TEMPORAL VARIATION IN RIVER NUTRIENT AND DISSOLVED LIGNIN PHENOL CONCENTRATIONS AND THE IMPACT OF STORM EVENTS ON NUTRIENT LOADING TO HOOD CANAL, WA.

Nicholas D. Ward, University of Washington School of Oceanography, Seattle, WA, nickward@uw.edu;
Jeffrey E. Richey, University of Washington School of Oceanography, Seattle, WA, jrichey@uw.edu;
Richard G Keil, University of Washington School of Oceanography, Seattle, WA, rickkeil@uw.edu

<u>Abstract</u> A year-long data set measuring dissolved nutrient, particulate nutrient, and dissolved lignin phenol concentrations in several temperate Pacific Northwest rivers, shows a strong correlation between river discharge rates and nutrient concentrations during significant storm events following a long dry period. Furthermore, dissolved lignin concentrations increase with river discharge during autumn and winter storms; systematic changes to C/V, S/V, and Ad/Al (v) ratios indicate a mobilization of relatively more woody/gymnosperm-derived and degraded material during storm events. Results from this study suggest that a shallow nutrient-rich pool of particulate matter accumulates in watersheds during long dry periods; this nutrient-rich particulate matter degrades in surface soils, creating a pool of accumulated dissolved nutrients in surface soils during periods of soil-saturation deficiency. Surface runoff during autumn and winter storms mobilizes the nutrient-rich particulate pool, whereas dissolved nutrients are mobilized from soils once the soil saturation deficiency is alleviated. This pool of shallow soil nutrients, secondary to a deep soil pool sustaining base flow conditions, is exhausted with successive winter storms; by spring there is little to no response in river nutrient concentrations and a dilution of dissolved lignin concentrations with increased rainfall and river flow.

INTRODUCTION

The magnitude of nutrient export from a watershed is closely coupled with the rate of water discharge. On a seasonal scale, there is a logarithmic relationship between river discharge and concentrations of dissolved Carbon and Nitrogen constituents (e.g. Guillaud, et al. 2007). Furthermore, recent studies have shown a tight coupling between river discharge rates and dissolved nitrogen and carbon concentrations on shorter timescales (e.g. Sigleo and Frick, 2003; Boyer et al, 1997). Addition of nutrient-rich freshwater has been shown to cause eutrophication in nutrient-limited estuarine or coastal systems, which in certain cases results in hypoxic events (Howarth and Marino, 2006; Rabalais, et al., 2001); 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.

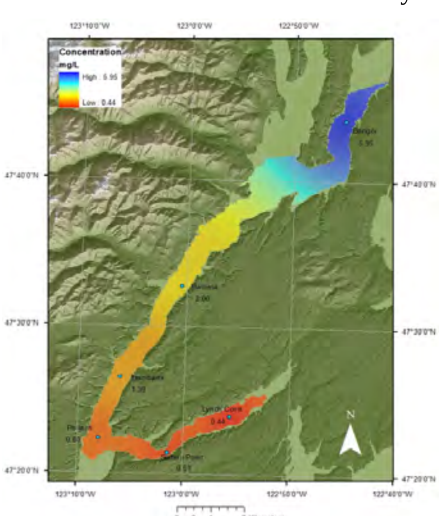

Figure 1. Dissolved O_2 concentrations in the Hood Canal. Sample sites for this study are the Skokomish and Union Rivers, which drain into the southwest and southeast corners of Hood Canal, respectively.

Observations in Hood Canal, WA—a branch of the fjord-like Puget Sound estuary—have shown that low dissolved Oxygen (DO) conditions in Hood Canal, especially in the southernmost Lynch Cove region (see figure 1), have become more persistent and widespread in recent decades compared to the 1930's to 1960's, resulting in increased frequency of hypoxic and fish kill events (Newton *et al*, 1995; Newton *et al* 2002). The Hood Canal Dissolved Oxygen Program Integrated Assessment and Modeling study (HCDOP-IAM) seeks to quantify the complex processes that contribute to low DO in Hood Canal, by utilizing marine models and a terrestrial Distributed Hydrology Soil-Vegetation Model (DHSVM). A subset of the HCDOP-IAM effort, this particular study seeks to better constrain river nutrient exports estimated by the DHSVM. The DHSVM, as it is, calculates total watershed nutrient export based on data gathered from monthly samplings from the 43 streams draining into Hood Canal; however, it is hypothesized that actual river-bound nutrient concentrations vary significantly on much shorter timescales than a monthly sampling is capable of representing due to large variation in rainfall and river flow. This hypothesis was explored by measuring river dissolved and particulate nutrient concentrations on several hour intervals during major storm events for an entire year. Stable isotope analysis of particulate N and C were measured to estimate the relative contributions of terrestrial, aquatic, and anthropogenic particulate organic matter (POM) sources. Furthermore, dissolved lignin phenol concentrations were measured to determine changes in dissolved organic carbon (DOC) composition throughout the course of a storm. This study seeks to describe the relationship between nutrient export and river discharge on a short time scale (hours) to enable the development of more accurate watershed chemical models, as well as increase understanding of river biogeochemical processes. Results from this study, as well as the described modeling study, can be applied to temperate river systems world-wide.

METHODS

Study Area The Hood Canal watershed (Figure 1) has a surface area of ~3,050 km^2, of which Hood Canal itself comprises 12%. The watershed can be separated into three zones: 1) the large mountainous watersheds of the Olympic Mountains with snowmelt dominated annual hydrographs, 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). Low DO conditions are most prevalent in the southernmost Lynch Cove region of Hood Canal due to its shallow bathymetry and resultant slow marine flushing rates (figure 1; Newton et al 2002). For this reason, this study focuses on the two rivers representative of those draining primarily into the Lynch Cove region, the Skokomish and Union Rivers.

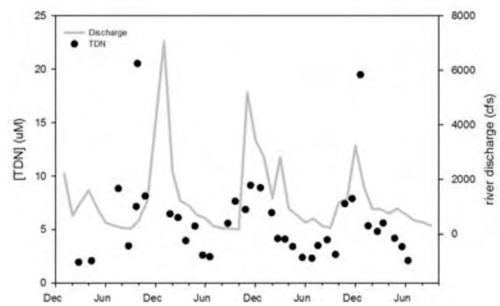

Figure 2. Monthly average TDN concentrations in the Skokomish River from 2005-2008. Peak TDN concentrations occur during winter months and reach a minimum during dry summer months.

The Skokomish River catchment, accounting for ~22% of the freshwater input into Hood Canal with a runoff rate of 3.2 m/yr, is situated in the southwest portion of the watershed, where annual precipitation rates are generally highest. The Skokomish catchment is sparsely populated with 0-4 people/km^2 and is primarily mature coniferous forest (46%) managed as national parks, national forest, or commercial forest (Steinberg et al. in review).

The Union River is a smaller stream, which drains into the southeast tip of Lynch Cove. The Union River and the numerous similar lowland draining streams account for ~24% of the freshwater input into Hood Canal with a runoff rate of 1.1 m/yr (Steinberg et al. in review). Compared to the Skokomish catchment, these lowland catchments have experienced more disturbance by clearing, suburban development, and wetland draining (McMurphy 1980, McCreary 1975, Ness and Fowler 1960). These watersheds have moderate population densities averaging 20 people/km^2. Dominant land use is primarily coniferous (~23% mature, ~15% young) and mixed deciduous (~30%) forests (Steinberg et al. in review); approximately 50% of the land covered by mixed deciduous forest consists of N_2-fixing red alder trees (L. McGeoch, unpubl. Data).

Sampling and Analysis Samples were collected on 3 or 4 hour intervals depending on forecasted storm duration using Teledyne ISCO autosamplers setup upstream of the Union and Skokomish River mouths. 24 samples were collected for each storm in acid-washed 1 L bottles, which were also pre-rinsed with river water prior to sampling. Storms were sampled over a 3 or 4 day period from October 2008 through October 2009 on the following start dates: 10/3/08, 10/31/08, 11/4/08, 1/6/09, 3/13/09, 3/16/09, 6/19/09, 9/4/09, and 10/13/09. Figure 2 was compiled using data from monthly sampling of the Skokomish River over a 3 year period. 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 (NO_3^-, NO_2^-, NH_4^+, SiO_4^{4-}, and PO_4^{3-}) were filtered through Whatman® cellulose acetate filters (0.45 µm), and analyzed on an Alpkem RFA/2 autoanalyzer. TDN and DOC was measured on a Shimadzu DOC analyzer after filtering through pre-combusted Whatman® GF/F glass fiber filters (0.7 µm nominal pore size) into pre-cleaned glass vials. Dissolved Organic Nitrogen (DON) concentrations were calculated by subtracting NO_3^-, NO_2^-, and NH_4^+ concentrations from TDN. For particulates, between 100 and 600 mL of stream water were filtered through pre-combusted Whatman® GF/F glass fiber filters, depending on sample turbidity. Particulates captured on the filters were then dried at 55 °C for 24 hours, acid-fumigated for 24 hours, re-dried at 55 °C, 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 PDZEuropa ANCA-GSL elemental analyzer. For Total Suspended Sediment (TSS) calculations, between 100 and 600 mL of stream water were filtered through pre-weighed/combusted Whatman® GF/F glass fiber filters, dried 55 °C for 48 hours, and weighed.

For dissolved lignin extraction, water samples were prefiltered through combusted Whatman® GF/F glass fiber filters and slowly (3 $mLmin^{-1}$) passed through 200 mg Waters Oasis HLB cartridges, which 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 ~1 drop/sec. 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 (MARS 5).

RESULTS

TDN and DOC Based on data collected monthly over a 3 year period, average TDN concentrations in the Skokomish and Union Rivers peak during winter months and reach a minimum during dry summer months (figure 2). TDN is typically comprised of about two-thirds nitrate and one-third DON, although the ratio of nitrate to DON generally increases with discharge during storm events (table 1). Results from storm samplings show that during the first significant storm (i.e. several days of consistent rainfall) after a dry summer, both TDN and DOC concentrations are tightly coupled with river discharge; both the Skokomish and Union Rivers saw a near-doubling of TDN and DOC concentrations with a doubling in river discharge during the 10/3/08 storm (figure 3). This strong coupling persisted through the November samplings (table 1), which saw a four-fold increase in river discharge and DOC and TDN concentrations over a several day period. After several months of consistent rainfall, the correlation between discharge and concentrations began to diminish, although still existed; during the January 2009 Union River sampling (figure 4), a 137% increase in river discharge only 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. Likewise, a 115% increase in discharge during the October 2009 sampling yielded a 92% and

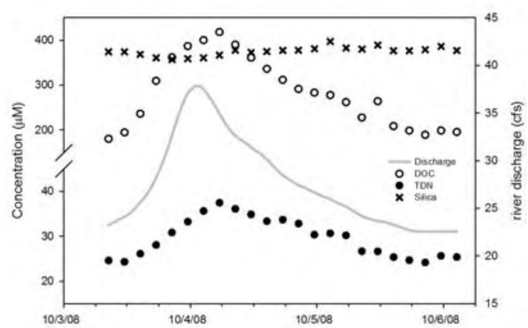

Figure 3. TDN, DOC and silica concentrations in the Union River during the first significant autumn storm of 2008.

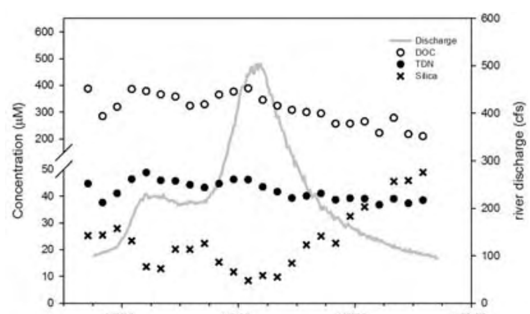

Figure 4. TDN, DOC, and Silica concentrations in the Union River during a winter 2009 storm.

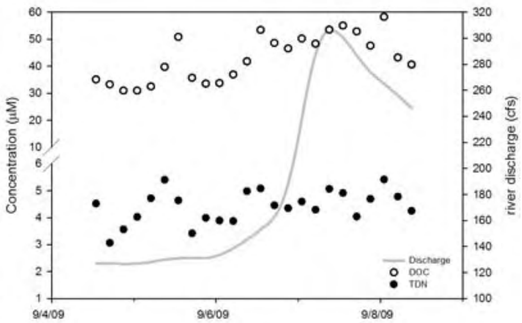

Figure 5. TDN, and DOC concentrations in the Skokomish River during a late summer storm

326% increase in TDN and DOC concentrations, respectively. 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. Surprisingly, TDN and DOC concentrations also remained fairly constant during the September 2009 sampling, with only a slight increase in DOC (figure 5); although river discharge increased significantly throughout the rain event, precipitation was patchy and inconsistent, meaning the soil was never able to significantly saturate with water. C to N and N to P ratios are positively correlated with river discharge in storms that show a coupling of nutrient concentrations with river discharge (i.e. October through January); the correlation between C/N and N/P ratios and discharge is strongest when the correlation between nutrient concentrations and discharge is strongest.

Dissolved Organic N, NO_3^-, NO_2^-, NH_4^+, SiO_4^{4-}, PO_4^{3-}

Dissolved NO_3^- concentrations followed the same pattern as TDN described above, showing a strong correlation with river discharge in autumn rain events that decreases in subsequent storms. In all storm events sampled throughout the year, SiO_4^{4-} concentrations decrease with increasing river discharge (e.g. figures 3 and 4). During autumn samplings, phosphate, ammonium, and nitrite concentrations also appear to increase with river discharge (figure 7). 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 previously. Phosphate, ammonium, and nitrite concentrations show a similar trend in winter storms (e.g. 1/6/09 sampling). As with NO_3^-, DON concentrations also increased with increasing river discharge in autumn and winter storms; this relationship diminished during spring and summer samplings (table 1). The ratio of NO_3^- to DON generally increased as river discharge increased in all sampled storms.

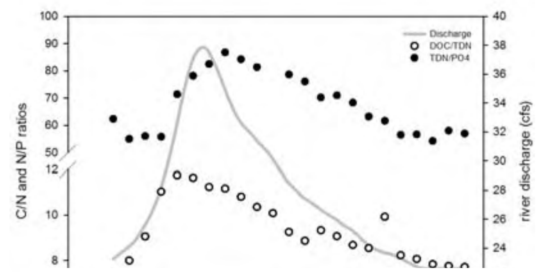

Figure 6. DOC/TDN and TDN/PO_4^{3-} ratios in the Union River during the first autumn storm in 2008

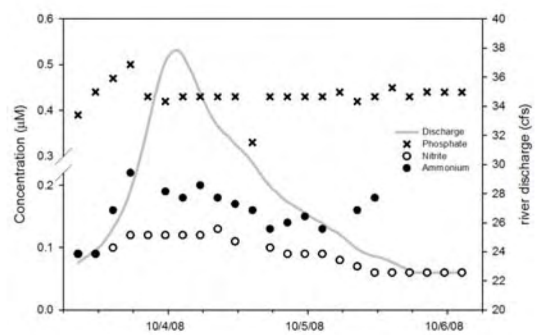

Figure 7. Dissolved Nitrite, Ammonium, and Phosphate concentrations in the Union River during the first significant autumn storm of 2008.

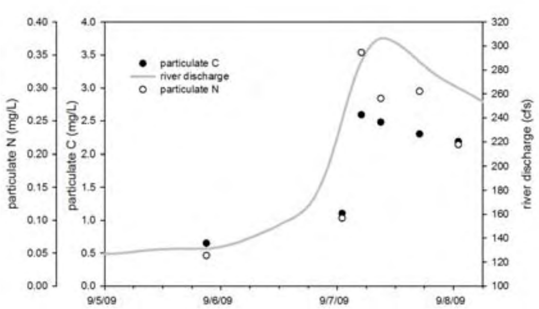

Figure 8. POC and PON concentrations in the Union River September 2009

Particulate C, N and TSSTSS concentrations showed a strong positive correlation with river discharge during all sampled storm events (table 1). 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 decreases in river flow. Similar to the observed trends in dissolved nutrient concentrations, particulate organic N and C (PON and POC) concentrations are highly correlated with river discharge

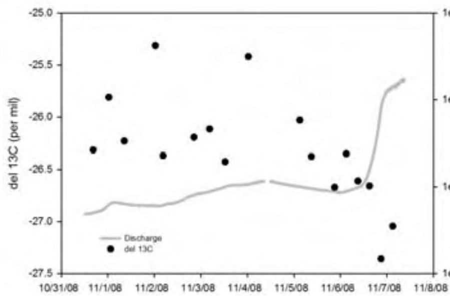

Figure 9. River discharge and ∂^{13}C in the Skokomish River during an autumn 2008

during autumn and winter storms (e.g. figure 8). As with dissolved concentrations, the coupling between particulate nutrient concentrations and river discharge was not observed in spring samplings and began to diminish after several major autumn storms (table 1). An interesting difference between dissolved and particulate nutrient concentrations is that POC and PON concentrations showed a strong correlation with discharge in the light rain event sampled in September 2009, whereas dissolved concentrations showed nearly no response (figures 5 and 8).

Stable isotope analysis of POC and PON revealed several notable trends, although results were generally more scattered than with the other measured parameters. ∂^{13}C generally decreased with increasing river discharge in all sampled storms, although, as with other parameters, this trend was most evident in autumn and winter samplings (figure 9; table 1). Throughout the year, ∂^{13}C values ranged from -25.3‰ to -29.2‰, indicating a primary input of C3 terrestrial OM. ∂^{15}N data did not show many clear trends; in most sampled storms ∂^{15}N values ranged from roughly +2‰ to +4‰, indicating a terrestrial source. However, the 9/4/09 and 1/6/09 storms showed a clear decrease in ∂^{15}N with increased discharge, ranging from +2.9‰ to -4.3‰ and +3.8‰ to -5.9‰ (table 1). Particulate C/N ratios did not show as clear of a trend as dissolved C/N ratios, however, C/N ratios generally increased with increased river discharge. Similar to dissolved ratios, this trend was most notable in autumn and winter samplings.

Dissolved Lignin Phenols As with DOC, the total concentration of dissolved lignin was highly correlated with river discharge during autumn storms (figure 10). With an increase in river discharge and subsequent increase in DOC and lignin concentrations, the total mass of lignin per mass of carbon (mg lignin/100 mg DOC) decreases (figure 10). As river discharge and lignin concentrations increase, there is an apparent increase in the ratio of cinnamyl to vannilyl phenols (C/V ratio) as well as a decrease in the ratio of syringal to vannilyl phenols (S/V ratio; figure 11). Furthermore, there is a systematic increase in the ratio of vannilyl acids to vannilyl aldehydes (Ad/Al (v)) throughout the autumn storm event (table 1). Similar results are seen during the 11/4/08 sampling (table 1).

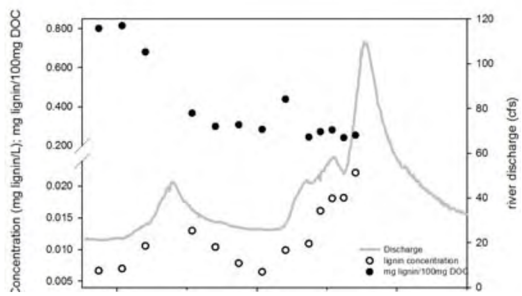

Figure 10. Total dissolved lignin concentrations, and the lignin to DOC ratio in the Union River during the first significant autumn storm of 2009

During the winter 1/6/09 sampling, lignin concentrations and the lignin to DOC ratio followed the same trend as mentioned above (table 1). However, contrary to the above results, Ad/Al (v) values decreased as river discharge increased. C/V ratios appeared to show a similar increase with river discharge, with no distinguishable trend in S/V ratios. During the 3/13/09 sampling, there appears to be a decrease in both total lignin concentrations and the lignin to DOC ratio (table 1). There is no distinguishable trend in S/V, C/V, and Ad/Al (v) during the 3/13/09 storm.

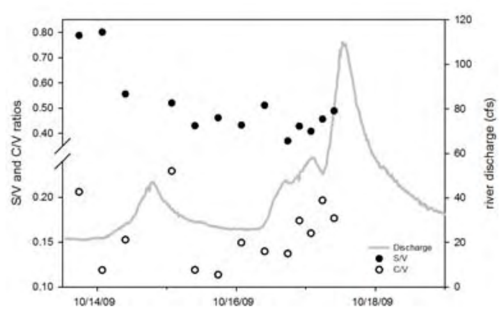

Figure 11. The S/V and C/V ratios of dissolved lignin phenols and in the Union River during the first significant autumn storm of 2009. As C/V increases material is more woody than leafy; as S/V decreases material is more gymnosperm-derived.

Table 1. Storm sampling data*

River	Date	Time	River flow (cfs)	DOC (µM)	TDN (µM)	SiO_4 (µM)	NO_3^- (µM)	PO_4^{3-} (µM)	DON (µM)	TSS mg/L	POC mg/L	PON mg/L	$\Delta^{13}C$ ‰	$\Delta^{15}N$ ‰	Total lignin mg/L	mg lignin/ 100mg DOC	S/V	C/V	Ad/Al(v)
SKOK	10/31/08	16:30	503	70	6.7	165	1.2	0.02	5.34	4.6	0.60	0.04	-26.3	2.1	6.5E-03	7.7E-03	0.58	0.16	1.20
SKOK	10/31/08	20:30	532	69	6.4	166	1.6	0.01	4.56	6.2					5.8E-03	7.0E-03	0.63	0.20	0.97
SKOK	11/1/08	0:30	622	65	4.3	166	0.8	0.02	3.16	7.7	0.66	0.10	-25.8	2.9	7.0E-03	8.9E-03	0.77	0.25	1.60
SKOK	11/1/08	4:30	658	68	7.9	166	2.0	0.01	5.49	6.0									
SKOK	11/1/08	8:30	634	59	4.7	166	1.2	0.01	3.34	9.3	0.98	0.07	-26.2	2.9	5.3E-03	7.5E-03	0.61	0.18	1.35
SKOK	11/2/08	0:30	604	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	610	52	4.9	169	1.4	0.00	3.26	2.2	0.71	0.04	-26.4	3.1	5.3E-03	8.4E-03	0.70	0.21	1.44
SKOK	11/2/08	8:30	640	51	4.0	170	1.5	0.00	2.28	2.4					4.9E-03	8.1E-03	0.75	0.22	1.43
SKOK	11/2/08	12:30	676	48	4.4	170	1.7	0.00	2.52	2.9					8.4E-03	1.5E-02	0.58	0.19	1.40
SKOK	11/2/08	16:30	750	52	4.4	171	1.6	0.00	2.67	1.4					8.6E-03	1.4E-02	0.70	0.28	1.14
SKOK	11/2/08	20:30	801	45	3.5	169	1.5	0.00	1.75	2.3	0.47	0.03	-26.2	3.8	9.4E-03	1.7E-02	0.63	0.20	0.95
SKOK	11/3/08	0:30	847	72	4.0	169	1.3	0.00	2.61	3.6					6.3E-03	7.4E-03	0.68	0.20	1.04
SKOK	11/3/08	4:30	881	51	3.8	171	0.9	0.00	2.65	2.8	0.62	0.04	-26.1	3.5	8.7E-03	1.4E-02	0.69	0.22	1.28
SKOK	11/3/08	12:30	1000	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	1070	64	3.8	160	1.1	0.01	2.41	9.5	0.60	0.03	-25.4	2.2	9.5E-03	1.4E-02	0.63	0.32	1.64
SKOK	11/4/08	15:00	1110	77	5.4	162	3.2	0.01	0.74	1.4					7.8E-03	7.2E-03	0.39	0.15	1.13
SKOK	11/4/08	21:00	1050	68	5.9	164	3.4	0.01	1.69	6.2					7.1E-03	5.8E-03	0.46	0.17	1.11
SKOK	11/5/08	3:00	1000	58	5.1	177	3.6	0.01	0.50	6.4	0.44	0.02	-26.0	3.5	1.1E-02	7.5E-03	0.44	0.17	1.09
SKOK	11/5/08	6:00	978	61	4.3	164	3.7	0.01	0.00		0.57	0.03	-26.4	3.0	1.0E-02	6.7E-03	0.54	0.17	1.96
SKOK	11/5/08	9:00	950	56	4.8	166	3.7	0.01	0.00	4.6					8.7E-03	5.5E-03	0.40	0.16	1.31
SKOK	11/5/08	21:00	881	49	4.5	177	3.4	0.01	0.00	3.6	0.38	0.09	-26.7	2.5	1.1E-02	6.3E-03	0.41	0.14	1.08
SKOK	11/6/08	3:00	888	50	4.8	165	3.5	0.01	0.00	3.7	0.34	0.02	-26.4	3.4	1.9E-02	1.2E-02	0.69	0.12	1.64
SKOK	11/6/08	9:00	985	55	4.5	164	3.6	0.00	0.00	3.3	0.51	0.03	-26.6	2.9	1.4E-02	9.0E-03	0.58	0.21	1.43
SKOK	11/6/08	15:00	1570	72	5.1	159	3.9	0.03	0.38	4.7	0.31	0.07	-26.7	3.1	1.2E-02	1.0E-02	0.62	0.15	1.52
SKOK	11/6/08	21:00	8010			135	7.2	0.09	0.00	117.8	2.81	0.29	-27.4	2.8	5.7E-03	1.0E-02	0.61	0.15	1.13
SKOK	11/7/08	3:00	13700	214	14.3	135	6.9	0.12	6.51	943.4	5.32	0.65	-27.0	2.6	4.7E-03	1.2E-02	0.44	0.15	0.98
SKOK	11/7/08	9:00	17200	156	10.3	145	6.4	0.10	3.21						6.3E-03	1.2E-02	0.45	0.18	1.03
UNIO	1/6/09	20:00	108	285	37.6	25	31.4	0.24	4.93	44.9	3.04	0.25	-27.1	3.8	3.6E-01	1.7E-02	0.54	0.29	1.88
UNIO	1/7/09	5:00	229	378	48.7	14	39.4	0.24	7.95	239.6	7.08	0.56	-28.0	-3.0	3.6E-01	2.4E-02	0.57	0.21	1.53
UNIO	1/7/09	17:00	217	329	43.1	22	35.4	0.22	6.65	83.1	9.38	0.81	-27.9	-4.4	6.7E-01	3.0E-02	0.12	0.05	1.13
UNIO	1/8/09	2:00	479	389	46.1	8	38.6	0.19	6.14	434.6	19.05	1.49	-27.8	-2.1	2.6E-01	1.8E-02	0.65	0.26	1.08
UNIO	1/8/09	11:00	311	308	39.2	15	34.1	0.16	4.29	379.5	8.90	0.79	-27.9	-5.9	2.6E-01	1.5E-02	0.64	0.26	1.19
UNIO	1/9/09	14:00	103	210	38.4	49	33.1	0.20	4.24	32.5	2.56	0.16	-26.9	1.8	2.8E-01	1.2E-02	0.89	0.20	0.99
SKOK	3/13/09	19:30	676	40	8.3	35	2.8	0.03	5.52	11.8	0.64	0.034	-25.3	2.8	1.2E-02	2.6E-02	0.61	0.09	0.89
SKOK	3/14/09	11:30	782	36	4.5	66	3.6	0.06	0.31	4.1	0.45	0.040	-27.4	3.3	8.1E-03	1.9E-02	1.54	0.84	0.37
SKOK	3/14/09	23:30	854	41	5.7	48	3.6	0.04	1.04	5.6	0.86	0.042	-28.1	3.3	9.8E-03	2.0E-02	0.69	0.18	1.26
SKOK	3/15/09	23:30	840	40	5.4	53	4.1	0.04	0.39	8.0	0.47	0.061	-25.8	3.4	3.4E-02	7.1E-02	0.04	0.01	0.13
SKOK	3/16/09	23:30	894	44	6.5	78	4.4	0.08	1.60	8.2	0.62	0.047	-28.3	2.0	5.9E-03	1.1E-02	0.70	0.18	1.07
SKOK	3/17/09	15:30	929	44	6.1	47	3.9	0.05	2.08	10.4	0.61	0.041	-26.6	2.3	6.8E-03	1.3E-02	0.83	0.25	2.20

UNIO	6/19/09	14:00	39	82	20.4	385	16.5	0.29	2.9	2.5					8.4E-03	8.5E-03	0.54	0.14	0.86
UNIO	6/20/09	6:00	48	88	21.6	406	17.5	0.33	3.2	1.4					9.0E-03	8.5E-03	0.66	0.23	0.71
UNIO	6/20/09	10:00	46	80	18.9	397	17.0	0.28	1.6	8.5					7.9E-03	8.2E-03	0.69	0.16	0.73
UNIO	6/20/09	14:00	40	87	20.4	399	17.1	0.31	3.2	1.6					6.8E-03	6.5E-03	0.50	0.13	0.76
UNIO	6/20/09	22:00	44	83	20.7	397	18.7	0.29	1.6	2.1					8.5E-03	8.5E-03	0.55	0.18	0.51
UNIO	6/21/09	2:00	48	85	22.0	397	19.0	0.28	2.7	1.9					6.7E-03	6.6E-03	0.54	0.14	0.91
SKOK	9/5/09	21:00	131	34	4.0	211	2.4	0.22	1.57	4.8	0.65	0.046	-26.2	2.9					
SKOK	9/7/09	1:00	223	50	4.6	202	3.0	0.14	1.54	15.5	1.10	0.103	-27.6	1.6					
SKOK	9/7/09	5:00	282	48	4.3	197	3.1	0.12	1.11	50.2	2.59	0.354	-28.9	0.5					
SKOK	9/7/09	9:00	308	54	5.1	195	3.8	0.11	0.68	65.3	2.48	0.284	-29.2	-4.3					
SKOK	9/7/09	17:00	293	53	4.0	196	3.6	0.13	0.22	42.0	2.30	0.295	-27.8	-2.3					
SKOK	9/8/09	1:00	267	58	5.4	200	3.9	0.15	0.82		2.18	0.214	-29.1	-3.5					
UNIO	9/5/09	19:00	23	97	18.7	399	17.4	0.51	0.64	3.9	0.67	0.056	-28.2	1.7					
UNIO	9/6/09	10:00	23	115	21.0	401	18.8	0.55	1.10	4.6	0.84	0.063	-26.8	2.1					
UNIO	9/6/09	16:00	32	131	18.5	392	17.5	0.50	0.90	4.2	0.65	0.098	-28.4	3.1					
UNIO	9/6/09	22:00	27	130	19.5	400	18.6	0.53	0.45	4.2	0.72	0.049	-26.6	2.7					
UNIO	9/7/09	4:00	25	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	24	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	23	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	24	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	21	69	19.1	397	12.5	0.31	6.3		0.84	0.119	-27.2	2.3	6.6E-03	8.0E-03	0.79	0.21	0.99
UNIO	10/14/09	1:45	22	71	19.4	395	13.0	0.28	6.0		0.66	0.043	-26.8	3.3	7.0E-03	8.2E-03	0.80	0.12	0.39
UNIO	10/14/09	9:45	28	129	20.4	384	11.9	0.40	8.2		0.88	0.065	-27.9	3.1	1.1E-02	6.8E-03	0.56	0.15	0.72
UNIO	10/14/09	17:45	45	310	30.6	346	17.3	0.41	12.8		2.45	0.214	-28.1	3.1					
UNIO	10/15/09	1:45	35	295	37.2	367	25.4	0.25	10.7		1.85	0.144	-28.1	3.4	1.3E-02	3.7E-03	0.52	0.23	0.72
UNIO	10/15/09	9:45	29	290	34.1	384	21.2	0.29	12.3		0.82	0.113	-28.4	3.1	1.0E-02	3.0E-03	0.43	0.12	0.77
UNIO	10/15/09	17:45	27	213	30.7	405	19.9	0.22	9.6		0.90	0.066	-26.8	3.2	7.8E-03	3.1E-03	0.46	0.11	0.73
UNIO	10/16/09	1:45	26	190	29.5	409	19.0	0.26	9.3		1.08	0.083	-27.5	3.5	6.5E-03	2.8E-03	0.43	0.15	0.70
UNIO	10/16/09	9:45	28	188	26.4	399	16.8	0.30	8.4		0.68	0.080	-27.2	3.4	9.9E-03	4.4E-03	0.51	0.14	0.95
UNIO	10/16/09	17:45	47	374	32.8	373	19.3	0.31	12.9		2.60	0.159	-28.3	2.7	1.1E-02	2.4E-03	0.37	0.14	1.22
UNIO	10/16/09	21:45	48	496	43.0	349	26.5	0.40	15.8		2.67	0.196	-26.8	3.8	1.6E-02	2.7E-03	0.43	0.17	1.06
UNIO	10/17/09	1:45	57	538	45.1	342	28.2	0.31	16.3		3.94	0.270	-28.1	3.1	1.8E-02	2.8E-03	0.41	0.16	0.95
UNIO	10/17/09	5:45	51	630	63.8	348	42.5	0.27	20.4		12.35	0.954	-28.6	3.0	1.8E-02	2.4E-03	0.46	0.20	1.03
UNIO	10/17/09	9:45	79	728	63.5	290	41.3	0.46	21.5		10.89	0.801	-28.5	2.6	2.2E-02	2.5E-03	0.49	0.18	0.71

*For a complete table with all data points and parameters measured, please contact the lead author.

DISCUSSION

Results from this year-long dataset suggest that in the Hood Canal watershed, nutrients accumulate in soils during long dry periods, and are mobilized during significant storm events that saturate surface soils. This pool of excess nutrients is exhausted by successive winter storms, and by late winter/early spring, there is relatively little increase in nutrient concentrations with increased river discharge. This suggests that one could consider the watershed to have two major nutrient pools—a deep soil pool supporting base flow nutrient concentrations, and a shallow soil pool, which accumulates nutrients during periods of low soil saturation (i.e. dry periods). Furthermore, the upper soil layers must be adequately saturated to mobilize these nutrients; for example, during the September 2009 sampling there was no significant increase in TDN concentrations with increased river discharge because rainfall was too inconsistent to saturate soils adequately enough to strongly mobilize the shallow dissolved nutrient pool (figure 5). Since TDN concentrations remained nearly constant and were not diluted like silica concentrations (i.e. base flow conditions), it is likely that nutrients from the shallow pool were only weakly mobilized. These results are consistent with 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 upper soil layers into the stream (Hornberger et al, 1994).

The observed correlation between river discharge and C/N and N/P ratios suggests that Carbon is more easily mobilized from surface soils than Nitrogen, and, likewise, Nitrogen is more easily mobilized than Phosphorous. These findings are consistent with results from studies showing that dissolved inorganic phosphorous is retained in sediments to a higher degree than nitrate because of its involvement in various precipitation and dissolution reactions (e.g Lucotte and d'Anglejan, 1988; Fox, 1989). The relative ease of mobilization of C versus N explains why DOC concentrations slightly increased with discharge in the September 2009 sampling, whereas TDN concentrations remained nearly constant. The observed decrease in Silica concentrations is the result of a dilution of base flow conditions by rapid shallow flow because Silica is far less soluble than Nitrogen, for example (Hill *et al*, 1999; Kennedy, 1971).

As expected, increased river flow mobilizes sediments, leading to a strong correlation between river discharge and total suspended sediment concentrations throughout the entire year. As with dissolved nutrient concentrations, POC and PON show strong correlation with river discharge during autumn and winter storms. This correlation diminishes by spring and summer samplings indicating that, as with dissolved nutrients, a shallow pool of particulates with high nutrient content accumulates during long dry periods. This nutrient-rich particulate pool is mobilized by surface runoff along with surface sediments rather than by the saturation of a sub-surface layer. For example, in the September 2009 sampling, POC and PON are highly correlated with river discharge, whereas dissolved nutrients are not.

Dissolved lignin phenol and particulate stable isotope analysis suggest that the shallow dissolved nutrient pool is derived from the shallow nutrient-rich particulate pool. Observed trends in dissolved lignin phenol concentrations and compositions indicate that relatively degraded plant material is mobilized with increasing soil saturation and river discharge during autumn and winter storms. The increase in C/V and decrease in S/V ratios with increasing river discharge indicate input of more woody/gymnosperm-derived material, and the increase in Ad/Al (v) suggests that this material is more highly degraded. Furthermore, decreases in ∂^{13}C with discharge may indicate input of more diagenetically altered particulate material. Lignin concentrations begin to decrease with additional river flow in the spring, indicating that the pool of shallow DOC has been mostly exhausted of lignin-derived organic matter. The above results from this study suggest that a shallow nutrient-rich pool of particulate matter accumulates in watersheds during long dry periods; this nutrient-rich particulate matter degrades in surface soils, creating a pool of accumulated dissolved nutrients in surface soils. Surface runoff during autumn and winter storms mobilizes the nutrient-rich particulate pool, whereas dissolved nutrients are mobilized from soils once soil saturation is no longer deficient. These accumulated nutrient pools dominate short term river nutrient concentrations by providing a strong correlation between river discharge and concentrations. After subsequent winter storms the pools of accumulated particulate and dissolved nutrients are depleted and river nutrient concentrations are dominated by base flow conditions, resulting in far less short-term variability in river nutrient concentrations.

In the context of the HCDOP-IAM modeling effort, this study suggests that storm-induced N surges can make a profound difference in total N export estimations depending on when monthly samples were taken. For example, rough estimates suggest that model export estimates for November 2007 should be a factor of 2 higher for the Skokomish River because the monthly sample was taken during a low point in the month's hydrograph. Likewise, export estimates for months that were sampled during above-average river flow conditions will be underestimated. 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. Furthermore, these results can be applied to temperate river systems worldwide to tackle a diverse set of topics.

REFERENCES

Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight. 1997. Response characteristics of DOC flushing in an alpine catchment. Hydrological Processes 11:1635-1647.

Fox, L. E. 1989. A model for inorganic control of phosphate concentrations in river waters. *Geochim. Cosmochim. Acta*. 53, 417-428

Guillaud, Jean-François, Alain Aminot[a], Daniel Delmas[b], Francis Gohin[a], Michel Lunven[a], Claire Labry[a] and Alain Herbland. 2007. Seasonal variation of riverine nutrient inputs in the northern Bay of Biscay (France), and patterns of marine phytoplankton response. Journal of Marine Systems Volume 72, Issues 1-4, July 2008, Pages 309-319 Oceanography of the Bay of Biscay

Hill, A.R., W.A. Kemp, J.M. Buttle and D. Goodyear. 1999. Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. Water Resources Research 35:811-821.

Hornberger, G. M., K. E. Bencala, and D. M. McKnight, Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, B*iogeochemistry, 25,* 147–165, 1994.

Howarth AND R. MARINO. 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. Limnol. Oceanogr. 51: 364–376.

Kennedy, V.C. 1971. Silica Variation in Stream Water with Time and Discharge. In J.D. Hem, ed., Nonequilibrium Systems in Natural Water Chemistry, pp. 95-130. American Chemical Society Advances in Chemistry 106, Washington, DC.

Lucotte, M. and d'Anglejan, B. 1988. Processes controlling phosphate adsorption by iron hydroxides in estuaries. *Chem. Geol.* 67, 75-83

McCreary FR (1975) Soil survey of Jefferson County area, Washington. USDA Soil Conservation Service, Washington DC

McMurphy CJ (1980) Soil survey of Kitsap County area, Washington. USDA Soil Conservation Service, Washington DC

Ness AO, Fowler RH (1960) Soil Survey of Mason County, Washington. USDA Soil Conservation Service in cooperation with Washington Agricultural Experiment Station, Washington DC

Newton, J.A., A.L. Thomson, L.B. Eisner, G.A. Hannach, and S.L. Albertson, 1995, Dissolved oxygen concentrations in Hood Canal: Are conditions different than forty years ago? In Puget Sound Research '95 Proceedings, Puget Sound Water Quality Authority, Olympia, WA, pp. 1002-1008.

Newton, J.A., S.L. Albertson, K. Van Voorhis, C. Maloy, and E. Siegel, 2002, Washington State Marine Water Quality in 1998 through 2000, Washington State Department of Ecology,Environmental Assessment Program, Publication #02-03-056, Olympia, WA.

Peterson, D.L., Schreiner, E.G., Buckingham, N.M. 1997. Gradients, vegetation and climate: spatial and temporal dynamics in the Olympic Mountains, U.S.A. Global Ecology and Biogeography. Letters, 6: 7-17

Rabalais, N.N., R.E. Turner, and W.J. Wiseman, Jr. 2001. Hypoxia in the Gulf of Mexico. J. Environ. Qual. 30:320–329

Sigleo and Frick, 2003 Sigleo, A.C., Frick, W.E., 2003. Seasonal variations in river flow and nutrient concentrations in a Northwestern USA watershed. In: Proceedings of the First Interagency Conference on Research in the Watersheds, October 2003, Benson, Arizona, USDA, pp. 370–376.

Steinberg, P.D., Brett, M.T., Bechtold, J.S., Richey, J.E., McGeoch, L.E., Osborne, S.N. In Review. The Influence of Watershed Characteristics on Nitrogen Export to Hood Canal, Washington, USA.