

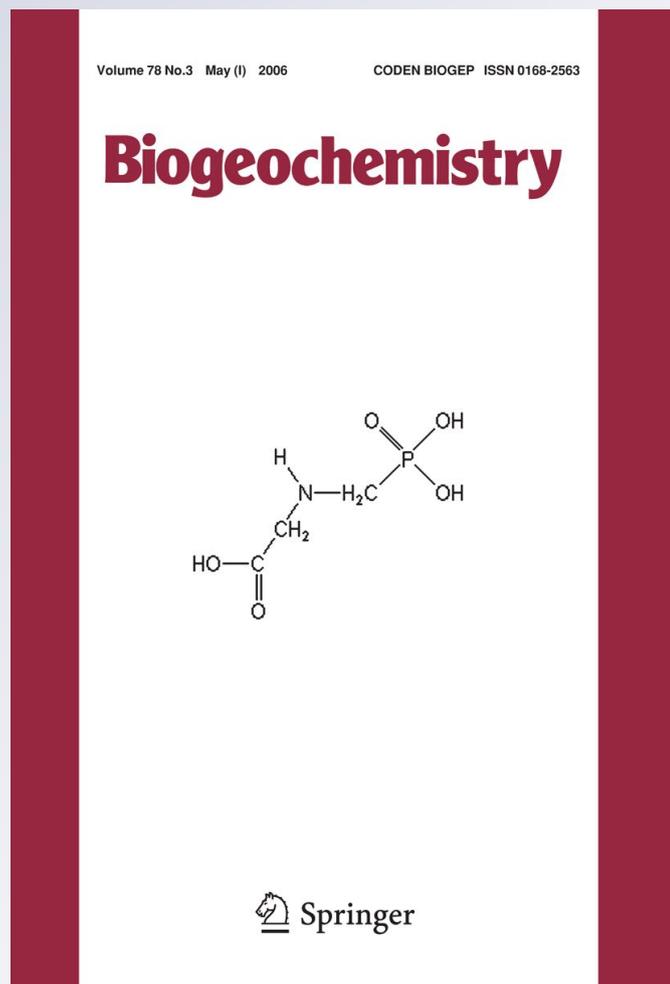
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# Temporal variation in river nutrient and dissolved lignin phenol concentrations and the impact of storm events on nutrient loading to Hood Canal, Washington, USA

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**Abstract** Rapid rainfall events can be responsible for a large proportion of annual nutrient and carbon loading from a watershed. The bioavailability of organic matter during these rapid loading events increases, suggesting that storms play a relevant role in the mobilization of potentially labile terrestrial carbon. A high correlation between river discharge rates and dissolved and particulate nutrient and carbon concentrations during autumn and winter storms was observed in several temperate Pacific Northwest rivers. Dissolved and particulate lignin concentrations also increased with river discharge; for example, in October 2009 dissolved lignin concentrations increased roughly 240% with a 200% increase in river discharge. During these storms a unique phenolic composition was observed for dissolved lignin that was rapidly mobilized from surface soils relative to the base flow of dissolved lignin. The observed increase in Ad/AI ratios with discharge indicates that rapidly mobilized dissolved lignin is more degraded than the base flow of dissolved lignin. Similarly, a marked increase in C/V ratios and decrease in the S/V ratio of dissolved lignin phenols with increasing river discharge was observed. These results may indicate a difference in source between mobilized and base flow pools, or, more likely, preferential degradation and

mobilization/retention of specific lignin phenols. The cumulative results from this year-long data set indicate that a shallow nutrient-rich pool of particulate and dissolved organic matter accumulates in watersheds during periods of soil-saturation deficiency (summer). Autumn and winter storms mobilize this pool of accumulated nutrients from surface soils, which is exhausted with successive winter storms.

**Keywords** Fluvial · Lignin · Mobilization · Nutrients · Organic carbon · Storm runoff

## Introduction

The magnitude of nutrient export from a watershed has been demonstrated to be closely coupled with the rate of water discharge on seasonal time scales (Guillaud et al. 2008). Studies have also shown a tight coupling between river discharge rates and dissolved nitrogen and carbon concentrations on timescales from days to weeks (e.g. Boyer et al. 1997; Hinton et al. 1998; Buffam et al. 2001; Sigleo and Frick 2003). Rapid loading events have been estimated to contribute to as much as 86% of annual OC export in forested watersheds (Raymond and Saiers 2010) and 71–85% of OC export in agricultural watersheds (Dalzell et al. 2007). Furthermore, it has been shown that organic matter (OM) biodegradability significantly increases

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with peak discharge in both temperate and high-latitude river systems, suggesting that storm events play a significant role in mobilization of potentially labile terrestrial carbon (Buffam et al. 2001; Holmes et al. 2008; Fellman et al. 2009). Small streams are the primary source of terrestrial material to river systems because of the tight land–water interface; rapidly changing conditions at this spatial scale leads to dynamic chemical conditions within the stream (Vannote et al. 1980; Peterson et al. 2001; McClain and Elsenbeer 2001).

Our understanding of downstream N cycling has been greatly improved by various  $^{15}\text{N}$  tracer studies, which allow the quantification of important processes such as nitrification and subsequent  $\text{NO}_3^-$  and  $\text{NH}_4^+$  uptake (e.g. Mulholland et al. 2000; Peterson et al. 2001; Webster et al. 2003; Deegan et al. 2011). Observations of short term compositional changes in stream OC such as increases in aromaticity, detected by specific UV absorbance, with peak discharge have allowed for a more detailed characterization of OC and hydrologic flowpaths (Hood et al. 2006; Vidon et al. 2008; van Verseveld et al. 2009). Spatial analysis suggests that distinct landscape units become functional during these hydrologic events, altering nutrient and dissolved organic carbon (DOC) mobilization dynamics throughout the course of a storm (Hinton et al. 1998; McGlynn and McDonnell 2003; Ocampo et al. 2006). However, the mechanistic mobilization dynamics of inorganic and organic constituents from the terrestrial biome are still not well constrained.

Input of nutrient-rich freshwater has been shown to cause eutrophication in nutrient-limited estuarine or coastal systems, which under certain conditions results in hypoxic events due to microbial respiration of sinking bloom-derived OM (Rabalais et al. 2001; Howarth and Marino 2006). Observations in Hood Canal, Washington—a branch of the Puget Sound estuary where this study is focused—have shown that low dissolved oxygen conditions in Hood Canal, especially in the southernmost Lynch Cove region (Fig. 1), have become more persistent and widespread in recent decades compared to the 1930s–1960s, resulting in increased frequency of hypoxic and fish kill events (Newton et al. 1995, 2002). One possible driver for the observed increase in frequency of hypoxic events is an increase in watershed nutrient loading rates. Changes in land use can have profound effects on the chemical composition of a stream and

greatly influence the potential for watershed nutrient delivery (Biggs et al. 2004; Thomas et al. 2004; Neill et al. 2006). Recent increases in urbanization and  $\text{N}_2$  fixing red alder tree prevalence has likely influenced the nutrient inventory of the Hood Canal watershed (Newton et al. 2002). Thus, understanding the timing and magnitude of river nutrient delivery is critical for predicting potential impacts of a watershed on the basin in which it drains. Furthermore, in order to assess the fate of terrestrially derived OM in the context of global biogeochemical cycling, it is crucial to first understand the mechanisms by which OM is mobilized from land into river systems.

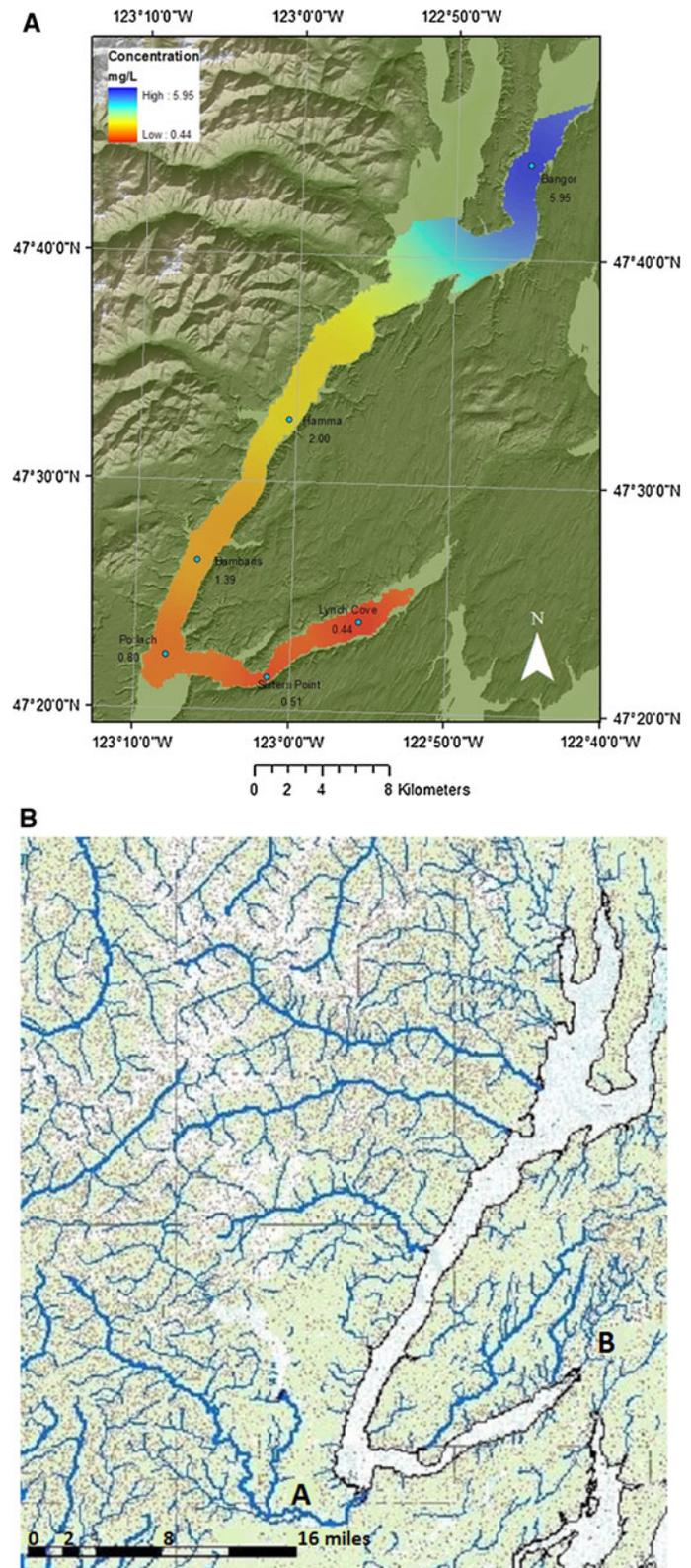
In this study, we measured variability in stream nutrient and OM concentration and composition at a fine temporal resolution in an effort to enhance our understanding of the dynamical coupling of hydrologic and geochemical fluxes into streams. Storm events were sampled over a three to 4 day period on a 3–4 h interval for an entire year in the Skokomish and Union Rivers, which drain into the Lynch Cove region of Hood Canal (Fig. 1). In addition to the measurement of dissolved nutrients and particulate OM, dissolved lignin phenol concentrations were measured to determine changes in the composition and source of DOC throughout the course of a storm. Lignin is a terrestrial biomarker unique to vascular plants that can be used as an indicator of the OM source (e.g. Hedges and Ertel 1982; Goñi and Hedges 1992); changes in phenolic ratios throughout a storm were used to determine variation in the composition of OM mobilized by base flow and rapid shallow flow. The goal of this study is two-fold: to assess the impact of short term storm events on nutrient loading rates and hypoxia in Hood Canal, Washington and to gain a better understanding of the mechanisms behind nutrient and OM mobilization in an effort to improve predictive capabilities concerning the fate of terrestrially derived material in the context of global biogeochemical cycling.

## Methods

### Study area

The Hood Canal watershed (Fig. 1) has a surface area of  $\sim 3,050 \text{ km}^2$ , of which Hood Canal itself comprises 12%. The watershed can be separated into three zones:

**Fig. 1** (Top) Modeled dissolved O<sub>2</sub> concentrations in the Hood Canal basin during the August 2006 hypoxic event (HCDOP Citizen Monitoring Data and UW Spatial Analysis Lab projection). (Bottom) Map of the Hood Canal drainage basin. Sample sites for this study are **a** the Skokomish River, which is relatively large, and **b** the Union River, which is representative of the many small streams that compose the Kitsap Peninsula watershed (PRISM Internet Map Server)



(1) the large mountainous watersheds of the Olympic Mountains with hydrographs dominated by snowmelt, (2) the Skokomish River (the largest catchment in the watershed), and (3) the smaller, lower elevation watersheds that dominate the Kitsap Peninsula and the southern, southeastern, and northwestern parts of Hood Canal. More than 60% of the total annual precipitation occurs between November and January, and less than 10% occurs between June and August (Peterson et al. 1997). Similarly, TDN concentrations in the Skokomish and Union Rivers peak during autumn and winter months and reach a minimum during dry summer months (Steinberg et al. 2010). Hood Canal is characterized by slow marine flushing rates. Low DO conditions are most prevalent in the southernmost Lynch Cove region of Hood Canal, where DO concentrations less than  $5 \text{ mg l}^{-1}$  were observed below the pycnocline every month of the year from 1998 to 2000 (Fig. 1; Newton et al. 2002). For this reason, we focused on the two rivers representative of those draining primarily into the Lynch Cove region, the Skokomish and Union Rivers.

The Skokomish River catchment, accounting for  $\sim 22\%$  of the freshwater input into Hood Canal with an average annual runoff rate of  $3.2 \text{ m/year}$  and discharge of  $37.6 \text{ m}^3/\text{s}$ , is situated in the southwest portion of the watershed, where annual precipitation rates are generally highest (Steinberg et al. 2010). The Skokomish catchment is sparsely populated with  $0\text{--}4 \text{ people/km}^2$  and is primarily mature coniferous forest (46%) managed as national parks, and national or commercial forest (Steinberg et al. 2010).

The Union River drains into the southeast tip of Lynch Cove. The Union River and the numerous similar lowland draining streams account for  $\sim 24\%$  of the freshwater input into Hood Canal with a runoff rate of  $1.1 \text{ m/year}$  (Steinberg et al. 2010). Compared to the Skokomish catchment, these lowland catchments have experienced more disturbance by clearing, suburban development, and wetland draining (Ness and Fowler 1960; McCreary 1975; McMurphy 1980). These watersheds have moderate population densities averaging  $20 \text{ people/km}^2$ . Dominant land use is primarily coniferous ( $\sim 23\%$  mature,  $\sim 15\%$  young) and mixed deciduous ( $\sim 30\%$ ) forests (Steinberg et al. 2010). Approximately 50% of the land covered by mixed deciduous forest consists of  $\text{N}_2$ -fixing red alder trees (L. McGeoch, unpublished data).

## Sampling and analysis

Samples were collected at three to 4 h intervals depending on forecasted storm duration using Teledyne ISCO autosamplers placed roughly 4 km upstream of the river mouths of the Union ( $47^\circ 27' 48.61''\text{N}$ ,  $122^\circ 49' 55.92''\text{W}$ ) and Skokomish Rivers ( $47^\circ 19' 09.73''\text{N}$ ,  $123^\circ 08' 22.47''\text{W}$ ). Water was pumped through Teflon tubing placed near the center of the river and fitted with a coarse mesh to exclude large debris (7 mm pore size). Twenty-four samples were collected for each storm in acid-washed 1 l polyethylene bottles, which were also pre-rinsed with river water prior to sampling. Upon completion of the autosampler sequence, samples were immediately placed on ice and transported to the lab for filtration and analysis. Significant storm events were sampled over a three or 4 day period from October 2008 through October 2009. Real-time river discharge data for the Skokomish River was obtained from USGS (<http://waterdata.usgs.gov/nwis/rt>). Union River discharge data was provided by the Hood Canal Salmon Enhancement Group (HCSEG).

Dissolved nutrient samples ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{SiO}_4^{4-}$ , and  $\text{PO}_4^{3-}$ ) were filtered through Whatman<sup>®</sup> cellulose acetate filters ( $0.45 \mu\text{m}$ ), and analyzed on an Alpkem RFA/2 autoanalyzer. TDN and DOC were measured on a Shimadzu DOC analyzer after filtering through pre-combusted Whatman<sup>®</sup> GF/F glass fiber filters ( $0.7 \mu\text{m}$  nominal pore size) into pre-cleaned glass vials. Dissolved organic nitrogen (DON) concentration was calculated by subtracting all inorganic nitrogen species from TDN. For particulates, between 100 and 600 ml of stream water (depending on turbidity) were filtered through pre-combusted Whatman<sup>®</sup> GF/F glass fiber filters. Particulates captured on the filters were then dried at  $55^\circ\text{C}$  for 24 h, acid-fumigated for 24 h, dried at  $55^\circ\text{C}$  for an additional 24 h, and packed in tin capsules. The samples were analyzed for N and C concentration and stable isotope ratios at UC-Davis Stable Isotope Facility on a PDZ Europa ANCA-GSL elemental analyzer. Total suspended sediment (TSS) was assessed by filtering between 100–600 ml of water through pre-weighed/combusted Whatman<sup>®</sup> GF/F glass fiber filters. The filters were then dried  $55^\circ\text{C}$  for 48 h, and reweighed.

Solid phase extraction of dissolved lignin was performed as described by Keil and Neibauer (2009); water samples were prefiltered through combusted

Whatman® GF/F glass fiber filters, acidified to pH 2 with HCl, and passed through 200 mg Waters Oasis HLB cartridges at a rate of 3 ml min<sup>-1</sup>. Solid phase extraction cartridges were pre-conditioned sequentially with 1 ml methanol, 1 ml ethyl acetate and 1 ml acidified (pH 2) MilliQ water. The solid phase was then eluted from the cartridge with 10 ml ethyl acetate at 3 ml/minute. Samples were analyzed via Gas Chromatography using an Agilent 6890N GC-FID following an alkaline CuO oxidation performed in a CEM Microwave Accelerated Reaction System as described by Goni and Montgomery 2000. Particulate lignin samples were analyzed in the same fashion; the Whatman® GF/F glass fiber filters used to measure TSS were placed directly into the Teflon microwave vessels to undergo CuO oxidation (Goni and Montgomery 2000). Combusted filters were used as blanks to assess any lignin signature present on the GF/F filters, which was nominal.

## Results

### Dissolved organic and inorganic constituents

During the first significant autumn storm (i.e. several days of consistent rainfall) after a dry summer, both TDN and DOC concentrations are tightly coupled with river discharge in both the Union and Skokomish Rivers (Figure 2, Table 2). For example, throughout the sampled 3 Oct 2008 storm, DOC and TDN concentrations increased from 42 and 4.2 to 193  $\mu\text{mol l}^{-1}$  and 12.6  $\mu\text{mol l}^{-1}$ , respectively, in the Skokomish River. The peak in both TDN and DOC concentrations occurred approximately 3–6 h after the peak in river discharge. This strong coupling persisted through the November samplings in the Union River. Although DOC and TDN concentrations increased with the large peak in discharge at the end of the November Skokomish River sampling, there was less correlation between discharge and DOC and TDN concentrations during smaller peaks in discharge throughout the week long sampling (Table 1).

After several months of consistent rainfall, the correlation between discharge and DOC and TDN concentrations began to diminish; for example, during the January 2009 Union River sampling, a 137% increase in river discharge yielded a 22 and 8% increase in TDN and DOC concentrations,

respectively, whereas a 62% increase in river discharge in the October 2008 sampling yielded an approximately 52 and 132% increase in TDN and DOC concentrations, respectively (Fig. 2). Furthermore, the correlation coefficients for the relationship between discharge and DOC and TDN concentrations decreases from October (DOC  $R^2 = 0.88$ ) to January (DOC  $R^2 = 0.27$ ) (Table 2). March and June 2009 samplings showed even less response in TDN and DOC concentrations to increased river discharge (Table 1); TDN and DOC concentrations did not move significantly from the average during these rainfall events and correlation constants, especially for TDN, remained low (Table 2). However, TDN concentrations also remained fairly constant during the September 2009 sampling, with a small increase in DOC in both rivers (Table 1). During this sampling, there was almost no correlation between river discharge and TDN and DOC concentrations in the Union River (DOC  $R^2 = 0.03$ ), whereas the Skokomish River showed a slight correlation between discharge and DOC concentrations (DOC  $R^2 = 0.51$ ) (Table 2). DOC:TDN, DOC:DON, TDN:PO<sub>4</sub><sup>3-</sup>, and DON:PO<sub>4</sub><sup>3-</sup> ratios are all positively correlated with river discharge in autumn and winter storms. The correlation between C:N and N:P ratios and discharge is strongest when the correlation between nutrient concentrations and discharge is strongest (Fig. 3).

Throughout the sampled 2008–2009 water year, TDN was on average composed of approximately 80% NO<sub>3</sub><sup>-</sup> and 17% DON in the Union River and 51% NO<sub>3</sub><sup>-</sup> and 43% DON in the Skokomish River (Table 1). Relative to inorganic N, DON contributes more to the TDN pool during wet autumn months than the rest of the year. For example, in the Skokomish River TDN is composed of 44% NO<sub>3</sub><sup>-</sup> and 52% DON from October through November whereas TDN is composed of 65% NO<sub>3</sub><sup>-</sup> and 27% DON from January through September (Table 1). Short term dissolved NO<sub>3</sub><sup>-</sup> concentrations followed the same pattern as TDN. DON concentrations also increased with increasing river discharge in autumn and winter storms; this relationship diminished during spring and summer samplings (Table 1). Peaks in both NO<sub>3</sub><sup>-</sup> and DON concentrations exhibited similar timing to TDN—peak concentrations occurred 3–6 h after peak river discharge. Phosphate concentrations increase only to a small extent prior to peak river flow, then level out, which is reflected in the N:P ratios discussed

**Table 1** Storm sampling data for the Union and Skokomish Rivers

River	Date	Time	River flow (m <sup>3</sup> /s)	DOC ( $\mu\text{mol l}^{-1}$ )	TDN ( $\mu\text{mol l}^{-1}$ )	SiO <sub>4</sub> <sup>-</sup> ( $\mu\text{mol l}^{-1}$ )	NO <sub>3</sub> <sup>-</sup> ( $\mu\text{mol l}^{-1}$ )	PO <sub>4</sub> <sup>3-</sup> ( $\mu\text{mol l}^{-1}$ )	DON ( $\mu\text{mol l}^{-1}$ )	TSS (mg l <sup>-1</sup> )	POC (mg l <sup>-1</sup> )	PON (mg l <sup>-1</sup> )	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	Total lignin (mg l <sup>-1</sup> )	S/V	CV	Ad/ Al (v)
SKOK	10/31/08	16:30	14.24	70	6.7	165	1.2	0.02	5.34	4.6	0.60	0.04	-26.3	2.1	6.5E-03	0.58	0.16	1.20
SKOK	10/31/08	20:30	15.06	69	6.4	166	1.6	0.01	4.56	6.2					5.8E-03	0.63	0.20	0.97
SKOK	11/1/08	0:30	17.61	65	4.3	166	0.8	0.02	3.16	7.7	0.66	0.10	-25.8	2.9	7.0E-03	0.77	0.25	1.60
SKOK	11/1/08	4:30	18.63	68	7.9	166	2.0	0.01	5.49	6.0								
SKOK	11/1/08	8:30	17.95	59	4.7	166	1.2	0.01	3.34	9.3	0.98	0.07	-26.2	2.9	5.3E-03	0.61	0.18	1.35
SKOK	11/2/08	0:30	17.10	49	3.5	169	1.2	0.00	2.19	2.2	0.63	0.04	-25.3	3.4				
SKOK	11/2/08	4:30	17.27	52	4.9	169	1.4	0.00	3.26	2.2	0.71	0.04	-26.4	3.1	5.3E-03	0.70	0.21	1.44
SKOK	11/2/08	8:30	18.12	51	4.0	170	1.5	0.00	2.28	2.4					4.9E-03	0.75	0.22	1.43
SKOK	11/2/08	12:30	19.14	48	4.4	170	1.7	0.00	2.52	2.9					8.4E-03	0.58	0.19	1.40
SKOK	11/2/08	16:30	21.24	52	4.4	171	1.6	0.00	2.67	1.4					8.6E-03	0.70	0.28	1.14
SKOK	11/2/08	20:30	22.68	45	3.5	169	1.5	0.00	1.75	2.3	0.47	0.03	-26.2	3.8	9.4E-03	0.63	0.20	0.95
SKOK	11/3/08	0:30	23.98	72	4.0	169	1.3	0.00	2.61	3.6					6.3E-03	0.68	0.20	1.04
SKOK	11/3/08	4:30	24.95	51	3.8	171	0.9	0.00	2.65	2.8	0.62	0.04	-26.1	3.5	8.7E-03	0.69	0.22	1.28
SKOK	11/3/08	12:30	28.32	55	4.1	169	0.8	0.00	3.17	4.5	0.71	0.05	-26.4	2.6				
SKOK	11/4/08	0:30	30.30	64	3.8	160	1.1	0.01	2.41	9.5	0.60	0.03	-25.4	2.2	9.5E-03	0.63	0.32	1.64
SKOK	11/4/08	15:00	31.43	77	5.4	162	3.2	0.01	0.74	1.4					7.8E-03	0.39	0.15	1.13
SKOK	11/4/08	21:00	29.73	68	5.9	164	3.4	0.01	1.69	6.2					7.1E-03	0.46	0.17	1.11
SKOK	11/5/08	3:00	28.32	58	5.1	177	3.6	0.01	0.50	6.4	0.44	0.02	-26.0	3.5	1.1E-02	0.44	0.17	1.09
SKOK	11/5/08	6:00	27.69	61	4.3	164	3.7	0.01	0.00		0.57	0.03	-26.4	3.0	1.0E-02	0.54	0.17	1.96
SKOK	11/5/08	9:00	26.90	56	4.8	166	3.7	0.01	0.00	4.6					8.7E-03	0.40	0.16	1.31
SKOK	11/5/08	21:00	24.95	49	4.5	177	3.4	0.01	0.00	3.6	0.38	0.09	-26.7	2.5	1.1E-02	0.41	0.14	1.08
SKOK	11/6/08	3:00	25.15	50	4.8	165	3.5	0.01	0.00	3.7	0.34	0.02	-26.4	3.4	1.9E-02	0.69	0.12	1.64
SKOK	11/6/08	9:00	27.89	55	4.5	164	3.6	0.00	0.00	3.3	0.51	0.03	-26.6	2.9	1.4E-02	0.58	0.21	1.43
SKOK	11/6/08	15:00	44.46	72	5.1	159	3.9	0.03	0.38	4.7	0.31	0.07	-26.7	3.1	1.2E-02	0.62	0.15	1.52
SKOK	11/6/08	21:00	226.8			135	7.2	0.09	0.00	117.8	2.81	0.29	-27.4	2.8	5.7E-03	0.61	0.15	1.13
SKOK	11/7/08	3:00	387.9	214	14.3	135	6.9	0.12	6.51	943.4	5.32	0.65	-27.0	2.6	4.7E-03	0.44	0.15	0.98
SKOK	11/7/08	9:00	487.1	156	10.3	145	6.4	0.10	3.21						6.3E-03	0.45	0.18	1.03
UNIO	1/6/09	20:00	3.06	285	37.6	25	31.4	0.24	4.93	44.9	3.04	0.25	-27.1	3.8	3.6E-01	0.54	0.29	1.88
UNIO	1/7/09	5:00	6.48	378	48.7	14	39.4	0.24	7.95	239.6	7.08	0.56	-28.0	-3.0	3.6E-01	0.57	0.21	1.53
UNIO	1/7/09	17:00	6.14	329	43.1	22	35.4	0.22	6.65	83.1	9.38	0.81	-27.9	-4.4	6.7E-01	0.12	0.05	1.13
UNIO	1/8/09	2:00	13.56	389	46.1	8	38.6	0.19	6.14	434.6	19.05	1.49	-27.8	-2.1	2.6E-01	0.65	0.26	1.08
UNIO	1/8/09	11:00	8.81	308	39.2	15	34.1	0.16	4.29	379.5	8.90	0.79	-27.9	-5.9	2.6E-01	0.64	0.26	1.19
UNIO	1/9/09	14:00	2.92	210	38.4	49	33.1	0.20	4.24	32.5	2.56	0.16	-26.9	1.8	2.8E-01	0.89	0.20	0.99
SKOK	3/13/09	19:30	19.14	40	8.3	35	2.8	0.03	5.52	11.8	0.64	0.034	-25.3	2.8	1.2E-02	0.61	0.09	0.89

**Table 1** continued

River	Date	Time	River flow (m <sup>3</sup> /s)	DOC (μmol l <sup>-1</sup> )	TDN (μmol l <sup>-1</sup> )	SiO <sub>4</sub> (μmol l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (μmol l <sup>-1</sup> )	PO <sub>4</sub> <sup>3-</sup> (μmol l <sup>-1</sup> )	DON (μmol l <sup>-1</sup> )	TSS (mg l <sup>-1</sup> )	POC (mg l <sup>-1</sup> )	PON (mg l <sup>-1</sup> )	Δ <sup>13</sup> C (‰)	Δ <sup>15</sup> N (‰)	Total lignin (mg l <sup>-1</sup> )	S/V	CV	Ad/Al (v)
SKOK	3/14/09	11:30	22.14	36	4.5	66	3.6	0.06	0.31	4.1	0.45	0.040	-27.4	3.3	8.1E-03	1.54	0.84	0.37
SKOK	3/14/09	23:30	24.18	41	5.7	48	3.6	0.04	1.04	5.6	0.86	0.042	-28.1	3.3	9.8E-03	0.69	0.18	1.26
SKOK	3/15/09	23:30	23.79	40	5.4	53	4.1	0.04	0.39	8.0	0.47	0.061	-25.8	3.4	3.4E-02	0.04	0.01	0.13
SKOK	3/16/09	23:30	25.32	44	6.5	78	4.4	0.08	1.60	8.2	0.62	0.047	-28.3	2.0	5.9E-03	0.70	0.18	1.07
SKOK	3/17/09	15:30	26.31	44	6.1	47	3.9	0.05	2.08	10.4	0.61	0.041	-26.6	2.3	6.8E-03	0.83	0.25	2.20
UNIO	6/19/09	14:00	1.10	82	20.4	385	16.5	0.29	2.9	2.5					8.4E-03	0.54	0.14	0.86
UNIO	6/20/09	6:00	1.36	88	21.6	406	17.5	0.33	3.2	1.4					9.0E-03	0.66	0.23	0.71
UNIO	6/20/09	10:00	1.30	80	18.9	397	17.0	0.28	1.6	8.5					7.9E-03	0.69	0.16	0.73
UNIO	6/20/09	14:00	1.13	87	20.4	399	17.1	0.31	3.2	1.6					6.8E-03	0.50	0.13	0.76
UNIO	6/20/09	22:00	1.25	83	20.7	397	18.7	0.29	1.6	2.1					8.5E-03	0.55	0.18	0.51
UNIO	6/21/09	2:00	1.36	85	22.0	397	19.0	0.28	2.7	1.9					6.7E-03	0.54	0.14	0.91
SKOK	9/5/09	21:00	3.71	34	4.0	211	2.4	0.22	1.57	4.8	0.65	0.046	-26.2	2.9				
SKOK	9/6/09	1:00	3.71	34	3.9	211	2.6	0.21	1.28						4.34E-03	0.14	0.11	1.02
SKOK	9/7/09	1:00	6.31	50	4.6	202	3.0	0.14	1.54	15.5	1.10	0.103	-27.6	1.6	7.48E-03	0.23	0.11	1.31
SKOK	9/7/09	5:00	7.99	48	4.3	197	3.1	0.12	1.11	50.2	2.59	0.354	-28.9	0.5	6.97E-03	0.25	0.16	1.18
SKOK	9/7/09	9:00	8.72	54	5.1	195	3.8	0.11	0.68	65.3	2.48	0.284	-29.2	-4.3	6.86E-03	0.26	0.14	1.42
SKOK	9/7/09	17:00	8.30	53	4.0	196	3.6	0.13	0.22	42.0	2.30	0.295	-27.8	-2.3	6.21E-03	0.48	0.17	0.86
SKOK	9/8/09	1:00	7.56	58	5.4	200	3.9	0.15	0.82		2.18	0.214	-29.1	-3.5				
UNIO	9/5/09	19:00	0.65	97	18.7	399	17.4	0.51	0.64	3.9	0.67	0.056	-28.2	1.7	7.40E-03	0.70	0.12	1.04
UNIO	9/6/09	10:00	0.65	115	21.0	401	18.8	0.55	1.10	4.6	0.84	0.063	-26.8	2.1	6.19E-03	0.25	0.13	1.90
UNIO	9/6/09	13:00	0.79	125	19.2	393	18.0	0.51	0.97	4.0					6.98E-03	0.36	0.19	1.07
UNIO	9/6/09	16:00	0.91	131	18.5	392	17.5	0.50	0.90	4.2	0.65	0.098	-28.4	3.1	6.28E-03	0.34	0.14	0.81
UNIO	9/6/09	19:00	0.85	130	18.6	394	17.7	0.51	0.87	3.5					5.72E-03	0.36	0.16	1.11
UNIO	9/6/09	22:00	0.76	130	19.5	400	18.6	0.53	0.45	4.2	0.72	0.049	-26.6	2.7	5.94E-03	0.30	0.15	1.00
UNIO	9/7/09	1:00	0.74	153	22.1	402	19.4	0.56	1.42	2.3					6.19E-03	0.27	0.16	1.27
UNIO	9/7/09	4:00	0.71	126	20.7	402	20.0	0.48	0.61	3.4	0.85	0.058	-26.5	2.0				
UNIO	9/7/09	10:00	0.68	124	21.0	407	19.7	0.53	0.79	3.1	0.67	0.105	-27.1	2.7				
UNIO	9/7/09	16:00	0.65	137	20.5	402	18.4	0.55	1.49	2.7	0.58	0.047	-26.5	3.7				
UNIO	9/7/09	22:00	0.68	177	23.6	391	19.7	0.63	3.58	6.4	1.01	0.104	-28.0	3.8				
UNIO	10/13/09	17:45	0.59	69	19.1	397	12.5	0.31	6.3		0.84	0.119	-27.2	2.3	6.6E-03	0.79	0.21	0.99
UNIO	10/14/09	1:45	0.62	71	19.4	395	13.0	0.28	6.0		0.66	0.043	-26.8	3.3	7.0E-03	0.80	0.12	0.39
UNIO	10/14/09	9:45	0.79	129	20.4	384	11.9	0.40	8.2		0.88	0.065	-27.9	3.1	1.1E-02	0.56	0.15	0.72
UNIO	10/14/09	17:45	1.27	310	30.6	346	17.3	0.41	12.8		2.45	0.214	-28.1	3.1				
UNIO	10/15/09	1:45	0.99	295	37.2	367	25.4	0.25	10.7		1.85	0.144	-28.1	3.4	1.3E-02	0.52	0.23	0.72

Table 1 continued

River	Date	Time	River flow (m <sup>3</sup> /s)	DOC (μmol l <sup>-1</sup> )	TDN (μmol l <sup>-1</sup> )	SiO <sub>4</sub> (μmol l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (μmol l <sup>-1</sup> )	PO <sub>4</sub> <sup>3-</sup> (μmol l <sup>-1</sup> )	DON (μmol l <sup>-1</sup> )	TSS (mg l <sup>-1</sup> )	POC (mg l <sup>-1</sup> )	PON (mg l <sup>-1</sup> )	Δ <sup>13</sup> C (‰)	Δ <sup>15</sup> N (‰)	Total lignin (mg l <sup>-1</sup> )	S/V	C/V	Ad/Al (v)
UNIO	10/15/09	9:45	0.82	290	34.1	384	21.2	0.29	12.3	0.82	0.82	0.113	-28.4	3.1	1.0E-02	0.43	0.12	0.77
UNIO	10/15/09	17:45	0.76	213	30.7	405	19.9	0.22	9.6	0.90	0.90	0.066	-26.8	3.2	7.8E-03	0.46	0.11	0.73
UNIO	10/16/09	1:45	0.74	190	29.5	409	19.0	0.26	9.3	1.08	1.08	0.083	-27.5	3.5	6.5E-03	0.43	0.15	0.70
UNIO	10/16/09	9:45	0.79	188	26.4	399	16.8	0.30	8.4	0.68	0.68	0.080	-27.2	3.4	9.9E-03	0.51	0.14	0.95
UNIO	10/16/09	17:45	1.33	374	32.8	373	19.3	0.31	12.9	2.60	2.60	0.159	-28.3	2.7	1.1E-02	0.37	0.14	1.22
UNIO	10/16/09	21:45	1.36	496	43.0	349	26.5	0.40	15.8	2.67	2.67	0.196	-26.8	3.8	1.6E-02	0.43	0.17	1.06
UNIO	10/17/09	1:45	1.61	538	45.1	342	28.2	0.31	16.3	3.94	3.94	0.270	-28.1	3.1	1.8E-02	0.41	0.16	0.95
UNIO	10/17/09	5:45	1.44	630	63.8	348	42.5	0.27	20.4	12.35	12.35	0.954	-28.6	3.0	1.8E-02	0.46	0.20	1.03
UNIO	10/17/09	9:45	2.24	728	63.5	290	41.3	0.46	21.5	10.89	10.89	0.801	-28.5	2.6	2.2E-02	0.49	0.18	0.71

For brevity, not all data is presented. For a complete table with all data points and parameters measured, please contact the lead author

previously. In all storm events sampled throughout the year, SiO<sub>4</sub><sup>4-</sup> concentrations decrease with increasing river discharge (Fig. 2; Table 1).

Total suspended sediments and particulate organic nitrogen and carbon

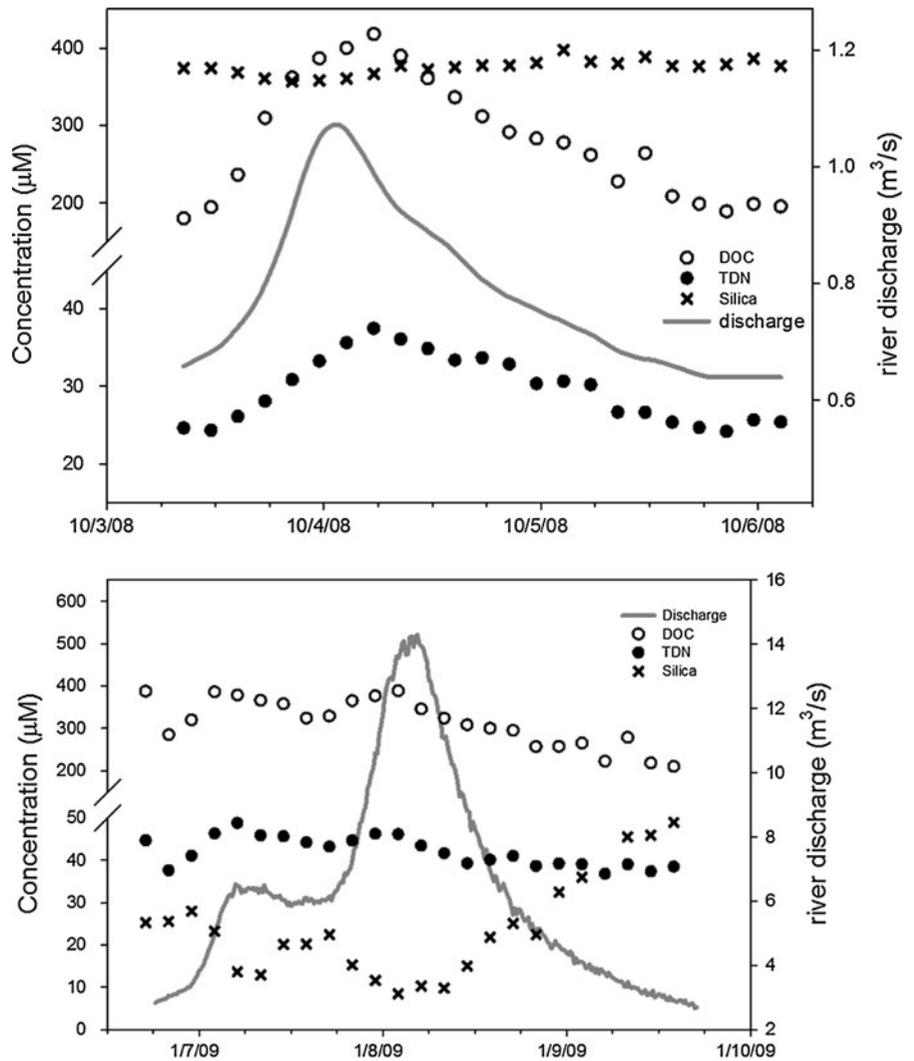
TSS concentrations were correlated with river discharge during all sampled storm events; *R*<sup>2</sup> values were above 0.80 for every sampled storm (Table 2). TSS concentrations generally reached a maximum simultaneously with or slightly prior to Peak River discharge, and began to drop several hours (~6–12 h) before river flow decreased. Similar to the observed trends in dissolved nutrient concentrations, particulate organic N and C (PON and POC) concentrations are strongly coupled with river discharge during autumn and winter storms (Fig. 4). As with dissolved nutrient concentrations, the coupling between particulate N and C concentrations and river discharge began to diminish after several major winter storms; for example, *R*<sup>2</sup> values for POC dropped from 0.94 in January to 0.01 in March (Table 2). A key difference between dissolved and particulate nutrient concentrations is that POC and PON concentrations peaked simultaneously or prior to peak river discharge similar to TSS.

Stable isotope analysis of POC revealed several notable trends. δ<sup>13</sup>C-POC generally became more depleted with increasing river discharge in all sampled storms. For example, δ<sup>13</sup>C-POC varied from -25.3 to -27.0‰ throughout the week long November sampling of the Skokomish River with the most depleted values occurring at peak discharge (Table 1). As with other measured parameters, this trend was most evident in autumn samplings. Throughout the year, δ<sup>13</sup>C-POC values ranged from -25.3 to -29.2‰, indicating a primary input of C<sub>3</sub> terrestrial OM.

Dissolved and particulate lignin phenols

As with DOC, the total concentration of dissolved lignin was correlated with river discharge during autumn storms (Fig. 5); data from the 13–17 October 2009 sampling showed the clearest trends and tightest correlations between discharge and the measured parameters (*R*<sup>2</sup> = 0.88), and will thus be considered to best represent autumn storm conditions. During this sampling, both DOC and dissolved lignin concentrations increased with discharge, however, the total mass

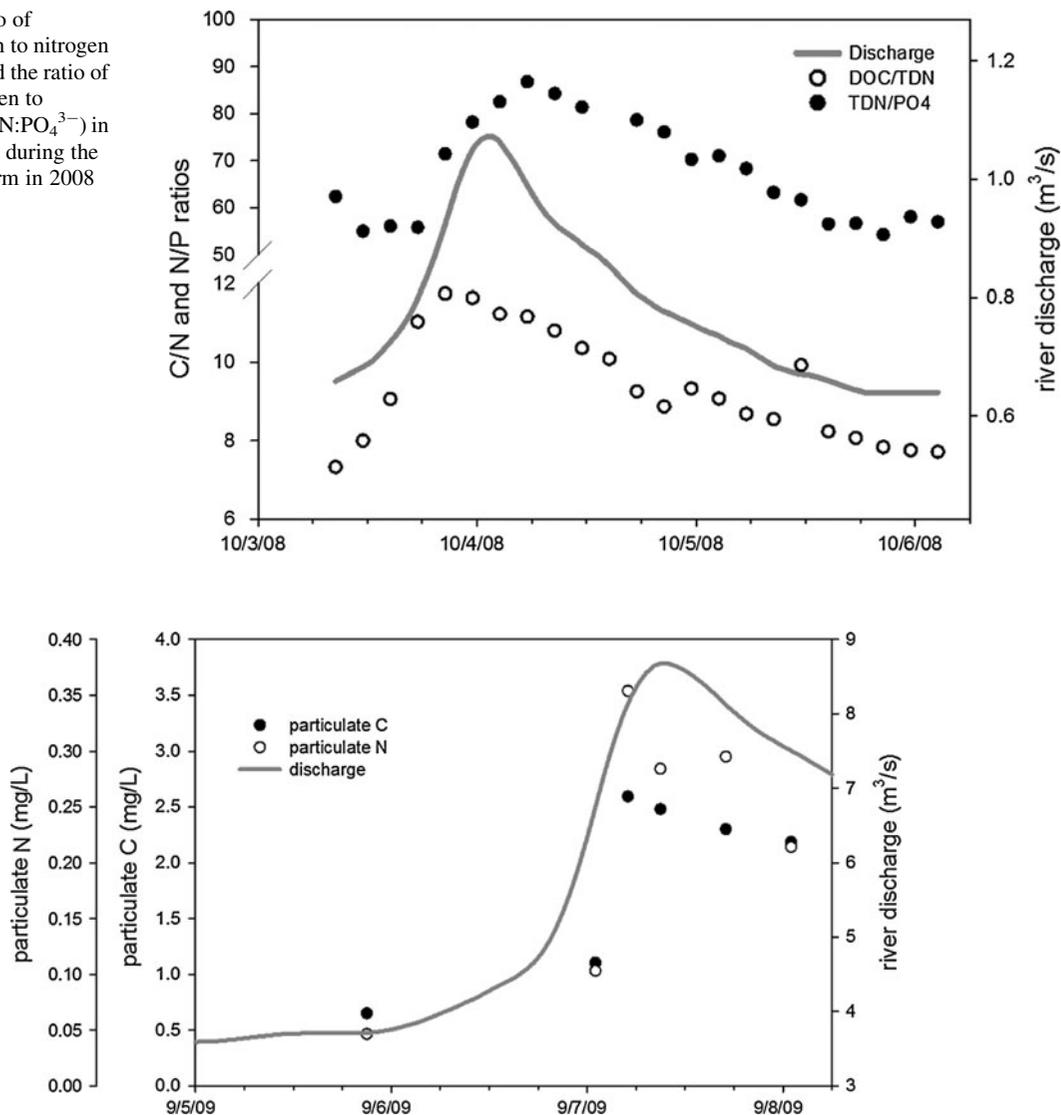
**Fig. 2** TDN, DOC, and silica concentrations in the Union River during the first significant autumn storm of 2008 (*top*), and a subsequent winter 2009 storm (*bottom*)



**Table 2** Correlation between river discharge and DOC, TDN, POC, PON, and TSS during sampled storms

River	Storm start date	DOC $R^2$	TDN $R^2$	POC $R^2$	PON $R^2$	TSS $R^2$
Union	3 Oct 2008	0.88	0.73			
Skokomish	2 Oct 2008	0.90	0.71			
Union	31 Oct 2008	0.87	0.92			
Skokomish	31 Oct 2008	0.11	0.11	0.96	0.96	0.84
Union	6 Jan 2009	0.27	0.33	0.94	0.94	0.86
Union	13 Mar 2009	0.73	0.38			
Skokomish	13 Mar 2009	0.50	0.28	0.01	0.19	0.80
Union	19 Jun 2009	0.11	0.13			
Union	4 Sep 2009	0.03	0.29			
Skokomish	4 Sep 2009	0.51	0.14	0.88	0.80	0.85
Union	13 Oct 2009	0.88	0.70	0.95	0.84	
Skokomish	13 Oct 2009	0.66	0.16			

**Fig. 3** The ratio of dissolved carbon to nitrogen (DOC:TDN) and the ratio of dissolved nitrogen to phosphorus (TDN:PO<sub>4</sub><sup>3-</sup>) in the Union River during the first autumn storm in 2008



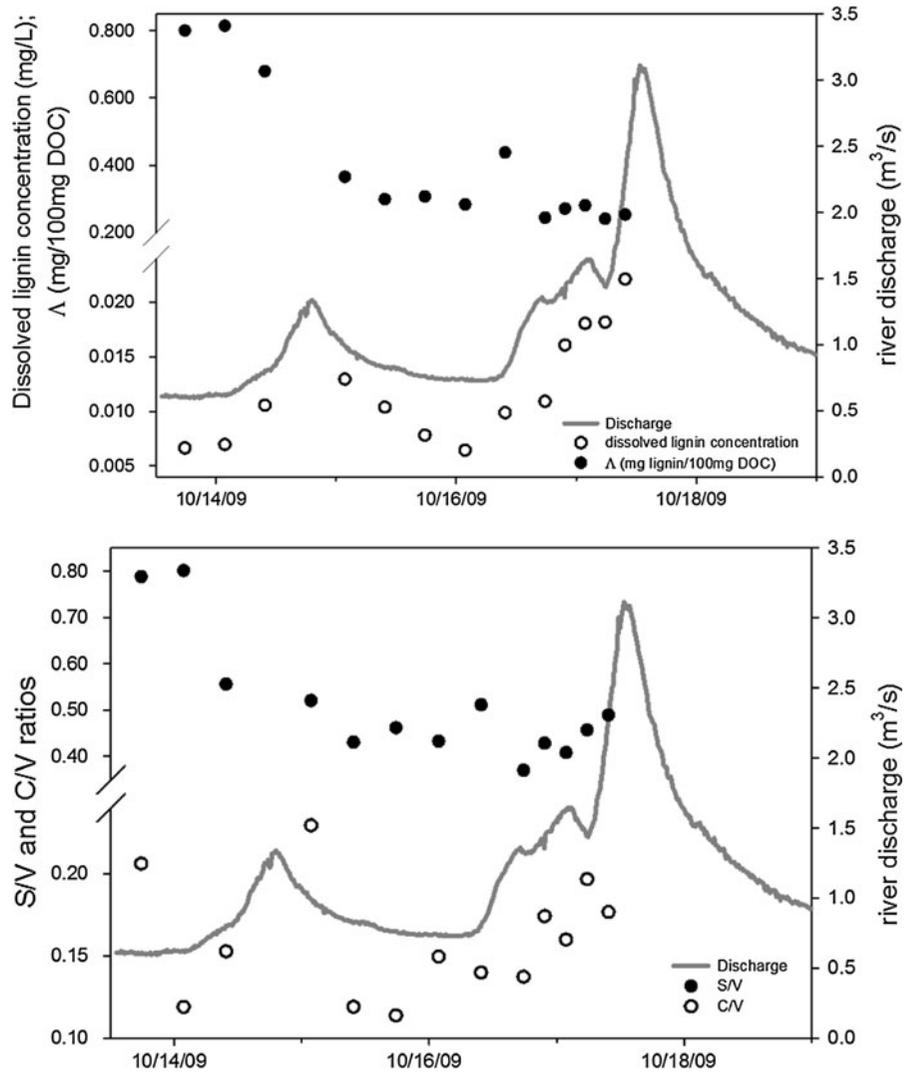
**Fig. 4** Particulate organic carbon and particulate organic nitrogen concentrations in the Union River September 2009

of dissolved lignin per mass of carbon (mg lignin/100 mg DOC) decreases, indicating a dilution of the DOC pool with non-lignin organic carbon (Fig. 5). During autumn storms there is an apparent increase in the ratio of cinnamyl to vanillyl phenols (C/V ratio) with increasing discharge as well as a decrease in the ratio of syringal to vanillyl phenols (S/V ratio; Fig. 5). Furthermore, there is a systematic increase in the ratio of vanillyl acids to vanillyl aldehydes [Ad/Al (v)] throughout the autumn storm event (Table 1). Similar results are seen during the November 2008 and January 2009 samplings in terms of lignin concentrations and

the ratio of lignin to DOC, although trends in C/V, S/V, and Ad/Al ratios are less distinguishable (Table 1). During the March 2009 sampling there appears to be a decrease in both total lignin concentrations and the lignin to DOC ratio and no distinguishable trends in Ad/Al (v), S/V, C/V, and (Table 1).

Particulate lignin concentrations were measured during the September 2009 storm. As with POC, total particulate lignin concentrations increased with increasing discharge (Fig. 6).  $\Lambda$ , or mg lignin per 100 mg POC, also increased with river discharge in contrast to observations in the ratio of dissolved lignin

**Fig. 5** Total dissolved lignin concentrations and the lignin to DOC ratio (*top*) and the ratio of syringal to vanillyl dissolved lignin phenols (S/V) and the ratio of cinnamyl to vanillyl dissolved lignin phenols (C/V) (*bottom*) in the Union River during the first significant autumn storm of 2009. As C/V increases material is more woody versus leafy; as S/V decreases material is more gymnosperm-derived versus angiosperm derived



to DOC (Fig. 5). Trends in the particulate lignin phenol ratios also showed opposite trends relative to dissolved lignin measurements during autumn storms (i.e. October 2009 sampling). With increasing discharge, S/V increased and both C/V and Ad/Al (v) decreased (Fig. 6).

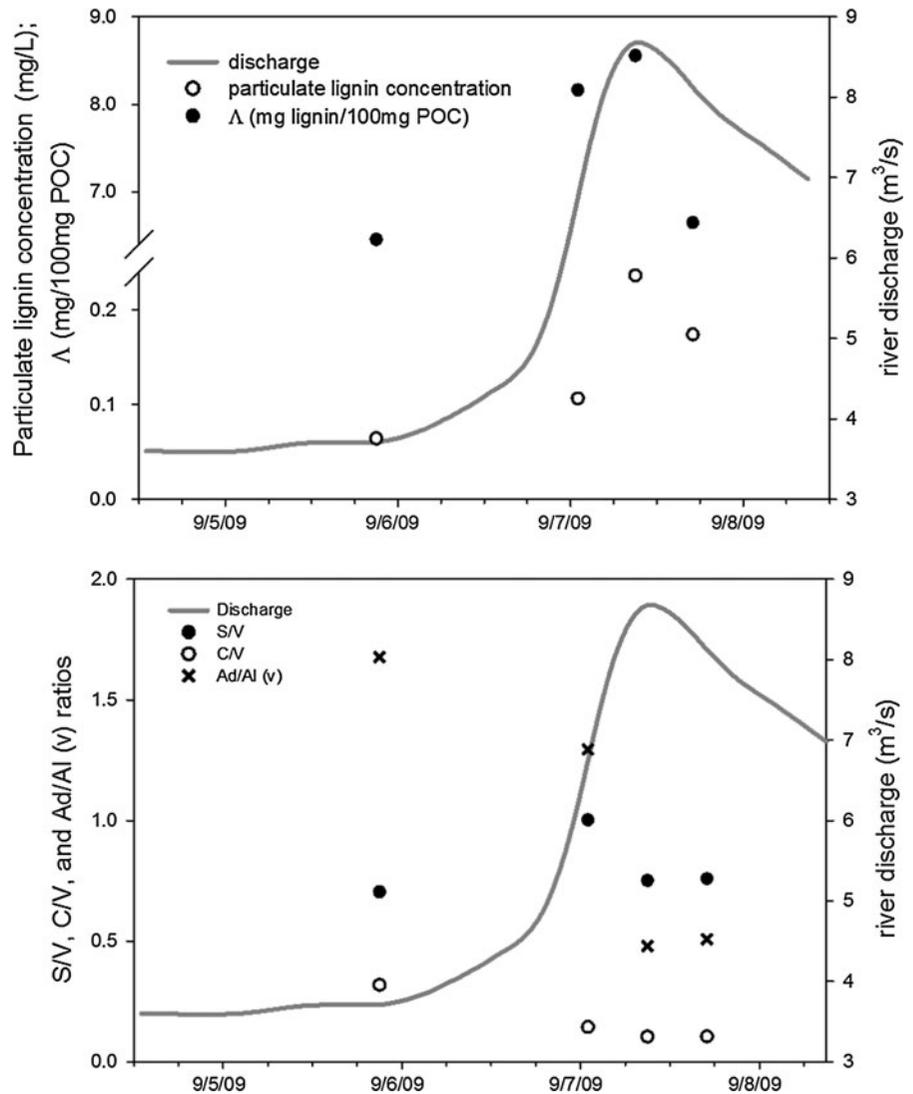
**Discussion**

**Nutrient accumulation and mobilization**

We suggest that nutrients accumulate in the upper soil layers in the Hood Canal watershed during long dry periods and are mobilized during autumn and winter

rainfall events. Excess nutrients are exhausted by successive winter storms. By late winter/early spring, nutrient concentrations exhibit little response to increased river discharge suggesting that the watershed has two distinct nutrient pools; (i) a deep soil nutrient pool that supports base flow nutrient concentrations throughout the year and (ii) an additional nutrient pool that accumulates in the shallow subsurface soil layer during periods of low soil saturation (i.e. summer dry periods) (Fig. 7). Hornberger et al. (1994) described the N-flushing hypothesis, which suggests that when the soil saturation deficit is high, nutrients accumulate in upper soil layers, and as the soil saturation deficit decreases, a saturated subsurface layer flushes nutrients from the

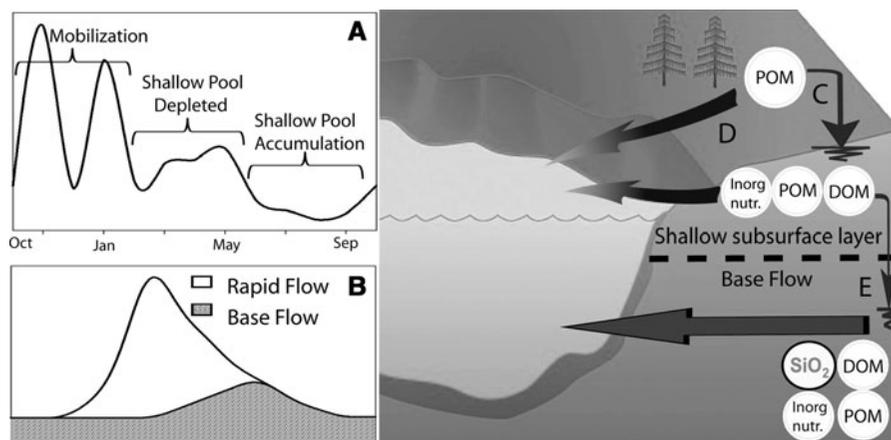
**Fig. 6** Total particulate lignin concentrations and  $\Lambda$ , or mg lignin/100 mg POC (*top*) and the particulate S/V, C/V, and Ad/Al (*v*) ratios (*bottom*) in the Skokomish River during the September 2009 storm



upper soil layers into the stream. The importance of hydrologic flowpaths through the uppermost OM rich soil layer in controlling soil OM concentrations has been demonstrated; during rapid rain events young OM has been shown to be flushed from upper soil layers, depleting soil OM concentrations and leaving behind older OM in deeper soil horizons (Schiff et al. 1998; van Verseveld et al. 2009). The 3–6 h time lag observed between peak river discharge and peak dissolved nutrient concentrations suggests that the accumulated shallow nutrient pool is mobilized by saturation of the shallow subsurface layer rather than by direct surface runoff. Based on end-member mixing models, Easthouse et al. (1992) estimated that base

flow largely consists of OM from deep soil layers, whereas 50–65% and 35–50% of the OM mobilized by peak flow originates from the B and O soil horizons, respectively. The observed decrease in silica concentrations in storms sampled throughout the year is the result of a dilution of base flow conditions; silica is relatively insoluble and is not mobilized by rapid shallow flow (Kennedy 1971; Hill et al. 1999).

As with dissolved nutrient concentrations, POC and PON are tightly correlated with river discharge during autumn and winter storms (Table 2). The correlation between POC and PON concentrations and river discharge diminishes by spring and summer samplings; for example the  $R^2$  value for POC drops from



**Fig. 7** *a* Nutrients accumulate in the shallow subsurface layer in dry summer months, are mobilized during autumn/winter storms, and are depleted from the accumulated shallow subsurface pool by late winter/spring. *b* Base flow is the sum of deep subsurface flow and delayed shallow subsurface flow (Ward and Robinson 1990). Rapid flow consists of surface runoff and shallow subsurface flow. *c* Particulate organic matter

(i.e. litterfall) degrades providing dissolved and particulate OM to the accumulated shallow subsurface nutrient/OM pool. *d* Surface and shallow subsurface material is mobilized by rapid flow leading to increased nutrient/OM concentrations during storm events. *e* Compounds that do not easily mobilize eventually fuel base flow chemical flux. Base flow of water provides a constant chemical flux to the river

0.96 in January 2009 to 0.01 in March 2009 (Table 2). The persistent correlation between discharge and TSS throughout the year supports the hypothesis that accumulated nutrients are completely leached out of soils by frequent winter storms. Thus, as with dissolved nutrients, a shallow pool of particulates with high nutrient content accumulates during long dry periods. Whereas dissolved constituents are mobilized primarily via saturation/solubilization of the sub surface soil layer, the occurrence of peak POC and PON concentrations simultaneously or prior to peak river discharge indicates that surficial processes such as displacement of discrete storage pools, surface runoff, and bank erosion are likely the primary means for mobilization of accumulated particulate nutrients and carbon. For example, in the September 2009 sampling POC and PON are moderately correlated with river discharge ( $R^2 = 0.88$  and  $0.80$  respectively), whereas dissolved nutrient concentrations are not (DOC  $R^2 = 0.51$ ; TDN  $R^2 = 0.14$ ; Table 2). Relative to later autumn storms, the September sampling occurred during a light rain event, which was likely not sufficient enough to saturate the upper soil layer and mobilize dissolved nutrients, whereas particulate material was mobilized by rapid surficial processes. For example, discharge in the Union River during the September 2009 sampling ranged from only  $0.65\text{--}0.91\text{ m}^3/\text{s}$ , whereas discharge

in the October 2009 sampling ranged from  $0.59$  to  $2.24\text{ m}^3/\text{s}$  (Table 1).

#### Organic matter characterization

Additional layers of complexity can be added onto the simple two nutrient pool model described above based on trends seen in carbon to nitrogen and lignin phenol ratios. Upon first inspection, the observed correlation between river discharge and DOC:DON ratios appears to indicate that the source of material to the shallow dissolved nutrient pool is of distinct origin from the source of the base flow pool; for example, material mobilized from the shallow soil pool has an elevated DOC:DON, which may indicate that the source of this pool is derived more from wood/vascular plant detritus than the base flow pool (Liaw and MacCrimmon 1977; Naiman and Sedell 1979). The increase in total dissolved lignin with discharge seems to support this, since lignin is unique to vascular plants (Sarkanen and Ludwig 1971). However, since the material in the base flow pool persists in soils longer than in the shallow pool it is also possible that the two pools are of similar origin and that the source signature has been altered by biogeochemical processes such as degradation and sorption (e.g. Aufdenkampe et al. 2001; Hernes et al. 2007).

Throughout autumn storms, the ratio of lignin to DOC decreases with increasing discharge. One explanation for the apparent enrichment of dissolved lignin in the deep base flow pool is that dissolved lignin is relatively more difficult to mobilize from soils than other dissolved organic carbon compounds; thus, other carbon compounds are more readily mobilized from soils into streams by rapid shallow flow. For example, Kaiser et al. (2004) observed that the hydrophobic fraction of lignin-rich DOM in soils is much less mobile relative to the hydrophilic fraction of DOM, composed primarily of carbohydrates, due to sorption of lignin-derived compounds by Al and Fe oxides–hydroxides. Easthouse et al. (1992) also observed a pronounced increase in the relative proportion of hydrophilic acids in stream water during an autumn storm event, followed by a lesser contribution in a subsequent storm. Another possible explanation is that the more rapidly cycled shallow pool of dissolved constituents has undergone less biodegradation than the deep base flow pool. Since few organisms are capable of directly consuming lignin, it is often considered relatively refractory compared to other carbon compounds (Trojanowski 1969; Crawford and Crawford 1980). However, the observed increase in the ratio of dissolved vanillyl acids to aldehydes [Ad/Al (v)] with increasing river discharge is contradictory to the above explanation. Upon biodegradation Ad/Al typically increases (Ertel and Hedges 1984; Hedges et al. 1988; Opsahl and Benner 1995), implying that DOM that is mobilized by storm events is more highly degraded than the base flow of DOM. In fact, many recent studies have begun to show that lignin in the dissolved phase is much more labile than once thought (Benner et al. 1991; Haddad et al. 1992; Opsahl and Benner 1995; Dittmar and Lara 2001; Otto and Simpson 2006).

It is likely that both biodegradation and sorption, which can be a rapid process relative to degradation (McKnight et al. 1992; Qualls and Haines 1992; Day et al. 1994; Aufdenkampe et al. 2001; Hernes et al. 2007), play an important role in the mobilization of dissolved carbon compounds. The observed data may imply that non-degraded dissolved lignin phenols (e.g. aldehydes) are relatively more difficult to mobilize from soils than their degraded counterpart (e.g. acids). The products of dissolved lignin degradation are mobilized by rapid shallow flow, whereas non-degraded dissolved lignin phenols are much less

soluble and persist in soils until further degradation. Prolonged exposure to water (i.e. base flow), on the other hand is capable of mobilizing the somewhat insoluble non-degraded dissolved lignin phenols similarly to silica mobilization. This hypothesis is in contrast to observations in high-latitude settings. Spencer et al. (2008) suggest that relatively less degraded OM, including lignin phenols, is released into high latitude rivers during spring flushing events. Cold winter temperatures prior to a high-latitude spring flushing, however, would inhibit OM degradation within soils, while drastic increases in river discharge may mobilize substantial amounts of OM regardless of its relative mobility. This DOC, however, has been shown to be highly labile once mobilized into the aquatic setting (Holmes et al. 2008). In contrast, biodegradation within soils is promoted during warm summer and autumn months in the temperate system studied here, allowing a preferential mobilization of more soluble/degraded OM during smaller peaks in discharge relative to high latitude spring flushings. Alternatively, it is possible that the less-degraded Ad/Al(v) signature of base flow dissolved lignin is unrelated to sorption processes and is simply an indicator that the deep soil horizons contain old, recalcitrant OM, whereas upper soil layers contain more fresh, labile OM that has been recently degraded. Numerous studies have shown that peaks in discharge release young labile OM relative to base flow (Schiff et al. 1998; Sanderman et al. 2009; van Verseveld et al. 2009).

The ratio of cinnamyl (C), vanillyl (V), and syringyl (S) phenols is an indicator of OM source; an increased C/V indicates a more non-woody than woody source and an elevated S/V indicates an angiosperm source (Hedges and Mann 1979; Hedges and Ertel 1982). Thus, the observed increase in C/V and decrease in S/V ratios of dissolved lignin with increasing river discharge indicates that the mobilized material contains more leafy/gymnosperm-derived compounds compared to the base flow of DOM. On the other hand, the systematic changes to C/V and S/V may indicate a preferential mobilization of cinnamyl phenols and retention of syringyl phenols relative to vanillyl phenols. Opposite trends in the ratio of lignin to OC, C/V, S/V, and Ad/Al (v) are observed in particulate lignin (Fig. 6). Perhaps compounds that are less likely to be mobilized by rapid flow are sorbed to the particulate

phase, which is either retained in soils or mobilized into the stream by surficial processes. However, particulate lignin data was only collected for one storm and is insufficient to entirely support the above hypothesis. It is likely that dissolved C/V and S/V ratios are controlled by the same mechanism described previously—preferential degradation of vanillyl versus syringyl phenols produces relatively more vanillyl acids (which are more easily mobilized than the non-degraded counterpart) than syringyl acids, for example. Likewise, it is possible that the shallow pool of young labile OM has simply undergone more degradation, and thus more phenolic fractionation, than the old refractory base flow pool.

The cumulative results from this year-long data set indicate that a shallow nutrient-rich pool of particulate and dissolved organic matter accumulates in watersheds during periods of soil-saturation deficiency (summer). Autumn and winter storms mobilize this pool of accumulated nutrients from surface soils, which is exhausted with successive winter storms. Results from this study will allow for more accurate nutrient and carbon export estimates from rivers with the development of more sophisticated watershed chemical models, which can be applied to river systems worldwide and used to tackle a diverse set of hydrological and biogeochemical issues. Furthermore, this unique high-resolution data set has contributed to a deeper understanding of the mechanisms involved in the mobilization of nutrients and OM from terrestrial biomes into river systems—a necessary step toward understanding the overall role of river systems in global biogeochemical cycling.

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