NITROGEN IN THE hlISSISSIPP1 RIVER BASIN:SOURCES AND FACTORS AFFECTING LOSS OF NITRATE TO THE RIVER"

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Nitrogen (N) is a naturally occurring element that is essential to plant growth and crop production. In a soil system, nitrate-N is continually supplied through mineralization of soil organic matter. Other sources of N include fertilizers, animal manures, municipal sewage wastes, agricultural and industrial wastes, atmospheric deposition. and dinitrogen fixation, all of which either occur as nitrate-N or can be converted to nitrate-N through mineralization and nitrification.

Sources of Nitrogen

The increased use of nitrogen fertilizers is being pointed to as a possible cause of water quality changes in the Mississippi River that lead to hypoxia in the Gulf of Mexico (Rabalais et al.. 1996). However, other sources of nitrogen in the Basin also contribute greatly to the total nitrogen inputs. Estimates of some of the inputs of nitrogen to the Mississippi Basin and its major tributary basins have been made by Battaglin et al. (1997) and have been reported for specific sections of the Basin by Goolsby et al. (1997). Based on the 11.6 million metric tons of N added annually to the Mississippi Basin (Table 1). approximately 51 % is from commercial fertilizer, 30% from livestock manure. 9% fixed by legumes, 5% from human domestic waste, and 4% deposited by rainfall. Municipal and industrial point discharges of N to rivers are estimated to contribute only 2 and 1% . respectively, to the total annual loading of N in the Basin. However. these discharges are often directly to rivers. whereas the oiher potential N sources are applied or generated at the land surface. Thus municipal and industrial point discharges of N to rivers could be the source of as much as 25% of the total N discharged to the Gulf of Mexico (Goolsby et al. 1997).

While most of the inputs of N to the Mississippi Basin can be estimated and the outputs in surface water can be measured, the actual sources of nitrate transported by the Mississippi River are unknown. How much is from this year's compared to last year's fertilizer is unknown. Similarly. the amount of nitrate coming directly from manures. legumes. soil organic matter, etc. is not known.

Fertilizer N use data. based on tons of fertilizer sold within each state, have been compiled annually since 1945. The amount of fertilizer used and the rate of application per crop acre for 9 midwestern states draining into the Mississippi River are shown in Figure 1. Although significant year-to-year variation exists. it is apparent that total fertilizer N use has increased little in this 9-state area (Illinois. Indiana. Iowa, Kansas. Minnesota, Missouri. Nebraska, South Dakota, and Wisconsin) since the early 1980's. Various mathematical

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models were applied to the data to determine when fertilizer use peaked or plateaued. The quadratic model indicated that fertilizer N use (sales) peaked in 1989. The linear response plateau (LRP) and quadratic response plateau (QRP) models indicated fertilizer N plateaued beginning in 1980 and 1987, respectively. These data refute the frequent statement of "increasing N fertilizer use in the Midwest".

Fig. 1. Fertilizer N used (sold) and rate of N application for the 9-state midwestern area draining into the Mississippi River Basin.

Transport and Temporal Variation of Nitrate

The transport of N from the Mississippi River to the Gulf of Mexico has averaged about 1.5 niillion metric tons per year since 1980 (Goolsby et al.. 1997). This flux represents about 13% of the estimated annual N input from all sources except soil N. About 60% of the annual N flus is nitrate and the remainder is mostly dissolved and particulate organic N. During the last 80 years, there has been a marked increase in the concentration of nitrate in the Lower Mississippi River that has been attributed to the increasing use of fertilizers (Turner and Rabalais, 1991). Before 1940. nitrate-N concentrations ranged from 0.2 to 0.4 mg/L; since 1940, they have ranged from 1.0 to 1.2 mg/L. In the last 10 to 15 years, however, nitrate concentrations remain high but do appear lo have stabilized.

Both the concentration and tlux of nitrate tend to be highest in the spring when streamflow is highest. This direct relationship between nitrate concentration and flow may result from leaching of nitrate from the soil during periods of high rainfall. Increased flows and elevated concentrations in agricultural tile drains also may contribute to this relationship (Goolsby et al., 1997).

Geographic Contribution of Nitrate

Based on data from 1987-92, disproportionately large quantities of nitrate in the Mississippi River, on average, were derived from the upper-basin States of Illinois, Iowa. and Minnesota (Antweiler et al., 1995). The data presented in Table 2 show that slightly more than one-half of total nitrate load in the entire Mississippi River Basin is derived from the Upper Mississippi River Basin, which supplies less than one-fourth of the total water. Conversely, the Ohio River supplies 41% of the total water, but only 21% of the total nitrate load.

Table 2. Geographic contribution of nitrate and water discharge in the Mississippi River Basin (adapted from Antweiler et al..

The median nitrate plus nitrite concentrations along the length of the Mississippi River for the period from 1970 through 1991 have been described by Moody and Battaglin (1995). Upstream from St. Paul, Minnesota, the median concentration of nitrate plus nitrite is 0.16 mg/L but then steadily increases step by step with each downstream addition of water from

the Minnesota (2.8 mg/L). Rock (2.9 mg/L). Iowa (5.5 mg/L), Des Moines (3.7 mg/L) , and Illinois (3.5 mg/L) Rivers. At Alton. Illinois, just upstream from the Mississippi-Missouri confluence near St. Louis, Missouri, the median concentration of nitrate and nitrite in the Mississippi River reaches a maximum of 2.6 mg/L. Downstream from Alton, the Missouri (1.1 mg/L) and Ohio Rivers (1.0 mg/L) successively dilute the nitrate and nitrite concentration so that it remains nearly constant at about 1.4 mg/L at gaging stations in the Lower Mississippi River. Although maximum concentrations for the Mississippi River have never exceeded the maximum contaminant level for drinking water of 10 mg/L, concentrations in several of the tributaries (Minnesota. Iowa. and Des Moines Rivers) in heavily farmed regions have exceeded the maximum contaminant level on occasion.

The geographic contribution within major tributaries to the Mississippi River can also vary greatly. Two Minnesota soil scientisrs (D. J. Mulla and A. P. Mallawatantri) have characterized the 10 million acre Minnesota River Basin that drains 12 major watersheds for the period from 1968 to 1994. Nitrate-N concentrations in the Minnesota River were qenerally less than 10 mg/L (MCL for drinking water) but vary considerably along the entire **^L** stretch. About 10% of all water quality monitoring samples exceeded the 10 mg/L standard in the eastern stretch that receives the greatest amount of rainfall, is dominated by intensive row-crop agriculture. and has significant portions of subsurface (tile) drained land. In the drier western stretch where discharge from tile drains is considerably less, no samples exceeded the standard. Three watersheds (Blue Earth, LeSueur, and Watonwan) alone account for 64% of the total nitrate-N load in the entire basin. yet they drain only 15% of the total basin area (Mulla et al., 1997). Six watersheds on the western side of the basin collectively generate only about 6% of the nitrate-N load.

Yield of nitrate-N (load divided by drainage basin area) ranged from about 0.3 Ib/A/yr on the western side of the basin to about 17.9 lb/A/yr in the Blue Earth. LeSueur, and Watonwan watersheds (Mulla et al., 1997). For the Minnesota River Basin as a whole. the yield of nitrate-N was about 7.2 Ib/A/yr. This compares to about 5.5 Ib for the Ohio River, 13.0 for the Iowa River, and 14.3 Ib/A/yr for the Illinois River.

Role of Agriculture

Agriculture has been identified frequently as a major contributor of nitrate-N to surface water. Stream-water collected from water years 1984 through 1993 for a portion of the Upper Mississippi River Basin were analyzed for nitrate-N (Kroening, 1996). Nitrate-N concentrations were significantly greater (2 to 6 mg/L) from those rivers which drain a large percentage of agricultural land compared to those which drain a larger percentage of forested land (0.1 to 0.5 mg/L). In the Mississippi River, mean concentrations were significantly greater (1.8 to 2.5 mg/L) down stream of the confluence with the Minnesota River (an agricultural watershed) than upstream (0.2 to 0.9 mg/L).

Keeney and DeLuca (1993) examined the nitrate-N concentrations in the Des Moines River in 1945. 1955. 1976. and from 1980 through 1990 and found that the average nitrate-N concentration has changed little in the last 45 years (5.0 mg/L in 1945 to 5.6 mg/L in 1980-90). They concluded that intensive agricultural practices that enhance mineralization of soil N coupled with subsurface tile drainage are the major contributors of nitrate-N rather

than solely fertilizer N.

Somewhat similar conclusions were drawn by David et al. (1997) who surmised that agricultural disturbance leading to high mineralization rates and N fertilization combined with tile drainage contributed significantly to nitrate export in the Embarras River in Illinois. In their 6-yr study, an average of 49% (range from 25 to 85%) of the large pool of nitrate remaining after harvest was leached through drain tiles and exported by the River. Precipitation exerted a tremendous influence on drainage losses with a few drays of high-flow events leading to most of the annual loss in some years.

Influence of **Precipitation**

Loading of nitrate-N into surface water is a function of transport volume (amount of water) and nitrate-N concentration in the transported water. The amount of drainage water leaving the landscape is largely a function of climate and soil properties. i.e., precipitation. texture, infiltration rate. etc. The effect of climate on subsurface drainage volume is abundantly clear in the following tile drainage studies. Annual tile drainage in a Minnesota study conducted on a Webster cl with continuous corn ranged from 1.3 to 26.6 inches per yr with an average of 11.7 inches (Randall and Iragavarapu. 1995). Drainage was least in 1989 when growing season precipitation was 35% below normal and greatest in 1991 when growing season precipitation was 51% above normal. In addition, drainage in the 3-yr dry period (1987-89) averaged only 1.7 inches compared to the following 3-yr wet period (1990- 92) when drainage averaged 21.6 inches. Similar findings were reported by Weed and Kanwar (1996) who measured tile drainage under both continuous corn and a corn-soybean rotation on Kenyon-Clyde-Floyd soils in Iowa. Averaged across four tillage systems, drainage in 1991 totaled 9.6 inches or 44% above the 1990-92 average. A 6-yr study conducted on a Normania clay loam at Lamberton, MN showed no tile drainage in 1988 and 1989 when annual precipitation was 69 and 76% of normal, respectively (Randall. et al., 1997). Drainage under continuous corn and a corn-soybean rotation averaged 0.9 inches in 1990. 8.8 inches in 1991. 5.6 inches in 1992, and 18.5 inches in 1993. Annual precipitation in those four years was 95, 125, 117, and 160% of normal, respectively. Data from these three studies clearly indicate the strong relationship between precipitation and volume of subsurface, tile drainage.

Influence of Soil **hlineralization**

Soils high in organic matter can mineralize a substantial amount of nitrate-N which is susceptible to loss in subsurface tile drainage. especially when wet years follow very dry years. Tile drainage from continuous corn plots that received only 18 Ih N/A/yr at Lamberton. MN contained annual flow-weighted nitrate-N concentrations of 13, 19, and 19 mg/L in 1973, 1974. and 1975. respectively (Gast et al.. 1978). No drainage occurred in 1976, an extremely dry year. In 1977. with slightly above-normal rainfall. nitrate-N concentrations averaged 28 mg/L from these plots. In a study at Waseca, MN. four plots were fallowed (no crop grown and no N applied) from 1987 through 1993. Nitrate-N concentration in the tile drainage water averaged 57 mg/L in 1990 following three dry years. Concentrations dropped to 38. 25, and 23 mg/L in 1991, 1992, and 1993, respectively (Randall. unpublished data). Based on data from these studies, high concentrations of

nitrate-N can easily be lost to tile drainage from high organic matter soils even if no N or very small amounts of N are applied, especially in wet years following dry years, which limited crop production. Hatfield (1996) found that nitrate-N concentrations in the Walnut Creek Watershed ranged from 15 to 20 mg/L throughout most of the year and stated that this loss is due primarily to the high organic matter content of the soils and their ability to mineralize N. Under these conditions. elevated levels of nitrate-N will be lost to drainage water regardless of soil or nutrient management practices.

Influence of Cropping Systenis

Nitrate-N concentrations in subsurface drainage water are related to crop rotation plus rate and timing of fertilizer N application (Baker and Melvin. 1994). Tile drainage water from row crop systems (continuous corn and a corn-soybean rotation) that were fertilized with N based on a soil nitrate test averaged between 14 and 40 mg nitrate-N/L from 1990 to 1993 at Lamberton, MN. In comparison, perennial crops (alfalfa and a CRP grass-alfalfa mix) gave nitrate-N concentrations ranging from 0.3 to 4 mg/L. Due to higher flow volumes from the plots planted to row crops, nitrate-N losses from the row crops ranged from 30 to 50X higher than from the perennial crops (Randall et al.. 1997). Nitrate-N concentrations under alfalfa were also shown to be much lower compared to corn or soybeans in Iowa (Baker and Melvin. 1994). Weed and Kanwar (1996) found higher nitrate-N losses from plots planted to continuous corn compared to a corn-soybean rotation in Iowa. In summary. these studies show substantially higher nitrate-N concentrations in row crops, especially continuous corn. compared to perennial crops that have a 7-month period of greater root activity (water and nutrient uptake) and where cycling of N is optimized.

Influence of Tillage

Studies conducted in Iowa showed that tillage methods have less effect on nitrate-N loss to drainage water than do crop rotations (Weed and Kanwar. 1996). Moldboard plowing gave the lowest flow volumes while ridge tillage and no tillage had the lowest nitrate-N concentrations. A 1 1-yr study with continuous corn at Waseca. MN showed similar results (Randall and Iragavarapu, 1995). Although slightly more water drained from the no-till plots. nitrate-N concentrations were slightly lower compared to moldboard plow plots. Thus. nitrate-N flux in subsurface drainage was not influenced by tillage system.

Influence of Rate and Time of N Application

Nitrogen was applied as 15-N depleted ammonium sulfate in the fall and spring for continuous corn during a 6-yr period at Waseca, MN. Corn yields from the late fall application (early November) of 120 and 180 Ib NIA averaged 8% lower than with spring (late April) application. In addition, annual losses of nitrate-N in the tile drainage water averaged 36% higher with fall application compared to spring application. Averaged across time of application, yields and nitrate-N losses in the drainage water were 17 and 30% higher for the 180-lb rate compared to the 120-lb rate. At the end of the study, 65% of the N being lost in the drainage from the 180-lb fall treatment was derived from the fertilizer, whereas only 15% of the N in the drainage water lost from the 120-lb spring treatment was derived from the fertilizer (Buzicky et al., 1983).

Anhydrous ammonia was applied in four treatments $|$ (late fall, late fall $+$ nitrapyrin. spring preplant, and split (40% preplant $+$ 60% sidedress)] to drainage plots at Waseca, MN from 1987 through 1993. Flow weighted nitrate-N concentrations across the four-yr flow period (1990-93) averaged 20, 17. 16, and 16 mg/L for the four treatments. respectively. Nitrate-N concentrations in 1990, following three dry years, were 3X higher than in 1993 - the fourth consecutive wet year. Corn yields were highest for the split treatment and lowest for fall applicarion without nitrapyrin. Yields were increased significantly in the very wet years by the addition of nitrapyrin to the fall application (Randall and Vetsch, 1995).

Split application of N does not always result in increased N efficiency and reduced nitrate losses. Baker and Melvin (1994) reported losses of nitrate-N to be higher for split application compared to a preplant application for continuous corn. Losses with split application for the corn-soybean rotation were lower in the year of application but tended to be higher in the following year when soybeans followed corn. Based on the data from these studies. fertilizer N management, particularly rate and time of application. plays a dominant role in the loss of nitrate-N to surface waters.

Steps Towards hlinimizing Nitrate-N Loss to Surface Waters

- 1) The most obvious but least economical way to reduce nitrate-N losses to surface water would be to abandon subsurface tile and surface ditch drainage systems. The reality of this measure is not likely. however, as crop production on millions of acres of poorly drained soils in the Corn Belt would be reduced markedly.
- 2) An alternative to present tile discharge systems would be to construct wetland restoration areas or denitrifying ponds where drainage water could be routed/"treated" to remove excess concentrations of nitrate before discharge into drainage ditches or rivers. This may be a cost-effective practice in strategic portions of drainage watersheds.
- 3) Fine-tune fertilizer N management. Applying the correct rate of N at the optimum time has been shown to have a substantial effect on nitrate-N losses.
- 4) Development of improved soil N testing methods to determine the availability of mineralizable N and carryover N from the previous crop would be helpful, especially following dry years, legumes. or past manure applications.
- **5)** Alternative cropping systems that contain perennial crops would also likely reduce nitrate-N losses. However, obtaining a market and a satisfaclory economic return are obstacles facing farmers at the present time.
- 6) Improved management of animal manure would help lower nitrate-N losses in livestock producing areas. Knowing the nutrient content and application rate of the manure. spreading it uniformly. and incorporating it in a timely manner would all lead to better management and confidence in manure N as a nutrient source.

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