

Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects

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Abstract. Distinct seasonal patterns in streamwater nutrient and dissolved organic carbon (DOC) concentrations are evident in the data record from 7 years of weekly sampling in the West Fork of Walker Branch (WB) and 4 years of weekly sampling in a nearby stream, upper White Oak Creek (WOC), both first-order streams in the Ridge and Valley Province of eastern Tennessee. Concentrations of NO_3 and soluble reactive phosphorus (SRP) in both streams showed a repeated pattern of annual maxima in summer and biannual minima in autumn and spring. Concentrations of DOC in WB exhibited distinct autumn maxima. To determine whether temporal variations in catchment hydrological processes could explain the seasonal nutrient and DOC variations in WB, we used an end-member mixing analysis involving Ca and SO_4 concentrations to separate stream discharge into three catchment flow paths of differing nutrient concentrations. Stream NO_3 , SRP, and DOC concentrations were predicted solely on the basis of temporal variation in the importance of these flow paths and measurements of nutrient concentrations for the different flow paths. Ratios of observed/predicted concentrations in stream water near 1.0 suggested that catchment effects alone explained streamwater concentrations, whereas ratios substantially different from 1.0 suggested that in-stream processes were important determinants of streamwater concentrations. Observed/predicted NO_3 and SRP concentration ratios showed repeated annual patterns with values closer to 1.0 during winter and summer (generally 0.8–1.2) and minima (<0.6) in spring and autumn, suggesting substantial in-stream net uptake at these times. Observed/predicted DOC concentration ratios were more variable and generally ≥ 1 but did show consistent autumn maxima (>2.5), indicating substantial in-stream DOC generation at this time. Observed/predicted ratios for all nutrients were generally less variable and were closer to 1.0 at high flow compared to low flow, suggesting that in-stream controls on streamwater chemistry are less important at high discharge than at low discharge. Our results indicate two general modes of control of stream nutrient concentrations: (1) catchment control via seasonal variation in the dominant hydrologic pathway (greater proportion of deep groundwater in summer), which produces lower winter and higher summer concentrations, and (2) in-stream control via high rates of net nutrient uptake during the spring (primarily by autotrophs) and autumn (primarily by heterotrophs).

Introduction

Understanding the controls on stream chemistry is important for questions concerning the management of streams and their catchments. Many studies have demonstrated the importance of terrestrial processes to stream water nutrient concentrations, and in fact, the chemistry of streams is often used to infer the status of nutrient cycling in the terrestrial ecosystems they drain. Weathering of parent material is known to be an important source of P to stream water [Dillon and Kirchner, 1975]. Perturbation studies of small catchments have demonstrated the importance of vegetation in retaining nutrient inputs and minimizing losses to streams [Likens *et al.*, 1977; Swank, 1988]. Studies of forest soils show that losses of dissolved inorganic nitrogen and phosphorus in drainage water are often very low owing to a combination of biological and

geochemical processes, including uptake by plants and heterotrophic microbes and adsorption to iron and aluminum oxides [Wood *et al.*, 1984; Johnson, 1992]. However, when rates of atmospheric N deposition are high, forests can eventually become N saturated [Aber *et al.*, 1989], resulting in high streamwater nitrate concentrations [Stoddard, 1994]. Thus streamwater N concentration (particularly the seasonal pattern) has been proposed as an indicator of terrestrial N saturation [Stoddard, 1994].

Fewer studies have focused on the role of in-stream processes as determinants of streamwater chemistry. McKnight and Bencala [1990] used relationships with major ions and an in-stream transport model to evaluate the relative importance of watershed and in-stream processes in controlling metal and DOC concentrations in streams. Indirect evidence of the importance of in-stream processes comes from observations that nutrient concentrations in streams are lower than in the groundwater feeding them [Grimm and Fisher, 1984; Ford and Naiman, 1989]. Mass balance studies of headwater streams or stream segments have indicated prolonged periods of net in-

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stream retention of nutrients punctuated by large net losses during storms [Meyer and Likens, 1979; Grimm, 1987]. Experimental radiotracer injections [Newbold *et al.*, 1983; Mulholland *et al.*, 1985; Tate *et al.*, 1995] and stable element additions [Triska *et al.*, 1989; Marti and Sabater, 1996] have demonstrated rapid in-stream uptake of nutrients by algae and microbes. In some streams adsorption by streambed sediments can also be an important regulator of inorganic P concentration [Meyer, 1979; Klotz, 1991; Tate *et al.*, 1995].

In a previous study in the West Fork of Walker Branch, Mulholland [1992] showed that streamwater nutrient concentrations varied seasonally, with highest concentrations in summer and lowest in late autumn and winter. Stream segment mass balances suggested that seasonal variation in in-stream nutrient immobilization rates might explain, at least partially, the seasonal differences in stream water nutrient concentrations. However, this previous study involved only monthly sampling over a period of 2 years. In this paper we present data from 7 years of weekly sampling in the West Fork of Walker Branch as well as from 4 years of weekly sampling in a nearby stream, White Oak Creek. We use a catchment flow path analysis to separate the effects of catchment hydrological processes from in-stream biogeochemical processes. This more comprehensive study confirms the findings from the previous study: that in-stream processes are important determinants of stream water nutrient concentrations and explain much of the strong seasonality in stream N, P, and DOC concentrations.

Study Sites

The study was conducted in the West Fork of Walker Branch and in upper White Oak Creek, two first-order streams on the U.S. Department of Energy's Oak Ridge National Environmental Research Park (latitude 35°58'N, longitude 84°17'W). The climate is typical of the humid southern Appalachian region. Mean annual temperature is 14.5°C, and mean annual rainfall is approximately 1400 mm, distributed relatively evenly throughout the year.

Both of the study streams drain hardwood forest catchments on Chestnut Ridge. Chestnut Ridge is underlain by the Knox Group, a 610-m-thick sequence of Cambrian and Ordovician siliceous dolomite that weathers rapidly to form deep soils with abundant chert [McMaster, 1963]. Soils are primarily Ultisols, with small areas of Inceptisols found in alluvial valleys adjacent to streams [Peters *et al.*, 1970]. Surface infiltration rates are very high, and rainfall infiltrates completely, even at the highest rainfall intensities [Luxmoore, 1983]. Surface soils have high hydraulic conductivity due to high macroporosity [Wilson and Luxmoore, 1988]; however, hydraulic conductivity declines rapidly with depth due to increasing clay content [Wilson *et al.*, 1989], and zones of perched saturation develop in the surface soil layers producing rapid lateral flow during larger storms [Mulholland *et al.*, 1990b]. The soils are acidic (pH 4.2–5.0) and low in exchangeable bases, nitrogen, and phosphorus.

The West Fork of Walker Branch (WB) drains a 38.4-ha catchment and at base flow is fed primarily by several springs. The stream was sampled approximately 300 m from its headwaters. Upper White Oak Creek (WOC) drains a 207-ha catchment about 2 km southwest of WB, and it is also fed primarily by several springs at base flow. Both streams have been the site of numerous ecological studies (WB: Elwood *et al.* [1981], Newbold *et al.* [1983], and Rosemond [1994]; WOC: Hill [1992] and Hill *et al.* [1995]). The West Fork of Walker Branch has

also been the site of a number of hydrological [Luxmoore *et al.*, 1990; Wilson *et al.*, 1991; Mulholland, 1993] and biogeochemical studies [Jardine *et al.*, 1990; Mulholland, 1992]. A more complete description of these streams can be found therein.

Methods

Grab samples of stream water were collected weekly about 60 m upstream from the weir on WB from 1989 through 1995. The samples were collected between 0900 and 1200 on Mondays prior to March 30, 1992, and on Tuesdays after that date. Measurements of pH (glass electrode), specific conductance (electrical conductivity bridge), and alkalinity (HCl titration to pH of 4.5) were made on unfiltered samples. Samples for chemical analyses were collected in polyethylene bottles, immediately returned to the laboratory and filtered (Nuclepore polycarbonate filters, 0.4- μ m pore size) within 3 hours of collection. Samples for major cations were acidified after filtration (0.5% HNO₃) and concentrations of Ca and Mg were measured by inductively coupled plasma emission spectrometry. Samples for major anions were refrigerated and SO₄ concentrations were determined by ion chromatography. Samples for dissolved organic carbon (DOC) were acidified after filtration (to pH < 3) and refrigerated. Concentrations of DOC were measured using an OI model 700 Total Carbon Analyzer (after CO₂ purging) prior to May 1992, and using a Shimadzu model 5000 Total Carbon Analyzer thereafter. Samples for nitrogen and phosphorus were refrigerated after filtration and analyzed within 3 days. Concentrations of NH₄ were measured by phenate colorimetry [American Public Health Association (APHA), 1992] and NO₂ + NO₃ were measured by Cu-Cd reduction followed by azo dye colorimetry [APHA, 1992], both using a Bran Lubbe TRAACS 800 autoanalyzer (detection limit of 1 μ gN/L). Because stream water was always well oxygenated (dissolved oxygen concentrations >6 mg/L) and because spot checks revealed very low NO₂⁻ concentrations (<2 μ gN/L), hereafter we refer to measurements of NO₂ + NO₃ as NO₃. Concentrations of soluble reactive phosphorus (SRP) were determined by the ascorbic acid-molybdenum blue method [APHA, 1992] using a 10-cm spectrophotometer cell to achieve low detection limits (0.5 μ gP/L).

Grab samples were collected approximately weekly from WOC 500 m upstream from the upper flume and approximately 800 m from the headwaters of this stream but upstream from its passage through the Oak Ridge National Laboratory complex. Only NH₄, NO₂ + NO₃, and SRP were measured on these samples, using the same methods and instrumentation as for WB, described above.

For WB data the effects of in-stream processes on nutrient and DOC concentrations were separated from those of catchment processes through an analysis that compared nutrient and DOC concentrations predicted from catchment flow paths with concentrations observed in the stream. Previous studies indicated that there are three dominant flow paths in the catchment and that these have distinctive Ca and SO₄ concentrations as well as different nutrient and DOC concentrations [Mulholland *et al.*, 1990b; Mulholland, 1993]. Mulholland [1993] showed that stream water concentrations of Ca and SO₄ in WB could be explained by a simple mixing of these three flow paths (sources of water): (1) water within bedrock fissures and cavities (bedrock zone) with high Ca and low SO₄ concentrations, (2) water within the permanently saturated zone immediately above the bedrock (saturated zone) with low Ca concentra-

tions and low SO_4 concentrations, and (3) water within transient saturated zones perched well above the permanent groundwater table (vadose zone) with low Ca concentrations and high SO_4 concentrations (and which contributes to stream discharge only during storm events). The relative contribution of each of these flow paths to stream discharge was determined using an end-member mixing analysis [Hooper *et al.*, 1990] that involves solving the following set of simultaneous equations:

$$[\text{Ca}]_1f_1 + [\text{Ca}]_2f_2 + [\text{Ca}]_3f_3 = [\text{Ca}]_s \quad (1)$$

$$[\text{SO}_4]_1f_1 + [\text{SO}_4]_2f_2 + [\text{SO}_4]_3f_3 = [\text{SO}_4]_s \quad (2)$$

$$f_1 + f_2 + f_3 = 1 \quad (3)$$

where subscripts 1, 2, and 3 refer to the three different flow paths; the subscript *s* refers to stream samples; *f* refers to the fraction of stream discharge contributed by each flow path; and [Ca] and $[\text{SO}_4]$ refer to the concentrations of each of these ions in water for each flow path. The existence of three flow paths in WB is supported by analysis of stream discharge recession curves following storm events [Mulholland, 1993].

Predicted stream nutrient and DOC concentrations based solely on the catchment flow path analysis (i.e., stream concentrations that are expected if only catchment hydrological and biogeochemical processes regulate stream chemistry) were determined for each sampling date in WB. The predicted nutrient and DOC concentrations were determined by computing the fraction of stream discharge contributed by each flow path (f_1, f_2, f_3), using the measured Ca and SO_4 concentrations, and then multiplying each fraction by the nutrient and DOC concentrations determined for each flow path and summing the products. Flow path chemistry (Ca, SO_4 , NO_3 , SRP, and DOC concentrations) was determined from measurements made over extended periods on each water source. Bedrock zone water chemistry was determined from weekly sampling of the largest and most hydrologically stable spring over the period from September 1993 to March 1995 ($n = 26\text{--}54$, depending on analyte). Saturated zone water chemistry was determined from samples collected from a groundwater well on the lower slope near the headwaters of the stream. Saturated zone samples for Ca and SO_4 were collected during the period from June 1990 to November 1990 ($n = 12$), and samples for nutrients and DOC were collected in December 1992, January 1993, and December 1996 ($n = 4$). Vadose zone water chemistry was determined from samples of lateral flow in the upper 2.5 m of soil collected during three storms in 1989 (January, March, and June) and one storm in 1991 (March) from a subsurface weir installed across the outlet of a 0.5-ha hillslope subcatchment. Volume-weighted concentrations were computed from measurements made on 4–6 samples collected during each storm, and the four volume-weighted storm concentrations were averaged. The predicted concentrations of stream nutrients and DOC were then compared with measured values on each date.

Measurements of mean daily water temperature and total daily photosynthetically active radiation (PAR) were made in WB and in WOC during 1995. Water temperature was measured using a Ryan thermograph, and PAR was measured using a LiCor quantum sensor and data logger. Water temperature was measured at 2-hour intervals, and mean PAR was recorded at 15-min intervals.

Results

Annual patterns of daily PAR in WB and WOC were closely related to the phenology of the deciduous forest vegetation (Figures 1a and 1b). Daily PAR reaching the stream increased steadily in winter and spring, peaking just before emergence of canopy leaves about day 100 (mid-April), after which daily PAR dropped sharply. Summer was the period of lowest PAR (days 150–300, June through September), with levels increasing somewhat after leaf fall, in late October. The spring peak in daily PAR was somewhat higher at the WOC site (approximately $18 \text{ mol quanta m}^{-2} \text{ d}^{-1}$) compared to that at the WB site (approximately $16 \text{ mol quanta m}^{-2} \text{ d}^{-1}$), whereas summer PAR was higher in WB.

Mean daily water temperatures show the typical pattern for northern hemisphere, temperate zone streams, with peak temperatures about day 240 (late August) (Figures 1c and 1d). The winter minimum is slightly lower and summer maximum slightly higher in WOC than in WB. A relatively large discharge of groundwater via springs moderates the annual temperature pattern in these streams.

Concentrations of NO_3 and SRP over a 7-year period in WB show a repeated pattern of annual summer maxima, lower concentrations during the period from midautumn to late spring, and biannual minima (Figures 2a and 2b). The early spring concentration minimum corresponds to the period of maximum PAR (March 1 to April 30), and the autumn minimum corresponds to the seasonal input of leaves to the stream, which usually peaks during the first week of November. The spring and autumn minima were somewhat more pronounced for NO_3 than for SRP, and the concentration minima for both nutrients were generally lower in autumn than in spring. The DOC concentration pattern in WB was somewhat more erratic, although in most years there was an autumn maximum (Figure 2c). In WOC, NO_3 and SRP concentrations also show summer maxima with minima in spring and autumn (Figure 3). As in WB, the concentration minima in WOC are somewhat more distinct for NO_3 than for SRP. Concentrations of NH_4 in both streams were usually very low ($<2 \mu\text{gN/L}$), showed no seasonal pattern and are not presented here.

Stream water concentrations of Ca and SO_4 generally plotted within the area bounded by a mixing region defined by three flow paths or water sources (Figure 4). The chemical compositions determined for each of these three flow paths are given in Table 1. The fractional importance of the bedrock zone flow path varied seasonally (Figure 5a) and was related to stream discharge (Figure 5b). At low discharge ($<10 \text{ L/s}$), which is the dominant condition during summer, bedrock zone flow contributed $>65\%$ of the stream discharge. However, the bedrock zone flow fraction declined with increasing discharge, and higher discharge conditions were more common in late autumn, winter, and early spring when evapotranspiration rates are low and soils are wetter.

Nutrient and DOC concentrations differed considerably for each flow path (Table 1). These differences in nutrient and DOC concentrations between different catchment flow paths were responsible for at least some of the variation in stream water concentrations. Ratios of nutrient and DOC concentrations measured in stream water to those predicted from catchment flow path analysis provided an estimate of how much of the variation in stream concentrations could be explained by variation in the pathway that water takes as it moves through the catchment to the stream. Observed/predicted concentra-

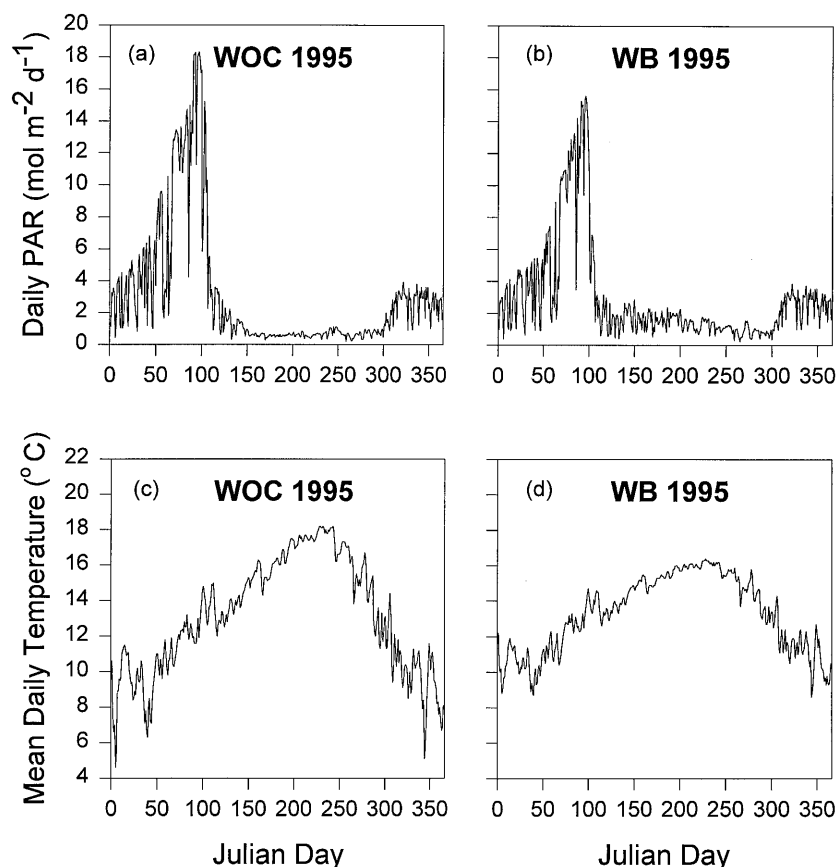


Figure 1. Daily PAR and mean daily water temperatures in the West Fork of Walker Branch (WB) and White Oak Creek (WOC) in 1995.

tion ratios near 1 indicated that catchment processes largely explain the variation in stream chemistry, whereas ratios <1 suggest in-stream depletion, and ratios >1 suggest in-stream generation. Stream samples collected during rainfall were excluded in this analysis because nutrient concentrations were strongly influenced by direct channel interception of through-fall, a highly transient water pathway not considered here. For example, concentrations of NO_3^- were considerably higher in samples collected during rainfall than at any other time. The exclusion of rainfall samples did not reduce the representation of high discharge periods in the analysis because peak discharge occurs well after rainfall ceases in WB [Mulholland *et al.*, 1990b; Mulholland, 1993]. Also, high discharge conditions were well represented in the data set despite the weekly sampling frequency because storm flow generally lasted for at least 3–4 days following the larger rainfall events [Mulholland *et al.*, 1990b]. Although peak storm flows were not represented in the data, the weekly sampling schedule included a representative number of high discharges associated with storm events each year.

Distinct seasonal patterns in observed/predicted ratios of NO_3^- and SRP were evident in WB (Figures 6a and 6b), with minima (generally <0.6) during spring and autumn and maxima during summer. Peak ratios during summer for NO_3^- were generally 1.2–1.3, suggesting net in-stream release, whereas peak ratios for SRP were generally 0.8–1.1, suggesting little net in-stream effect on concentrations. The pattern in observed/predicted DOC ratios was considerably different than for N and P. DOC ratios were generally >1 , with relatively large

values (2.5–10) observed during autumn, suggesting large net in-stream release of DOC at this time. Summer was also generally a period of net DOC release (ratios >1), while ratios in winter and spring were variable but closer to 1.

To evaluate whether uncertainty in the calculated flow path fractions or in flow path nutrient and DOC concentrations affects the most prominent results of the observed/predicted analyses (the large overprediction of stream nutrient concentrations in late autumn and early spring and the large underprediction of stream DOC concentrations during summer and autumn using flow path considerations only), we repeated the analyses based on measured variation in end-member chemistry. First, overestimates of the importance of the bedrock flow path during the higher discharge periods (typically late autumn through early spring) might produce the patterns observed. This condition might result from underestimation of Ca concentration and overestimation of SO_4^{2-} concentration for the bedrock flow end-member, as is suggested in Figure 4 (i.e., some stream data points plotted just to the upper left of the mixing region). To evaluate effects of this uncertainty, flow path fractions were recalculated using bedrock end-member Ca and SO_4^{2-} concentrations that bounded all stream data (32 and 1.6 mg/L, respectively) and the mixing analyses for stream nutrient and DOC concentrations were repeated. Second, uncertainty in the nutrient and DOC concentrations of the different flow paths might affect the seasonal pattern in observed/predicted ratios. In particular, overestimation of NO_3^- and SRP concentrations in the vadose and saturated zone flow paths and underestimation of DOC concentrations in all flow paths

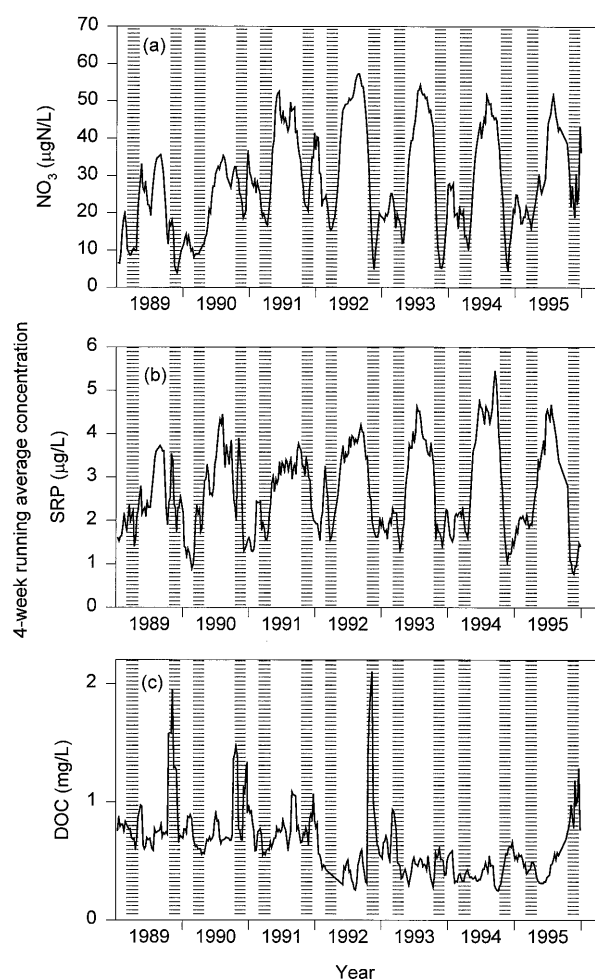


Figure 2. Four-week running averages of NO_3 , SRP, and DOC concentrations in WB determined on weekly grab samples over a 7-year period from 1989 to 1995. The vertical shading denotes the spring period of maximum PAR (March 1 through April 30) and the autumn period of maximum leaf input (October 15 through December 15).

would tend to reduce the most prominent seasonal minima and maxima in observed/predicted ratios and thus reduce the significance of in-stream effects. To evaluate this source of uncertainty, predicted stream water nutrient and DOC concentrations were recalculated using the mean minus the standard deviation as the NO_3 and SRP concentrations for vadose and saturated zone flow paths and the mean plus the standard deviation as the DOC concentrations for all flowpaths (Table 1). Plots of the results of these two alternative analyses showed similar seasonal patterns in observed/predicted ratios for stream water nutrient and DOC concentrations (Figure 6), indicating that the results are robust given these uncertainties.

The observed/predicted ratios of NO_3 , SRP, and DOC were more variable at low discharge but tended to converge toward 1 at high discharge (Figure 7). This effect was greatest for DOC and lowest for NO_3 .

We estimated the effect of in-stream processes on the annual fluxes of NO_3 , SRP, and DOC in WB by comparing fluxes determined from observed stream water concentrations to fluxes calculated using concentrations predicted from the flow path analyses. The observed/predicted annual flux ratios for NO_3 and SRP were <1 for all years, except for NO_3 in 1991

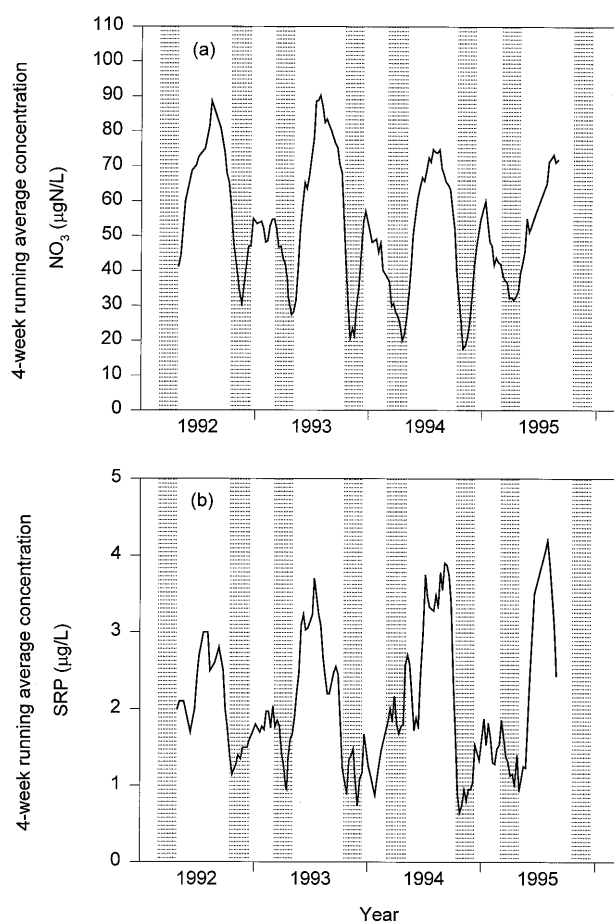


Figure 3. Four-week running averages of NO_3 and SRP concentrations in WOC determined from weekly grab samples over the period from March 1992 to September 1995. The vertical shading denotes the spring and autumn periods as defined in Figure 2.

(Table 2). For DOC flux, observed/predicted ratios were more variable. In 1992 the DOC flux ratio was considerably >1 , suggesting net in-stream production, and in 1994 the DOC flux ratio was considerably <1 , suggesting net in-stream consumption. On average, over the 5-year period from 1991 to 1995, measured NO_3 flux was about 17% lower and SRP flux was about 31% lower than it would have been in the absence of in-stream processes.

Discussion

Multiyear records of NO_3 and SRP concentrations in WB and WOC show two distinct seasonal patterns: (1) high summer concentrations and generally lower concentrations in the other seasons and (2) distinct concentration minima in early spring and late autumn (Figures 2 and 3). The higher summer concentrations and lower concentrations during the cooler seasons appear to be largely a result of variation in hydrological processes occurring in the catchment. Stream water nutrient concentrations predicted from knowledge of the relative importance and nutrient concentrations of different flow paths were closer to observed concentrations during summer and winter, particularly for SRP (Figure 6). For NO_3 , observed/predicted concentration ratios were consistently >1 during summer, suggesting that in-stream net remineralization (remi-

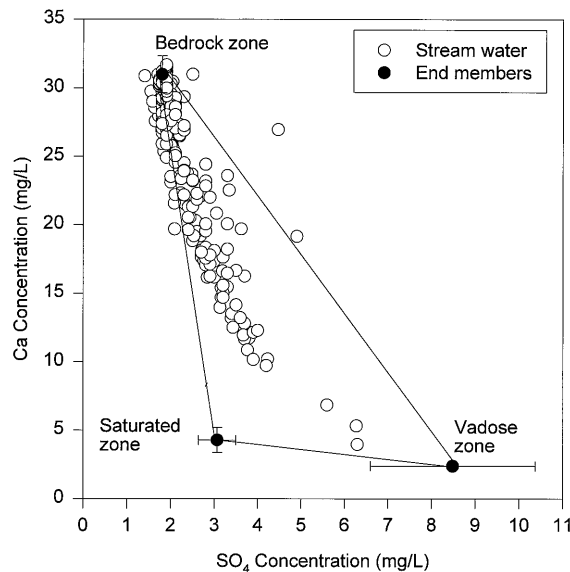


Figure 4. End-member mixing diagram for WB showing concentrations of Ca and SO_4 in stream water and in the proposed flow paths (water sources) contributing to stream discharge.

neralization in excess of uptake) also contributed to the higher stream water NO_3 concentrations at this time.

Stream water NO_3 and SRP concentrations were generally high in summer because most of the stream discharge is generated by the bedrock zone flow path during this period of lower flow. Soils are drier in summer owing to high rates of evapotranspiration, and stream discharge is sustained largely by contributions of groundwater from bedrock fissures and cavities via springs. The dolomitic bedrock is a known source of PO_4 to drainage water, but the source of the higher NO_3 concentrations in this flow path is unknown [Mulholland, 1992].

During the cooler months a greater fraction of stream discharge is generated via the saturated groundwater zone above

Table 1. Mean Chemical Concentrations Determined for Different Flow Paths (Water Sources) in Walker Branch Watershed and Used in the End-Member Mixing Analyses

Solute	Flow Path		
	Vadose Zone*	Saturated Zone†	Bedrock Zone‡
Ca	2.40 (0.17, 4)	4.29 (0.92, 12)	31.0 (1.35, 54)
SO_4	8.49 (1.89, 4)	3.07 (0.43, 12)	1.83 (0.04, 26)
NO_3	5.0 (7.0, 4)	6.8 (3.1, 4)	46.0 (3.0, 54)
SRP	0.9 (0.7, 4)	1.7 (0.7, 4)	5.0 (0.7, 52)
DOC	1.8 (0.5, 4)	0.7 (0.2, 4)	0.2 (0.1, 49)

Standard deviation and n are given in parentheses. Values for Ca, SO_4 , and DOC are mg/L, and values for NO_3 and SRP are $\mu\text{gN/L}$ and $\mu\text{gP/L}$, respectively.

*Mean of volume-weighted mean concentrations from four storm events (January, March, and June 1989 and March 1991).

†Ca and SO_4 values are means of samples collected from a groundwater well during the period from June to November 1990. Nutrient and DOC values are means of samples collected in December 1992, January 1993, and December 1996.

‡Mean of samples from a spring collected during base flow over the period from September 1993 to March 1995.

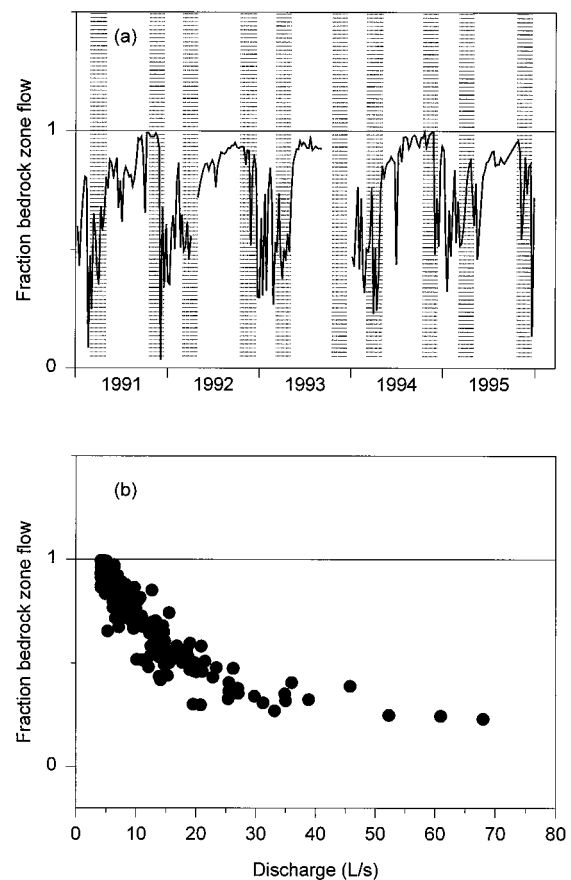


Figure 5. Contribution of bedrock zone flow path as a fraction of total stream discharge in WB calculated from end-member mixing analysis using Ca and SO_4 concentrations and plotted (a) over time and (b) against stream discharge. Breaks in the curve in Figure 5a are the result of missing data on SO_4 concentration.

the bedrock and from the soil vadose zone as transient perched water tables develop and produce lateral flow in soil macropores following rainfall [Mulholland *et al.*, 1990b; Mulholland, 1993]. As evapotranspiration rates decline sharply after autumn leaf fall, subsequent rainfall increases soil moisture levels producing greater flow along the upper two flow paths, which increases both total stream discharge as well as the fractional contributions of these flow paths to stream discharge. Concentrations of NO_3 and SRP in vadose zone water and in the saturated groundwater zone are very low, probably as a result of highly efficient uptake and retention of these nutrients by forest vegetation and the heterotrophic microbial community in the litter and upper soil layers. Despite relatively high NO_3 concentrations in rainfall (often $>1 \text{ mgN/L}$), NO_3 concentrations in vadose zone water are always low ($<25 \mu\text{gN/L}$), even during rainfall events and during the winter as well as the growing season [Mulholland *et al.*, 1990b]. This suggests that NO_3 immobilization is very rapid and that heterotrophic microbes play an important role. Soils remain unfrozen and relatively warm during most of the winter in these catchments (mean soil temperature at 15 cm depth in WB during the months of January and February in 1993–1995 was 6.4°C ; P. J. Hanson, unpublished data, 1993–1995), and autumn leaf fall contributes a large supply of labile organic carbon to soil microbes at this time. For PO_4 , adsorption to iron and aluminum

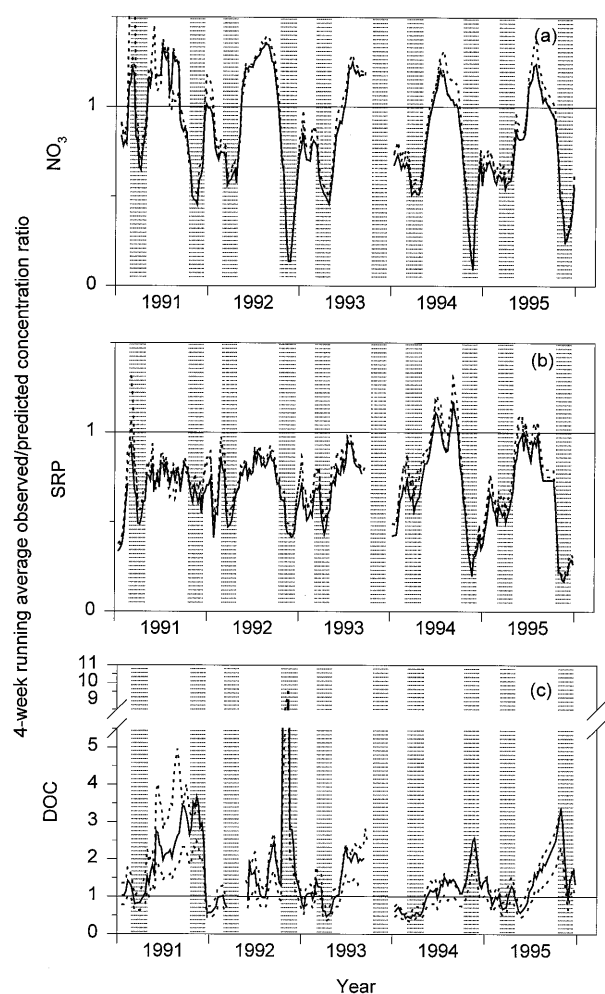


Figure 6. Four-week running averages of observed/predicted ratios for NO_3 , SRP, and DOC concentrations in WB. Predicted concentrations were based on a Ca- SO_4 end-member mixing analysis to determine flow path contribution and the nutrient and DOC concentrations determined for different flow paths. The solid line is for the flow path separation based on mean flow path chemistry (Table 1), and the dotted lines are for two alternative analyses evaluating effects of uncertainties in flow path chemistry: (1) a flow path separation based on bedrock flow path Ca of 32 mg/L and SO_4 of 1.6 mg/L and (2) predicted stream concentrations using NO_3 and SRP concentrations of mean minus standard deviation for vadose and saturated zone flow paths, and DOC concentrations of mean plus standard deviation for all flow paths (see text). Stream samples collected during rainfall were not included in the analysis. Vertical shading denotes spring and autumn periods as defined in Figure 2. Breaks in the curves are the result of missing data on SO_4 concentration.

oxides in the mineral soil also strongly limits its concentration in soil drainage water [Wood *et al.*, 1984].

Variation in the importance of different flow paths, either between catchments or temporally within a catchment, has been shown to be a primary contributor to variation in major ion chemistry and the acid/base status of streams [Hooper *et al.*, 1990; Ross *et al.*, 1994; Rice and Bricker, 1995]. In catchments where the dominant subsurface flow paths are relatively shallow (laterally through the upper soil layers), drainage waters are often more acidic due to the lack of base cations and

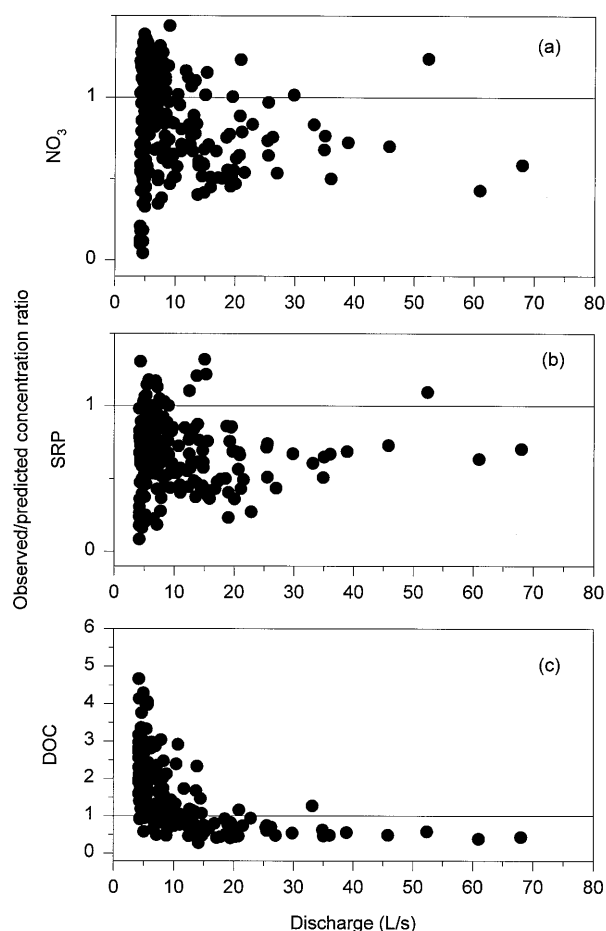


Figure 7. Observed/predicted ratios of NO_3 , SRP, and DOC concentrations in WB plotted against stream discharge.

alkalinity contributed by bedrock weathering. For nutrients, seasonal variation in forest stream concentrations have been attributed to seasonal variations in nutrient uptake by terrestrial vegetation [Foster *et al.*, 1989]. However, few studies have explicitly examined the effect of catchment flow path variation on stream water nutrient concentrations. Pringle *et al.* [1993] showed that geothermal groundwater flow paths account for

Table 2. Ratios of Observed/Predicted Annual Fluxes of NO_3 , SRP, and DOC for Walker Branch Calculated From the Weekly Measured and Predicted Concentrations and the Stream Discharge at the Time of Sampling

Year	Flux Ratio		
	NO_3	SRP	DOC
1991	1.04	0.70	0.98
1992	0.89	0.69	1.17
1993	0.80	0.67	0.97
1994	0.71	0.70	0.61
1995	0.73	0.64	0.92
5-year mean (S.D.)	0.83 (0.14)	0.68 (0.03)	0.93 (0.20)

The ratios are observed or predicted concentration multiplied by discharge and summed over the annual period. Only dates for which both measured and predicted concentrations were available were included in these analyses. Samples during rainfall were excluded from the analyses. S.D., standard deviation.

much of the spatial variation in stream SRP concentrations in one area of Costa Rica. *Peters* [1994] showed that stream water NO_3 concentrations rose during July storms at Panola Mountain, Georgia, presumably because of an increase in the importance of surface flow paths and leaching of nitrate that had accumulated in the upper soil during the preceding dry periods when uptake by vegetation was reduced. Our results from Walker Branch indicate that variation in the relative importance of different catchment flow paths, particularly shallow lateral flow through the upper soils and deep flow that permits geochemical interaction with the bedrock, can result in substantial temporal variation in streamwater nutrient concentrations. However, our results differ from those of *Peters* [1994] in that the shallow flow path in WB contains the lowest nutrient concentrations.

The spring and autumn minima in stream NO_3 and SRP concentrations evident in both WB and WOC appear to be the result of in-stream processes. Consistent minima in observed/predicted concentration ratios during early spring and late autumn in WB (generally <0.6) suggest that there is considerable in-stream net immobilization of the NO_3 and SRP supplied by drainage water from the catchment at these times. In streams draining deciduous forest catchments, spring and autumn are likely to be the periods of most intense biological demand for nutrients. Light levels in the stream are highest in the spring just prior to emergence of the canopy leaves (Figure 1) and blooms of filamentous algae (e.g., *Batrachospermum* sp.) are commonly observed in WB and WOC during March through the middle of May. Primary production in WB [Marzolf *et al.*, 1994] and WOC (W. R. Hill *et al.*, manuscript in preparation) is highest during March and April, presumably resulting in higher nutrient uptake by algae at this time. In midautumn, leaf fall provides a source of organic matter with low nutrient/carbon ratios to the stream, thus increasing the demand for stream water nutrients by the fungi and bacteria that rapidly colonize and decompose the leaves.

The results presented here support the findings of previous studies in WB. Nutrient mass balances computed at monthly intervals across a 140-m segment showed large net uptake of inorganic N and P during the autumn, winter, and spring and net release during summer [Mulholland, 1992]. Experiments involving injections of radioactive PO_4 tracers to stream water have shown very high rates of uptake and very short PO_4 uptake lengths after leaf fall in autumn and much lower uptake rates and longer uptake lengths in summer [Mulholland *et al.*, 1985; Mulholland *et al.*, 1990a]. D'Angelo and Webster [1991] found the same seasonal pattern in PO_4 uptake length for streams at the Coweeta Hydrologic Laboratory in North Carolina. McDowell and Asbury [1994] reported that periods of higher leaf litter input to a forest stream in Puerto Rico were associated with lower stream water concentrations of NO_3 . Sharp longitudinal declines in SRP concentrations downstream from large springs in WB, presumably due to biological uptake, were observed during autumn and spring but were absent in summer [Mulholland and Rosemond, 1992].

The seasonal pattern of nutrients in WB and WOC contrasts sharply with the seasonal pattern observed in deciduous forest streams at higher latitudes, suggesting differences in flow path dynamics or in-stream processes with latitude. Streams in the White Mountains of New Hampshire [Vitousek, 1977], the Catskill Mountains of New York [Murdoch and Stoddard, 1992], and the Turkey Lakes Watershed of Ontario [Foster *et al.*, 1989] all have maximum NO_3 concentrations during the

winter or early spring with no evidence of spring and autumn minima. Winter maxima and summer minima in stream nitrate concentrations have been attributed to the effect of seasonal differences in nitrogen uptake by the deciduous forest, and this pattern forms the foundation of the proposed framework for evaluating nitrogen saturation in forested catchments [Aber *et al.*, 1989; Stoddard, 1994]. In contrast to the northern pattern, but similar to that for the Oak Ridge streams, winter minima and summer maxima in NO_3 concentrations were observed in a stream draining an undisturbed control watershed at Coweeta, North Carolina [Swank, 1988]. Nitrate concentrations remained very low during all seasons in streams draining Panola Mountain in the Piedmont region of Georgia, although increases during storms were observed [Peters, 1994].

We suggest that there is a fundamental difference between northern and southern temperate forest streams in the seasonality of nutrient concentrations. In northern forest streams the temporal nutrient patterns appear to be largely controlled by seasonality in uptake by the deciduous terrestrial vegetation (i.e., high uptake rates during summer growth and low uptake during winter dormancy). However, in southern forest streams nutrient concentrations are influenced by year-round uptake in catchment soils (particularly uptake by soil heterotrophs) and by in-stream uptake associated with seasonally pulsed algal growth and litter decomposition. Higher concentrations during the summer in southern streams are primarily a result of a greater importance of deeper groundwater flow paths, the concentrating effects of low discharge, and in-stream nutrient regeneration rates that exceed in-stream nutrient uptake at this time of low algal growth rates and low inputs of fresh detritus.

The seasonal pattern in DOC concentration in WB was considerably more variable than those for NO_3 and SRP, although autumn maxima were observed in most years (Figure 2). The autumn DOC maxima were likely a result of net in-stream production of DOC as suggested by relatively high observed/predicted concentration ratios at this time (Figure 6). Relatively high summer observed/predicted DOC ratios suggest that in-stream production of DOC was also an important determinant of stream water DOC at this time as well. Winter observed/predicted ratios for DOC were closer to 1, suggesting that catchment processes were the primary determinant of stream water DOC in winter.

In general, temporal and spatial variations in stream DOC concentrations have been attributed largely to catchment hydrological and biogeochemical processes [Mulholland, 1997], although McKnight and Bencala [1990] showed that in-stream sorption of DOC to iron and aluminum oxides on the streambed can be substantial in acidic streams. Stream DOC concentrations have been positively linked to the relative importance of surface and shallow subsurface flow paths through organic-rich soils and sediments, either as a result of inputs from areas with high water tables such as wetlands and riparian soils [Eckhardt and Moore, 1990; Fiebig *et al.*, 1990] or shifts in the dominant flow paths from deeper routing of drainage water to shallow lateral flow during storm events or snowmelt [McDowell and Wood, 1984; Hornberger *et al.*, 1994]. Our results suggest that in-stream production of DOC can also be an important determinant of stream DOC concentration. In-stream production of DOC by algae can result in diel fluctuations in stream DOC concentrations [Kaplan and Bott, 1982], but the lack of maxima in observed/predicted DOC concentrations in spring (Figure 6), when algal production is maximum [Marzolf *et al.*, 1994], suggests little effect of algae on stream

water DOC concentrations in WB. Feeding by invertebrate detritivores can produce DOC in streams [Meyer and O'Hop, 1983], and it is likely that this process as well as physical leaching of fresh leaf litter entering the stream was responsible for the autumn DOC maxima in WB.

The approach that we used to separate the effects of catchment and in-stream processes on nutrient and DOC concentrations in WB was based on the assumption that the end-member mixing analysis provides a reasonable estimate of stream concentrations expected if only catchment processes were important. Convergence of observed/predicted ratios toward 1 at high stream discharge, particularly for SRP and DOC (Figure 7), supports this assumption. We would expect that at high discharge, in-stream processes would tend to be less important regulators of streamwater concentrations because shorter water residence times and lower surface/volume ratios within the stream channel should reduce the effect of in-stream biological processes. Our approach also relies on accurate estimates of nutrient and DOC concentrations for each flow path and that these be relatively constant. We are relatively confident in our estimates of nutrient and DOC concentrations in vadose zone and bedrock zone flow paths because they are based on numerous samples over extended periods of time. A "flushing effect" that results in declining DOC concentrations in soil water and stream water over time during snowmelt has been reported for some catchments [Hornberger *et al.*, 1994; Boyer *et al.*, 1996]. However, extended periods of high runoff do not appear to produce a similar flushing effect in WB, as indicated by equally high DOC concentrations in vadose zone water during two large, successive storms (within a 7-day period) during 1989 [Mulholland *et al.*, 1990b].

We are somewhat less confident about nutrient and DOC concentrations in the saturated zone flow path because these are based on only four samples (Table 1). Nonetheless, the measured NO_3 , SRP, and DOC concentrations for the saturated zone flow path were consistent with our expectations, which were based on known physical characteristics of the catchment. We expected SRP concentrations in the saturated zone flow path to be more similar to concentrations in the vadose zone than those in the bedrock zone because the saturated zone Ca concentrations indicated very little interaction between this flow path and the bedrock. Also, we expected the saturated zone DOC concentrations to be more similar to DOC concentrations in the bedrock zone than concentrations in the vadose zone because water in the saturated zone has passed through much of the DOC-adsorbing portion of the soil profile (B horizon). Finally, when we recalculated predicted stream water concentrations using more extreme values for flow path chemistry based on variation in the measurements, the dominant seasonal patterns in observed/predicted concentration ratios remained the same. Thus the results of our mixing analyses appear to be robust, despite some uncertainty in flow path chemistry.

The observed/predicted annual flux analyses suggested that in-stream processes resulted in net removal of about 17% of the NO_3 flux from the catchment to the stream and net removal of about 32% of the SRP flux from the catchment to the stream in WB (Table 2). It is likely that stream nutrient storage is in approximate steady state over annual periods, and the in-stream reductions in NO_3 and SRP fluxes were probably offset by increases in the flux of organic forms of these nutrients or, in the case of NO_3 , denitrification loss. Increases in the ratio of organic/total N and P concentrations from upstream to

downstream have been observed in previous studies of WB [Mulholland, 1992], suggesting net conversion of inorganic to organic fluxes of nutrients.

In conclusion, our results show that catchment flow path dynamics and in-stream uptake and release of nutrients and DOC strongly influence the concentrations of these solutes in streams. Seasonality in catchment flow paths and in-stream processes resulting primarily from the phenology of terrestrial vegetation and stream algal and microbial communities can produce consistent annual patterns of nutrient and DOC concentrations in forest streams.

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