Exhibit 11

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Decadal-scale export of nitrogen, phosphorus, and sediment from the Susquehanna River basin, USA: Analysis and synthesis of temporal and spatial patterns

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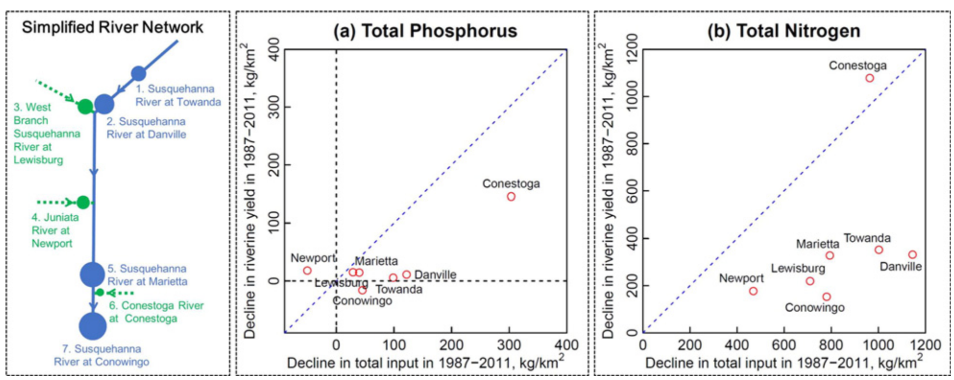
HIGHLIGHTS

- N, P, and SS loads were estimated for seven sites in the Susquehanna River basin.
- N, P, and SS loads have dropped at all Susquehanna sites above Conowingo Reservoir.
- Smaller annual declines in riverine load than source input suggest legacy sources.
- Dissolved and particulate species show chemostasis and mobilization, respectively.
- Yields of all species correlate positively with the fraction of non-forested area.

GRAPHICAL ABSTRACT



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ABSTRACT

The export of nitrogen (N), phosphorus (P), and suspended sediment (SS) is a long-standing management concern for the Chesapeake Bay watershed, USA. Here we present a comprehensive evaluation of nutrient and sediment loads over the last three decades at multiple locations in the Susquehanna River basin (SRB), Chesapeake's largest tributary watershed. Sediment and nutrient riverine loadings, including both dissolved and particulate fractions, have generally declined at all sites upstream of Conowingo Dam (non-tidal SRB outlet). Period-of-record declines in riverine yield are generally smaller than those in source input, suggesting the possibility of legacy contributions. Consistent with other watershed studies, these results reinforce the importance of considering lag time between the implementation of management actions and achievement of river quality improvement. Whereas flow-normalized loadings for particulate species have increased recently below Conowingo Reservoir, those for upstream sites have declined, thus substantiating conclusions from prior studies about decreased reservoir trapping efficiency. In regard to streamflow effects, statistically significant log-linear relationships between annual streamflow and annual constituent load suggest the dominance of hydrological control on the inter-annual variability of constituent export. Concentration-discharge relationships revealed general chemostasis and mobilization effects for dissolved and particulate species, respectively, both suggesting transport-limitation conditions. In addition to affecting annual export rates, streamflow has also modulated the relative importance of dissolved and particulate fractions, as reflected by its negative correlations with

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dissolved P/total P, dissolved N/total N, particulate P/SS, and total N/total P ratios. For land-use effects, period-of-record median annual yields of N, P, and SS all correlate positively with the area fraction of non-forested land but negatively with that of forested land under all hydrological conditions. Overall, this work has informed understanding with respect to four major factors affecting constituent export (*i.e.*, source input, reservoir modulation, streamflow, and land use) and demonstrated the value of long-term river monitoring.
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1. Introduction

Chesapeake Bay has experienced persistent summer hypoxia conditions that have been attributed to a combination of excessive nutrient and sediment inputs from its watershed (Kemp et al., 2005; Shenk and Linker, 2013) and density-driven vertical stratification (Murphy et al., 2011; Pritchard and Schubel, 2001). Reduction of nitrogen (N), phosphorus (P), and sediment loadings has therefore been a long-standing focus of Chesapeake watershed management, which has been reinforced recently with the promulgation of Chesapeake Bay Total Maximum Daily Loads (TMDLs) (U.S. Environmental Protection Agency, 2010) and state-wide efforts to establish watershed implementation plans (Linker et al., 2013a; Shenk and Linker, 2013).

Among the tributaries to Chesapeake Bay, Susquehanna River is the largest (Hagy et al., 2004; Murphy et al., 2011; Zhang et al., 2015) (Fig. 1). It is one of nine major tributaries that collectively account for over 90% of river input above the head of tides and which have a total non-tidal drainage area that accounts for ~78% of the bay's total watershed area (Belval and Sprague, 1999; Langland et al., 1995). Of this total non-tidal drainage, the Susquehanna River contributed 62% of streamflow, 65% of total N (TN), 46% of total P (TP), and 41% of suspended sediment (SS) between 1979 and 2012 (Zhang et al., 2015). The relatively lower fractional contributions of TP and SS reflect historical trapping by the Lower Susquehanna River Reservoir System (LSRRS). This system, however, has become less capable of retaining sediment and particulate nutrients in recent years as it approaches sediment storage capacity (Hirsch, 2012; Zhang et al., 2013; Zhang et al., 2016).

For rivers with concentration-discharge monitoring data, water-quality analyses have often focused on how concentration varies with not only time, discharge, and season, but also with changes in source inputs (*e.g.*, fertilizer, manure, point sources, and atmospheric deposition), system function (*e.g.*, reservoirs), land use, and hydro-climatic factors (Harris, 2001; Howarth et al., 2012; Sobota et al., 2009; Sprague et al., 2000). For the Chesapeake watershed, a multi-party collaboration is underway within the Chesapeake Bay Program partnership to seek explanations for water-quality changes in Chesapeake tributaries (Keisman et al., 2015). In this context, our work is intended as a cursory examination of various types of data available for the Susquehanna River basin (SRB). Specifically, a recently developed statistical method for estimating daily loads was combined with some relatively simple and traditional mass-balance and concentration-discharge (C-Q) approaches to (a) accurately estimate riverine concentration and loading based on sparse monitoring data; (b) evaluate riverine loading trends by better accommodating inter-annual streamflow variability; (c) examine relationships between estimated concentration and streamflow for categorizing export patterns; and (d) analyze factors affecting constituent export, *e.g.*, source inputs, reservoir modulation, streamflow, and land use. This work demonstrates that the traditional approaches, despite some important shortcomings, can nonetheless be useful toward understanding some of the most important patterns and controls of constituent export. While more sophisticated approaches have become available for evaluating riverine export (*e.g.*, Ai et al., 2015; Chen et al., 2014; Green et al., 2014; Hale et al., 2015) and others are under development (even among our own team), we have considered these methods as beyond the current scope, and reserve their application for future work.

In the above context, we have undertaken a comprehensive evaluation of (1) temporal trends of nutrient and sediment loadings at seven long-term monitoring locations and (2) spatial variations of nutrient and sediment budgets of major sub-basins in the SRB. Specifically, we have focused on addressing four motivating questions:

Q_1: What have been the general patterns of temporal trends in riverine nutrient/sediment loadings? In particular, have trends been consistent (a) across all seven monitoring locations and (b) between dissolved and particulate species?

Q_2: What have been the general trends in watershed source inputs and how have their magnitudes compared with those in riverine loadings?

Q_3: Which sub-basins have been net sources (or storages) of loadings and what has been the role of streamflow on constituent export?

Q_4: How do sub-basins compare in regard to constituent yield (*i.e.*, loading per area) and how do differences relate to those in land use distribution?

This work offers a unique opportunity to understand these aspects for a large watershed. First, long-term river monitoring data are available at multiple locations across this watershed, which allowed combined temporal and spatial analyses. In addition, the well-documented data on watershed source inputs fostered a quantitative comparison of changes in source input and changes in riverine yield. Moreover, the contrasting land use distributions of the sub-basins facilitated an evaluation of land-use effect on export. Finally, we were also able to compare the upstream sub-basins with re-analysis of the previously studied downstream reservoir system (*i.e.*, the LSRRS) to better highlight and confirm temporal aspects of the LSRRS's modulation of loadings. Overall, this work should help inform the management of Chesapeake Bay's largest tributary and also foster comparisons with rivers in other geographical regions (within the Chesapeake watershed and beyond) for better understanding patterns and controls of constituent export.

2. Methods

2.1. Study area and data

The non-tidal SRB covers portions of New York, Pennsylvania, and Maryland, USA. (Fig. 1). The basin's outlet at Conowingo Dam has been monitored by the U.S. Geological Survey (USGS) since the late 1970s. This site is about 10 miles from the river mouth and receives 99% of the streamflow from the entire SRB (Belval and Sprague, 1999). Upstream and in Pennsylvania, six sites have been monitored by the Susquehanna River Basin Commission (SRBC) since the mid-1980s. Among them, Towanda, Danville, and Marietta monitor the mainstem of Susquehanna River, whereas Lewisburg, Newport, and Conestoga monitor the West Branch Susquehanna River, Juniata River, and Conestoga River, respectively, all of which are tributaries to the Susquehanna (Fig. 1). Details of these sites are summarized in Table 1.

At each site, daily streamflow data were compiled from the USGS National Water Information System (NWIS) Web Interface (U.S. Geological Survey, 2014a). Water-quality concentration data were compiled from the USGS NWIS for Conowingo and from the SRBC website

(Susquehanna River Basin Commission, 2014) for the six upstream sites. These data included concentration measurements for SS, TP, TN, dissolved phosphorus (DP), and dissolved nitrogen (DN). Temporal coverages of these water-quality samples are summarized in Table S1. The average number of sampled days ranges between 25.5 and 40.4 per year. The samples at each site were collected across the full range of hydrological conditions in each year and comprised at least one sample in each month of the year and 8 targeted samples during times of stormflow (*i.e.*, periods of elevated discharge).

2.2. Statistical method for loading estimation: WRTDS

To provide reasonable estimates of daily concentrations – as needed for estimation of daily and annual loads – it is necessary to augment these relatively sparse water-quality concentration data through statistical treatments. Typically, daily concentrations are estimated on the basis of correlations of concentration over three parameters: time, season, and discharge (*e.g.*, Cohn et al., 1989). For this work, we applied a method recently adopted by the USGS called "Weighted Regressions on Time, Discharge, and Season (WRTDS)" (Hirsch et al., 2010). This approach has been shown to offer better performance than prior regression-based methods because it does not rely on those methods' problematic assumptions about the homoscedasticity of model errors, constancy of seasonal trends in concentration, or constancy of the concentration-discharge relationship (Chanat et al., 2016; Hirsch et al., 2010; Moyer et al., 2012).

In general, WRTDS can produce two types of concentration and loading estimates, which are called "*true-condition*" and "*flow-normalized*" estimates, respectively. True-condition estimates are model-based approximations of the real history of riverine concentration or loading and are relevant to understanding actual downstream impacts. By contrast, the flow-normalization method uses the full history of flows on the given calendar date to effectively remove the effects of interannual streamflow variability. It should therefore better reflect the effects of changes in source inputs and system function (Hirsch et al., 2010). Because this method considers flow data from the entire record, it requires more computational effort than the true-condition estimates (Hirsch and De Cicco, 2015).

At each site, WRTDS was run using the *EGRET* (Exploration and Graphics for RivEr Trends) version 2.2.0 (Hirsch and De Cicco, 2015) to produce both the true-condition and flow-normalized concentration and loading estimates for each day in the record for each water-quality species (*i.e.*, SS, TP, TN, DP, and DN). For all WRTDS runs, we used the default settings specified by the user guide (Hirsch and De Cicco, 2015) — see details in the online Supplementary material. The daily loading estimates were averaged to obtain annual loading estimates for each calendar year between the start year (various among sites; see Table S1) and 2013. In addition, particulate phosphorus (PP) and particulate nitrogen (PN) loadings were inferred by subtracting DP and DN from TP and TN loadings, respectively. Annual yields for each site were calculated by dividing the annual loading estimates by their respective drainage areas. Long-term median loadings and yields for each site are provided in Table S2. Finally, annual true-condition loadings for each site were divided by their respective annual discharges to estimate annual flow-weighted concentrations ($C_{\text{Annual-FW}}$).

For each WRTDS run, residual plots were generated to evaluate model performance (not shown). These plots showed that unaccounted residuals from WRTDS generally have no structural relationship with time, discharge, or season. All derived estimates from this work, along with the river monitoring data, are stored at the publicly accessible Johns Hopkins University Data Archive (Zhang and Ball, 2016). Additionally, loads for TN, TP, and SS for all seven sites can be downloaded from the USGS-designated website (U.S. Geological Survey, 2014b).

2.3. Trend and mass-balance analyses

To address the four questions posed in Section 1, we conducted two major types of analysis based on WRTDS estimates: "*trend analysis*" and "*mass-balance analysis*". Questions Q_1 and Q_2 were aimed toward better understanding when and where riverine loadings have changed. For such "*trend analysis*," we focused on the synthesis of WRTDS *flow-normalized* estimates. To better understand these riverine trends, we compiled and analyzed watershed source input data made available to us by the Chesapeake Bay Program Office (CBPO) (Shenk and Linker, 2013). These data are used as input to the Chesapeake Bay Watershed Phase 5.3.2 model — see http://ches.communitymodeling.org/models/CBPhase5/index.php for details. The most relevant of these data for our purposes are: atmospheric deposition data (estimated using developed regression models — see Grimm and Lynch (2005) and Linker et al. (2013a) for details); fertilizer and manure application data (estimated using agricultural census data); and data for point-source contributions (including significant/non-significant dischargers, industrial flows, and combined sewer overflows). For each of these four major categories

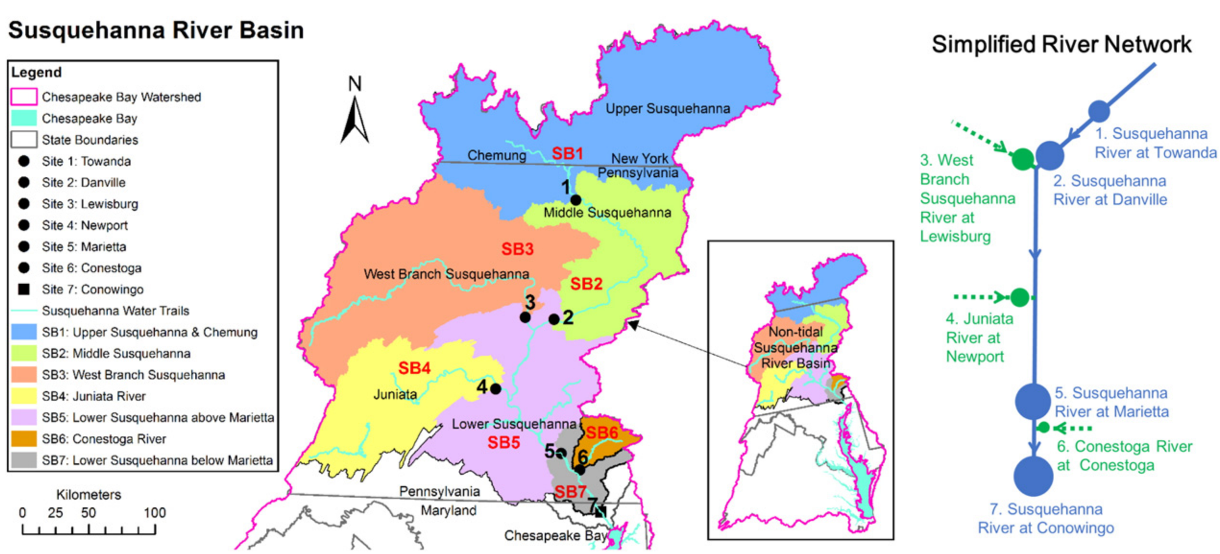

Fig. 1. Map of the Susquehanna River basin (SRB), showing the seven long-term monitoring sites (No. 1–7) and the seven sub-basins (SB1–SB7). Conowingo (#7) is the non-tidal SRB's outlet. Inset shows the SRB's location within the Chesapeake Bay watershed. The diagram of "Simplified River Network" shows four sites on the river mainstem and three sites on the tributaries to Susquehanna River. See Table 1 for details of the sites and sub-basins.

(and several minor others), the CBPO has estimated monthly source inputs from each drainage basin between 1984 and 2011.

Questions Q_3 and Q_4 were aimed toward better understanding the relative contributions of loadings from the Susquehanna sub-basins and the effects of streamflow and land use on constituent export. For these questions, "*mass-balance analysis*" was conducted using WRTDS *true-condition* estimates. This type of analysis is particularly suitable to the non-tidal SRB because of the well-positioned locations of the monitoring sites (Fig. 1). Specifically, we divided the non-tidal SRB into seven sub-basins (SBs), namely, Upper Susquehanna River plus Chemung River (SB1), Middle Susquehanna River (SB2), West Branch Susquehanna River (SB3), Juniata River (SB4), Lower Susquehanna River above Marietta (SB5), Conestoga River (SB6), and Lower Susquehanna below Marietta (SB7) (Fig. 1, Table 1). Note that SB7 covers the LSRRS and its vicinity. The seven sub-basins range between 1,217 and 20,194 km^2 in drainage area. For each sub-basin, riverine input constituent load is the flux entering its river reach, including the flux passing the monitoring site at the upstream limit of the reach and the tributary flux entering that reach, if monitored. Output load is the flux passing the monitoring site at the downstream limit of the reach. The output load was subtracted from riverine input load to determine whether each sub-basin was a net source (*i.e.*, riverine output > riverine input) or net storage (*i.e.*, riverine output < riverine input) (Table 1). This analysis assumes that WRTDS load estimation can approximately reproduce actual mass-balance relations across sites, which is an expected but not mathematically certain condition. Research is underway to better understand uncertainties and imprecisions of such estimates — irrespective of these concerns, however, the mass-balance results presented herein should shed some useful insights on relative loading contributions among sub-basins.

3. Results

3.1. Temporal trends in flow-normalized riverine loadings

To compare loading trends across all seven long-term sites for particulate and dissolved constituents, we summarized flow-normalized (FN) modeled loadings for SS, TP, DP, PP, TN, DN, and PN in Fig. 2. By integrating out the effects of inter-annual variability in streamflow, these FN loadings (Fig. 2b–h) show much smoother trends than true-condition loadings or streamflow (Fig. 2a). FN-modeled loadings of SS show overall downward trends at all sites except Conowingo (Fig. 2b). Among these sites, Conestoga had the highest early-period SS yield but also showed the strongest decline in FN loading. By contrast, Conowingo shows a clear rise since around 2000.

FN-modeled trends of TP, DP, and PP are shown in Fig. 2c, d, and e, respectively. At all sites except Conowingo, TP has shown general overall declines over time, but with some short periods of stable or slightly rising loads (Fig. 2c). These TP declines are accompanied by declining FN-modeled PP loading since the late 1990s (Fig. 2e) and by declining FN-modeled DP loading in both earlier (1986–1993) and more recent (2005–2013) periods (Fig. 2d). In comparison, FN-modeled PP trends (Fig. 2e) have closely followed those of SS (Fig. 2b), with high correlations at each site (linear correlation coefficients: 0.47–0.92; median: 0.83), which reflects the critical role of sediment in PP transport. As in the case of SS, Conestoga had the highest early-period yields of TP and PP (see Table S4) and showed the strongest declines in FN-modeled TP and PP loadings. By contrast, FN loadings of TP and PP at Conowingo exhibit clear rises in recent decades.

FN-modeled trends of TN, DN, and PN are shown in Fig. 2f, g, and h, respectively. TN loadings show steady declines at all sites except Conowingo (Fig. 2f) and these declines have been primarily driven by declines in DN loadings (Fig. 2g). Among these sites, Towanda results show the strongest fractional decline in FN loadings of TN and DN, whereas the Conestoga estimates show the strongest absolute decline in TN yield (Table S4). For PN, FN estimates of loading show declines at all sites except Conowingo, with Conestoga showing the strongest decline (Fig. 2h). In contrast with the upstream sites, Conowingo results show steady (but slight) rises in DN and TN loadings in recent years and a much stronger rise in PN loading throughout the study period.

3.2. Comparison of changes in riverine yield and source input

To further evaluate riverine loading trends in the context of management, it is useful to consider the contemporary histories of watershed

Table 1
Details of the long-term monitoring sites and sub-basins in the Susquehanna River basin.[a]

Monitoring sites							
Index in Fig. 1	USGS site number	Site name (short name)	Drainage area, km^2	Upstream land use (percent)			
				Urban	Agricultural	Forested	Other
1	01531500	Susquehanna River at Towanda, PA (*Towanda*)	20,194	4	35	60	1
2	01540500	Susquehanna River at Danville, PA (*Danville*)	29,060	5	33	60	2
3	01553500	West Branch Susquehanna River at Lewisburg, PA (*Lewisburg*)	17,734	2	15	81	2
4	01567000	Juniata River at Newport, PA (*Newport*)	8,687	2	28	69	1
5	01576000	Susquehanna River at Marietta, PA (*Marietta*)	67,314	4	30	64	2
6	01576754	Conestoga River at Conestoga, PA (*Conestoga*)	1,217	14	60	23	3
7	01578310	Susquehanna River near Conowingo, MD (*Conowingo*)	70,189	2	29	67	2
Sub-basins							
Index in Fig. 1	Sub-basin name	Calculation of net export	Drainage area, km^2	Upstream land use (percent)			
				Urban	Agricultural	Forested	Other
SB1	Upper Susquehanna River & Chemung River	Towanda (site #1)	20,194	4.0	35.0	60.0	1.0
SB2	Middle Susquehanna River	Danville (#2) − Towanda (#1)	8,866	7.3	28.4	60.0	4.3
SB3	West Branch Susquehanna River	Lewisburg (#3)	17,734	2.0	15.0	81.0	2.0
SB4	Juniata River	Newport (#4)	8,687	2.0	28.0	69.0	1.0
SB5	Lower Susquehanna River above Marietta	Marietta (#5) − Newport (#4) − Lewisburg (#3) − Danville (#2)	11,834	6.0	46.6	44.7	2.7
SB6	Conestoga River	Conestoga (#6)	1,217	14.0	60.0	23.0	3.0
SB7	Lower Susquehanna River below Marietta	Conowingo (#7) − Marietta (#6) − Conestoga (#5)	1,658	NA[b]	NA	NA	NA

[a] Modified from Table 3 and Table 8 in Sprague et al. (2000).
[b] Not available.

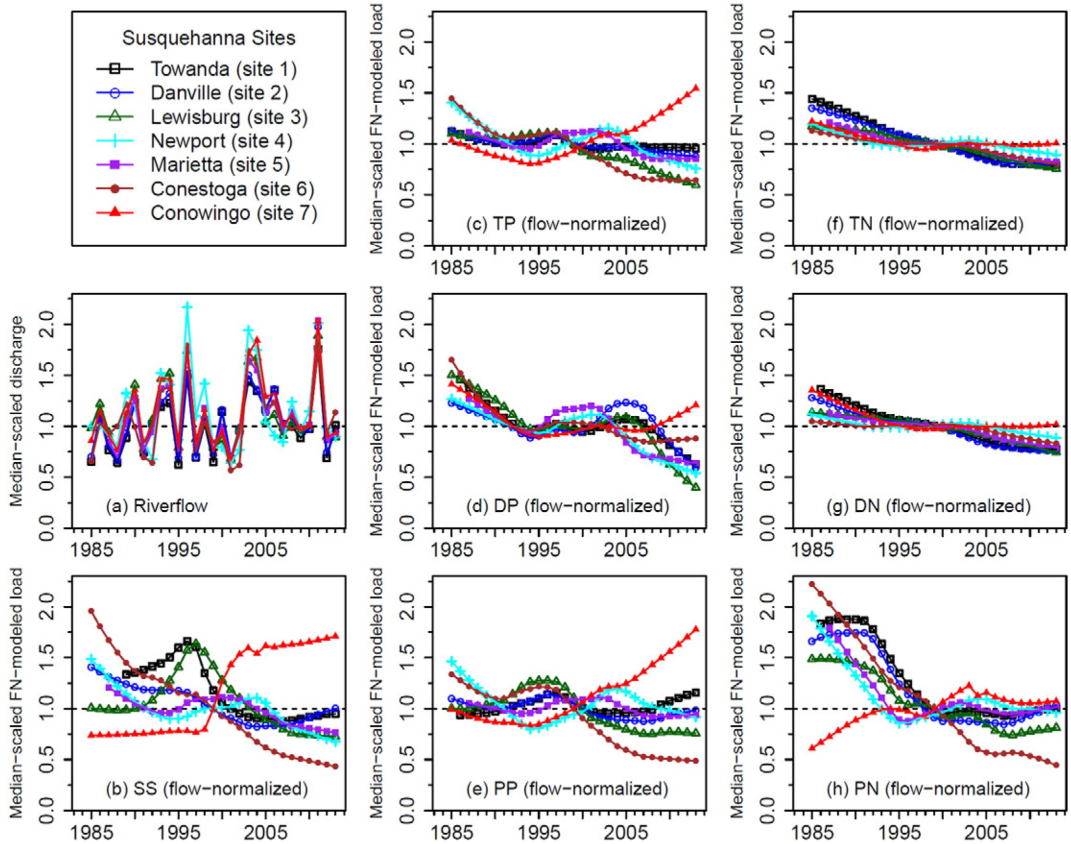

Fig. 2. Reconstructed time series of (a) annual discharge and annual *flow-normalized* (*FN*) loadings of (b) SS, (c) TP, (d) DP, (e) PP, (f) TN, (g) DN, and (h) PN at the seven Susquehanna sites. To aid comparison, all *y-axis* values have been scaled by respective long-term annual medians (see Table S2).

source input. Toward this end, input data for major source categories between 1984 and 2011 are plotted together with our riverine estimates in Fig. 3 for TP and Fig. 4 for TN. Period-of-record averages of annual riverine conditions (*i.e.*, river flow, concentration, and yield) and annual source inputs for the period of 1987–2011 are summarized in Table S3, which is the longest period that has data at all sites. In addition, the period-of-record change in source input yield (Δ_{Input}) for each site was quantified, *i.e.*, $\Delta_{\text{Input}} = 2011$ yield − 1987 yield. Similarly, the period-of-record change (Δ) was quantified for each individual source input. These changes, along with the initial (1987) and final (2011) conditions, are summarized in Table S4 and discussed below.

For TP, total source inputs have declined generally at all sites except Newport (Fig. 3, Table S4). Among the other six sites, the decline for Conestoga ($\Delta_{\text{Input}} = -304$ kg km^{-2}) is much greater than those for

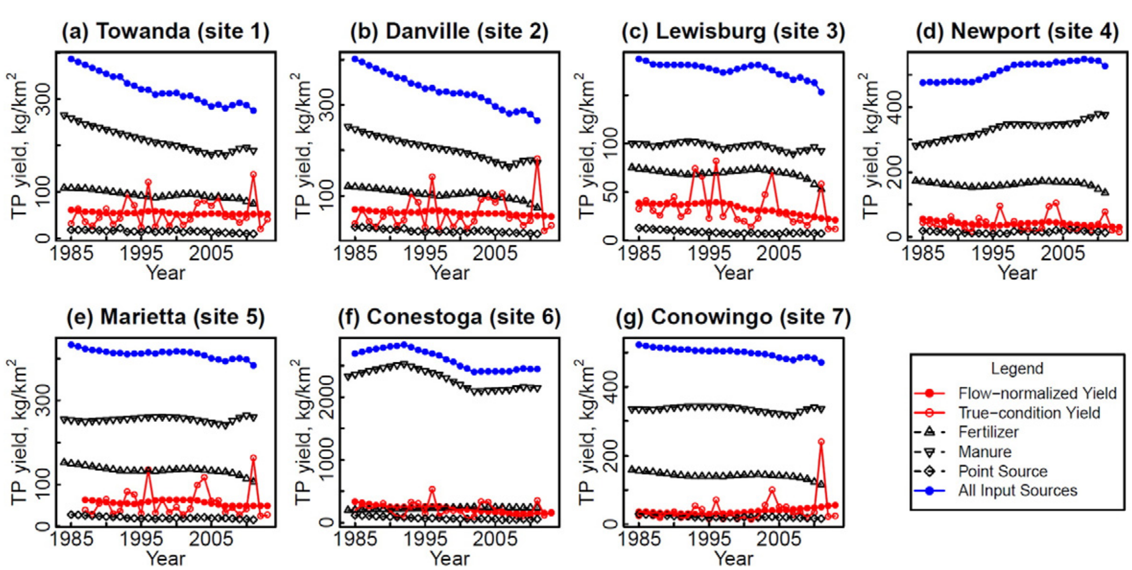

Fig. 3. Reconstructed time series of WRTDS-estimated TP riverine yield (flow-normalized and true-condition estimates) and yields from major source inputs (fertilizer, manure, point source, and sum of all sources) for the seven Susquehanna sites: (a) Towanda, (b) Danville, (c) Lewisburg, (d) Newport, (e) Marietta, (f) Conestoga, and (g) Conowingo. Note that the *y-axis* scale varies with plot.

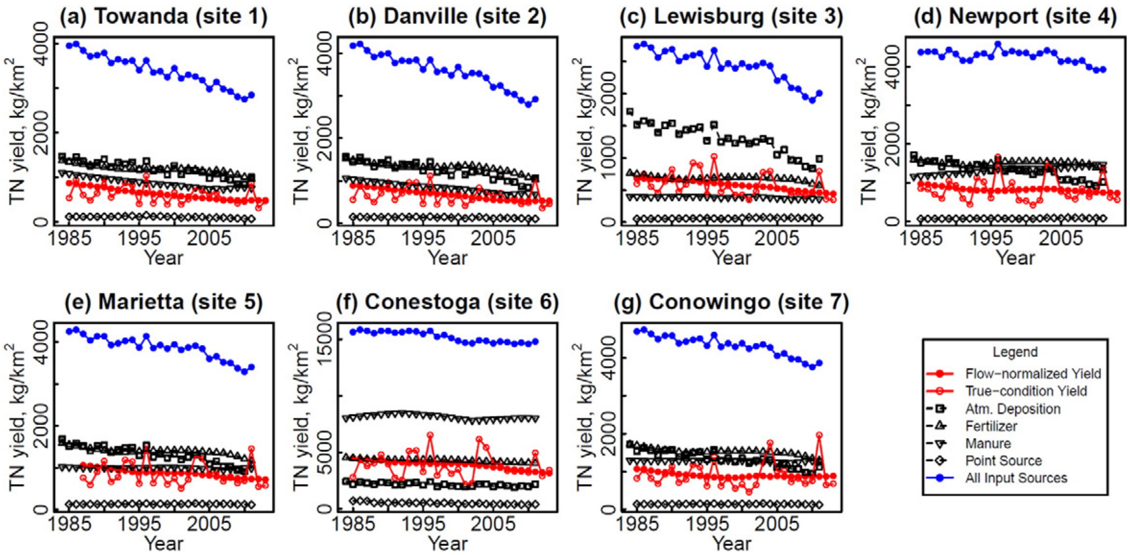

Fig. 4. Reconstructed time series of WRTDS-estimated TN riverine yield (flow-normalized and true-condition estimates) and yields from major source inputs (atmospheric deposition, fertilizer, manure, point source, and sum of all sources) for the seven Susquehanna sites: (a) Towanda, (b) Danville, (c) Lewisburg, (d) Newport, (e) Marietta, (f) Conestoga, and (g) Conowingo. Note that the *y-axis* scale varies with plot.

the other sites (-29 to -122 kg km^{-2}; Table S4). Individual sources showed negative Δ for 17 of 21 source-site combinations (Table S4), with only the following exceptions: fertilizer at Conestoga ($+23$ kg km^{-2}) and manure at Newport ($+83$ kg km^{-2}), Marietta ($+10$ kg km^{-2}), and Conowingo ($+3$ kg km^{-2}). Of the various source categories, declines in estimated manure input contributed the most to overall declines in estimated total input at Conestoga, Danville, and Towanda, whereas declines in fertilizer contributed the most to the overall declines in total input at Conowingo, Marietta, and Lewisburg. The only positive Δ_{Input} (total input) occurs at Newport ($+51$ kg km^{-2}), which is entirely attributable to manure rise.

For TN, total source inputs have declined consistently at all sites (Fig. 4, Table S4). Danville has the largest decline (-1146 kg km^{-2}) and Newport has the smallest (-469 kg km^{-2}) (Table S4). For individual sources, 25 of 28 source-site combinations have negative Δ (Table S4), with positive Δ only for manure at Newport ($+266$ kg km^{-2}) and for point source at Newport ($+13$ kg km^{-2}) and Lewisburg ($+11$ kg km^{-2}). Atmospheric deposition showed consistent declines at all sites and with similar Δ (-356 to -552 kg km^{-2}) for all sites except Conestoga, where Δ was much smaller (-87 kg km^{-2}). Fertilizer showed consistently negative Δ at all sites, while manure and point source showed negative Δ at most sites, with the few exceptions noted above. Of these, the positive Δ in manure at Newport ($+266$ kg km^{-2}) is the most substantial and has counteracted a substantial portion of the negative Δ in atmospheric deposition (-552 kg km^{-2}). Among the individual sources, declines in estimated atmospheric deposition have had the greatest contribution to overall declines in estimated total input at all sites except Conestoga (Table S4).

For purposes of comparison to the Δ_{Input} values, we calculated the period-of-record (1987–2011) changes in flow-normalized riverine yield ($\Delta_{\mathrm{FN\text{-}Yield}}$). The $\Delta_{\mathrm{FN\text{-}Yield}}$ values for TP and TN are negative for all cases except TP at Conowingo (Table S4). For both TP and TN, Conestoga had the strongest decline among all sites (-146 kg P km^{-2} and $-1{,}078$ kg N km^{-2}). The $\Delta_{\mathrm{FN\text{-}Yield}}$ values are shown against the Δ_{Input} values in Fig. 5, from which it is evident that $\Delta_{\mathrm{FN\text{-}Yield}}$ values are consistently lower. For quantitative comparison, their ratios, *i.e.*, $\Delta_{\mathrm{FN\text{-}Yield}}/\Delta_{\mathrm{Input}}$, were calculated as a simple description of the fraction of source

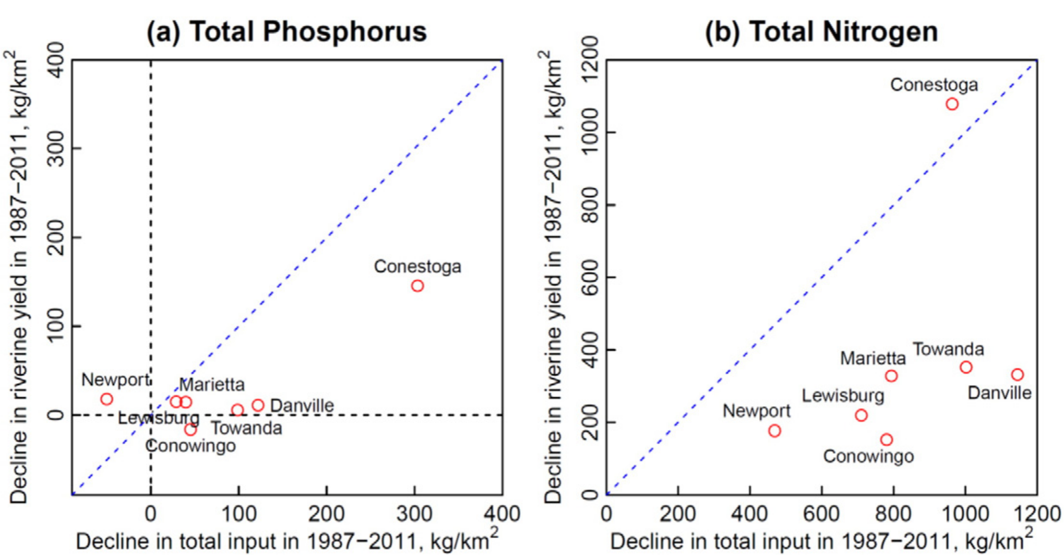

Fig. 5. Comparison between declines in total source input and declines in flow-normalized riverine yield for the seven Susquehanna sites for the period of 1987–2011. See Table S3 for details. The blue diagonal line indicates the 1:1 reference line.

reduction that has been realized in the riverine yield decline. For TP, these ratios are 0.52, 0.48, 0.37, 0.09, and 0.06 for Lewisburg, Conestoga, Marietta, Danville, and Towanda, respectively. Notably, the ratio is negative for both Conowingo (−0.35) and Newport (−0.35). For TN, the ratios are 1.12, 0.41, 0.38, 0.35, 0.31, 0.29, and 0.20 for Conestoga, Marietta, Newport, Towanda, Lewisburg, Danville, and Conowingo, respectively. In general, these ratios are <1.0 (13 of 14 cases).

3.3. Mass balances of sub-basins and effects of streamflow on export

To examine whether all Susquehanna sub-basins have been net loading sources (*i.e.*, riverine output > riverine input), we calculated true-condition annual net loading for each constituent between 1985 and 2013 for each sub-basin (Fig. 6). The results show that all six upstream sub-basins (*i.e.*, SB1–SB6) have been net exporters for nutrients and sediment in almost every year throughout the last three decades, including dry years. In contrast, the most downstream sub-basin, SB7 (Lower Susquehanna River below Marietta), shows negative values that reflect net accumulations of N, P, and SS, as expected for this reservoir-dominated sub-basin (Fig. 6). Rises in the SB7 plots, however, are observed in recent decades, especially for particulate species, suggesting that SB7 may soon become a net neutral or net positive source of nutrients and sediment to the downstream reach.

Peaks for streamflow and all constituents have occurred concurrently in SB1–SB6, with all plots showing a striking similarity in the timing of significant export (Fig. 6). To further examine the dominance of hydrological control on constituent export, we analyzed the relationships between annual loading (L_{Annual}) and annual discharge (Q_{Annual}). Despite considerable scatter with some site-species combinations, strong linear $\log[L_{Annual}] \sim \log[Q_{Annual}]$ relationships (p-value < 0.01) are observed for all species at all sites (Fig. S1). Thus Q_{Annual} alone is a strong predictor of L_{Annual}. Within this context, and given the definition of load ($L = QC$ or $\log[L] = \log[Q] + \log[C]$), a slope of 1.0 would be expected for conditions of constant concentration, and deviations from this value are indicative of the nature of C-Q relationships. An alternative approach to investigate such effects is to directly examine concentration data, as is done in Fig. S2, where we have plotted annual flow-weighted concentration ($C_{Annual\text{-}FW}$, calculated as L_{Annual}/Q_{Annual}) against area-normalized annual discharge, $(Q/A)_{Annual}$. Note that this annual averaging helps mitigate some of the issues associated with the fact that C-Q relationships can vary with time and season and also depend on time of sampling within a hydrograph (*e.g.*, during rising and falling limbs), which can be an especially important problem for high-discharge events that are only sparsely sampled. Nonetheless, we have identified years with extreme-discharge events in Fig. S2 as a means of qualitatively looking for outliers. Evidently, these specific years (1996, 2004, 2011) fall within the general trend. Overall, the approximately linear slope of $\log[C_{Annual\text{-}FW}] \sim \log[(Q/A)_{Annual}]$ can coarsely reveal whether export patterns follow dilution (slope < 0), chemostasis (slope ~ 0), or mobilization (slope > 0) (Godsey et al., 2009; Stallard and Murphy, 2014). For our sites, the results show general chemostasis effects for dissolved and dissolved-dominated species (*i.e.*, DN, TN, and DP) but mobilization effects for particulate and particulate-dominated species (*i.e.*, PN, TP, PP, and SS) (Fig. 7; S2).

Considering the above distinction between particulate and dissolved constituents, streamflow may have played an important role in modulating the relative importance of dissolved and particulate fractions. To verify such effects, we have plotted ratios of annual DP to annual TP loads (DP/TP), annual DN to annual TN loads (DN/TN), and annual PP to annual SS loads (PP/SS) against $(Q/A)_{Annual}$ for each site and observed general negative correlations (Fig. 8a–c). Moreover, as a means of considering nutrient loadings in the context of algal growth, we plotted

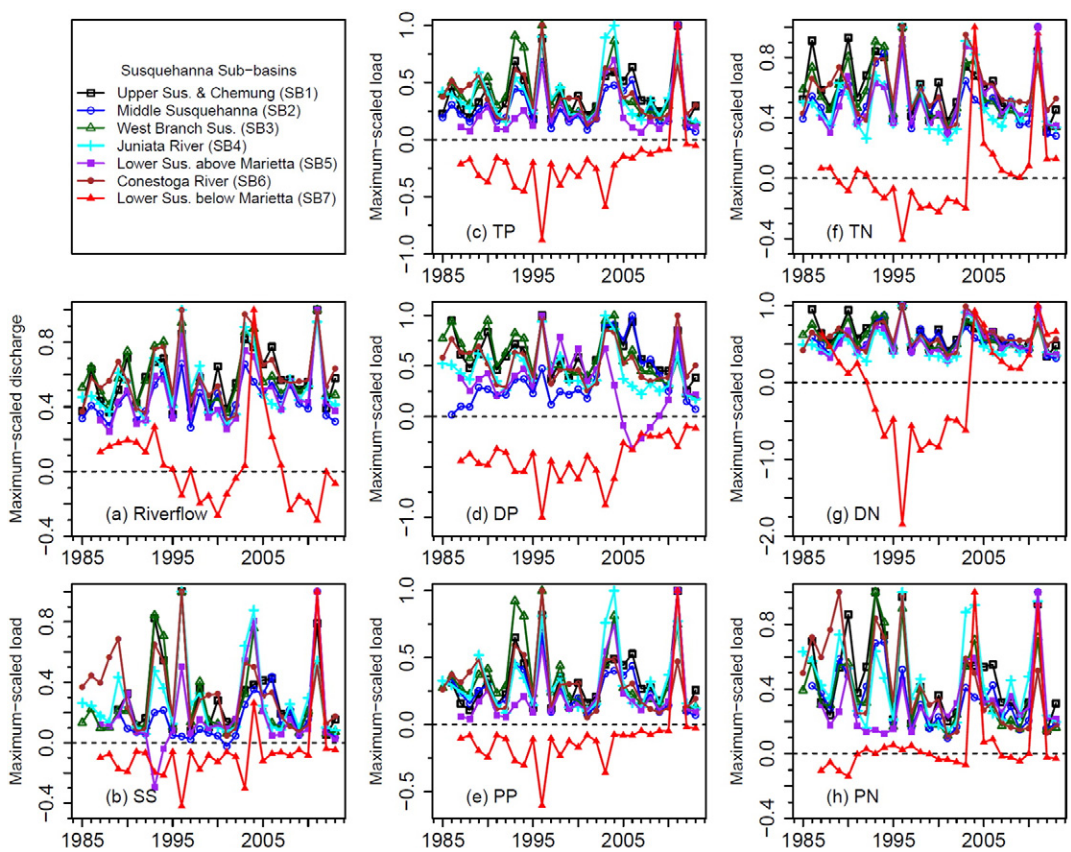

Fig. 6. Reconstructed time series of (a) annual discharge and annual *true-condition* net contributions of (b) SS, (c) TP, (d) DP, (e) PP, (f) TN, (g) DN, and (h) PN by the seven Susquehanna sub-basins. To aid comparison, *all y-axis* values have been scaled by respective long-term annual maxima.

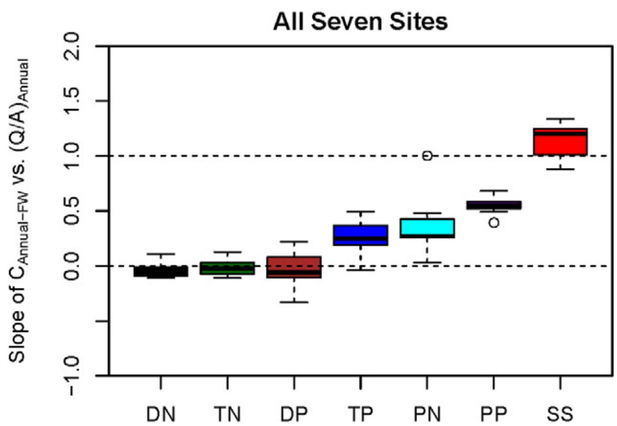

Fig. 7. Fitted linear slopes for relations between annual flow-weighted concentration ($C_{\text{Annual-FW}}$) and area-normalized annual discharge ($[Q/A]_{\text{Annual}}$) on log-log scale at the seven Susquehanna sites for each water-quality constituent. Detailed data and slope fits are presented in Fig. S2 of the online Supplementary material.

TN/TP molar ratio against area-normalized discharge on both annual (Fig. 8d) and daily (Fig. 8e) scales. (The daily ratios are considered more representative of instantaneous ratios than the annual ratios.) Following the convention of Qian et al. (2000), we classified the TN/TP molar ratios into three nominal categories with respect to possible nutrient limitation: (1) P-limitation (TN/TP > 20), (2) co-limitation by both N and P (10 ≤ TN/TP ≤ 20), and (3) N-limitation (TN/TP < 10). We emphasize that these categories are nominal only — although based on the classic Redfield ratio (Redfield, 1958), the cut-off values do not reflect any actual knowledge about limitations in the given systems. Rather, our interest is in the comparative ratios and trends. In these regards, both plots show generally lower TN/TP ratios during high discharge at the Susquehanna sites, including differences in regard to the nominally limiting nutrient. Notably, the daily ratio follows a clear spatial gradient, with values increasing from upstream to downstream sites and with Conowingo consistently having the highest ratio (Fig. 8f).

3.4. Relative contributions by sub-basins and effects of land use on export

To compare the relative contributions of sub-basins to the total annual loadings at Conowingo (*i.e.*, delivered loading from the non-tidal SRB to Chesapeake Bay) between 1985 and 2013, we quantified the fractional contributions (FCs) of each sub-basin for each species — see Fig. 9. (Note that FCs of these seven sub-basins always sum up to one in each year and that the negative FCs of SB7 [Lower Susquehanna River below Marietta] correspond to net storage in the reservoir system.) For streamflow, SB1 (Upper Susquehanna River & Chemung River) and SB3 (West Branch Susquehanna River) have the highest FCs throughout the last three decades as they have the largest drainage areas (Table 1). Consistent with the large area, SB1 also has the highest FCs for SS, TP, DP, and PP. SB3, however, has generally low FCs for all constituents. Another major deviation between rankings of streamflow FC and constituent FC is observed with SB5 (Lower Susquehanna River above Marietta). This sub-basin is about 60% of SB1 in drainage area (Table 1), but it has the highest FCs for all N species (*i.e.*, TN, DN, and PN) and the second highest FCs for all P species (*i.e.*, TP, DP, and PP) that are only slightly lower than those of SB1. In comparison to SB5, SB7 (Lower Susquehanna River below Marietta) is also located in the Lower Susquehanna area and dominated by agricultural land; however, this reservoir-dominated sub-basin does not export constituents in a similar way. Instead, various species are at least partially retained.

To further quantify the relationships between constituent export and land use, we plotted the period-of-record medians of $(Q/A)_{\text{Annual}}$ and annual constituent yield against area fractions of major land uses, namely, non-forested (*i.e.*, agricultural, urban, and others) and forested (Fig. 10). (SB7 was excluded from this analysis to remove the complication of reservoir effects.) Simple linear regressions were developed between log-transformed median annual yield and area fractions of land uses. Due to data limitation (number of sub-basins = 6), our linear models involve only one explanatory variable and thus cannot account for interactions between "forested" and "non-forested" lands or for any additional variability that is associated with different categories of "non-forested" lands. Nonetheless, this simple approach can provide some qualitative insights on land-use effects. In general, period-of-

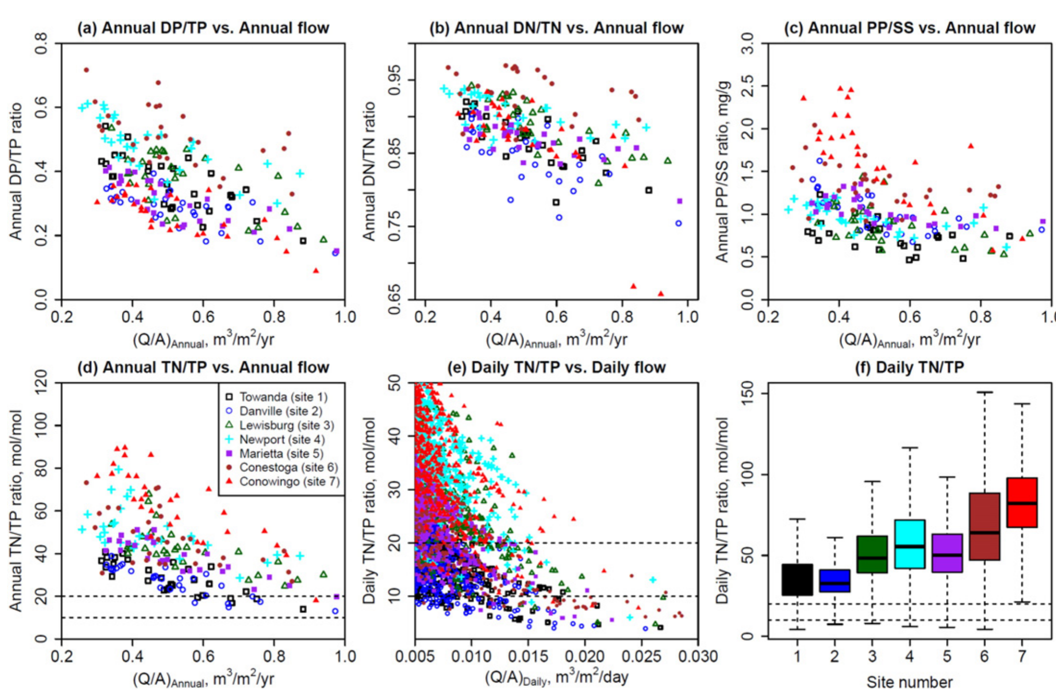

Fig. 8. Relations between area-normalized annual discharge ($[Q/A]_{\text{Annual}}$) and annual ratios of (a) DP/TP, (b) DN/TN, (c) PP/SS, and (d) TN/TP at the seven Susquehanna sites. Plot (e) shows relations between area-normalized daily discharge ($[Q/A]_{\text{Daily}}$) and daily TN/TP ratio for each site. Plot (f) summarizes the daily TN/TP ratio at each site with boxplots. The region between dashed lines in plots (d)-(f) represent the nominally co-limitation condition by both N and P (*i.e.*, 10 ≤ TN/TP ≤ 20).

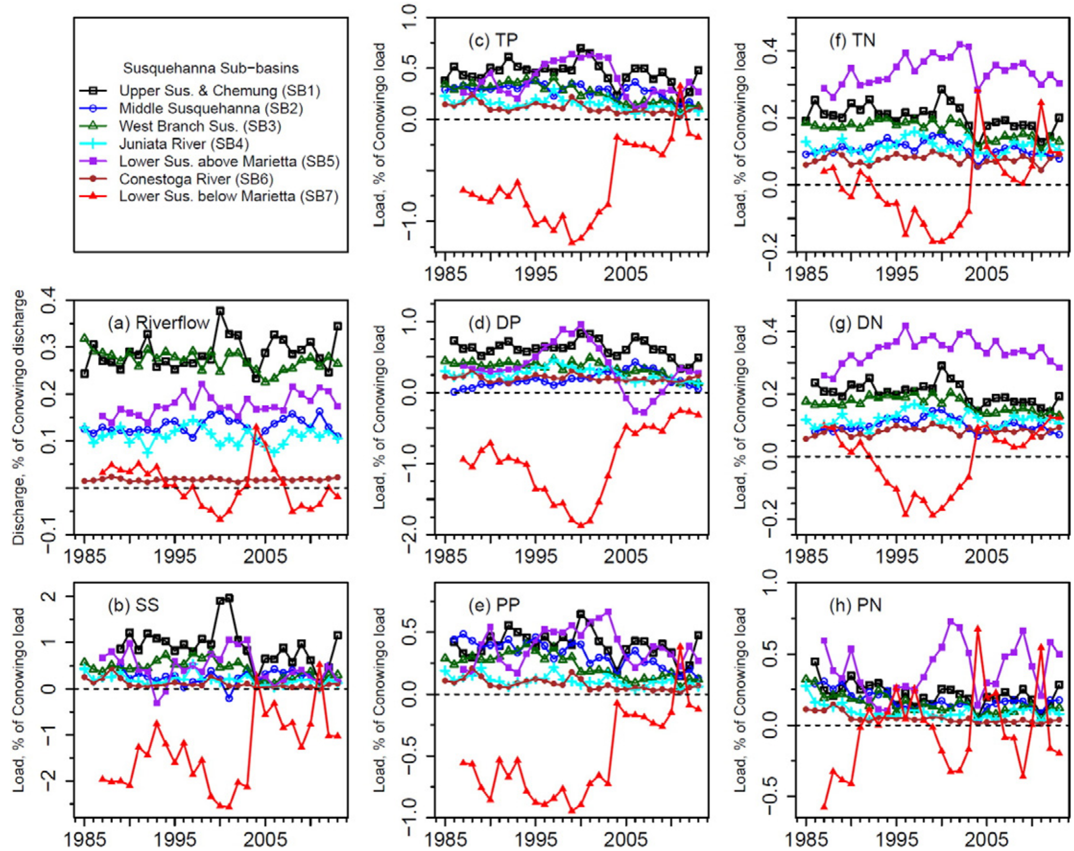

Fig. 9. Fractional contributions (FC) of each sub-basin to (a) annual discharge and annual *true-condition* loadings of (b) SS, (c) TP, (d) DP, (e) PP, (f) TN, (g) DN, and (h) PN at Conowingo (river fall-line). Note that FCs of all sub-basins sum up to one in each year.

record median of $(Q/A)_{Annual}$ is almost invariant between land use types. In contrast, median annual yields of N, P, and SS are strongly affected by land uses: the median annual yields correlate positively with the area fraction of non-forested land but negatively with that of forested land.

To evaluate land-use effects under different hydrological conditions, we categorized each year in the period of 1987–2013 to three flow classes, *i.e.*, wet, average, and dry years. These were determined according to the ranking of annual-average streamflow: the highest 30%, the lowest 30%, and the middle 40% are classified as "wet," "dry," and "average," respectively. Correlation analyses presented above (Fig. 10) were then separately conducted on subsets of data corresponding to each flow class. Results for non-forested land show positive effects on log-transformed median yields for all species under all three flow classes, with generally similar slopes but different intercepts — wet years always have much larger intercepts than average or dry years (Fig. S3). For forested land, the slopes between log-transformed median yields and area fraction are consistently negative under all three flow classes, and intercepts are again larger in wet years than average or dry years (Fig. S4).

4. Discussion

4.1. Temporal trends in flow-normalized riverine loadings

FN-modeled loadings show general declines for all species (*i.e.*, dissolved, particulate, and total) at all Susquehanna sites upstream of Conowingo Reservoir in the last three decades (Section 3.1; Fig. 2). The general consistency in timing and magnitude across sites indicates that changes have been relatively uniform spatially, presumably reflective of basin-wide effects from management controls. Although it is difficult to establish causation (which is beyond the scope of this work), we list below some major management actions that have possibly affected the observed trends. For SS (Fig. 2b), the general declines may reflect improvements in land management practices with respect to control of sediment sources and transport. For P, the declines in DP (Fig. 2d) at least partially benefited from the implementation of a P-detergent ban in Pennsylvania since 1990 (Litke, 1999) and nutrient removal technology upgrade at WWTPs since the 1980s (Chesapeake Bay Program, 1998; Chesapeake Executive Council, 1998). For example, point source input at Marietta is calculated to have declined by 172,000 kg between 1995 and 2011, which is 51% of the estimated decline in DP riverine loading over the same period (336,000 kg). In comparison, the PP declines (Fig. 2e) are more reflective of nonpoint source controls, including at least fertilizer and manure reductions and P-based nutrient management (Weld et al., 2002). For TN (and DN), the declines (Fig. 2f–g) are likely related to historical controls on point sources (particularly WWTP upgrade) and nonpoint sources (*e.g.*, fertilizer and manure applications) (Chesapeake Bay Program, 1998; Chesapeake Executive Council, 1998) and measures taken in response to the Clean Air Act and associated reductions in nitrogen oxide emissions from coal-fired power plants and automobiles (Eshleman et al., 2013; Linker et al., 2013b).

In contrast with the upstream sites, Conowingo showed clear rises in FN loadings of SS, TP, PP, and PN in recent years (Fig. 2), re-affirming the trends documented previously (Hirsch, 2012; Zhang et al., 2013). Complementary to these FN-modeled trends, true-condition estimates for SB7 (Lower Susquehanna River below Marietta) show decreased net annual storage in recent decades, especially for particulate constituents (Section 3.3; Fig. 6). These results collectively suggest declining trapping performance by the LSRRS (mainly Conowingo Reservoir) and possibly associated effects on biogeochemical transformations (*e.g.*, mineralization, biotic uptake, burial in sediments, denitrification) during the (presumably declining) residence time in the reservoir. As sediment

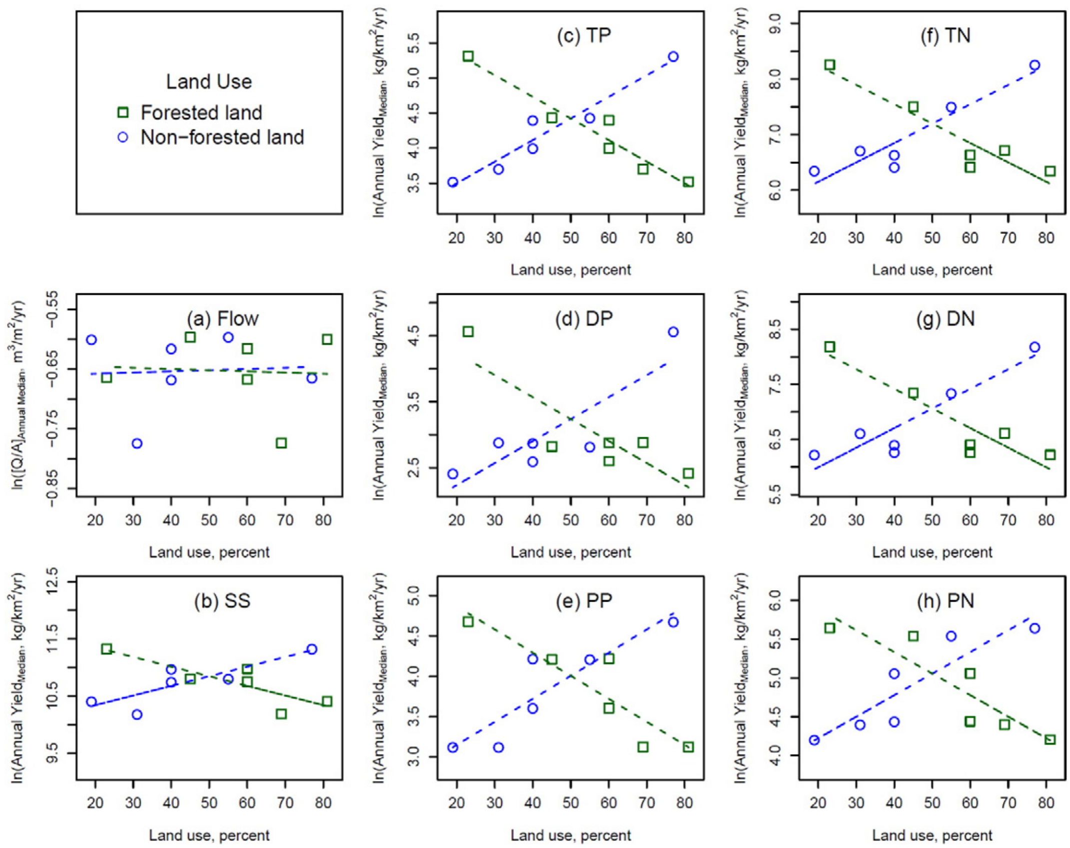

Fig. 10. Relations between area fractions of two types of land use (*i.e.*, forested and non-forested) and log-transformed period-of-record medians of (a) area-normalized annual discharge ($[Q/A]_{\text{Annual Median}}$) and annual *true-condition* loadings of (b) SS, (c) TP, (d) DP, (e) PP, (f) TN, (g) DN, and (h) PN in the seven Susquehanna sub-basins. Each point represents one sub-basin. Dashed lines are linear fits.

accumulates in the reservoir, cross-sectional area becomes less available for flow, thereby increasing the average horizontal flow velocity, decreasing the vertical depth from water surface to sediment bed, and increasing the relative importance of wind-induced turbulence. In this regard, our parallel work focusing on the reservoir reach has used several different approaches to demonstrate that decreased reservoir trapping has occurred under a wide range of flow conditions — see Zhang et al. (2016). To further understand these processes and the associated effects on reservoir modulation of upstream inputs, which is of growing concern to watershed managers (Friedrichs et al., 2014; The Lower Susquehanna River Watershed Assessment Team, 2014), continued monitoring and research is indispensable. Toward this end, one major research project is already underway (Blankenship and Wheeler, 2016; University of Maryland Center for Environmental Science, 2016).

4.2. Comparison of changes in riverine yield and source input

Our evaluation of the source input changes (Section 3.2) provides additional evidence that is useful for explaining the riverine trends. For both TP (Fig. 3) and TN (Fig. 4), total source input and the major individual sources have declined in the drainage basins of most sites. For individual sources, the largest declines are generally associated with manure or fertilizer for TP and atmospheric deposition for TN. Two notable anomalies are observed, however. One anomaly is manure input at Marietta, which has risen for both TN and TP. These rises may be explained by an increase in estimated animal numbers (by ~1.6% yr^{-1}) in the Juniata River basin, as estimated from data provided by the CBPO (Yactayo, 2015). The other anomaly is atmospheric deposition at Conestoga, for which the decline was much smaller than the other sites. This spatial difference can be related to increases in estimated ammonia deposition associated with more intense agricultural activities in the Conestoga River basin (Shenk, 2015).

The $\Delta_{\text{FN-Yield}}/\Delta_{\text{Input}}$ ratios provide a simple quantitative measure of the fraction of source reduction that has been realized in the riverine yield decline (Fig. 5). The generally positive ratios (12 of 14 cases) indicate that riverine yield has indeed declined in response to source reductions in different parts of the SRB. Several anomalies are noted. For TP, both Conowingo and Newport show negative ratios. For Conowingo, the negative ratio reflects a positive change in TP yield despite a negative change in source input, owing to declines in TP retention within Conowingo Reservoir (see Section 4.1). For Newport, the negative ratio reflects a negative change in TP yield despite a positive change in source input that is more difficult to explain — at this site, the result may imply enhanced nutrient processing in the Juniata River basin. For TN, Conowingo has the smallest ratio, reflecting decreased retention of the PN fraction within the reservoir. By contrast, Conestoga has the highest ratio (1.12) among all sites, reflecting an overall decline in riverine yield even greater than that in source input. Note that, however, Conestoga is a small basin and thus the quality of source input data may not be as high as for the larger basins. Considering all sites except Conowingo and Conestoga, $\Delta_{\text{FN-Yield}}/\Delta_{\text{Input}}$ ratio has a coefficient of variation of 2.4 for TP but only 0.14 for TN, which implies that, in the absence of information from other types of data or process-based modeling, TN is much more predictable from source input than is TP.

A consistent pattern is that $\Delta_{\text{FN-Yield}}/\Delta_{\text{Input}}$ ratios are generally <1.0 (13 of 14 cases), reflecting the fact that riverine outputs at the Susquehanna sites have remained relatively constant despite strong changes in source inputs. We note that similar patterns have been documented for other watersheds within the Chesapeake Bay, Mississippi River, and Lake Erie basins, and that prior authors have speculated that such results could reflect continuing contributions from legacy sources (Basu et al., 2010; Jarvie et al., 2013; Meals et al., 2009; Sharpley et al., 2013). We speculate that our results may similarly reflect such sources. For the Chesapeake region, the legacy stores primarily comprise groundwater for N (Bachman et al., 1998; Sanford and Pope, 2013), surface soils and river sediments for P (Ator et al., 2011; Sharpley et al., 2013), and stream corridors and reservoir beds for sediment (Gellis et al., 2008; Walter and Merritts, 2008). These legacy stores originated primarily from agricultural fertilizer applications (Brush, 2009; Meals et al., 2009; Sharpley et al., 2013) and historical land clearances (Gellis et al., 2008; Langland, 2015) and can be released during high flow and erosional events.

Definitive confirmation of such "legacy effects" for our sites may not be possible without complete understanding of the sources and sinks (*e.g.*, plant uptake, denitrification) and of the processes controlling constituent accumulation and release. (Included in such concerns, for example, would be the uncertainties and accuracies of the currently available data for source input and possible over-statement of the assumed efficiency of implemented best management practices.) Nonetheless, some authors have come to other conclusions about the causes of similar trends at other locations. In particular, Basu et al. (2010) observed generally low inter-annual variability in reconstructed time series of $C_{Annual\text{-}FW}$ at their study sites (within the Mississippi-Atchafalaya River and Baltic Sea basins) and attributed this observation to legacy sources created by long histories of anthropogenic inputs that greatly exceeded removal mechanisms. Although also not confirmed directly through mass-balance calculations, others (*e.g.*, Gellis et al., 2008; Jarvie et al., 2013; Sharpley et al., 2013) have posited similar hypotheses, and other studies have provided supporting data. For example, legacy sources have been reported to contribute as much as over half of riverine TP and TN fluxes in some Chinese agricultural watersheds (Chen et al., 2014; Chen et al., 2015). Additionally, a major fraction (median = 48%) of riverine TN load at 36 Chesapeake sites was estimated to come from baseflow contributions (Bachman et al., 1998). For our seven sites, results show temporal invariance in $C_{Annual\text{-}FW}$ at all sites for dissolved species (DN, TN, and DP) and at all sites except Conestoga and Lewisburg for particulate species (PN, TP, PP, and SS) (Fig. S5). These patterns are consistent with a similar conclusion of so-called "biogeochemical stationarity" (Basu et al., 2010; Thompson et al., 2011) and is similarly speculated to reflect the effects of legacy sources. The management implication is that short-term water-quality improvement in Susquehanna River should not be expected to follow a "one-to-one" correspondence with reduction of contemporary source inputs (*e.g.*, fertilizer and manure) and that larger long-term gains may follow only after the depletion of legacy sources. (In this regard, the relatively strong decline in $C_{Annual\text{-}FW}$ for particulate species at Conestoga and Lewisburg likely reflects some combination of strong decline in source inputs and depletion of legacy sources.) Overall, our results reinforce the importance of considering lag time between the implementation of management actions and achievement of river quality improvement. Such lag times may be on the order of years to decades for N and P (Jarvie et al., 2013; Sanford and Pope, 2013; Sharpley et al., 2013) and much longer for upland sediment management practices in watersheds with large transport-length scales (Pizzuto et al., 2014).

4.3. Mass balances of sub-basins and effects of streamflow on export

Mass-balance analysis of true-condition estimates reveals a striking similarity among all six sub-basins upstream of Conowingo Reservoir with respect to the timing of significant exports (Section 3.3; Fig. 6). This suggests similar conditions of rainfall and material processing in SB1–SB6 and implies that Q_{Annual} is the principal factor controlling L_{Annual}, with relatively less influence from other factors (*e.g.*, seasonally-varying biogeochemical processes). The statistically significant linear slopes for $\log[L_{Annual}] \sim \log[Q_{Annual}]$ confirm the dominance of hydrological control on the inter-annual variability of constituent exports (Fig. S1), which suggests generally transport-limitation conditions, as has also been similarly observed with other watersheds (*e.g.*, Alvarez-Cobelas et al., 2008; Alvarez-Cobelas et al., 2009; Basu et al., 2010; Howarth et al., 2012; Howarth et al., 2006; Sobota et al., 2009).

Despite the above commonality of hydrological control, dissolved and particulate species exhibit markedly distinctive export behaviors based on the fitted linear slopes of $\log[C_{Annual\text{-}FW}] \sim \log[(Q/A)_{Annual}]$. Specifically, dissolved species are dominated by chemostasis effects (slope ~ 0), whereas particulate species are dominated by mobilization effects (slope > 0) (Fig. 7; S2). A likely explanation is that dissolved species are dominated by processes of subsurface transport, storage, and mixing that are relatively homogeneous over a range of spatial and temporal scales (Gall et al., 2013; Harman, 2015; Kirchner and Neal, 2013), whereas particulate species are dominated by surface transport that are more susceptible to episodic exports. In both cases, the general lack of dilution patterns indicates that none of these constituents has been supply-limited, implying sufficient storage of excess constituent mass in these sub-basins. This finding is consistent with the "legacy sources" hypothesis discussed in Section 4.2.

In addition to affecting the annual export rates of dissolved and particulate constituents, streamflow has also played an important role in modulating the relative importance of dissolved and particulate fractions (Fig. 8). This analysis was limited to annual estimates for describing general patterns and constraining seasonal effects. The observed negative correlations between $(Q/A)_{Annual}$ and annual DP/TP and annual DN/TN ratios (Fig. 8a–b) likely reflect surface mobilization of particulate (inorganic and organic) fractions during high discharges (Pionke et al., 2000; Sharpley et al., 1999). In this context, DN has always been the dominant fraction (>70%) of TN, whereas DP has been only a minor fraction of TP except during very low flows. The negative correlation between $(Q/A)_{Annual}$ and annual PP/SS (Fig. 8c) is expected given that (1) transported sediments contain a higher fraction of fine-sized particles during low flows and (2) finer sediments have higher specific surface areas for P absorption (Horowitz et al., 2012; Zhang et al., 2015). The negative correlation between streamflow and TN/TP molar ratio (Fig. 8d–e) indicates that high-flow flushing affects P to a larger degree than N. In regard to the nominally limiting nutrient (Fig. 8d, 8e), the lower TN/TP ratios during high discharges is an issue of interest that is consistent with the different export mechanisms for the two species. The spatial trend of daily TN/TP, which increases from upstream to downstream sites (Fig. 8f), imply incrementally more net export of TN than TP as one moves from upstream to downstream reaches of Susquehanna River over the study period. The implication is that the TN-to-TP mass ratio for contributions from the downstream river reaches and surrounding watersheds are greater than those from the upstream counterparts. Two possible scenarios, for example, could include (1) greater P contributions from steeper terrain in upstream watersheds or (2) greater N contributions from downstream agricultural lands. These are speculations only, however, and other scenarios are also possible. More definitive understanding would require additional data collection and study.

4.4. Relative contributions by sub-basins and effects of land use on export

The relative contributions of each sub-basin to total non-tidal SRB load are consistent with expectations based on relative drainage area and dominant land use (Section 3.4; Fig. 9). For SB3 (West Branch Susquehanna River), its relatively large drainage area but low FCs for all types of constituents reflect the facts that SB3 has the highest fraction of forested area (81%) and that forested land should have relatively lower source inputs and higher assimilation capacity than non-forested land. By contrast, SB5 (Lower Susquehanna River above Marietta) has a relatively small area (60% of SB1) but high FCs for constituents, reflecting its larger fraction of agricultural area (47% compared to 35% in SB1) and smaller fraction of forested area (45% compared to 60% in SB1). This disproportionally larger contribution by SB5 is consistent with previous findings (Ator et al., 2011) and deserves management considerations. In contrast with SB5, the patterns of SB7 (Lower Susquehanna River below Marietta) effectively demonstrate that nutrient/sediment export has been significantly modulated by major human modulation of the landscape, *i.e.*, river damming. Particularly, various N and P species can be at least partially retained within the reservoir through particle sedimentation and algal uptake, followed by processes of bacterial degradation, denitrification, and burial in sediments (Friedl and Wüest, 2002; Jossette et al., 1999). Moreover, the SB7 results also illustrate that such reservoir modulation (retention and release) has varied considerably as it approaches sediment storage capacity.

The follow-up analysis (Fig. 10) has developed regression models between log-transformed period-of-record median yield and area fractions of land uses. The results show that period-of-record median yields of N, P, and SS all correlate positively with the area fraction of non-forested (*i.e.*, human-disturbed) but negatively with that of forested land (Fig. 10). Moreover, these land-use effects are observed under all three flow classes, but with consistently larger intercepts during wet years (Figs. S3–S4). This latter aspect may relate to both (a) increased mobilization of surface and sub-surface constituents and (b) decreased biogeochemical assimilation (*e.g.*, less denitrification or biotic uptake) that could result from shorter transit times during high-flow conditions (Alvarez-Cobelas et al., 2009; Howarth et al., 2006). These findings on land-use effects are particularly relevant to management of the SRB and also consistent with published findings elsewhere (*e.g.*, Harris, 2001; Jordan et al., 1997; Sobota et al., 2009; Worrall et al., 2012).

5. Conclusions

This paper provides a comprehensive evaluation of nutrient and sediment exports from multiple locations in the Susquehanna River basin over the last three decades. Our work has demonstrated the value of long-term data and the utility of "traditional" approaches of trend analysis, mass-balance calculation, and examination of C-Q relations for understanding riverine export. This synthesis of temporal and spatial patterns has provided information on four major factors affecting constituent export, namely, source input, reservoir modulation, streamflow, and land use, as summarized below:

(1) "*Source input*": Nutrient and sediment riverine loadings have generally declined at sites in Susquehanna River upstream of Conowingo Reservoir. These declines seem to have followed contemporary source input reductions. However, the generally <1.0 $\Delta_{FN\text{-}Yield}/\Delta_{Input}$ ratios and the general temporal invariance of $C_{Annual\text{-}FW}$ at these sites suggest the possibility of legacy contributions, as proposed by other investigators in prior major watershed studies. These results reinforce the importance of considering lag time between the implementation of management actions and achievement of river quality improvement.

(2) "*Reservoir modulation*": The contrast of mass-balance results in sub-basin SB7 with multiple upstream sub-basins effectively demonstrates how a major reservoir system (the LSRRS) has caused this sub-basin to behave far differently than any of the upstream reaches. As previously discussed in prior papers, the data indicate substantial retention of particulate species within the LSRRS, but with retention rates decreasing over time as the reservoir approaches sediment storage capacity. Consequently, flow-normalized loadings for particulate species have increased recently below Conowingo Reservoir, despite general declines at upstream sites.

(3) "*Streamflow*": Statistically significant linear $\log[L_{Annual}] \sim \log[Q_{Annual}]$ relationships at the monitoring sites suggest the dominance of hydrological control on the inter-annual variability of constituent exports. The associated $\log[C_{Annual\text{-}FW}] \sim \log[(Q/A)_{Annual}]$ patterns generally show chemostasis effects for dissolved species and mobilization effects for particulate species, both implying transport-limited (as opposed to source-limited) conditions. In addition to affecting annual export rates, streamflow has also affected the relative importance of dissolved and particulate fractions, as reflected by the negative correlations between $(Q/A)_{Annual}$ and DP/TP, DN/TN, PP/SS, and TN/TP ratios.

(4) "*Land use*": The relative contributions of the sub-basins are consistent with expectations based on relative drainage area and dominant land use. Period-of-record median annual yields of N, P, and SS all correlate positively with the area fraction of non-forested land but negatively with that of forested land, and these patterns are observed under all hydrological classes.

These findings with respect to factors affecting riverine export are consistent with prior studies on a broad range of watersheds. These results have direct bearing toward better management of this large watershed and the attainment of Chesapeake Bay TMDLs. Moreover, our approaches are transferable to other Chesapeake tributaries and to rivers in other geographical regions. Last but not least, this work effectively illustrates how science-based management can benefit from maintaining open-access to high quality long-term monitoring data at multiple locations in watersheds.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.03.104.

Appendix B. List of abbreviations

$\Delta_{FN\text{-}Yield}$	period-of-record change in flow-normalized riverine yield, in ML^{-2}
Δ_{Input}	period-of-record change in source input yield, in ML^{-2}
$C_{Annual\text{-}FW}$	annual flow-weighted concentration, in ML^{-3}
CBPO	Chesapeake Bay Program Office
DN	dissolved nitrogen
DP	dissolved phosphorus
EGRET	Exploration and Graphics for RivEr Trends (an *R* package)
FC	fractional contribution
FN	flow-normalized (estimates)
L_{Annual}	loading of constituent, in MT^{-1}
N	nitrogen
NWIS	National Water Information System Web Interface (managed by USGS)
P	phosphorus
PN	particulate nitrogen
PP	particulate phosphorus
Q_{Annual}	annual discharge, in L^3T^{-1}
$(Q/A)_{Annual}$	area-normalized annual discharge, in L/T

$(Q/A)_{Daily}$	area-normalized daily discharge, in L/T
SB	sub-basin
SRB	Susquehanna River basin
SRBC	Susquehanna River Basin Commission
SS	suspended sediment
TMDL	Total Maximum Daily Load
TN	total nitrogen
TP	total phosphorus
USGS	U.S. Geological Survey
WRTDS	weighted regressions on time, discharge, and season
WWTP	wastewater treatment plant

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