Biogeochemistry (2008) 91:177–199
DOI 10.1007/s10533-008-9279-3

Estimation of nitrogen inputs to catchments: comparison of methods and consequences for riverine export prediction

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Received: 12 June 2008 / Accepted: 18 November 2008 / Published online: 10 December 2008

Abstract Catchment nitrogen (N) budgets are a valuable tool to assess relative magnitude of N inputs and predict losses via riverine export. However, a range of computational approaches may be chosen, potentially affecting the modeled relationship between inputs and exports. To determine the influence of various assumptions and computational details on the effectiveness of N input estimates in predicting riverine N export, we compared eight separate net anthropogenic N input budgets and one soils compartment budget for each of 18 Lake Michigan catchments. N input estimation methods that took into account seasonal fluctuations in livestock numbers and estimated crop N-fixation by legume yield rather than area harvested best predicted river N export. The average annual river export of N from the 18 catchments ranged from less than 300 kg N km^{-2} year^{-1} in forested areas to more than 800 kg-N km^{-2} year^{-1} in agricultural catchments and 1,580 kg-N km^{-2} year^{-1} in small urban catchments. Using the most effective model ($R^2 = 0.95$, median prediction error = 1.8%) riverine N exports were found to account for 21% of N inputs. Other methods predicted riverine N exports less well ($R^2 = 0.61$–0.73), bias was greater, and the fractional export of N inputs by rivers decreased to $\sim$13%. The soil N budget also was a less effective predictor of river export. This comparison demonstrates that N budgeting that incorporates more detailed description of agricultural N sources can substantially improve prediction of riverine N exports from catchments with a wide range of landscape characteristics.

Keywords Nitrogen · NANI · N Export · River · Catchment · Nutrient budget · Nutrient loading · Lake Michigan

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Introduction

Inputs of anthropogenic nitrogen (N) in excess of the processing and storage capacity of terrestrial ecosystems result in N export to aquatic ecosystems, causing a long cascade of detrimental impacts (Galloway et al. 2002; Galloway et al. 1996). Serious consequences include groundwater contamination, surface-water acidification, biodiversity loss, eutrophication, and hypoxia (Carpenter et al. 1998; Galloway et al. 2003; Rabalais et al. 2002; Vitousek et al. 1997). Export of N into coastal areas due to high riverine nitrogen discharges has resulted in eutrophication and hypoxia in coastal waters including the Chesapeake Bay (Boynton et al. 1995) and the Gulf of Mexico (Rabalais et al. 2002; Scavia et al. 2004).

To better understand how human activities affect nitrogen inputs to catchments and export by rivers, N budgets have been constructed at various spatial scales using a NANI (Net Anthropogenic Nitrogen Input) approach (e.g., North Atlantic Ocean, Howarth et al. 1996; coterminous United States, Jordan and Weller 1996; multiple river basins of the Northeastern U.S., Boyer et al. 2002; the state of Illinois, David and Gentry 2000). NANI is estimated using a mass balance approach by summing inputs of fertilizer, atmospheric deposition, plant N-fixation, and N imported as food and feed, less estimated outputs from N volatilization and N exported as food and feed. In addition to the NANI approach at the catchment scale, some N mass balance estimates have restricted the system boundary to the soils compartment (Burkart and James 1999). Most such studies find a high correlation between net N inputs to catchments and riverine N exports across a wide range of spatial settings, and a substantial excess of anthropogenic N inputs relative to riverine export (Van Breemen et al. 2002). However, such studies also agree that estimates of net N input terms contain considerable uncertainty and potential bias, because estimates of N sources, losses, and the net N input balance can vary widely depending on the definition of the system boundary, the assumptions and approximations used to estimate N flows, and on the quantity and quality of available data over space and time (Boyer et al. 2002; David and Gentry 2000; Howarth et al. 1996; Meisinger and Randall 1991).

These uncertainties in estimating net N inputs may affect the magnitude of the correlation between N inputs and riverine N export (Jordan and Weller 1996; McIsaac et al. 2002). For example, using Monte Carlo simulation, Jordan and Weller (1996) determined that the strength of the correlation between N inputs and riverine export of total N (TN) was most sensitive to estimates of the terms for crop consumption by humans and animals, fertilizer application, and N production from corn and soybean. Comparison of alternative N budgeting approaches also can provide insight into which methods best explain variation in N exports from catchments and the contribution of individual N sources to river export loads. By systematically adding internal N flux terms to NANI budgets for the Lower Mississippi Basin and by subtracting them from comprehensive N budgets, McIsaac et al. (2002) found that the widely used NANI approach had the highest power to predict riverine nitrate N fluxes, accounting for 95% of variation in export, in comparison with 14 other net N input formulations.

Our primary goal was to compare various methods for the estimation of anthropogenic N inputs to catchments to determine whether refinements of computational approach can result in improved estimation of catchment loadings, based on the relationship between N inputs and river export of N. For 18 catchments of the Lake Michigan Basin (LMB), we first quantified net anthropogenic N inputs using eight models based on the NANI approach and one based on the soil compartment only. Because a principal application of N input estimation is to develop predictive models of river TN export, and the strength of such models implies successful prediction of catchment loadings, we then compared the performance of regression models in predicting riverine TN exports based on alternative estimates of N inputs. We find that N budgeting that incorporates more detailed description of agricultural N sources can substantially improve prediction of riverine N exports from catchments across a variety of settings of land uses, agricultural practices, and human activities in the Lake Michigan basin.

Methods

Study area

We selected 18 of the 25 catchments of the LMB based on their wide range of land use and the availability of riverine TN export data. Catchment boundaries were delineated upstream of the lowermost USGS gauging station on each river with adequate water quality data, using 30-m National Elevation Dataset (Fig. 1). Land cover data were derived from the Geographic Information Retrieval and Analysis System (GIRAS) land use and land cover (LULC) and the National Land Cover Data (NLCD) (MRLC 1995; U.S. EPA 1998). Climate data including precipitation and temperature were obtained from the PRISM historical climate GIS data set (4 km × 4 km) (Daly and Gibson 2002a, b), and grid values within each catchment were averaged over 5-year intervals using ArcGIS 9.0.

The drainage area, land use, population density, annual average water discharge, and precipitation for

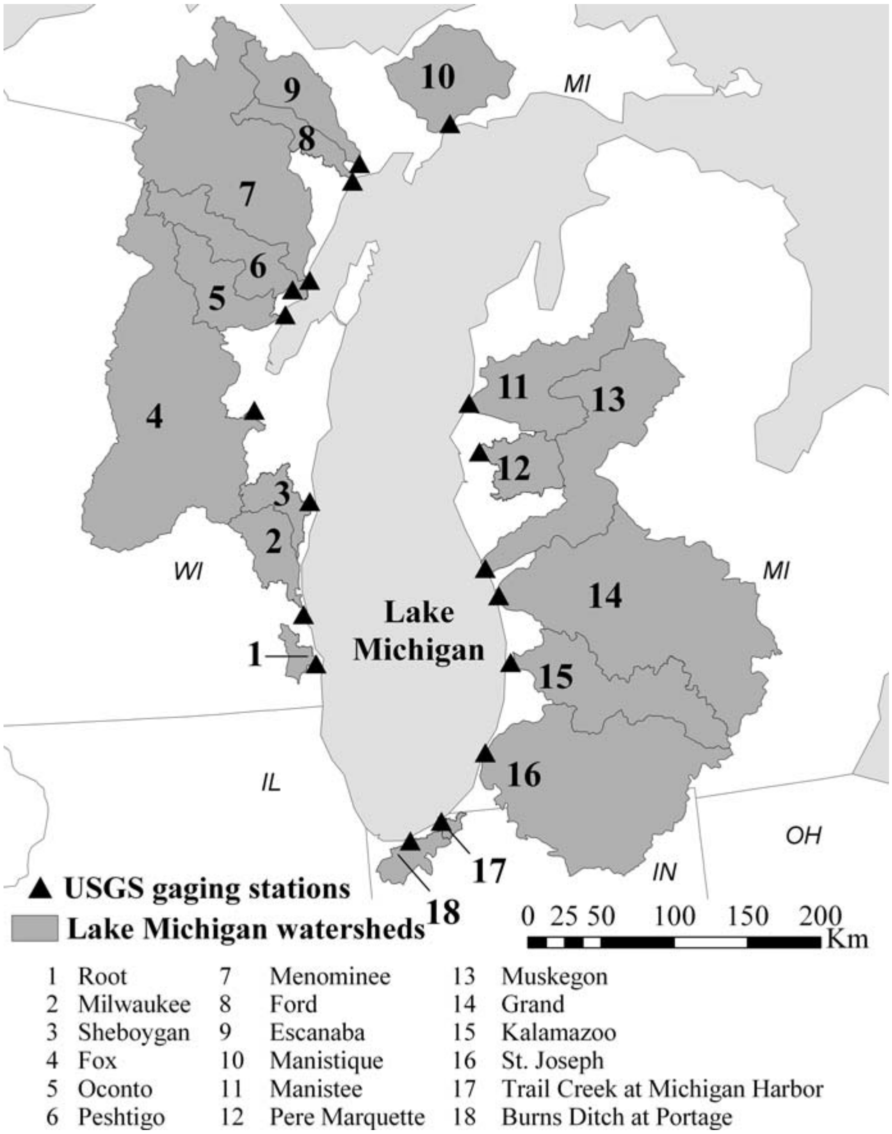


Fig. 1 The 18 Lake Michigan catchments used for N budgeting. Boundaries were delineated upstream of USGS stations (denoted with *triangles*) where streamflow and water quality were measured during 1972–1992

each catchment are summarized in Table 1. Individual catchments varied greatly in size, from 153 km^2 for Trail Creek to 15,825 km^2 for the Fox River. Combined land use across the 18 focal catchments was 43% agricultural, 37% forest, 12% wetland, and 6% urban. Catchments in the northern LMB, including the Manistee, Manistique, and Menominee, are dominated by undisturbed land (forest and wetland) (all above 70%). The Sheboygan, St. Joseph, Grand River, and Kalamazoo in southern LMB are examples of highly agricultural (75–82%) catchments. Catchments of the southern LMB, including the Root, Trail Creek, and Burns Ditch, are highly urbanized (19, 19.6, and 20% urban, respectively).

Nitrogen budgets

Nitrogen inputs to catchments were estimated using eight alternative sets of assumptions and calculations for the NANI approach (Howarth et al. 1996, Boyer et al. 2002), and one estimate restricted to the soils compartment (Burkart and James 1999), for a total of nine models. Annual N budgets were separately constructed for each of five agricultural census years (1974, 1978, 1982, 1987, and 1992) for which river TN export was also available; thus a total of 810 nitrogen budgets were constructed (nine computational approaches * 18 catchments * 5 years). Because the focus of the present study is to compare

Table 1 Catchment, climatic, and land use characteristics for the 18 catchments of the Lake Michigan Basin, averaged over five agricultural census years from 1974 to 1992

ID	Catchment	USGS station	Area (km^2)	Mean temperature (°C)	Mean flow (mm/year)	Mean precipitation (mm/year)	Population density (capita/km^2)	Land use			
								Agric (%)	Forest (%)	Urban (%)	Wetland (%)
1	Root	4087242	510	8.8	354	901	397	76.7	3.1	19.0	0.1
2	Milwaukee	4087010	1,818	8.0	289	843	201	73.9	7.9	12.2	4.6
3	Sheboygan	4086000	1,106	8.1	235	856	31	82.0	7.2	2.5	7.0
4	Fox	4085059	15,825	7.1	259	801	32	51.1	27.2	2.4	13.3
5	Oconto	4071775	2,543	6.1	279	798	10	27.5	52.1	0.7	17.2
6	Peshtigo	4069500	2,797	5.8	259	783	9	20.7	54.7	0.9	21.7
7	Menominee	4067651	10,541	5.0	291	780	7	7.1	73.1	0.7	16.3
8	Ford	4059500	1,165	5.2	313	810	3	7.1	53.5	0.2	39.0
9	Escanaba	4059000	2,253	5.0	326	846	9	5.4	66.7	1.1	23.6
10	Manistique	4049500	883	5.7	456	834	3	5.0	49.5	0.3	40.2
11	Manistee	4126000	4,343	6.7	462	832	8	18.3	73.1	1.0	5.9
12	Pere Marquette	4122500	1,764	7.3	360	909	8	17.6	71.2	0.7	8.1
13	Muskegon	4122150	6,941	6.9	349	819	27	33.6	47.7	2.8	11.3
14	Grand	4120250	14,292	8.6	296	838	85	75.4	13.9	5.5	3.7
15	Kalamazoo	4108670	5,164	8.8	365	899	83	75.1	12.6	6.1	4.2
16	St. Joseph	4102533	12,095	9.4	368	922	68	80.4	9.3	5.5	2.4
17	Trail Creek	4095380	153	10.0	510	969	237	50.0	27.7	19.6	0.5
18	Burns Ditch	4095090	857	10.1	389	970	286	63.7	13.3	20.0	1.1

the performance of nine alternative N budgeting models based on their ability to predict spatial variation in riverine TN export across the 18 catchments, for this analysis we averaged both N inputs and river exports over time. An analysis of temporal variation will be reported in a subsequent paper.

NANI is estimated at the catchment scale based on the difference between anthropogenic N inputs (atmospheric N deposition, crop N fixation, fertilizer use, and food and feed imports) and outputs (volatilization of ammonia from three sources: applied fertilizer, animal manure and crop senescence; and export of food and feed). The NANI approach only considers N that is either newly fixed within the system or is transported into a system from outside sources. To avoid double counting of N inputs, no recycling terms such as animal N manure, human waste, and re-deposition of locally derived ammonia are included in NANI estimates. In contrast, soil N budgets include animal N manure as an input of N into the system. In addition, soil N budgets exclude estimates of N imported in food, because it would be consumed by humans and presumably treated by municipal wastewater plants, and thus bypass the soil compartment and directly enter the aquatic system. Similarly, N from imported feed was excluded from soil N budgets because it enters the agricultural food chain and eventually reaches the soil, mainly as applied animal manure. Thus, the specific inputs to soil N budgets included N fertilizer, crop N fixation, atmospheric N deposition, and animal N manure, while outputs included NH_3 volatilization and crop N harvest.

Computational differences among the eight NANI models included alternative methods of estimating crop N-fixation (yield vs. area), animal population size (dynamic vs. steady-state), and data aggregation (area- vs. land use-weighting) (Fig. 2a). The estimate of annual average animal population size influences the magnitude of net import or export of N in food and feed, animal manure production (used only in the soil budget), and volatilization of N from animal manure. Previous studies have identified this

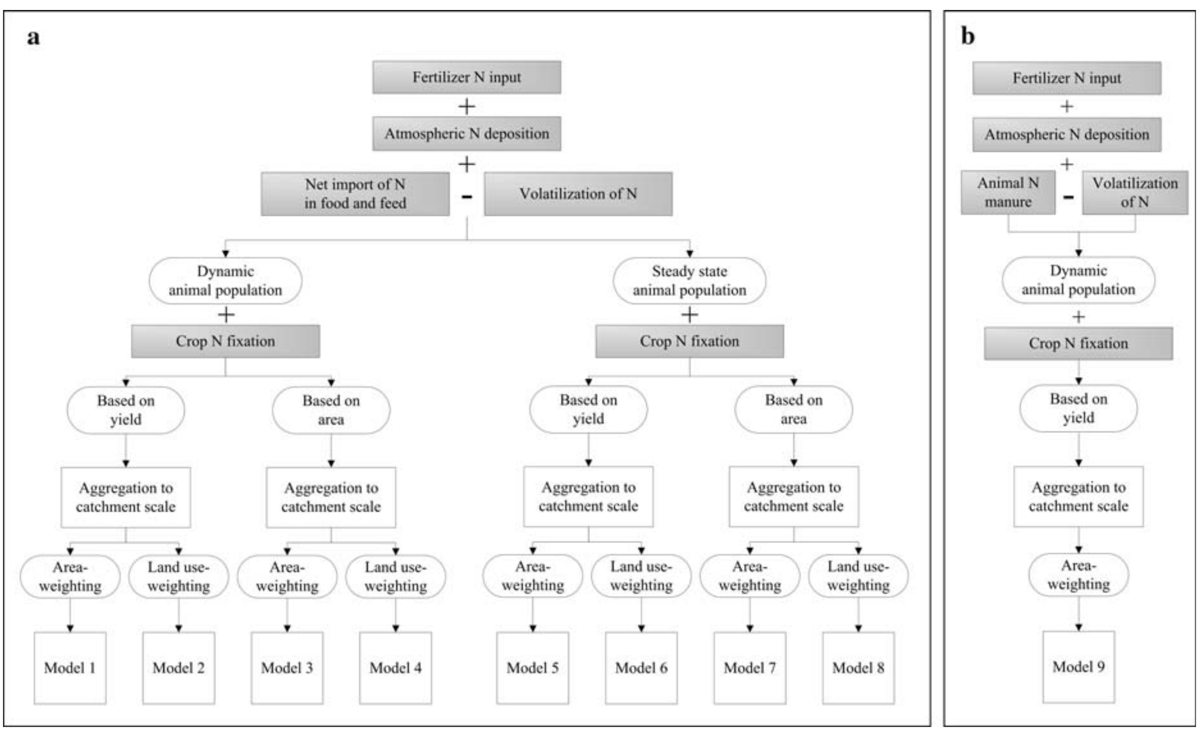


Fig. 2 Two flowcharts illustrating how **a** The eight NANI and **b** One soil N input estimates were obtained for the 18 Lake Michigan catchments. Fertilizer and atmospheric N inputs are the same for each estimate. Alternative methods are the result of whether (1) the animal population is dynamic or steady state, (2) crop N-fixation is estimated based on area or yield, and (3) county-level data is aggregated to the catchment by area- or land use-weighting. *Shaded boxes* represent the five main components of NANI and soil N budgets

component of NANI as most subject to uncertainty and errors, along with crop N fixation (Boyer et al. 2002; David and Gentry 2000; Goolsby et al. 1999). County-level estimates of N fluxes were aggregated to the catchment scale using two different weighting methods: (1) the fraction of land that is included within the catchment boundary (hereafter referred to as area-weighting), and (2) the fraction of the relevant land use type, such as crop or urban land, lying within each catchment (hereafter referred to as land use-weighting).

To limit the number of alternative models, for the soil N budget (model 9) we estimated crop N fixation based on yield, net volatilization of ammonia and animal N manure based on the dynamic livestock model, and used only the area-weighted method to scale from counties to catchments (Fig. 2b).

N fertilizer inputs

County-level estimates of N fertilizer use (1974–1982) and sales (1987) were obtained from USGS Branch of Systems Analysis (Alexander and Smith 1990) and USGS Water Resources Division (WRD) (Battaglin 1994), respectively. For 1992, statewide N fertilizer sales data from the Fertilizer Institute (TFI 1992–2002) were converted to the county level using the ratio of county to state expenditures for commercial fertilizer taken from the 1992 Census of Agriculture (U.S. Bureau of the Census 1995), following the method of Battaglin (1994).

County-level fertilizer estimates were aggregated to the catchment level using two allocation methods. Area-weighted sums were computed based on the proportion of each county included in each catchment. The land use-weighted estimate was computed from the ratio of the fertilized area of each county within a catchment to the total area of each county treated with fertilizer. We estimated fertilized area based on a classification of cultivated lands (1992 NLCD) and a classification of agricultural land types (LULC) to determine areas expected to receive fertilizer.

Total atmospheric N deposition

Annual precipitation-weighted mean wet deposition of NH_4^+ and NO_3^- and dry deposition of particulate ammonium (NH_4^+), gaseous nitric acid (HNO_3), and particulate nitrate (NO_3^-) were obtained for all sites in five states (IL, IN, OH, MI, and WI) for the years 1980–2004 from NADP/NTN and for the years 1989–2004 from CASTNET, respectively (CASTNET 2006; NADP 2006). Dry deposition for 1980–1988 was estimated from total wet deposition using ratios of dry to wet deposition (NH_4^+, 0.14; HNO_3, 0.51; NO_3^-, 0.51) developed using data from 11 sampling sites that simultaneously measured dry and wet deposition from 1989 through 2004. For the years prior to 1980, total atmospheric deposition of NO_3 and NH_4 was extrapolated using historical trends in national nitrous oxide (NO_X) emission (U.S. EPA 2000; 2003) and NH_3 emission (Van Aardenne et al. 2001) based on the relationship between emission and atmospheric deposition of NO_3 and NH_4 for 1981–2004 (David and Gentry 2000).

Atmospheric organic nitrogen (AON) can be a substantial input of N (Neff et al. 2002). For this study, new inputs of dust AON and organic nitrates were estimated to be one-half of the median value of 20 kg-N km^{-2} year^{-1} from AON dust deposition monitoring and one-half of 110 kg-N km^{-2} year^{-1} from the TM_3 model (Neff et al. 2002). Similar to the historical inorganic N extrapolations, historical changes in organic nitrate deposition for the period 1974–1992 were extrapolated based on estimates of national emission of NO_X because studies have shown that NO_X is an important source, producing organic nitrates from chemical reaction with reactive hydrocarbons (Muthuramu et al. 1994; Neff et al. 2002; Roberts 1990).

The values of total inorganic N plus net organic N in dry and wet deposition, averaged over 5 year increments at NADP/NTN sample stations, were used to generate an N-deposition surface covering the 18 Lake Michigan catchments. This surface was created by inverse distance weighted interpolation (Tidwell et al. 2004) and the grid values within each catchment were averaged using ArcGIS 9.0.

Net trade of N in food and feed

N supply from animal and crop production in excess of estimated demand by humans and livestock is assumed to be exported. Thus, net trade of N in food and feed was calculated by subtracting human and animal N consumption from crop and animal N production. Positive and negative net balances represent import and export of N in food and feed, respectively.

Human N consumption was estimated by multiplying annual human population estimates by per capita N consumption rates. Per capita N consumption was obtained from estimates of annual per capita protein consumption at the national level from the USDA Economic Research Service (U.S. Department of Agriculture 2006), multiplied by 0.16 (protein fraction of N).

Estimation of animal feed requirements and animal products in trade can be complicated when the farm residence time for livestock is variable. For beef and milk cattle, sheep and lambs, horses and breeding fowl, seasonal fluctuations in numbers are assumed to be minimal, and continuous replacement offsets mortality and sale of animals that are no longer productive. For these livestock groups, year-end inventory data are assumed to be representative of the population throughout the year. However, some livestock groups reside on a farm during only part of the year, including hogs, pigs and most poultry, and then are exported to market. For these groups, year-end inventory data may over-estimate the N trade associated with livestock.

We compared two estimates of average annual livestock population size to determine the amounts of animal N products and animal N consumption. The static animal population method assumes that population numbers for all livestock types do not vary over the year, so that year-end inventory numbers from the USDA Census of Agriculture are representative of average numbers for all livestock types (Boyer et al. 2002). The dynamic animal population estimate takes into account the life cycle of farm animals during the year (Kellogg et al. 2000), and results in a lower population estimate in most cases.

Equation 1 estimates the annual average number of livestock during a year based on a weighted sum of end-of-year inventory and annual sales data, taking into account differences in residence times among categories of livestock.

$$\mathrm{AL} = \left\{ \left(\mathrm{Inventory} \times \frac{1}{\mathrm{Cycles}} \right) + \left(\frac{\mathrm{Sales}}{\mathrm{Cycles}} \times \frac{\mathrm{Cycles} - 1}{\mathrm{Cycles}} \right) \right\} \tag{1}$$

where AL is the annual average number of livestock, inventory is the number from the end-of-year inventory data, sales is the number of animals from sales data, and cycles is the duration of the life cycle (365 days divided by the number of days from birth to market) per year. Data on sales and inventory of livestock were obtained from the Census of Agriculture from 1974 to 1992, and the eighteen classes of animals used for this estimation are listed in Table 2. To estimate livestock N consumption, animal-specific N consumption rates from the National Research Council (NRC 1984, 1985, 1998) and from Van Horn et al. (1996) were combined with estimates of average livestock numbers derived using the dynamic and static methods, respectively (Table 2).

To estimate food and feed production within individual catchments, crop product N content from Lander et al. (1998) and Jordan and Weller (1996) was combined with county-level crop yield data from the Census of Agriculture for various crop types (Table 3). Assumptions about crop product lost to spoilage or other causes as well as allocation of crop products to animals and humans were applied as described in Boyer et al. (2002). Animal production was estimated on the basis of slaughtered livestock sales data, combined with N content of their edible portion and the varying weight of slaughtered livestock by year. The N content of the edible portion was obtained from the USDA National Nutrient Database for Standard Reference (U.S. Department of Agriculture 2005), and annual average live weights of cattle, calf, swine, sheep, and lambs for each state (IN, IL, MI, and WI) for the period from 1974 to 1992 were obtained from USDA NASS state-level annual and monthly livestock slaughter summary reports (USDA/NASS 2006). Animal N production also was estimated as the difference between animal N feed consumption and animal N excretion under the static model (Table 2). For additional computational details, see Han (2007).

Animal N manure and NH_3 volatilization

Agricultural sources of volatilized NH_3 considered in this study include applied manure, fertilizer, and the senescing leaves of crops. To estimate NH_3 emissions from animal manure, manure N was calculated by multiplying the estimates of average annual livestock populations by N excretion rate, and the resultant

Table 2 The rates of N excretion, N emission, and N consumption for each of the livestock classes estimated under the dynamic and static livestock models

Dynamic livestock model						Static livestock model			
Livestock group	Life cycle[a] (days)	Average live weight[b] (kg-N km^{-2} $year^{-1}$)	Excretion rates[a] (kg-N km^{-2} $year^{-1}$)	Consumption rates[c] (kg-N km^{-2} $year^{-1}$)	Emission rates[d] (kg-N km^{-2} $year^{-1}$)	Livestock group	Excretion rates[e] (kg-N km^{-2} $year^{-1}$)	Consumption rates[e] (kg-N km^{-2} $year^{-1}$)	Emission rates[f] (kg-N km^{-2} $year^{-1}$)
Milk cow	365	650.0	104.0	130.8	26.0	Milk cow	121.0	156.0	18.8
Breeding herd	365	460.0	59.8	60.9	4.8	Beef cow	58.0	66.8	18.8
Beef calf	150	98.0	9.8	19.9	0.8				
Dairy calf		98.0	6.7	10.6	0.5				
Beef heifer	150	403.0	28.2	40.5	2.3				
Milk heifer	150	489.0	34.2	43.5	2.7	Young cattle	NA	NA	10.7
Beef stocker	200	266.0	26.6	37.6	10.6				
Dairy stocker	200	266.0	18.6	37.6	7.4				
Fattened cattle	146	403.0	48.0	50.3	19.2				
Breeding hog	365	114.0	9.1	13.8	4.7	Hog and pig	5.8	8.5	4.2
Slaughter hog	182	34.0	5.8	24.0	3.0				
Layer	365	2.2	0.7	0.8	0.3	Layer	0.6	0.8	0.2
Pullet	162	1.5	0.4	0.4	0.2				
Broiler	60	1.7	0.7	0.8	0.3	Broiler	0.1	0.1	0.1
Breeding turkey	365	8.5	1.7	2.1	0.8	Turkey	0.4	0.6	0.7
Slaughter turkey	182	6.4	1.6	2.1	0.7				
Sheep	365	NA	8.4	14.5	5.6	Sheep	5.0	6.0	2.8
Horse	365	NA	40.0	44.8	9.3	Horse	40.0	44.8	10.0

Note that the static model includes fewer livestock categories

Sources: [a]Kellogg et al. 2000; [b]USDA/NASS 2006; [c]NRC 1984,1985,1998; [d]U.S. EPA 2005; [e]van Horn 1998; [f]Battye et al. 1994

Table 3 N content of harvested crops and the partitioning ratios used to classify crops as livestock feed or human food, by commodity

Crop type	Yield unit (YU)	Nitrogen content (kg-N/YU)	Fraction of crops fed to humans (%)	Fraction of crops fed to animals (%)	Proportion remaining after handling loss (%)
Field corn for grain	Bushel	0.80	4	96	90
Field corn for silage	Ton	3.22	0	100	100
Wheat	Bushel	0.50	61	39	90
Oats	Bushel	0.27	6	94	90
Barley	Bushel	0.41	3	97	90
Sorghum for grain	Bushel	0.44	0	100	90
Sorghum for silage	Bushel	6.70	0	100	100
Irish potatoes	Cwt.	0.16	100	0	90
Rye for grain	Bushel	0.49	17	83	90
Alfalfa hay	Ton	22.87	0	100	100
Other hay	Ton	9.86	0	100	100
Soybean	Bushel	1.61	2	98	90
Crop pasture	Acre	2,000.00	0	100	90
Non-crop pasture	Acre	1,000.00	0	100	90

Modified from Lander et al. (1998) and Jordan and Weller (1996)

values were then multiplied by emission factors for eighteen individual livestock categories (Table 2). The parameters used for manure production and emission for each livestock class were derived from Kellogg et al. (2000); Lander et al. (1998), and the EPA emission inventory report (U.S. EPA 2005). Volatilization was estimated under the static livestock method by multiplying NH_3 emission factors (Battye et al. 1994) by estimates of the average livestock population.

Volatilization losses from fertilizer were calculated as a percentage of fertilizer application in each catchment: 15% for urea, 2% for ammonium nitrate, 8% for nitrogen solution, 1.0% for anhydrous ammonia, and 4.4% for other combined fertilizers (Battye et al. 1994; Goebes et al. 2003). To account for N volatilized as ammonia from plants during crop senescence, especially at the end of the growing season, we used crop acreage data from the USDA Census of Agriculture, assuming volatilization rates to be 6,000 kg-N km^{-2} $year^{-1}$ for corn, 4,500 kg-N km^{-2} $year^{-1}$ for soybean, and 3,500 kg-N km^{-2} $year^{-1}$ for wheat (Goolsby et al. 1999). Hay was assumed to be harvested before the end of growing period and thus N volatilized from hay was not estimated.

Due to the short life span of NH_3 in the atmosphere, some fraction of volatilized N is likely to be redeposited within the area where it was emitted rather than transported out of the system. Following Boyer et al. (2002), we assumed that 75% of NH_3 emissions are re-deposited locally and the remaining 25% are exported. Net atmospheric N deposition was estimated by reducing total atmospheric N deposition by 25% to account for assumed losses to volatilization. We acknowledge that using a fixed volatilization rate of 25% is a source of uncertainty in our estimates of net N deposition. This should not have much effect in catchments where net atmospheric nitrogen deposition is a relatively small fraction of total N inputs, but could be of greater concern for forested catchments.

Crop N fixation

Legumes considered for this study included soybean, alfalfa, other non-alfalfa hay, and pasture. Crop N fixation associated with non-alfalfa hay and pasture was estimated by multiplying the harvested land area in each case by the average of published N fixation rates for non-alfalfa hay (11,600 kg-N km^{-2} $year^{-1}$) and crop pasture (1,500 kg-N km^{-2} $year^{-1}$) (Boyer et al. 2002; Burkart and James 1999).

The amounts of N fixed by soybean and alfalfa, the principal legumes within the LMB, were estimated by two approaches, area and yield. Following Boyer et al. (2002) we estimated N fixation from the product of area cultivated and the average rate of N fixation in U.S. agricultural production system measured by ^{15}N isotope dilution (soybean, 9,600 kg-N km^{-2} $year^{-1}$; alfalfa, 21,800 kg-N km^{-2} $year^{-1}$). Because the amount of N fixed by legumes per unit area may vary as function of yield (Barry et al. 1993) and soil N availability (Coale et al. 1985; David et al. 1997; Meisinger and Randall 1991), some studies have adopted an approach based on estimates of legume N yield and the percentage of this N that can be attributed to fixation (Barry et al. 1993; David et al. 1997; McIsaac and Hu 2004; Meisinger and Randall 1991). These authors argue that crop yield is the factor that best aggregates variables associated with crop, soil, and climatic conditions including available soil moisture, vigor of stand, density, and other management factors. Following the yield-based approach of Meisinger and Randall (1991), we calculated crop N fixation as the product of estimates of soybean and alfalfa N yield and the percentage of this N that can be attributed to fixation.

Because total N fixation by legumes includes the amount fixed and the amount taken up from the soil (NRC 1993), and the proportion of total legume N derived from fixation varies as a function of soil N availability (Meisinger and Randall 1991), we estimated the amount of N mineralized from soil organic matter (OM) using information from State Soil Geographic maps (STATSGO) (U.S. Department of Agriculture 1994) following the method put forth by Goolsby et al. (1999) and modified by Han (2007) to estimate soil organic N of the upper soil horizon.

Since the upper 30 cm of soil generally is considered the surface soil and is most readily influenced by agricultural activities, we estimated the soil organic N of this upper soil horizon. The mass of OM in the upper 30 cm of soil for each of $\sim$205 STATGO map units in the LMB was calculated as the product of the average soil bulk density, average percent OM content (each determined form the high and low reported values), and volume. Soil N content was estimated to be 3% of soil OM (Stevenson 1994), and to be mineralized at a rate of 2% per year in cultivated soil (Gentry et al. 1998). Finally, soil N mineralization for each map unit was aggregated to the corresponding watershed using area-weighting.

Data aggregation and final budgets

Except for catchment-level estimates of total atmospheric N deposition, all estimates of N inputs and outputs for NANI computations were based on county-level statistics and reapportioned to catchments using both area-weighting and land use-weighting. For the latter, the relevant land use types included cropland to apportion crop N production, urban area to apportion estimates of county-level human N consumption, and both cropland and urban lawns and golf courses to apportion estimates of county-level fertilizer for each catchment.

For soil N budgets, the sum of the estimates of agricultural N inputs and outputs were applied only to cropland, whereas N inputs from atmospheric N deposition were applied to the entire land area. Thus, the area-weighted estimate of soil N balance for each catchment was calculated by summing the area-weighted estimates of total atmospheric deposition (normalized by the total area of each catchment) plus the area-weighted estimates of total agricultural net N inputs (calculated as fertilizer N + crop N fixation + animal N manure—net volatilization of N). The area-weighted estimates were quantified by aggregating the county-level estimates of total agricultural net N inputs weighted by the fraction of cropland lying within each catchment, and finally normalized by the total area of each catchment unit.

Riverine TN concentrations and fluxes

Available data for river TN concentrations in Lake Michigan tributaries for 1970–1995 were retrieved from the USGS National Water Information System (NWIS), and the U.S. EPA Storage and Retrieval System (STORET). Due to limited data on TN concentrations over the target period as well as discontinuities in data records, we sometimes used TN concentrations from multiple monitoring stations if they were located close (within $\sim$1 km) to the corresponding USGS gauging station. Daily river discharge data were obtained from the USGS National Water Data Storage and Retrieval System (WATSTORE) (Table 1). Figure 3 illustrates time series of TN concentration and discharge data for four

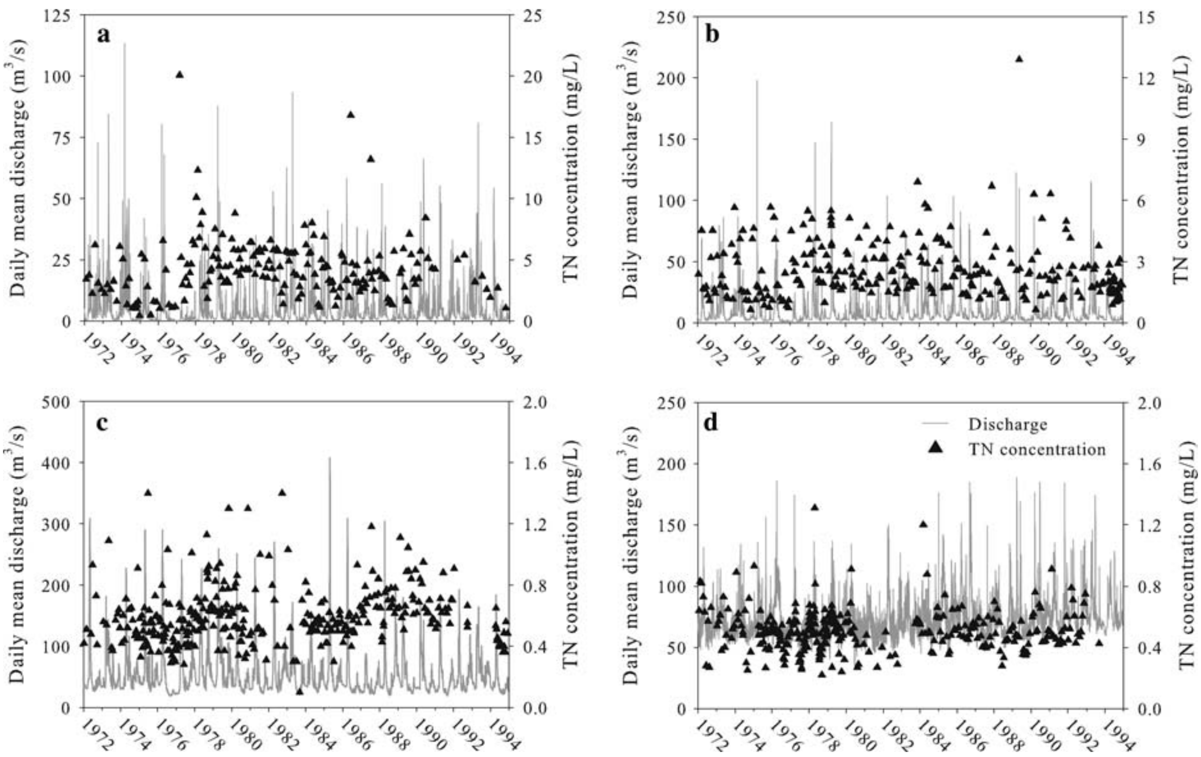


Fig. 3 TN concentration (mg/L, denoted with *black triangles*) in daily flows (m^3/s, denoted with *gray lines*) used for estimation of annual TN load illustrated for four tributaries [**a** Root (urbanized), **b** Sheboygan (agricultural), **c** Manistique (wetland), **d** Manistee (forested)] from January 1972 through December 1994

different rivers, representing forested (Manistee), urbanized (Root), agricultural (Sheboygan), and wetland (Manistique) catchments.

We estimated annual loads of TN exported from each tributary from TN concentrations and daily discharge using the USGS Estimator Regression Model (Cohn et al. 1989). The model was calibrated using multiple regressions between daily loads (estimated by multiplying daily average discharge by instantaneous concentration) and daily average discharges and the time of the year. With the exception of several catchments (Root in 1974, Menominee in 1982 and 1992, Ford in 1992, Escanaba in1974) that had few data points, approximately monthly concentration estimates were available for most catchments. To compensate for the limited quantity of TN concentration data we estimated TN export for each calendar year after first calibrating this model with 5 years of continuous data. For example, 1982 TN export was estimated by calibrating the model using 1980–1984 TN concentrations and daily discharge data.

Statistical analysis

Regression analysis was used to compare prediction of riverine N export across the 18 Lake Michigan catchments using individual N inputs, catchment characteristics (e.g. human population density, percent land cover in catchments), and total N inputs. The primary purpose of these regressions was simply to determine which method of estimating N inputs best predicted river TN exports for the 18 catchments. We applied the same exponential and linear regression approach to the nine alternative estimates of net N inputs for all catchments because some prior studies have found an exponential model to result in a better fit. To evaluate regression models we examined goodness-of-fit, as measured by the R^2 value and root mean square error (RMSE) using SPSS 15.0 (SPSS Inc. 2007). We also carried out an analysis of prediction errors following Alexander et al. (2002), which assesses the accuracy of prediction in terms of variability and bias. This analysis uses the difference between predicted and measured values of stream N export, expressed as a percentage of the measured export, and evaluates model accuracy through comparisons of the median and range of errors.

Results

Crop N fixation

Yield-based estimates of rates of fixation per unit area by soybean and alfalfa ranged from 3,773 to 13,159 kg-N km^{-2} year^{-1} and from 10,894 to 21,641 kg-N km^{-2} year^{-1}, respectively, and varied from catchment to catchment depending on estimates of soil N mineralization and legume yield (Table 4). All are within the ranges summarized by the NRC (1993) for rates of N fixation in soybean (1,500 to ~31,000 kg-N km^{-2} year^{-1}) and alfalfa (7,000 to ~60,000 kg-N km^{-2} year^{-1}) from various literature sources. Rates of crop N fixation from the area-based approach do not vary by catchment and tend to be mid-range (9,600 kg-N km^{-2} year^{-1}) for soybean and higher for alfalfa (21,800 kg-N km^{-2} year^{-1}), in comparison with yield-based estimates.

N input to each catchment from crop fixation ranged from 73 kg-N km^{-2} year^{-1} in the Manistique to 3,259 kg-N km^{-2} year^{-1} in the Sheboygan based on yield, and from 105 kg-N km^{-2} year^{-1} to 3,597 kg-N km^{-2} year^{-1} based on area (values are averages of area-(Table 5) and land use-(Table 6) weighting estimates). Our estimates fall within the reported range of other studies for forested catchments of the northeastern U.S. (70–370 kg-N km^{-2} year^{-1}, Howarth et al. 2006), and major agricultural catchments in the upper and middle Mississippi River Basins (1,930 to ~3,470 kg-N km^{-2} year^{-1}, Goolsby et al. 1999) using the same method. Similarly, our estimates of legume fixation based on yield are consistent with those in Illinois estimated by McIsaac and Hu (2004) using the same method.

Crop N fixation estimates were slightly higher using the area-based approach except where soybean-

Table 4 Estimates of average soil N mineralization rate and the corresponding proportion of plant N from N fixation by soybean and alfalfa hay for the 18 Lake Michigan watersheds, based on the yield-based method of Meisinger and Randall (1991)

ID	Catchment	Soil N mineralization (kg-N km^{-2} year^{-1})	Proportion of plant N from fixation		Crop N fixation rate[a]	
			Soybean (%)	Alfalfa (%)	Soybean (kg-N km^{-2} year^{-1})	Alfalfa (kg-N km^{-2} year^{-1})
1	Root	6,861	0.73	0.83	10,947	20,860
2	Milwaukee	6,726	0.74	0.84	10,800	20,685
3	Sheboygan	7,343	0.71	0.81	10,511	19,574
4	Fox	6,771	0.74	0.84	10,882	18,799
5	Oconto	5,471	0.75	0.80	10,775	16,844
6	Peshtigo	7,007	0.72	0.82	10,595	15,265
7	Menominee	7,926	0.68	0.78	8,232	12,847
8	Ford	13,688	0.53	0.73	4,031	11,507
9	Escanaba	9,608	0.59	0.69	4,427	10,894
10	Manistique	12,422	0.57	0.77	3,773	12,168
11	Manistee	3,935	0.81	0.84	9,292	11,793
12	Pere Marquette	4,092	0.80	0.84	8,819	15,075
13	Muskegon	4,955	0.77	0.82	9,999	13,569
14	Grand	6,547	0.75	0.85	11,027	19,516
15	Kalamazoo	4,843	0.78	0.82	10,835	18,530
16	St. Joseph	4,922	0.77	0.82	11,563	18,635
17	Trail Creek	3,677	0.82	0.85	10,781	18,191
18	Burns Ditch	8,430	0.65	0.75	13,159	21,641

[a] For comparison, the area-based estimates using the method of Boyer et al. (2002) are 9,600 kg-N km^{-2} year^{-1} for soybean and 21,800 kg-N km^{-2} year^{-1} for alfalfa

Table 5 Principal N inputs to the 18 catchments of the Lake Michigan Basin including comparisons of alternative estimation methods using area-weighting allocation

ID	Catchment	Crop N fixation		N fertilizer	Total atmos. dep.	Net N vol. as NH_3		Net atmos. deposition		Net import of N in food and feed		Animal N manure		Crop N export
		Based on yield	Based on area			Dynam.	Steady-state	Dynam.	Steady-state	Dynam.	Steady-state	Dynam.	Steady-state	
1	Root	1,906	1,825	2,088	846	432	414	414	432	1,374	1,679	937	1,808	3,255
2	Milwaukee	2,953	3,108	2,352	803	524	443	279	360	−1,513	1,126	2,745	5,163	4,739
3	Sheboygan	3,256	3,594	3,801	760	601	507	159	253	−2,237	1,107	3,202	6,186	5,421
4	Fox	1,979	2,229	2,000	717	367	317	350	400	−1,572	400	1,843	3,628	3,378
5	Oconto	1,079	1,337	952	667	185	153	482	514	−815	329	1,093	2,075	1,794
6	Peshtigo	478	641	460	647	73	62	574	585	−321	164	448	874	751
7	Menominee	235	340	153	630	25	22	605	608	−156	16	178	332	353
8	Ford	284	451	299	657	26	22	631	635	−157	6	190	340	397
9	Escanaba	70	104	35	632	4	4	628	628	24	39	41	66	100
10	Manistique	76	110	38	696	3	4	693	692	−44	−16	34	64	96
11	Manistee	318	524	291	835	33	30	802	805	−160	−3	196	351	422
12	Pere-Marquette	433	589	651	853	69	63	784	790	−270	−1	311	578	634
13	Muskegon	818	1,201	663	849	104	91	745	758	−515	11	571	1,068	1,150
14	Grand	1,755	1,802	2,754	956	453	422	503	534	−1,244	−509	1,282	2,186	3,141
15	Kalamazoo	1,369	1,448	2,449	958	441	424	517	534	−931	−467	1,179	1,990	2,810
16	St. Joseph	1,986	1,903	3,868	951	649	640	302	311	−1,831	−1,473	1,442	2,404	4,193
17	Trail Creek	2,966	2,304	5,265	938	718	720	220	218	−4,156	−3,697	832	1,525	5,568
18	Burns Ditch	2,094	1,924	6,090	938	688	693	250	245	−2,573	−2,695	434	681	4,509

All numbers in kg-N km^{-2} $year^{-1}$

Table 6 Principal N inputs to the 18 catchments of the Lake Michigan Basin including comparisons of alternative estimation methods, and river export of TN using land use-weighting allocation

ID	Catchment	Crop N fixation		N fertilizer	Total atmos. dep.	Net N vol. as NH_3		Net atmos. deposition		Net import of N in food and feed		Animal N Manure		Crop N export
		Based on yield	Based on area			Dynam.	Steady-state	Dynam.	Steady-state	Dynam.	Steady-state	Dynam.	Steady-state	
1	Root	2,267	2,169	2,385	846	502	482	344	364	−375	238	1,075	2,061	3,806
2	Milwaukee	2,826	2,976	2,243	803	499	421	305	382	−1,441	1,086	2,627	4,941	4,530
3	Sheboygan	3,262	3,600	3,812	760	602	508	158	252	−2,464	912	3,205	6,188	5,432
4	Fox	1,908	2,149	1,936	717	354	307	362	410	−1,502	387	1,769	3,482	3,254
5	Oconto	961	1,192	844	667	165	136	502	531	−710	308	972	1,847	1,589
6	Peshtigo	640	869	558	647	95	81	552	565	−439	209	593	1,162	998
7	Menominee	202	295	127	630	19	16	611	614	−135	−6	141	258	296
8	Ford	180	283	150	657	14	12	643	645	−130	−40	116	197	253
9	Escanaba	96	140	46	632	6	5	626	627	−37	−6	57	91	137
10	Manistique	69	100	34	696	3	3	693	693	−42	−18	30	57	88
11	Manistee	260	438	242	835	26	24	809	811	−152	−28	156	278	345
12	Pere-Marquette	282	388	474	853	44	41	809	812	−180	−8	198	369	413
13	Muskegon	809	1,187	639	849	101	87	747	761	−469	49	566	1,056	1,123
14	Grand	1,775	1,828	2,780	956	457	425	499	530	−1,280	−524	1,302	2,221	3,171
15	Kalamazoo	1,371	1,453	2,458	958	443	425	515	533	−852	−394	1,196	2,013	2,816
16	St. Joseph	1,898	1,794	3,729	951	626	621	325	330	−1,652	−1,460	1,312	2,108	3,880
17	Trail Creek	1,799	1,396	3,182	938	435	436	503	502	−1,374	−1,266	504	924	3,377
18	Burns Ditch	1,807	1,660	5,181	938	595	599	343	339	−1,701	−1,882	373	585	3,888

All numbers in kg-N km^{-2} $year^{-1}$

corn rotation was the primary form of agriculture (the Root catchment and southern regions of the LMB including St. Joseph, Trail Creek, and Burns Ditch). Overall, highest N fixation was found along the western side and the south shore of Lake Michigan. There was a strong correlation between cropland cover (percent area in total cropland) and N input from crop N fixation ($R^2 = 0.74$). The correlation increased slightly when only the area in soybean and alfalfa was considered ($R^2 = 0.85$).

Fertilizer

Most estimates of N fertilizer inputs derived using land-use weighting to apportion county-level values to catchments were slightly larger than those using area-weighting across the 18 catchments (Tables 5, 6). However, differences between the two methods were negligible in most cases, with the exception of Trail Creek and Ford River, where estimates were substantially lower based on land use-weighting in comparison with area-weighting. Application of N fertilizer, normalized by total catchment area, varied greatly among the 18 catchments, ranging from 35 kg-N km^{-2} year^{-1} in the Escanaba catchment to 6,090 kg-N km^{-2} year^{-1} in the Burns Ditch catchment, based on area-weighting allocation (Table 5). Spatial variation in N fertilizer use was better explained by variation in harvested corn acreage ($R^2 = 0.84$) as a percent of each catchment than by percent total cropland ($R^2 = 0.57$), presumably because corn receives more N fertilizer than other common crops.

Net atmospheric N deposition

Total depositional N inputs from the atmosphere exceeded total net losses of N to the atmosphere via volatilization from agricultural sources (animal manure, crop senescence, and fertilizer), resulting in net atmospheric N input for all catchments of the LMB. Spatial variation in net atmospheric N deposition is modest in comparison with agricultural sources such as N fertilizer use and crop N fixation, ranging from 159 to 802 kg-N km^{-2} year^{-1} based on the dynamic livestock model (Table 5).

The net atmospheric N deposition input showed a relatively high positive correlation with the fraction of undisturbed land, quantified as forest plus wetland area ($R^2 = 0.61$), and a negative correlation with the fraction of land area in agriculture ($R^2 = 0.56$). This is because atmospheric N deposition varies little across all catchments whereas N losses due to volatilization vary more and are highest from the more agricultural catchments.

Net import of N in food and feed

Differences in net import of N in food for humans due to alternative allocation methods were negligible for most catchments, with the exception of catchments of small size and varied land use (Root, Trail Creek, and Burns Ditch). However, estimates of animal N consumption and animal N products differed substantially between dynamic and static estimates for some catchments, resulting in large discrepancies between methods in estimates of the net import of N in food and feed (Tables 5, 6). This difference can be attributed to lower livestock population estimates computed by the dynamic versus static animal inventories. The magnitude of the difference varied by catchment and by which state a catchment was located in, rather than by the percentage of a catchment used for agriculture, suggesting regional differences in livestock management practices.

Comparison of N input estimates

The average of the eight NANI estimates for LMB catchments ranged from 775 to 1,082 kg-N km^{-2} year^{-1} in forested regions (catchments 7–10 in Table 7), from 3,728 to 6,770 kg-N km^{-2} year^{-1} in agricultural regions (catchments 3, 14–16 in Table 7) and from 4,077 to 5,588 kg-N km^{-2} year^{-1} in small urban and agricultural mixed catchments (catchments 1, 2, 17, and 18 in Table 7). N inputs were highest when estimated using the steady-state livestock model, and lowest using the soil budget. Differences among estimates across the eight NANI models were consistently greater (ranging from −48 to +60% of the average value) in the agricultural western region of the LMB and were smallest in the forested northern catchments (−20 to +24% of the average value). However, the difference among the eight estimates of NANI does not appear to be strongly related to the percentage of a catchment used for cropland. For example, estimates of net N inputs across the nine models were significantly different

Table 7 Total net N inputs for the 18 catchments estimated by the eight NANI models and the soil N budget model, averaged for the census years from 1974 to 1992, and river export of TN, averaged over the same time period

ID	Catchment	Model[a]									River TN export
		1	2	3	4	5	6	7	8	9	
1	Root	5,782	4,621	5,701	4,523	6,105	5,254	6,024	5,156	2,090	1,588
2	Milwaukee	4,071	3,933	4,226	4,083	6,791	6,537	6,946	6,687	3,590	657
3	Sheboygan	4,979	4,768	5,317	5,106	8,417	8,238	8,755	8,576	4,997	811
4	Fox	2,757	2,704	3,007	2,945	4,779	4,641	5,029	4,882	2,794	381
5	Oconto	1,698	1,597	1,956	1,828	2,874	2,644	3,132	2,875	1,812	369
6	Peshtigo	1,191	1,311	1,354	1,540	1,687	1,972	1,850	2,201	1,209	224
7	Menominee	837	805	942	898	1,012	937	1,117	1,030	818	206
8	Ford	1,057	843	1,224	946	1,224	935	1,391	1,038	1,007	211
9	Escanaba	757	731	791	775	772	763	806	807	674	216
10	Manistique	763	754	797	785	790	778	824	809	745	290
11	Manistee	1,251	1,159	1,457	1,337	1,411	1,285	1,617	1,463	1,185	228
12	Pere-Marquette	1,598	1,385	1,754	1,491	1,873	1,560	2,029	1,666	1,545	298
13	Muskegon	1,711	1,726	2,094	2,104	2,250	2,258	2,633	2,636	1,647	293
14	Grand	3,768	3,774	3,815	3,827	4,534	4,561	4,581	4,614	3,153	777
15	Kalamazoo	3,404	3,492	3,483	3,574	3,885	3,968	3,964	4,050	2,704	579
16	St. Joseph	4,325	4,300	4,242	4,196	4,692	4,497	4,609	4,393	3,405	850
17	Trail Creek	4,295	4,110	3,633	3,707	4,752	4,217	4,090	3,814	3,715	832
18	Burns Ditch	5,861	5,630	5,691	5,483	5,734	5,445	5,564	5,298	4,359	1,225

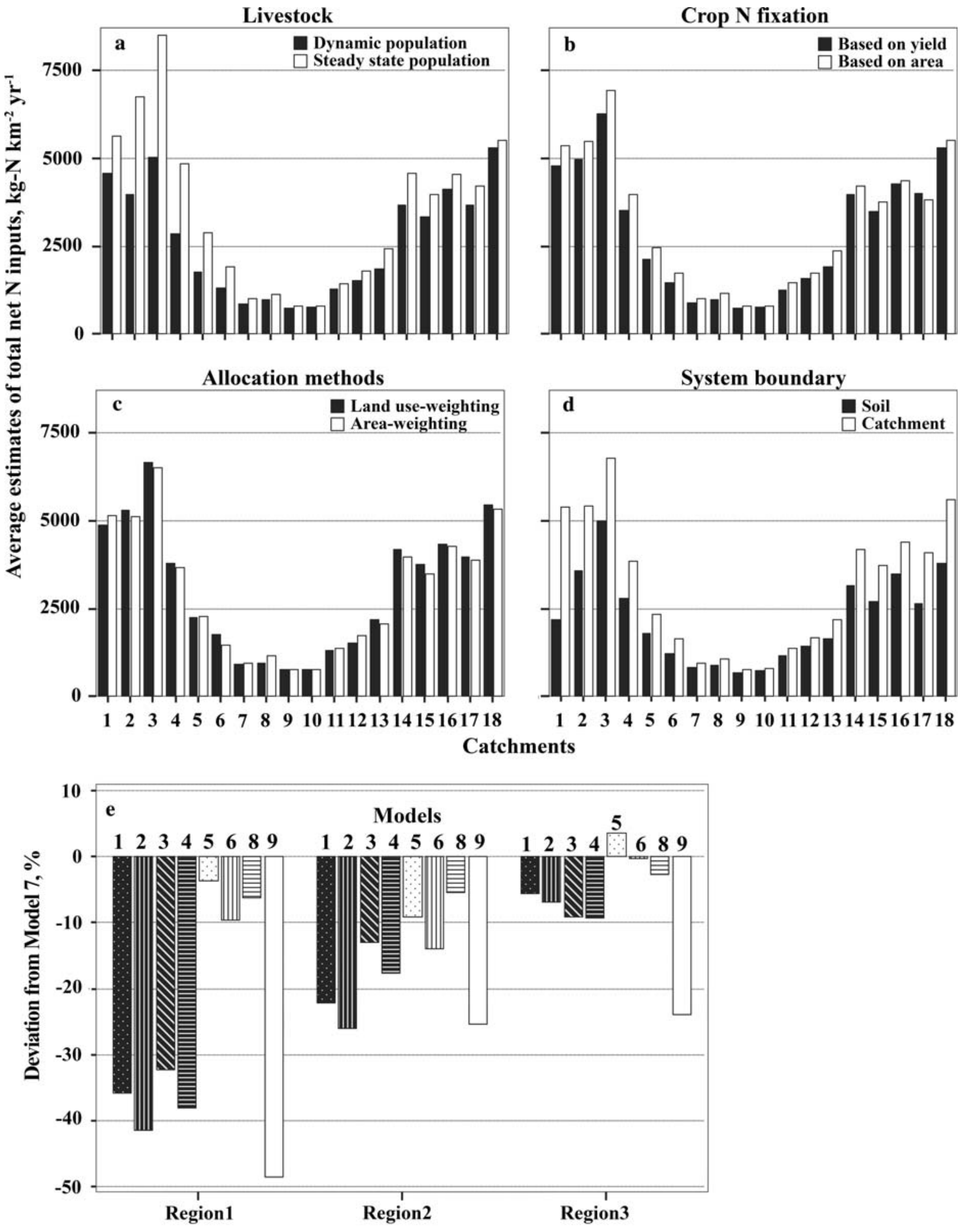
[a] Models 1 through 8 use the NANI budgeting approach (Fig. 2a), and Model 9 is based on the soil budget (Fig. 2b)

from each other for the agricultural western region of the LMB (one-way ANOVA, $p = 0.037$), but not for the agricultural southeast of the LMB. Overall, NANI was correlated with the extent of land in agriculture ($R^2 = 0.88$).

NANI estimates were most sensitive to whether animal populations were treated as steady state or dynamic (Fig. 4a). This influenced our estimates of animal N manure production, animal N consumption, volatilization of N from animal manure, and animal N food production. Estimates of NANI based on the dynamic livestock model were marginally lower than those based on the steady-state model ($p = 0.094$, one-way ANOVA) for the agricultural southwestern region of the LMB. Differences in estimates of NANI between computational choices related to crop N fixation (Fig. 4b; $p = 0.809$) as well as spatial allocation methods (Fig. 4c; $p = 0.65$) did not differ significantly.

Net N inputs to the soil compartment of each catchment ranged from 674 to 4,997 kg-N km^{-2} year^{-1} (Table 7) and in general were significantly lower than N inputs estimated by NANI methods (Fig. 4d; $p = 0.029$, one-way ANOVA). The largest discrepancy between NANI estimates and soil N budgets was seen in the highly urbanized catchments with relatively large human populations ($p = 0.003$). In contrast, differences between NANI and soil budgets were marginally significantly for agricultural catchments ($p = 0.068$) and not significant for forested catchments ($p = 0.231$). Most NANI estimates and the

Fig. 4 Comparison of N input estimates illustrating the influence of various computational choices. **a** Dynamic (*solid bars*) versus steady-state (*open bars*) livestock accounting, based on the average of models 1–4 versus the average of model 5–8. **b** Crop N-fixation based on yield (*solid bars*) versus area (*open bars*), based on the average of models 1,2,5,6 versus model 3,4,7,8. **c** Aggregation by land use (*solid bars*) versus area-weighting (*open bars*) spatial allocation based on the average of models 2,4,6,8 versus model 1,3,5,7. **d** N inputs for the soil compartment (*solid bars*) versus the catchment NANI method (*open bars*), based on model 9 versus model 1–8. **e** Relative differences between models based on comparing each against Model 7 which is similar to the traditional NANI budgeting method for three regions of the LMB [Region1: agricultural western (catchments 1–5), Region2: forested northern (catchments 6–12), Region3: agricultural eastern (catchments 13–18)]


Livestock
a
Dynamic population
Steady state population
Crop N fixation
b
Based on yield
Based on area
Allocation methods
c
Land use-weighting
Area-weighting
System boundary
d
Soil
Catchment
Average estimates of total net N inputs, kg-N km^{-2} yr^{-1}
0
2500
5000
7500
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Catchments
e
Models
1 2 3 4 5 6 8 9
Deviation from Model 7, %
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0
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-40
-50
Region1
Region2
Region3

soil N estimate were lower than obtained using model 7, which most closely approximates the traditional NANI method. Models 1–4 differed most, and the deviation was greatest for highly agricultural watersheds emphasizing livestock production (see Region 1 in Fig. 4e).

Relationship between N inputs and riverine TN export

The average annual export of TN from the 18 catchments ranged from less than 300 kg-N km^{-2} year^{-1} in forested areas to more than 800 kg-N km^{-2} year^{-1} in agricultural catchments, and was highest in small, urbanized catchments (Table 7). The latter exported as much as 1,588 kg-N km^{-2} year^{-1}, about five times higher than the amount of N exported from forested catchments.

Riverine TN export appeared to be directly related to land use, and was positively related to disturbed land (urbanized and intensively cultivated; $R^2 = 0.71$) and negatively related to extent of forested land ($R^2 = 0.64$). Spatial variation in river export of TN is better described by NANI ($R^2 = 0.81$) than by any individual input variables, although fertilizer application was the best individual input term ($R^2 = 0.56$).

To determine which computational approach best predicted riverine TN exports, we compared all nine estimates of total net anthropogenic N inputs to the 18 Lake Michigan catchments, after averaging across years (Fig. 5). For the resulting 18 regressions (9 net N input models * 2 regressions, linear and exponential), an exponential regression using NANI from Model 1 gave the strongest statistical relationship between inputs and exports ($R^2 = 0.94$) (Fig. 5a). Exponential regression models using NANI models

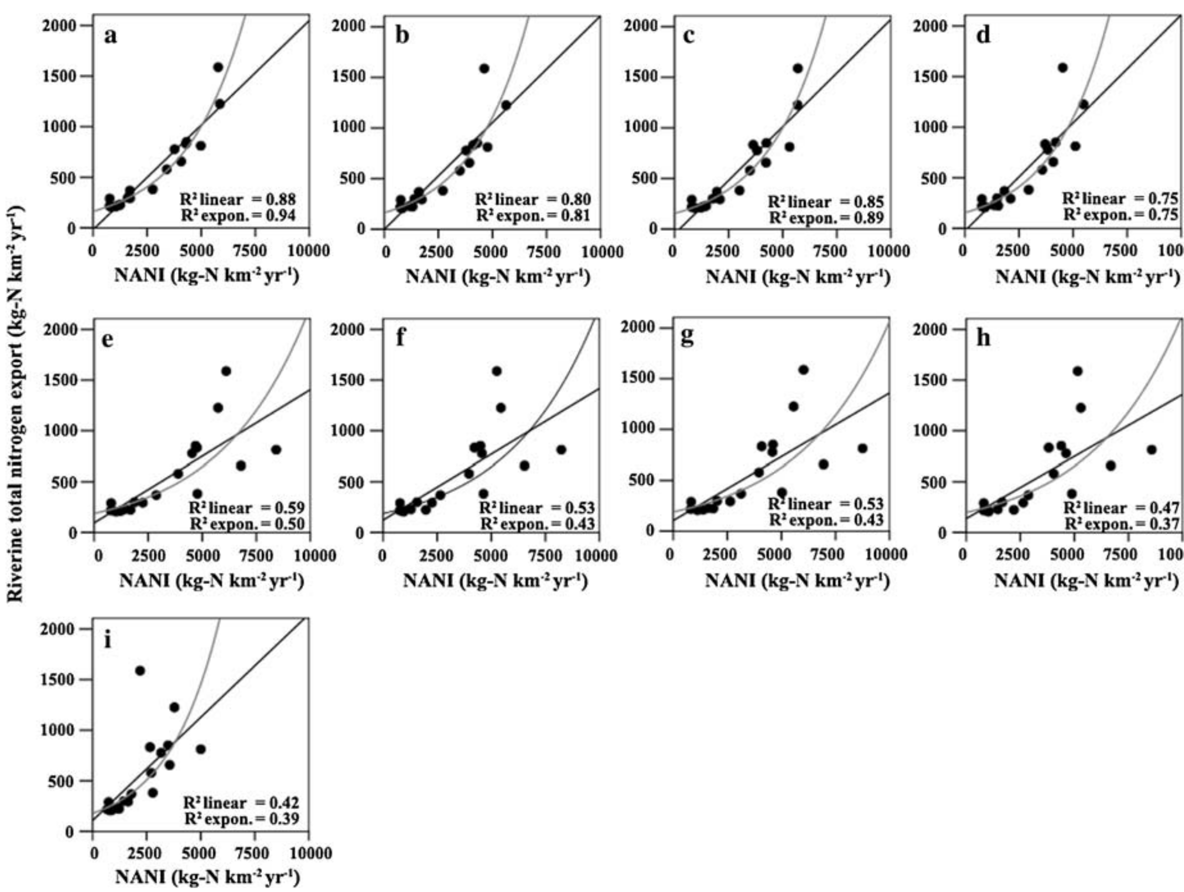

Fig. 5 Comparison of exponential and linear regressions estimating riverine TN exports from N inputs across the 18 catchments. **a**–**h** Correspond to NANI estimates from models 1 to 8, and **i** represents the estimate based on the soil compartment

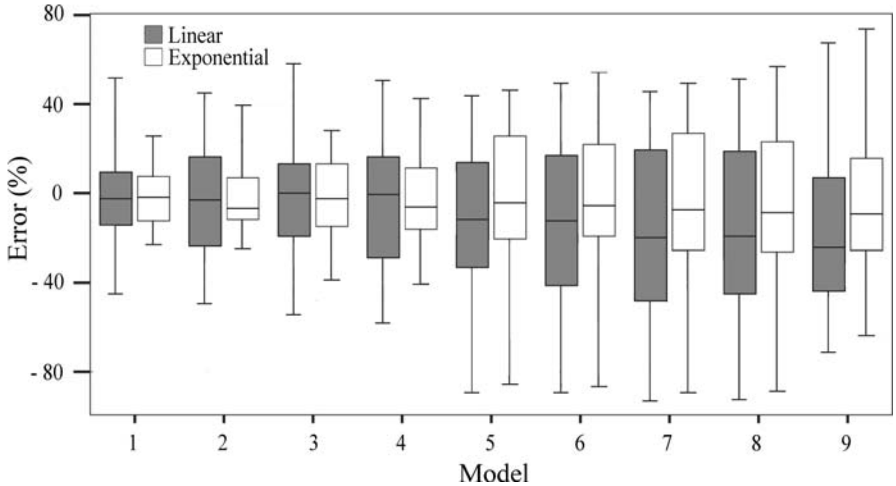

Fig. 6 *Box plots* showing errors in the prediction of riverine TN exports from the application of the nine linear (*filled boxes*) and exponential (*empty boxes*) regression models to the 18 Lake Michigan watersheds, each using an alternative estimate of N inputs based on different computation and assumptions. The *lower and upper edges* of the box represent the 25th and 75th percentiles, respectively. The *lower and upper whiskers* are drawn to the minimum and maximum values

1–4 based on the dynamic livestock population model always reported higher values of R^2 (Fig. 5) and lower values of RMSE compared with models 5–8 based on steady-state livestock populations. Similarly, the fit of exponential regressions using NANI models where crop N fixation was estimated based on yield was always better than those based on area. However, statistical fits and RMSE did not differ between area-weighted and land use-weighted allocation methods. In addition, regression models using net soil N input consistently had poor fits (linear $R^2 = 0.42$, exponential $R^2 = 0.39$) in comparison with regressions using catchment NANIs.

Comparison of model accuracy using the median and interquartile range (IQR) of the distribution of errors provides further evidence of model performance (Fig. 6). The exponential model based on NANI derived from Model 1 (dynamic animal population, crop N fixation based on yield, and area-weighting) has appreciably the highest precision (IQR = 22.4%) and the lowest bias (median error = −1.9%) in the prediction of nitrogen export. In addition, both linear and exponential regressions using NANI based on the dynamic livestock population model (models 1 through 4, Fig. 5a–d) resulted in smaller bias of prediction errors as well as higher precision, in comparison with regressions based on the steady-state livestock model (model 5 through 8, Fig. 5e–h). Moreover, a strong asymmetry in prediction errors as well as large negative median errors (−12.1 to −19.6%) for the linear regressions using NANI from models 5–8 indicates that those models tend to under-predict riverine TN exports for more catchments than they over-predict.

The fraction of NANI exported as riverine TN also varied depending on NANI estimation method. For Model 1, the fractional delivery of NANI as riverine N exports averaged 0.21 and varied among catchments from 0.14 to 0.38 with a standard error of 0.013. Model 7, similar to the approach used by Howarth et al. (1996) and Boyer et al. (2002), showed a lower fractional delivery with an average value of 0.13, and varied among catchments from 0.08 to 0.35 with a standard error of 0.016.

Discussion

Nitrogen inputs to the catchments of the LMB varied widely in relation to land use, were much higher in agricultural than forested catchments, and were highest in small mixed urban and agricultural catchments. Our estimates fall within the reported range from forested catchments of Maine (Howarth et al. 2006) to agricultural catchments in the Mississippi River Basin (Burkart and James 1999). Estimates of riverine TN exports for the 18 Lake Michigan catchments fall within the reported range of recent estimates for forested catchments of the northeastern U.S. (314–404 kg-N km^{-2} year^{-1}), (Boyer et al. 2002), major agricultural catchments in Illinois (500–2,400 kg-N km^{-2} year^{-1}) (David and Gentry 2000), and mixed urban and agricultural catchments (1,755 kg-N km^{-2} year^{-1}, Boyer et al. 2002).

Comparison of methods of N input estimation

The choice of method for estimation of N inputs to catchments influenced the magnitude of N inputs, and the extent of this effect varied by catchment. Computational adjustments to the NANI approach that took into account seasonal fluctuations in livestock numbers resulted in lower estimates than when end-of-year inventories were used. The discrepancies between the different livestock models were modest among urbanized catchments but pronounced among agricultural and forested catchments, especially in the southwestern LMB. Estimates of NANI that used area-based crop N fixation usually were higher than yield-based values, although the difference was not statistically significant. However, discrepancies between land-use and area-weighted allocation methods were negligible, suggesting that N inputs are, in effect, uniformly distributed within catchments. Soil compartment estimates of N inputs were consistently lower than NANI estimates, and this was especially true for urban catchments. This is not surprising, because the soil N budget only accounts for agricultural N inputs and outputs directly transferred to or from the soil, and does not consider N inputs or outputs from urban sources such as municipal and industrial discharge.

The extent of difference among NANI estimates from agricultural catchments also varied widely with agricultural practices. For example, the largest difference among the eight NANI estimates was observed in the catchments of the western region of the LMB, which have high numbers of those livestock categories that fluctuate most during a year (young cattle, poultry, and pigs raised for meat products), in comparison with crop-producing agricultural catchments located in Indiana and Michigan. The relatively poor fit between N inputs and river export for NANI models 5–8 (Fig. 5e–h) is largely due to the significantly higher estimates of N inputs under the steady-state livestock model in comparison with the dynamic model. This is most evident for catchments 2, 3, and 4, where livestock are primarily those categories that have shorter life cycle residency.

Prediction of river export from alternative N budgets

Our finding that riverine TN exports are better explained by NANI than any single input term is consistent with previous results (Boyer et al. 2002; Howarth et al. 1996; Jordan and Weller 1996; McIsaac et al. 2002). Prior studies have found strong correlations between net anthropogenic loading of N to catchments and river export of TN (Boyer et al. 2002; Caraco and Cole 1999; David and Gentry 2000). Furthermore, we also found that computational adjustments that took into account seasonal fluctuations in livestock numbers, and estimated crop N fixation by yield rather than by area of harvested legume, improved the statistical fit of NANI-TN export regressions. Average estimates of NANI based on Model 1, which included these adjustments and an exponential fit, accounted for 95% of spatial variation in average riverine TN exports with the smallest bias and variability in prediction errors.

The relationship between NANI estimated using the steady-state livestock model and riverine N export begins to diverge from linear at NANI higher than ~3,700 kg-N km^{-2} year^{-1} (Fig. 5e–h), and this divergence is more pronounced in catchments in the southern and southeastern regions of the LMB compared with those in the western region, resulting in more scatter. This supports the conclusion that NANI estimated by Model 1 is an excellent descriptor of long-term spatial variation in riverine TN export across the 18 Lake Michigan catchments.

Factors influencing the relationship between catchment N input and river export

Characteristics of the study catchments likely influence the importance of these adjustments to NANI computations. In the 16 catchments of the Northeastern U.S. reported by Howarth et al. (2006) and Boyer et al. (2002), most of the study area was forested (70%) and only three catchments exceeded 30% agriculture (maximum 35%), whereas ten of the 18 LMB catchments had >30% agricultural land (maximum 80%). In addition, while agricultural practices in the northeastern U.S. catchments relies mainly on livestock husbandry and thus high import of N for animal feed, those of the LMB varied widely, from grain to livestock, resulting in diverse patterns of net trade of N. When we apply Model 7, which most closely resembles the Howarth–Boyer model, to catchments of the LMB, N inputs accounted for only 53% of spatial variation in riverine TN exports across the 18 catchments and the fraction of nitrogen inputs exported by rivers fell to $\sim$13% of N inputs. This suggests that the traditional NANI approach lacks sufficient detail to estimate N inputs and outputs accurately for highly agricultural catchments occurring within an agricultural production system that varies across space at a relatively fine scale.

Environmental variables may also affect the fractional export of river N. Howarth et al. (2006) reported that catchments having lower precipitation and discharge export a lower fraction of their N inputs to rivers. Combining data from the 16 northeastern catchments studied by Howarth et al. with 12 catchments of the southeastern U.S., Schaefer and Alber (2007) found that the percent of N exported decreased as an exponential function of mean temperature, with a breakpoint between 11 and 12°C, below which fractional delivery of NANI varied little and above which it increased with rising temperature. They argued that the lower fractional export of N for the southeastern compared to the northeastern U.S. catchments may be explained by differences in denitrification rates due to different temperatures. However, mean temperature did not account for variation in riverine N export as a percentage of NANI for either the 16 northern or 12 southern catchments separately. For the 18 catchments of the LMB, using our model 1, we found no relationship between the fractional delivery of NANI by rivers and any of the variables of mean precipitation ($R^2 = 0.058$, $p = 0.335$), discharge ($R^2 = 0.007$, $p = 0.75$), or temperature ($R^2 = 0.001$, $p = 0.75$). However, using model 7, which is most similar to Howarth et al. (2006)'s method, we found a positive relationship between the fractional delivery of NANI by rivers and mean annual water discharge ($R^2 = 0.307$, $p = 0.017$), but not with either mean precipitation ($R^2 = 0.100$, $p = 0.201$) or temperature ($R^2 = 0.001$, $p = 0.902$). This may indicate that the influence of environmental factors on the fractional delivery of anthropogenic N inputs should be more cautiously interpreted, especially for highly diversified landscapes of small catchments, because the errors or uncertainty in estimates of anthropogenic N input or riverine N exports may lead to misinterpretation of the fate of the missing N as well as which factors are influential.

In the present study, based on R^2 comparisons and an error analysis, river TN export across the 18 LMB catchments was slightly better predicted using an exponential rather than a linear model (see Figs. 5, 6), and only when NANI was estimated using the dynamic livestock model. The stronger predictive capacity of exponential relative to linear regression models may suggest that high N inputs from human activities exceed the capacity of the terrestrial and aquatic systems to process and store nitrogen inputs. Jordan and Weller (1996) also observed a non-linear relationship between net anthropogenic N inputs and riverine nitrate fluxes for U.S. rivers in the 1980s, finding that higher NANI estimates were associated with higher riverine discharges of nitrate for regions receiving more than 2,000 kg-N km^{-2} year^{-1}. Similarly, Aber et al. (2003) found that nitrogen losses from forested catchments in the northeastern U.S. increased dramatically and non-linearly as atmospheric deposition exceeded $\sim$700 kg-N km^{-2} year^{-1}. Both studies can be interpreted as evidence of nitrogen saturation. Several explanations may account for the finding that relationships are linear in some studies and exponential in others. Both N inputs and river exports are subject to estimation error (David and Gentry 2000; McIsaac et al. 2002; Meisinger and Randall 1991) and authors have used either nitrate or TN as the export term, both of which may affect the statistical relationship.

In conclusion, our comparison of anthropogenic nitrogen inputs to catchments using eight variants of the NANI approach as well as a soils compartment model demonstrates clearly that differences among N budgeting models can markedly influence the estimation of N inputs. Computational methods that incorporate more detailed description of agricultural N sources, including the dynamic structure of livestock populations and variation in crop N fixation, led to improved prediction of riverine TN exports. This was especially noticeable when applied to catchments with a wide variety of landscape characteristics such as land use, geology, and climate.

Acknowledgments This work was supported by grants and a fellowship from the University of Michigan School of Natural

Resources and Environment and a Rackham Discretionary Fund. We are grateful to Dan Brown, George Kling, Don Scavia, and Nathan Bosch for their insights and comments and to two anonymous reviewers for their very helpful comments.

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