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A Daily Time Series Analysis of Stream Water Phosphorus Concentrations Along an Urban to Forest Gradient

MICHAEL T. BRETT*
SARA E. MUELLER
GEORGE B. ARHONDITSIS

Department of Civil and Environmental Engineering
Box 352700
University of Washington
Seattle, Washington, 98195, USA

ABSTRACT / During a 1-year period, we sampled stream water total phosphorus (TP) concentrations daily and soluble reactive phosphorus (SRP) concentrations weekly in four Seattle area streams spanning a gradient of forested to urban-dominated land cover. The objective of this study was to develop time series models describing stream water phosphorus concentration dependence on seasonal variation in stream base flows, short-term flow fluctuations, antecedent flow conditions, and rainfall. Stream water SRP concentrations varied on average by ±18% or ±5.7 μg/L from one week to another, whereas TP varied ±48% or ±32.5 μg/L from one week to another. On average, SRP constituted about 47% of TP. Stream water SRP concentrations followed a simple sine-wave annual cycle with high concentrations during the low-flow summer period and low concentrations during the high-flow winter period in three of the four study sites. These trends are probably due to seasonal variation in the relative contributions of groundwater and subsurface flows to stream flow. In forested Issaquah Creek, SRP concentrations were relatively constant throughout the year except during the fall, when a major salmon spawning run occurred in the stream and SRP concentrations increased markedly. Stream water SRP concentrations were statistically unrelated to short-term flow fluctuations, antecedent flow conditions, or rainfall in each of the study streams. Stream water TP concentrations are highly variable and strongly influenced by short-term flow fluctuations. Each of the processes assessed had statistically significant correlations with TP concentrations, with seasonal base flow being the strongest, followed by antecedent flow conditions, short-term flow fluctuations, and rainfall. Times series models for each individual stream were able to predict ~70% of the variability in the SRP annual cycle in three of the four streams (r^2 = 0.57–0.81), whereas individual TP models explained ~50% of the annual cycle in all streams (r^2 = 0.39–0.59). Overall, time series models for SRP and TP dynamics explained 82% and 76% of the variability for these variables, respectively. Our results indicate that SRP, the most biologically available and therefore most important phosphorus fraction, has simpler and easier-to-predict seasonal and weekly dynamics.

Anthropogenic activities often degrade lake or stream water quality. This degradation can be caused by discharges of industrial or municipal wastewater treatment plant effluent into surface waters. This point-source pollution is easily identified and quantified, and point-source phosphorus (P) loading to lakes and rivers has been greatly reduced since the implementation of the 1972 Clean Water Act. However, there has been less success in controlling diffuse, non-point-sources (NPSs) of pollution, which are currently usually unregulated and are considered to be the main cause of lake, stream, and coastal area eutrophication in the United States (NRC 1992; USEPA 1996; Carpenter and others 1998). In lakes, phosphorus is the most common regulator of primary production, and excessive P inputs can cause eutrophication (Vollenweider 1976; Schindler 1977; Edmondson 1994). Increased nutrient inputs can stimulate noxious algal blooms and increase macrophyte growth, significantly reducing the aesthetic quality of lakes and streams (Welch 1992). Cyanobacteria blooms, which are strongly associated with eutrophication, can also cause taste and odor problems in drinking water supplies (Falconer 1999), and toxins produced by cyanobacteria blooms might even be a causative agent for certain cancers (Ding and others 1999).

KEY WORDS: Stream water quality; Urban; Phosphorus dynamics; Statistical models; Forest; Bioavailable phosphorus

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*Author to whom correspondence should be addressed; *email:* mtbrett@u.washington.edu

Urbanization increases phosphorus transport by artificially accentuating naturally occurring erosion processes. P transport occurs in groundwater (Jordan and others 1993), but most P is transported in particulate form sorbed to soil particles (Peterjohn and Correll 1984), which, in turn, is associated with suspended sediment transport (Leonard and others 1979; Pacini and Gächter 1999). Kronvang and others (1997), Hatch and others (1999), and Pacini and Gächter (1999) found particulate phosphorus (PP) and suspended sediment (SS) transport were both strongly associated with high discharge events. High-flow events mobilize large amounts of sediments due to stream bank/bed erosion and are the primary drivers for P export to receiving water bodies. Urbanization can also increase stream nutrient transport by supplying anthropogenic P sources from lawn fertilizers, septic fields, pet wastes, and construction sites. The loss of forested cover from urbanization minimizes the recycling and removal of inorganic nutrients (particularly nitrogen), due to the reduction in the microbial and vegetative processes that immobilize nutrients in forest litter and soils (Wahl and others 1997). Despite having a watershed only one-third the size of the forested catchment, Wahl and others (1997) found an urbanized creek's soluble reactive phosporus (SRP) load was nearly five times greater than that for an adjacent forested creek due to both higher runoff volume and higher stream water SRP concentrations. Kluesener and Lee (1974) estimated that approximately 80% of the annual total phorphorus (TP) input to Lake Wingra, Madison, Wisconsin, was from urban runoff. They also found that constituent concentrations were highest during the ''first flush'' of a storm (usually the first 15 min) due to accumulation of pollutants on impervious surfaces during antecedent dry periods. The National Urban Runoff Program (US EPA 1990) found storm water runoff had a median TP concentration of 420 μg/L at 22 sites across the United States.

Particulate phosphorus (PP) is, in most cases, a dominant fraction of stream P loads (Leonard and others 1979; Meyer and Likens 1979; Hatch and others 1999; Pacini and Gächter 1999), but varies greatly in its biologically availability (Dorich and others 1984; Broberg and Persson 1988; Hatch and others 1999; Pacini and Gächter 1999). Bioavailable P (BAP) is defined as the sum of immediately available P and P that can be transformed into an available form by naturally occurring physical, chemical, and biological processes (Boström and others 1988). SRP is directly available for algal uptake and correlates most strongly with BAP as determined in algal growth bioassays (Boström and others 1982; Hatch and others 1999). The size of the sediment particles to which PP is bound is critical because this determines the rate at which particles will settle once they reach the stream/lake interface (i.e., their physical availability). Large sand-sized particles will rapidly settle out of the water column and can become permanently lost to lake sediments, whereas smaller particles like silts and clays will stay suspended much longer, rendering the phosphorus bound to these particles more available for biological uptake (Cowen and Lee 1976; Dorich and others 1984; Hatch and others 1999; Pacini and Gächter 1999). Pacini and Gächter (1999) also found that because the mineralogy of small and large particles differs greatly, the type of chemical bonds PP is associated with varies strongly with particle size. Large sand-sized particles (>50 μm in diameter) contained mostly refractory nonextractable phosphorus, whereas the smallest particles (~6 μm in diameter) contained high proportions of NaOH extractable phosphorus indicating P bound to organic matter (Pacini and Gächter 1999).

Watershed urbanization is one of the greatest threats to the biological integrity of lakes and streams in the Puget Sound ecoregion (May and others 1997). This region has experienced rapid population growth since the 1960s, and this high rate of growth is projected to continue into the future. As the Puget Sound population grows, urban and especially suburban areas expand into forested watersheds. Most of this development will take place as low- to medium-density residential housing and associated connecting roads and small commercial developments. The Pacific Northwest is dominated by moderately well-drained glacial outwash soils and has a humid climate and low-intensity rainfall. Historically, these conditions generated runoff predominantly via subsurface flow processes because of the absorbent coniferous forest soils, which provided interception storage and evapotranspiration (Booth 1991; Schueler 1994). As these forests are converted to urban areas, the absorbent soil layers are stripped away, soil is compacted, and impervious layers are created. The imperviousness of many urban areas increases storm water discharge causing stream channel down cutting and associated erosion, and even small rainfall events are capable of washing accumulated pollutants into surface waters. Riparian corridors that once partially protected creeks are often greatly reduced (May and others 1997). Riparian vegetation contributes large woody debris (LWD) to stream channels, and LWD, in turn, performs critical functions such as dissipating stream flow energy, protecting stream banks, stabilizing streambeds, and storing sediment (Abbe and Montgomery 1996; Naiman and Decamps 1997).

When riparian vegetation is cleared, channel erosion increases, and in combination with increased runoff, consequences for stream dynamics are magnified (Booth 1990). Impervious surfaces (such as roads, parking lots, and roofs) and lawns with shallow soils generate more runoff during storms and deliver the runoff more quickly via constructed drainage networks (Kluesener and Lee 1974; Hollis 1975; Schueler 1994; Burges and others 1998; Konrad 2000). Discharges once associated with large, multiyear or multidecade storm events can inundate urban basins one or more times per year (Neller 1988; Booth 1991).

The objective of this study was to examine the impact of urban land cover relative to forest land cover on intra-annual variability in phosphorus transport in the humid northwest region of North America. We sampled stream water TP concentrations daily and SRP concentrations weekly in four Seattle area streams with a catchment land-cover gradient spanning predominantly forested to highly urban. Additionally, we developed time series models describing stream water phosphorus concentration as a function of several flow characteristics. Seasonal variations in stream base flow, short-term flow fluctuations, antecedent flow conditions, and rainfall were used as predictor variables. With these models, we explored phosphorus predictability and compared SRP and TP seasonal and weekly dynamics in order to develop more reliable predicts of phosphorus loading. Development of robust methodologies for predicting stream nutrient dynamics and reduction of prediction uncertainty are important steps during tehevaluation of alternative management schemes.

Study Sites

The Vashon ice flow of 14,000 years ago created the glacial outwash areas common throughout the Puget Sound area. The region is underlain primarily by low-permeability till, lacustrine deposits, and bedrock, on which a more permeable soil has developed in the forest root zone since deglaciation (Booth 1990). The catchments studied lie within the benchlike area of glacial moraine and outwash plains of the Puget Sound lowlands. Old-growth forests originally covered these catchments, but logging, which began in the mid-1800 s, and suburban development, especially since the 1960 s, has resulted in a reduced area of second-growth forest dominated by Douglas fir and red alder. The Puget Sound lowlands are characterized by a rolling topography. The catchments of the steams studied are dominated by the Alderwood–Everett soil series. This series is described as (1) moderately deep to very deep, (2) moderately well drained to somewhat excessively drained, and (3) nearly level to very steep soils each on till plains, terraces, and outwash plains (USDA 1983; Goldin 1992). The climate of the Puget Sound region is classified as marine west coast, which means that it is greatly influenced by winds from the Pacific Ocean and by the Puget Sound. There is a distinct rainy season, which usually occurs between the months of October and April. The average annual precipitation ranges from 100 to 150 cm, with 70–80% of the annual precipitation (mostly as rain) falling during the late fall, winter, and early spring.

Issaquah Creek drains a relatively undeveloped watershed of Lake Sammamish (Figure 1). It is located in the foothills of the Cascades, and because of the higher elevation of the watershed, it can receive up to twice as much rainfall per land area as the other catchments studied. The Issaquah Creek catchment area is 109 km^2, and the channel extends 25 km from its headwaters to Lake Sammamish. Catchment elevations range from about 905 m above mean sea level (AMSL) near the headwaters to 10 m AMSL at the confluence with Lake Sammamish. This catchment is undergoing rapid urban development in its lower reaches. There is also a hatchery on this creek to which large populations of sockeye and king salmon return to spawn in the fall. North Creek drains a fairly developed basin located primarily in Snohomish County (Figure 1). The catchment area is about 72 km^2, and the channel extends 20 km from its origin to its confluence with the Sammamish River. Elevations in the watershed range from about 158 m AMSL near the headwaters to approximately 6 m AMSL at the mouth. The headwaters are created by surface runoff from a highly urbanized commercial/high-density residential area. There are also 253 mapped wetlands with a total area of 6.6 km^{2,} which are located primarily along the floodplain and tributaries (SCSWM 1994). Numerous hobby farms exist in the catchment, mostly located in the eastern part of the catchment. Approximately 27.5% of the watershed is zoned as rural-residential and lacks sanitary sewer access (SCSWM 1994). Swamp Creek drains a large area that also has some heavy commercial development. The catchment has an area of 64 km^2 and is being urbanized from a historic rural and forested state. This 24-km-long stream originates at an elevation of 137 m AMSL and flows into the Sammamish River, near Lake Washington, at 6 m AMSL. The watershed consists of mildly rolling topography and has several wetlands in it. Thornton Creek drains a highly urbanized area in the northern part of Seattle (Figure 1). The basin is classified as mostly single

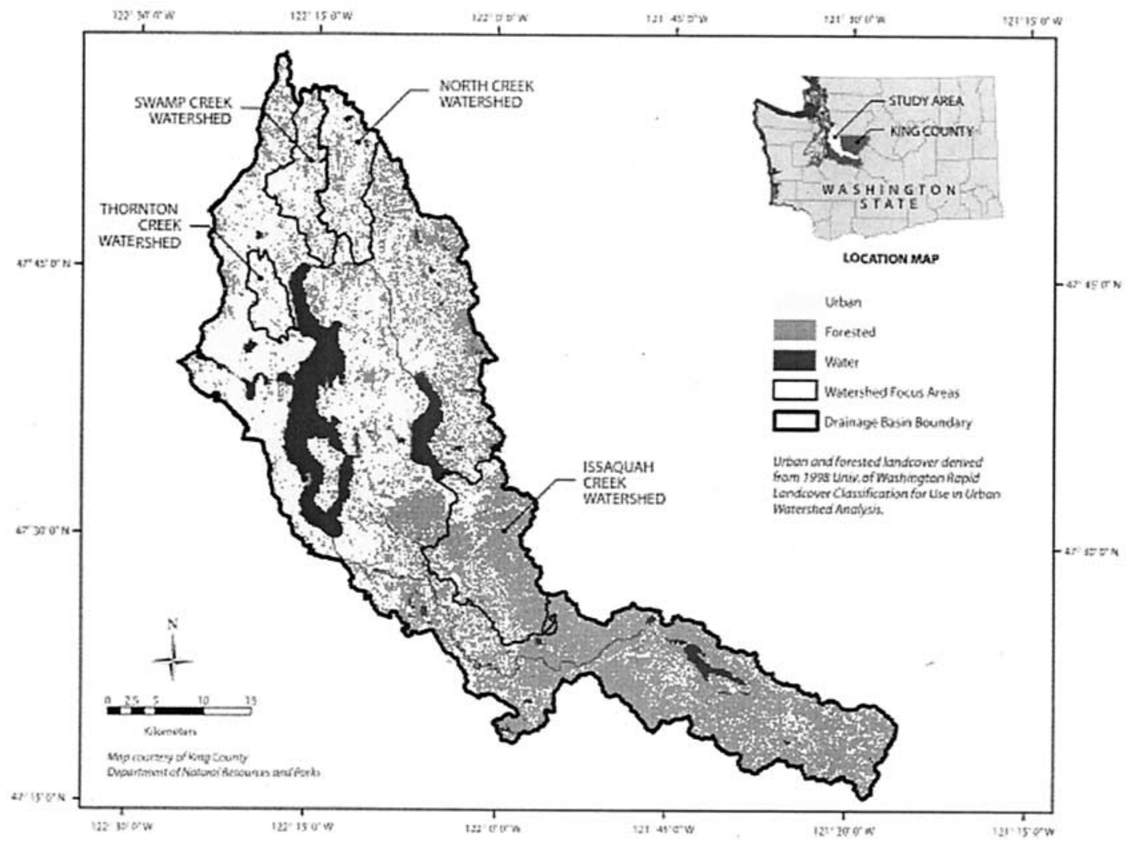

Figure 1. A map of the four study catchments and their land-cover characteristics.

Table 1. Catchment characteristics for each of the four streams assessed in this study

	Watershed area (km^2)	Mean flow (m^3/s)	Mean slope (degrees)	Glacial	Volcanic	Alluvium	Sedimentary	Forest	Grass/shrub/crop	Water/bare soil	Sum of urban
Issaquah	145	3.99	10	66.9%	18.4%	5.6%	4.9%	73.3%	4.1%	0.6%	22.0%
North	74	1.75	2.7	96.5%	0.0%	3.5%	0.0%	27.0%	9.0%	2.3%	61.5%
Swamp	63	1.1	3.1	96.0%	0.0%	4.0%	0.0%	27.9%	8.1%	2.0%	62.0%
Thornton	29	0.32	3.5	96.8%	0.0%	3.2%	0.0%	6.5%	6.2%	0.4%	87.1%

Note. The slope and geological characterizations were for the entire watershed, whereas the land-cover classifications were generated using a 340-m buffer width. For additional details on these catchments, see Brett and others (in press).

family and multifamily residential but also includes significant areas of commercial development and light industry. The 29-km^2 catchment has a 9-km-long channel and several tributaries. The stream has its headwaters at 80 m AMSL elevation and discharges into Lake Washington at 6 m AMSL.

Methods

Watershed Analysis

Land-cover patterns for the study area were analyzed as described in Brett and others (2005). Briefly, we used a Landsat satellite image, obtained in 1998 for the Puget Sound lowlands of northwestern Washington State, with a resolution of 30 m (each pixel represented 900 m^2). The land-cover classes were chosen to reflect categories that can be readily distinguished in the satellite data and to represent important watershed characteristics. The final classified image contained the seven land-cover categories: forest, grass/shrub/crop, water, bare soil, urban forest, urban grassy, and urban paved. The stream layer network and watershed subbasin delineation were obtained from the combination of a digital elevation

Table 2. Average nutrient concentrations for the four study streams

Parameter	Units	Issaquah Creek	Swamp Creek	North Creek	Thornton Creek
Soluble Reactive Phosphorus					
Man ± SD	μg/L	16.8 ± 5.5	31.0 ± 8.9	43.8 ± 8.9	34.3 ± 9.0
Geometric mean	μg/L	16.2	29.7	42.9	33.2
Vol. wt. average	μg/L	15.4	28.2	41.8	32.3
n		43	47	51	47
Total Phosphorus					
Mean ± SD	μg/L	38.5 ± 14.7	59.0 ± 23.3	88.8 ± 26.0	84.4 ± 32.1
Geometric mean	μg/L	36.5	55.9	85.8	80.0
Vol. wt. average	μg/L	41.7	62.6	90.8	96.9
n		337	346	356	355

model (DEM) and the Washington Department of Natural Resources stream network map. The land-cover characteristics (using a 340-m buffer width) along with the slope and geological substrate for each of the four catchment areas are provided in Table 1 (for further methodological details and data see Brett and others 2005).

Water Quality Sampling

An Isco 3700 Portable Sampler, which holds 24, 1-L polypropylene bottles, was used to collect the stream water samples. The intake tube stream depth was chosen to best represent well-mixed conditions without getting dislodged by objects floating downstream. Flow within the channel was assumed to be turbulent and vertically well mixed. During a 1-year period, TP samples were collected on a daily basis, whereas SRP samples were only collected on weekly because SRP samples have a 24-h holding time and the autosampler was tended weekly. Our sample set was between 92% and 98% complete for TP and between 83% and 98% complete for SRP (see Table 2). The missing TP samples are primarily due to periodic autosampler jamming, and the missing SRP samples are due to jamming and a delay in the initiation of SRP sample collection. The autosampler was programmed to collect water samples every 8 h; however, only the sample collected at 6 AM daily was saved for TP analyses. Once brought back to the laboratory, samples were transferred to acid-washed 125-mL high-density polypropylene bottles and analyzed for TP within a few days. The SRP samples were filtered through 0.45-μm surfactant-free cellulose acetate membrane filters immediately after being brought back to the laboratory, transferred to acid-washed 125-mL bottles, and frozen until analysis.

Precipitation and Discharge Data

Precipitation data was collected from the SeaTac (47° 45′ N - 122° 30′ W and 137 m) and Sandpoint (47° 41′ N - 122° 15′ W and 18 m) weather stations monitored by the National Weather Service. Discharge data was obtained from the United States Geologic Survey for Issaquah (station ID# 12121600) and Thornton (ID# 12128000) creeks, from King County for Swamp Creek (ID# 12127100), and from Snohomish County for North Creek (ID# 12126000) in daily average and 15-min increments.

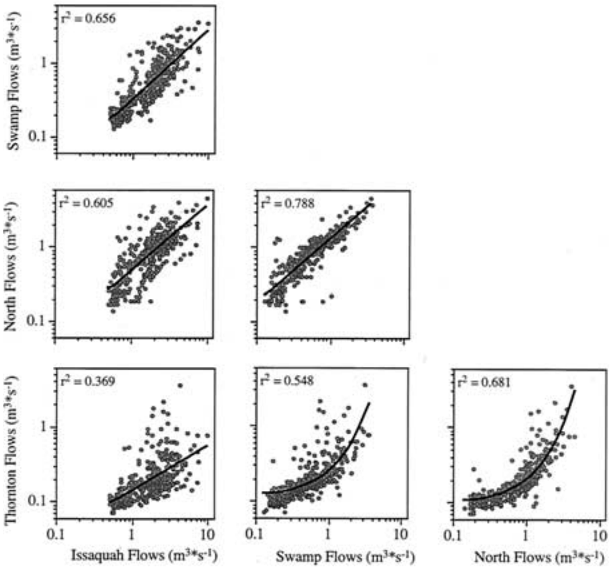

Figure 2. A correlation matrix for stream flows (m^3/s) in the four study sites during the August 15, 2000 to August 15, 2001 study period.

Phosphorus Analyses and Quality Control

The TP assay followed the Standard Methods (APHA 1998) ascorbic acid method after persulfate digestion (SM4500-P-B, E). Orthophosphorus, or SRP, was assayed colorimetrically according to the ascorbic acid method (SM4500-P F) (APHA 1998). Matrix spikes and laboratory duplicates were carried out on at least 5% of all samples.

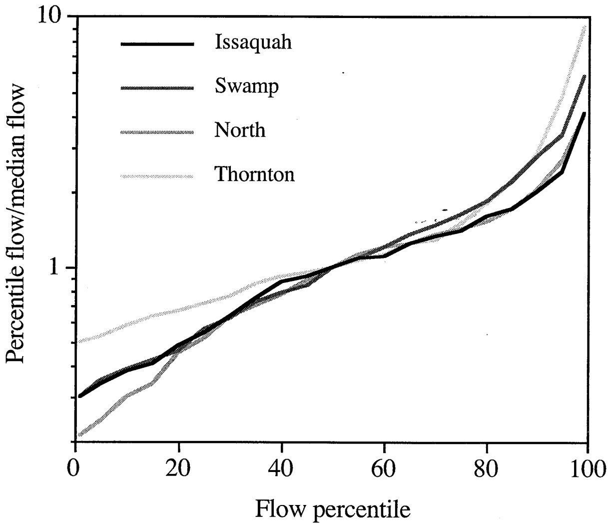

Figure 3. The distribution of relative stream flows for the four study sites during this investigation. The relative stream flow was calculated as the observed stream flow on each date divided by the median stream flow for the whole year.

Results

Flow Variability

The streams selected for this study represent highly urbanized conditions (Thornton Creek), mixed land-cover conditions (North and Swamp creeks), and predominantly forested conditions (Issaquah Creek). Figure 2 shows a flow correlation matrix for these streams using daily average flow data for each. This figure shows that Swamp Creek and North Creek had the most similar flow regimes ($r^2 = 0.79$) and Issaquah Creek and Thornton Creeks had the least similar flow regimes ($r^2 = 0.38$). It is also interesting to note that the relationship between Thornton Creek and Swamp and North creeks flows was sharply curvilinear at higher flows, with relatively higher flows observed in Thornton Creek under these conditions. When the flows of these streams are normalized to their own annual median flows (Figure 3) to show overall relative variability in annual peak and minimum flows, one can see that both peak and minimum flows were highest in Thornton Creek. It is generally known that urban streams, with their higher catchment impervious area, have high relative peak flows (Booth 1991; Schueler 1994). However, it is also generally believed that urban streams have lower relative minimum base flows due to reduced hydrologic infiltration, which is also caused by the greater impervious surface area. Recently, some authors have suggested that urban streams might, in fact, have higher minimum flows due to leakage from potable water and sewerage pipes and irrigation of residential lawns and landscaping (Alley and others 2002). Swamp Creek had a similar pattern to its relative flow distribution as Issaquah Creek; however, it had larger relative peak flows. North Creek also had a relatively similar flow pattern compared to Issaquah Creek, but it had lower relative minimum flows. Although the flow regimes were overall the most similar between Swamp and North creeks (Figure 2), they differed in that both peak and minimum relative flows were higher in Swamp Creek (Figure 3). The lower relative minimum flows in North Creek could suggest greater utilization of groundwater in this catchment during the summer low-flow period, and the lower peak flows suggest that greater infiltration occurs in this catchment.

Because we planned to use seasonal fluctuations in base flow as one of our explanatory variables, we calculated a monthly (31-day) running median value from the raw daily average flow data for each stream (Figure 4). We then fit a sinusoidal function to the monthly running median value of the annual daily flow time series (see Figure 4). This function predicted the prevailing base flow in a stream during any specified time of the year. Although the seasonal based flow term provided only a coarse fit to the $\log_{10}$ transformed daily flow data [$r^2 = 0.44 \pm 0.15$ (± 1 SD)], it provided a quite good fit to the respective monthly running median flows [$r^2 = 0.86 \pm 0.03$] (see Figure 4).

Mean Phosphorus Concentrations

Table 2 shows the mean ± 1 SD phosphorus concentrations for the streams sampled. Issaquah Creek had the lowest SRP and TP concentrations and North Creek had the highest concentrations for these fractions. SRP [mean coefficient of variaton (CV) = 27%] was, in general, less variable than TP (mean CV = 36%). Because SRP was only sampled weekly and TP was sampled daily, we also compared week-to-week variability for both SRP and TP. Overall SRP varied on average by ±18% or ±5.7 μg/L from one week to another, whereas TP varied ±48% or ±32.5 μg/L from one week to another. Because flow fluctuations have a very strong impact on stream nutrient export and concentrations often vary with flow, a flow-weighted nutrient concentration is the best measure of "typical" stream nutrient concentrations (e.g., Johnson 1979; Stow and Borsuk 2003). However, in many cases, a complete flow record is not available and it is, therefore, necessary to estimate "typical" stream nutrient concentrations using only periodically observed concentrations. For example, when summarizing the King County long-

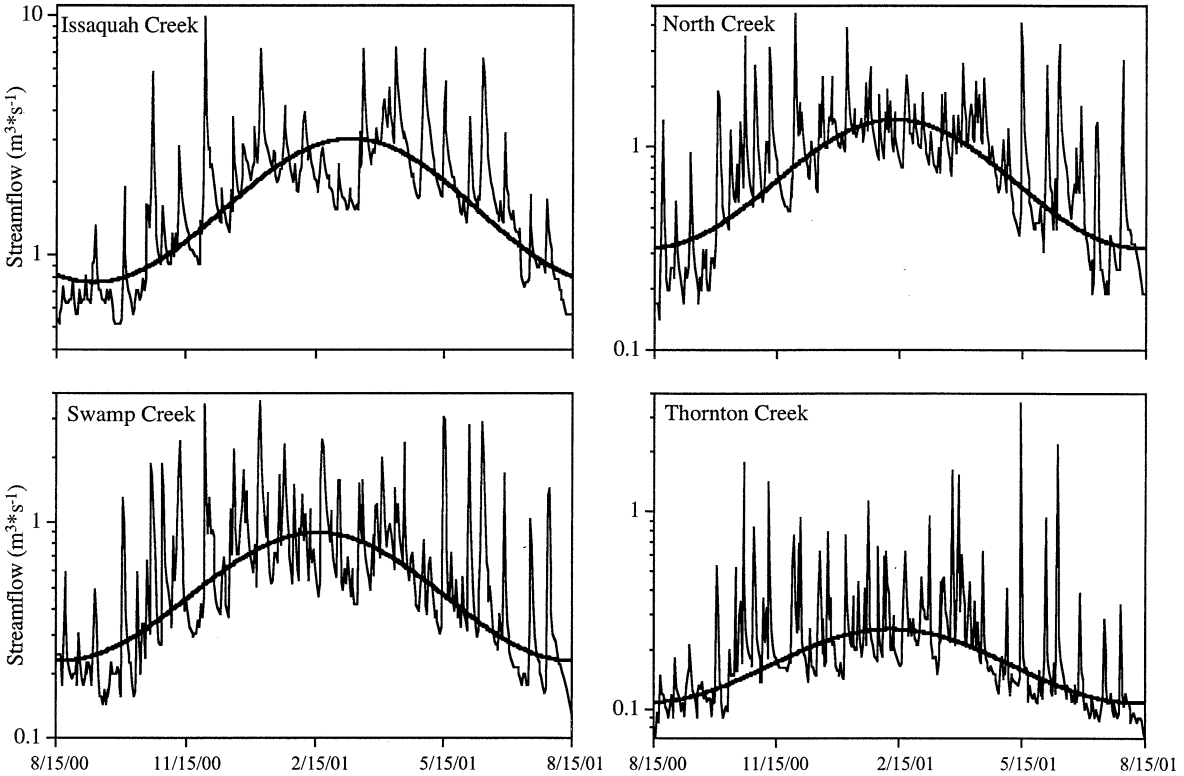

Figure 4. The annual time series of observed mean daily stream flows for each stream. The sinusoidal function fits the 30-day running median stream flow.

term record of stream nutrient concentrations (Brett and others 2005), only a partially complete record of stream flow data was available. For this reason, Brett and others (2005) used the geometric mean of approximately 120 observations collected monthly over a 10-year period to represent typical nutrient and sediment concentrations in the streams they assessed. Because we have both a complete flow record and a very detailed record of stream nutrient concentrations, we were able to compare the relationship between the flow-weighted nutrient concentration and other estimates of ''typical'' nutrient concentrations. For TP, the simple arithmetic mean gave, on average, a 7.5 ± 3.9% (± 1 SD) underestimate of the flow-weighted concentration, whereas the geometric mean gave an 11.5 ± 4.3% underestimate (Table 2). For SRP, the simple arithmetic mean gave, on average, a 7.1 ± 2.1% overestimate of the flow-weighted concentration, whereas the geometric mean gave a 4.0 ± 1.3% overestimate (Table 2). Unfortunately, these results do not suggest a general solution to the problem of estimating the most likely flow-weighted nutrient concentration in the absence of comprehensive flow data.

Statistical Time Series Models

One of the objectives of this study was to determine what proportion of the daily time series for TP and SRP dynamics could be predicted using multiple regression models. Ultimately, this dataset will also be used to calibrate mechanistic process-based models of catchment phosphorus transport. We based our statistical models on the assumption that nutrient transport in our study sites was primarily related to seasonal variation in base flows, rapid changes in stream flow (i.e., spikeness), antecedent flow conditions, and rainfall. Although it could have been insightful, we did not attempt to characterize periphyton nutrient uptake because this would have required us to take into account periphyton biomass, stream temperature, light availability, and invertebrate grazing on periphyton dynamics and we did not have sufficient data to characterize these parameters.

Seasonal variation in base flows is caused by variation in the relative contribution of groundwater (as opposed to subsurface flows and overland flows) to stream flow (Jordan et al. 1997). Since ground water is generally believed to have higher nutrient concentrations (especially dissolved nutrients) than rainwater and associated overland and subsurface flows (Winter 1978; Vanek 1987; Millham and Howes 1994), we can expect to observe higher nutrient concentrations during periods when stream flows are dominated by groundwater contributions (i.e., during the summer dry period). Conversely, rapid changes in stream flows can be expected to result in greater nutrient transport (especially for nutrients associated with particles) because these flow spikes can mobilize instream sediments and their associated nutrients due to channel scouring (Novotny 2003). Antecedent flow conditions can impact stream nutrient concentrations by either allowing nutrients to accumulate in the stream channel and catchment (if conditions are dry) or washing off nutrients (if conditions are wet). Rainfall can impact stream nutrients because when rainfall is sufficiently intense, overland flow and resulting erosion will occur (Novotny 2003).

The Seasonal term in our regression model equaled the previously described predicted base flow at any given time:

$$\text{Seasonal} = \text{Predicted base flow}/\text{Median flow} \qquad (1)$$

We described flow spikes using the $\log_{10}$ ratio of a day's flow divided by the preceding day's flow accordingly:

$$\text{Spikeness} = \log_{10}(\text{Flow}_t/\text{Flow}_{t-1}) \qquad (2)$$

We characterized antecedent flow conditions by taking the $\log_{10}$ ratio of the geometric mean of the flow on days 2-4 preceding a given day divided by the flow on that day accordingly:

$$\text{Antecedent flow} = \log_{10}(\text{Geomean flow}_{t-2\text{ to }4}/\text{Flow}_t) \qquad (3)$$

We did not include the preceding day's flow in our measure of antecedent flow conditions because this would have made the antecedent index strongly correlated with the flow spikeness index. We characterized rainfall as the mean of the rainfall for the preceding day and the day the stream sample was collected accordingly:

$$\text{Rainfall} = \text{Mean}(\text{Rainfall}_{t-1}, \text{Rainfall}_t) \qquad (4)$$

This approach was used to predict the actual SRP concentrations in these streams, as well as log(TP), because TP concentrations were moderately log normally distributed in these streams. We also tested alternative terms to those described above. For example, we tested the alternative ''spikeness'' term minimum{0, $\log_{10}(\text{Flow}_t/\text{Flow}_{t-1})$} because we expect rapidly rising flows to have a greater impact TP concentrations that rapidly falling flows. We also tested the alternative antecedent term maximum{0, $\log_{10}(\text{Geomean flow}_{t-2\text{ to }4}/\text{Flow}_t)$}, to more fully isolate the spikeness and antecedent terms. However, neither of these alternative formulations markedly changed the fit or prediction error compared to terms 1–4 listed above. Our statistical analyses were performed using SPSS® version 10 for Mac.

The observed SRP concentration time series and the multiple regression model predicted SRP concentrations are depicted in Figure 5. This figure shows that both the observed SRP time series and the predicted SRP concentrations follow a smooth sine-wave-type seasonal pattern with high concentrations during the summer low-flow period and low concentrations during the winter high-flow period. The multiple regression model indicates that all of the explained variation is attributable to the seasonal base flow term, with the spikeness, antecedent, and rainfall terms all insignificant (Table 3). The fit between the time series model and the raw SRP time series for Issaquah Creek was the poorest of all the models assessed. This was probably the case because there appeared to be a strong impact of salmon spawning on Issaquah October–November SRP concentrations, and there was very little variation in Issaquah SRP concentrations the remainder of the year. However, because there was less variation in Issaquah SRP concentrations, the residual error of the model estimates for this stream was similar to that obtained for the other streams. The results of these SRP time series models suggest that the predominant factor regulating annual variation in stream SRP concentrations in Thornton, North, and Swamp creeks was the relative contribution of groundwater to stream flows, which was high during the summer (when very little rainfall occurred) and lower during the winter.

The annual daily time series for TP concentrations and the multiple regression model predicted TP concentrations are depicted in Figure 6, and described in Table 3. With the exception of Issaquah Creek, the TP time series models gave substantially weaker fits to the observed concentration time series compared to the SRP results. The weakest TP time series model was obtained for Thornton Creek, which was the most urban and also had the greatest variability in flows and TP concentrations. Also, in contrast to the results obtained for SRP, almost all of the terms examined (seasonal base flow, spikeness, antecedent flow, and rainfall) were statistically significant for each stream-specific time series model. For three of the four models, the seasonal base flow term had

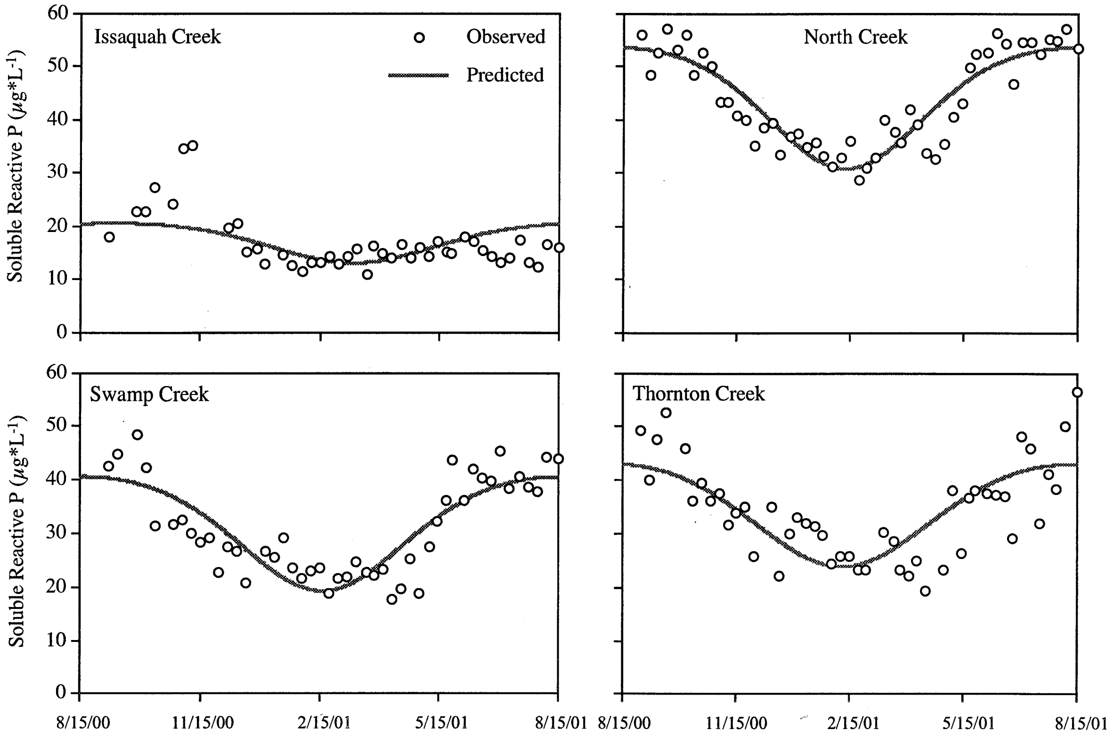

Figure 5. The annual time series of observed weekly stream water SRP concentrations. The gray curve describes the predicted concentrations according to the stream-specific statistical time series models presented in Table 3.

the greatest impact on predicted TP concentrations. This is probably due to the strong impact of the seasonal term on stream SRP concentrations because, on average, SRP constituted 47 ± 5% of the stream water TP. Antecedent conditions had, on average, the second strongest impact on TP fluctuations, and rainfall, although significant in three of four cases, had the weakest impact for all models.

We also developed an overall statistical time series model for stream SRP concentrations using an additional term (i.e., each stream's flow weighted SRP concentration). This model predicted SRP concentrations at any time of the year in a given stream based on the normalized predicted base flow and the stream's weighted SRP concentration. Because Seattle area stream SRP concentrations are moderately highly correlated to catchment land cover (Brett and others 2005), this approach could be used to provide season-specific predictions for all streams in the Seattle area. Figure 7 and Table 3 show that this model was able to predict a large portion of the overall seasonal variability for the four streams (r^2 = 0.82). The stream flow-weighted SRP concentration and the seasonal base flow fluctuation terms were the only statistically significant predictors for SRP concentrations. Despite the fact that the flow-weighted SRP concentration had the most important impact on predicted SRP concentrations, the overall model provided fits for each of the individual streams, which were virtually identical to the previously discussed stream-specific SRP time series models (Figure 5).

Finally, we developed an overall time series model for stream TP concentrations (Figure 8 and Table 3), as described earlier for SRP. This model had an overall fit (r^2 = 0.76) that was clearly stronger than the fit for the individual TP time series models. The overall TP time series model differed from the overall SRP time series model in that it also included significant terms for each of the parameters considered. The stream flow-weighted TP concentration term had the strongest impact on predicted TP concentrations, followed by the seasonal base flow term, antecedent flows, flow spikeness, and rainfall (Figure 8). Despite the fact that the flow-weighted TP concentration was the most important term in this model, the overall model provided fits for each of the individual streams that were nearly as strong as the previously discussed stream-specific TP time series models (i.e., the average r^2 for the overall model applied to each stream was 0.45, whereas the average r^2 for the specific stream models was 0.50).

Table 3. The structure and fit for the statistical time series models of stream water total and soluble reactive phosphorus concentrations

Term	Units	Issaquah Creek	Swamp Creek	North Creek	Thornton Creek	Overall model	Day-Specific overall models
Soluble Reactive Phosphorus							
Coefficients							
Intercept	μg/L	23.0	47.8	60.4	56.9	16.1	
Seasonal	Unitless	−5.0	−14.4	−14.3	−21.5	−12.5	
Spikeness	Unitless	NS	NS	NS	NS	NS	
Antecedent	Unitless	NS	NS	NS	NS	NS	
Rainfall	cm/day	NS	NS	NS	NS	NS	
Flow wt. conc.	μg/L	—	—	—	—	0.974	
Overall r^2		0.260	0.723	0.814	0.571	0.817	
Residual mean square	μg/L	4.6	4.7	3.9	6.0	5.4	
Semi-partial r^2 values							
Seasonal		0.267	0.712	0.801	0.560	0.569	
Spikeness		NS	NS	NS	NS	NS	
Antecedent		NS	NS	NS	NS	NS	
Rainfall		NS	NS	NS	NS	NS	
Flow wt. Conc.						0.746	
Total phosphorus							
Coefficients							
Intercept	log(μg/L)	1.63	1.90	2.06	2.06	0.106	0.096 ± 0.101
Seasonal	Unitless	−0.061	−0.150	−0.120	−0.149	−0.114	−0.112 ± 0.006
Spikeness	Unitless	0.248	0.133	0.119	0.128	0.131	0.138 ± 0.027
Antecedent	Unitless	−0.322	−0.140	−0.085	−0.177	−0.152	−0.149 ± 0.024
Rainfall	cm/day	0.047	0.052	0.045	NS	0.0430	0.0425 ± 0.0387
log(flow wt. conc.)	log(μg/L)					0.995	0.999 ± 0.055
Overall r^2		0.427	0.586	0.572	0.386	0.756	0.763 ± 0.028
Residual Mean Square	log(μg/L)	0.100	0.086	0.071	0.107	0.096	0.096 ± 0.004
Semi-partial r^2 values							
Seasonal		0.147	0.465	0.479	0.168	0.254	
Spikeness		0.066	0.071	0.065	0.047	0.046	
Antecedent		0.166	0.138	0.063	0.098	0.095	
Rainfall		0.034	0.045	0.044	NS	0.023	
log(flow wt. Conc.)	log(μg/L)					0.691	

Note. This table presents the results of models predicting concentrations in each individual stream and for the entire dataset. The overall model for stream water TP concentrations predicted the log(TP concentration). The day-specific overall TP models utilized one-seventh of the TP dataset to generate seven different time series models in order to minimize the serial correlation in the residuals of the overall TP model generated using the entire dataset; the values reported for the day-specific TP models were mean ± 1 SD.

The results of a Durbin–Watson test indicated the residual errors of our overall daily stream water TP concentration model were autocorrelated. This was also the case for our stream-specific TP models and, to a much lesser extent, for our SRP concentration time series models. Positive autocorrelation of residual errors, as was the case in our study, is of concern because it can cause an underestimate of the error variance and an overestimate of the overall strength of the model (Stow and Borsuk 2003). We were able to largely overcome this autocorrelation problem by building the overall TP model using only data from every seventh day [i.e., day-of-the-week-specific models, in a manner similar to that employed by Stow and Borsuk (2003)]. Although this solved the autocorrelation problem, it created an inference problem because it was not clear which day-specific TP time series model (e.g., Monday, Tuesday, etc.) was most appropriate for the entire dataset. Therefore, we compared the performance and structure of the seven different day-specific TP time series models to that of the original overall daily TP model (see Table 3). Interestingly and somewhat surprisingly, the average coefficients obtained for the 7-day-specific TP models were nearly identical to those obtained for the overall daily model. Furthermore, the average r^2 values and model error estimates were also nearly identical to those for the daily model. Based on these results, we inferred that although the Durbin–Watson statistic indicated our model errors were autocorrelated, this did not, in fact, cause the strength of our model to be overestimated.

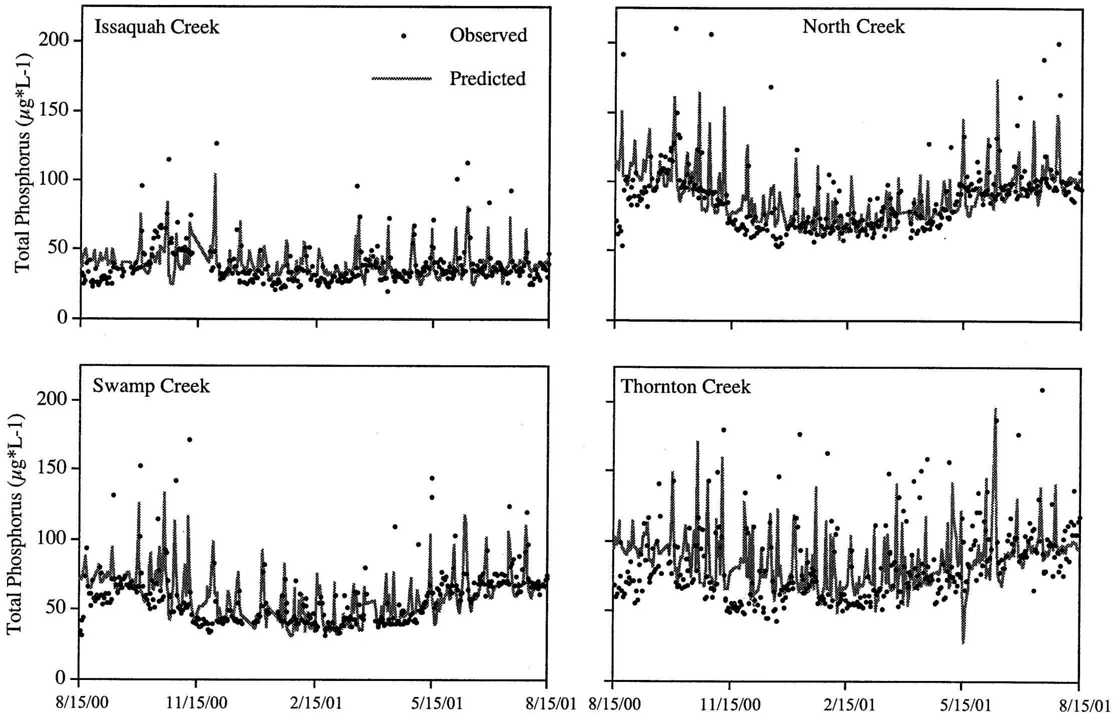

Figure 6. The annual time series of observed weekly stream water TP concentrations. The gray curve describes the predicted concentrations according to the stream-specific statistical time series models presented in Table 3.

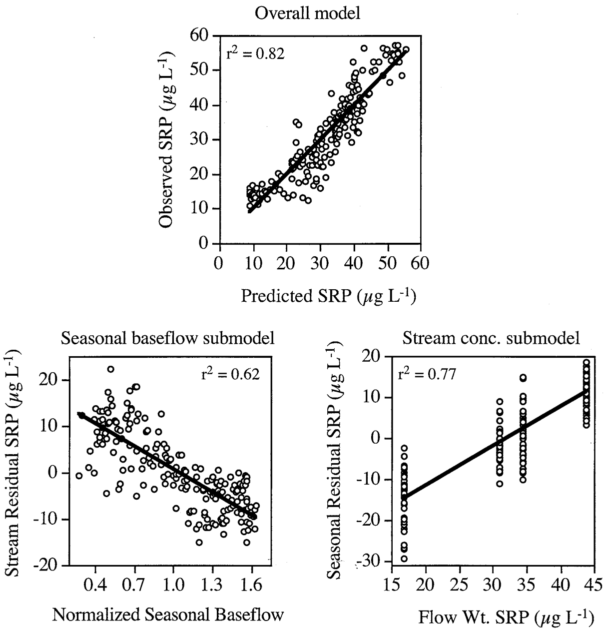

Figure 7. The overall statistical time series model for SRP. This overall model aggregates the data for all four streams into a single statistical model as described in Table 3.

Discussion

The most important result from this study is that Seattle area stream water SRP concentrations follow a smooth cycle that is easily described by a seasonally based sine wave. Terms describing short-term flow fluctuations, antecedent conditions, and rainfall impacts on SRP concentrations were in all cases nonsignificant. Stream water SRP concentrations were higher during the summer dry period when groundwater inputs dominate stream flows and decreased during the winter when groundwater inputs are diluted by overland flows and especially recent subsurface flows. The increase in stream SRP concentrations from winter to summer conditions averaged 61 ± 22% (± 1 SD) for the trends observed in North, Swamp, and Thornton creeks. This strong annual cycle in stream water SRP concentrations is similar to trends reported for a much coarser data analysis of Seattle area stream water quality (Brett and others 2005). The between-stream differences in average SRP concentrations were attributable to previously noted (Brett and others 2005) trends between stream water nutrients and catchment land cover. An overall time series model that included a term describing seasonal impacts and site-specific impacts on stream SRP concentrations was able to

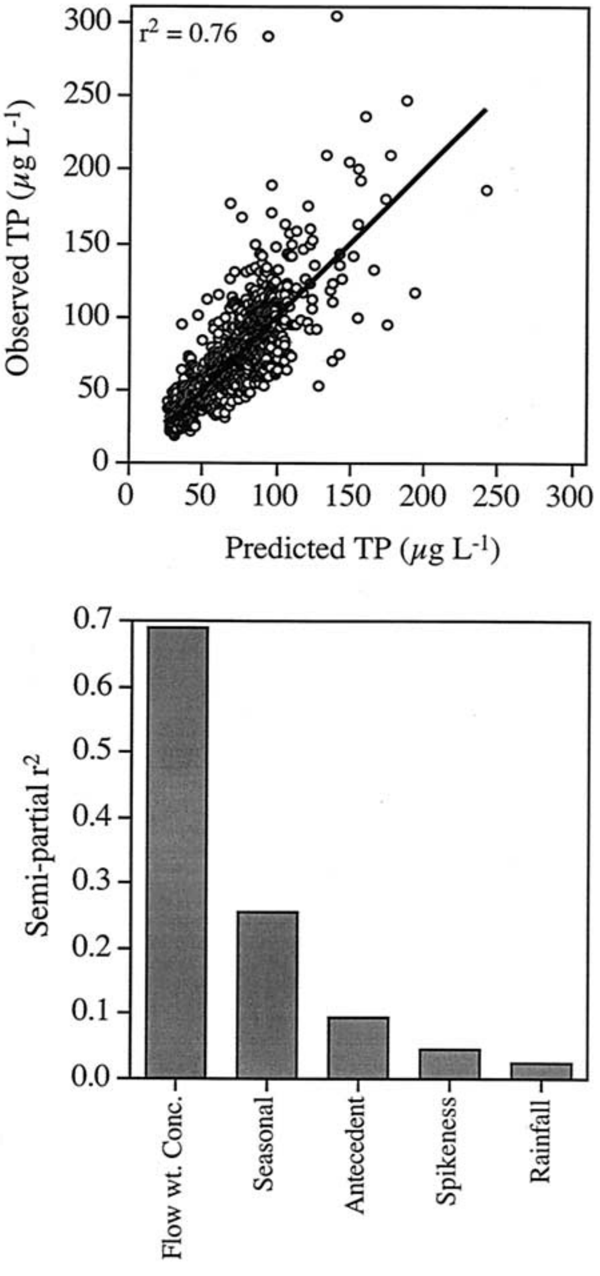

Figure 8. The overall statistical time series model for TP. This overall model aggregates the data for all four streams into a single statistical model as described in Table 3.

explain 82% of the variability in SRP concentrations for the entire dataset. Interestingly, there was minimal loss of predictive power for this overall SRP time series model for each stream compared to the site-specific SRP models. The site-specific time series models for these four streams also had high predictive power (r^2 = 0.57–0.81) in three of four cases. In the one case (i.e., Issaquah Creek) where the time series model only had a weak fit to the observed SRP trends, the actual residual error of this particular model's estimates was similar to the prediction error for the other models (see Table 3). This was the case because Issaquah Creek had, for the most part, very little annual variation in stream water SRP concentrations. Thus, although the site-specific model for this stream had a weak fit, it still provided predictions that were close to actual values most of the time. The exception to this generality occurred during the fall, when Issaquah Creek SRP and TP concentrations were much higher than either the site-specific or overall time series models predicted and was probably due to a salmon spawning run at that time. Several studies have shown Pacific salmon carcasses can act as important nutrient sources for small streams (Cederholm and others 1999; Chaloner and others 2002), and although less studied, it is also plausible that salmon redd construction might mobilize nutrients by resuspending fine sediments within the stream channel.

Although the overall SRP time series model might seem to have limited utility because it requires prior knowledge about average stream water SRP concentrations, this information is easily attainable for area streams with only a modest initial sampling effort (i.e., 6–12 samples/year for 1 or 2 years). In fact, this information is already available for virtually every sizable stream in King County, and in cases where streams have not been previously sampled, this information can be predicted using already established stream nutrient/catchment land-cover relationships (Brett and others 2005). Once an estimate of stream SRP concentration is obtained, our results suggest that over the annual cycle, SRP concentrations will be at a minimum during the winter, reach a maximum during the summer, and vary little from week to week. These trends are important because SRP is the most biologically available phosphorus fraction for algae and bacteria. The simple annual cycle of stream water SRP concentrations, the fact that this fraction constitutes about half of all phosphorus, and the fact that SRP concentrations can be easily predicted suggest the most important phosphorus fraction is easily predictable in the streams we studied.

In contrast to the results obtained for the SRP time series models, the short-term and seasonal TP dynamics were complex and more difficult to predict. The site-specific TP time series models gave weaker fits ($r^2 \approx$ 0.50) to the observed data than did most of the site-specific SRP models ($r^2 \approx 0.70$), and in almost all cases, the TP time series models included significant coefficients for each of the terms considered (seasonal cycle, short-term flow fluctuations, antecedent conditions, and rainfall). Because TP concentrations were significantly positively related to stream flows, high flows and high TP concentrations tended to coincide. For example, 28.6 ± 4% (± 1 SD) of the annual TP load (calculated as the sum of all observed concentrations multiplied by daily flows) occurred during only 5% of all days in these streams. The weakest TP time series model was obtained for Thornton Creek, which had the most variable TP and stream flow dynamics. On an encouraging note, the overall TP time series model gave satisfactory predictions ($r^2 = 0.76$), without a major loss of predictability for the specific streams. This suggests that phosphorus transport was affected by the same processes in a similar manner in each of the streams. The fact that TP transport appears to be generalizable across streams also has important implications, because it suggests that a single time series model structure might be appropriate for all Seattle area streams.

Ideally, our study would have measured total dissolved phosphorus (TDP) and TP instead of SRP and TP. TDP equals the sum of SRP and dissolved organic P (DOP), and the difference between TP and TDP can be used to estimate particulate P (PP). This is important because PP and TDP have very different transport mechanisms and biological availability, whereas SRP or DOP are much more similar. For example, it is generally assumed that SRP is entirely bioavailable, DOP is almost entirely bioavailable, and PP has very widely ranging bioavailability depending on a variety of factors (see below). A recent study of phosphorus speciation and concentration changes during storm events in Seattle area urban, mixed land cover, and forest stream types (Brattebo 2003) showed that SRP and TDP concentrations were nearly constant during storm events in these streams, whereas TP and especially PP concentrations fluctuated dramatically during rapid changes in stream hydrographs. If we coarsely estimate PP as the difference between TP and SRP for the present dataset, which falsely lumps the more stable DOP fraction with PP, we find that the ‘‘pseudo PP’’ concentrations in our streams fluctuated far more on a daily or weekly basis than did either SRP or TP.

Overall, the results of the present study are quite consistent with those of Brett and others (2005), who looked at long-term (i.e., decadal) average stream nutrient concentrations as a function of land cover and season, and Brattebo (2003), who investigated hourly fluctuations in phosphorus concentration and speciation for different stream land-cover types during storm events. Brett and others (2005) found that long-term average stream water SRP and TP concentrations were moderately strongly correlated with catchment land-cover type ($r^2 \approx 0.60$), with streams draining urban-dominated catchments having on average about 110% higher phosphorus concentrations than streams draining forested catchments. This study also found that stream water SRP concentrations tended to be much higher during the summer than during the winter. Brattebo study of phosphorus transport during storm events found that SRP and TDP concentrations were quite stable even when stream flows fluctuated dramatically, whereas PP and, to a lesser extent, TP concentrations changed markedly during different phases of the storm hydrograph. Brattebo also found that DOP accounted for 20–40% of TDP in Seattle area streams.

In general, our results lead to a discussion about whether water quality managers should be most concerned with SRP or TP transport to lakes from streams. On a positive note, our overall time series models seem to be moderately good at predicting both SRP and TP concentrations. However, the vast majority of limnological analyses have focused on TP loading to lakes, as opposed to simply looking at dissolved phosphorus loading. This is a conservative approach, but it is not clear if it is also the most appropriate on a case-by-case basis. The literature on the bioavailability of phosphorus is in unanimous consent that dissolved phosphorus (and especially the reactive phase) is almost entirely bioavailable (Reynolds and Davies 2001). In contrast, the bioavailability of PP, another major component of TP, seems to vary greatly depending on its source and the characteristics of the particles with which this phosphorus is associated. Phosphorus attached to particles derived from catchments without extensive agricultural activity tends to have low biological availability (Ellis and Stanford 1988; Hatch and others 1999), whereas a much higher portion of the PP derived from agricultural catchments with intense fertilizer application is bioavailable (Sharpley 1993). Particulate P in wastewater treatment plant effluent that has only undergone primary and secondary treatment is much more bioavailable than PP in effluent from treatment plants with advanced tertiary treatment for phosphorus removal (Ekholm and Krogerus 1998).

As previously mentioned, the size of particles with which phosphorus is associated also has a great impact on both the physical and chemical properties of this PP (Dorich and others 1984; Broberg and Persson 1988; Hatch and others 1999; Pacini and Gächter 1999). Large sand-sized particles will tend to settle out of the water column very rapidly [on the order of 20 m/day; Broberg and Persson (1988)], will have relatively low phosphorus content on a per mass basis, and will predominantly contain refractory nonextractable phosphorus (Pacini and Gächter 1999). For these reasons, one can probably ignore the eutrophication potential for phosphorus associated with large-sized particles. Conversely, small-sized particles like clays and silts will settle slowly (unless they coagulate/flocculate into larger particles) and will have relatively high phosphorus content and more easily extracted phosphorus, especially if from agricultural catchments (Pacini and Gächter 1999). In a study of phosphorus bioavailability in streams draining the Lake Tahoe watershed, algal growth in bioassay experiments was weakly correlated to the amount of PP in the clay/silt size fraction and not at all correlated with PP in the sand size fraction (Hatch and others 1999). Soils in the Lake Tahoe watershed are probably less nutrient enriched due to external loading than are soils in the Lakes Washington/Sammamish watershed; however, both the Lake Tahoe and Lakes Washington/Sammamish watershed soils are probably much less nutrient enriched than typical agricultural soils. Similar to the results obtained for Lake Tahoe tributaries, Ellis and Stanford (1988) concluded that only a very small fraction (6%) of the PP in fine sediments transported to Flathead Lake by the Flathead River was bioavailable. Moreover, a recent review by Ekholm (1998) concluded that TP is a poor estimator of biological available P.

Conclusions

Eutrophication management using total maximum daily loads (TMDLs) has received increasing attention, especially regarding the control of non-point-sources on a watershed basis (USEPA 2000). Basic components of the TMDL development process are the establishment of maximum allowable nutrient loadings for specific water bodies. However, the inherent prediction uncertainty of natural systems along with the need for cost-effectiveness and an adequate degree of social and political acceptability make TMDL evaluation and optimal management plan selection difficult (Borsuk et al. 2002). Thus, careful consideration of site-specific characteristics and identification of the basic ecological structures and natural processes that underlie water body dynamics are important ways to decrease the economic costs and environmental risks of management decisions (USEPA 2000). The findings of our study have important management implications in this regard. For example, SRP concentrations in Seattle area streams are probably a much more sensitive indicator of eutrophication potential in area lakes (Edmondson 1994; Arhonditsis and others 2003) than are stream water TP concentrations. Here, we showed that stream water SRP concentrations are also relatively easy to predict using land cover and seasonal stream flow fluctuations. Hence, it is feasible to generate both seasonal and long-term estimates of bioavailable phosphorus loading to Seattle area lakes, which, in turn, will enable a realistic evaluation of alternative management schemes. However, it should emphasized that many factors regulate the bioavailability of PP, and some forms of PP can certainly exacerbate surface water eutrophication. The relatively small number of studies in the literature that have actually measured the bioavailability of PP and the difficulties inherent when predicting TP (and especially PP) dynamics are the major challenges for establishing such a long-term prognostic tool. An essential next step would be a detailed assessment of the bioavailability of the particulate phosphorus fraction in area streams as a function of stream/catchment land-cover characteristics. This information would increase our understanding of the effects of land-use changes and increased urbanization on lakes, and thus facilitate the selection of best management practices and the development of local non-point-source nutrient control programs.

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