

Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed

Shuiwang Duan,¹ Sujay S. Kaushal,¹ Peter M. Groffman,² Lawrence E. Band,³ and Kenneth T. Belt⁴

Received 3 June 2011; revised 22 December 2011; accepted 27 December 2011; published 1 March 2012.

[1] Watershed export of phosphorus (P) from anthropogenic sources has contributed to eutrophication in freshwater and coastal ecosystems. We explore impacts of watershed urbanization on the magnitude and export flow distribution of P along an urban-rural gradient in eight watersheds monitored as part of the Baltimore Ecosystem Study Long-Term Ecological Research site. Exports of soluble reactive phosphorus (SRP) and total P (TP) were lowest in small watersheds with forest and low-density residential land use ($2.8\text{--}3.1\text{ kg}^{-1}\text{ km}^{-2}\text{ yr}^{-1}$). In contrast, SRP and TP exports increased with watershed impervious surface coverage and reached highest values in a small urban watershed ($24.5\text{--}83.7\text{ kg}^{-1}\text{ km}^{-2}\text{ yr}^{-1}$). Along the Gwynns Falls, a larger watershed with mixed land use, the greatest proportion of SRP (68%) and TP (75%) was contributed from the lower watershed, where urban areas were the dominant land use. Load duration curve analysis showed that increasing urbanization in watersheds was associated with shifts in P export to high-flow conditions ($>2\text{ mm d}^{-1}$). SRP concentrations during low-flow conditions at urban headwater sites were highest during summer and lowest during winter. This seasonal pattern was consistent with sediment incubation experiments showing that SRP release from sediments was temperature dependent. Our results suggest that shifts in streamflow and alterations in water temperatures owing to urbanization and climate can influence stream water P concentrations and P export from urban watersheds.

Citation: Duan, S., S. S. Kaushal, P. M. Groffman, L. E. Band, and K. T. Belt (2012), Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed, *J. Geophys. Res.*, 117, G01025, doi:10.1029/2011JG001782.

1. Introduction

[2] Human alteration of the global nitrogen (N) and phosphorus (P) cycles has contributed to increased coastal eutrophication, harmful algal blooms and alterations in aquatic food webs [Ryther and Dunstan, 1971; Smil, 2000; Kemp *et al.*, 2005]. It is generally assumed that P is a limiting nutrient for freshwater eutrophication and N is a limiting nutrient for coastal eutrophication [Ryther and Dunstan, 1971; Howarth and Paerl, 2008; Turner *et al.*, 2006]. Recent studies have shown that P can also be a limiting nutrient in marine waters owing to excessive N loading, however [e.g., Sylvan *et al.*, 2006; Howarth and Marino, 2006]. Urbanization is a widespread and rapidly growing form of land use change, and it has led to elevated P concentrations and exports from watersheds [Dillon and

Kirchner, 1975; Norvell *et al.*, 1979; Tufford *et al.*, 2003; Petrone, 2010]. In some cases, increases in P concentrations resulting from urbanization are comparable to those observed in agricultural watersheds [Omernik, 1976; Fink, 2005].

[3] Recent estimates show that a large proportion of P delivered to the Chesapeake Bay originates from point (e.g., municipal and industrial wastewater) and nonpoint sources (e.g., surface runoff and in-stream sediment) corresponding to agriculture and urban/suburban land use [Russell *et al.*, 2008]. Urbanization not only enhances P inputs to watersheds [Norvell *et al.*, 1979; Alvarez-Cobelas *et al.*, 2009], but it also alters urban hydrology [e.g., Paul and Meyer, 2001] which has been shown to increase the temporal variability of nitrogen export [e.g., Kaushal *et al.*, 2008; Shields *et al.*, 2008; Kaushal *et al.*, 2010b]. Changes in P export in response to urban hydrologic alteration have not been well studied relative to nitrogen dynamics, although P export is likely sensitive to hydrologic alteration. Urbanization can also influence stream temperatures owing to deforestation, discharges from power plants and wastewater treatment facilities, and runoff from impervious surfaces [Kaushal *et al.*, 2010a, and references therein], which can potentially influence P cycling in aquatic systems. Prior studies have shown that temperature affects SRP levels in aquatic systems

¹Earth System Science Interdisciplinary Center, Department of Geology, University of Maryland, College Park, Maryland, USA.

²Cary Institute of Ecosystem Studies, Millbrook, New York, USA.

³Department of Geography, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, USA.

⁴Baltimore Field Station, Northern Research Station, Forest Service, U.S. Department of Agriculture, Baltimore, Maryland, USA.

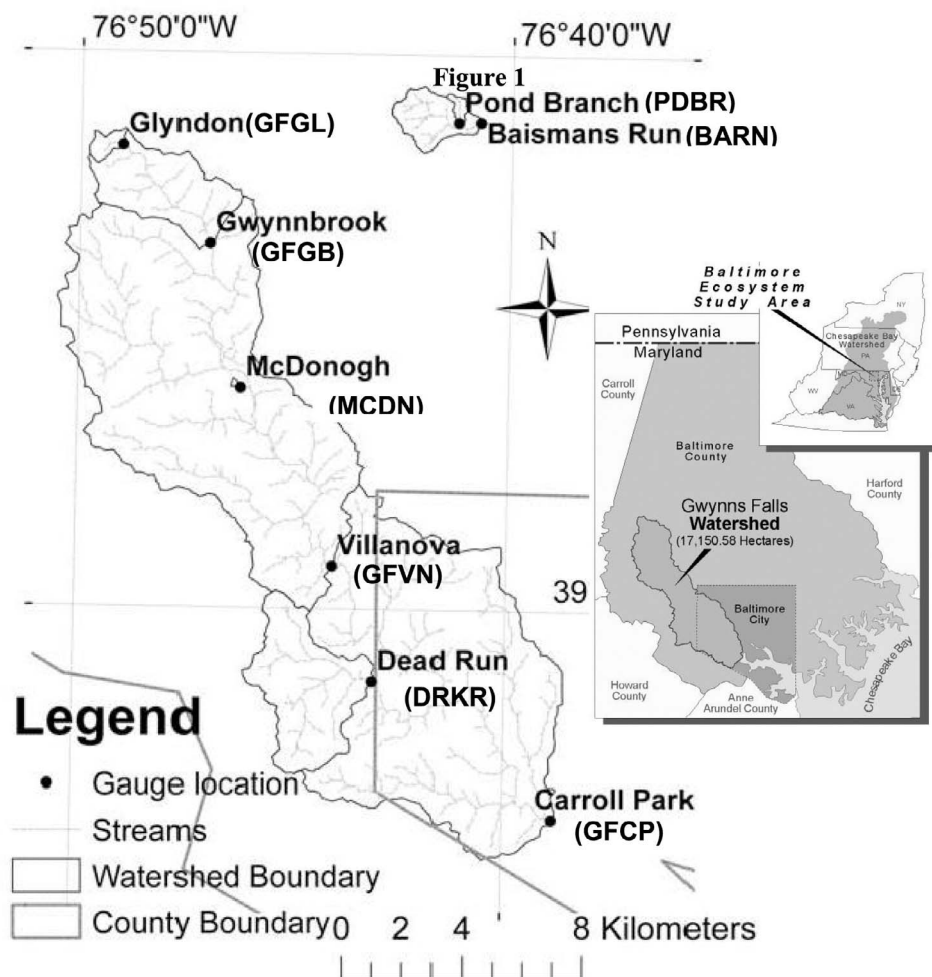


Figure 1. Map of the Gwynns Falls and Baisman Run watersheds, indicating the study sites and subwatersheds in each stream.

via biotic and/or abiotic processes [Barrow, 1979; Froelich, 1988; Correll *et al.*, 1999; James and Barko, 2004]. Equilibrium phosphate concentrations with soil particles and the solubility of phosphorus minerals (e.g., hydroxylapatite) are temperature dependent [Barrow, 1979; Prakash *et al.*, 2006]. Temperature also increases the rates of SRP sorption and desorption from particles [Froelich, 1988] and favors the formation of environmental conditions (e.g., anoxic) at which SRP fluxes from sediments and soils can be enhanced [House and Denison, 2002; James and Barko, 2004; Solim and Wangane, 2009].

[4] Here, we investigated the effects of altered stream hydrology and temperature on P concentrations and exports across an urban-to-rural gradient in the Chesapeake Bay watershed. We hypothesized that: (1) altered hydrology has increased the temporal variability of P export from urban watersheds, with P dominantly exported during high-flow periods and that (2) elevated temperatures in urban streams enhances the release of phosphorus from sediments to the water column. The effect of stream hydrology on P export was examined by analyzing cumulative frequency distributions of daily P export. The influence of stream temperature was investigated by examining seasonal changes in P concentration and performing temperature-controlled sediment

incubation experiments. Characterizing the magnitude and temporal variation in P export in urbanizing watersheds is needed to improve future forecasting and watershed scale restoration efforts aimed at reducing P export and improving P retention.

2. Materials and Methods

2.1. Study Sites

[5] Streams in the present study were sampled as part of the National Science Foundation funded Baltimore urban Long-Term Ecological Research project (LTER), the Baltimore Ecosystem Study (BES; see <http://beslter.org>). Most of the sites were located in the Gwynns Falls watershed (76° 30', 39° 15'), a 17,150 ha watershed in the Piedmont physiographic province that drains into the northwest branch of the Patapsco River that flows into the Chesapeake Bay (see Figure 1 and Table 1). The headwaters of the Gwynns Falls are dominated by suburban and residential land use in Baltimore County with the middle and lower reaches extending into urban areas of Baltimore City. Four of the sites, Glyndon (GFGL), Gwynnbrook (GFGB), Villa Nova (GFVN) and Carroll Park (GFCP), are located along the main stem of the Gwynns Falls and traverse a rural/suburban to urban

Table 1. Characteristics and P Exports of Gwynns Falls Main Channel Watershed (Segments), Selected Small Watersheds, and Nearby Reference Watershed^a

							Export (kg km ⁻² yr ⁻¹)	
Land Use/Context		Area (km ²)	Land Use (%)			Runoff (m)		
			Impervious	Forest	Agricultural		SRP	TP
Main Channel Reaches								
Glyndon	suburban	0.8	19.0	19.0	5.0	0.34	9.2	48.4
Gwynnbrook	suburban	11.0	15.0	17.0	8.0	0.41	4.6	14.5
Villa Nova	suburban/urban	84.2	17.0	24.0	10.0	0.42	4.2	33.6
Carroll Park	urban	170.7	24	18.0	6.0	0.45	9.3	83.7
Small- and Medium-Sized Watersheds								
McDonough	agriculture	0.1	0.0	26.0	70.0	0.35	11.6	24.6
Dead Run	urban	14.3	31.0	5.0	2.0	0.58	6.3	24.5
Pond Branch	forested	0.38	0.0	100.0	0.0	0.46	1.1	2.8
Baisman Run	low residential	3.8	0.3	71.0	2.0	0.41	1.2	3.1

^aWatershed land cover and impervious surface data are from *Shields et al.* [2008] and the National Land Cover Database.

gradient. McDonough (MCDN) is a small tributary of the Gwynns Falls draining a watershed dominated by row crop agriculture (corn, soybeans) between the Glyndon and Gwynnbrook stations. Dead Run (DRKR) is an urbanized tributary of the Gwynns Falls between the Villa Nova and Carroll Park stations. Baisman Run (BARN) and Pond Branch (POBR) are predominantly forested watersheds located in the nearby Gunpowder Falls watershed. Baisman Run is a mix of forest and low-density residential development, while Pond Branch serves as a small forested reference watershed. Population density varied between subwatersheds of the BES LTER site from 2.5 persons per hectare to 19.8 persons per hectare (in 1990) with the lower subwatersheds being the most densely populated. The Gwynns Falls is served by city or county sanitary sewer lines, while homes in the Baisman Run watershed have on-site wastewater disposal (septic) systems. There were no wastewater treatment plants upstream of any sites considered in this paper.

2.2. Data Collection and Analysis

[6] Stream discharge was continuously monitored by the U.S. Geological Survey at all stations. Streams were sampled weekly with no regard to flow conditions. Filtered (0.45 micron) samples were analyzed for soluble reactive phosphorus (SRP) and unfiltered samples were analyzed for total phosphorus (TP). Following collection, samples were transported to the Cary Institute of Ecosystem Studies (IES), Millbrook, New York, for chemical analysis. SRP was analyzed on a Lachat Quikchem 8000 flow injection analyzer using the ascorbic acid-molybdate blue method [Murphy and Riley, 1962]. TP was analyzed by persulfate digestion followed by SRP analysis [Ameel et al., 1993]. Standards, made from KH₂PO₄ ranged from 2 to 200 ppb, and the limit of detection was 1.5 ppb. Values below this were set to 1.5 $\mu\text{g P L}^{-1}$. If the value for TP was more than 0.01 mg P L⁻¹ but below the SRP concentration, the TP value for that sample was assumed to be the same as the SRP value. One blank of laboratory deionized water was prepared each week and stored along with the samples. Once every six weeks field spike blanks (100 ppb) were prepared for filtered samples at three stations: Carroll Park, Villa Nova, and Glyndon. Check standards (20 and 200 ppb) made from Na₅P₅O₁₀ were processed along with each batch of TP samples. Each week's samples ranged

from close to detection limits at the forested reference site, to values over 1,000 $\mu\text{g P/L}$ at the urban sites. All data are posted on the BES WWW site <http://beslter.org>.

[7] Stream discharge and chemistry data for most sites covered the period between October 1998 to September 2007, with a shorter period (October 1999 to September 2007) for the Baisman Run and McDonough watersheds. This period covered a range of climate conditions, including severe drought in 2002 (57% of normal precipitation) and a period of high (132% of normal) precipitation in water year 2003 (<http://www.weather.gov/climate>). The effects of these hydroclimatic changes on the study watersheds have been described previously for the Gwynns Falls [e.g., Kaushal et al., 2008; Shields et al., 2008].

[8] We estimated TP and SRP loads for nonsampled days using the U.S. Geological Survey software Load Estimator (LOADEST; <http://water.usgs.gov/software/loadest/>). LOADEST was developed to calculate mass exports of sediment and chemical constituents to the Chesapeake Bay from input files consisting of continuous average daily flow data and discrete concentrations using a multiple parameter regression model with bias corrections incorporated into the program [Cohn et al., 1992; R. L. Runkel et al., Load estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers: Techniques and methods book 4 (U.S. Geological Survey, 2004). It is now a publicly available software program developed to estimate water quality constituent loads in streams and rivers. In this study, the measurements of SRP or TP concentrations and streamflow for each station were used for model calibrations. An automated model selection option was used to choose the "best" model from the set of predefined models (0 to 9) to obtain the lowest value of Akaike Information Criterion. These models, which contained up to seven parameters, captured the dependence of concentrations on both discharge and season (the sine and cosine terms) and any long-term trend. Average daily discharge data for the study period were also prepared for the run of LOADEST so that daily fluxes of SRP or TP were estimated for the whole study period, once the model had been calibrated. From the returning files, results from the adjusted maximum likelihood estimates (AMLE) were used to modify loading equations to correct for transformation bias. LOADEST was run with a daily time step for the period 2000–2007, and daily estimates were compiled by water year (October in prior year to September) to produce

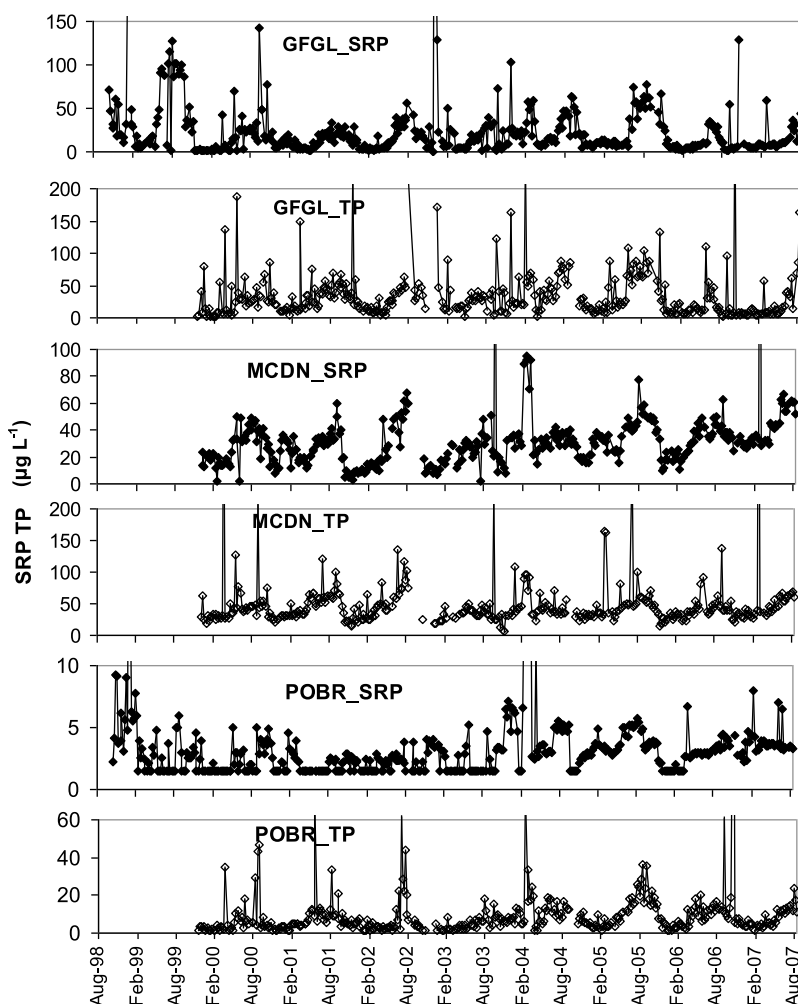


Figure 2. Soluble reactive phosphorus (SRP) and total phosphorus (TP) concentrations at three headwater sites. SRP values are indicated by solid diamonds, and TP values are indicated by open diamonds.

annual export estimates that were normalized per drainage area. The values (loads and watershed area) of the segments between two stations along the main stem of the Gwynns Falls were calculated by subtracting the values of the upstream station from those of the downstream station. Percentages for GFGB, GFVN, or GFCE include loads from smaller drainages included within these watershed segments; that is, GFGL, GFGB, and GFCE, respectively.

[9] Results were evaluated against land use and land cover data in export flux form. Flow and nutrient cumulative export curves of TP and SRP export were also computed from daily flow or estimated daily exports for each site, using the method described by *Shields et al.* [2008]. Cumulative export curves show the percent of accumulated water or nutrient mass exported at different runoff levels. To characterize cumulative export, cumulative daily flow, cumulative SRP or TP loads were graphed versus runoff. The daily cumulative flow or cumulative nutrient loadings were then normalized by the total loadings over the entire period.

2.3. Sediment Incubation Experiments to Investigate Temperature Effects

[10] Sediment and water samples were collected on 2 April 2010 from four sites along the Gwynns Falls main stem

(GFGL, GFGB, GFVN and GFCE), as well as from three tributaries: POBR (forest), MCDN (agriculture) and DRKR (urban). In the laboratory, the sediments were sieved through a 2 mm sieve, and the fraction that passed the sieve was then homogenized and stored at 4°C. The sediments were incubated in four chambers with temperature set at 4, 15, 25, and 35°C.

[11] At each temperature, 200 g of wet sediment and 450 mL of unfiltered stream water were added to 500 mL glass flasks. The water and sediment were well mixed, and the flasks were left stationary at 4°C for 2 to 4 days to wait for the particles to settle. Stream water samples without sediment additions were prepared in 500 mL flasks at the same time as controls. The flasks were then placed in environmental control chambers for incubation experiments. The flasks were kept in the dark and were gently stirred with a shaker table. During the 2 day incubations, 30 mL of water was collected at 0, 6, 12, 24, and 48 h increments and filtered in situ through 25 mm Whatman GF/F filters in a syringe filter. SRP concentrations in the filtered water were measured colorimetrically using a spectrophotometer [*Kaushal and Lewis, 2005*]. Chloride (Cl^-) was measured with a Dionex ICS-1500 ion chromatograph, and was used as a conservative tracer to normalize the effect of evaporation, which may

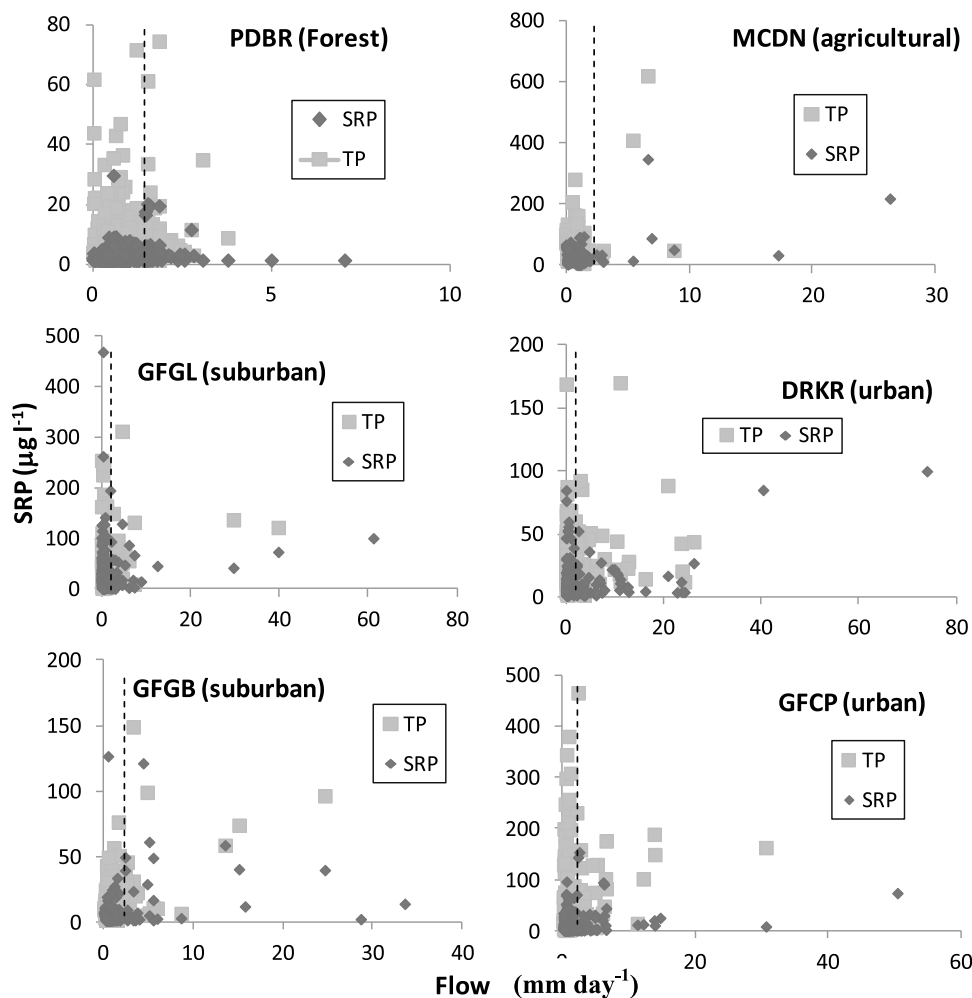


Figure 3. Plots of SRP (diamonds) and TP (squares) concentrations versus water flow at selected sites with different types of land use.

change water volume and SRP concentrations during the incubations. The concentration difference between the water-sediment mixture and the water-only control was assumed to represent P release from sediments. SRP release rates were calculated by simple linear regression of SRP concentrations versus incubation times.

2.4. Statistics

[12] Differences in P export across varying land uses and differences in sediment SRP flux in the incubation experiments were tested using Dunnett's post hoc test for ANOVA in the SPSS statistical software system. Relationships between P export and land use were tested using Spearman's correlation with $\alpha = 0.05$. Spearman's correlation was used in case assumptions of normality were not met.

3. Results

3.1. Temporal Patterns in Phosphorus Concentrations

[13] Figure 2 presents actual measurements of SRP and TP concentrations in 3 headwater streams (area $< 0.8 \text{ km}^2$) that showed distinct seasonal changes. In the suburban (GFGL) and agricultural (MCDN) headwater sites of the Gwynns Falls, SRP and TP concentrations were highest during August (summer) and lowest during February (winter).

ANOVA analysis also showed that the values in summer (July to September) were significantly higher than those of winter (January to March) ($p < 0.05$). This seasonal pattern was also observed at downstream sites the Gwynns Falls main stem (GFGB, GFVN and GFCE) but became increasingly variable owing to short-term oscillations (not shown). SRP concentrations at POBR (forested) were close to detection limits ($2 \mu\text{g L}^{-1}$) and no seasonal variation was observed, but there was a distinct seasonal pattern for TP.

[14] Figure 3 shows changes in SRP or TP concentrations (actual measurements) with streamflow. No significant relationships were observed between SRP or TP concentrations and streamflow at any site. At forest (POBR) and low-density residential sites (BARN), the highest SRP concentrations appeared to be during median streamflow. At urban and urban/suburban sites, the highest SRP and TP concentrations occurred at base flows, but an increase in SRP concentration from middle to high flow was also observed (e.g., GFGL, GFCE and DRKR).

3.2. Sediment Incubation Experiments to Investigate Temporal Patterns

[15] Both final SRP concentrations (at 48 h) and sediment release rates increased with temperature at all sites ($p < 0.05$

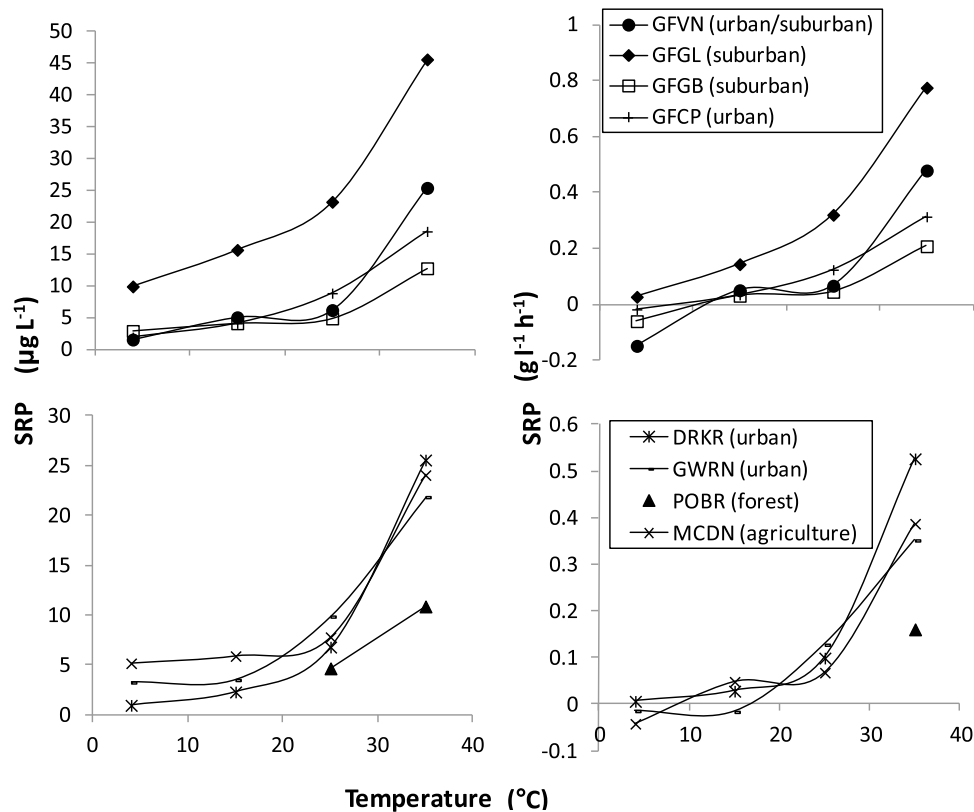


Figure 4. Changes in final SRP concentration (at 48 h) and SRP release rate with water temperature in sediment incubation experiments. The results of POBR at 4, 15, and 25°C are not presented because fine particles did not settle out of solution.

for linear regressions; see Figure 4). Increases in concentrations and release rates were low at lower temperatures (from 4°C to 15°C), and larger values occurred at higher temperatures (from 25°C to 35°C). SRP concentrations and sediment release rates were always highest at GFGL and lowest at POBR (Figure 4), and this difference was consistent with routine measurements of SRP concentrations in streams. In contrast to incubations with sediment, the incubations with water only showed no significant changes in SRP concentrations with time or temperature.

3.3. Cumulative Frequency Distributions of Phosphorus Exports

[16] The water duration curves displayed marked variation along the rural-urban gradient (Figure 5). The forested reference site (POBR) and low-density residential site (BARN) exhibited similar characteristics to each other and had substantial proportions (85% and 75%) of water export under low- to moderate-flow conditions (<2 mm d⁻¹). In the agricultural watersheds (MCDN), less water (71%) was exported across this flow range. More urbanized watersheds (GFGB, GFGL and DRKR) displayed considerably different export characteristics, with decreasing proportions (53%, 38% and 25%) of the overall export occurring during low- to moderate-flow conditions. Table 2 also shows that the runoff at 50% and 80% of cumulative flow also increased in the same sequence.

[17] The SRP and TP load duration curves at the forested (POBR) and low-density residential (BARN) sites

followed a similar pattern to the water duration curves. However, the urban/suburban sites exhibited considerably different export characteristics, with less SRP (25%, 20% and 18%) and TP (10%, 7% and 13%) exported during low- to moderate-flow conditions (<2 mm d⁻¹), relative to the water duration curves. SRP and TP duration curves for these 3 urban/suburban sites clustered together, while the curves at the agricultural (MCDN) site were between the urban/suburban and forest/low residential site types. Similarly, the runoff at 20%, 50% and 80% of cumulative SRP and TP exports also differed between urban/suburban and forested/low residential land use ($p < 0.01$, one-way ANOVA; see Table 2).

3.4. Annual P Exports

[18] The mean annual P exports over the period of 2000 to 2007 displayed marked variability along the urban-rural gradient (Table 1). Lowest SRP and TP exports were found in the forested reference and low-density residential watersheds (POBR and BARN) and were 2.8 kg TP km⁻² yr⁻¹ (1.1 for SRP) and 3.2 kg TP km⁻² yr⁻¹ (1.2 for SRP), respectively. Higher SRP values were found in the following watersheds: MCDN (agricultural), GFPC segment, and GFGL (urban/suburban) and were 11.3, 9.3, and 9.2 kg km⁻² yr⁻¹, respectively. SRP exports increased with increasing impervious surface coverage plus agricultural land use, and decreased with more forest cover (Figure 6; $p < 0.01$). Similarly, highest TP exports were found in GFPC (urban) watersheds, followed by GFGL (suburban), and

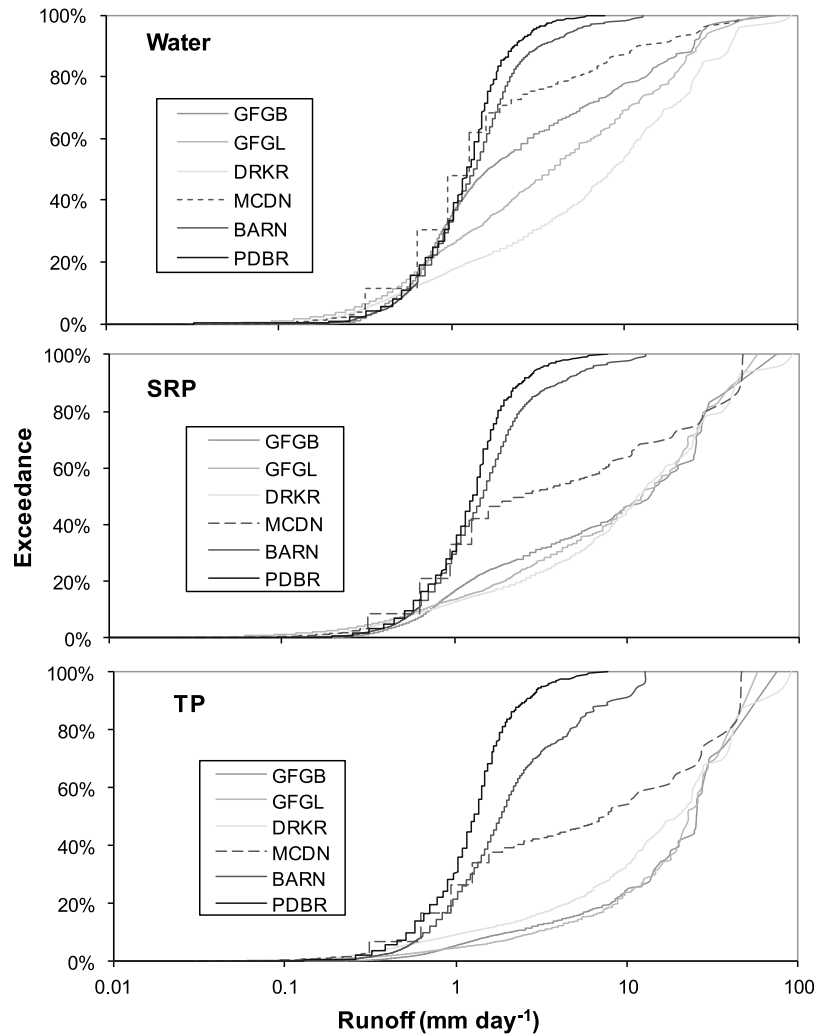


Figure 5. Cumulative flow duration and SRP and TP export as a function of runoff in small subwatersheds. Data for large watersheds (GFVN and GFPC) are not shown. Runoff is normalized per unit area and is shown in units of mm d^{-1} .

Table 2. Runoff Values When 20%, 50%, and 80% of Water, SRP, and TP Were Exported From Selected Subwatersheds^a

	Watershed/Land Use					
	POBR/Frosted (mm d^{-1})	BARN/Residential (mm d^{-1})	MCDN/Agricultural (mm d^{-1})	GFGB/Suburban (mm d^{-1})	GFGL/Suburban (mm d^{-1})	DRKR/Urban (mm d^{-1})
<i>Water</i>						
20%	0.7	1.0	0.6	0.7	0.7	1.3
50%	1.2	1.4	1.3	1.6	3.6	8.5
80%	1.8	2.2	5.0	13.1	18.8	25.3
<i>SRP</i>						
20%	0.8	0.8	0.6	1.2	2.0	2.4
50%	1.3	1.5	2.5	13.8	12.3	11.5
80%	1.8	2.4	28.2	28.9	29.3	36.0
<i>TP</i>						
20%	0.8	0.8	0.9	8.0	8.8	4.5
50%	1.3	1.9	1.9	25.3	22.7	19.8
80%	1.9	4.7	36.1	39.0	39.3	41.9

^aData are from Figure 5.

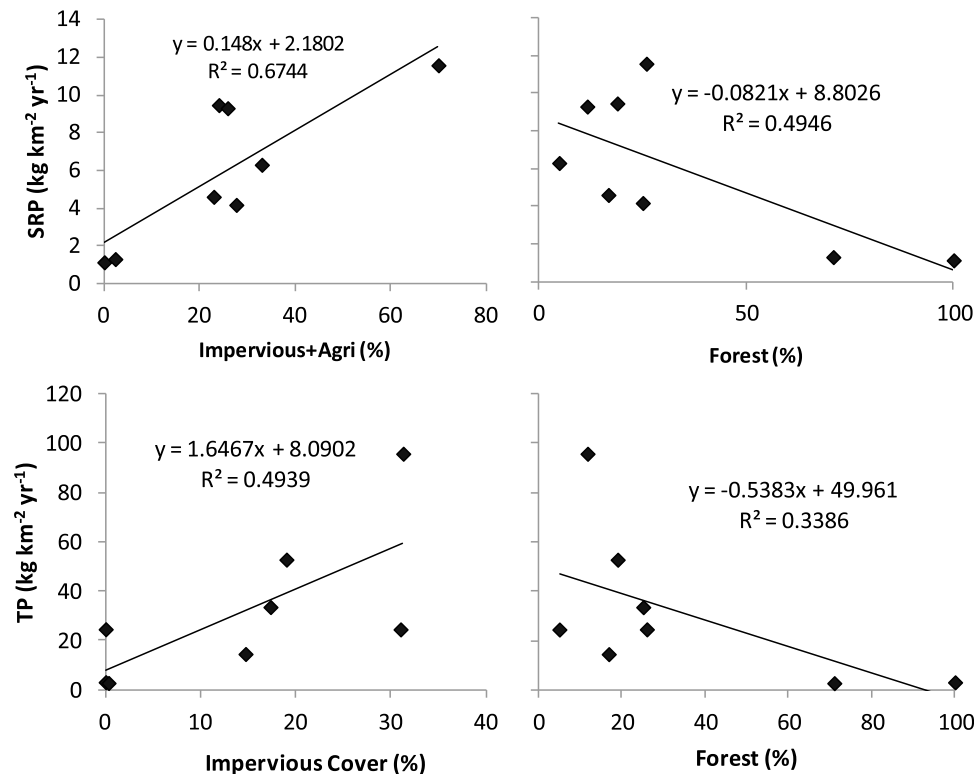


Figure 6. Correlation between phosphorus export (SRP and TP) and land use. Impervious + Agri is the total percent of impervious cover and agricultural land use. GFGB, GFVN, or GFCP refer to specific segment drainage areas along the urban rural gradient in the Gwynns Falls watershed.

DRKR (urban) and were 83.7, 48.4, and 24.5 $\text{kg km}^{-2} \text{yr}^{-1}$, respectively. TP exports increased with increasing impervious surface coverage and decreased with increasing forest cover (Figure 6; $p < 0.01$).

[19] Annual SRP and TP loads of the Gwynns Falls exhibited large variability, generally following the trend of water discharge: higher during wet years (2003 and 2004) and lower during dry years (2002; see Figure 7). On average, the more urbanized portion of watershed below the suburban/urban boundary (GFVN), exported half (51%) of the water, but disproportionately more of the total loads of both SRP (68%) and TP (75%). This distribution is different from nitrogen [e.g., *Groffman et al.*, 2004; *Kaushal et al.*, 2008; *Shields et al.*, 2008], which was exported disproportionately higher from the rural/suburban headwaters of the watershed.

4. Discussion

4.1. Watershed Urbanization and Annual Phosphorus Export

[20] Environmental factors that control watershed P exports have been widely examined [e.g., *Dillon and Kirchner*, 1975; *Behrendt and Opitz*, 1999; *Withers and Jarvie*, 2008; *Alvarez-Cobelas et al.*, 2009]. These factors includes watershed geology [*Dillon and Kirchner*, 1975], runoff regime [*Petrone*, 2010], surface water area [*Alvarez-Cobelas et al.*, 2009], and land use/land cover [*Norvell et al.*, 1979; *Line et al.*, 2002; *Tufford et al.*, 2003]. Characteristics of the stream network and channel (e.g., drainage density, stream size and mean depth) may influence

upstream and downstream patterns in P export because they affect erosion of stream banks [e.g., *Kirchner*, 1975; *Withers and Jarvie*, 2008]. In this study, runoff and stream size seemed relatively unimportant for regulating P export. There was no correlation between TP or SRP exports and surface runoff or watershed area ($p > 0.05$). We cannot determine how changes in stream characteristics (stream size and depth) from upstream to downstream influence P export, because changes in stream size are confounded with changes in land use in this study. However, we observed strong correlations of SRP and TP exports with impervious surface cover (ISC; see Figure 6), an “indicator” variable for urbanization [*Kaushal et al.*, 2008; *Shields et al.*, 2008]. The linkage of P export with land use in this study is comparable to the conclusions of many prior studies showing that urbanization and agriculture have greatly increased annual P export in a variety of streams and rivers globally [e.g., *Dillon and Kirchner*, 1975; *Norvell et al.*, 1979; *Line et al.*, 2002; *Tufford et al.*, 2003; *Petrone*, 2010]. An increase in TP exports from forested to agricultural to urban land use was also observed in watersheds in Connecticut and Australia (Table 3). Compared to larger rivers in the Chesapeake Bay watershed, TP exports from Gwynns Falls were somewhat lower (Table 3) likely because there were no intentional sewage discharges by municipal wastewater treatment plants in the Gwynns Falls watershed.

[21] The linkage of high P export with urban land use (Figure 6) and disproportionately higher P contributions from the most urbanized areas of the Gwynns Falls (the segment from Villa Nova to Carroll Park (Figure 7) may be related to

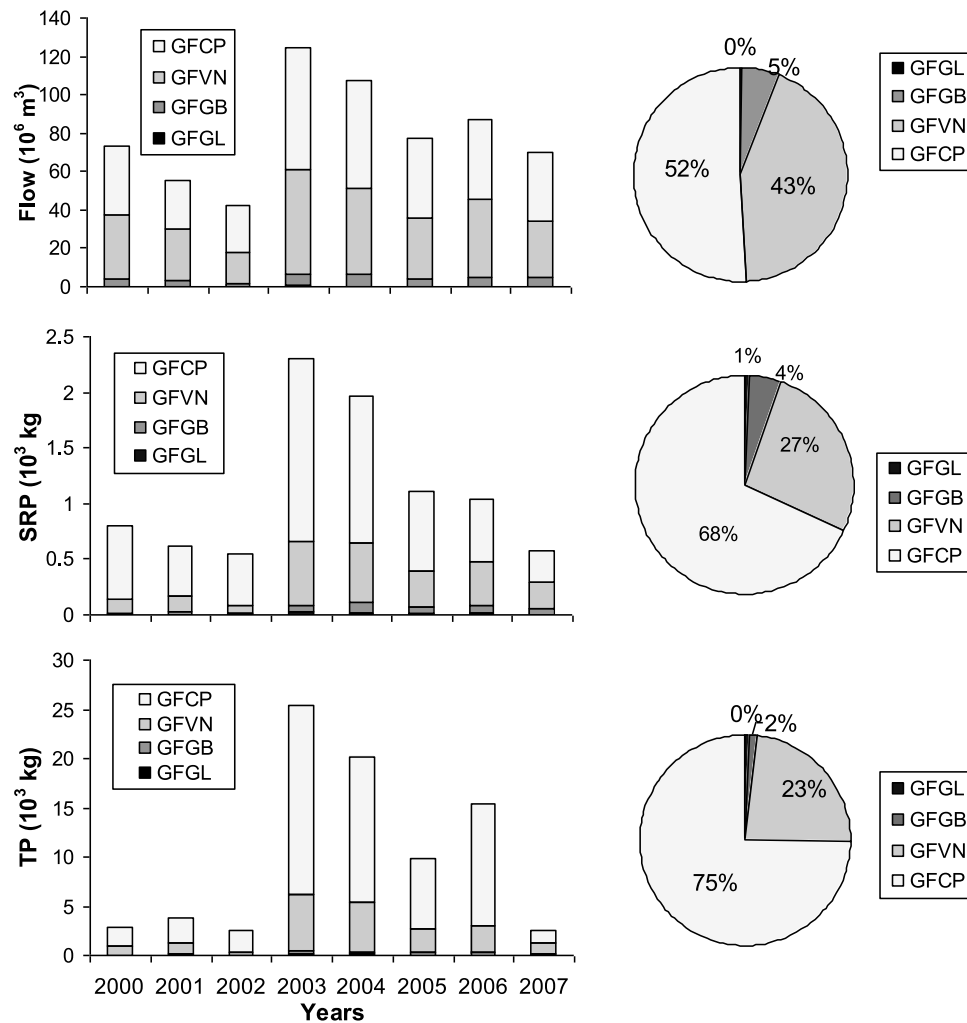


Figure 7. Annual loads of water, SRP, and TP exported from the Gwynns Falls (left) from 1999 to 2007 and (right) average percentage of inputs from four segments of the watershed. Percentages for GFGB, GFVN, or GFCEP include loads from smaller drainages included within these watershed segments; that is, GFGL, GFGB, and GFCEP, respectively.

leaky sewers, a common P source in urban areas). This lower Gwynns Falls watershed includes small urban watersheds such as Dead Run, Gwynns Run (high in P export but data are not shown), and other polluted streams draining Baltimore City. Gwynns Run has been shown to be highly contaminated with sewage [Kaushal *et al.*, 2011], and a major sewer leak to this stream (GFGR) was identified and repaired in April 2004. Nitrate isotope data also showed substantial wastewater contributions from other urbanized watersheds, GFCEP, DRKR and GFGL, which also had higher P export (Table 1) [Kaushal *et al.*, 2011]. Divergent

sources may explain different spatial distributions of N and P inputs along segments of the Gwynns Falls. For N, chemical fertilizers from agricultural land use (in the upper Gwynns Falls) are generally considered as a dominant N source [Groffman *et al.*, 2004; Kaushal *et al.*, 2011]. Fertilizers could also be a source of P, but P loss from soil is generally minor relative to nitrogen. Thus, nitrate concentrations decrease longitudinally with increasing urbanization [Kaushal *et al.*, 2011], while for P the opposite longitudinal pattern was observed. The high TP concentrations in urban watersheds may be attributed to storm

Table 3. Total Phosphorus Exported From Watersheds With Different Land Use

Stream/River Name	Dominant Land Use			References
	Forest	Agricultural	Urban/Suburban	
Gwynns Falls/Baisman Run	2.8–3.1	24.6	14.5–83.7	this study
Connecticut watersheds	10	54	170	Norvell <i>et al.</i> [1979]
U.S. rivers	23	94	112	Beaulac and Reckhow [1982]
Swan-Canning, Australia	<3	3–15	5–40	Petrone [2010]
Choptank River		14–67		Boynton <i>et al.</i> [1995] and Fisher <i>et al.</i> [1998]

water-induced bank erosion, lack of P retention on impervious surface [Withers and Jarvie, 2008] and temperature-induced SRP release from sediment and soils (discussed in section 4.3). Additionally, a large area of farmland in the Gwynns Falls watershed was transformed to urban areas with impervious surfaces during the 20th century (http://www.ohio.edu/people/dyer/LULC_change.html). Fink [2005] showed that change from cropland to urban land use can significantly increase TP export, as a result of loss of P-enriched soils due to flashy urban hydrology. This replacement may likely be another reason for the high P export rates in some urban watersheds here and in prior studies.

4.2. Effect of Urbanization on the Timing of P Export

[22] The effect of urbanization on stream hydrology and drainage structure has been widely reported in the literature [e.g., Paul and Meyer, 2001; Walsh et al., 2005; Elmore and Kaushal, 2008]. In addition to increases in runoff volume, urbanization accelerates the timing of storm events, forming a typically “flashy” hydrograph relative to less disturbed streams. This change in discharge is due to the improved hydraulic efficiency of an urbanized area, as a result of changes made to the watershed (e.g., impervious land surface and storm water pipes) and stream channel (channelization). Approximately 90% of headwater streams in Baltimore City are buried and converted into storm drains which can alter hydrologic connectivity [Elmore and Kaushal, 2008]. In this study, we found a strong coupling between cumulative flow distribution as a function of runoff and the extent of watershed impervious coverage (Figure 5 and Table 2). This showed that storm events play a more important role in water export with increasing watershed urbanization. In addition to urbanization, other watershed characteristics (e.g., watershed size) may also play a role, but appeared to not be so important in the present study. For example, if watershed size dominated stream hydrology, cumulative flow from the DRKR watershed (larger size) should be more evenly distributed than that of GFGL (smaller size) because of increased buffering effects of a larger watershed on flow peaks (although the distribution also depends on catchment shape and other variables); the same should have been observed for BARN (larger) and POBR (smaller), but was not.

[23] The effect of urbanization on the timing of P export was similar to patterns of streamflow (Figure 5). Therefore, storm events in urban areas affect the export patterns of water and P. Hydrological control of P export was also supported by the significant correlations between estimated daily P export and daily streamflow (SRP: $r^2 = 0.67\text{--}0.93$, $p < 0.01$; TP: $r^2 = 0.55\text{--}0.77$, $p < 0.01$). This may be expected because P load is a product of concentration and streamflow. On an annual basis, streamflow has also been shown to be one of the most important factors controlling nutrient exports from the Gwynns Falls, with large variability in loads across wet and dry years (Figure 7) [Kaushal et al., 2008; Shields et al., 2008]. However, we observed that the patterns of cumulative SRP and TP export did not exactly follow that of cumulative flow distribution (Figure 5 and Table 2), ascribed to the relationships between phosphorus concentration and discharge (Figure 3). For urban/suburban watersheds, the elevated high P concentrations during base flows could be attributed to the sewage leaks as suggested by nitrate

isotopes, and then decreased at moderate flows owing to dilution [Kaushal et al., 2011]. However, the SRP and TP concentrations during storm events were not as low as expected from a dilution curve but increased from middle to high flows as a result of sanitary sewer surcharging. This change may cause more P to be exported during high-flow events in urban watersheds. The mechanisms are not completely clear, but one additional possibility may be that SRP that was stored in the channel sediment pore water was remobilized to streams during high flows. Particulate P is more likely controlled by sediment transport, and particulate P concentrations typically increase with streamflow [Withers and Jarvie, 2008]. As a result more P was exported by urban streams during high-flow events and SRP/TP exports shifted more toward large runoff events relative to the flow duration curves.

[24] Our findings regarding how altered hydrology affects P export may have remedial implications. Our results show that most of the SRP (75–82%) and TP (87–93%) were exported under high-flow conditions ($>2\text{ mm d}^{-1}$) in urban/suburban watersheds. Thus, strategies that prioritize reducing P export during high-flow events should be the most effective way to reduce annual P loadings from urban watersheds. Storm water best management practice techniques (BMPs), which are used to reduce stormflow, could potentially be an effective way to reduce phosphorus export when P primarily originates from nonpoint sources. However, the effect of BMPs might be limited if the main P sources were from subsurface leaky sewers and sanitary sewer overflows during high flows [Kaushal et al., 2011].

4.3. Temperature Effects on Seasonal Changes in P Concentrations

[25] The pronounced seasonal changes in SRP concentration in the 2 headwater streams (GFGL and MCDN in Figure 2), with highest concentrations in summer and lowest concentrations in winter, suggest that SRP concentration in these headwater streams may be driven by changes in stream temperature. Other variables that influence SRP concentrations in aquatic ecosystems, including flow conditions, tributary-by-tributary “dilution,” biotically mediated changes in pH and dissolved oxygen [Withers and Jarvie, 2008, and references within; Duan et al., 2010] may also cause such seasonal change in SRP [James and Barko, 2004; Solim and Wanganeo, 2009]. For example, the relatively high SRP concentrations during summer could be attributed to low flow during this season, an idea supported by the trend of decreasing SRP concentrations with increasing streamflow at the urban sites (Figure 3). However, base flow SRP concentration during other seasons was not high, suggesting that dilution was not the only mechanism. In addition, prior studies [e.g., Jensen et al., 2006] have shown SRP release with increasing chloride concentrations in coastal areas. Salinization and chloride concentrations in the Gwynns Falls urban/suburban sites show a well-developed seasonality as a result of applications of road salt during winter [Kaushal et al., 2005]. However, SRP concentration were high during summer in the present study and varied inversely with chloride (which was highest during winter), thus precluding the effect of high chloride on SRP release.

[26] Sediment incubations in this study showed that SRP concentration and SRP release rate are temperature dependent, suggesting that temperature-dependent SRP release from sediment may be an important mechanism underlying seasonal changes in SRP. Prior sorption shaking experiments with riverine sediment have also revealed that organic river substrates can be a source of SRP, and there can be temperature enhanced sediment SRP desorption [e.g., *Schulz and Herzog*, 2004]. Here, our incubation data can be used to investigate seasonal variations in SRP concentrations, after we calibrate them with average stream depth at base flow and assume that water-sediment interactions at the end of our experiments reached the same state as in the streams. By using a linear regression (Figure 4), we estimated SRP concentrations at the GFGL site to be $21.3 \mu\text{g l}^{-1}$ at an average summer temperature of 21.5°C [Kim, 2007]. We estimated SRP concentration to be $30.2 \mu\text{g l}^{-1}$ at a maximum summer temperature of 27.9°C . Figure 2 shows that most SRP values in August (summer) were within this range. Similarly, we estimate winter SRP concentrations to be 7.4 to $9.2 \mu\text{g l}^{-1}$, which were also close to most measurements. The reason for lack of SRP seasonality at POBR is unclear, and one possibility is that the SRP concentrations at this forested site were close to detection limits ($<2 \mu\text{g P}$) and the seasonal changes could not easily be observed.

[27] Prior studies have shown that the mechanisms for temperature effects on sediment buffering could be biotic and/or abiotic [Froelich, 1988; Correll et al., 1999; Duan et al., 2010]. The studies of Barrow [1979] and Prakash et al. [2006] show that the zero equilibrium phosphate concentration (EPC₀) of particles and the solubility of phosphorus minerals (e.g., hydroxylapatite) are temperature dependent. Temperature also increases the rates of SRP sorption and desorption from particles [Froelich, 1988]. However, the stimulating effects of warm water temperatures on biotically mediated biogeochemical processes in stream sediments could also be a major driver behind the seasonality observed in the incubation experiments. For example, fast oxidation of organic matter at higher temperatures [White et al., 1991] could lead to lower dissolved oxygen concentration and formation of anoxic conditions that favor SRP fluxes from sediments [James and Barko, 2004; Solim and Wangane, 2009]. The same biotic and abiotic processes could occur in soils, and soil SRP buffering is also likely important because of the wider distribution of soils than stream sediments. Because small headwater streams have larger water-sediment contact areas and were more likely affected by groundwater inputs from soils, temperature-SRP/TP coupling may have been more apparent in headwater streams (Figure 2). This coupling became less substantial downstream as water-sediment contact area decreased.

5. Conclusions

[28] Urbanization significantly increased phosphorus (SRP and TP) exports from watersheds to streams. The high TP exports from urban areas (an order of magnitude higher than forest land use) suggests that P retention in urban watersheds should still be a priority for P load reductions in order to control eutrophication in the Chesapeake Bay watershed. Wastewater treatment plant improvements have greatly reduced P loads from point P sources to the Chesapeake Bay

in recent decades [e.g., D'Elia et al., 2003]. In the future, efforts to control TP inputs may need to focus on nonpoint sources as well.

[29] Changes in hydrology patterns in urban streams alter the pattern of phosphorus export, with more P exported during high-flow events. Current research has focused on the effects of seasonal climate variability on P export and nutrients delivered during the spring high-flow period; these can result in spring algal blooms and summer hypoxia [Kemp et al., 2005]. In addition, future management efforts may need to include measuring and managing pulses of nutrients associated with increasing streamflow variability in urban areas [Kaushal et al., 2008, 2010b]. Storm water best management practices might be an effective way to reduce phosphorus export, and management of sewer leaks during high flows may also be needed for remediating sanitary sewer overflows (SSOs).

[30] The correlations between SRP and water temperature from incubation experiments suggest that P release from sediments and soils (and other processes that are temperature dependent) may play a role in shaping the seasonal patterns of SRP concentrations and export from small streams. Rising stream water temperatures, due to interactions between urbanization and global warming [e.g., Kaushal et al., 2010a], may influence base flow SRP concentrations and P dynamics. Because base flow conditions dominate during the growing season and the growth of freshwater algae is generally P limited, rising temperatures may have an increasingly strong influence on urban stream ecosystems in the future.

[31] **Acknowledgments.** This research was supported by grants from the National Science Foundation (NSF) LTER program (NSF DEB-9714835 and 0423476), NSF DBI 0640300, NSF CBET 1058502, Maryland Sea Grant SA7528085-U, Maryland Sea Grant NA05OAR4171042, Maryland Sea Grant R/WS-2, and NASA NNX11AM28G. The authors thank Alysia Koufus Perry, Jessica Hopkins, Alex Kalejs, Emilie Stander, Nathan Forand, Alan Lorefice, Evan Grant, Amanda Thimmayya, Dan Dillon, and Lisa Martel for help with field sampling and laboratory and data analysis and Edward Doheny (USGS) for his work with the stream gauges and flow data between 1998 and 2007. Casey Sperling assisted with the laboratory sediment incubation experiments.

References

- Alvarez-Cobelas, M., S. Sanchez-Carrillo, D. G. Angeler, and R. Sanchez-Andres (2009), Phosphorus export from catchments: A global view, *J. North Am. Benthol. Soc.*, **28**, 805–820, doi:10.1899/09-073.1.
- Ameel, J. J., R. P. Axler, and C. J. Owen (1993), Persulfate digestion for determination of total nitrogen and phosphorus in low nutrient waters, *Am. Environ. Lab.*, **10**, 1–11.
- Barrow, N. J. (1979), Three effects of temperature on the reactions between inorganic-phosphate and soil, *J. Soil Sci.*, **30**, 271–279, doi:10.1111/j.1365-2389.1979.tb00984.x.
- Beaulac, M. N., and K. H. Reckhow (1982), An examination of land use—Nutrient export relationships, *J. Am. Water Resour. Assoc.*, **18**, 1013–1024, doi:10.1111/j.1752-1688.1982.tb00109.x.
- Behrendt, H., and D. Opitz (1999), Retention of nutrients in river systems: Dependence on specific runoff and hydraulic load, *Hydrobiologia*, **410**, 111–122, doi:10.1023/A:1003735225869.
- Boynton, W. R., J. H. Garber, R. Summers, and W. M. Kemp (1995), Inputs, transformations and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries, *Estuaries*, **18**, 285–314, doi:10.2307/1352640.
- Cohn, T. A., D. L. Caulder, E. J. Gilroy, L. D. Zynjuk, and R. M. Summers (1992), The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay, *Water Resour. Res.*, **28**, 2353–2363, doi:10.1029/92WR01008.
- Correll, D. L., T. E. Jordan, and D. E. Weller (1999), Effects of precipitation and air temperatures on phosphorus fluxes from Rhode River

- watersheds, *J. Environ. Qual.*, 28, 144–154, doi:10.2134/jeq1999.00472425002800010017x.
- D'Elia, C. F., W. R. Boynton, and J. G. Sanders (2003), A watershed perspective on nutrient enrichment, science and policy in the Patuxent River, Maryland: 1960–2000, *Estuaries*, 26, 171–185, doi:10.1007/BF02695960.
- Dillon, P. J., and W. B. Kirchner (1975), The effects of geology and land use on the export of phosphorus from watersheds, *Water Res.*, 9, 135–148, doi:10.1016/0043-1354(75)90002-0.
- Duan, S., R. Amon, T. S. Bianchi, and P. H. Santschi (2010), Temperature control on soluble reactive phosphorus in the lower Mississippi River?, *Estuaries Coasts*, 34, 78–89, doi:10.1007/s12237-010-9284-3.
- Elmore, A. J., and S. S. Kaushal (2008), Disappearing headwaters: Patterns of stream burial due to urbanization, *Front. Ecol. Environ.*, 6, 308–312, doi:10.1890/070101.
- Fink, J. C. (2005), The effect of urbanization on Baird Creek, Green Bay, Wisconsin, MSc thesis, Dep. of Environ. Sci. and Policy, Univ. of Wisc.-Green Bay, Green Bay. [Available at http://www.uwgb.edu/watershed/fink/Fink_Thesis_TOC.pdf].
- Fisher, T. R., K.-Y. Lee, H. Berndt, J. A. Benitez, and M. M. Norton (1998), Hydrology and chemistry of the Choptank River Basin, *Water Air Soil Pollut.*, 105, 387–397, doi:10.1023/A:1005001525063.
- Froelich, P. N. (1988), Kinetic control of dissolved phosphate in natural rivers and estuaries—A primer on the phosphate buffer mechanism, *Limnol. Oceanogr.*, 33, 649–668, doi:10.4319/lo.1988.33.4 part 2.0649.
- Groffman, P. M., N. L. Law, K. T. Belt, L. E. Band, and G. T. Fisher (2004), Nitrogen fluxes and retention in urban watershed ecosystems, *Ecosystems*, 7, 393–403, doi:10.1007/s10021-003-0039-x.
- House, W. A., and F. H. Denison (2002), Exchange of inorganic phosphate between river waters and bed-sediments, *Environ. Sci. Technol.*, 36, 4295–4301, doi:10.1021/es020039z.
- Howarth, R. W., and R. Marino (2006), Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over 3 decades, *Limnol. Oceanogr.*, 51, 364–376, doi:10.4319/lo.2006.51.1 part 2.0364.
- Howarth, R. W., and H. Paerl (2008), Coastal marine eutrophication: Control of both nitrogen and phosphorus is necessary, *Proc. Natl. Acad. Sci. U. S. A.*, 105, E103, doi:10.1073/pnas.0807266106.
- James, W. F., and J. W. Barko (2004), Diffusive fluxes and equilibrium processes in relation to phosphorus dynamics in the upper Mississippi River, *River Res. Appl.*, 20, 473–484, doi:10.1002/rra.761.
- Jensen, H. S., T. Bendixen, and F. Ø. Andersen (2006), Transformation of particle-bound phosphorus at the land-sea interface in a Danish estuary, *Water Air Soil Pollut. Focus*, 6, 547–555, doi:10.1007/s11267-006-9038-1.
- Kaushal, S. S., and W. M. Lewis Jr. (2005), Fate and transport of dissolved organic nitrogen in minimally disturbed streams of Colorado, USA, *Biogeochemistry*, 74, 303–321.
- Kaushal, S. S., P. M. Groffman, G. E. Likens, K. T. Belt, W. P. Stack, V. R. Kelly, L. E. Band, and G. T. Fisher (2005), Increased salinization of fresh water in the northeastern United States, *Proc. Natl. Acad. Sci. U. S. A.*, 102, 13,517–13,520, doi:10.1073/pnas.0506414102.
- Kaushal, S. S., P. M. Groffman, L. E. Band, C. A. Shields, R. P. Morgan, M. A. Palmer, K. T. Belt, C. M. Swan, S. E. G. Findlay, and G. T. Fisher (2008), Interaction between urbanization and climate variability amplifies watershed nitrate export in Maryland, *Environ. Sci. Technol.*, 42, 5872–5878, doi:10.1021/es800264f.
- Kaushal, S. S., G. E. Likens, N. A. Jaworski, M. L. Pace, A. M. Sides, D. Seekell, K. T. Belt, D. H. Secor, and R. L. Wingate (2010a), Rising stream and river temperatures in the United States, *Front. Ecol. Environ.*, 8, 461–466, doi:10.1890/090037.
- Kaushal, S. S., M. L. Pace, P. M. Groffman, L. E. Band, K. T. Belt, P. M. Meyer, and C. Welty (2010b), Land use and climate variability amplify contaminant pulses, *Eos Trans. AGU*, 91(25), 221–222, doi:10.1029/2010EO250001.
- Kaushal, S. S., P. M. Groffman, L. E. Band, E. M. Elliott, C. A. Shields, and C. Kendall (2011), Tracking nonpoint source nitrogen pollution in human-impacted watersheds, *Environ. Sci. Technol.*, 45, 8225–8232, doi:10.1021/es200779e.
- Kemp, W. M., et al. (2005), Eutrophication of Chesapeake Bay: Historical trends and ecological interactions, *Mar. Ecol. Prog. Ser.*, 303, 1–29, doi:10.3354/meps303001.
- Kim, H. J. (2007), Temperatures of urban streams: Impervious surface cover, runoff, and the importance of spatial and temporal variations, MSc thesis, Dep. of Civ. and Environ. Eng., Univ. of Md., Baltimore Cty., Baltimore.
- Kirchner, W. B. (1975), An examination of the relationship between drainage basin morphology and the export of phosphorus, *Limnol. Oceanogr.*, 20, 267–270, doi:10.4319/lo.1975.20.2.0267.
- Line, D. E., N. M. White, D. L. Osmond, G. D. Jennings, and C. B. Mojonnier (2002), Pollutant export from various land uses in the upper Neuse River Basin, *Water Environ. Res.*, 74, 100–108, doi:10.2175/106143002X139794.
- Murphy, J., and J. P. Riley (1962), A modified single solution method for determination of phosphate in natural waters, *Anal. Chim. Acta*, 27, 31–36, doi:10.1016/S0003-2670(00)88444-5.
- Norvell, W. A., C. R. Frink, and D. E. Hill (1979), Phosphorus in Connecticut lakes predicted by land use, *Proc. Natl. Acad. Sci. U. S. A.*, 76, 5426–5429, doi:10.1073/pnas.76.11.5426.
- Omernik, J. M. (1976), The influence of land use on stream nutrient levels, *Rep. EPA-600/2-76-014*, Environ. Prot. Agency, Washington, D. C.
- Paul, M. J., and J. L. Meyer (2001), Streams in the urban landscape, *Annu. Rev. Ecol. Syst.*, 32, 333–365, doi:10.1146/annurev.ecolsys.32.081501.114040.
- Petrone, K. C. (2010), Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan-Canning River system, southwestern Australia, *J. Geophys. Res.*, 115, G01016, doi:10.1029/2009JG001051.
- Prakash, K. H., R. Kumar, C. P. Ooi, P. Cheang, and K. A. Khor (2006), Apparent solubility of hydroxyapatite in aqueous medium and its influence on the morphology of nanocrystallites with precipitation temperature, *Langmuir*, 22, 11,002–11,008, doi:10.1021/la0621665.
- Russell, M. J., D. E. Weller, T. E. Jordan, K. J. Sigwart, and K. J. Sullivan (2008), Net anthropogenic phosphorus inputs: Spatial and temporal variability in the Chesapeake Bay region, *Biogeochemistry*, 88, 285–304, doi:10.1007/s10533-008-9212-9.
- Ryther, J. H., and W. M. Dunstan (1971), Nitrogen, phosphorus, and eutrophication in coastal marine environments, *Science*, 171, 1008–1013, doi:10.1126/science.171.3975.1008.
- Schulz, M., and C. Herzog (2004), The influence of sorption processes on the phosphorus mass balance in a eutrophic German lowland river, *Water Air Soil Pollut.*, 155, 291–301, doi:10.1023/B:WATE.0000026535.27164.56.
- Shields, C. A., L. E. Band, N. Law, P. M. Groffman, S. S. Kaushal, K. Savvas, G. T. Fisher, and K. T. Belt (2008), Streamflow distribution of non-point source nitrogen export from urban-rural catchments in the Chesapeake Bay watershed, *Water Resour. Res.*, 44, W09416, doi:10.1029/2007WR006360.
- Smil, V. (2000), Phosphorus in the environment: Natural flows and human interferences, *Annu. Rev. Energy Environ.*, 25, 53–88, doi:10.1146/annurev.energy.25.1.53.
- Solim, S. U., and A. Wanganeo (2009), Factors influencing release of phosphorus from sediments in a high productive polymictic lake system, *Water Sci. Technol.*, 60, 1013–1023, doi:10.2166/wst.2009.445.
- Sylvan, J. B., Q. Dortch, D. M. Nelson, A. F. M. Brown, W. Morrison, and J. W. Ammerman (2006), Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation, *Environ. Sci. Technol.*, 40, 7548–7553, doi:10.1021/es061417t.
- Tufford, D. L., C. L. Samarghitan, H. N. McKellar, D. E. Porter, and J. R. Hussey (2003), Impacts of urbanization on nutrient concentrations in small southeastern coastal streams, *J. Am. Water Resour. Assoc.*, 39, 301–312, doi:10.1111/j.1752-1688.2003.tb04385.x.
- Turner, R. E., N. N. Rabalais, and D. Justic (2006), Predicting summer hypoxia in the northern Gulf of Mexico: Riverine N, P, and Si loading, *Mar. Pollut. Bull.*, 52, 139–148, doi:10.1016/j.marpolbul.2005.08.012.
- Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan II (2005), The urban stream syndrome: Current knowledge and the search for a cure, *J. North Am. Benthol. Soc.*, 24, 706–723.
- White, P. A., J. Kalff, J. B. Rasmussen, and J. M. Gasol (1991), The effect of temperature and algal biomass on bacterial production and specific growth rate in freshwater and marine habitats, *Microb. Ecol.*, 21, 99–118, doi:10.1007/BF02539147.
- Withers, P. J. A., and H. P. Jarvie (2008), Delivery and cycling of phosphorus in rivers: A review, *Sci. Total Environ.*, 400, 379–395, doi:10.1016/j.scitotenv.2008.08.002.

L. E. Band, Department of Geography, University of North Carolina at Chapel Hill, CB 3220 Saunders Hall, Chapel Hill, NC 27599, USA.

K. T. Belt, Baltimore Field Station, Northern Research Station, Forest Service, U.S. Department of Agriculture, 5523 Research Park Dr., Ste. 350, Baltimore, MD 21228, USA.

S. Duan and S. S. Kaushal, Earth System Science Interdisciplinary Center, Department of Geology, University of Maryland, 5825 University Research Ct., Rm. 4049, College Park, MD 20740, USA. (sduan@umd.edu)

P. M. Groffman, Cary Institute of Ecosystem Studies, Box AB, 2801 Sharon Tpke., Millbrook, NY 12545, USA.