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Anthropogenic Inputs of Nitrogen and Phosphorus and Riverine Export for Illinois, USA

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ABSTRACT

Agricultural nonpoint sources are important contributors of N and P to surface waters. We determined N and P net anthropogenic inputs for Illinois, examining changes during the last 50 yr and linkages to surface water export of N and P. Inputs (fertilizer, atmospheric deposition, and N_2 fixation) were compared to exports (grain export, after accounting for animal and human consumption, plus animal product export) from 1945 through 1998 using state-reported data on fertilizer sales, crop production, and human and animal populations. Large inputs of N were found beginning about 1965, coinciding with increased N fertilizer applications (about 800 000 Mg N yr^{-1}). The N input (about 400 000 Mg N yr^{-1}) was 8.6 million Mg N for the 1979 to 1996 crop years, with a corresponding riverine flux of 4.4 million Mg N (51% of net anthropogenic inputs discharged by rivers). Using literature estimates of field and in-stream denitrification, we could account for nearly all of the missing N in a mass balance. For P, a different pattern was found for state net anthropogenic inputs with a large input from 1965 to 1990, and on average no net inputs since 1990. For rivers, we estimated that 16% of the total N load and 47% of the total P load was from sewage effluent. We estimate that Illinois contributed 15 and 10% of the annual total N and P loads of the Mississippi River, respectively, and that any reduction strategy in Illinois must address agricultural sources.

NONPOINT pollution of surface waters from N and P inputs is well established in the United States, with agricultural and urban activities constituting the major sources (Carpenter et al., 1998). This has lead to widespread eutrophication of surface waters, causing degradation of aquatic ecosystems and problems such as toxic algal blooms, loss of oxygen, fish kills, and loss of biodiversity (Carpenter et al., 1998). Nitrogen also can be a concern in drinking water supplies, due to methemoglobinemia in infants and more recently concerns about linkages to non-Hodgkin's lymphoma (Ward et al., 1996). Nonpoint sources of N and P are difficult to measure and regulate because of the large land areas involved and extreme temporal variability due to weather (Carpenter et al., 1998).

Recently, many efforts have been made to construct N and P balances for watersheds of various sizes in attempts to relate inputs to nonpoint contributions to surface waters (e.g., Jordan and Weller, 1996; Howarth et al., 1996; van Eerdt and Fong, 1998; Bennett et al., 1999; Burkart and James, 1999; Cahoon et al., 1999). These balances have included inputs from row crop agriculture, animal production, human consumption of food, and sewage production. Howarth et al. (1996) related net anthropogenic inputs (the terrestrial nutrient balance) to export by river systems, examining all watersheds that drain into the North Atlantic. They found a strong linear relationship between riverine fluxes of total N and the sum of net anthropogenic inputs (fertilizer application, atmospheric deposition of oxidized N forms, fixation by leguminous crops, and the import/export of N in agricultural products) and that riverine fluxes of N were about 25% of these inputs. Caraco and Cole (1999) developed a simple model that used point source N loading (sewage inputs) combined with fertilizer and NO_y (inorganic oxides of N) deposition for 35 large rivers throughout the world that had a 1000-fold variation in NO_3^-–N export. They found that their model explained NO_3^-–N export well ($r^2 > 0.8$), with about 20% of fertilizer plus NO_y deposition inputs exported in rivers as NO_3^-–N.

These types of studies and improved understanding of nonpoint pollution are needed because human inputs of N and P are greatly increasing worldwide. In a recent synthesis, Vitousek et al. (1997) indicated that humans have doubled the rates of N inputs to terrestrial systems, with input rates still increasing. Much of this increase was estimated to be from fertilizer applications and use of leguminous crops (Vitousek et al., 1997). In forest ecosystems, there is great concern about N saturation, which leads to NO_3^-–N losses in drainage waters (Aber et al., 1998; Fenn et al., 1998). The greatest input of N in these systems is from atmospheric deposition and there is concern when NO_3^-–N concentration in drainage waters reach 0.1 to 1 mg N L^{-1} (Aber et al., 1998). Agricultural lands, on the other hand, are essentially all intentionally N saturated (from fertilizer and N_2 fixation inputs) in order to maximize crop production, leading to NO_3^-–N concentrations >10 mg N L^{-1}, particularly in tile drained areas of the Midwest (David et al., 1997). Tile drainage provides a linkage between agricultural fields and rivers in much of the midwestern Cornbelt. Therefore, in much of the USA, further studies are needed to relate N and P fluxes in agricultural production to riverine fluxes.

Another impact of nonpoint inputs of N and P to large river systems is alterations in the composition and functioning of estuarine and nearshore ecosystems (Vitousek et al., 1997). Increases in N and P carried by the Mississippi River to the Gulf of Mexico have been linked to fertilizer applications in the drainage basin (Turner and Rabalais, 1991). This resulting eutrophication has

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many potential effects on coastal plankton food webs (Turner and Rabalais, 1991, 1994; Turner et al., 1998), including hypoxia (Rabalais et al., 1991) and anoxia episodes.

It is generally found that inputs of N to terrestrial systems exceed riverine export (Howarth et al., 1996; David et al., 1997), leading to surplus or missing N in mass balances. Howarth et al. (1996) and Howarth (1998) proposed that much of this N is lost to the atmosphere by denitrification in the sediments of wetlands, lakes, and rivers. If this hypothesis is correct, then total losses of N from terrestrial systems are even greater than the fluxes of N in large river systems would suggest (Kellman and Hillaire-Marcel, 1998). Much of this loss from N-enriched river systems may be as N_2O (Seitzinger and Kroeze, 1998; McMahon and Dennehy, 1999), which is a greenhouse gas and is important in the breakdown of stratospheric ozone. In-field denitrification also may account for much of the surplus or missing N, and needs to be included in mass balances.

In order to understand these sources and sinks, we have conducted studies linking N and P export to surface waters with agricultural activities both at the field (Gentry et al., 1998) and small watershed scale (David et al., 1997; Xue et al., 1998) in Illinois. Illinois is a predominately agricultural state, dominated by corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr) row crops, with extensive artificial tile drainage in about 4 000 000 ha of the soils in the state (Fausey et al., 1995). Taken together, these factors should lead to high exports of N and P from nonpoint sources in the state to surface waters. However, there have been no estimates made of net anthropogenic N and P inputs and linkages to riverine export for the state of Illinois, an important component of the Mississippi River drainage.

We estimated N and P inputs and outputs, including riverine fluxes, for the state of Illinois. This approach can be used as a heuristic tool in identifying gaps in our knowledge concerning the fate of N and P. Our goal was to examine long-term changes in N and P inputs and outputs, and determine Illinois' current contribution of these nutrients to the Mississippi River. Understanding the role of a large agricultural state such as Illinois in contributing to export of N and P by river systems will help demonstrate the importance of addressing nonpoint pollution by agriculture. As the USEPA begins to look to states to possibly regulate themselves, an approach such as the one used in this study can provide a framework for setting state level priorities in reducing N and P nonpoint sources.

MATERIALS AND METHODS

Terrestrial Nitrogen and Phosphorus Net Anthropogenic Inputs

We used annual Illinois Agricultural Statistics (Illinois Department of Agriculture, 1945–1998) for 1945 through 1998 to estimate agricultural inputs and outputs of N and P. The surface area of Illinois is 146 000 km^2, with approximately 93 000 km^2 of row crop agriculture. Inputs included atmospheric deposition, fertilizer, and N_2 fixation by crops and grasses. Outputs included crop grain and animal product export (in excess of human consumption). Crop grain export was reduced by human and animal consumption, which provided an overall net export of food and feeds from the state.

Values for wet atmospheric deposition were calculated from annual averages of all National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites (three to seven sites each year) in the state from 1980 through 1997 (NADP, 1999), with 1998 estimated using the 1997 value. The average areal NO_3^-–N flux from the NADP sites was then multiplied by the area of the state. Only wet deposition of NO_3^-–N was considered a net input; NH_4^+–N was treated as an internal, recycled flux and not included in our net anthropogenic inputs (Howarth et al., 1996). Dry deposition of HNO_3 and NO_3^-–N was estimated as 70% of wet based on recent estimates from the U.S. Environmental Protection Agency (USEPA) Clean Air Status and Trends Network (CASTNet) of 14 sites in the Mississippi River basin where wet deposition was co-located (G.B. Lawrence, 1999, personal communication). Prior to 1980, we used estimates of national emissions of nitrogen oxides to scale NO_3^-–N deposition in 10 yr intervals from 1940 through 1970 (USEPA, 1999). The average of emissions from 1980 through 1996, a period when emissions were stable, was taken as a baseline (1940 emissions were 31% of this baseline). Because deposition inputs are a minor component of the Illinois N budget, this method is sufficiently accurate. Phosphorus in deposition was not included because the limited data that was available suggested that inputs were small. Wet deposition of PO_4^{3-}–P at Bondville, IL averaged only 0.02 kg P ha^{-1} yr^{-1} for 1995 through 1998 (V. Bowersox, unpublished data).

Fertilizer N and P inputs were derived from annual sales data (July though June basis) in the state of all forms of each fertilizer (Illinois Agricultural Statistics, 1945–1998). Sales include all fertilizer used for agriculture as well as that sold for lawns, golf courses, or gardens. To estimate the current proportion of N fertilizer used for non-agricultural purposes, we used the approximate number of golf courses in Illinois (650) with the average area of greens and tees, fairways, and rough per course (2, 10, and 10 ha, respectively) with their corresponding fertilization rates (244, 195, and 147 kg N ha^{-1} yr^{-1}, respectively) (B. Branham, 1999, personal communication). For lawn N fertilization, we used satellite land cover analysis data (Luman et al., 1995) and assumed all urban grassland and low density urban areas were lawns (356 000 ha) and were fertilized with 97 kg N ha^{-1} yr^{-1} (B. Branham, 1999, personal communication). This amount of N fertilizer would have been included in the fertilizer sales, so it was not additional N added to the state.

Yearly crop production for corn, soybean, wheat (*Triticum aestivum* L.), and oat (*Avena sativa* L.) were from state statistics. Production estimates were corrected for moisture content, and N and P concentrations were used to determine grain N and P contents of each crop for each year. Grain N concentrations were calculated using an average protein concentration in the grain (10, 40, and 12% for corn, soybean, and wheat, respectively) (Sinclair and DeWit, 1975; Smith, 1984) and the average mass ratio of N to grain protein (1:6.25). These values yielded grain N concentrations of 1.6% for corn, 6.4% for soybean, and 1.9% for wheat. For oat, the protein concentration of the groat + hull was estimated at 12.75% for an N concentration of 2.0% (F. Kolb, 1999, personal communication). Average grain P concentrations used were 3.35, 6.75, 3.75, and 4.0% for corn, soybean, wheat, and oat, respectively (Peterson et al., 1975; Smith, 1984; Raboy et al., 1984; Johnson and Mattern, 1987; Mallarino, 1996). To estimate soybean N_2 fixation, we assumed 50% of the aboveground N in the plants was from N_2 fixation (Johnson et al., 1975; Harper, 1987).

Uptake of N into the nongrain aboveground portions of the soybean plant were estimated using an N harvest index of 80% (Crafts-Brandner et al., 1984). Belowground biomass of both corn and soybean was not considered in our net inputs, and was assumed to mineralize each year, having no major effect on our budgets. This estimate follows our previous approach for soybean and belowground transfers (David et al., 1997). Nonsoybean N_2 fixation was estimated at 218 kg N ha^{-1} yr^{-1} for alfalfa (*Medicago sativa* L.), 116 kg N ha^{-1} yr^{-1} for other N_2-fixing grasses, and 15 kg N ha^{-1} yr^{-1} for pasture (Jordan and Weller, 1996). Land in alfalfa and other N-fixing grasses was from the Illinois Agricultural Statistics (1945–1998) and pasture land was calculated as the difference between total farm area minus row crops, alfalfa, and other hay (this area has steadily decreased from 49 000 km^2 in 1945 to 18 000 km^2 in 1998).

Human consumption of food was estimated from yearly U.S. Census Bureau population data for Illinois, combined with per capita consumption of N and P in food. The per capita estimates were made using nutritional data by human age classes for protein and P (Interagency Board for Nutrition Monitoring and Related Research, 1995) and assuming the mass ratio of N to protein is 1:6.25. Census data by age class in 1996 for Illinois were combined with the nutritional data, which provided per capita values of 4.53 and 0.46 kg yr^{-1} of N and P consumed, respectively, for the population of Illinois. These per capita values were then used with census population data for 1945 through 1998.

Animal consumption and manure N and P fluxes were calculated using annual average counts of dairy cows, cattle, hogs, chickens, and turkeys on Illinois farms from the Illinois Agricultural Statistics (1945–1998), along with N and P consumption in animal feed and production of manure. The manure estimates do not enter into the overall N and P net inputs, but are useful in comparison with other fluxes. Data on both intake of N and P and excretion was from Van Horn et al. (1996) for dairy cows and from Thomas and Gilliam (1977) for chickens, turkeys, and cattle. For manure production by hogs, Soil Conservation Service (1992) data were used and combined with Thomas and Gilliam's (1977) data on animal product N and P to estimate intake. Dairy cows and cattle also were assumed to obtain part of their diets from hay and grazing and part from grain (food concentrates). We used values for the percentage of the grain in their total diet of 25% for cattle and 40% for dairy cows (Jordan and Weller, 1996; D. Faulkner, 1999, personal communication). All hay produced in Illinois was assumed to be used for animal production, and the remaining N and P demand was assumed to be from grazing (Jordan and Weller, 1996).

Overall net anthropogenic inputs of N and P were calculated as inputs (fertilizer, deposition, N_2 fixation) minus outputs (net grain export of N or P, animal product export). Net grain export was calculated as total grain N and P, minus the amounts consumed by humans or animals in the state, following procedures of Howarth et al. (1996).

Table 1. River systems, location and station number of discharge and water quality data, drainage area, and fraction of drainage area in Illinois used in estimating export of N and P by surface waters from Illinois.

River system	Gage location	Station number†	Drainage area	Fraction in Illinois
			km^2	%
Big Muddy	Murphysboro	05599500	5 618	100
Embarras	Ste. Marie	03345500	3 926	100
Illinois	Valley City	05586100	69 264	93
Kaskaskia	Venedy Station	05594100	11 378	100
Little Wabash	Carmi	03381500	8 034	100
Rock	Joslin	05446500	24 732	46

† U.S. Geological Survey unique identification number.

Surface Water Nitrogen and Phosphorus Loads

Export of total N and P for all surface waters in Illinois to the Mississippi River was estimated for the 1979 through 1997 water years. Daily flow data from USGS gaging stations on the six major river systems in the state (USGS, 1999; Table 1) were combined with Illinois Environmental Protection Agency water quality data (NO_3^-–N, total N, and total P) to estimate daily and yearly loads. Water quality data were collected every six weeks during this period, and daily values were estimated by linear interpolation (expand procedure, SAS Institute, 1993). The method used connects successive water quality values with straight lines (a linear spline). Because these rivers are generally large with slow day-to-day changes in flow, this approach was used rather than relating concentration to discharge, because we found generally poor discharge/concentration relationships. This problem is probably due to large year-to-year variation in the concentrations of N and P in many surface waters of Illinois, as we observed in the upper Embarras River (David et al., 1997). Our values for the Illinois River differed only 3% from estimates made by Lurry and Dunn (1997), who used discharge/concentration relationships. The six rivers accounted for 72% of the state's surface area (after drainage areas outside of Illinois were removed for two of the rivers). Because the six river basins were well distributed throughout the state, we assumed that these rivers were representative of the missing area and multiplied their total export by a factor of 1.4. Organic and NH_4^+–N were not available for the Embarras River, so the average of the two other river systems with similar NO_3^-–N loads were used (Rock and Illinois Rivers) to estimate these N forms and therefore total N (i.e., 73% of total N was as NO_3^-–N in the Embarras River).

We compared our yearly estimates of N and P export by Illinois rivers with the load in the Mississippi River at the southern tip of Illinois, at a point that would include the inputs from the Ohio River. We used flow and N and P concentration data for the Mississippi River at Thebes (calculated as described above for the rivers in Illinois) and added to them the yearly load in the Ohio River at Metropolis, IL, calculated by Lurry and Dunn (1997) for 1979 through 1994 and by us for 1995 through 1997 using the same data sources and techniques as described above.

Sewage effluent also was estimated for the state based on annual population data (U.S. Census Bureau) and calculated per capita N and P values from treatment plants. We used an estimate that 87.7% of the state population was sewered (Van der Leeden et al., 1990) and that the effluent was a direct input into surface waters. Per capita sewage N and P values were estimated from monthly 1998 data for the Urbana–Champaign Sanitary District (T. Bachman, 1999, personal communication) and from 1997 and 1998 data for the Metropolitan Water Reclamation District of Greater Chicago (C. Lue-Hing, 1999, personal communication). Two plants serve 126 000 people in Urbana–Champaign and include some industrial inputs. We obtained annual average flow weighted values of 3.1 kg N yr^{-1} and 0.52 kg P yr^{-1} per capita leaving the plants. One of the two plants removes P, which lowered the per capita export to 0.14 kg P yr^{-1}, whereas the other does not, so the per capita loss was 0.7 kg P yr^{-1}. For Chicago, we obtained monthly data from three plants that serve 4.5 million people (38% of the population of the state) and include a large industrial base. Annual per capita values were 4.37 and

0.63 kg yr^{-1} of N and P, respectively, which were higher than the Urbana–Champaign plants for N, and similar for P to the plant that does not have removal technology. In our calculations we used per capita values from the Chicago plants for both N and P for the 64% of the population living in northeastern Illinois. For the remaining 36% of the Illinois population we used Urbana–Champaign average values of N and the higher P value (0.7 kg P yr^{-1}).

Howarth et al. (1996) used an annual N per capita value of 3.3 kg N yr^{-1}, lower than the Chicago plants. Terrio (1995) included an estimate that 23 600 and 4900 Mg of total N and P, respectively, were discharged annually to streams as sewage effluent in the upper Illinois River basin, based on 1988 Chicago treatment plant fluxes. Using the 1988 population of the six Illinois counties in this area (7.2 million people), per capita values of 3.3 and 0.68 kg yr^{-1} of N and P, respectively, were obtained from the Terrio (1995) discharge values. All of these estimates for P were similar and suggest that sewage effluent P export per capita has: (i) not changed recently and (ii) can be estimated accurately by using average per capita values and the population estimates of an area. For N, per capita values for Chicago treatment plants for 1997 and 1998 were higher than other estimates. We used these higher values to be conservative and not underestimate the contribution of sewage effluent to Illinois surface waters in the northeastern area of the state.

Potential Errors and Limitations of Data

This type of N and P budgeting and mass balance approach is subject to many assumptions and limitations in the available data. On the input side, fertilizer inputs from sales data are well documented and are the largest and best known input. For N, N_2 fixation is the second most important input and this estimate is uncertain. Rates of N_2 fixation are highly variable from year-to-year and there are many values in the literature (NRC, 1993). Rather than use a range of values, as was done by the NRC (1993), we used typical or average values from the literature and adjusted them for actual yields. However, in a given year these values could be substantially off and therefore we regard N_2 fixation as the input with the largest degree of uncertainty. Deposition is the other input for N and wet deposition is measured at many sites in Illinois. Dry deposition is much more variable, but due to the magnitude of this input compared with fertilizer and N_2 fixation, any errors would be of minor consequence.

Outputs in grain can be estimated well from literature values of N and P concentrations and state values of measured grain harvest. Although year-to-year effects from growing season weather and differences in varieties can affect N and P concentrations, we believe these estimates to be accurate on the scale of a state-level analysis. Animal and human consumption can be accurately estimated from numbers of animals or people and typical food consumption. Sewage data were calculated from several plants in the state that included a large percentage of the population and therefore should be representative of the entire state.

For riverine loads, values were calculated from daily river flow and concentration data collected on a 6 wk basis. Unfortunately, as for most studies of this type, more intensive data were not available. Therefore, storm discharges may have been underestimated, particularly for particulate forms of nutrients. We assume that our load calculations are conservative, and that actual export may be somewhat higher, particularly for P. However, as discussed previously, this is less of a problem for the larger river systems included in our analysis.

Finally, we used literature estimates for processes such as denitrification. This important loss of N is not well measured, and our estimated large flux rates through this process document the need for improved measurements and methods for estimating denitrification loss of N from soils and surface waters.

Although many of the values we used were estimates from the literature and are subject to large errors and uncertainty, taken together we believe we have a good representation of the N and P balances in the state, and how they relate to riverine export. In addition, a long-term analysis such as we have calculated here helps to reduce the variability that may occur in one year. Finally, this type of analysis indicates where we need further study and measurements to reduce errors in important fluxes.

RESULTS AND DISCUSSION

State Nitrogen Net Anthropogenic Inputs—Long Term Trends

Nitrogen fertilizer use in Illinois began following World War II and increased greatly through the 1960s and 1970s, where it has since leveled off at about 850 000 Mg N yr^{-1} (Fig. 1). Fertilizer N use is now the largest input of N to the state (~60% of total inputs), with N_2 fixation second (~35%) and deposition (~5%) a small component of total inputs. In the 1940s fertilizer was <1% of N inputs, with most (89%) from N_2 fixation. As was typical of agriculture in the USA, there was a change from manure applications and crop rotation of legumes as sources of N to applications of inorganic N fertilizer. The plant species responsible for N_2 fixation also have changed, with soybean increasing during this time from about 25% of the total N_2 fixation in 1945 to 80% in 1998. We estimated that N fertilizer used by golf courses and for lawns was 2600 and 34 800 Mg N yr^{-1} for the state, or about 0.3 and 3.9% of total fertilizer sales, respectively. This is no doubt an overestimate, because it assumes that all urban grassland is fertilized each year, but demonstrates that agricultural use of N fertilizer is the dominant use. In addition, we would expect that N losses from golf courses and lawns to be less than agricultural land, due to the permanent nature of the vegetation and use of multiple small applications each year. Indeed, Gold et al. (1990) found that fertilized lawn treatments caused small losses of N compared with losses from septic systems and corn production, supporting these conclusions. In addition, a recent review by Cohen et al. (1999) also found little effect of golf courses on surface water quality.

In the 1940s, much of grain N produced in Illinois was eaten by animals or humans in-state (~80% of grain N), which has deceased to about 11% in the 1990s (Fig. 1). States such as Illinois are able to now export large amounts of grain, which removes a large amount of the N added to the state each year. Animal and human consumption therefore are currently a small part of the Illinois N budget, due to the decreasing populations of animals and low human population compared with the amount of agricultural production in the state. The major grain crops also have changed during the last 50 yr, from a more diverse rotation that included oat and

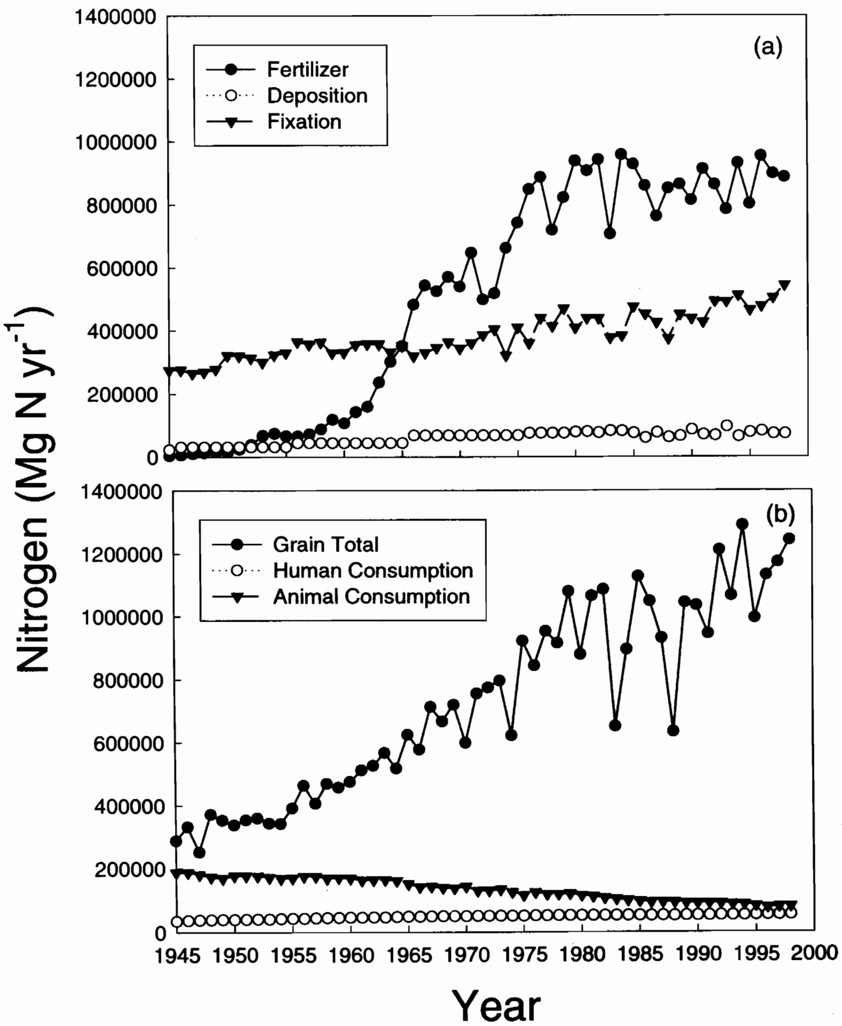

Fig. 1. Annual N (*a*) inputs from fertilizer N, atmospheric deposition of wet and dry oxidized N, N_2 fixation and (*b*) N removals as harvested N in grain and human and animal consumption of grain N in Illinois from 1945 through 1998.

wheat to one that is dominated by corn and soybean (Fig. 2).

These changes in inputs and outputs of N have led to large, but variable, net inputs (or surpluses) of N each year (Fig. 2). The net anthropogenic inputs were greatest during the 1980s, and are currently about 400 000 Mg N each year. Large net N inputs were generated during poor crop years, such as the drought years of 1983 and 1988. Part of the N that is retained in Illinois from crop production is returned as animal manure or sewage effluent (Fig. 2). Animal manure flux of N has steadily decreased from the 1940s, whereas sewage effluent has increased with the population of the state (from 7.6 million in 1945 to 12 million in 1998), although sewage effluent N is small in comparison with other N fluxes.

Other recent studies on N balances also have found large net inputs to terrestrial ecosystems using similar approaches (Jordan and Weller, 1996; Howarth et al., 1996; Jordan et al., 1997). A study using 1987 crop data for the entire USA found a large surplus of N, with Illinois one of the states with the largest surplus (NRC, 1993). Illinois ranked from first to third nationally in the size of the balance, depending on the N_2 fixation rate used. The balance the NRC (1993) estimated for Illinois ranged from 402 000 to 597 000 Mg of N for 1987, and our estimate of 430 000 Mg N for 1987 is within their values.

State Phosphorus Net Anthropogenic Inputs—Long Term Trends

State P net anthropogenic inputs are not similar to N, suggesting that each fertilizer must be examined independently. Phosphorus fertilizer use did follow that of N, however, with large increases through the 1960s and 1970s, reaching a peak of 233 000 Mg of P in 1977 (Fig. 3). Recent P applications (1987 to 1998) are approximately 160 000 Mg P, about 75% of peak application rates. Phosphorus harvested in grain also has increased with increasing fertilization since 1945, with most of the grain P currently in corn and soybean (Fig. 4).

Interestingly, net anthropogenic P inputs were approximately zero in the 1940s and 1950s, as it was again recently (1990s) (Fig. 4). In the 1940s net P inputs were zero because the limited fertilizer application was appar-

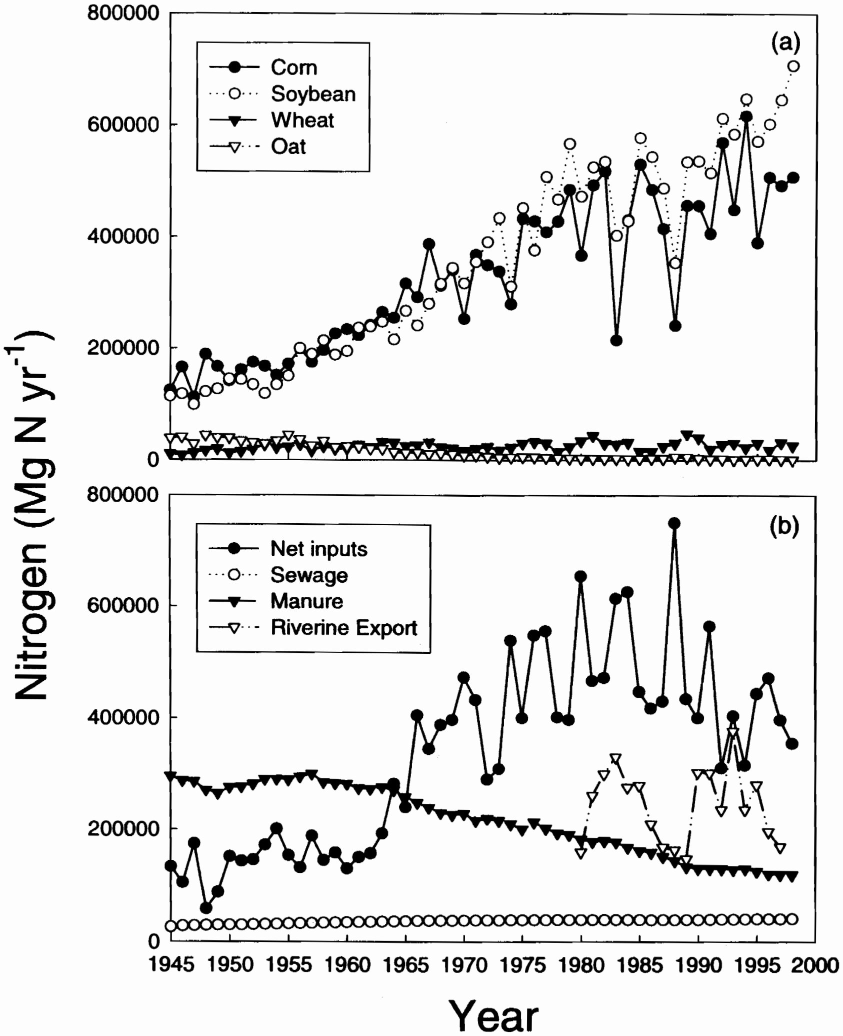

Fig. 2. Annual (*a*) grain N in corn, soybean, wheat, and oat and (*b*) the net anthropogenic inputs (sum of fertilizer + deposition + N_2 fixation minus net export of grain N), sewage effluent discharge of N, manure N, and total export by all Illinois rivers of total N in Illinois from 1945 through 1998.

ently taken up by crops, which were then eaten by animals. The manure closed the cycle in that P was reapplied to the land. The recent P cycle is balanced because fertilization has decreased to the point where it matches that of net grain export. However, during the last 50 yr there was a 25 yr period where the net inputs would indicate that large surpluses must have accumulated. The cumulative net P inputs for 1945 to 1998 suggests a surplus of 2.2 million Mg of P, or about 230 kg P ha^{-1} of row crop area in the state. Most of this P is still likely found in Illinois soils, although it may not be evenly distributed.

Riverine Flux of Nitrogen and Phosphorus

Export of N and P by all Illinois rivers was estimated for the 1980 through 1997 water years (Fig. 2 and 4). The average total N load for Illinois rivers was 244 000 Mg N yr^{-1}, and for total P was 14 200 Mg P yr^{-1} (Table 2). Yearly loads of N were mostly affected by water flux (driven by precipitation), which tends to obscure direct linkages to the N balance (Lucey and Goolsby, 1993; David et al., 1997). There were no apparent trends in loads of N or P during this time period. The large flux of N by rivers in 1993 was similar to the net N inputs for 1992 and 1993. However, this large flux of N followed some of the highest positive net inputs found in our analysis and may represent delayed export of NO_3^-–N by large amounts of precipitation in the 1993 water year. Keeney and DeLuca (1993) and David et al. (1997) found similar relationships for NO_3^-–N export and N balances for smaller watersheds.

Estimated average total N flux for each of the major river systems in Illinois varied from as little as 5 kg N ha^{-1} yr^{-1} (Big Muddy River) to as much as 24 kg N ha^{-1} yr^{-1} (Embarras River) (Fig. 5). For the state as a whole, the average flux was 17 kg N ha^{-1} yr^{-1} for the 18-yr period. The fraction of NO_3^-–N of total N in surface waters was 72% for all systems, and ranged from 32% in the Big Muddy River to 77% in the Illinois River. There was a major difference in both total N flux and percentage of NO_3^-–N of total N among the six river systems. The Illinois and Rock had the largest N fluxes with most of their N as NO_3^-–N (69–77%),

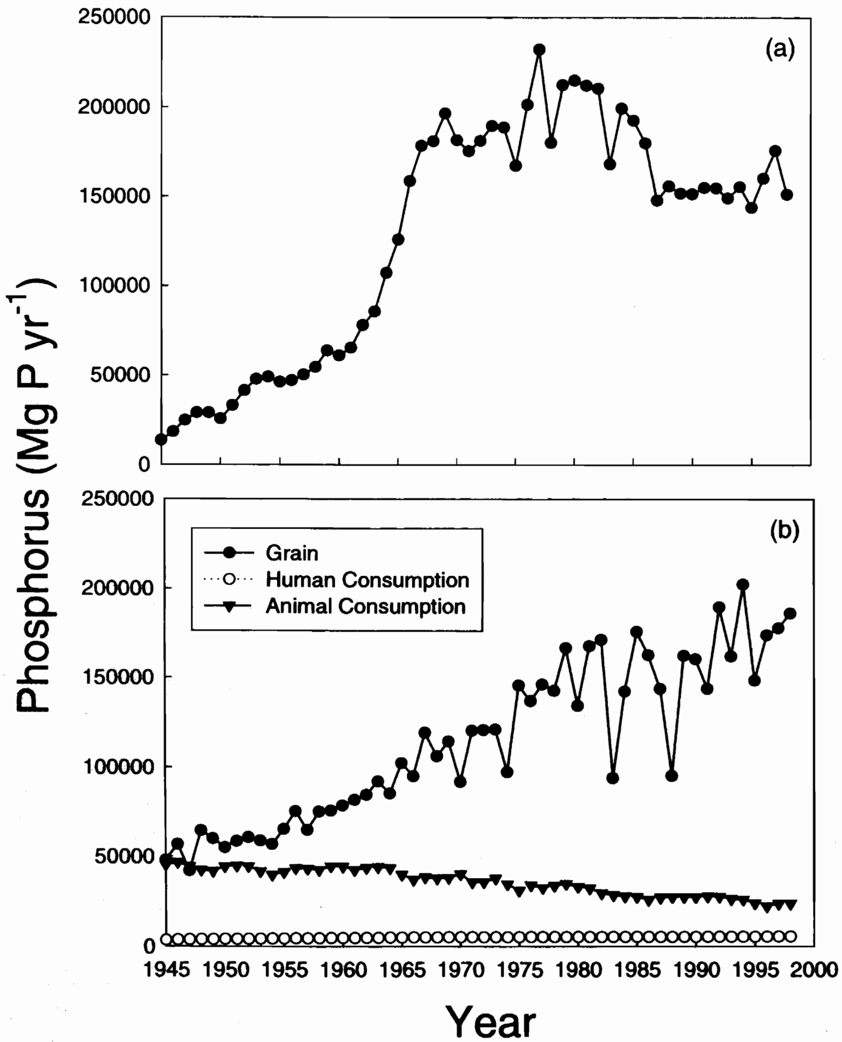

Fig. 3. Annual (*a*) fertilizer P and (*b*) harvested P in grain and human and animal consumption of grain P in Illinois from 1945 through 1998.

whereas the Little Wabash, Kaskaskia, and Big Muddy had smaller fluxes of total N and only 32 to 51% of total N as NO_3^-–N. We believe that these differences in NO_3^-–N as a percent of the N load were due to variation in in-stream denitrification, which is discussed later. However, the amount of tile drainage in each watershed also could affect the loss of N to rivers, with more intensively tile drained watersheds having larger fluxes of N.

Phosphorus fluxes were generally uniform for the six river systems (Fig. 5), ranging from 0.7 to 1.1 kg P ha^{-1} yr^{-1}, with 38% of total P in dissolved forms and 62% in particulate forms. For all surface waters in the state the flux was 1.0 kg ha^{-1} yr^{-1}, with 46% of total P in dissolved forms. However, because we used concentration data collected every 6 wk, we may have underestimated losses of particulate P (Jordan et al., 1986). This underestimate would likely be more of a concern in the small watersheds of our study (Embarras, Big Muddy) that had more variability in discharge, compared with the larger systems. Therefore, we consider our riverine export flux calculations to be minimum estimates.

We compared our estimated annual streamflow and export of N and P from all Illinois rivers with the load of the Mississippi River at several locations (Table 2). To obtain an estimate of N and P loads in the Mississippi at the southern tip of Illinois, we summed the loads of the Ohio River at Metropolis and the Mississippi at Thebes. No other sizable tributaries are found between these stations and the Ohio and Mississippi Rivers confluence. For the 1980 to 1997 water years we estimated average loads of 1 374 000 and 117 000 Mg N and P, respectively, in the Mississippi River. The contribution of Illinois rivers to the total Mississippi load was 18 and 12% for N and P, respectively. For streamflow, Illinois was estimated to contribute 9.6% of the flow, demonstrating a disproportionate contribution of N and P. The first gaged site on the Mississippi River below where the Ohio River enters was at Memphis, TN. Loads and streamflow estimated by Lurry and Dunn (1997) compared well with our combined Ohio and Mississippi River estimates.

Dunn (1996) calculated the total load of N and P exported to the Gulf of Mexico by the Mississippi River by summing the Mississippi and Atchafalaya Rivers, because the latter has about 1/3 of the Mississippi River

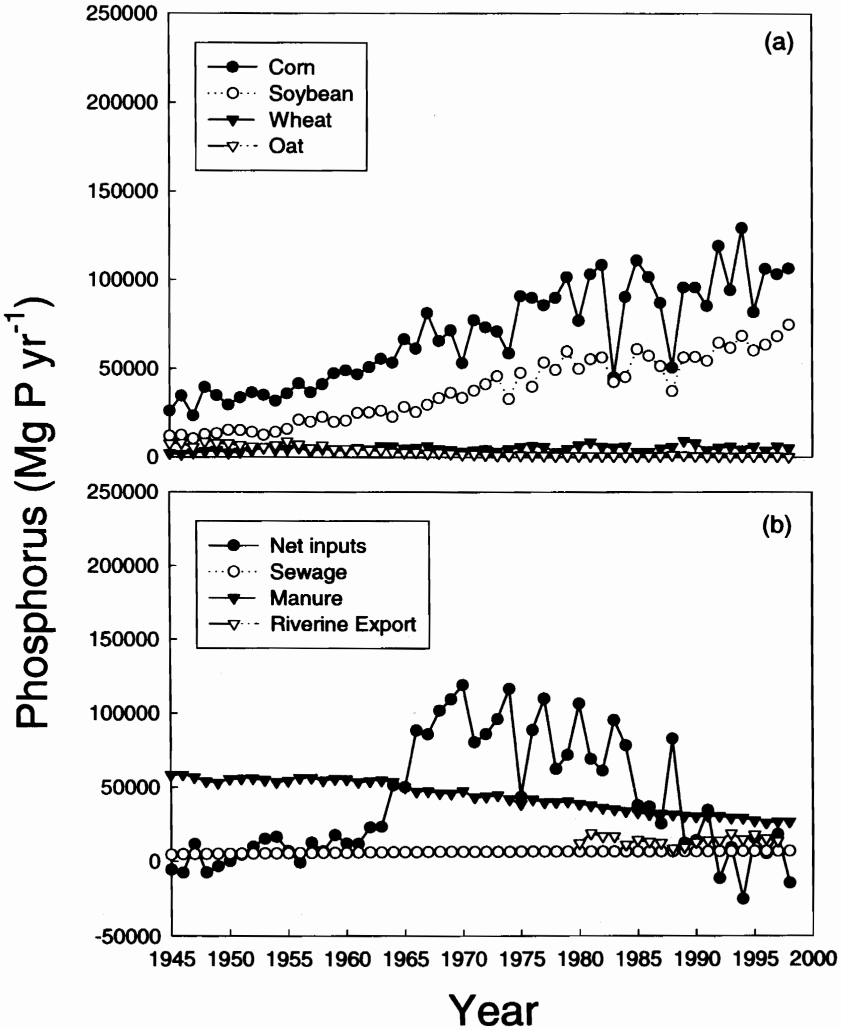

Fig. 4. Annual (*a*) grain P in corn, soybean, wheat, and oat and (*b*) the net anthropogenic inputs (fertilizer minus net export of grain P), sewage effluent discharge of P, manure P, and total export by all Illinois rivers of total P in Illinois from 1945 through 1998.

discharge diverted into it (Turner and Rabalais, 1991). Therefore, the sum of N and P fluxes from both rivers can be used to estimate total fluxes to the Gulf of Mexico by the Mississippi River drainage. For the entire Mississippi drainage area, Illinois contributed 15 and 10% of the annual total N and P loads, respectively, but only 6.7% of the streamflow.

An important direct input of N and P to surface waters is sewage effluent. Howarth et al. (1996) estimated that for all North America basins an average of 12% of the total N load was as sewage, with about 9% for the Mississippi River basin. Our estimate was that 16% of the total N and 47% of the total P loads in Illinois rivers were from sewage for 1980 through 1997. For N, this amount is greater than the estimates from Howarth et al. (1996), probably because of the effect of the Chicago metropolitan area, where 64% of the population in the state is found. We estimated that 21% of the Illinois River N load was from sewage effluent, compared with 14% for other rivers in the state. For P, estimates of the sewage effluent contribution to river export were 70% for the Illinois River and 33% for all other rivers in the state. This suggests that for a river with a large population that discharges sewage effluent into it (such as the Illinois River), about one-fifth of the N and two-thirds of the P was from effluent. However, in less-populated areas dominated by agriculture, such as

Table 2. Mean annual total N and total P loads for the sum of Illinois River systems and selected comparison sites in the Mississippi River system.

Location	Water years of record	Mean annual streamflow	Total N load	Total P load
		10^9 m^3 yr^{-1}	— 10^3 Mg yr^{-1} —	
Illinois Rivers	1980–1997	47	244	14.2
Mississippi River —Thebes, IL	1980–1997	217	830	70.2
Ohio River —Metropolis, IL	1980–1997	270	544	46.6
Sum of Mississippi & Ohio Rivers	1980–1997	487	1374	117
Mississippi River —Memphis, TN†	1974–1994	504	1379	113
Mississippi River‡	1978–1993	488	1216	102
Atchafalaya River‡	1978–1993	210	430	43.4
Sum	1978–1993	698	1646	145

† From Lurry and Dunn (1997).
‡ From Dunn (1996).

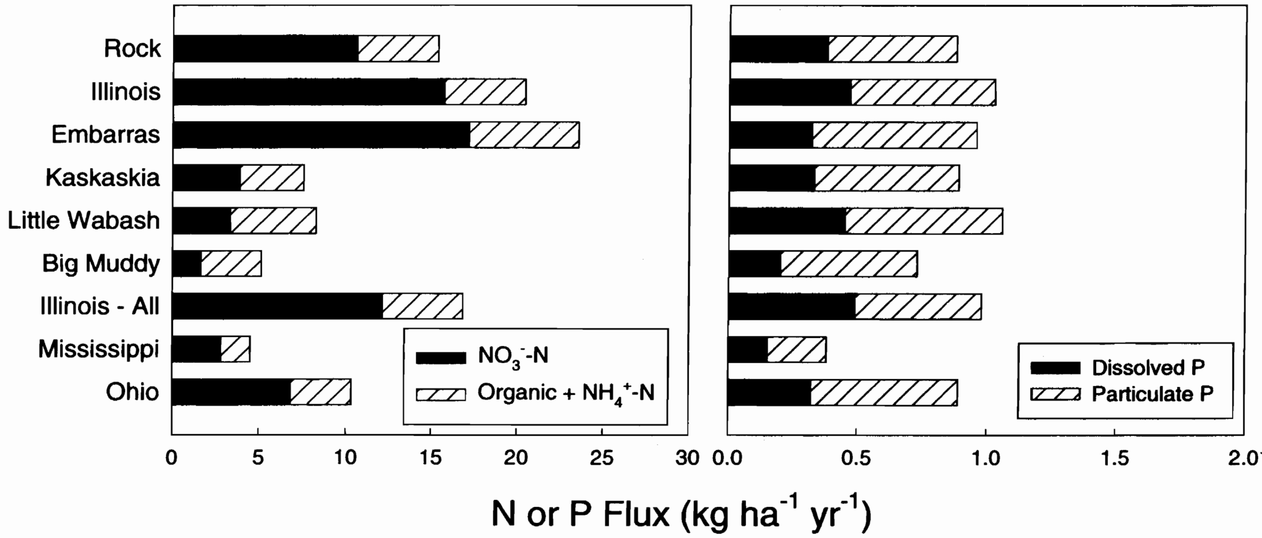

Fig. 5. Average annual total N and P flux of the six major river systems in Illinois from 1980 to 1997, the overall average for the state, and the Ohio (at Metropolis, IL) and Mississippi (at Thebes, IL) Rivers included for comparison. Also shown is the fraction of total N as NO_3^-–N and organic N + NH_4^+–N and fraction of total P in dissolved and particulate forms.

northwestern, central, and southern Illinois, we estimated that about 86% of the N and 67% of the total P were from agricultural surface runoff and subsurface tile drainage flow. Recently Xue et al. (1998) found that relatively large amounts of P can be transported through tile drainage in central Illinois and that this may be an important loss of P from soils in addition to surface runoff.

Manure N and P is decreasing, but was still an important transfer of N and P in the state (Fig. 2 and 4). Amounts of N and P generated in raw manure are still much greater than sewage effluent N and P fluxes. However, manure is applied to the land following handling where about 50% of the N is probably lost as NH_3 (Jordan and Weller, 1996), versus the direct input of sewage effluent into rivers. Most of this N and P is probably taken up either by row crops or by grasses in pasture lands and therefore is not thought to be an important input to Illinois surface waters.

Another way of comparing the relative importance of an agricultural state such as Illinois with others in the region or to other large regions is to compare net anthropogenic inputs for a drainage basin with the riverine flux. Howarth et al. (1996) used this approach for all drainages that enter the North Atlantic Ocean and we added our estimate for Illinois to this figure (Fig. 6). Howarth et al. (1996) found a strong linear relationship between net inputs and riverine flux, with about 20% of net inputs found as riverine export each year. Treating Illinois as a watershed led to a net anthropogenic input (average of 32 kg N ha^{-1} yr^{-1} for 1980 to 1997) similar to most other regions, but a substantially higher export flux of N (average of 17 kg N ha^{-1} yr^{-1} for 1980 to 1997), or about 51% of net inputs. However, the range in both the net anthropogenic inputs and riverine flux demonstrates that any given year could have a very different value. This analysis also suggests how all subwatersheds in a region do not contribute N evenly. The Mississippi River drainage had an overall net anthropogenic input of 22 kg N ha^{-1} yr^{-1} and a riverine flux of about 5 kg N ha^{-1} yr^{-1}, 22% of inputs (Howarth et al., 1996). Our estimates for N flux from Illinois surface waters are therefore much greater than the overall Mississippi basin, as our analysis has shown for N as well as P (Fig. 5). The average 51% of net inputs exported by surface waters is also much greater than other intensively studied regions, such as the Chesapeake Bay basin, where Jordan et al. (1997) found that most subwatersheds discharged between 15 and 30% of net inputs. This makes sense however, in that Illinois has a much greater percentage of land area in intensive agriculture with extensive areas of tile drainage that can lead to high NO_3^-–N losses than the Mississippi basin as a whole, or the Chesapeake Bay basin.

We also applied the Caraco and Cole (1999) model to our summary data for 1980 through 1997. This model adds sewage inputs to a fraction (watershed export coefficient) of fertilizer and NO_y inputs to determine river export of NO_3^-–N, with the fraction a function of runoff. They found that with increasing runoff more of the inputs were found as river exports. With our estimated runoff of 0.32 m for the state, the fraction of fertilizer and deposition NO_3^-–N inputs that the Caraco and Cole (1999) model would estimate in river export was 16%. Combined with sewage inputs, we therefore obtained an estimated river export of 912 kg NO_3^-–N km^{-2} yr^{-1} for the state of Illinois using their model, compared with the actual river export of 876 kg NO_3^-–N km^{-2} yr^{-1}. This suggests that their model provided an excellent fit to our NO_3^-–N river export data and that knowing only sewage, fertilizer, and deposition inputs can provide a good estimate of the average NO_3^-–N load in a river, when runoff is used to adjust the loss rates. Grain harvest, N_2 fixation, and manure production are not needed in this approach.

Caraco and Cole (1999) suggest that two reasons their hydrologically dominated model works across variable watersheds is because some inputs affect organic N export more (e.g., N_2 fixation) and that many factors important on a plot or small watershed are not important

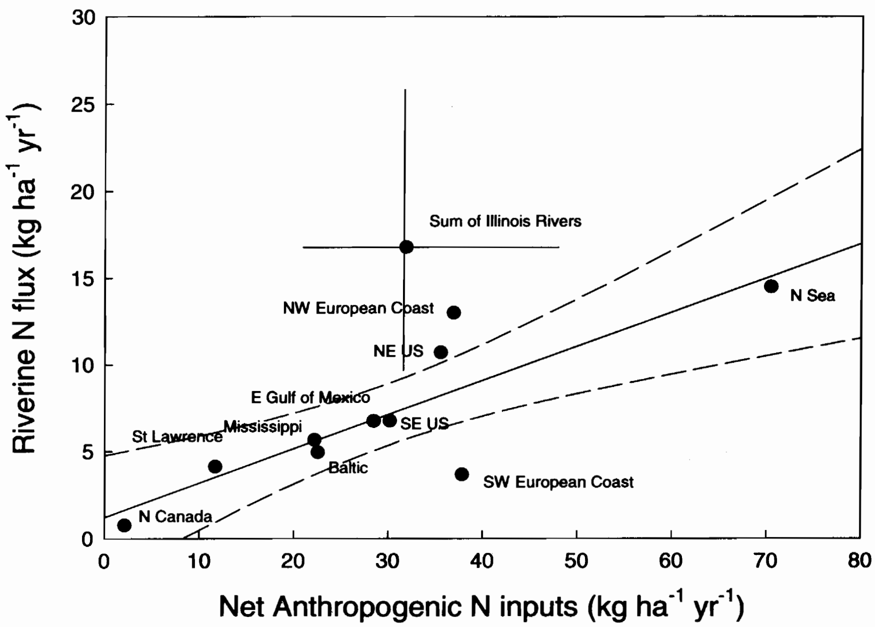

Fig. 6. Net anthropogenic N inputs (sum of anthropogenic N deposition, fertilizer, N_2 fixation by crops, and net import or export of N in food and feed) compared with riverine N flux for all basins that drain into the North Atlantic (adapted from Howarth et al., 1996) and Illinois (mean of 1980 through 1997) considered as one basin. The lines through the Illinois point represent the range found in the 18-yr period of data used.

on a regional scale. This model may work well for Illinois because it does account for larger exports of water to surface waters due to tile drainage, through the watershed export coefficient. In addition, when average data are used from many years, the effects of outputs such as harvest export and denitrification are reduced. These outputs tend to vary greatly from year-to-year and can influence the N balance and also lead to differences in NO_3^-–N export by rivers. The Howarth et al. (1996) approach did not work well compared with the Caraco and Cole (1999) model, even though we did use the same summary period of average data for Illinois. The major difference between the two models is the use of net inputs by Howarth et al. (1996), versus gross inputs with an adjustment for hydrology by Caraco and Cole (1999).

Fate of Missing Nitrogen and Phosphorus

We cannot account for all of the net anthropogenic inputs of N and P summed for 1979 through 1996 (Table 3). For N, the net input was estimated at greater than 8.6 million Mg N, compared with a corresponding riverine export of 4.4 million Mg N. This leaves 4.2 million Mg N of net inputs unaccounted for. Most net input calculations of N by other researchers have had similar pools that could not be accounted for (e.g., Jordan and Weller, 1996; Howarth et al., 1996). Although there are many possible ways to account for this missing N, we believe the most likely fate is denitrification, both of NO_3^-–N in fields and from in-stream processing. If we use an estimate of 10% of fertilizer and 35% of N in the riverine flux (from Howarth et al., 1996) denitrified during an average year, our N sources balance our sinks within 2%. This approach seems reasonable based on several points. First, from field and laboratory studies denitrification is known to be an important loss of N following fertilization (e.g., Parkin et al., 1987; Seech and Beauchamp, 1988; Mulvaney et al., 1997). It is extremely variable in space due to *hot spots* (Parkin et al., 1987) and time due to rainfall events (Sexstone et al., 1985). Therefore, we know that field denitrification losses vary greatly from field-to-field and year-to-year. Our estimate of 10% for 18 yr of record no doubt underestimates some years and overestimates others, but the long-term nature of our approach hopefully reduces the importance of temporal variability and reflects the importance of this N sink. Second, Howarth et al. (1996) used various approaches to estimate river denitrification at 20% of N flux and lake or reservoir losses at 50%. These seem to make sense based on our six river systems in Illinois. Two of the three river systems with the lowest NO_3^-–N fluxes (Big Muddy and Kaskaskia Rivers) have major reservoirs in their drainage basins, which could greatly reduce NO_3^-–N concentrations and flux rates. Third, and finally, other potential sinks for this surplus N seem unlikely, and below are discussed further.

Changes in soil N pools could affect our N balances, if mineralization and immobilization rates are not equal during various time periods (Aldrich, 1980). We did

Table 3. Summary N and P additions for Illinois from 1979 to 1996 and 1980 through 1997 water years for losses.

Source	Total N	Total P
	Mg N	Mg P
Additions of N		
Net anthropogenic inputs	8 574 000	739 000
Losses of N		
Riverine flux	4 395 000	255 000
Fertilizer denitrification†	1 560 000	
In-stream denitrification‡	2 370 000	
Sum of losses	8 321 000 (97% of net inputs)	255 000 (35% of net inputs)

† Estimated as 10% of fertilizer application.
‡ Estimated at 35% of river N load (from Howarth et al., 1996).

not include estimates of these rates, because they are extremely variable and not known on a yearly basis. Instead we assumed that no major changes have occurred in soil N pools, which would suggest that mineralization rates equal immobilization. For the 18-yr period of our riverine flux and N surplus comparison, we have no evidence nor data to make alternate assumptions. Recently, Drinkwater et al. (1998) found no significant changes in soil N pools of a conventional corn and soybean rotation during a 15-yr period. This is the type of production system used in Illinois and supports our approach. However, to demonstrate the magnitude of N change needed in agricultural soils, we can divide the surplus N by the ha of row crops in the state, which gives a value of 451 kg N ha^{-1} for the 18 yr, or 25 kg N ha^{-1} yr^{-1}. Given that N pools in agricultural soils range from 2000 to 10 000 kg ha^{-1} down to 1.5 m, it is possible that some of the added N accumulated as organic N forms in the soils, which would be difficult to measure. More studies such as that conducted by Drinkwater et al. (1998) are needed to help establish bounds on this potential sink or source of N.

Another potential sink is volatilization of N from plant tissues (Francis et al., 1993). However, more recent work by Francis et al. (1997) suggests that NH_3 is lost and gained from corn foliage during the reproductive period, but is not thought to be a net sink to the atmosphere. At various times the corn foliage may be actively gaining and losing NH_3, but the net result is no loss from the plant/soil system. Therefore, we did not include plant volatilization as a net loss of N from the state of Illinois.

For P, a different fate of the missing P is hypothesized. The long-term P balance shown previously for Illinois suggests a P input and output balance in the 1940s through 1960s, a large surplus added as fertilizer for about 25 yr, and then an input/output balance again in the 1990s. What is the fate of the P that accumulated based on our balance? We know that some was lost by sewage effluent discharges and surface and subsurface soil losses from agricultural fields. For example, the net balance for the 18-yr period used for the previous N evaluation was 739 000 Mg P, with export by rivers of 255 000 Mg P (Table 3). Riverine export accounts for 35% of the surplus P. The remainder of the surplus P is probably still sorbed or immobilized in agricultural soils. Phosphorus is retained well by soils and only small amounts are removed by surface runoff or leaching (Sims et al., 1998; Xue et al., 1998). In much of the drained soils in Illinois we believe that soils enriched in P are found in low-lying areas where soil deposition occurs above the tiles and that some of this P is transported through the tile lines (Xue et al., 1998, 1999). Because Illinois soils are generally rich in Ca with a pH of 6 to 6.5, much of the P is thought to be retained as Ca phosphates with some Fe and Al phosphates (Chang and Jackson, 1958).

Bennett et al. (1999) determined a P balance for the Lake Mendota watershed in Wisconsin. They also found that soils in the watershed had accumulated large amounts of P from fertilizer inputs, as indicated by increased soil test values that compared well with their estimated surplus P. Their calculated loss by hydrologic export was only 6% of surplus P, much less than our 35% estimate. This difference may have been partly due to sewage effluent inputs, which Bennett et al. (1999) did not include in their analysis. If we removed sewage effluent P from our river export, only 18% of surplus P was removed by rivers. This is still three times the percentage of surplus P removed found by Bennett et al. (1999) and extensive tile drainage export in Illinois soils may have been responsible.

Surface water bottom sediments may be another important source or sink for N or P (Mayer et al., 1999) and are carried by rivers as part of the total N and P load. Our riverine fluxes of N and P are based on all forms and therefore include suspended particulate (or sediment) N and P. However, we cannot evaluate the role of surface water bottom sediments as sinks or sources of N and P based on previous loading rates and treat bottom sediments as being in steady state with water column N and P with no major fluxes to our budgets.

Finally, groundwater may be a sink for some of the surplus N (but not P) in Illinois. However, compared with many states, Illinois has fine-textured soils that are poorly drained and require extensive artificial drainage for crop production. Approximately 35% of Illinois is tile drained (Fausey et al., 1995) and this artificial drainage helps route drainage waters directly into surface waters (David et al., 1997; Gentry et al., 1998). Therefore, in the highest density agricultural areas of Illinois, we would expect most surplus N to be transported to surface waters, rather than lost through deep seepage to aquifers.

Mass balance diagrams using our calculated fluxes and estimates based on the discussion above demonstrate that for both N and P, fertilizer in and grain export out dominate the balances (Fig. 7 and 8). For N, N_2 fixation and denitrification (both in-field and in-stream) are also major fluxes and the overall mass balance averaged during the 18 yr is small (+13 Mg N yr^{-1}). Riverine export of N is a dominant flux and represents the second largest loss of N from the state. For P, riverine export is small compared with fertilizer and net grain export and a large increase in the P pool was estimated (+27 Mg P yr^{-1}), relative to overall inputs. These diagrams illustrate the major fluxes in N and P, as well as indicating where further research is needed to reduce uncertainty (large fluxes in italics).

Environmental Implications

Our results suggest that Illinois will continue to contribute fluxes of N and P to the Mississippi River similar to those we determined for the 1980 through 1997 period. Nitrogen inputs are still much larger than exports and are dominated by fertilizer inputs, and about half of this N is transported from the state in surface waters. Turner and Rabalais (1991) also concluded that changes in Mississippi River water quality during this century were from changes in fertilizer use. Our budgets from

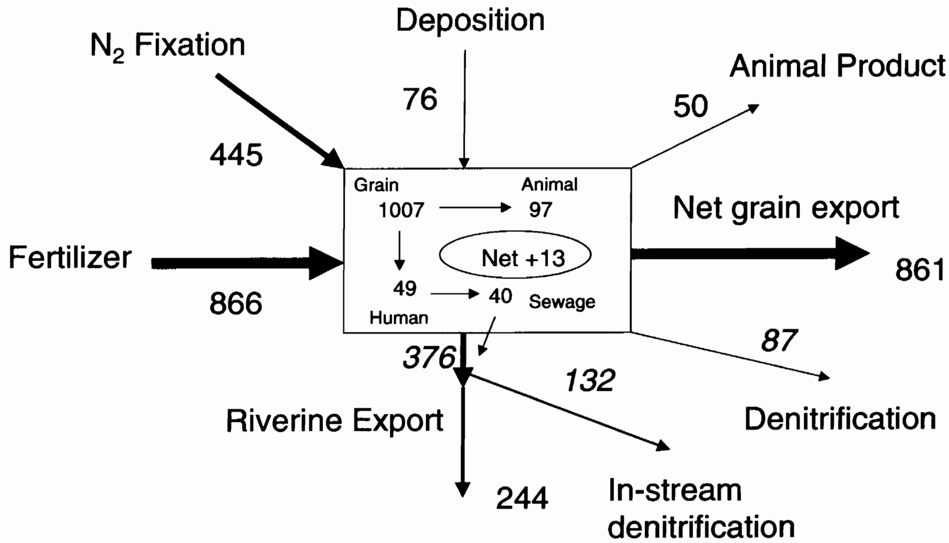

Fig. 7. Mass balance diagram for N showing inputs and outputs, averaged for 18 yr (1979 through 1996 for terrestrial fluxes, 1980 through 1997 water years for riverine export). Box represents state of Illinois, and fluxes inside the box are for total grain N harvest, consumption by animals and humans, sewage effluent produced, and the net difference in inputs and outputs each year. Not shown is animal consumption of N from forages and pastures. Fluxes are proportional to thickness of lines, and numbers in italics are fluxes calculated from literature estimates. All units are 1000 Mg N yr^{-1}.

1945 through 1998 would strongly support this conclusion for Illinois.

Denitrification would seem to be removing large amounts of N from both soils and surface waters and we need to know the fate of this N to fully determine human impacts on N fluxes (Weller and Jordan, 1996). Seitzinger and Kroeze (1998) recently estimated the global production of N_2O from aquatic ecosystems and estimated that rivers and estuaries could account for 20% of the global anthropogenic N_2O emissions. Based on their review of the literature, they used an N_2O emission factor of 0.3% (N_2O:N_2). If we use this emission factor, our in-stream estimate of denitrification released as N_2O would equate to 390 Mg N per year. McMahon and Dennehy (1999) determined that annual emissions of N_2O from the South Platte and Potomac Rivers (about 250 Mg N yr^{-1}) were similar in magnitude to the emissions from all of the primary and secondary municipal sewage treatment plants in the U.S. (about 800 Mg N yr^{-1}, from Czepiel et al., 1995). With only 0.3% of all missing N emitted as N_2O our estimates are larger than McMahon and Dennehy's (1999) values. High N fertilization rates also can lead to increased N_2O emissions from soils (Eichner, 1990; Matson et al., 1998) and add greatly to the emissions from river processes. Clearly, more studies are needed on the fate of all missing N with respect to denitrification to determine how agriculture in Illinois and throughout the Midwest may be contributing to global N_2O emissions.

Another implication of our results is that N losses from agricultural fields may be much larger than the riverine fluxes suggest, due to in-stream losses of N. The amount of N we estimated to be lost by in-stream denitrification would equal 9 kg N ha^{-1} yr^{-1} for all of

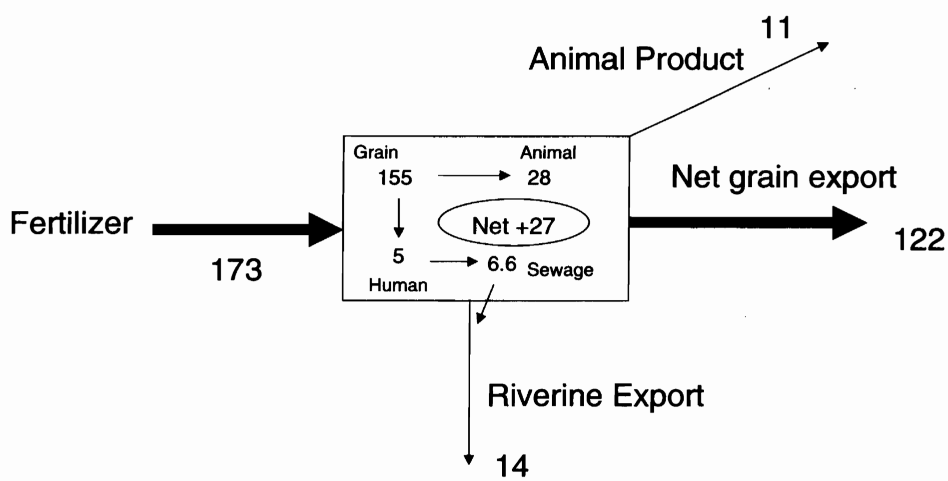

Fig. 8. Mass balance diagram for P showing inputs and outputs, averaged for 18 yr (1979 through 1996 for terrestrial fluxes, 1980 through 1997 water years for riverine export). Box represents state of Illinois and fluxes inside the box are for total grain P harvest, consumption by animals and humans, sewage effluent produced, and the net difference in inputs and outputs each year. Not shown is animal consumption of N from forages and pastures. Fluxes are proportional to thickness of lines. All units are 1000 Mg P yr^{-1}.

Illinois and possibly as much as 14 kg N ha^{-1} yr^{-1} if the source was row crop agriculture in the state. We had estimated that about 17 kg N ha^{-1} yr^{-1} was lost from the entire state (Fig. 5) and adding an in-stream denitrification component for agricultural land (and increasing the state loss per ha assuming the source is only row crop agriculture) would boost this loss to 41 kg N ha^{-1} yr^{-1}. In the 1995 through 1997 water years we measured tile N exports in a 30 ha field in east-central Illinois of 38 to 64 kg N ha^{-1} yr^{-1} (Gentry et al., 1998) and 25 to 44 kg N ha^{-1} yr^{-1} in a small watershed where in-stream processing would be limited (David et al., 1997), so these estimates seem reasonable.

For P, we would predict that export by rivers will continue at current flux rates, despite the recent decline in fertilizer applications. Although inputs and outputs are now balanced, the large pool of P likely built up in the soil will probably continue to be lost at current rates. Only a small amount of this large P pool is removed annually in dissolved and particulate forms, so that it will take either increased crop removals or slow removal by surface runoff and subsurface drainage to deplete it. Both of these removal mechanisms are likely to deplete soil P pools slowly. In addition, sewage effluent will continue to contribute an important fraction of the P in surface waters, particularly for the Illinois River. Correll (1999) recently reviewed the important role of P as a rate limiting nutrient in surface waters and concluded that total P was the best measurement and is what would need to be regulated, rather than orthophosphate.

Finally, riverine flux of N and P may have important effects on coastal water eutrophication. For the 18-yr period of water flux, we obtained a molar N:P ratio of 38 (data from Table 3), exactly the same ratio as Howarth et al. (1996) reported for the overall Mississippi River basin. Therefore, it appears that the N and P quality of Illinois river discharges are consistent with the overall Mississippi River basin. Ratios above 16 are thought to promote P limitation of phytoplankton growth, whereas ratios below 16 result in N limitations, because the typical N:P ratio in phytoplankton biomass is 16 (Redfield, 1958). However, because many biogeochemical processes occur in coastal waters that alter the forms and availability of these nutrients, these ratios must be viewed as relative indicators and are useful on a comparison basis (Howarth et al., 1996). In addition, ratios of silicate to N also are important in coastal food webs (Turner et al., 1998), but we did not have silicate data available.

CONCLUSIONS

Long-term mass balances of N and P for the state of Illinois show that for N large surpluses have been and continue to occur on an annual basis (last 30 yr) and that for P current inputs equal outputs, but that large surpluses did occur for approximately 25 yr (1965 to 1990). Surface water N in Illinois appears to be dominated by agricultural sources, with the most important input being N fertilizer (application rates have been relatively constant the last 20 yr). Phosphorus in surface waters is mainly from agricultural sources (P fertilizer is the input) in all rivers except the Illinois, but sewage effluent also is an important contributor. Export of N and P by Illinois surface waters seems unlikely to change given current conditions. Illinois contributes a large fraction of the N and P loads found in the Mississippi River (which probably is typical of other Cornbelt states) and needs to be considered as part of any strategy to decrease exports to the Gulf of Mexico. Such a strategy would have to focus on agricultural nonpoint sources of N and P. Inputs of N likely are lost both in agricultural fields following fertilization and in rivers and reservoirs by denitrification. Although reducing N loads in rivers, denitrification could greatly contribute to global N_2O emissions.

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REFERENCES

Aber, J., W. McDowell, K. Nadelhoffer, A. Magill, G. Bernston, M. Kamakea, S. McNulty, W. Currie, L. Rustad, and I. Fernandez. 1998. Nitrogen saturation in temperate forest ecosystems. BioScience 48:921–933.

Aldrich, S.R. 1980. Nitrogen in relation to food, environment, and energy. Spec. Publ. 61. Agric. Exp. Stn., College of Agric., Univ. of Illinois at Urbana–Champaign.

Bennett, E.M., T. Reed-Andersen, J.N. Houser, J.R. Gabriel, and S.R. Carpenter. 1999. A phosphorus budget for the Lake Mendota watershed. Ecosystems 2:69–75.

Burkart, M.R., and D.E. James. 1999. Agricultural-nitrogen contributions to hypoxia in the Gulf of Mexico. J. Environ. Qual. 28:850–859.

Cahoon, L.B., J.A. Mikucki, and M.A. Mallin. 1999. Nitrogen and phosphorus imports to the Cape Fear and Neuse River basins to support intensive livestock production. Environ. Sci. Technol. 33: 410–415.

Caraco, N.F., and J.J. Cole. 1999. Human impact on nitrate export: An analysis using major world rivers. Ambio 28:167–170.

Carpenter, S.R., N.E. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Applic. 8:559–568.

Chang, S.C., and M.L. Jackson. 1958. Soil phosphorus fractions in some representative soils. J. Soil Sci. 9:109–119.

Cohen, S., A. Svrjcek, T. Durborow, and N. LaJan Barnes. 1999. Water quality impacts by golf courses. J. Environ. Qual. 28:798–809.

Correll, D.L. 1999. Phosphorus: A rate limiting nutrient in surface waters. Poultry Sci. 78:674–682.

Crafts-Brandner, S.J., F.E. Below, J.E. Harper, and R.H. Hageman. 1984. Effect of nodulation on assimilate remobilization in soybean. Plant Physiol. 76:452–455.

Czepiel, P. P. Crill, and R. Harriss. 1995. Nitrous oxide emissions from municipal wastewater treatment. Environ. Sci. Technol. 29: 2352–2356.

David, M.B., L.E. Gentry, D.A. Kovacic, and K.M. Smith. 1997. Nitrogen balance in and export from an agricultural watershed. J. Environ. Qual. 26:1038–1048.

Drinkwater, L.E., P. Wagoner, and M. Sarrantonio. 1998. Legume-based cropping systems have reduced carbon and nitrogen losses. Nature 396:262–265.

Dunn, D.D. 1996. Trends in nutrient inflows to the Gulf of Mexico from streams draining the conterminous United States, 1972–93. U.S. Geological Survey Water-Resources Investigations Report 96-4113. U.S. Geological Survey, Austin, TX.

Eichner, M.J. 1990. Nitrous oxide emissions from fertilized soils: Summary of available data. J. Environ. Qual. 19:272–280.

Fausey, N.R., L.C. Brown, H.W. Belcher, and R.S. Kanwar. 1995. Drainage and water quality in Great Lakes cornbelt states. J. Irrig. Drain. Eng. 121:283–288.

Fenn, M.E., M.A. Poth, J.D. Aber, J.S. Baron, B.T. Bormann, D.W. Johnson, A.D. Lemly, S.G. McNulty, D.F. Ryan, and R. Stottlemyer. 1998. Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. Ecol. Applic. 8:706–733.

Francis, D.D., J.S. Schepers, and A.L. Sims. 1997. Ammonia exchange from corn foliage during reproductive growth. Agron. J. 89: 941–946.

Francis, D.D., J.S. Schepers, and M.F. Vigil. 1993. Post-anthesis nitrogen loss from corn. Agron. J. 85:659–663.

Gentry, L.E., M.B. David, K.M. Smith, and D.A. Kovacic. 1998. Nitrogen cycling and tile drainage NO_3^- loss in a corn/soybean rotation. Agric. Ecosyst. Environ. 68:85–97.

Gold, A.J., W.R. DeRagon, W.M. Sullivan, and J.L. Lemunyon. 1990. Nitrate-nitrogen losses to groundwater from rural and suburban land uses. J. Soil Water Conserv. 45:305–310.

Harper, J.E. 1987. Nitrogen metabolism. p. 497–533. *In* J.R. Wilcox (ed.) Soybeans: Improvement, production, and uses. 2nd ed. Agron. Monogr. 16. ASA, CSSA, and SSSA, Madison, WI.

Howarth, R.W. 1998. An assessment of human influences on fluxes of nitrogen from the terrestrial landscape to the estuaries and continental shelves of the North Atlantic Ocean. Nutrient Cycling Agroecosystems 52:213–223.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Zhao-Liang. 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Biogeochemistry 35:75–139.

Illinois Department of Agriculture. 1945–1998. Illinois Agricultural Statistics. Illinois Agricultural Statistics Service, Springfield.

Interagency Board for Nutrition Monitoring and Related Research. 1995. Third report on nutrition monitoring in the United States. Vol. 2. Prepared by the Life Sciences Research Office, Federation of American Societies for Experimental Biology. U.S. Government Printing Office, Washington, DC.

Johnson, J.W., L.F. Welch, and L.T. Kurtz. 1975. Environmental implications of N fixation by soybeans. J. Environ. Qual. 4:303–306.

Johnson, V.A., and P.J. Mattern. 1987. Wheat, rye, and triticale. p. 133–182. *In* R.A. Olson and K.J. Frey (eds.) Nutritional quality of cereal grains: Genetic and agronomic improvement. Agron. Monogr. 28. ASA, CSSA, and SSSA, Madison, WI.

Jordan, T.E., D.L. Correll, and D.E. Weller. 1997. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. J. Environ. Qual. 26:836–848.

Jordan, T.E., J.W. Pierce, and D.L. Correll. 1986. Flux of particulate matter in the tidal marshes and subtidal shallows of the Rhode Island estuary. Estuaries 9:310–319.

Jordan, T.E., and D.W. Weller. 1996. Human contributions to terrestrial nitrogen flux. BioScience 46:655–664.

Keeney, D.R., and T.H. DeLuca. 1993. Des Moines River nitrate in relation to watershed agricultural practices: 1945 versus 1980s. J. Environ. Qual. 22:267–272.

Kellman, L., and C. Hillaire-Marcel. 1998. Nitrate cycling in streams: using natural abundances of NO_3^-–$\Delta^{15}N$ to measure *in-situ* denitrification. Biogeochemistry 43:273–292.

Lucey, K.J., and D.A. Goolsby. 1993. Effects of climatic variations over 11 years on nitrate-nitrogen concentrations in the Raccoon River, Iowa. J. Environ. Qual. 22:38–46.

Luman, D., M. Joselyn, and L. Suloway. 1995. The land cover database of Illinois 1991–1995 [Online]. Available at http://www.inhs.uiuc.edu/igis/illinois/stats.htm (verified 11 March 1999).

Lurry, D.L., and D.D. Dunn. 1997. Trends in nutrient concentration and load for streams in the Mississippi River basin, 1974–94. Water-Resources Investigations Report 97-4223. U.S. Geological Survey, Austin, TX.

Mallarino, A.P. 1996. Evaluation of optimum above-ground phosphorus supplies for corn by analysis of plant parts. Agron. J. 88:376–380.

Matson, P.A., R. Naylor, and I. Ortiz-Monasterio. 1998. Integration of environmental, agronomic, and economic aspects of fertilizer management. Science 280:112–115.

Mayer, T., C. Pitacek, and L. Zahini. 1999. Sediments as a source of nutrients to hypereutrophic marshes of Point Pelee, Ontario, Canada. Water Res. 33:1460–1470.

McMahon, P.B., and K.F. Dennehy. 1999. N_2O emissions from a nitrogen-enriched river. Environ. Sci. Technol. 33:21–25.

Mulvaney, R.L., S.A. Khan, and C.S. Mulvaney. 1997. Nitrogen fertilizers promote denitrification. Biol. Fertil. Soils 24:211–220.

National Atmospheric Deposition Program. 1999. Annual deposition data for Illinois monitoring sites [Online]. Available at http://nadp.sws.uiuc.edu/nadpdata/multsite.asp?state=IL (verified 12 April 1999).

National Research Council. 1993. Soil and water quality: An agenda for agriculture. Committee on Long-Range Soil and Water Conservation, Board on Agriculture. National Academy Press, Washington, DC.

Parkin, T.N., J.L. Starr, and J.J. Meisinger. 1987. Influence of sample size on measurement of soil denitrification. Soil Sci. Soc. Am. J. 51:1492–1501.

Peterson, D.M., J. Senturia, V.L. Youngs, and L.E. Schrader. 1975. Elemental composition of oat groats. J. Agric. Food Chem. 23:9–13.

Rabalais, N.N., R.E. Turner, W.J. Wiseman, Jr., and D.F. Boesch. 1991. A brief summary of hypoxia on the northern Gulf of Mexico continental shelf: 1985–1988. p. 35–47. *In* R.V. Tyson and T.H. Pearson (eds.) Modern and ancient continental shelf anoxia. Spec. Publ. 58. Geological Society, London.

Raboy, V., D.B. Dickinson, and F.E. Below. 1984. Variation in seed total phosphorus, phytic acid, zinc, calcium, magnesium, and protein among lines of *Glycine max* and *G. soja*. Crop Sci. 24:431–434.

Redfield, A.C. 1958. The biological control of chemical factors in the environment. Am. Sci. 46:205–221.

SAS Institute. 1993. SAS/ETS User's Guide, Version 6. 2nd Edition. SAS Inst., Cary, NC.

Seech, A.G., and E.G. Beauchamp. 1988. Denitrification in soil aggregates of different sizes. Soil Sci. Soc. Am. J. 52:1616–1621.

Seitzinger, S.P., and C. Kroeze. 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Global Biogeochemical Cycles 12:93–113.

Sexstone, A.J., T.B. Parkin, and J.M. Tiedje. 1985. Temporal response of soil denitrification rates to rainfall and irrigation. Soil Sci. Soc. Am. J. 49:99–103.

Sinclair, T.R., and C.T. DeWit. 1975. Comparative analysis of photosynthate and nitrogen requirement in the production of seeds by various crops. Science 189:565–567.

Sims, J.T., R.R. Simard, and B.C. Joern. 1998. Phosphorus loss in agricultural drainage: Historical perspective and current research. J. Environ. Qual. 27:277–293.

Smith, L.M. 1984. Seed development, metabolism, and composition. p. 13–52. *In* M.B. Tesar (ed.) Physiological basis of crop growth and development. ASA, CSSA, and SSSA, Madison, WI.

Soil Conservation Service. 1992. Agricultural waste management field handbook. Chapter 4, part 651. USDA SCS, Washington, DC.

Terrio, P.J. 1995. Water-quality assessment of the upper Illinois River basin in Illinois, Indiana, and Wisconsin: Nutrients, dissolved oxygen, and fecal-indicator bacteria in surface water, April 1987 through August 1990. Water-Resources Investigations Rep. 95-4005. U.S. Geological Survey, Urbana, IL.

Thomas, G.W., and J.W. Gilliam. 1977. Agro-ecosystems in the USA. Agro-Ecosystems 4:182–243.

Turner, R.E., N. Qureshi, N.N. Rabalais, Q. Dortch, D. Justic, R.F. Shaw, and J. Cope. 1998. Fluctuating silicate:nitrate ratios and coastal plankton food webs. Proc. Natl. Acad. Sci. USA 95:13048–13051.

Turner, R.E., and N.N. Rabalais. 1991. Changes in Mississippi River water quality this century. BioScience 41:140–147.

Turner, R.E., and N.N. Rabalais. 1994. Coastal eutrophication near the Mississippi river delta. Nature 368:619–621.

United States Environmental Protection Agency. 1999. National emission trends, 1900–1996 [Online]. Available at http://www.epa.gov/ttnchie1/trends96/chapter3.pdf (verified 26 July 1999).

United States Geological Survey. 1999. Daily stream flow data [Online]. Available at http://www-il.usgs.gov/nwis-w/IL/ (verified 12 April 1999).

Van der Leeden, F., F.L. Troise, and D.K. Todd. 1990. The water encyclopedia second edition. Lewis Publ., Chelsea, MI.

van Eerdt, M.M., and P.K.N. Fong. 1998. The monitoring of nitrogen surpluses from agriculture. Environ. Pollut. 102:227–233.

Van Horn, H.H., G.L. Newton, and W.E. Kunkle. 1996. Ruminant nutrition from an environmental perspective: Factors affecting whole-farm nutrient balance. J. Anim. Sci. 74:3082–3102.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Applic. 7:737–750.

Ward, M.H., S.D. Mark, K.P. Cantor, D.D. Weisenburger, A. Correa-Villaseñor, and S.H. Zahm. 1996. Drinking water nitrate and the risk of non-Hodgkin's lymphoma. Epidemiology 7:465–471.

Xue, Y., M.B. David, L.E. Gentry, and R.J. Hudson. 1999. Reply to "Comment on 'Kinetics and modeling of dissolved phosphorus export from a tile-drained agricultural watershed' by Y. Xue, M.B. David, L.E. Gentry, and D.A. Kovacic. J. Environ. Qual. 27:917–922 (1998)." J. Environ. Qual. 28:1046–1047.

Xue, Y., M.B. David, L.E. Gentry, and D.A. Kovacic. 1998. Kinetics and modeling of dissolved phosphorus export from a tile-drained agricultural watershed. J. Environ. Qual. 27:917–922.