

The influence of impoundments on nutrient budgets in two catchments of Southeastern Michigan

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Abstract N and P budgets quantify inputs and outputs of nutrients at the catchment scale to allow evaluation of inputs and outputs as well as inferences about transport and processing based on unaccounted-for nutrients. N and P budgets were constructed for two catchments in southeastern Michigan with markedly different numbers of impoundments, over two years, to evaluate the influence of impoundments on nutrient fluxes from each catchment. The Huron, with 88 impoundments >10 ha, stored $156 \text{ kg P km}^{-2} \text{ y}^{-1}$, while the Raisin (with 14 impoundments) had a net export of $102 \text{ kg P km}^{-2} \text{ y}^{-1}$. The Huron catchment also stored and denitrified more N than the Raisin catchment – $2,418 \text{ kg N km}^{-2} \text{ y}^{-1}$ compared to $1,538 \text{ kg N km}^{-2} \text{ y}^{-1}$. Riverine export of N and P also varied markedly between the catchments, with the Huron River exporting 288 kg N and $7 \text{ kg P km}^{-2} \text{ y}^{-1}$ and the Raisin River exporting $1,268 \text{ kg N}$ and $34 \text{ kg P km}^{-2} \text{ y}^{-1}$. We then re-calculated budget results from previous studies using the approach of the present study, altering input and outputs fluxes as well as system boundaries to obtain comparable budgets. For these comparable budgets, annual P outputs on average accounted for 77% of inputs whereas N outputs accounted for only 39% of N inputs. Across catchments, the percent of inputs exported by the river averaged 16% for N and 5% for P, indicating more effective retention of P than N.

Keywords Catchment · Impoundments · Mass balance · Nitrogen · Nitrogen budget · Phosphorus · Phosphorus budget · Rivers

Introduction

To improve our understanding of nutrient dynamics at the catchment scale, recent studies have developed catchment nitrogen (N) and phosphorus (P) budgets that account for inputs and outputs of these nutrients (Baker and Richards 2002; Boyer et al. 2002; David and Gentry 2000; Goolsby et al. 1999). These previous studies illuminate sources and fates of N and P in catchments across the U.S., and permit inferences about the transport and processing of nutrients within catchments. A general finding is that much of the N and P inputs are unaccounted for, indicating storage of these nutrients or the presence of additional output fluxes not considered in the budget. One potential mechanism for this observed storage and loss is removal of N and P in impoundments; however, no budgeting studies to date have explored catchment-scale effects of impoundments on river export of nutrients.

Research demonstrating the capacity of impoundments to remove N and P is mounting. Stanley and Doyle (2002) discussed the potential benefits of impoundments in removing nutrients from river systems, and argued that P settling and N denitrification were the primary mechanisms. Hillbricht-Ilkowska (1999) claimed that impoundments were “disturbing

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inserts” in the framework of the river continuum concept, providing places for N and P removal. Their comparison of 17 impoundments and 10 stream reaches in Eastern Europe documented NO_3 production in stream reaches and NO_3 removal in impoundments. In a large reservoir and its upstream reach in agricultural Illinois, Wall et al. (2005) found high NO_3 loss rates due to denitrification within an impoundment. In their study of 35 large rivers around the world, Caraco and Cole (1999) found a close relationship between N inputs and river export for most rivers. Three of the rivers had 3-fold lower river N exports than predicted by the model, which was attributed to the presence of large reservoirs with long residence times. Suspended sediment particles with their associated P have been shown to quickly settle from the water as velocity decreases during the transition from a lotic to lentic system (Kufel 1993). P stored in the sediments of an impoundment remains in place unless internal P loading (due to desorption of sediment P or decomposition of organic matter) exceeds P sedimentation (Hillbricht-Ilkowska 1999), or the dam that created the impoundment is removed, causing sediments to be mobilized (Hart et al. 2002). Vorosmarty et al. (2003) estimated that impoundments trapped more than 50% of sediment flux in regulated rivers around the world, further confirming the important

role of impoundments in reducing P loads through settling of P adsorbed to sediments.

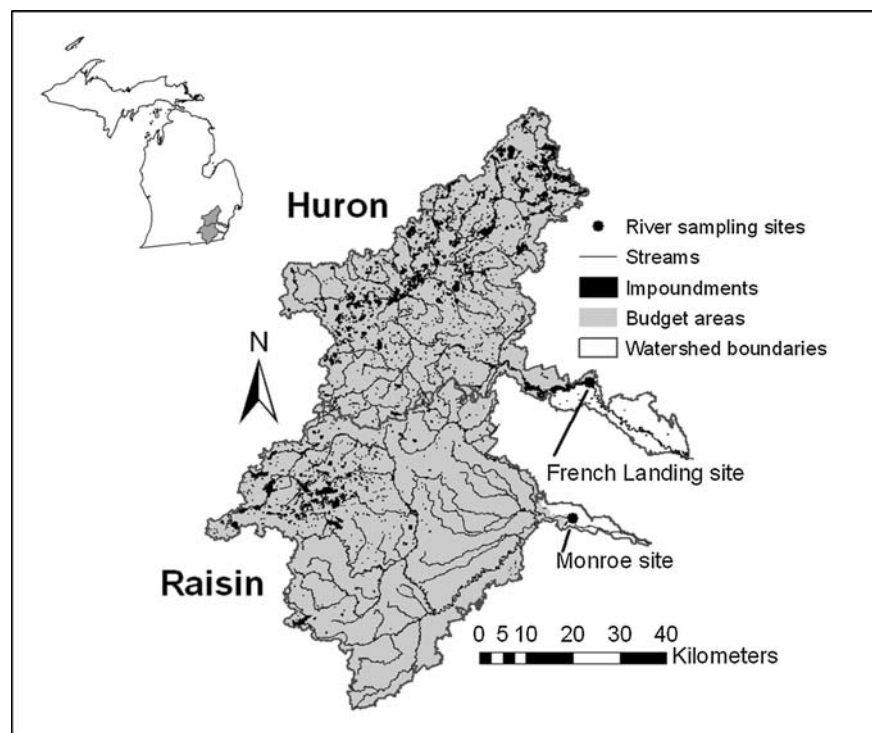
The present study compares two catchments in southeastern Michigan, the Huron and Raisin, which differ in land use and extent of impoundments, to investigate nutrient processing and transport at the catchment scale. To determine the influence of impoundments on river export of nutrients, we compared N and P budgets for the Huron and Raisin. To assess the generality of our results, we constructed comparable budgets from results of prior studies using the approach of the present study. We found that catchments with more impoundments export fewer nutrients, that catchment inputs generally were highly correlated to river export, and that the catchments retained P more effectively than N.

Methods

Study area

The Huron (2,377 km²) and Raisin (2,737 km²) are catchments of mixed land use in southeastern Michigan that drain into the western end of Lake Erie (Fig. 1). They are characterized by hilly to moderately

Fig. 1 Huron and Raisin catchments in southeastern Michigan. Shaded areas denote the region on which budgets are based, and are defined by drainage area above French Landing and Monroe sampling sites, respectively



undulating topography in their upper catchments, underlain with moraines, till deposits, and outwash plains. The lower portions of the Huron and Raisin are underlain by sands and clays from glacial Lake Erie (Knutilla and Allen 1975). These two adjacent catchments fall within 3 ecoregions, the Southern Michigan/Northern Indiana Till Plains, the Huron/Erie Lake Plain, and the Eastern Corn Belt Plains (Omernik 1987). Land use in the two catchments is similar with both being largely agricultural (Table 1), but the Huron has less agriculture and more forest and urban land area compared to the Raisin. Precipitation is slightly higher in the Huron catchment, but river water yields are lower. This likely is due to more evapotranspiration in forested areas and evaporation from impoundments in the Huron catchment.

Both catchments originate in “lake district” areas, but their middle and lower sections differ notably in degree of river impoundment. The Huron catchment has a total of 88 impoundments that have surface areas of at least 10 ha, while the Raisin has only 14 impoundments of this size. These river impoundments are both artificial (created by dams) and natural (lakes), and most are controlled through dam operations or lake level control

Table 1 Characteristics of the Huron and Raisin catchments for nutrient budget areas. Note the large difference between the Huron and Raisin in the number of impoundments and the water residence time for each catchment

Characteristic	Huron	Raisin
Catchment budget area (km ²)	2,191	2,673
Precipitation (mm/y)		
2004	893	866
2005	830	786
Average (1995–2005)	889	848
Stream yield (mm/y)		
2004	196	236
2005	184	218
Average (1995–2005)	185	254
Land cover (2001)		
Forest	26.5%	10.5%
Agriculture	41.8%	75.2%
Urban	10.0%	3.6%
Wetland	14.5%	7.8%
Water	4.4%	1.5%
Other	2.8%	1.5%
Number of impoundments	88	14
Water residence time (days)	139	9

structures. This discrepancy in number of impoundments leads to a large difference in water residence times for the mainstem channel of each river network.

Huron and Raisin nutrient budgets

N and P budgets were developed for each catchment following methods described in Boyer et al. (2002) for N and Baker and Richards (2002) for P, with slight modifications described below. Catchment N budgets included inputs (atmospheric deposition, fertilizer application, N fixation in agricultural and natural lands), system storage (the N stock or pool stored in the catchment), and outputs (NH_x volatilization, export of food and feed, and river export) (Fig. 2). Boyer et al.’s (2002) methodology was modified by the inclusion of NH_x volatilization as an output rather than combining it in net atmospheric deposition, and also by the inclusion of food and feed as an export rather than an input due to lower consumption needs and higher crop production in the Huron and Raisin compared to northeastern U.S. catchments studied by Boyer et al. (2002). Note that denitrification was not included in the budget, but its potential inclusion is discussed later. P budgets included inputs (atmospheric deposition, fertilizer and manure application, point source river discharge, and sludge application to agricultural lands), system storage (the P stock or pool stored in the catchment), and two outputs (crop export and river export) (Fig. 3). Nutrient budgets differ not only in input and output terms, but also in how the system or accounting unit is defined. In P budgets we included the soils and water inside the defined catchment. This is a modification from Baker and Richards (2002), who included only the soils compartment as the defined system. The system boundary in the N budgeting approach is defined

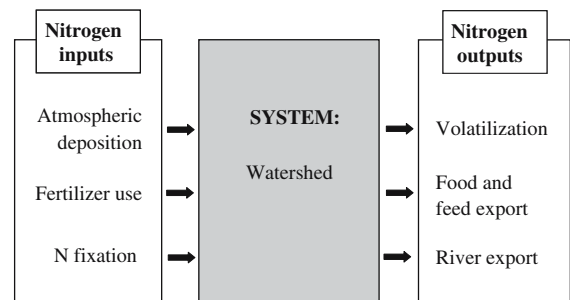


Fig. 2 Conceptual diagram for nitrogen budget including inputs, system, and outputs

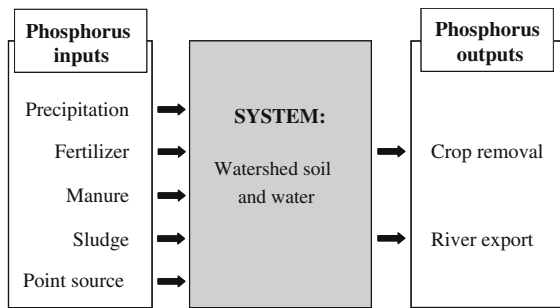


Fig. 3 Conceptual diagram for phosphorus budget including inputs, system, and outputs

more broadly. Within the defined catchment, the system included water and soil, the air above the land and water surface, as well as everything living in the water, soil, and air. This is an important distinction because the difference in system boundaries dictates inclusion of certain inputs and outputs. In the P budget, for example, manure application was a new input of P into the system, whereas in the N budget, manure application was considered internal cycling and thus not included in input or output calculations. A more detailed description of budgeting methodology can be found in Bosch (2007).

Atmospheric deposition and NH_x volatilization

Atmospheric deposition included both inorganic and organic deposition. Data for wet inorganic N deposition in the forms of nitrate (NO_3^-) and ammonium (NH_4^+) were obtained from the National Atmospheric Deposition Program (NADP 2006), which has an active sampling site in Ann Arbor, Michigan, centrally located to both catchments. Dry inorganic N deposition data were available for the same sampling site from the EPA Clean Air Status and Trends Network (CASTNET 2006), and included fluxes of nitric acid (HNO_3), NO_3^- , and NH_4^+ . Atmospheric organic nitrogen (AON) deposition has been shown to consistently make up 30% of total N deposition (Neff et al. 2002). Following Boyer et al. (2002), we assumed that only half of this deposited AON is from outside of the catchment, so AON was estimated as 15% of total N deposition.

NH_x volatilization represents a loss of N to the atmosphere and out of the system. This N emission is produced by livestock operations and fertilizer application. Livestock population statistics (NASS 2006) for dairy cows, beef cattle, young cattle, pigs and

hogs, sheep and lambs, horses and ponies, layer chickens, broiler chickens, and turkeys in the 2 catchments were combined with literature NH_x emission rates (Battye et al. 1994 as reported in Boyer et al. 2002) to calculate volatilization from animal waste. Volatilization losses from fertilizers were calculated as a percentage of application in each catchment—15% for urea, 0.1% for anhydrous ammonia, and 2% for other combined fertilizers (Battye et al. 1994 as reported in Boyer et al. 2002).

Only atmospheric deposition of P in wet deposition from rainfall was considered in the P budgets. We used the value of $14.1 \text{ kg P km}^{-2} \text{ y}^{-1}$ previously estimated by Baker and Richards (2002) for catchments around Lake Erie.

Fertilizer application

Catchment N and P fertilizer application was estimated from state fertilizer consumption data (Terry and Kirby 2005, 2006) and state- and county-level farmer fertilizer expenses from the USDA National Agricultural Statistics Service (NASS 2006). State fertilizer consumption data were distributed among counties within the state based on proportion of the total statewide farmer expenses that the county represented. Catchment fertilizer application was estimated by multiplying the proportion of each county within the catchment by each county's total fertilizer consumption and summing this result for all counties in the catchment. This procedure was used for translation of all county-level data into catchment data when necessary in various budget fluxes.

Manure application

Manure application was considered as a budget input only for P, and was considered internal system processing in N budgets because of the way the system boundaries were defined in the budgeting approaches. Manure applications were estimated based on county-level data similar to fertilizer application estimation. Livestock populations of dairy cows, beef cattle, young cattle, pigs and hogs, sheep and lambs, goats, horses and ponies, layer chickens, broiler chickens, and turkeys (NASS 2006) were combined with animal-specific excretion rates and nutrient contents (OSU 2006) to estimate manure production and subsequent application to agricultural fields.

Sewage disposal

As with manure inputs, human waste was an input only in P budgets and was considered as internal cycling within the system in N budgets. Human waste with associated P enters municipal wastewater treatment plants (WWTPs) and either becomes sludge or is directly discharged into receiving waters. In the WWTPs of the Huron and Raisin catchments, about 95% of incoming P is incorporated into sludge (J. Johnson, personal communication) and the other 5% is a point source discharge into rivers. Most WWTPs in southeastern Michigan apply this sludge to agricultural fields, and the remainder incinerate their sludge and deposit the ashes in landfills. Effluent P loads were obtained for all active point source dischargers (most of which are WWTPs) in each catchment from the EPA Permit Compliance System database. These point P discharge sources were summed for both catchment budget areas. WWTP dischargers that applied sludge to land (MDEQ 2005) were assumed to apply 19 times (95%/5%) the amount of P that is discharged to the river.

Nitrogen fixation

N fixation associated with agricultural lands as well as non-agricultural vegetation was another important N input into the Huron and Raisin catchments. Fixation rates used in this study were taken directly from Boyer et al. (2002). Land cover areas were obtained from the USDA National Agricultural Statistics Service for crops (NASS 2006), 2001 land cover data from the NOAA Coastal Change Analysis Program (CCAP 2005) for grassland and wetland, and USDA Forest Service Forest Inventory and Analysis Program was used to quantify black locust (*Robinia pseudoacacia*) forest stands (FIAP 2006). Fixation rates were combined with land cover areas as in Boyer et al. (2002) to calculate N-fixation in each catchment.

Crop export and food & feed export

Crop product P content (Kellogg et al. 2000) was combined with county-level crop yield data (NASS 2006) to calculate crop export P (Baker and Richards 2002). Food and feed export of N was calculated as crop and animal production minus human and animal

consumption requirements (Boyer et al. 2002). A human N consumption rate of $4.53 \text{ kg N person}^{-1} \text{ y}^{-1}$ (David and Gentry 2000) along with 2004 and 2005 population estimates from the U.S. Census Bureau were used to estimate human N consumption. Animal-specific N consumption rates from several sources (Luginbuhl et al. 1998; Ritchie 1994; UMES 1995; Van Horn 1998) were combined with livestock population statistics (NASS 2006) to estimate animal N consumption. Crop N production was estimated identically to crop P production, using crop product N content (Kellogg et al. 2000) and the same crop yield statistics. Animal production was based on the difference between animal consumption and animal excretion as in Boyer et al. (2002). Animal N excretion rates were calculated in the same way as manure P applications, but using manure N production rates (OSU 2006).

River export

Annual river export loads for 2004 and 2005 were estimated for each catchment based on N and P concentrations from direct water sampling and stream discharge data (Fig. 4). Daily river export concentrations of N and P are available at the Monroe sampling site on the Raisin (Fig. 1) nearly continuously for 1983-present from the monitoring programs of the National Center for Water Quality Research at Heidelberg College. Only scattered N and P data were available for the Huron River from municipal, state, and USGS sources. For this reason, we collected water samples biweekly for nutrient analysis at French Landing near the mouth of the Huron River from 2003 to 2006. Biweekly samples were supplemented with additional sampling during major storm events to evaluate a variety of flow conditions. For the Raisin catchment, daily mean discharge data were collected from the USGS gage on the Raisin River near Monroe (station # 04176500). Discharge data for the Huron River were obtained from dam operators at French Landing Dam in Belleville, MI, and compared with the nearby USGS gage site at Ann Arbor (station # 04174500) for verification.

Annual river export loads were estimated for the Raisin River at Monroe and the Huron River at French Landing Dam using AutoBeale, which is an implementation of the Beale Ratio Estimator (Richards 1998). This estimation procedure first computes an average

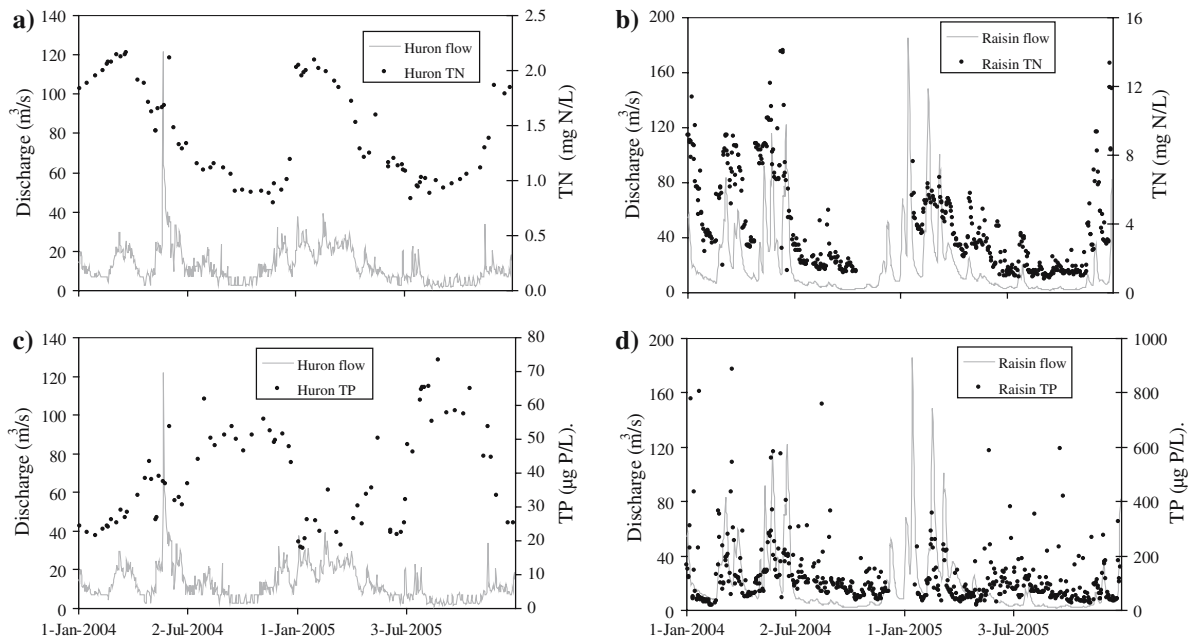


Fig. 4 Daily mean discharge (m^3/s), TN concentration (mg N/L), and TP concentration ($\mu\text{g P/L}$) for the Huron (French Landing site) and Raisin (Monroe site) Rivers over the 2004 and 2005

calendar years. Four panels represent: (a) Huron TN and discharge, (b) Raisin TN and discharge, (c) Huron TP and discharge, and (d) Raisin TP and discharge

daily load based on dates with concentration data and then adjusts this average daily load according to the proportion of the annual flow included within the subset of dates with corresponding concentration data. This adjusted average daily load is then multiplied by 365 to obtain an annual load estimate. Use of AutoBeale allowed breaking of the year into several time intervals, each with their own average daily load, to account for seasonal and flow differences throughout the year.

Nutrient concentrations were determined using standard automated colorimetric procedures on a Technicon Auto Analyzer II as detailed by Davis and Simmons (1979). Ammonia (NH_4) was determined by the phenate method based on the indophenol blue reduction. Nitrate/nitrite (NO_3) was determined by the cadmium reduction method based on the azo dye reaction. Soluble reactive phosphorus (SRP) was determined by the molybdate/ascorbic acid method based on the formation of a phosphomolybdate blue complex. Total phosphorus (TP) and total dissolved phosphorus (TDP) (Menzel and Corwin 1965) as well as total dissolved nitrogen (TDN) (D'Elia et al. 1977) were determined like SRP and nitrate/nitrite respectively, after digestion with potassium persulfate in an autoclave. Samples for total particulate nitrogen

(TPN) were processed through pre-combusted (4 h at 450°C) Whatman GF/F filters and frozen until analysis. Prior to analysis filters were thawed and dried at 80°C for 24h. TPN concentrations were then determined on a Carlo-Erba model 1110 CHN elemental analyzer. Monitoring data for the Raisin catchment did not include TDN or TPN, but total Kjeldahl nitrogen (TKN), NO_3 , and NH_4 were included. TN concentrations were then calculated for the Raisin catchment by summing TKN and NO_3 . Total organic nitrogen (TON) was calculated as TN minus NO_3 and NH_4 .

Re-calculation of budgets from other studies using the reference method

Comparing the results of this investigation to similar budget studies allows conclusions to be broadened beyond southeast Michigan and identifies limitations of current budgeting approaches. However, among-study comparison of nutrient inputs and outputs as well as the proportion of inputs accounted for as budget outputs is difficult because of differences in budgeting methods. This was addressed by employing a number of assumptions and approximations in order to reconstruct all budgets to be consistent with the

budgeting approach used for the Huron and Raisin, which is considered the “reference method” for the remainder of this paper.

In addition to the Huron and Raisin, phosphorus budgets were constructed for the State of Illinois, the Maumee and Sandusky catchments in northern Ohio, the Muskingham and Minnesota catchments in the Mississippi Basin, and the entire Mississippi Basin using the reference method. Baker and Richards (2002) did not include surface waters in their system definition for the Maumee and Sandusky, and they assumed point source discharges were transported to the river mouth without any load reduction. To adjust the original budgets, point source discharges were added back into the river export loads and also included as an input. David and Gentry’s (2000) P budget methodology for the state of Illinois is similar to those used for N budgets, in which system boundaries include above-ground terms, and fluxes are combined to form net input and output fluxes. Few of the inputs and outputs included in the Huron and Raisin P budget approach were explicitly included by David and Gentry (2000), so re-calculation of their budgets to conform with the reference method was only an approximation. Though Goolsby et al. (1999) did not formally construct P budgets, most of the important inputs and outputs are reported, so it is possible to re-calculate their budgets. Reported fertilizer application rates, manure application rates, and point source discharges were used from David and Gentry (2000) and Goolsby et al. (1999) for the state of Illinois, Muskingham, Minnesota, and the entire Mississippi basin. Point source discharge and manure application for Illinois were interpolated from time series plots included in David and Gentry (2000). A precipitation rate of $14 \text{ kg P km}^{-2} \text{ y}^{-1}$ was added as well as sludge inputs based on Baker and Richards (2002). Crop and river P exports were reported for all 4 of these geographic units except crop export for the state of Illinois, which was estimated from the crop export rate for the Illinois River catchment ($1,353 \text{ kg P km}^{-2} \text{ y}^{-1}$) included in Goolsby et al. (1999).

To enable comparisons between prior studies and N budgets for the Huron and Raisin, analogous budgets were re-calculated for the state of Illinois and three catchment units in the Northeast (Mohawk, Rappahannock, and all the northeastern U.S. catchments combined), using input and output fluxes provided in David and Gentry (2000) and Boyer et al.

(2002) to accord with the reference method. The Muskingham, Minnesota, and the entire Mississippi Basin could not be included in these budget comparisons because the approach of Goolsby et al. (1999) defined system boundaries differently and included different fluxes. Since Boyer et al. (2002) used a net term for atmospheric deposition, N lost to NH_x volatilization had to be added to the northeastern catchments for comparison to the present study. Fortunately, these fluxes were explicitly included in Boyer et al. (2002). N fixation included in budgets was the sum of agricultural and natural (forest and wetland) N fixation, except for the state of Illinois, which only reported agricultural N fixation. N in food and feed was included as an input flux for the three northeastern U.S. units and as an output flux for the Huron and Raisin catchments as well as Illinois. NH_x volatilization from fertilizer and animal waste was not included in David and Gentry (2000) for Illinois, so this flux was estimated using the proportion of NH_x volatilization to fertilizer application for the Raisin catchment, which was 0.013.

Results

Huron and Raisin nitrogen budgets

Atmospheric N deposition contributed 22% of N inputs to the Huron catchment and only 12% of all inputs to the Raisin catchment over the two year study period (Table 2). Deposition rates were considered to be the same for both catchments because the closest deposition monitoring station was central to both catchments. Inorganic wet deposition accounted for 61% of the total atmospheric deposition, and inorganic dry and organic deposition contributed 24% and 15%, respectively. Wet deposition of NH_4^+ and NO_3^- was lower in 2005 when the catchments experienced below-average rainfall, and total dry deposition was higher in 2005. Nitric acid was the largest contributor to N in dry deposition.

Nitrogen fertilizer was the largest single input of N to both catchments, accounting for 42% of N inputs into the Huron catchment and 54% of inputs to the Raisin. Application rates per unit area of N in fertilizer were more than two times higher in the more agricultural Raisin catchment compared to the Huron catchment. Most fertilizer N was applied as

Table 2 Atmospheric N deposition for Huron and Raisin catchments ($\text{kg N km}^{-2} \text{y}^{-1}$)

	2004	2005
Inorganic wet deposition		
Ammonium	301	250
Nitrate	327	283
Total	628	533
Inorganic dry deposition		
Nitric acid	166	191
Nitrate	12	10
Ammonium	36	46
Total	214	246
Organic deposition		
Total	149	138
Total deposition	991	918

anhydrous ammonia, with minor contributions from urea (3%) and other forms (14%).

Nitrogen fixation in agricultural, wetland, and forested lands was another important source of N to both catchments (Table 3). Overall, N fixation accounts for about 35% of total N inputs to both catchments, and row-crop agricultural land provided a large majority

Table 3 Nitrogen fixation in agricultural and natural lands of each catchment ($\text{kg N km}^{-2} \text{y}^{-1}$)

	Huron		Raisin	
	2004	2005	2004	2005
Agricultural fixation				
Cropland	1,268	1,241	2,561	2,515
Pasture/Grassland	266	266	85	85
Total	1,534	1,508	2,646	2,600
Natural fixation				
Forest	21	21	22	22
Wetland	44	44	17	17
Total	65	65	40	40

Table 4 Food and feed consumption and production of N for each catchment as well as overall export ($\text{kg N km}^{-2} \text{y}^{-1}$)

		Human consumption	Animal consumption	Crop production for animals	Crop production for humans	Animal production for humans	Export in food and feed
Huron	2004	1,061	725	2,036	127	225	602
	2005	1,071	670	2,116	142	198	716
Raisin	2004	269	1,389	5,490	409	444	4,684
	2005	271	1,431	5,962	448	463	5,171

of N fixation. NH_x volatilization only accounted for 4% of the Huron's outputs, and only 1% of the Raisin's outputs. Most of this volatilization was from livestock-associated emissions rather than from volatilization of fertilizers.

Food and feed export was the largest output for both catchment N budgets, making up 67% of N outputs for the Huron and 79% for the Raisin. N production by crops and livestock exceeded N consumption needs for humans and animals in both catchments during 2004 and 2005 (Table 4). N production from wheat was the most important crop N source to humans in both catchments, and soybean crop N production was the largest source to livestock. River export loads of total N were over four times larger for the Raisin compared to the Huron (see below). Nitrate/nitrite accounted for most of the TN exported from each catchment via river export.

All inputs and outputs were aggregated to produce N budgets for the Huron and Raisin catchments for 2004 and 2005 (Table 5). A greater proportion of inputs were accounted for in outputs from the Raisin catchment (80%) than the Huron catchment (22%). Assuming the difference between inputs and outputs represents losses of N due to storage and denitrification, the Huron stored and denitrified $2,418 \text{ kg N km}^{-2} \text{y}^{-1}$ compared to $1,538 \text{ kg N km}^{-2} \text{y}^{-1}$ for the Raisin. Total N inputs were approximately two times higher for the Raisin catchment because of higher fertilizer application and crop N fixation. Total N outputs were nearly six times higher in the Raisin catchment compared to the Huron catchment, due primarily to high exports of agricultural products.

Huron and Raisin phosphorus budgets

Inputs of P from precipitation were small, accounting for only 3% of all P inputs to the Huron catchment

Table 5 Complete N budget for each study catchment for calendar years 2004 and 2005 ($\text{kg N km}^{-2} \text{y}^{-1}$)

	Atmospheric deposition	Nitrogenous fertilizer application	N fixation in forest lands	N fixation in agriculture lands	Total N inputs	Volatilization	Food & feed export	River export	Total N outputs	% N inputs accounted for as outputs	% of N inputs exported by stream
Huron 2004	991	1,886	65	1,534	4,477	39	602	293	935	21	6.5
Huron 2005	918	1,805	65	1,508	4,295	36	716	282	1,033	24	6.6
Raisin 2004	991	4,258	40	2,646	7,935	54	4,684	1,471	6,209	78	18.5
Raisin 2005	918	4,084	40	2,600	7,641	55	5,171	1,065	6,292	82	13.9

and 2% to the Raisin. The same rate was used for both catchments ($14 \text{ kg P km}^{-2} \text{y}^{-1}$). Fertilizer application was the largest single input of P, accounting for 56% of total P inputs to the Huron catchment and 71% for the Raisin. There was more than twice as much fertilizer applied in the Raisin catchment relative to the Huron. Manure inputs to the system contributed about one-fifth of total P inputs for each catchment. The Raisin had higher manure inputs because of larger livestock populations.

Human waste inputs to the catchments consisted of point source effluents directly into receiving waters and sludge application to agricultural fields. Point source discharge made up a very small portion of total P inputs to the system, about 1.2% in the Huron and 0.4% in the Raisin. Approximately 98% of P from point source discharges came from municipal WWTPs rather than industrial facilities in both catchments. Sludge application contributed 21% and 7% of P inputs for the Huron and Raisin, respectively. Thus, there was more sludge than animal manure P applied to agricultural fields in the more urban Huron catchment.

Crop export was a much larger P output than was riverine P export in both catchments. Crop export from the Raisin catchment was about 3 times higher than estimated for the Huron catchment. Corn and soybean crops accounted for most crop P exported

from each catchment. River exports accounted for only 2% and 3% of the total outputs for the Huron and Raisin catchments, respectively. Raisin River P exports were about five times higher than those of the Huron.

Combining all inputs and outputs into a P budget (Table 6) shows that more P inputs are accounted for as outputs in the Raisin catchment than in the Huron, as was seen for N. In fact, the Raisin catchment exported more P than it received as inputs in both 2004 and 2005. Assuming the difference between inputs and outputs represents P storage, the Huron stored $156 \text{ kg P km}^{-2} \text{y}^{-1}$, while the Raisin had a net export of $102 \text{ kg P km}^{-2} \text{y}^{-1}$. Considering both catchments, more of the inputs are accounted for in the outputs for the P budgets (96%) than are accounted for in the N budgets (59%). Total P inputs to the Raisin were about twice those to the Huron catchment, due to higher fertilizer and manure application rates in the Raisin catchment.

Huron and Raisin N and P river exports

River nutrient export as a percentage of total inputs was higher for N than for P (Tables 5, 6). Combining both catchments and years, river export accounted for about 2.6% of P inputs, versus 11.4% of N inputs.

Table 6 Complete P budget for each study catchment for calendar years 2004 and 2005 ($\text{kg P km}^{-2} \text{y}^{-1}$)

	Rainfall	Fertilizer	Manure	Sludge	Point source discharge	Total P inputs	Crop export	River export	Total P outputs	% P inputs accounted for as outputs	% P inputs exported by rivers
Huron 2004	14	293	95	101	6	509	316	8	323	63	1.5
Huron 2005	14	258	86	106	6	469	337	6	343	73	1.2
Raisin 2004	14	668	170	65	4	921	907	41	948	103	4.5
Raisin 2005	14	591	173	59	3	841	991	27	1,018	121	3.3

Stoichiometric N:P ratios were 8.9 for total inputs and increased to 38 in river export. Comparing catchments, river export was a threefold larger percentage of both P and N inputs in the Raisin than in the Huron, due to much higher river TN and TP export loads in the Raisin. Examination of the specific forms of N and P in river export revealed that more of TP export was SRP in the Raisin, compared to the Huron catchment (Table 7). TON and NH_4 accounted for much larger portions of TN loads in the Huron compared to the Raisin catchment. Nitrate/nitrite, however, was relatively more important in the Raisin TN load compared to the Huron.

Budget comparisons with other studies

Several broad observations can be made after applying the reference method to P budgets from the eight geographic units described previously. P outputs as a percentage of inputs ranged from 60% in the Sandusky catchment to 112% in the Raisin catchment, and averaged 77% (Table 8). Thus, about a fifth of P coming into these systems was unaccounted for or missing based on a common method of estimation.

Table 7 Riverine N and P export from study catchments ($\text{kg P km}^{-2} \text{y}^{-1}$ and $\text{kg N km}^{-2} \text{y}^{-1}$)

		SRP	TP	TON	NO_3	NH_4	TN
Huron	2004	1.0	8	132	144	18	293
	2005	0.4	6	107	161	14	282
Raisin	2004	8.8	41	141	1,313	17	1,471
	2005	6.9	27	174	873	19	1,065

Table 8 Comparison of P budgets for various catchments and geographic areas after adjusting results from other studies so they are comparable to the “reference method” P budget described in this study ($\text{kg P km}^{-2} \text{y}^{-1}$)

Geographic unit	Rain	Fertilizer	Manure	Sludge	Point source disch.	Total P inputs	Crop export	River export	Total P outputs	% P inputs accounted for as outputs	% P inputs exported by rivers
Huron catchment ^a	14	275	90	103	6	489	326	7	333	68	1.3
Raisin catchment ^a	14	630	172	62	3	881	949	34	983	112	3.9
Maumee catchment ^b	14	1,550	450	43	14	2,071	1,115	135	1,250	60	6.5
Sandusky catchment ^b	14	1,470	360	27	10	1,881	1,175	140	1,315	70	7.4
State of Illinois ^c	14	1,180	240	136	68	1,638	1,353	100	1,453	89	6.1
Muskingham catchment ^d	14	322	372	151	66	925	581	61	642	69	6.6
Minnesota catchment ^d	14	872	460	5	5	1,356	1,028	32	1,060	78	2.4
Mississippi basin ^d	14	346	336	41	20	757	466	42	507	67	5.5

Sources: ^aThis study; ^bBaker and Richards (2002); ^cDavid and Gentry (2000); ^dGoolsby et al. (1999)

The percentage of missing P did not correlate well with any of the fluxes or with extent of cropland. However, total P inputs and outputs were tightly correlated ($R^2 = 0.80$), and river export was highly correlated to total P inputs ($R^2 = 0.83$) when compared broadly across these eight geographic units. The fraction of P inputs exported by rivers ranged from 1.3% to 7.4%, with an average of 5%.

As with P budgets, N budgets for the six geographic units described above varied substantially (Table 9). N outputs as a fraction of inputs ranged from 14% in the Rappahannock catchment to 80% in the Raisin, averaging 39%. Thus, on average, the majority of N inputs were unaccounted for or missing using the reference method. Outputs as a fraction of inputs were strongly correlated with the proportion of cropland ($R^2 = 0.84$). Total inputs and outputs for N were tightly correlated ($R^2 = 0.92$), and river export was correlated to total N inputs ($R^2 = 0.74$). The fraction of N inputs exported by the river ranged from 6.6% to 22.9% of total inputs, with an average of 16%.

Discussion

Huron and Raisin nutrient fluxes

Quantification of N and P budgets for the Huron and Raisin provided insight into the origin, transport, and fate of N and P in these two southeastern Michigan catchments. For the two catchments and two years of study, on average, more of the inputs were accounted

Table 9 Comparison of N budgets for various catchments and geographic areas after adjusting results from other studies so they are comparable to the “reference method” N budget described in this study ($\text{kg N km}^{-2} \text{y}^{-1}$)

Geographic unit	Atmos. dep.	Fert. app.	N fixation	Food & feed import	Total N inputs	Volatil.	Food & feed export	River export	Total N outputs	% N inputs accounted for as outputs	% N inputs exported by rivers
Huron catchment ^a	954	1,846	1,586		4,386	37	659	288	984	22	6.6
Raisin catchment ^a	954	4,171	2,663		7,788	55	4,928	1,268	6,250	80	16.3
Mohawk catchment ^b	1,130	411	1,309	624	3,474	56		795	851	24	22.9
Rappahannock catchment ^b	1,028	1,030	1,716	607	4,381	134		470	604	14	10.7
All NE U.S. catchments ^b	1,067	474	907	748	3,196	108		718	826	26	22.5
State of Illinois ^c	520	5,930	3,050		9,500	77	6,240	1,670	6,407	68	17.6

Sources: ^a This study; ^b Boyer et al. (2002); ^c David and Gentry (2000)

for as measurable outputs for P (96%) than for N (59%). Much of this difference is likely due to the exclusion of denitrification as an output flux, as discussed below. A greater fraction of inputs were accounted for as outputs for both N and P in the Raisin catchment compared to the Huron. It is probable that this greater imbalance in the Huron catchment is due to greater removal of N and P via impoundments.

River exports of N and P differed considerably as a fraction of nutrient budgets and between the Huron and Raisin catchments. Combining both catchments and years, river export on average accounted for about ten times more of total inputs of N (11.4%) than P (2.6%). Stoichiometric ratios for N:P in inputs compared to river export confirm that substantially less P is exported from these two catchments by river transport than is true for N, suggesting that proportionally more P than N is stored in either the terrestrial or aquatic parts of the catchment. This was expected since P is considered the primary limiting nutrient in freshwater systems. Comparing the two catchments, the Huron stored more P than the Raisin and also stored and/or denitrified more N. The greater number of impoundments in the Huron catchment is the most likely explanation for these differences, allowing more P to settle out of the water column and more N to be denitrified as suggested by Stanley and Doyle (2002).

The inference that impoundments are the primary reason why smaller proportions of catchment N and P inputs are exported through the Huron River is supported by other work in these and other catchments. Comparison of input and output loads above and below impoundments and across river reaches in the Huron and Raisin documented that impoundments

consumed N and P whereas stream reaches showed no removal (Bosch 2007). Increased nutrient removal in impoundments was attributed to N loss through denitrification in sediments, long-term settling of P, and longer residence times of water, allowing more time for processing to occur. Direct sampling showed that two adjacent impoundments in the Huron catchment together removed 18% and 32% of TN and TP annual loads, respectively. In addition, model simulations using the Soil and Water Assessment Tool (SWAT) showed that P and N export loads would approximately double if all impoundments were removed from the Huron watershed (Bosch 2007). In a survey of 27 impoundments across Ohio, Indiana, and Illinois, Walker and Kuhner (1978) reported a median annual TP removal of 47% and TN removal of 23%. David et al. (2006) found that 19% of TN inputs were removed in an agriculturally influenced impoundment in Illinois. In a global study of 35 large rivers which compared catchment N inputs and river export, Caraco and Cole (1999) discovered substantially decreased export of N in the three rivers which contained large impoundments. Substantial N and P removal in the numerous impoundments of the Huron catchment provides a likely explanation for the relatively low N and P river export.

Differences in nutrient retention between forested and agricultural ecosystems could provide an alternative explanation for low N and P export through the Huron River, relative to the Raisin River. The River Raisin has a greater proportion of its area in agricultural use and less forested land compared to the Huron (Table 1). In a comparison of N and P fluxes in cropland versus forested riparian ecosystems in Maryland, Peterjohn and Corell (1984) found much

greater retention of N and P in forested ecosystems, relative to those dominated by agricultural practices. Pregitzer et al. (2004) observed that leaching losses of inorganic and organic N from northern hardwood forests were small, apparently because the majority of atmospheric N deposition was retained by plant and microbial sinks. With proportionally more forested and less agricultural land in the Huron catchment, it is reasonable to expect that more N and P would be retained within terrestrial ecosystems, thus reducing nutrient delivery to stream channels via groundwater or subsurface flow.

Comparisons with other studies

The majority of N entering the various geographic units was missing or unaccounted for in catchment outputs when compared using the reference method. In contrast, only about one-fifth of P inputs were unaccounted for in measured outputs. This difference likely is at least partly due to the absence of a denitrification flux in N budgets, as well as more storage of P than N within catchments. Unlike P budgets, N outputs as a fraction of N inputs were strongly correlated with the proportion of cropland, indicating that N storage and removal increased as the extent of agricultural land in the catchment declined. Presumably this missing N was lost from the system via denitrification, although storage is also a possibility. Total inputs and outputs were tightly correlated for both P and N budgets, which is expected if the budgets are reasonably accurate. Since the percent of inputs exported by the river was three times higher for N than P, these catchments retain P more effectively than N. The Huron had the lowest percent of riverine export for both N and P, which likely is due to the many impoundments in the Huron relative to most other catchments.

Howarth et al. (1996) and Boyer et al. (2002) each reported that rivers typically export about 25% of their net inputs. Our estimates of river export percentages using the reference method were not directly comparable to these values. To compare their results to N budgets for the Huron and Raisin catchments and the state of Illinois, NH_x volatilization and food and feed export fluxes were subtracted from total N inputs to calculate total net N inputs as Boyer et al. (2002) used. Using comparable calculations to those reported in Boyer et al. (2002), the Huron River exported only 8% of catchment net inputs of N, which is lower than

any of the 16 northeastern U.S. catchments. The more agricultural Raisin and catchments in Illinois exported 45% and 52% of net N inputs in their rivers, respectively, which were higher percentages than any catchments included in Boyer et al. (2002). This indicates that this 25% generalization does not apply broadly, possibly because the 16 catchments in the northeastern U.S. included in Boyer et al. (2002) do not represent the diversity of land use proportions, geology, extent of impoundment, or climate that is present in other catchments.

Budgeting uncertainty and limitations

Although budgets were constructed with the best data available, there were some fundamental gaps due to unmeasured inputs or outputs. For example, P budgets did not include human waste inputs from septic tanks, which may be important as large proportions of each catchment that we studied are unsewered. Because septic inputs are difficult to estimate, this term commonly is omitted (Baker and Richards 2002; David and Gentry 2000). Using information from local county officials and population census data, we roughly estimated the number of people in each catchment that were serviced by septic tanks. We then multiplied these population numbers by a human P loading rate of $2.74 \text{ kg P y}^{-1} \text{ person}^{-1}$ (Goolsby 1999). Inclusion of this additional P in the budget estimates lowers the percentage of inputs accounted for as outputs (to 43% and 98% for the Huron and Raisin respectively, see Table 6) and implies greater P storage in the system.

The N budget approach used in this study and others (Boyer et al. 2002; David and Gentry 2000) does not include denitrification as a catchment output because of the large degree of uncertainty associated with this flux. If we estimate denitrification output fluxes for soil, ground water, and surface water based on Seitzinger et al. (2006), N outputs from the Huron catchment would account for 82% of inputs, rather than 22%, and N outputs from the Raisin would exceed inputs (111% vs. 80%). Overall, then, the Huron stores more P than the Raisin and also stores and denitrifies more N compared to the Raisin. The much greater number and extent of impoundments in the Huron catchment is the most likely cause for these differences, presumably allowing more P to settle out of water column and more N to be denitrified.

N and P catchment budgeting approaches vary widely, making it difficult to synthesize results and make comparisons. Budget approaches differ in how the system is defined, in what fluxes are considered to be internal to the system versus inputs or outputs from the system, and in which fluxes are excluded because they are considered insignificant or highly uncertain. There is also variation in how some fluxes are combined to form net fluxes. Our efforts to compare budgets from different studies by applying a common estimation approach suggests the value of further efforts to develop a standardized approach to N and P budget calculation.

Conclusion

For the Huron and Raisin catchments and 2004 and 2005 budget years, a greater fraction of inputs were accounted for as outputs for P budgets (96%) than for N budgets (59%). The amount of missing N is consistent with rough estimates of denitrification. Comparing the two catchments, it is clear that the Huron catchment overall stored more P than the Raisin, and also stored and denitrified more N. It is likely that the many impoundments in the Huron catchment allowed the river to remove a greater percentage of N and P from the water, compared to the Raisin.

Comparison of input and output fluxes from the Huron and Raisin with findings of other studies, supported by the construction of comparable budgets for geographic units included in these studies, corroborated Huron and Raisin budget results and allowed some synthesis. On average, P outputs accounted for 77% of inputs, whereas quantifiable N outputs only accounted for 39% of inputs. In addition, these values vary widely. As in the case of the Huron and Raisin catchments, inclusion of denitrification as an additional N output flux likely would significantly increase the proportion of inputs that could be accounted for as outputs. The percent of inputs exported by the river averaged 16% for N and 5% for P, indicating that these catchments retain P more effectively than N.

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