitrogen Balance in and Export from an Agricultural Watershed

Mark B. David,* Lowell E. Gentry, David A. Kovacic, and Karen M. Smith

ABSTRACT

Surface water nitrate (NO_3^-) pollution from agricultural production is well established, although few studies have linked field N budgets, NO_3^- loss in tile drained watersheds, and surface water NO_3^- loads. This study was conducted to determine field sources, transport, and river export of NO_3^- from an agricultural watershed. The Embarras River watershed at Camargo (48 173 ha) in east-central Illinois was investigated. The watershed is a tile-drained area of fertile Mollisols (typical soil is Drummer silty clay loam, a fine-silty, mixed mesic Typic Haplaquoll) with primary cropping of maize (*Zea mays* L.) and soybean (*Glycine max* L.). Agricultural field N sources and sinks, tile drainage NO_3^- concentrations and fluxes, and river NO_3^- export were estimated for the entire watershed. Large pools of inorganic N were present following each harvest of maize and soybean (average of 3670 Mg N yr^{-1} over a 6-yr period). The source of most of the inorganic N was divided between N fertilizer and soil mineralized N. High concentrations of NO_3^- were found in four monitored drainage tiles (5–49 mg N L^{-1}), and tile concentrations of NO_3^- were synchronous with Embarras River NO_3^- concentrations. High flow events contributed most of the yearly NO_3^- loss (24.7 kg N ha^{-1} yr^{-1}) from tile drained fields in the 1995 water year (1 Oct. 1994 through 30 Sept. 1995) where high rainfall events occurred in a low overall precipitation year (in one tile 21% of the annual load was exported in 1 d). During the 1996 water year, NO_3^- export in tiles was much higher (44.2 kg N ha^{-1} yr^{-1}) due to greater precipitation, and individual days were less important. On average, about 49% (average of 1688 Mg N yr^{-1} over a 6-yr period) of the field inorganic N pool was estimated to be leached through drain tiles and seepage and was exported by the Embarras River, although depending on weather and field N balances this ranged from 25 to 85% of the field N balance over the 6-yr period. It seems likely that agricultural disturbance (high mineralization inputs of N) and N fertilization combined with tile drainage contributed significantly to NO_3^- export in the Embarras River.

NITRATE contamination of surface and groundwaters is of environmental concern throughout agricultural areas of the USA. High inputs of N fertilizer are required to support intensive row-crop agriculture, particularly for corn in the Midwest where fertilizer application rates are typically 100 to 200 kg N ha^{-1} yr^{-1}. It is difficult to maintain the fine balance of available N required to satisfy crop needs and at the same time minimize leaching losses, even though fertilization combined with soil mineralization can provide large amounts of inorganic N (Keeney and DeLuca, 1993). Under optimal growing season conditions and fertilizer N application rates, the crop grain yield contains typically only about 50% of the added fertilizer N (Oberle and Keeney, 1990).

Throughout many areas of the Midwest and in particular in much of Illinois, agricultural fields are drained with subterranean tiles (perforated pipe) to allow farming to be practical and economically viable (Fausey et al., 1995). In Illinois alone, about 4 000 000 ha are tile drained, representing 35% of all Illinois cropland (USDA, 1987). As early as the late 1960s, studies on tile drainage waters showed high concentrations of N, mostly as NO_3^- (Willrich, 1969). Kohl et al. (1971) used ^{15}N proportions in various N pools to estimate that 55 to 60% of the NO_3^- found in surface waters of a typical Illinois corn/soybean watershed was from applied fertilizer not used by the crop. Many studies since these early reports have clearly shown that tile drainage waters contain high concentrations of N as NO_3^-, often much greater than the USEPA drinking water standard of 10 mg N L^{-1} (e.g., Lowrance et al., 1984; Logan et al., 1994; Fausey et al., 1995). Few studies have examined N transport from undisturbed, grassland ecosystems in the Midwest to estimate precultivation concentrations and loss of N to surface waters. Recently, however, Dodds et al. (1996) found that the annual N transport averaged 0.16 kg N ha^{-1} yr^{-1} from several tallgrass prairie watersheds in Kansas, with NO_3^- concentrations ranging from 0.01 to 0.39 mg N L^{-1}. This demonstrated the tight cycling of N in the grasslands that once dominated much of the central USA, despite their high soil organic C and N contents (Dodds et al., 1996), and clearly contrasts the large increase in NO_3^- concentrations and flux due to intensive agriculture.

Recent studies have estimated both farm N budgets (Barry et al., 1993) and large watershed N sources (Keeney and DeLuca, 1993) to evaluate NO_3^- inputs to ground- and surface waters, respectively. Barry et al. (1993) used a simplified N budget where they looked at many inputs and outputs of N, and assumed total soil-N remained constant from one rotation to the next. They found this method gave useful estimates of potential NO_3^- leaching, despite the major assumptions made. One of their major uncertainties was atmospheric deposition of NH_3 from on-farm sources (Barry et al., 1993). Also, high levels of denitrification (up to 62 kg N ha^{-1} yr^{-1} for continuous corn) were estimated by examining differences between N present at harvest and the amount of N leached.

Keeney and DeLuca (1993) took a different approach to estimating N sources. They attempted to use flow and NO_3^- measurements in the Des Moines River to identify the effect of agricultural practices on NO_3^- concentrations. Concentrations and agricultural practices in the 1980s were compared to the 1940s in a 3 194 000-ha basin. They concluded that intensive agricultural activities in 1945 and 1980 to 1990 were the major source of river NO_3^-, and not entirely N fertilizer (Keeney and DeLuca, 1993). The primary source of N from intensive agricultural activities was thought to be mineralization from soil disturbance coupled with tile drainage. Since most of the land was already under cultivation and tiled by 1945, the major disturbance had been made leading

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Abbreviations: USGS, U.S. Geological Survey; ANI, added N interaction.

to little change in river NO_3^- concentrations in the period of 1945 to the 1980s. This occurred in spite of the increase in N fertilization rates from 0.4 to 219 kg ha^{-1} yr^{-1} in 1945 and 1990, respectively (Keeney and DeLuca, 1993). The additional fertilizer N has led to a doubling of residual inorganic N in croplands between 1945 and 1990, although this has not apparently led to an increase in river NO_3^- concentrations. Keeney and DeLuca (1993) attributed the lack of change in river NO_3^- concentrations to the current buffering capacity of the watersheds compared to poor manure management, higher soil erosion rates, and possibly greater N mineralization rates in the 1940s.

These types of studies have illustrated the complexity in determining the source of NO_3^- in rivers of the Midwest, particularly in areas artificially drained. Therefore, we evaluated agricultural N fluxes and sources of river NO_3^- in a predominately tile drained agricultural watershed in east-central Illinois, estimating N sources due to agricultural practices mediated through drainage tiles. Our goal was to better understand the impact of current agricultural practices combined with tile drainage on river NO_3^- concentrations.

DESCRIPTION OF THE UPPER EMBARRAS RIVER WATERSHED

The Embarras River originates in the urban areas of Champaign and Urbana, IL, and ultimately drains 48 173 ha when it passes through Camargo, IL, the site of a U.S. Geological Survey (USGS) gauging station (Fig. 1). The watershed is predominately in row-crop agriculture (91%), with approximately 46 to 49% of the area in maize and 41 to 44% in soybean production from 1990 to 1995. Approximately 4.5% of the watershed is urban, and 2.9% is in roads. The remainder is woodlands (0.6%), grass (0.5%), water (0.6%), and homesites (0.3%). Because soils in east-central Illinois are highly valued for crop production, livestock production is almost nonexistent in the watershed. There is no large source of sewage effluent from any waste water treatment plants along this section of the river; Champaign-Urbanas effluent does not enter this basin. Average annual stream flow of the Embarras River at Camargo averaged 4.7 m^3 s^{-1} (1961–1995), with minimum and maximum daily flows of 0 and 174 m^3 s^{-1} (LaTour et al., 1996).

Soils of this area developed from Wisconsinan till that supported primarily prairie vegetation. Estimated forest and prairie vegetation before settlement in Champaign County were 6.3 and 93.7% of the land area, respectively (Iverson et al., 1989). The Mollisols in the area formed in 100 to 150 cm of loess over medium to fine-textured till. Drummer (fine-silty, mixed mesic Typic Haplaquolls) silty clay loams and closely related soils (Flanagan-Catlin) are dominant in the watershed and surrounding counties, where slopes are nearly level providing poor drainage without tiling. The flat topography and need for tile drainage is clearly demonstrated by the small 38 m fall in elevation over the 35 km main branch of the Embarras River, for a channel slope of approximately 0.1%. Tile drainage was estimated to be 75 to 80% of the total land area using infrared photographs to show tile lines combined with geographic information system land estimates of effective area drained near each line (R. Cooke, 1997, personal communication). In addition, it was estimated that 70% of the watershed area was included in drainage districts, further supporting the density of tile systems. We used a range of 70 to 85% tile drainage in some of our calculations, based on the above

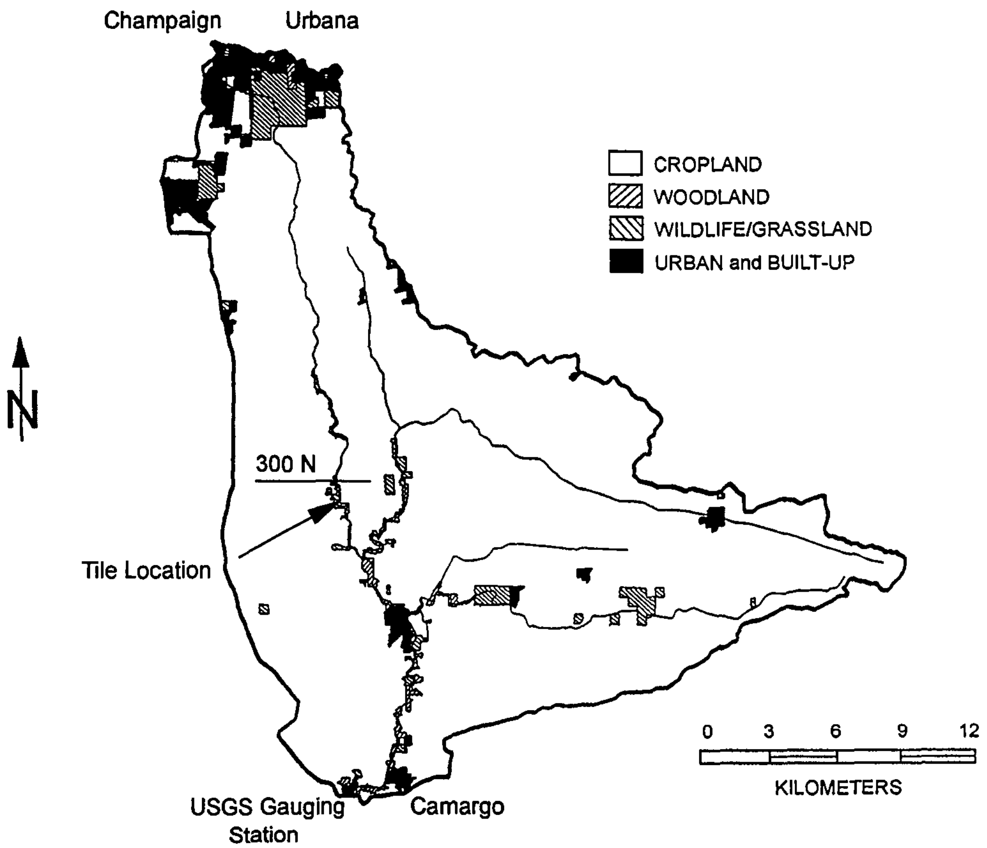

Fig. 1. Map showing Embarras River and landuse in the Camargo watershed. Also shown are the 300N and Camargo gauge sampling sites, as well as the location of the four tiles monitored.

estimates. This watershed is typical of several counties in east-central Illinois in terms of soils, slopes, tile drainage systems and cropping patterns, which allows us to use county information for constructing watershed budgets. East-central Illinois is a rather homogeneous area of flat croplands with poorly drained soils in maize/soybean rotations.

METHODS

River and Tile Flow and Nitrate Concentrations

We used Embarras River daily average flow data for the 1991 through 1996 water years measured at the USGS gauging station at Camargo (39° 47′30″N, 88° 11′10″W) to determine daily and annual water volumes for the watershed (Maurer et al., 1992, 1993, 1994; LaTour et al., 1995, 1996). Daily precipitation data were obtained from measurements at Urbana, IL, at the headwaters of the watershed. Nitrate values in stream waters over the 6-yr period were obtained from a variety of sources, and ranged from excellent to poor in quality. For the 1991 water year, we used USGS measurements that were made nine times during the year. For 1992 water year and the first 2 mo of the 1993 water year (i.e., October 1991 through December 1992), no direct measurements were available anywhere on the river, and we used seasonal averages from the previous 5-yr period. Since December 1992 we have made weekly or biweekly NO_3^- concentration measurements on grab samples at a site 15 km upriver (designated as 300N on Fig. 1) from Camargo. Nitrate was determined following filtration (Whatman GF/C glass fiber filter, 1.2 μm) using an ion chromatograph (Dionex 2000i, Sunnyvale, CA) with a detection limit of 0.05 mg N L^{-1}. Ammonium and NO_2^- were determined on each filtered sample using colorimetric techniques (APHA, 1989). In addition, on selected samples organic N was determined by Kjeldahl digestion and detection of NH_4^+ using an automated phenate method (APHA, 1989). Since June 1993, we have measured river NO_3^- concentrations at Camargo weekly to biweekly from grab samples, again using ion chromatography. Camargo and the 300N locations were highly correlated ($r^2 = 0.86$, $n = 35$, $P < 0.0001$), and we used the 300N site to estimate Camargo NO_3^- concentrations for the period of December 1992 through June 1993. Therefore, our best estimates of NO_3^- concentrations in the river are from December 1992 through the 1996 water year, and our weakest estimate is for the 1992 water year. Because NO_3^- concentrations in the river change more on a seasonal than weekly basis, we felt these values could be used to make accurate estimates of daily NO_3^- loss.

We calculated daily NO_3^- loss in flow by expanding our measurements to predict concentrations throughout the time period, multiplying concentration by flow and summing for each day. During extremely high flow events (>50 m^3 s^{-1}, which occurred on 32 d during the 6- yr period) NO_3^- concentrations in the Embarras River were generally diluted by surface runoff, so we reduced preflood concentrations by 50% during these major events. This reduction was based on measurements made during several major storm and flow events during 1993 to 1996. For example, during 17 to 19 May 1995 a major event occurred. On 16 May 1995, before the event, NO_3^- in the river at 300N was 8.8 mg N L^{-1}. Peak flow occurred on 17 to 19 May, and NO_3^- concentrations ranged from 3.1 to 6.9 (mean of 4.4, $n = 5$) during the period at this location; this was 50% of the concentration before high flow. Other events had similar patterns, supporting our use of a 50% reduction.

In addition to sampling Camargo and the 300N river location, we determined NO_3^- concentrations from October 1993 through September 1996 where the headwaters of the river emerge from Champaign and Urbana, reflecting urban runoff. Headwater flow was obtained weekly from a staff gauge over a 1-yr period and flow was estimated based on stage height and channel contours. These weekly flow measurements were then related to flow at Camargo, and that relationship used to predict daily urban flow for 1995 and 1996 water years.

At the 300N river location, outlets of four drainage tiles from corn and soybean fields (predominately Drummer series soils) were fitted with weirs, pressure transducers, and data loggers to record stage height on a 15-min basis. In addition, water samplers (ISCO, Inc., Lincoln, NE) were used to obtain flow proportional solution samples during runoff events. Samples were collected as often as every 15 min during major flow, or as far apart as once a week during low flow. The ISCOs were therefore set to collect more samples than were needed to characterize NO_3^- on each hydrograph, ensuring that we had complete coverage of each event. All four tiles were fully instrumented throughout the 1995 and 1996 water years, and samples were collected when there was flow. In addition, during the 1993 and 1994 water years two of the tiles had weekly grab samples collected and flow estimated by bucket collection per unit time. Three of the tiles (WT1, CN1, and WT2) together drained an area of 40 ha, whereas tile CN2 drained 25 ha. The size of the subsurface watershed was estimated by determining the extent of tile drainage (from probing, aerial photographs, and a tiling contractor who installed many of the tiles) combined with an estimate of the effective area of influence of the drain tiles (100 m) (Kurein, 1995). Using a geographic information system with survey data and the above tile information and area of influence, we were able to assign effective drainage areas to the tile system. However, in several places effective drainage areas overlapped, and we could not clearly assign the area to one tile vs. another. Therefore, although we know the total area drained, we cannot assign some areas to a particular tile.

The 40 ha watershed was in a maize/soybean rotation in which maize was cultivated in 1993 and 1995. Although this watershed is divided and owned by two farmers, they were on the same crop rotation during our study and employed similar cultivation and management practices. Both fields were planted with similar genetic material, planted and harvested together, and received the same N fertilizer rate of 135 kg N ha^{-1} of anhydrous ammonia (for maize). However, one field did receive a solution of $(NH_4)_2SO_4$ (6-0-0-6) at a rate of 135 kg N ha^{-1} in February of 1995, rather than anhydrous ammonia. The 25-ha watershed drains land planted to both crops and therefore tile drainage from this watershed integrated N loss from two different cropping systems simultaneously (anhydrous ammonia was applied at a rate of 197 kg N ha^{-1} for maize production). Overall, the watersheds had similar soils under drainage (Drummer series), slopes (0–3%), crops (maize/soybean rotations), and density of drainage areas as the Camargo watershed and surrounding counties.

All tile solution samples were filtered (Whatman GF/C) and analyzed for NO_3^-, NH_4^+, and NO_2^-, using the same techniques as for all river samples. In addition, on selected tile samples organic N was determined as discussed previously. As with the river samples, daily and yearly loss of NO_3^- was estimated using flow and concentration measurements.

Although NH_4^+, NO_2^-, and organic N were measured on samples, these N forms were not included in river or tile budgets because of their small contribution to total N. Ammonium and NO_2^- were never more than 1% of total N in any samples, and organic N was generally <1% in tile and <2 to 3% in river samples. Only during high river flow was organic N a greater proportion of total N, due to surface runoff. Because we were constructing an inorganic N budget, and surface runoff brings soil particles (and organic N) into the river and is an unknown input, we did not include these N forms in our budgets. Therefore, all estimates presented are for NO_3^- only, but do include nearly all total N.

Agricultural Nitrogen Budgeting

The inorganic N budget for the Camargo agricultural watershed was estimated by summing the inputs or sources of mineral N for each crop and subtracting the total amount of N removed by plant uptake in both the grain and stover (aboveground only). Data were not available to estimate below-ground stover N in maize or soybean. For maize the inputs were fertilizer, soil mineralization, and wet deposition of N. For the soybean crop, the inputs were soil mineralization and wet deposition. The contribution of N to the soybean crop through the process of symbiotic N_2 fixation is discussed below. The overall N budget for the watershed represented the net gain or loss of inorganic N from the soil for the area planted in each crop in a given year. Crop areas planted to maize (range of 21 181–23 394 ha between 1990 and 1995) and soybean (19 743–21 205 ha), fertilizer rates (D. McNaught, 1996, personal communication), and grain yields (Illinois Department of Agriculture, 1996) were obtained for Champaign County, and were scaled to the Camargo watershed, which falls primarily in Champaign County, with the southern areas in Douglas County. Most fertilization in this area is with anhydrous ammonia at a rate of 197 kg N ha^{-1}. We assumed that the Camargo watershed had the same proportion of planting and yields as that for Champaign County.

Average maize and soybean yields for Champaign County were used to determine total grain N accumulation in the Camargo watershed. Total grain N for the maize and soybean crop in the watershed was calculated based on the average protein concentration in the grain of each crop (10% for maize and 40% for soybean, F. Below, 1996, personal communication) and the average N ratio of concentration to grain protein (1:6.25). These average values produced grain N concentrations of 1.6% for maize and 6.4% for soybean. Growing season conditions can affect protein in grain whereby higher yields tend to have lower protein in grain and vice versa, however, we consider this variation to be negligible. Uptake of N into nongrain aboveground portions of the plant were estimated using a N harvest index of 70% for maize, and 80% for soybean (F. Below, 1996, personal communication). Both below-ground maize and soybean (nonsymbiotically fixed N) biomass N was not considered in our balance, and was assumed to mineralize each year and therefore have no major effect on our budgets.

The total N accumulated by the soybean crop was a combination of soil uptake and symbiotic N_2 fixation. Symbiotic N_2 fixation was not measured in the watershed, therefore a direct N input from fixation could not be determined. However, in midwestern soils there have been several estimates of symbiotic N_2 contributions to soybean biomass, with various studies indicating that about 50% of the N is fixed (Johnson et al., 1975; Harper, 1987). Therefore, to calculate the amount of soybean grain N accumulated solely by soil uptake, we estimated that 50% of the total grain N was the result of N_2 fixation, and this amount was subtracted from the total grain and stover N accumulation. The input to soil from fixation occurs after the microbial degradation of the soybean root system and shoot residue. This N would be part of soil mineralization in the following year and would be in part the cause for the increase in mineralized N in areas planted to corn the following year.

Precipitation N inputs were obtained from an NADP site (Bondville) located near the watershed. Nitrate and NH_4^+–N in wet deposition were summed for each water year of the study.

Mineralization of soil organic N was estimated for the watershed using measurements made on fields near the 300N river sampling site (the same fields where tile drainage was sampled). Detailed mineralization measurements were made using the buried-bag technique (Eno, 1960; Paschke et al., 1989), and were found to be 88 kg N ha^{-1} yr^{-1} under soybean during the 1994 water year (David et al., 1996). For maize, we added 45 kg N ha^{-1} yr^{-1} to the soybean estimate (Kurtz et al., 1984; Bundy et al., 1993), due to increased mineralization from soybean stover, for an estimate of 133 kg N ha^{-1} yr^{-1}. The calculated mineralization rates would include N mineralized from either soybean fixed residual N or that from maize stover. These estimates compare well to those estimated by Keeney and DeLuca (1993) using data from Bremner (1967), where they obtained a range of 40 to 120 kg N ha^{-1} yr^{-1}.

RESULTS AND DISCUSSION

Embarras River Nitrate

Flow in the Embarras River varied seasonally, typically with lowest flow during the summer and early fall, and highest flow during winter and spring (Fig. 2). It is a flashy watershed, responding quickly to rainfall events. During the 6-yr period evaluated, instantaneous flow varied from 0 to 228 m^3 s^{-1}. The greatest daily mean was during the 1994 water year, at 174 m^3 s^{-1}. Runoff varied from 260 mm yr^{-1} in 1995 to 662 mm yr^{-1} in 1993, and ranged from 26% (1995) to 51% (1994) of precipitation (Table 1). Although flow was low during most years in August through October due to high evapotranspiration rates, during the summer of 1993 there was always substantial flow due to high rainfall throughout the summer.

Nitrate concentrations in the river at the Camargo gauging station ranged from below detection to 15.1 mg N L^{-1} during the 1992 through 1996 water years (Fig. 3). Typically, concentrations were in the 8 to 10 mg N L^{-1} range throughout this period. Concentrations at the site 15 km upriver (300N) followed the same trend as the Camargo site, although they were on average 10% less, which may reflect the smaller drainage area. Nitrate concentrations changed little over weekly to monthly time periods, but did change seasonally depending on flow. During the extreme low flow periods of late summer to early fall, concentrations declined to $<$0.05 mg N L^{-1}, probably due to denitrification in the nearly stagnant water combined with lack of tile inputs (discussed later). Concentrations of NO_3^-–N were also low during early spring of 1994, 1995, and 1996, slowly increasing through the spring and peaking in late May to June of each year. During the extremely wet year of 1993, this pattern was not evident with concentration having little variation during the year. Other studies in the Midwest have shown a similar temporal pattern in riverine NO_3^-–N concentrations (e.g., Lucey and Goosby, 1993).

When examined on a daily basis, NO_3^- export ranged from below detection to as much as 63.4 Mg N d^{-1} (Fig. 2 and Table 1). Although concentrations were reduced

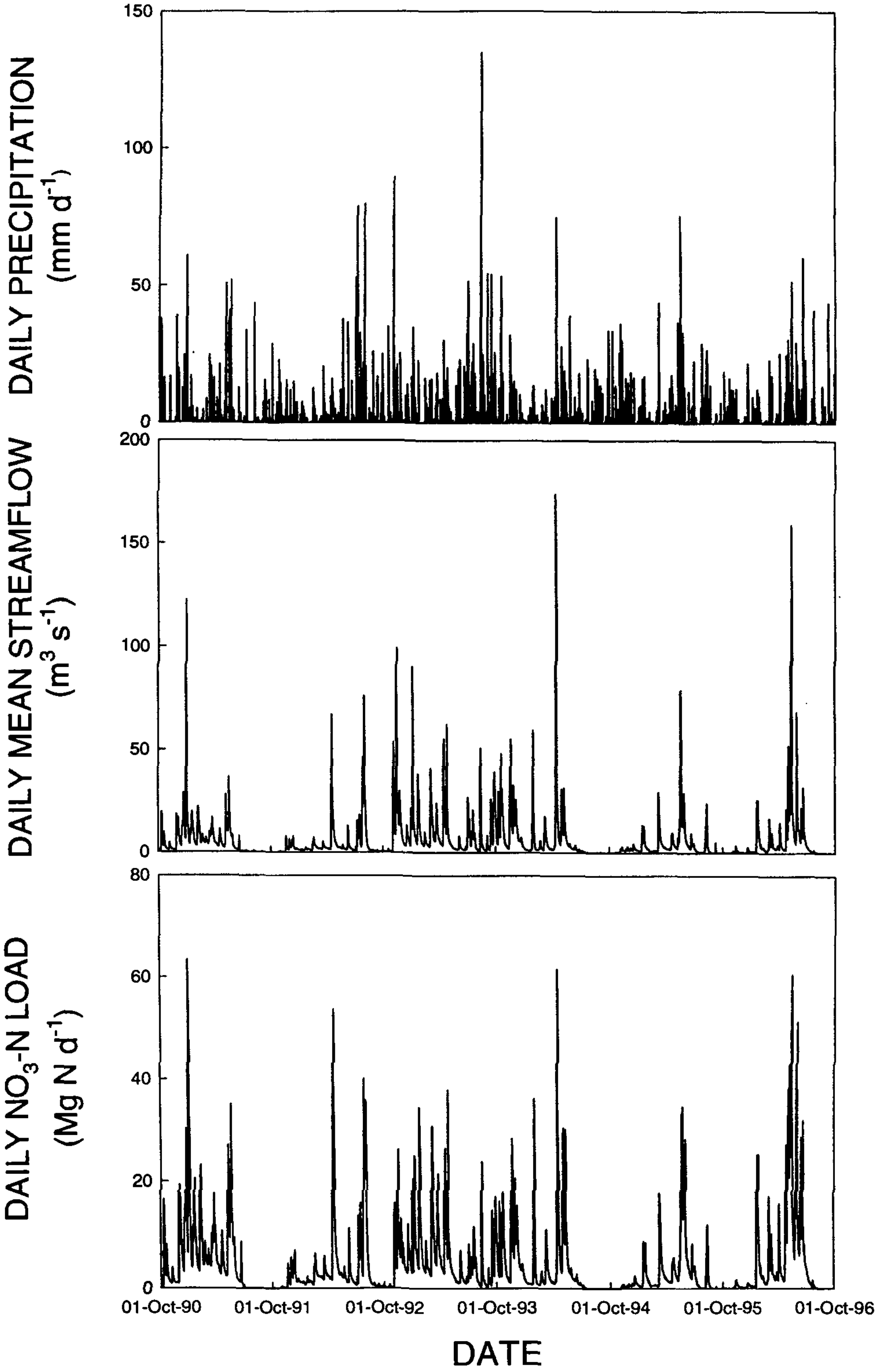

Fig. 2. Daily (1) precipitation at Urbana, IL, (2) average flow of the Embarras River at the Camargo gauging station, and (3) NO_3^- export of the Embarras River for the 1991–1996 water years.

during extremely high flow events (>50 m^3 s^{-1}), these periods produced such large volumes of water that large amounts of N were exported. For example, the 61.7 Mg N d^{-1} exported on 12 Apr. 1994 contributed 3.9% of the total yearly export of NO_3^-. Similar percentages were found each year during the period of study (Table 1). We calculated the number of days to reach 75% of the annual export of N at Camargo for each water year, and obtained values ranging from 59 to 134 days.

During the 1994, 1995, and 1996 water years, the contribution of urban runoff from Champaign-Urbana was estimated at 22, 9, and 26 Mg N yr^{-1}, which was 1.4, 0.9, and 1.3% of the export at Camargo (Table 1). Nitrate concentrations in the river at these sources were gener-

Table 1. Annual precipitation at Urbana, runoff for the Embarras River at Camargo, and NO_3^- export by the Embarras River for the Camargo watershed in east-central Illinois. Estimated NO_3^- input to the Embarras River from Champaign-Urbana is also presented for three water years. Water years begin 1 October and end on 30 September of the following year.

Water year	Precipitation	Runoff, % of precipitation	Embarras River NO_3^- load: Camargo	Embarras River NO_3^- load: Champaign-Urbana	Days to 75% of Camargo export	Maximum daily at Camargo, % of yearly
	mm yr^{-1}	mm yr^{-1}	Mg N yr^{-1}	Mg N yr^{-1}	d	Mg N d^{-1}
1991	1053	388 (37)	2068		109	63.4 (3.1)
1992	1056	268 (25)	1321		89	53.7 (4.1)
1993	1548	662 (43)	2210		134	37.9 (1.7)
1994	949	487 (51)	1602	22	82	61.7 (3.9)
1995	994	260 (26)	979	9	72	34.6 (3.5)
1996	956	397 (42)	1948	26	59	60.6 (3.1)

ally about 1 to 2 mg N L^{-1}. This demonstrates that agricultural land is the source of nearly all the NO_3^- in the river at Camargo, rather than urban inputs. This same conclusion has been reached in other agricultural watersheds (e.g., Keeney and DeLuca, 1993).

Tile Nitrate

The four monitored drain tiles had NO_3^- concentrations ranging from 5 to 49 mg N L^{-1} during the study period (Fig. 3). Before October of 1994, however, we only collected grab samples from tiles WT1 and CN1 and samples were not obtained during most events. During the 1995 and 1996 water years we sampled the tiles during all events, and concentrations of NO_3^- increased to as much as 49 mg N L^{-1} in tile WT1 during a major precipitation event. Tile NO_3^- concentrations were similar to the overall Embarras River both at 300N and Camargo. For example, when there was no tile flow during late summer of 1994, concentrations of NO_3^- in the river were <0.05 mg N L^{-1}. When tiles began to flow in November of 1994, NO_3^- concentrations in the river immediately responded and were similar to the tile concentrations. During the summer of 1995, tile flow stopped in early July and river NO_3^- again decreased to <0.05 mg N L^{-1}. Although there was great variability in tile NO_3^- concentrations during 1995 and 1996 due to storm events, the overall pattern in the tiles was similar to that in the river. We examined the relationship between average daily flow weighted NO_3^- concentration (tile WT1, which had the longest record) and river NO_3^- at Camargo over a 33 mo period (n = 1007). Days were not used when the river flow was >50 m^3 s^{-1}, because this is when surface runoff is important and the river dilutes. The close relationship obtained (r = 0.83, n = 999, $P < 0.0001$) suggests that this one tile had a similar pattern in NO_3^- concentrations as the river, explaining 70% of the variation. Other tiles follow the same pattern (Fig. 3), and it seems clear that tiles along the Embarras River are the source of most of the NO_3^-, with river concentrations responding directly to tile flow.

The four tiles varied greatly in their flow, ranging from 12 694 to 56 320 m^3 yr^{-1} during the 1995 water year, and 18 960 to 102 122 m^3 yr^{-1} during 1996, a much wetter year (Table 2). This was due to the varied source areas they drain, which were difficult to establish due to the complex drainage patterns for each tile that led to overlap of effective drainage areas. On a daily basis, NO_3^- export from the tiles was as much as 148 kg N d^{-1} during the high flow period of May 1995 in tile WT2 (Fig. 4).

During the 1995 water year, which was the lowest runoff year of the five evaluated in this study, nearly all of the tile NO_3^- leached during record rainfall in May. For tile WT2, 9 d of flow contributed 75% of the annual export of 689 kg N. However, for tile CN1 that had comparatively low flow, 47 d of flow were required to yield 75% of the total exported N (105 kg). During the 1996 water year, when there was greater rainfall and higher flows and N loss, the days to 75% of annual export ranged from 45 to 69 d. This is remarkably greater than the 1995 water year, and reflects the complexity in inorganic soil N pools and precipitation in controlling daily export of NO_3^-.

High flow events in these tile systems can therefore be extremely important contributors to NO_3^- export depending on the year. For tile WT2, the maximum daily export was 148 kg N, about 21% of the annual load (Table 2). During the 1996 water year with greater overall flow, the maximum daily amounts in the tiles ranged from 3.4 to 4.9% of the annual NO_3^- load. If intense rainfall occurs before the crop can use the applied fertilizer, large amounts can be leached in short time periods. Nitrate concentrations increased with increasing flow during these storm events, which contributed to the high daily exports. This pattern and concentration range of NO_3^- leaching is similar to other tile drained areas of the Midwest under corn/soybean rotations (Kladivko et al., 1991; Logan et al., 1994).

Annual export of N from the tiles during the 1995 water year ranged from 105 to 689 kg N, and from 237 to 999 kg N in 1996. This large variability in N export from adjacent tiles was a result of tile length and area drained. The 1995 loads were obtained during a relatively dry year, except for the rainfall in May. We could not separate the individual drainage areas of tiles WT1, CN1, and WT2, but together they drained about 40 ha, leading to a 29.2 kg N ha^{-1} N export in 1995. For tile CN2 in 1995, the export was estimated at 20.2 kg N ha^{-1}. Corresponding values for the wetter 1996 water year were 48.3 and 40.0 kg N ha^{-1}. Other studies have found similar NO_3^- concentrations and exports in tiles from a variety of locations and cropping systems (Logan and Schwab, 1976; Logan et al., 1980, 1994; Kladivko et al., 1991; Fausey et al., 1995; Drury et al., 1996), although these are highly dependent on flow.

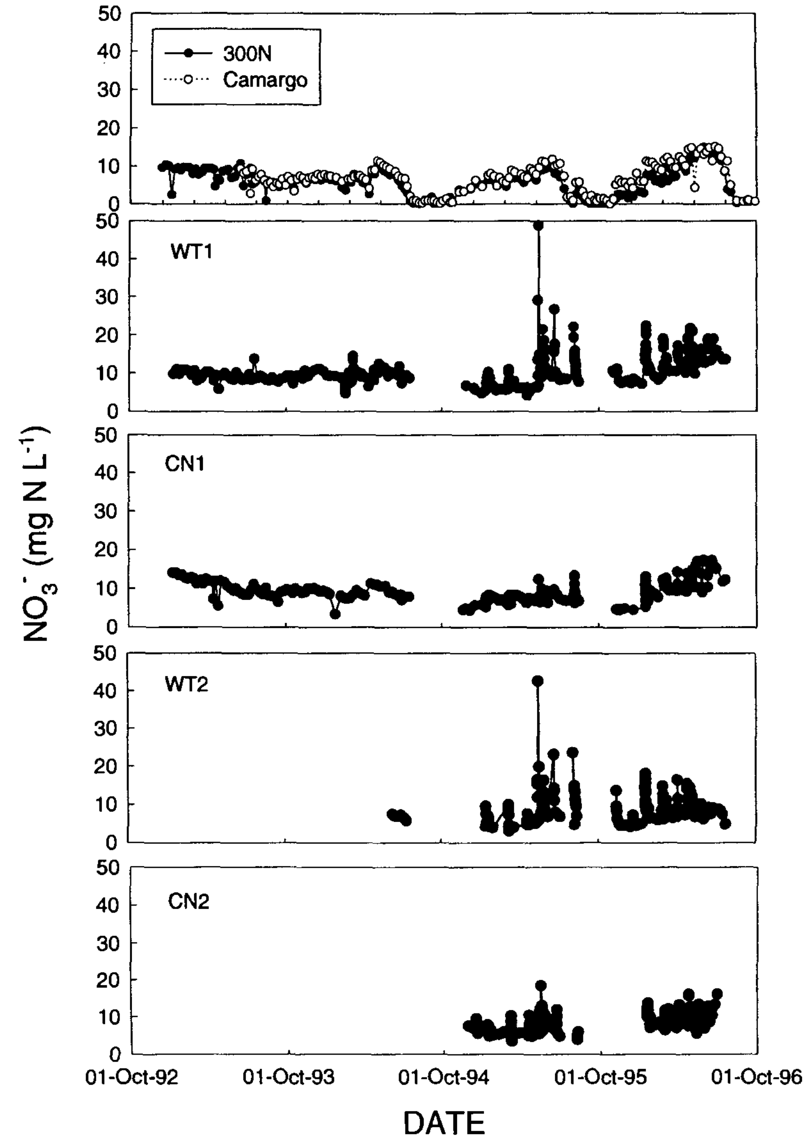

Fig. 3. Nitrate concentrations in the Embarras River at the Camargo gauging station and 300N location, and concentrations in agricultural drainage tiles near the 300N location.

Watershed Agricultural Nitrogen Budget

We estimated the input and outputs of corn/soybean agricultural fields on the Camargo watershed from 1990 through 1995 (Table 3). Fertilizer was the largest source of maize mineral N, which ranged from 4164 to 4599 Mg N yr^{-1}. Soil mineralization was estimated to provide from 2754 to 3041 Mg N yr^{-1} to maize, about 66% of the fertilizer input. Grain export of N varied with growing conditions, and ranged from a high of 3282 Mg N in 1992 to a low of 1683 in 1991. The stover N pool varied in proportion to the grain N pool, ranging from 721 to 1406 Mg N. Sources minus sinks of N therefore followed a similar pattern as plant uptake in the stover plus grain export, with a low of 2976 Mg N in 1992 to a high of 5116 in 1991.

For soybean the largest input was soil mineralization, which was estimated to be 88 kg N ha^{-1} with totals ranging from 1737 to 1866 Mg N yr^{-1} for the entire watershed (Table 3). After subtracting symbiotically fixed N in grain and stover, the soybean area balance ranged from +242 to −524 Mg N. This suggested that soybean production used most of the mineralized N in the soils, and may have used some residual inorganic N as well. Although soybean production results in a net removal of inorganic N from the soil (Heichel and Barnes, 1984), N applications to maize are usually adjusted for N supplied by the previous soybean crop. In midwestern states, an N credit of 45 kg N ha^{-1} is often used to lower the N application rate for the following maize crop (Kurtz et al., 1984). However, N credits following soybean production vary with soil type and year. Silt loams provide greater N contribution from the breakdown of soybean residue than sandy loams due to increased leaching losses of NO_3^- in sandy soils before crop uptake in the subsequent year (Bundy et al., 1993).

In addition, several studies show that the addition of N fertilizer to soils enhances the mineralization rate (added N interaction, ANI), thereby increasing overall mineralization of N (Azam et al., 1993; Jenkinson et al.,

Table 2. Annual flow and NO_3^- export for four tiles draining corn/soybean agricultural land in the Camargo watershed in east-central Illinois for the 1995 and 1996 water years.

Water year and tile	Flow	NO_3^- load	No. of days to reach 75% of annual NO_3^- load	Maximum daily NO_3^- load, % of annual
	$m^3\ yr^{-1}$	kg N yr^{-1}	d	kg N d^{-1}
1995				
WT1	29 135	374	26	76 (20)
CN1	12 694	105	47	18 (17)
WT2	54 874	689	9	148 (21)
CN2	56 320	506	23	73 (15)
1996				
WT1	57 688	860	45	42 (4.9)
CN1	18 960	237	69	8 (3.4)
WT2	94 155	837	56	42 (5.0)
CN2	102 122	999	46	36 (3.6)

1985; Rao et al., 1991). To account for this enhanced mineralization from the soybean contribution and ANI, we used a measured estimate of 133 kg N ha^{-1} for N mineralization during maize (David et al., 1996).

When maize and soybean areas were combined on the entire watershed, excess inorganic N was estimated as high as 5359 Mg N (127 kg N ha^{-1}) following the 1991 harvest, and as low as 2585 Mg N (59 kg N ha^{-1}) in 1992. In a field study of N pools in the Camargo watershed, similar residual pools of inorganic N were directly measured (by KCl extraction of inorganic N) during 1994 and 1995 (David et al., 1996), further supporting this budget approach. The large differences in inorganic N pools were due primarily to the variability in maize removal of N in grain (yields ranged from a low of 4.7 Mg ha^{-1} in 1991 to a high of 9.0 Mg ha^{-1} in 1992) combined with uptake in nongrain aboveground biomass. The low maize grain N removal in 1991 and 1995 were due to overall lack of plant N uptake during dry growing conditions that produced the highest soil inorganic N pools at harvest. In 1992, yields and plant N accumulation were the greatest during the 6-yr period and resulted in the lowest amount of inorganic N carryover. Therefore, if yields are reduced by drought, large soil inorganic N pools can accumulate and increase the likelihood of NO_3^- leaching during the following winter and spring before crop uptake.

Using our budget approach we can also examine the efficiency of N uptake by the crops in this watershed. The overall utilization of N sources for the entire watershed (comparing fertilizer, mineralization, and wet deposition to nonfixed N removed by aboveground portion of the crop) was 61% over the 6-yr period, with a range of 43 to 73%. Remaining inorganic N, which varied from 27 to 57% of the sources for a given year, was the amount available for leaching into tiles and the river (see below). Efficiency of N use varied considerably, however, between maize and soybean. The maize crop on average over the 6-yr study accumulated 48% of the inorganic N (range of 32–61%), whereas soybean accumulated 112% (range of 87–120%). Based on this analysis soybean production would deplete the soil pool of both mineralized inorganic N as well as residual inorganic N (values >100%), whereas maize production

Table 3. Annual inorganic sources and sinks of N for the Camargo watershed in east-central Illinois, 1990 to 1995.

Input/Output	1990	1991	1992	1993	1994	1995
	Mg N					
Maize						
N fertilizer	4506	4417	4490	4351	4599	4164
Soil mineralization†	2980	2921	2969	2877	3041	2754
Wet deposition	160	114	136	138	131	129
Total sources	7646	7453	7596	7366	7772	7047
Plant uptake-Stover	1154	721	1406	1137	1373	787
Export of grain	2692	1683	3282	2652	3204	1837
Total sinks	3845	2404	4688	3789	4577	2624
Sources-sinks	3869	5116	2976	3644	3265	4487
Soybean						
Soil mineralization	1737	1737	1866	1774	1774	1746
Wet deposition	138	100	126	126	113	121
Total sources	1875	1838	1992	1899	1887	1867
Plant uptake-Stover‡	403	319	477	458	482	400
Export of grain‡	1611	1276	1907	1832	1928	1600
Total sinks	2014	1595	2383	2289	2410	2000
Sources-sinks	−139	242	−391	−390	−524	−133
Net for watershed	3730	5359	2585	3254	2741	4354

† Symbiotic N_2 fixation from the previous years soybean crop was considered an N input to maize production through increased N mineralization.
‡ N accumulation from soil uptake of inorganic N only—the contribution to grain and stover N from symbiotic N_2 fixation was estimated to be 50% of total plant N accumulation and was subtracted from grain and stover values.

would add to it. Soybean uptake efficiency maybe overestimated, because during highly productive years: (i) more N in the plant could be derived from N_2 fixation, and (ii) soil mineralization could add larger amounts of inorganic N to the soil. Harper (1987) noted a range in N_2 fixation by soybean of 25 to 50% of N uptake, Johnson et al. (1975) determined N_2 fixation rates of 80 to 100 kg N ha^{-1} yr^{-1} (48% of aboveground biomass N), and Barry et al. (1993) estimated N_2 fixation in soybean was about 50% of total uptake. We used an average of 50% because values were not available for each year of our study, and this proportion is supported by the literature cited above. It is likely, however, that the N_2 fixation rate varies greatly from year to year in soybean, decreasing as the availability of inorganic N increases (Johnson et al., 1975). We also used a soil mineralization rate of 88 kg N ha^{-1} yr^{-1} that was based on 1 yr of measurements at one site. This rate no doubt varies considerably, and is probably higher during highly productive crop years due to favorable soil conditions for microbial activity.

Keeney and Deluca (1993) did a similar analysis for an Iowa watershed, and found that in 1990 only 43% of the inorganic N was used by the crop, much lower than our 1990 value of 61%. This difference is clearly shown by the small amount of N they estimated in crop plants (24 and 104.9 kg N ha^{-1} yr^{-1} for soybean and maize, respectively). Our estimate of N removed by maize in 1990 was 168 kg N ha^{-1} yr^{-1}, whereas for soybean the nonfixed N in the plant was 102 kg N ha^{-1} yr^{-1}. Therefore, it would appear that our cropping systems in east-central Illinois were much more efficient than those in central Iowa. However, without comparing yields (yields were not given in Keeney and Deluca, 1993) it is difficult to determine why this large difference in efficiency and plant N was observed.

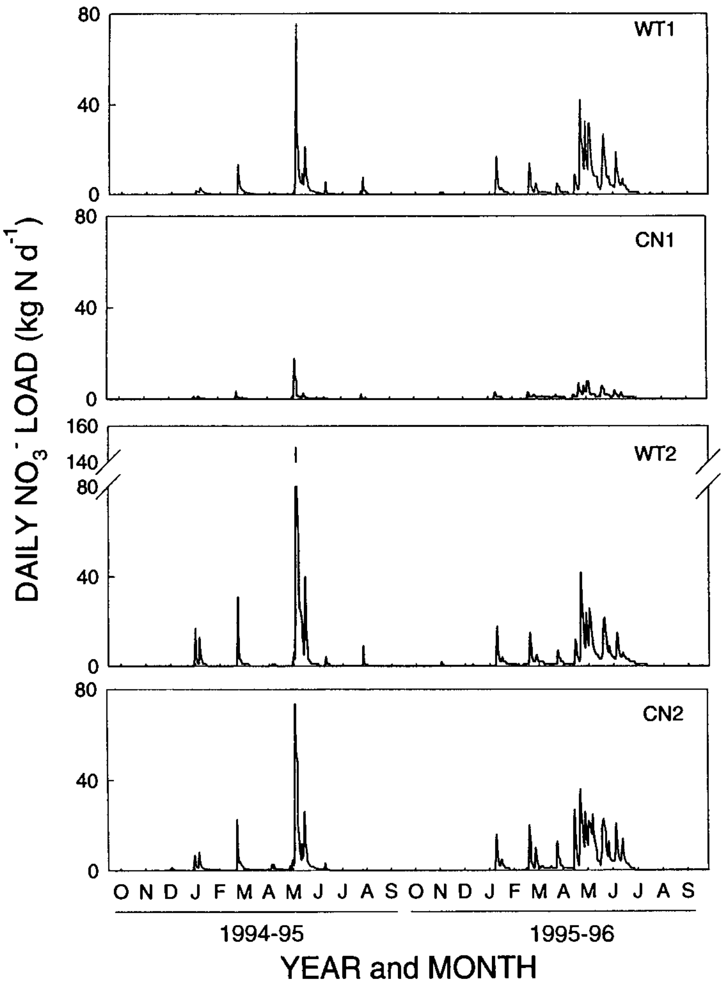

Fig. 4. Daily NO_3^- export from agricultural drainage tiles during the 1995 and 1996 water years.

Relationship between Land Usage and River Nitrate

We have demonstrated that tile drainage contributes NO_3^- to the Embarras River. To further investigate the linkage between agricultural production and river NO_3^- export, we compared the overall field N budget to river export the following year (Fig. 5). River N export ranged from 25 to 85% of the field N balance in a given water year, with an average of 49%. The water year of 1993, when 662 mm of precipitation was in runoff, followed the highest harvest that led to the smallest residual N pool. However, due to the high rainfall, tile drain flow, and runoff, the N export by the river was the greatest and was similar to the field N balance for that year. This probably reflects loss of N stored in the fields from the previous growing season (1991), when a large pool of residual N was estimated, with only a small amount found in the river due to limited precipitation and runoff (only 268 mm of runoff). The field N balance and river export are linked by hydrology. During years of below-average precipitation, NO_3^- is not removed by tile drainage and the total export is low, as occurred following the 1991 and 1994 harvests. Kladivko et al. (1991) and Logan et al. (1994) also concluded that tile drainage losses of NO_3^- are highly dependent on climatic effects, and that significant time lags in NO_3^- leaching through tiles can occur during periods of limited rainfall. Lucey and Goolsby (1993) also reached a similar conclusion for the Raccoon River in Iowa, but only compared fertilizer additions to NO_3^- in the river.

If (i) tile drainage in the 1995 water year provided all of the river NO_3^-, (ii) our monitored tiles were typical of all tiles in the watershed (24.7 kg N ha^{-1} yr^{-1} for the 1995 water year), and (iii) between 70 to 85% of the cropped land (average 42 628 ha) in the Camargo watershed were tile drained, total export would be 737 to 895 Mg N for the 1995 water year. In the 1996 water year, with an average tile N export of 44.2 kg N ha^{-1} yr^{-1}, the range would be 1319 to 1601 Mg N. Our estimated values for the export of N from the Camargo watershed were 979 and 1948 Mg N for the 1995 and 1996 water years, respectively (Table 1). This again suggests that tiles do provide most of the rivers NO_3^- load, with the remainder probably from seepage or surface runoff.

When summed for the 6-yr period of 1990 to 1995, the field N balance was 22 023 Mg N, and the river export was 10 128 Mg N. It is apparent that both mineralized N and fertilizer N contributed to the NO_3^- in tile drainage, and therefore to the river export. Nitrate loss through tile drainage occurs whenever high precipitation leads to tile drain flow, whether during the winter or summer. The large mineral N pool in these soils at any given time is composed of both fertilizer and mineralized N,

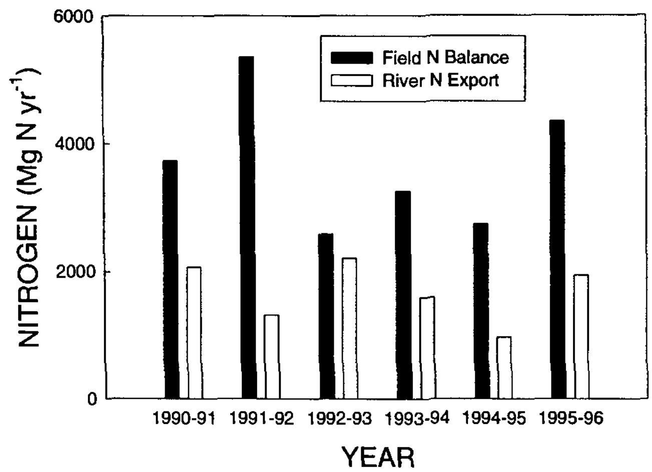

Fig. 5. Yearly agricultural field N balance following each harvest and Embarras River export of NO_3^- for the water year following the harvest for the period 1990–1996.

and both are susceptible to leaching. Even if N fertilization were reduced or eliminated, the overall disturbance from agricultural production in the Embarras River watershed would still lead to high NO_3^- concentrations and export, depending on the timing of precipitation events. Keeney and DeLuca (1993) reached a similar conclusion in their Iowa study on a much larger watershed without the advantage of tile drainage exports.

One unanswered aspect of our study is the fate of the 11 895 Mg N that was estimated as not being taken up by the crop or exported by the tiles into the river. There are several possibilities, including: NH_3 volatilization after fertilization (Terman, 1979; Bock, 1984), denitrification in the field (Lowrance, 1992; Barry et al., 1993), post-anthesis volatile plant N losses (Francis et al., 1993), leaching into groundwater, seepage, and riparian zone uptake or denitrification (Groffman et al., 1991; Haycock and Pinay, 1993; Nelson et al., 1995), belowground stover uptake (roots), or a change in the soil N pool. In addition, our estimates of mineralization rates could be high, as we would expect them to vary based on yearly temperature and moisture patterns. However, data are not available to better estimate mineralization rates in individual fields or across a watershed at this time, although studies are suggesting this may be possible (e.g., Saint-Fort et al., 1990). All of the above N sinks and sources could contribute at various times depending on weather and leaching patterns in individual fields. Using typical total N pools for this area, we estimated that the Camargo watershed had a total soil N pool (0–100 cm) of about 400 000 Mg N. Therefore, the 11 895 Mg N unaccounted for over the 6-yr period would only be about 3.1% of total soil N. It seems likely that some of the N was lost by one of the processes listed above, and that perhaps the overall N status of the soils increased to some extent. For example during 1995, fertilizer was generally applied before the heavy rains of May. Because soil temperatures had warmed (17, 16.0, and 14.2°C at 0.05, 0.2, and 0.4 m, respectively) and crop uptake of N had not begun, conditions were good for denitrification. This may have greatly reduced the mineral N pool in the watershed, but not affected crop production because of the poor growing conditions later in the year (moisture limitations).

CONCLUSIONS

By estimating a budget of N sources and sinks (i.e., fertilizer application, soil mineralization, and grain harvest) in a large agricultural watershed we determined that large pools of inorganic N were present in the soil following harvest. The source of the inorganic N was divided between N fertilizer and soil mineralized N. On average, about 49% of this NO_3^- was leached through drain tiles and was exported by the Embarras River, although this ranged from 25 to 85% of the field N balance over a 6-yr period depending on weather (i.e., precipitation). High flow events led to large exports of N in tiles and in the river. Only a few days of high flow events can lead to most of the annual loss of NO_3^- from a tile-drained field in some years. It seems likely that agricultural disturbance leading to high mineralization rates and N fertilization combined with tile drainage contributed significantly to NO_3^- export in the Embarras River.

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