

Spatial and temporal patterns of dissolved nitrogen and phosphorus in surface waters of a multi-land use basin

Daniel M. Evans · Stephen H. Schoenholtz ·
Parker J. Wigington Jr · Stephen M. Griffith ·
William C. Floyd

Received: 24 April 2013 / Accepted: 5 September 2013 / Published online: 18 September 2013
© Springer Science+Business Media Dordrecht 2013

Abstract Research on relationships between dissolved nutrients and land-use at the watershed scale is a high priority for protecting surface water quality. We measured dissolved nitrogen (DN) and ortho-phosphorus (P) along 130 km of the Calapooia River (Oregon, USA) and 44 of its sub-basins for 3 years to test for associations with land-use. Nutrient concentrations were analyzed for spatial and seasonal patterns and for relationships with land-use and stream discharge. Ortho-P and DN were higher in lower-elevation sub-basins dominated by poorly drained soils and agricultural production compared with higher-elevation sub-basins dominated by well-drained soils and forests. Eight lower basins had at least one sample period with nitrate-N > 10 mg L⁻¹. The Calapooia River had lower concentrations of dissolved nutrients compared with lower sub-basins, often by an order of magnitude. Dissolved organic N represented a greater proportion of DN in the upper forested sub-basins. Seasonal nutrient concentrations had strong positive correlations to the percent of a sub-basin that was managed for agriculture in all seasons

(*p* values ≤ 0.019) except summer. Results suggest that agricultural lands are contributing to stream nutrient concentrations. However, poorly drained soils in agricultural areas may also contribute to the strong relationships that we found between dissolved nutrients and agriculture.

Keywords Surface waters · Dissolved nutrients · Land management · Dissolved nitrogen · Phosphorus · Multi-land use · Landscape scale · Rivers · Streams

Introduction

Surface water quality is a growing concern in Oregon's Willamette River Basin because 70 % of Oregon's expanding population lives within this basin and relies on surface waters for market and non-market amenities. Research addressing nutrients in global surface waters and their relationship with land-use is a high priority, particularly in basins with a predominance of

D. M. Evans (✉)
Dept. of Crop and Soil Environmental Sciences, Virginia Tech, 330 Smyth Hall, Blacksburg, VA 24061, USA
e-mail: daniel76@vt.edu

S. H. Schoenholtz
Virginia Water Resources Research Center, Virginia Tech, 210 Cheatham Hall, Blacksburg, VA 24061, USA
e-mail: stephen.schoenholtz@vt.edu

P. J. Wigington Jr
US-EPA, 200 S.W. 25th St, Corvallis, OR 97333, USA
e-mail: wigington.jim@epa.gov

S. M. Griffith
USDA-ARS, 3450 SW Campus Way,
Corvallis, OR 97330, USA
e-mail: Steve.Griffith@ars.usda.gov

W. C. Floyd
Ministry of Forests, Lands and Natural Resource
Operations, 2100 Labieux Rd,
Nanaimo, BC V9T 6E9, Canada
e-mail: william.floyd@gov.bc.ca

agriculture and forestry, which have the potential to increase surface water nutrient levels (Binkley and Brown 1993; Jordan et al. 1997; Dinnes et al. 2002). Nitrogen (N) and phosphorus (P) often limit productivity of aquatic ecosystems. Consequently, increases of the inorganic, more bio-available forms of N and P above background levels can lead to growth of nuisance algae and aquatic plant growth, often resulting in negative impacts to surface waters such as eutrophication (Nixon 1995; US-EPA 1996; Carpenter et al. 1998; Bennett et al. 2001).

Land-use has been linked to export of N and P into aquatic systems (Bonn et al. 1996; Jordan et al. 1997; Howarth et al. 2002; Wernick et al. 1998; Donner et al. 2004; Brett and Hartley 2005; Pellerin et al. 2006). Strong positive relationships are often noted between amount of agriculture in a basin and surface water nutrient concentrations (Dillon and Kirchner 1975; Johnson et al. 1997; Howarth et al. 2002; Pellerin et al. 2006; Poor and McDonnell 2007; Floyd et al. 2009). However, few studies address these relationships in multiple land-use settings in western North America. The Willamette Basin is distinct from more highly studied watersheds, such as the Chesapeake Bay and Mississippi River Basins, because of a unique climate, low atmospheric deposition of nutrients (NADP, National Atmospheric Deposition Program, <http://nadp.sws.uiuc.edu/data/>), and prevalence of poorly drained soils in the lower area of the basin.

This study was conducted in the Calapooia River Basin, a major tributary within the greater Willamette Basin. The Calapooia Basin has a similar mix of land uses as the Willamette Basin and has been reported to have high dissolved nutrient levels in the main river channel (Bonn et al. 1996; ODEQ 1996; Floyd et al. 2009). Forestry and agriculture, particularly grass seed production, are the primary land uses, with rural residential and urban development as minor components. The objectives of this study were to (1) perform basin-wide synoptic sampling of dissolved nitrogen (DN) and ortho-P in the Calapooia River and its tributaries, (2) analyze for spatial and temporal trends in these concentrations, and (3) determine the areas in the basin that are likely contributing relatively high levels of nutrients to surface waters. Sampling at biweekly to monthly intervals was maintained for three water years (2004–2006) to address seasonal and annual variations of dissolved nutrients and to evaluate associations between land-use, soils, stream discharge, and dissolved nutrient concentrations in 44 independent sub-basins within the Calapooia River Basin.

Methods

Site description

The Calapooia River, spanning 130 km and draining 966 km², flows westward out of the western Cascade Mountains in the southern Willamette River Basin, a region with generally dry, hot summers and cool, wet winters. Atmospheric N deposition is low (1–3 kg N ha⁻¹ year⁻¹) due to the lack of large anthropogenic sources between the basin and the Pacific Ocean (NADP, National Atmospheric Deposition Program, <http://nadp.sws.uiuc.edu/data/> (verified Feb. 10, 2011)). The Calapooia Basin has a distinctly different climate, as well as land-use, geology, and stream morphology in its lower versus upper reaches. Average yearly precipitation in the lower Calapooia Basin is 914 mm and in the upper is 1,524 mm with 80 % occurring from October through March (Woodward et al. 1998; Urich and Wentz 1999). The lower Calapooia Basin is generally flat with average slopes ranging from 0 to 5 %, low perennial stream drainage densities, and mean river gradients of 0.11 %, with sections of constrained and unconstrained, braided river channels. Grass seed grown in concert with sheep grazing is the primary management regime with a few cattle and poultry operations. Rural residential housing and small towns are prevalent in the lower Calapooia Basin. Poorly drained soils comprised of well-sorted, fine sediments dominate the lower Calapooia Basin (Table 1). The upper Calapooia Basin is comprised of steep, well-defined hillslopes with a mean river gradient of 2.4 % and a generally constrained river channel. The geology in the upper Calapooia Basin is comprised of weathered volcanic rock, such as basalts, andesites, and tuffs with well-drained rocky soils. The primary land-use is timber production by private enterprises with short-rotation (~40 years) Douglas-fir (*Pseudotsuga menziesii*) management using clearcutting as the primary silvicultural treatment. Fertilization of these forest stands is common, though fertilization is not known to have occurred during our study period. The uppermost reaches of the basin are owned and managed by the U.S. Forest Service for multiple uses with recreation trails, remnant mixed old-growth forest stands, and long-rotation forest management. The geology in the upper Calapooia Basin is comprised of weathered volcanic rock, such as basalts, andesites, and tuffs with well-drained rocky soils.

Field methods

A basin-wide synoptic water-quality sampling regime was conducted for three water years starting in October of 2003 and ending in September of 2006, including 41 sample runs. Seventy-five sampling sites were selected to cover the range of land uses in the Calapooia Basin (Fig. 1) with 31 on the mainstem of the river and 44 at the outlets of independent tributaries (Floyd 2005; Evans 2007; Floyd et al. 2009). All sites were sampled between storms on a bi-weekly to monthly basis to capture seasonal baseflow conditions. Samples were collected in acid-washed, 250-ml plastic bottles within a 10-h period to ensure similar flow conditions for each sample. Samples were collected using a weighted depth-integrated rope sampler or a grab sample technique. River sections that were >10 m in width had multiple samples taken across the channel that were then composited and sub-sampled in the field.

Laboratory methods

Water samples were stored at 4 °C if analyzed within 48 h of sampling or frozen at –20 °C if analyzed after 48 h. Before analysis, samples were vacuum filtered using 0.45 µm filters. Total nitrogen (TN) was analyzed using a PC-controlled total organic carbon analyzer using the catalytic thermal decomposition and chemiluminescence method (Shimadzu Corp., Kyoto, Japan) with a minimum detection limit of 0.04 mg N L⁻¹. Nitrate-N, ammonium-N, and ortho-P were analyzed using a Lachat Quick Chem 4200 analyzer (Lachat Instruments, Loveland, Colorado). Minimum detection limits for nitrate- and ammonium-N for the Lachat were 0.1 mg N L⁻¹ from October 2003 through February 2004 and 0.04 mg N L⁻¹ thereafter. Minimum detection limits for ortho-P were 0.01 mg P L⁻¹. We use a conservative approach and report the detection limit whenever a measured value is below detection limit. Dissolved organic nitrogen (DON) was calculated by subtracting nitrate-N and ammonium-N from TN.

Land-use and stream discharge

The percent of each sub-basin in agriculture (%AG) was estimated using 30-m Landsat imagery provided by the Pacific Northwest Ecosystem Research Consortium (PNW-ERC, available at www.fsl.orst.edu/pnwerc/wrb/access.html). Percent area of sub-

basin in agriculture includes grass seed, row crops, orchards, nurseries, pasture, hay fields, and Christmas tree farms. Percent of sub-basins with woody vegetation (%WV) was delineated using higher resolution 30-cm ortho-rectified airphotos flown in the spring of 2000 by Linn County, OR. Poorly drained soils were delineated using the STATSGO and SSURGO databases provided by the PNW-ERC. We used soil hydrogroup D, defined as having a high water table or shallow depth to impervious layers, fine texture, and a high clay content, to delineate poorly drained soils (%PD). Because discharge data were not available for the Calapooia River during our study period, discharge at Wiley Creek (134.2 km²), the nearest gauged stream adjacent to the Calapooia Basin, was used for an estimate of reference discharge over the course of the study and is heretofore referred to as discharge (United States Geological Survey; <http://water.usgs.gov/data/>). Precipitation data were gathered from the nearest long-term climate station at Cascadia, OR (Natural Resources Conservation Service; <http://www.wcc.nrcs.usda.gov/cgibin/precip.pl?state=oregon>). Annual mean precipitation for Cascadia, OR, based on 30 years of record is 1,640 mm. The 2003–2004 water year was near average with 1,630 mm of precipitation. The 2004–2005 water year was drier, with 35 mm less precipitation than the 30-year mean and a few substantial spring storms. The 2005–2006 water year was 29 mm wetter than the 30-year mean with a series of strong late fall storms and an average spring. These precipitation patterns are apparent in the discharge at Wiley Creek observed during the study period (Fig. 2).

Data analysis

Seasonal mean DN concentrations in the mainstem of the Calapooia River and the 44 sub-basins were examined for spatial and temporal trends. Seasons were defined as 3-month periods beginning with the start of the water year on October 1st. Associations between seasonal concentrations of dissolved nutrients and land-use/land-cover were examined using Pearson's correlation coefficients. Preliminary analysis revealed strong associations (p values<0.0001) between %AG and %WV ($r=0.95$) and between %AG and %PD ($r=0.85$). Due to the strength and linearity of these associations, we use %AG as the explanatory variable for correlation analysis. It is important to note that, within

Table 1 Independent sub-basin characteristics in the Calapooia River Basin, Oregon

Site ID	Elevation (m)	Basin area (km ²)	% Woody vegetation	% Agriculture	% Poorly drained soils
1	745.4	13.38	100.0	0.0	0.0
2	754.3	4.94	100.0	0.0	0.0
4	662.9	3.93	100.0	0.0	5.1
6	547.1	15.38	100.0	0.0	2.9
12	537.5	3.73	100.0	0.0	10.8
15	425.5	3.46	100.0	0.0	6.2
16	424.3	8.61	100.0	0.0	2.6
18	409.6	7.19	100.0	0.0	0.0
23	360.1	5.00	100.0	0.0	0.0
26	0.0	7.86	100.0	0.0	4.6
27	364.0	4.64	100.0	0.0	0.0
28AA	284.0	6.48	100.0	0.0	1.6
29	283.5	5.71	100.0	0.1	7.4
30	277.5	9.38	100.0	0.0	9.2
47	280.1	4.32	100.0	0.0	23.0
48	234.4	3.12	100.0	0.0	0.0
50	177.5	7.52	98.3	1.8	0.0
51	172.4	3.97	93.9	6.2	2.1
55	167.6	6.89	79.3	19.7	1.2
56	164.3	8.49	72.7	27.3	14.5
57	191.9	13.42	32.7	67.1	11.3
59	151.3	12.38	92.8	7.2	14.8
64	140.5	5.26	93.8	6.3	1.3
65	117.2	3.06	52.4	47.6	2.6
67	118.1	18.34	93.6	6.5	34.0
70	74.1	7.69	0.8	98.7	19.2
71	58.8	14.03	10.4	88.6	34.2
63A-1	179.7	19.51	99.6	0.5	43.0
63X	154.7	16.69	94.0	6.1	60.6
68A	79.2	28.47	31.1	20.6	79.1
68B	82.6	26.67	14.8	44.1	62.2
68C	75.3	15.67	2.6	91.9	70.3
68H	84.2	15.44	7.6	74.6	22.8
68I	75.8	3.39	0.2	99.8	86.0
69A	129.4	23.63	96.3	3.8	94.5
69C	84.7	22.59	8.7	90.8	81.1
69D	100.8	27.89	3.8	95.0	77.6
72A	74.9	9.79	1.0	97.9	83.0
73A	70.8	7.89	1.3	98.7	57.9
74A	69.8	7.25	1.1	98.1	85.3
74B	66.9	9.99	1.3	98.3	83.6
75A	83.8	32.22	72.4	27.5	26.0
75C	83.3	16.99	3.7	90.5	67.3
75D	66.0	21.02	3.2	94.1	70.0

Area not in agriculture or woody vegetation is urban or sub-urban development. Site ID letters indicate independent sub-drainages

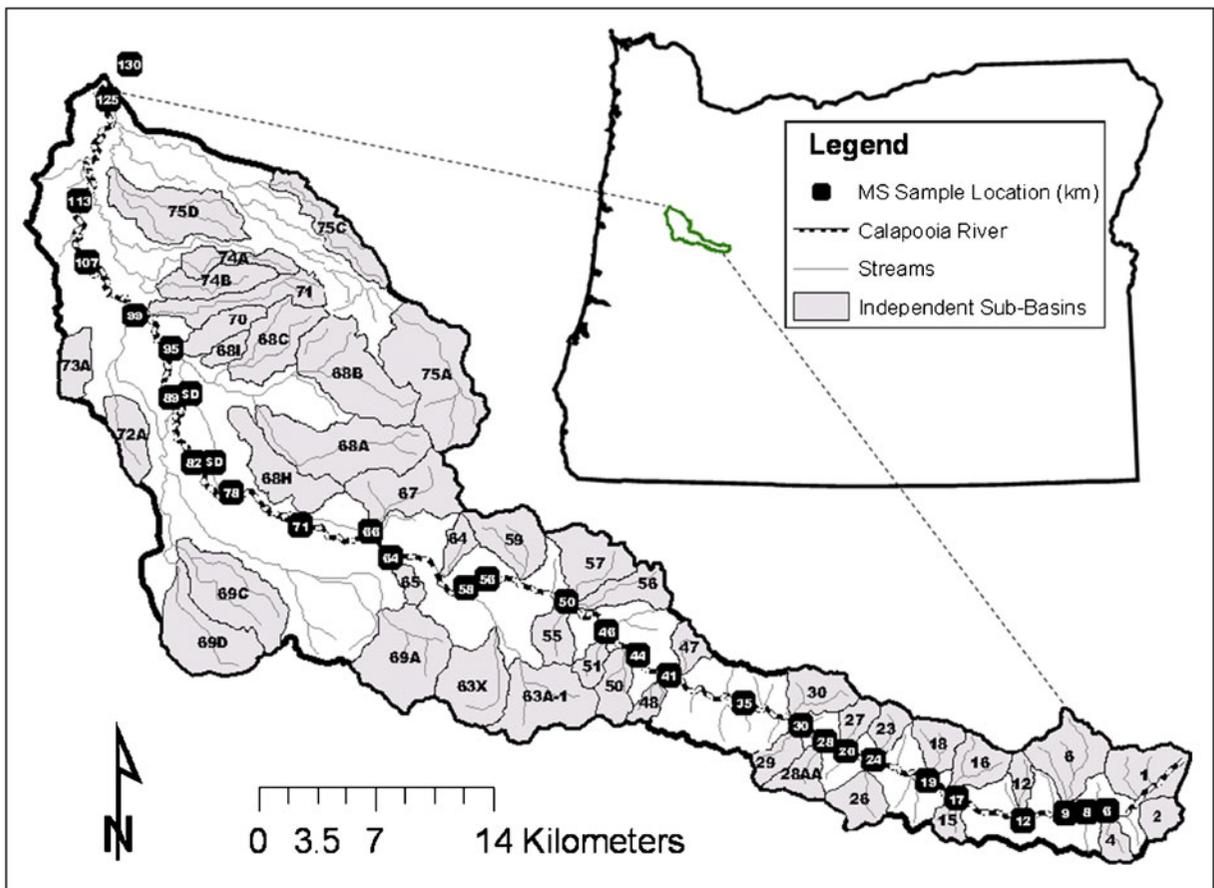


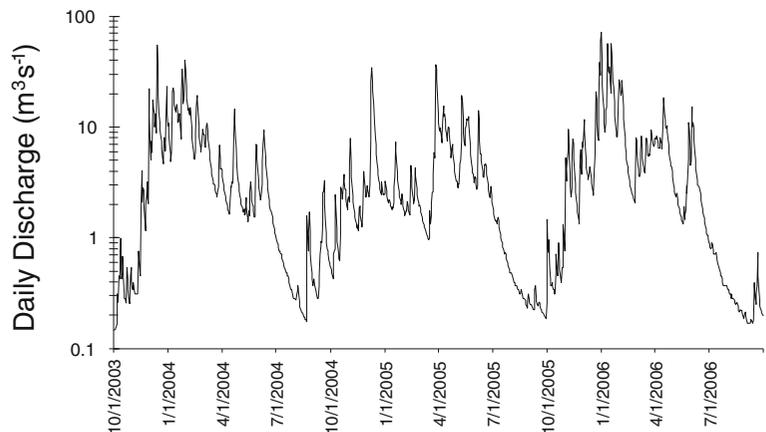
Fig. 1 Location of the Calapooia River Basin in Oregon and synoptic sampling points on the mainstem (MS) of the Calapooia River and 44 sub-basins

the Calapooia Basin, the flat, poorly drained soils have developed in low-lying areas where agricultural operations are predominant and pre-existing vegetation has been removed. Therefore, any results addressing associations between %AG and dissolved nutrients

may be influenced by relationships among %PD, %WV, and %AG.

Because precipitation trends and seasonal flow regimes may affect dissolved nutrient concentrations, we conducted a series of simple linear regression analyses

Fig. 2 Wiley Creek mean daily discharge for 3-year study period



intended to describe the relationship between dissolved nutrient concentrations and stream discharge and to explore the predictive value of stream discharge on concentration of dissolved nutrients. We used reference discharge at the time of sampling (daily mean) to predict stream nutrient concentrations in two classes: sub-basins dominated by agriculture ($\geq 90\%$ of area) or sub-basins dominated by woody vegetation ($\geq 90\%$ of area). Eleven sub-basins were dominated by agriculture, and 24 were dominated by woody vegetation. Nine were intermediate and were not used for this analysis.

Results

Dissolved nitrogen

Strong temporal trends and spatial patterns are evident in the DN concentrations in 44 sub-basins of the Calapooia River (Fig. 3). During the fall and winter in the lower Calapooia Basin, mean seasonal TN concentrations exceeded 10 mg L^{-1} in nine sub-basins and peaked above 14 mg L^{-1} during two water years. Ammonium-N rarely exceeded detection limits in the sub-basins above 68B and 68C and was a small component of TN for all sub-basins during all seasons and years, except for three agriculturally dominated lower sub-basins. Nitrate-N concentrations increased notably below sub-basin 64. Above this sub-basin, nitrate-N concentrations were consistently $<0.5 \text{ mg L}^{-1}$ with most measurements $<$ detection limits. In fall and winter months at locations below sub-basin 64, nitrate-N concentrations were higher, with eight lower basins having at least one sample period with nitrate-N exceeding the US Environmental Protection Agency surface drinking water guideline for nitrate-N of 10 mg L^{-1} (US-EPA 1996).

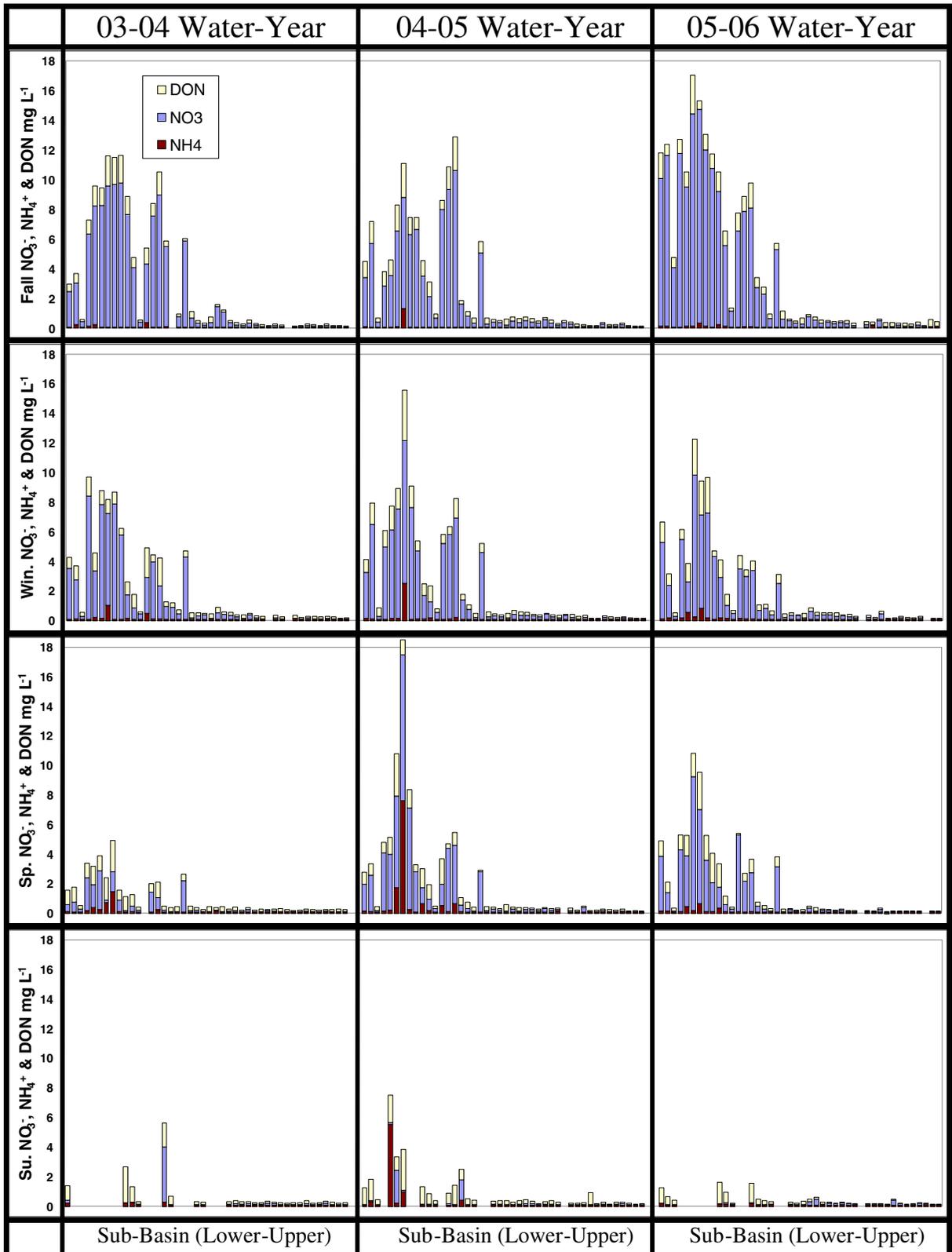
Dissolved organic N did not have a clear seasonal trend in the sub-basins (Fig. 3), but it did have a spatial pattern. Concentrations of DON above sub-basin 64 were low with values rarely exceeding 0.20 mg L^{-1} . Below sub-basin 64, DON concentrations were higher with mean seasonal values often exceeding 1.0 mg L^{-1} . Ratios of DIN/DON varied across the sub-basins, with higher DIN/DON ratios occurring in the lower sub-basins than in the upper sub-basins in the fall, winter, and spring, indicating that DIN dominates in the lower sub-basins and DON provides a relatively larger contribution of DN in the upper sub-basins.

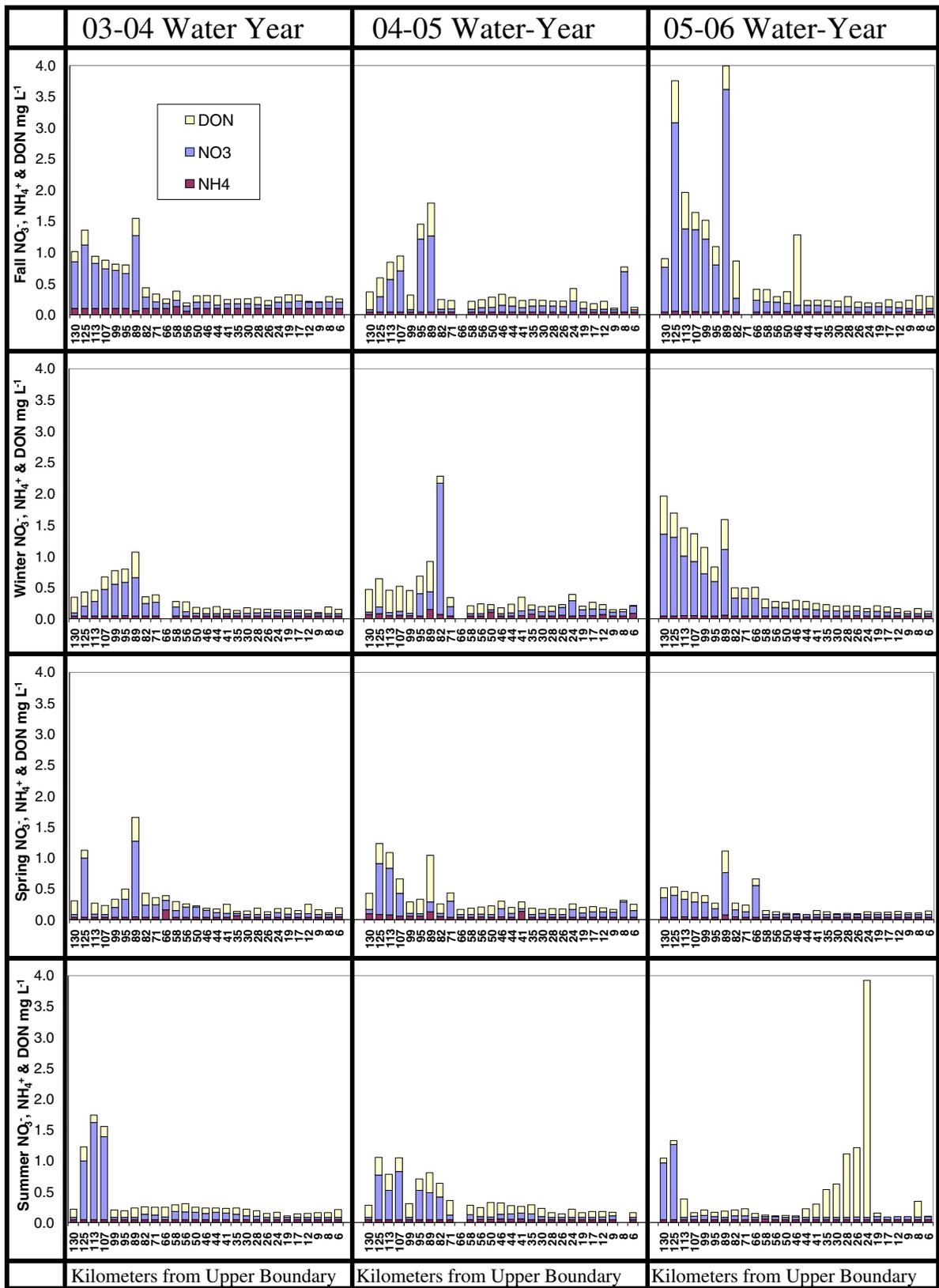
Fig. 3 Total dissolved nitrogen (DN), dissolved organic N (DON), ammonium-N, and nitrate-N concentrations averaged per season (Summer (Su), Spring (Sp), Winter (Win), Fall) for three water years in 44 sub-basins of the Calapooia River, Oregon. Each bar represents an independent sub-basin graphed in order from the bottom of the watershed on the left side of each graph. Total DN is represented by the total height of each bar

Strong temporal and longitudinal trends were also evident for DN concentrations in the mainstem of the Calapooia River (Fig. 4). Concentrations of TN in the lower reaches were consistently an order of magnitude less than sub-basins that discharge to it. The upper reaches of the Calapooia River had TN concentrations that were lower (often by an order of magnitude) when compared with the lower reaches. Peak TN values occurred below river km 89 with mean seasonal concentrations between 0.5 and 4.0 mg L^{-1} in the fall and winter. Maximum individual measurements of 8.64 mg L^{-1} at river km 89 in the fall of the 2005–2006 water year and 11.58 mg L^{-1} at river km 24 in the summer of the 2005–2006 water year were observed.

Nitrate-N comprised the largest component of TN in the Calapooia River, particularly in the lower sections of the river (Fig. 4). Nitrate-N concentrations were consistently higher in the lower sections of the river for all seasons and all years with peak values occurring in the fall and winter. The highest measured concentration for nitrate-N in the mainstem of the river was 7.67 mg L^{-1} in the fall of the 2005–2006 water year at river km 125. Nitrate-N concentrations increased substantially below river km 82 and 89 in the fall, winter, and spring.

In the mainstem of the Calapooia River, ammonium-N rarely exceeded detection limits above river km 89 in any season or year and was generally a small portion of TN at sample locations in the lower reaches (Fig. 4). Concentrations of DON were also low compared with nitrate-N, with higher DON concentrations in the lower reaches of the river and higher DON concentrations in the fall and winter periods compared with spring and summer (Fig. 4). One exception to this pattern occurred in the summer of 2006 when one sample period showed a notable spike of DON of 11.54 mg L^{-1} at river km 24, with reduction of this concentration evidenced at downstream sample points. Dissolved organic N contributed a greater portion of TN in the upper reaches of the river, where TN values were lower.





◀ **Fig. 4** Total dissolved nitrogen (DN), dissolved organic N (DON), ammonium-N, and nitrate-N concentrations averaged per season for three water years in the mainstem of the Calapooia River, Oregon. Each bar represents a location along the mainstem of the river graphed in order from the bottom of the watershed on the left side of each graph. Total DN is represented by the total height of each bar

Phosphorus

Mean seasonal ortho-P concentrations also showed distinct spatial patterns across the sub-basins of the Calapooia River, with higher values at lower sub-basins (Fig. 5). In all seasons and years, upper sub-basins mean seasonal ortho-P concentrations were lower than 0.02 mg L^{-1} with many at or near the detection limit of 0.01 mg L^{-1} . There were 28 instances of mean seasonal ortho-P concentrations exceeding 0.1 mg L^{-1} . Fall had ten sub-basins with at least one seasonal mean ortho-P $>0.1 \text{ mg L}^{-1}$, with five in winter and spring and eight in summer. All but three of these occurrences were in the lower sub-basins. Ortho-P concentrations were lower in the mainstem of the Calapooia River relative to the sub-basins that discharge to it, with 3-year mean ortho-P concentrations at the mainstem sample locations ranging from 0.011 to 0.023 mg L^{-1} and an overall 3-year mean of 0.012 mg L^{-1} (SE=0.0023). At the confluence with the Willamette River, the 3-year mean ortho-P concentration in the Calapooia River was 0.015 mg L^{-1} (SE=0.0024).

Nutrient associations with land-use and discharge

Nitrate-N, ammonium-N, DON, and ortho-P all had significant positive associations with %AG (Table 2). In fall, winter, and spring, nitrate-N increased as %AG increased in the sub-basins. Pearson correlation coefficients were all ≥ 0.79 for these seasons and were all significant (p values ≤ 0.0001). However, the association between %AG and nitrate-N was not significant in the summer months (p value=0.12). Ammonium-N and %AG had significant associations in all seasons with correlation coefficients ranging from 0.37 to 0.40 ($0.006 \leq p$ values ≤ 0.019). Dissolved organic N increased as %AG increased in all seasons and water years with correlation coefficients ≥ 0.84 (p values < 0.0001). Ortho-P also had significant positive correlations with %AG in all years (p values ≤ 0.01).

Reference stream discharge was a significant positive predictor of nitrate-N in our regression models for streams

dominated by either WV or AG (p values < 0.0001) (Table 3). Discharge was also a significant negative predictor of ortho-P in the AG-dominated streams (p value=0.005) but was not a significant predictor for ortho-P in WV-dominated streams or for ammonium-N and DON in either WV- or AG-dominated streams. Variability was high in all of the regression models with the all-model $R^2 \leq 0.079$.

Discussion

Dissolved nitrogen

The clear spatial patterns showing higher DN concentrations in the lower sub-basins of the Calapooia River Basin, which are dominated by agriculture, are consistent with similar studies addressing land-use and DN (Omernik 1976; Johnson et al. 1997; Brett and Hartley 2005; Pellerin et al. 2006; Floyd et al. 2009). The low concentrations of DN in the upper sub-basins are also consistent with the low DN concentrations and yields reported by Vanderbilt et al. (2003) in the H.J. Andrews Research Forest adjacent to the Calapooia Basin. One explanation for these low DN concentrations in the upper Calapooia sub-basins is that the soils in this system tend to be N-deficient and are often dominated by rock and coarse fragments (Evans et al. 2011). This leads to efficient utilization of available N in these forested systems with minimal leaching of N (Fredriksen 1972; Henderson et al. 1979; Vanderbilt et al. 2003). The lower concentrations of DN in the lower mainstem of the Calapooia River compared with sub-basins may be caused by a dilution effect of water with low DN concentration from the upper area of the Calapooia Basin mixing with waters of higher DN concentration in the lower sub-basins. With our data, we could not determine an explanation for the spike of DON in the summer of 2006 or higher DN concentrations in other seasons or years at river km 24, as this site is in a forested environment and no fertilization is known to have occurred.

We observed that, as reference discharge increases, nitrate-N concentrations generally tend to increase, which is supported by work in the Appalachian Mountains (Buffman et al. 2001) and in the Adirondack Mountains (McHale et al. 2000). This relationship may occur because of increased hydrological connection between the sources of nitrate-N in terrestrial

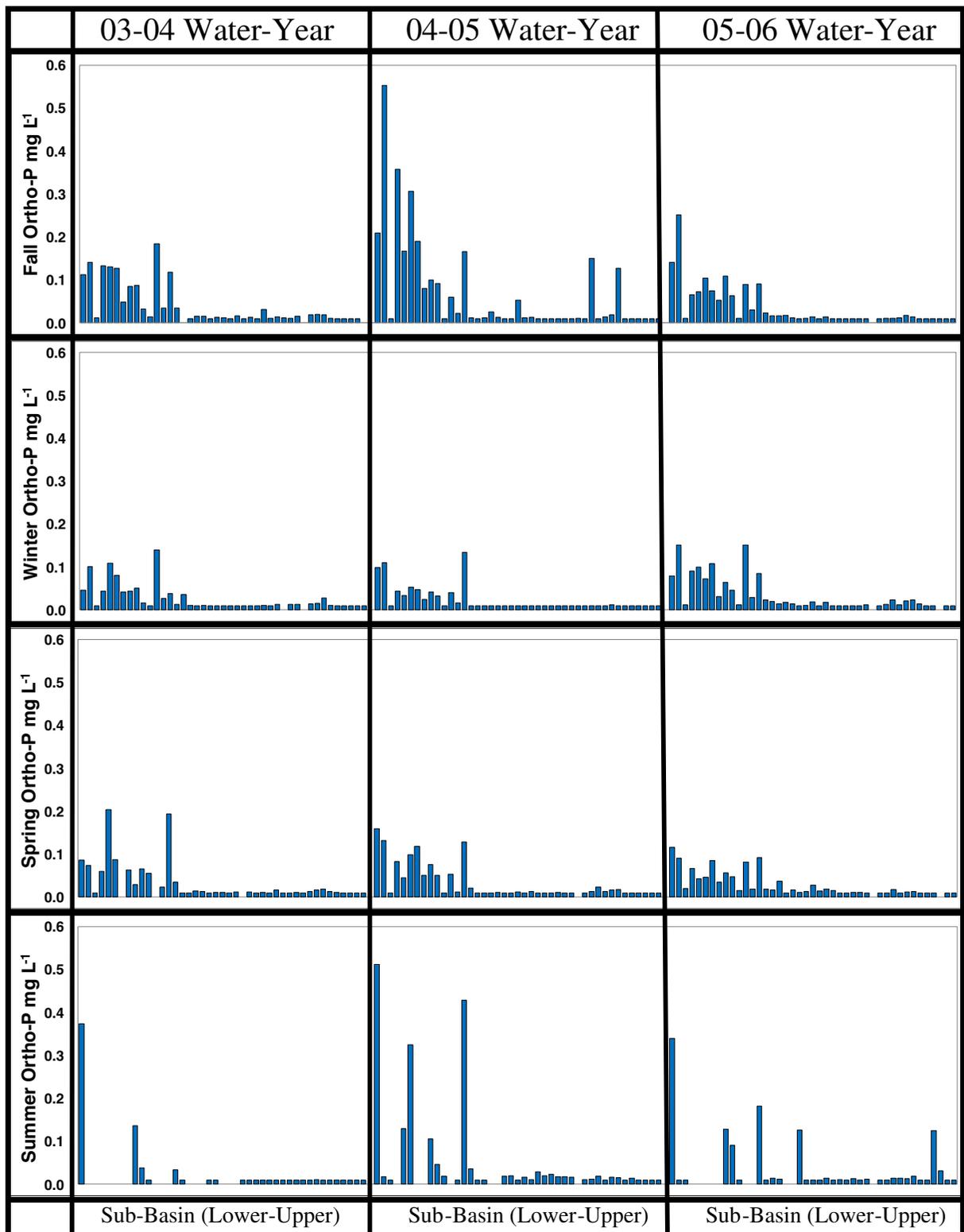


Fig. 5 Ortho-P concentrations averaged per season for three water years in the mainstem of the Calapooia River, Oregon. Each bar represents a location along the mainstem of the river graphed in order from the bottom of the watershed on the left side of each graph

Table 2 Pearson correlation coefficients describing associations between fraction of area of 44 independent sub-basins in agriculture and mean seasonal nutrient concentrations in the Calapooia River Basin, Oregon during 3 years

	Nitrate-N (mg L ⁻¹)	Dissolved organic N (mg L ⁻¹)	Ammonium- N (mg L ⁻¹)	Ortho-phosphorus (mg L ⁻¹)
Fall (<i>r</i> , (<i>p</i>), and <i>n</i> values)	r=0.91; <i>p</i> value=(<0.0001); <i>n</i> =44	0.90; (<0.0001); 44	0.40; (0.0077); 44	0.74; (<0.0001); 43
Winter (<i>r</i> , (<i>p</i>), and <i>n</i> values)	0.85; (<0.0001); 44	0.87; (<0.0001); 44	0.37; (0.0125); 44	0.55; (0.0001); 42
Spring (<i>r</i> , (<i>p</i>), and <i>n</i> values)	0.79; (<0.0001); 44	0.88; (<0.0001); 44	0.41; (0.0061); 44	0.38; (0.01); 42
Summer (<i>r</i> , (<i>p</i>), and <i>n</i> values)	0.26; (0.12); 38	0.84; (<0.0001); 38	0.38; (0.0194); 38	0.58; (0.0001); 33

systems that have accumulated during the dry summer months and the expanded surface water network that

develops during high precipitation and flow events (Hewlett and Hibbert 1967; Dunne and Black 1970).

Table 3 Regression models for mean daily reference stream discharge on 44 independent sub-basin nutrient concentrations measured monthly during 3 years

	Coefficient	Standard error	<i>p</i> value	<i>R</i> ²
Nitrate-N, AG dominated				
Intercept	3.000	0.332	<0.0001	
Discharge	0.207	0.048	<0.0001	0.053
Root mean square error				3.574
Nitrate-N, WV dominated				
Intercept	0.085	0.006	<0.0001	
Discharge	0.010	0.001	<0.0001	0.079
Root mean square error				0.142
Ammonium-N, AG dominated				
Intercept	0.224	0.065	0.0007	
Discharge	0.005	0.009	0.576	0.001
Root mean square error				0.700
Ammonium-N, WV dominated				
Intercept	0.042	0.001	<0.0001	
Discharge	0.00001	0.00001	0.951	0.00001
Root mean square error				0.019
DON, AG dominated				
Intercept	1.055	0.095	<0.0001	
Discharge	0.024	0.014	0.075	0.010
Root mean square error				1.028
DON, WV dominated				
Intercept	0.154	0.006	<0.0001	
Discharge	0.001	0.001	0.266	0.001
Root mean square error				0.123
Ortho-P, AG dominated				
Intercept	0.172	0.017	<0.0001	
Discharge	-0.007	0.002	0.005	0.025
Root mean square error				0.189
Ortho-P, WV dominated				
Intercept	0.015	0.001	<0.0001	
Discharge	-0.0002	0.0002	0.334	0.001
Root mean square error				0.026

N for woody vegetation-dominated (WV) is 886 samples and for agriculture-dominated (AG) is 310

DON dissolved organic nitrogen

The compounded effect of increased nitrate-N concentrations at periods of high discharge suggests that yield of DN from the Calapooia River into the Willamette River is greatest during the wet fall through spring months.

Dissolved organic N concentrations do not decrease as sharply as nitrate-N in the summer months, which is consistent with the work of Willett et al. (2004) in Wales and Arheimer et al. (1995) in Sweden and Finland. This may be due to increased biological activity in the summer months, leading to increased in-stream processing of particulate organic N (Arheimer et al. 1995). Low-flow conditions in the summer also allow for lesser amounts of DON to produce higher concentrations.

The relatively high proportion of DN contributed by DON in the upper Calapooia Basin is supported by research in the adjacent H.J. Andrews Research Forest. In a long-term study, Vanderbilt et al. (2003) found that DON was the predominant form of N that was exported in six small forested sub-basins. In a meta-analysis involving 348 watersheds across North America, Pellerin et al. (2006) found similar results showing that DON accounted for half of the DN in forested watersheds. In 100 streams in South America, Perakis and Hedin (2002) observed DON to be the primary form of N export in unpolluted forests. The primary hypothesis explaining the dominance of DON export in forested watersheds focuses on soil and stream processes favoring more rapid removal and transformation of DIN than DON (Vanderbilt et al. 2003).

We found higher DN concentrations and higher DIN/DON ratios in the lower sub-basins compared with the upper sub-basins, often by an order of magnitude. Therefore, the relative yield of N as DON from the upper sub-basins is quite small when compared with the yield of N as DON from lower sub-basins. Although DON concentrations increased in sub-basins in the lower Calapooia Basin, the proportion of DN that was comprised of DON decreased. The remainder of DN was comprised primarily of an increased proportion of nitrate-N in the lower sub-basins. This pattern was also reported by Pellerin et al. (2006) in a multi-continent meta-analysis. The increased levels of DN and DON are generally thought to come from increased N loading in agriculture- and urban-dominated sub-basins (Johnson et al. 1997; Pellerin et al. 2006) and from changes in hydrologic function that deliver DN to aquatic systems (Brett and Hartley 2005; Poor and McDonnell 2007).

The predominance of poorly drained soils in the lower Calapooia Basin may exacerbate these patterns by shifting hydrological flowpaths overland and delivering nutrients directly to surface waters during wet seasons (Wigington et al. 2005).

Ortho-phosphorus

In the upper forested sub-basins of the Calapooia River, mean ortho-P concentrations were at or slightly above detection limits of 0.01 mg P L^{-1} (Fig. 5). These values are consistent with the low ortho-P concentrations recorded in the adjacent undisturbed reference watersheds at the H.J. Andrews Experimental Forest with a mean of $0.022 \text{ mg P L}^{-1}$ (Martin and Harr 1988). Surprisingly, we also found that the mean ortho-P concentrations in the mainstem of the Calapooia River were near detection limits, even at the confluence with the Willamette River.

Because P is not a direct threat to human health in drinking water, a guideline based on avoiding nuisance plant and algae growth of 0.1 mg L^{-1} for total P (TP) has been promoted by the US-EPA (1986) and has generally been used as a standard for fresh surface waters (Bonn et al. 1996; Binkley and Brown 1993). Although we do not have TP measures, all of our upper sub-basins and mainstem sample points fall well below this guideline based on our ortho-P measures. In contrast, many of the Calapooia Basin's agriculturally dominated sub-basins had mean ortho-P values higher than this TP guideline. Yet, it is clear that these higher ortho-P concentrations in the lower sub-basins are effectively diluted upon mixing with the mainstem of the Calapooia River.

We observed increased concentrations of ortho-P in the lower sub-basins to the Calapooia River and strong, consistent correlations with %AG. This relationship has also been reported in the Pudding River Basin, another major tributary within the Willamette River Basin (Bonn et al. 1996) and in 34 watersheds in southern Ontario (Dillon and Kirchner 1975). Stream discharge was a significant negative predictor of ortho-P concentrations in streams dominated by agricultural land uses, which was not expected because of the tendency of P to move into stream systems adsorbed to eroded soil (Sharpley et al. 1993; Brett and Hartley 2005). Because water samples were collected at baseflow conditions, our sampling may have neglected higher concentrations of more mobile nutrients that

increased during storm events, thereby weakening the associations that we found between nutrients such as ortho-P and stream discharge.

Land-use and nutrients

The strong positive correlations between %AG and nutrient concentrations in Calapooia River sub-basins are similar to results found across North America (Bonn et al. 1996; Jordan et al. 1997; Brett and Hartley 2005; Pellerin et al. 2006; Poor and McDonnell 2007; Floyd et al. 2009). Causes of increased nutrient flux from agricultural systems are well documented, with tillage, artificial drainage, and fertilization as often-cited practices of concern. Tillage increases the amount of mineralization that occurs at a given site due to the general increase of microbial activity after tillage and the associated oxidation of soil organic matter (Randall et al. 1997; Dinnes et al. 2002; Nelson et al. 2006). Timing, type, and amount of fertilization with N- and P-containing compounds are relevant because of the possibility of nutrients in these compounds being delivered to surface water and shallow groundwater. Loss of N can occur when N-sinks such as vegetation and microbial uptake are inadequate to utilize or transform additional N (Griffith et al. 1997a, b; Dinnes et al. 2002). Loss of P can occur when pools of soil P are high or when surface soil erosion delivers P directly to streams (Sharpley et al. 1993; Brett and Hartley 2005). Installation of tile drains generally lowers the water table, which increases the oxygen content of soils and enhances conditions for nitrifying bacteria and accelerates delivery of DN to receiving waters (Warren 2002).

Research has also identified nutrient management concerns on a more local level that may play a role in the Calapooia Basin. Horneck and Hart (1988) noted that areas of the Willamette Valley of western Oregon are often fertilized at rates up to 30 % more than local extension service recommendations. Other local researchers have stressed the importance of timing for tillage and fertilization. Spring treatments have been recommended in preference to fall applications because of the late fall and winter rains in the Willamette Valley and subsequent likelihood to leach nitrate-N to groundwater and surface water in excess of system needs (Nelson et al. 2006). In the Willamette Basin, Griffith et al. (1997a) recommended balancing N application with needs of growing crops based on indices such as growing degree days, and Nelson et al. (2006) stressed the importance of balancing applications of fertilizer to

background levels of available N in soils caused by natural changes in N mineralization resulting from climatic and soil conditions. In a study conducted in the poorly drained soils of the lower Calapooia Basin, Wigington et al. (2003) supported these conclusions and stated that appropriate rates and timing of fertilizer may be more effective at reducing leaching of nitrate-N from grass seed fields than establishing and retaining grassed riparian management zones. Floyd et al. (2009) addressed effects of woody vegetation and poorly drained soils at different spatial scales in the Calapooia Basin. They found significant differences in relationships between nutrients and land-use at different spatial scales but noted that these differences were not large and likely not to be biologically relevant, and they emphasized the importance of interacting effects among poorly drained soils, woody vegetation, and agricultural management in the Calapooia Basin.

Conclusions

During our study period, many lower sub-basins of the Calapooia River Basin had concentrations of nitrate-N that were higher than the EPA standard for drinking water and ortho-P concentrations were above EPA guidelines for avoiding nuisance aquatic plant growth. However, DN and ortho-P concentrations were lower than accepted EPA guidelines in the mainstem of the river, likely due to dilution of the lower sub-basin water with water from the upper forested part of the basin and samples being collected during baseflow conditions. We expect that comparable patterns exist in basins with similar climatic regimes, geology, soils, and land-use/land-cover signatures. Strong, consistent, positive associations were evident between the amount of agriculture in a sub-basin and dissolved N and P concentrations. However, agriculture in the Calapooia Basin occurs predominately on soils that are poorly drained. These soils enhance the tendency to deliver nutrients to aquatic systems due to stream channel expansion and overland flow during wet periods, and may contribute to the strong relationships that we found between dissolved nutrients and %AG. Critical-source-area strategies (Pionke et al. 2000) based on addressing locations in the landscape that exhibit high soil N or P and tendency to flood in the winter months may be helpful for reducing inputs of nutrients into surface waters.

Further investigation should be focused on plot-scale studies in agriculture-dominated sub-basins to determine the extent that suggested nutrient management strategies, such as spring fertilization or fertilization based on background N mineralization, can shift nutrient dynamics and minimize export. Additionally, attention should be given to effects of in-stream processing on N and P components as they move through multi-land use aquatic systems. It is likely that nutrient spiraling within the system is a factor determining amounts and distributions of N and P components in the system at any point in time or space. For example, it is uncertain how much of the DON in the upper areas of the Calapooia Basin is being utilized in the aquatic system or converted to DIN and transported downstream.

This research also highlights the need for watershed-scale studies that address nutrients across multiple land-uses. Reducing nutrient concentrations in any system through changes in management or regulation requires an understanding of the range of nutrient concentrations that occur throughout the system and identification of local scenarios that result in high concentrations. This study indicated that N and P concentrations and components can vary widely among seasons and water years because of natural factors that are beyond the control of land managers. Efforts to reduce or regulate nutrients must address this large temporal variability and any watershed-specific hydrologic features that interact with management objectives.

Acknowledgments This research was supported by the Forest Research Laboratory Fish and Wildlife Habitat in Managed Forests Research Program at Oregon State University and the USDA Agricultural Research Service. In-kind support was provided by the US Environmental Protection Agency through the time of one of the co-authors. This manuscript has been subjected to agency review and approved for publication. We thank Mabelle Nelson and Donald Streeter for providing lab and field support. The use of trade, firm, or corporation names in this manuscript is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the USDA Agricultural Research Service or the U.S. Environmental Protection Agency of any product or service to the exclusion of others that may be suitable.

References

- Arheimer, B., Anderson, L., & Lepisto, A. (1995). Variation of nitrogen concentration in forested streams-influences on flow, seasonality and catchment characteristics. *Journal of Hydrology*, 179, 281–304.
- Bennett, E. M., Carpenter, S. R., & Caraco, N. F. (2001). Human impact on erodible phosphorus and eutrophication: A global perspective. *Bioscience*, 51(3), 227–234.
- Binkley, D., & Brown, T. C. (1993). Forest practices as nonpoint sources of pollution in North America. American Water Resources Association. *Water Resources Bulletin*, 29(5), 729–740.
- Bonn, B. A., Wentz, D. A., & Hinkle, S. R. (1996). Willamette Basin, Oregon-nitrogen in streams and ground water, 1980–1990. USGS Open-File Report 96–227.
- Brett, M. T., & Hartley, D. M. (2005). Non-point-source impacts on stream nutrient concentrations along a forest to urban gradient. *Environmental Management*, 35, 330–342.
- Buffman, I., Galloway, J. N., Blum, L. K., & McGlathery, K. J. (2001). A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. *Biogeochemistry*, 53, 269–306.
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications*, 8(3), 559–569.
- Dillon, P. J., & Kirchner, W. B. (1975). The effects of geology and land use on the export of phosphorus from watersheds. *Water Research*, 9(2), 135–148.
- Dinnes, D. L., Darlen, D. L., Jaynes, D. B., Kasper, T. S., Hatfield, J. L., Colvin, T. S., & Cambardella, C. A. (2002). Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils. *Agronomy Journal*, 94, 153–171.
- Donner, S. D., Kucharik, C. J., & Foley, J. A. (2004). Impact of changing land use practices on nitrate export by the Mississippi River. *Global Biogeochemical Cycles*, 18, 1–21.
- Dunne, T., & Black, R. D. (1970). Partial area contributions to storm runoff in a small New England watershed. *Water Resources*, 5(2), 438–445.
- Evans, D. M. (2007). Dissolved nitrogen in surface waters and nitrogen mineralization in riparian soils within a multi-land use basin. MS Thesis. Oregon State University.
- Evans, D. M., Schoenholtz, S. H., Wigington, J. P., & Griffith, S. M. (2011). Nitrogen mineralization in riparian soils along a river continuum within a multi-landuse basin. *Soil Science Society of America Journal*, 75(2), 719–728.
- Floyd, W. C. (2005). Seasonal relationships between dissolved nitrogen and landuse/landcover and soil drainage at multiple spatial scales in the Calapooia Watershed, Oregon. MS Thesis. Oregon State University.
- Floyd, W. C., Schoenholtz, S. H., Griffith, S. M., Wigington, P. J., & Steiner, J. J. (2009). Nitrate-nitrogen, land/use/land cover, and soil drainage associations at multiple spatial scales. *Journal of Environmental Quality*, 38, 1473–1482.
- Fredriksen, R. L. (1972). Nutrient budget of a Douglas-fir forest on an experimental watershed in western Oregon. In: Research on coniferous forest ecosystems, proceeding of a symposium, Bellingham, WA. 23–34 March 1972, 115–131.
- Griffith, S. M., Alderman, S. C., & Streeter, D. J. (1997a). Italian ryegrass and nitrogen source fertilization in western Oregon in two contrasting climatic years. I. Growth and seed yield. *Journal of Plant Nutrition*, 20(4–5), 419–428.
- Griffith, S. M., Alderman, S. C., & Streeter, D. J. (1997b). Italian ryegrass and nitrogen source fertilization in western Oregon in two contrasting climatic years. II. Plant nitrogen

- accumulation and soil nitrogen status. *Journal of Plant Nutrition*, 20(4–5), 429–439.
- Henderson, G. S., Swank, W. T., Waide, J. G., & Grier, C. C. (1979). Nutrient budgets of Appalachian and Cascade region watersheds: A comparison. *Forest Science*, 24(3), 385–397.
- Hewlett, J. D., & Hibbert, A. R. (1967). Factors affecting the response of small watersheds to precipitation in humid areas. In W. E. Sopper & H. W. Lull (Eds.), *International symposium on forest hydrology* (pp. 275–290). Oxford: Pergamon.
- Horneck, W. R., & Hart, J. M. (1988). A survey of nutrient uptake and soil test values in perennial ryegrass and turf type tall fescue fields in the Willamette Valley. In H. W. Youngberg (Ed.), *Seed production research* (pp. 13–14). Corvallis: Oregon State University, Department of Crop and Soil Science.
- Howarth, R. W., Boyer, E. W., Pabich, W. J., & Galloway, J. N. (2002). Nitrogen use in the United States from 1961 to 2000 and potential future trends. *Ambio*, 31, 88–96.
- Johnson, L. B., Richards, C., Host, G. E., & Arthur, J. W. (1997). Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology*, 37, 193–208.
- Jordan, T. E., Correll, D. L., & Weller, D. E. (1997). Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. *Journal of Environmental Quality*, 26, 836–848.
- Martin, C. W., & Harr, R. D. (1988). Logging of mature Douglas-fir in western Oregon has little effect on nutrient output budgets. *Canadian Journal of Forest Resources*, 19, 35–43.
- McHale, M. R., Mitchell, M. J., McDonnell, J. J., & Cirimo, C. P. (2000). Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen. *Biogeochemistry*, 48, 165–184.
- Nelson, M. A., Griffith, S. M., & Steiner, J. J. (2006). Tillage effects on nitrogen dynamics and grass seed crop production in Western Oregon, USA. *Soil Science Society of America Journal*, 70, 825–831.
- Nixon, S. W. (1995). Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia*, 41, 199–219.
- Omernik, J. M. (1976). The influence of land use on stream nutrient levels. US-EPA. 600/3-76-014.
- ODEQ (1996). Oregon department of environmental quality: Oregon water quality index report for upper Willamette basin water years. 1986–1995.
- Pellerin, B. A., Kaushal, S. S., & McDowell, W. H. (2006). Does anthropogenic nitrogen enrichment increase organic nitrogen concentrations in runoff from forested and human-dominated watersheds? *Ecosystems*, 9, 852–864.
- Perakis, S. S., & Hedin, L. O. (2002). Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. *Nature*, 415, 416–419.
- Pionke, H. B., Gburek, W. J., & Sharpley, A. N. (2000). Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. *Ecological Engineering*, 14(4), 325–335.
- Poor, C. J., & McDonnell, J. J. (2007). The effects of land use on stream nitrate dynamics. *Journal of Hydrology*, 332(1–2), 54–68.
- Randall, G. W., Huggins, D. R., Russelle, M. P., Fuchs, D. J., Nelson, W. W., & Anderson, J. L. (1997). Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa, and row crop systems. *Journal of Environmental Quality*, 26, 1240–1247.
- Sharpley, A. N., Daniel, T. C., & Edwards, D. R. (1993). Phosphorus movement in the landscape. *Journal of Production Agriculture*, 6, 492–500.
- Uhrich, M. A., & Wentz, D. A. (1999). Environmental setting of the Willamette Basin, OR. USGS Water Resource Investigation Report. 97-4082-A.
- U.S. EPA (1986). Quality criteria for water. Rep 440/9-86-001, U.S. Govt. Print Office. Washington D.C.
- U.S. EPA (1996). National strategy for the development of regional nutrient criteria: EPA 822-B-00-002.
- Vanderbilt, K. L., Lajtha, K., & Swanson, F. J. (2003). Biogeochemistry of unpolluted forested watersheds in the Oregon Cascades: Temporal patterns of precipitation and stream nitrogen fluxes. *Biogeochemistry*, 62, 87–116.
- Warren, K. (2002). Transport of water and solutes from tile-drained fields in the Willamette Valley, Oregon: A field scale study. Master of Science Thesis, Corvallis: Oregon State University, 127 pp.
- Wernick, B. G., Cook, K. E., & Schreier, H. (1998). Land use and stream-water nitrate dynamics in an urban–rural fringe watershed. *Journal of the American Water Resources Association*, 34, 639–650.
- Willett, V. B., Reynolds, B. A., Stevens, P. A., Ormerod, S. J., & Jones, D. L. (2004). Dissolved organic nitrogen regulation in freshwaters. *Journal of Environmental Quality*, 33, 201–209.
- Wigington, P. J., Griffith, S. M., Field, J. A., Baham, J. E., Horwath, W. R., Owen, J., Davis, J. H., Rain, S. E., & Steiner, J. J. (2003). Nitrate removal effectiveness of a riparian buffer along a small agricultural stream in western Oregon. *Journal of Environmental Quality*, 32, 162–170.
- Wigington, P. J., Moser, T. J., & Lindeman, D. R. (2005). Stream network expansion: A riparian water quality factor. *Hydrological Processes*, 19, 1715–1721.
- Woodward, D. G., Gannett, M. W., & Vaccaro, J. J. (1998). Hydrogeologic framework of the Willamette lowland aquifer system. Oregon and Washington. U.S. Geological Survey Professional Paper 1424-B.