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The influence of watershed characteristics on nitrogen export to and marine fate in Hood Canal, Washington, USA

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Abstract Hood Canal, Washington, USA, is a poorly ventilated fjord-like sub-basin of Puget Sound that commonly experiences hypoxia. This study examined the influence of watershed soils, vegetation, physical features, and population density on nitrogen (N) export to Hood Canal from 43 tributaries. We also linked our watershed study to the estuary using a salinity mass balance model that calculated the relative magnitude of N loading to Hood Canal from watershed, direct precipitation, and marine sources. The overall flow-weighted total dissolved N (TDN) and particulate N input concentrations to Hood Canal were 152 and 49 μg l^{-1}, respectively. Nitrate and dissolved organic N comprised 64 and 29% of TDN, respectively. The optimal regression models for TDN concentration and areal yield included a land cover term suggesting an effect of N-fixing red alder (*Alnus rubra*) and a human population density term (suggesting onsite septic system (OSS) discharges). There was pronounced seasonality in stream water TDN concentrations, particularly for catchments with a high prevalence of red alder, with the lowest concentrations occurring in the summer and the highest occurring in November–December. Due to strong seasonality in TDN concentrations and in particular stream flow, over 60% of the TDN export from this watershed occurred during the 3 month period of November–January. Entrainment of marine water into the surface layer of Hood Canal accounted for ≈98% of N loading to the euphotic zone of this estuary, and in a worst case scenario OSS N inputs contribute ≈0.5% of total N loading. Domestic wastewater discharges and red alders appear to be a very important N source for many streams, but a minor nutrient source for the estuary as a whole.

Keywords Hood Canal · Puget Sound · Stream chemistry · Nitrogen · Red alder · Onsite septic systems · Eutrophication · Hypoxia

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Introduction

Since the Industrial Revolution, human activities have doubled the loading of mineralized nitrogen (N) to terrestrial ecosystems (Vitousek et al. 1997;

Green et al. 2004). On a global scale the most significant anthropogenic inputs to the reactive N cycle include fertilizers, wastewater discharges, urban/suburban runoff, and NO_x and NH_3 loading to the atmospheric from fossil fuel combustion and agriculture (Vitousek et al. 1997; Paerl et al. 2002; Galloway et al. 2004). Excessive terrestrial N loading can lead to soil N saturation, decreased tree productivity, enhanced N leaching into surface and groundwaters (Fenn et al. 1998), and in some cases dramatically increased loading to receiving lakes, rivers and estuaries (Howarth et al. 1996; Boyer et al. 2006).

Intact conifer-dominated watersheds are usually N limited (Sollins et al. 1980; Triska et al. 1984; Hedin et al. 1995), discharge proportionally more dissolved organic than inorganic N (Perakis and Hedin 2002), and have low areal N yields (Perakis and Hedin 2002; Cairns and Lajtha 2005). Areas subjected to timber harvest and other disturbances are often re-colonized by early successional nitrogen-fixing species such as alder (*Alnus* spp.). Red alder (*Alnus rubra*), a prevalent deciduous tree in the Pacific northwest region of North America, can fix 100–200 kg N ha^{-1} $year^{-1}$ (Binkley et al. 1994). Since alders often grow in riparian areas adjacent to surface and subsurface flow paths, high soil and litterfall N concentrations can lead to increased stream water N concentrations (Hurd et al. 2001; Compton et al. 2003; Hurd and Raynal 2004). Increased stream water N yields due to alders have been noted in the coastal range of Oregon (Compton et al. 2003), the Olympic Peninsula in Washington (Bechtold et al. 2003), the Adirondack Mountains in New York (Hurd et al. 2001; Hurd and Raynal 2004), forests of Wisconsin (Younger and Kapustka 1983), and fens in Germany (Busse and Gunkel 2002).

Our study was initiated as part of a broader effort to understand hypoxic events and associated fish-kills in Hood Canal. Hood Canal is an N-limited, deep, stratified fjord-like sub-basin of the Puget Sound estuary with a shallow sill blocking deep-water tidal exchange at its marine boundary (Newton et al. 1995). Dissolved oxygen (DO) concentrations in the deep waters of Hood Canal decline during the summer due to strong density stratification and the settling/decomposition of phytoplankton from the euphotic zone, and low summer/fall DO concentrations have been observed since the 1950s (Collias et al. 1974). Nearly all of the lower reaches of the Hood Canal watershed have been logged or cleared at least once, and are dominated by red alders. Furthermore, while population density in the Hood Canal watershed is quite low, i.e., <20 individuals km^{-2}, much of the population is concentrated along the shorelines, and all domestic wastewater discharges within the watershed are treated by on-site septic (OSS) systems.

The overall objectives of our study were to determine the loading of dissolved nitrogen by source into Hood Canal, and to assess that loading relative to marine sources. We examined the extent to which watershed characteristics (e.g., soils, land cover, physical features and population density) predict stream water N concentrations and nutrient export to Hood Canal from its tributaries. We then linked the watershed to the Canal, using a salinity mass balance to estimate marine upwelling flows, and assessed the magnitudes of watershed N export to the surface mixed layer of Hood Canal relative to marine sources (i.e., estuarine circulation).

Study area

The Hood Canal (Fig. 1) watershed has a surface area of $\sim$3,050 km^2, of which Hood Canal itself comprises 12%. The watershed can be separated into three zones: (1) the large snowmelt dominated catchments of the Olympic Mountains, (2) the Skokomish River, and (3) the many smaller rain dominated catchments of the Kitsap Peninsula and Hood Canal lowlands. Dominant land uses/covers in the lowland catchments are re-growth conifer, deciduous mixed forests, and suburban and semi-rural development (Table 1). Areas mapped as deciduous mixed forest usually have a closed upper canopy that is composed of ca. 50% red alder (L. Porensky, unpubl. data). The upper elevations are within the Olympic National Park and are nearly pristine conifer forests. The middle elevations are part of Olympic National Forest, 76% of which has been logged (Peterson et al. 1997).

The lowland catchments have more disturbance from forest clearing, wetland draining and suburban development. In this watershed, over 60% of precipitation occurs between November and January and less than 10% occurs between June and August. Freshwater inputs to Hood Canal averaged 170 m^3 s^{-1} during the water years 1990 to 2006. The first study year (i.e., 2005) was somewhat drier than average, whereas 2005

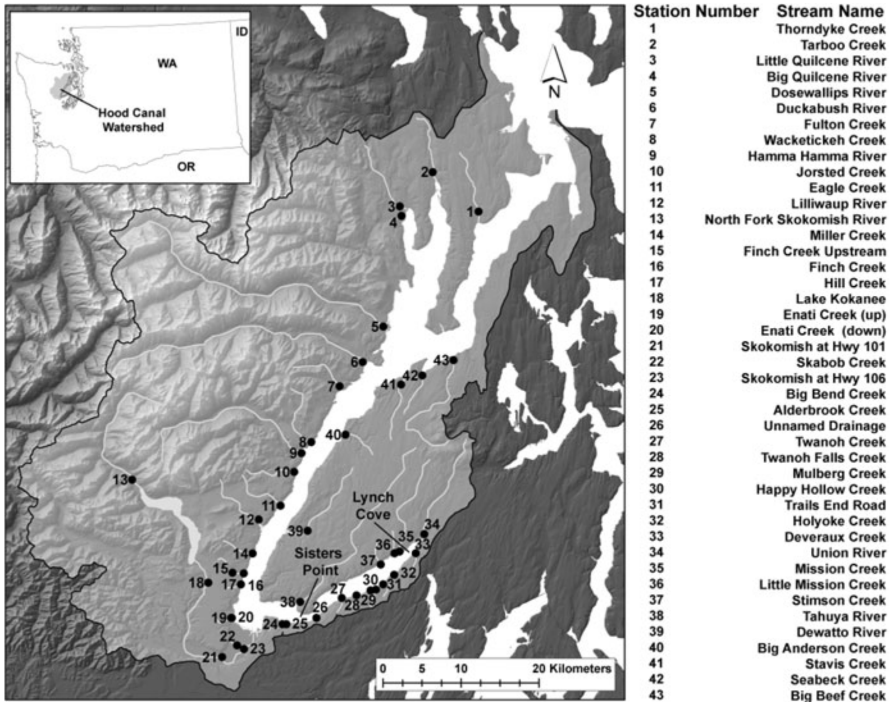


Fig. 1 Map showing the location of the 43 sampled tributaries in the Hood Canal watershed, Washington

Table 1 Physical characteristics, and land cover and soil types for the five regions of the Hood Canal watershed

	Skokomish River[a]	Diversion from North Fork Skokomish	Other Olympic Mountain catchments	Sampled Kitsap/lowland catchments	Unsampled Kitsap/lowland catchments
Physical characteristics					
Catchment area (km^2)	375	254	985	578	618
Mean elevation (m)	428	808	543	186	118
Average slope (%)	40.2	52.9	44.0	14.8	17.1
Average discharge (1990–2006) ($m^3\ s^{-1}$)	37.6	21.9	69.5	19.6	20.7
Average runoff (1990–2006) ($m\ year^{-1}$)	3.2	2.7	2.2	1.1	1.1
Population density ($people\ km^{-2}$)	3.6	3.8	3.8	20	45
Land cover					
Mature coniferous forest (%)	46.4	58.3	49.9	41.3	23.7
Deciduous mixed forest (%)	8.8	3.8	7.3	16.9	29.3
Grass/shrubs/crops/early regrowth (%)	8.6	5.3	7.6	8.1	9.4
Young coniferous forest (%)	9.7	3.6	7.9	13.3	15.1
Low and high density urban (%)	1.4	0.9	1.3	2.2	4.6
Soil types					
Entisols (weakly developed soils) not derived from till	41.3	64.5	45.3	38.3	51.0
Soils influenced by ash (andic soils and andisols)	56.2	45.4	53.0	6.5	15.1
Soils derived from glacial till	13.8	12.5	13.4	49.5	29.7
Rock outcrops	6.4	14.4	8.8	0.1	0.0

[a] Skokomish River does not include that area of the North Fork Skokomish River upstream of upstream of Cushman Dam

was the wettest year in the last 50. Average annual runoff ranges from 3.2 m $year^{-1}$ in the Skokomish River catchment to 1.1 m $year^{-1}$ in the lowlands (Table 1). The mountainous areas of the watershed are sparsely populated (i.e., $\approx$4 people km^{-2}), and the lowlands have moderate population densities ($\approx$20 people km^{-2}) with areas of higher population density along the shoreline especially within Lynch Cove (Table 1).

Methods

Basin attributes

A USGS 30 m resolution digital elevation model (DEM) was used to create the stream network, delineate catchment boundaries, and calculate watershed areas, mean elevation and slope. Soils data (SSURGO 2006) were used to construct a soil matrix of chemical and physical characteristics and taxonomic information for each soil type. Land cover was classified, via a supervised classification of a 30 m resolution Landsat Enhanced Thematic Mapper Plus (ETM+) image from July 30, 2000 (NASA Landsat Program 2001), with at least 10 ground-truth reference sites used for each the land cover type. Urban areas were masked based on their location in the PRISM 2002 landcover map (Alberti et al. 2004), and subalpine forests were masked based on their proximity to snow-covered areas. To estimate this land cover classification's accuracy, 100 randomly located test points were referenced against aerial photographs from 2003, which suggested that the final product had a classification accuracy of >90%.

Population estimates for each catchment were generated by disaggregating 2000 US Census block data using normalized difference vegetation index (NDVI) scores (sensu Imhoff et al. 2000; Koh et al. 2006), derived from the previously mentioned Landsat image. The PRISM 2002 land cover classification was used to subdivide the original NDVI raster into three component rasters, including areas expected to have zero population (e.g., steep slopes), suburban areas (with 90% of the population) and rural areas (with 10% of the population). Within the suburban and rural rasters, the population for each census block was divided among individual pixels based on the difference between each pixel's NDVI value and the mean NDVI value of the census block.

Field and laboratory procedures

Forty-three streams, accounting for 88% of the overall watershed's hydrologic yield, were sampled monthly from January 2005 to December 2006. The unsampled areas of the watershed (which accounted for 22% of the surface area and 12% of the hydrologic yield) consisted of small, undifferentiated shoreline catchments. Grab samples were collected in 0.1 M HCl acid-washed bottles pre-rinsed with streamwater. Dissolved nutrient samples (NO_3^-, NH_4^+) were filtered through Whatman® cellulose acetate filters (0.45 μm pore size), and analyzed on an Alpkem RFA/2 autoanalyzer. TDN was measured on a Shimadzu DOC analyzer after filtering through pre-combusted Whatman® GF/F glass fiber filters (0.7 μm). For particulates, 100–600 ml of stream water, depending on turbidity, was filtered through GF/F filters. Particulates captured on the filters were dried at 55°C for 24 h, acid-fumigated for 24 h, re-dried at 55°C, and packed in tin capsules. The samples were analyzed for N and C concentration at the UC-Davis Stable Isotope Facility using a PDZEuropa ANCA-GSL elemental analyzer.

Streamflow estimation

Fourteen of the 43 streams, which accounted for 68% of the total watershed area, including all large Olympic Mountain rivers, had daily mean flow records. The ungaged areas were narrow shoreline catchments and small to medium size tributaries entirely within the lowlands. Streamflows for the ungaged catchments were estimated by classifying each drainage by hydroclimatic region and then applying the mean of the areal daily runoff rates for a particular region.

Loading rates

Monthly freshwater dissolved nutrient loads to Hood Canal were estimated by multiplying the monthly mean streamflows by the actual monthly grab sample concentrations for the 39 sampling sites that were direct discharges (i.e., not upstream of other sample locations) to Hood Canal accordingly: Loading = $\sum$monthly conc. $\times$ mean monthly flow $\times$ 30.4. The flow-weighted mean concentrations were used as the response variable in regression models, these were calculated accordingly; flow-weighted concentration = $\sum$monthly conc. $\times$ mean monthly flow/$\sum$mean monthly flow.

To fill-in missing data we used the three streams which had the most similar monthly patterns compared to the stream with the missing data to generate regression based estimates for the missing value and we then took the average of these estimates to represent the missing data. Before the fill-in process, the 24-month by 43-stream dissolved constituent concentration matrices were 78% complete. The monthly arithmetic mean of concentrations measured in the four most populated Kitsap watersheds (Big Beef, Seabeck, Tahuya, and Union) were used to estimate each month's concentration for the unsampled portions of the Hood Canal watershed. These streams had average population densities (49 people km^{-2}) and deciduous mixed forest (21%), which were similar to those of the unsampled region (46 people km^{-2} and 29%, respectively) (Table 1).

Principal component analyses

Since the number of potential regression model predictor variables ($n = 33$) was quite high compared to the number of sites sampled ($n = 43$) and some of the predictor variables were collinear, we used principal component analysis (PCA) to first select the most important variables for model development. The three main types of data (physical properties, land cover, soils) were treated separately in three independent PCAs, and all principal components were rotated using the Varimax algorithm with Kaiser normalization using SPSS® version 16.0.

Multiple regression models

Multiple regression models were developed using the key variables identified by the PCAs (Jassby 1999) and population density as predictor variables and the annual flow-weighted concentrations as response variables. A MatLab (v 7.1) script was developed to test the significance of all possible regression models for each response variable. The most probable models were selected from all significant (α values <0.05) models using the Akaike information criterion (Akaike 1970; Burnham and Anderson 2002).

Monte Carlo simulations were used to partition the N load from the watershed to Hood Canal from the various sources identified as being important in our most probable TDN concentration models. Each repetition of these simulations drew from the coefficient random normal distributions based on the mean ± SD obtained from the regression models. These coefficients were then multiplied by the corresponding catchment characteristics (e.g., vegetation type) for each tributary and divided by the sum to generate partial contributions from the prospective sources. These partial contributions to stream TDN concentrations were then multiplied by the observed catchment annual loading. The total TDN load associated with each term in the original regression models was then summed across the entire watershed. This process was repeated 10,000 times.

Salinity box model of N inputs to hood canal

We used water and salinity mass balance equations to partition the N load to the surface mixed layer of Hood Canal from marine, watershed and atmospheric sources. Our salinity box model was similar to other box models for the entire Puget Sound basin (Mackas and Harrison 1997; Babson et al. 2006). The equations were applied separately to Lynch Cove east of Sister's Point (shown in Fig. 1) and to the mainstem Hood Canal (from Sister's Point to Admiralty Inlet). The Lynch Cove portion of Hood Canal suffers the most severe oxygen stress, and the watershed draining to Lynch Cove has a much higher population density and N concentrations (see "Results" below) than the overall watershed. The salinity mass balance for Lynch Cove was calculated as follows:

$$Q_{\mathrm{SF}} = Q_{\mathrm{UP}} + Q_{\mathrm{FW}}, \text{ and}$$

$$Q_{\mathrm{SF}} * S_{\mathrm{SF}} = Q_{\mathrm{UP}} * S_{\mathrm{UP}} + Q_{\mathrm{FW}} * S_{\mathrm{FW}},$$

where Q represents flow, S represents salinity, and the subscripts SF, UP and FW represent the surface layer, upwelling water and freshwater inputs, respectively. Using field data for S_{UP}, S_{FW} and Q_{FW}, we solved these equations for the upwelling flow (Q_{UP}) accordingly:

$$Q_{\mathrm{UP}} = \frac{Q_{\mathrm{FW}}}{\left(\frac{S_{\mathrm{UP}}}{S_{\mathrm{SF}}} - 1\right)}.$$

The mainstem Hood Canal equations are similar except there is an additional input of water and salt:

the seaward outflow from the surface mixed layer of Lynch Cove. After calculating the upwelling flow into the surface box, the upwelling DIN load was calculated as a product of the upwelling flow and the DIN concentration at depth. The total load to the euphotic zone was the sum of the N loads from upwelling, watershed discharges, and rain and dry DIN fallout onto the estuary's surface.

Marine salinities and DIN concentrations used in the box models were obtained from the Hood Canal Dissolved Oxygen Program (http://www.hoodcanal.washington.edu), hereafter referred to as HCDOP (2008). Salinities for the Hood Canal mainstem and Lynch Cove box models were obtained from four Oceanic Remote Chemical-optical Analyzers (HCDOP 2008). Marine DIN concentrations were based on an average of 2005–2006 monthly discrete samples from the HCDOP citizen-monitoring network (HCDOP 2008). The rainwater DIN concentration was estimated as a distance weighted average from four regional National Atmospheric Deposition Program sites (NADP 2008). Dry DIN fallout was estimated as a distance weighted average from three regional Clean Air Status and Trends Network sites (CASTNET 2008).

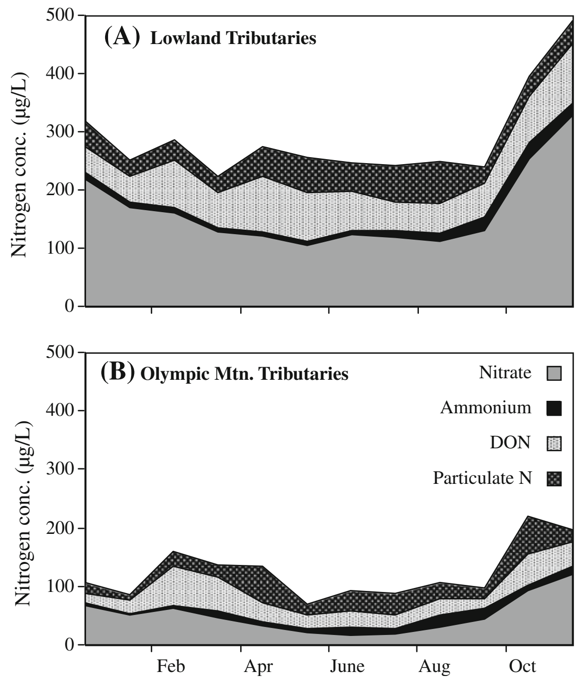


Fig. 2 Two-year average concentrations of PN, NH_4^+, DON, and $NO_2^- + NO_3^-$ observed in **a** lowland streams (32 streams), and **b** Olympic Mountain watersheds (Big Quilcene, Dosewallips, Duckabush, Hamma Hamma, Little Quilcene)

Results

Seasonal and regional trends in concentrations and export

The seasonal patterns for the dominant nitrogen fractions in the lowland streams and Olympic Mountain tributaries are shown in Fig. 2. The flow-weighted TDN concentration for the entire watershed was 152 μg l^{-1} for the 2-year sampling period (Table 2). Annual TDN export was 700 metric tons (MT) in 2005 and 698 metric tons in 2006, despite the fact that total flow was 29% higher in 2006. The North Fork of the Skokomish River had similar areal N loading compared to other Olympic Mountain catchments (1.7 and 1.9 kg ha^{-1} $year^{-1}$, respectively), and the mainstem Skokomish had the highest yield (4.2 kg N ha^{-1} $year^{-1}$). The estimated N yields for the sampled and unsampled lowland areas were 2.1 and 3.2 kg ha^{-1} $year^{-1}$, respectively.

Most of the TDN load was in the form of NO_3^-, particularly during the wet months. Watershed flow-weighted TDN and NO_3^- concentrations were positively correlated with monthly mean flow ($r = 0.49$ and 0.57, respectively). From November to February, NO_3^- constituted ≈70% of the monthly TDN load, whereas during the summer NO_3^- comprised 53% of TDN. Dissolved organic nitrogen comprised 34% of the TDN load during the summer, but declined to 21% of TDN during November–February. Ammonium and nitrite constituted a minor fraction of TDN (6 and 1%, respectively). Particulate nitrogen (PN) constituted 24% of the TN load (Table 2), and peaked during the wet season when sediment transport was the highest. However, as a proportion of TN, PN was greatest in the summer.

Due to the combined effect of two-fold higher TDN concentrations which peaked in December, and eight-fold higher flows which peaked in January, greater than 60% of TDN export from this watershed to the mainstem Hood Canal and Lynch Cove occured during the 3 months of November–January (Fig. 3). Conversely, only 15% of TDN export from the watershed occurred during the 5 month period from June to October. The annual TDN time series

Table 2 Regional flow-weighted mean nitrogen concentrations, annual loading rates, and area-normalized loading rates based on the 2005–2006 monthly grab samples

	NO_3	NH_4	NO_2	DON	PN	DIN	TDN	TON	TN
Flow-weighted mean concentrations (μg l^{-1})									
N Fork Skokomish diversion	22	10.0	0.4	38	36	33	72	75	108
Skokomish River	71	9.5	2.9	22	81	83	106	103	186
Other Olympic Mountain rivers	61	7.6	0.4	38	34	69	108	72	142
Kitsap/lowland watersheds	198	12.7	0.9	72	37	212	283	108	319
Unsampled Kitsap/lowland watersheds[a]	325	12.7	1.0	114	43	339	452	157	495
Overall flow-weighted concentration	97	9.5	1.2	44	49	108	152	93	201
Loads (MT $year^{-1}$)									
N Fork Skokomish diversion	14	6.2	0.23	24	22	20	44	46	67
Skokomish River	95	12.8	3.95	30	109	111	141	139	250
Other Olympic Mountain rivers	109	13.5	0.63	68	60	124	192	128	252
Kitsap/lowland watersheds	86	5.5	0.37	31	16	92	122	47	138
Unsampled Kitsap/lowland watersheds[a]	144	5.6	0.42	50	19	150	199	69	218
Total annual load	447	44	5.6	202	226	496	699	429	925
Percentage of total load (%)	48	5	1	22	24				
Loading rates (kg $year^{-1}$ ha^{-1})									
N Fork Skokomish diversion	0.5	0.24	0.01	0.9	0.9	0.8	1.7	1.8	2.6
Skokomish River	2.8	0.38	0.12	0.9	3.2	3.3	4.2	4.1	7.5
Other Olympic Mountain rivers	1.1	0.14	0.01	0.7	0.6	1.3	1.9	1.3	2.6
Kitsap/lowland watersheds	1.5	0.10	0.01	0.5	0.3	1.6	2.1	0.8	2.4
Unsampled Kitsap/lowland watersheds[a]	2.3	0.09	0.01	0.8	0.3	2.4	3.2	1.1	3.5
Whole watershed loading rates	1.8	0.15	0.02	0.7	0.8	2.0	2.7	1.5	3.3

[a] Concentrations shown for Unsampled Kitsap/lowland watersheds are based on monthly averages of those from the four most populated catchments in the region (Big Beef, Seabeck, Tahuya, Union)

shows concentrations increased dramatically during November and December as flow increased, but that TDN concentrations dropped off markedly in January even as flow continued to increase (Fig. 3). A similar pattern was observed in Lynch Cove, although in that region flow peaked in December.

Statistical models of watershed effects on nutrients

The normalized coefficient loadings for the three separate principal component analyses (i.e., soils, vegetation type, and watershed physical characteristics) are shown in Table 3. The soils data matrix was reduced to three principal components that together explained 79% of the soils variance (Table 3). The soil variables most strongly correlated with soils_PC1 were volcanic and spodosol soils, and rock outcrops. The soil types highly correlated with soils_PC2 were hydric, histic/histosol and wetland soils, as well as soil water capacity. Soils_PC3 was highly positively correlated with weakly developed soils not derived from glacial till (e.g., entisols and inceptisols), and highly negatively correlated with glacially indurated (till) soils. Two land cover principal components explained 50 and 31%, respectively, of the total land cover variance. Landcover_PC1 was highly positively correlated with deciduous mixed forest and negatively correlated with mature coniferous forest. Landcover_PC2 was strongly correlated with open forest/regrowth, which comprised 9% of the watershed. The watershed physical characteristics matrix was reduced to a single principal component that explained 85% of the total variance (Table 3). The four physical characteristics were highly collinear and had similar strong coefficient loadings on physical_PC1.

Based on these PCA results, six watershed characteristics, as well as population density, were

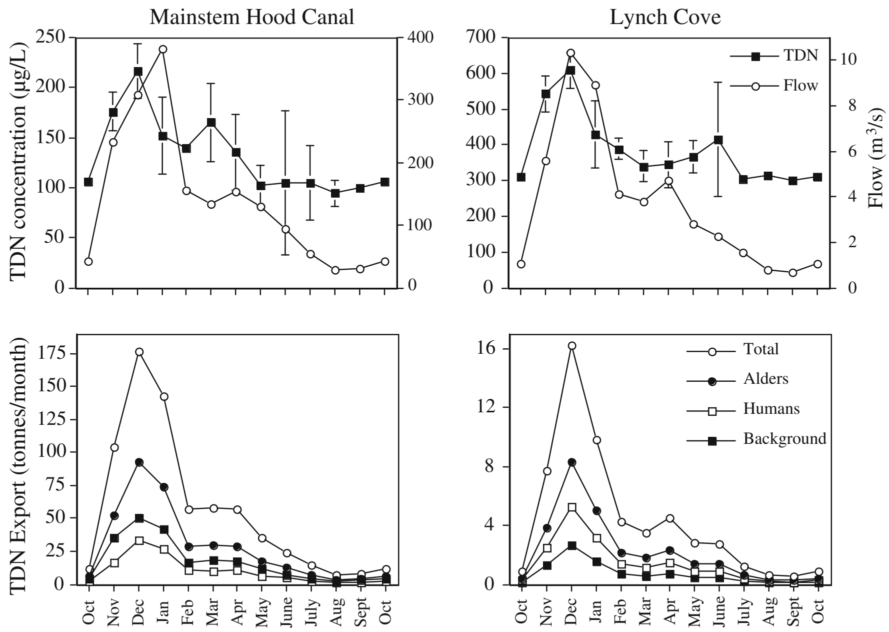


Fig. 3 The average monthly time series for the TDN concentrations and stream flow (*upper panels*) and TDN export (*lower panels*) for the mainstem Hood Canal (*left panels*) and Lynch Cove region (*right panels*) of this estuary. The error bars presented for the TDN concentrations are ±1 SD. The various curves presented in the loading panels represent total TDN export to the euphotic zone of the estuary, and partial TDN loadings attributable to red alders, humans and natural background conditions according to the regression model presented in Table 6

selected for regression model development. These included volcanic soils (soils_PC1), hydric soils (soils_PC2), indurated till (soils_PC3), deciduous mixed forest (landcover_PC1), open forest regrowth (landcover_PC2), and slope (physical_PC1). A correlation matrix of these characteristics shows that with the exception of volcanic soils and slope, the variables used for regression modeling were independent (Table 4). Because of the correlation between volcanic soils and slope, only slope was considered when developing regression models. Using these results, multiple regression models were developed for each chemical constituent.

Because NO_3^- was the dominant N fraction in the sampled streams, the optimal regression models for NO_3^-, DIN, TDN and TN concentrations were quite similar and included a positive coefficient for deciduous mixed forest and population density, or alternatively deciduous mixed forest and glacial till (Table 5). The regression models for DON, PN and TON were all associated with the presence of hydric soils within the different stream catchments (Table 5). The areal export models for NO_3^-, DIN and TDN were a function of population density and deciduous mixed forest, whereas the areal models for DON and TON were a function of hydric soils and slope (Table 5).

To highlight the effects of vegetation and population density on TDN concentrations, Fig. 4 shows the distribution of monthly TDN concentrations in the 10 catchments with the largest percentage area in deciduous mixed forest (panel A) and the 10 catchments with the most mature coniferous forest (panel B). TDN concentrations were generally quite low in the catchments dominated by mature conifer, and much higher and more seasonally variable in the catchments with a high proportion of deciduous mixed forest. Furthermore, in the deciduous mixed forest streams there was a very pronounced peak in TDN during late November–December. Figure 4 also shows the distribution of monthly TDN concentrations in the 10 most (panel C) and least (panel D) densely populated catchments. TDN was much higher in the catchments with high population density, and there was a modest peak in late fall concentrations.

Monte Carlo simulations

Two plausible regression models for TDN explained similar variance, i.e., a model based on deciduous mixed forest and population density and a model based on deciduous mixed forest and glacial till (Table 5). To determine what portion of the annual TDN load is attributable to each term in these models and to account for uncertainty in these models, we ran Monte Carlo simulations. We used our actual field data to estimate N export from the watershed to the

Table 3 The partial coefficient loadings (as *r* values) for the soils, land cover, and physical characteristics principal component analyses

Soil types and characteristics PCA	% Hood Canal watershed in each soil type	Soils_PC1	Soils_PC2	Soils_PC3
Percent of variation explained within PCA		34.3	28.7	15.6
Percent area with weakly developed soils (entisols excluding till)	41	−0.26	−0.09	**0.89**
Log(percent catchment area with volcanic soils)	33	**0.95**	−0.03	0.19
Percent catchment area with till soil	18	−0.43	0.06	**−0.85**
Log(percent catchment area in rock outcrops)	12	**0.91**	−0.17	−0.03
Log(percent catchment area in riverwash/water)	4.9	0.37	**0.60**	0.06
Log(percent catchment area with hydric soils)	2.8	−0.02	**0.93**	−0.17
Log(percent catchment area in spodosol soils)	2.5	**0.78**	−0.26	−0.14
Log(percent catchment area with wetland mineral soils)	2.3	0.01	**0.88**	−0.21
Log(percent catchment area with histosols/histic soils)	0.6	−0.03	**0.88**	0.22
Depth-integrated soil organic matter	–	0.53	0.55	0.37
Depth-integrated soil cation exchange capacity	–	**−0.73**	−0.26	0.48
Depth-integrated soil water capacity	–	−0.13	**0.81**	−0.10
Soil bulk density (36–60 inches below surface)	–	**−0.91**	−0.28	0.02
Depth averaged percent clay (mean)	–	**0.66**	0.19	0.34

Land cover types PCA	Watershed in each land cover type (%)	LC_PC1	LC_PC2
Percent of variation explained within PCA		50.1	30.5
Mature coniferous forest	49	**−0.80**	−0.59
Deciduous/mixed forest	10	**0.96**	−0.08
Grass/shrubs/crops/early regrowth	7.9	0.42	0.38
Young coniferous forest	7.9	0.42	0.21
Sub-alpine forest	5.9	−0.34	−0.14
Open forest/regrowth	5.2	0.09	**−0.92**
Marsh/wetland/shoreline/shallow water	5.1	−0.11	0.10
Snow/ice	2.8	−0.32	−0.14
Bare ground/clearcut	2.7	−0.08	−0.04
Water	1.8	−0.09	0.00
Low density urban	1.0	0.22	0.22
Cloud	0.7	−0.05	−0.26
High density urban	0.2	0.08	0.26
Cloud shadow	0.1	0.34	−0.20

Physical characteristics PCA	Physical_PC1
Percent of variation explained within PCA	84.9
Log(watershed area)	**0.82**
Log(elevation)	**0.86**
Mean slope (%)	**0.81**
Log(mean annual flow 2005–2006)	**0.90**

The soils, land cover and physical characteristics most strongly associated with a particular PC are indicated in bold

Table 4 Correlation matrix on the variables originally selected for multiple regression

	Volcanic soils	Log(hydric soils)	Till	Deciduous mixed forest	Open forest regrowth	Slope
Log(hydric soils)	−0.12					
Till	−0.52	0.18				
Deciduous mixed forest	−0.28	0.56	0.28			
Open forest regrowth	−0.32	−0.03	0.11	0.11		
Slope	0.90	−0.32	−0.43	−0.45	−0.27	
Population density	−0.43	0.17	0.47	0.18	0.00	−0.41

Volcanic soils were removed from the regression independent variable matrix after finding this term was highly correlated with slope

Table 5 The significant multiple regression equations for the various nitrogen species with AIC weight >10%

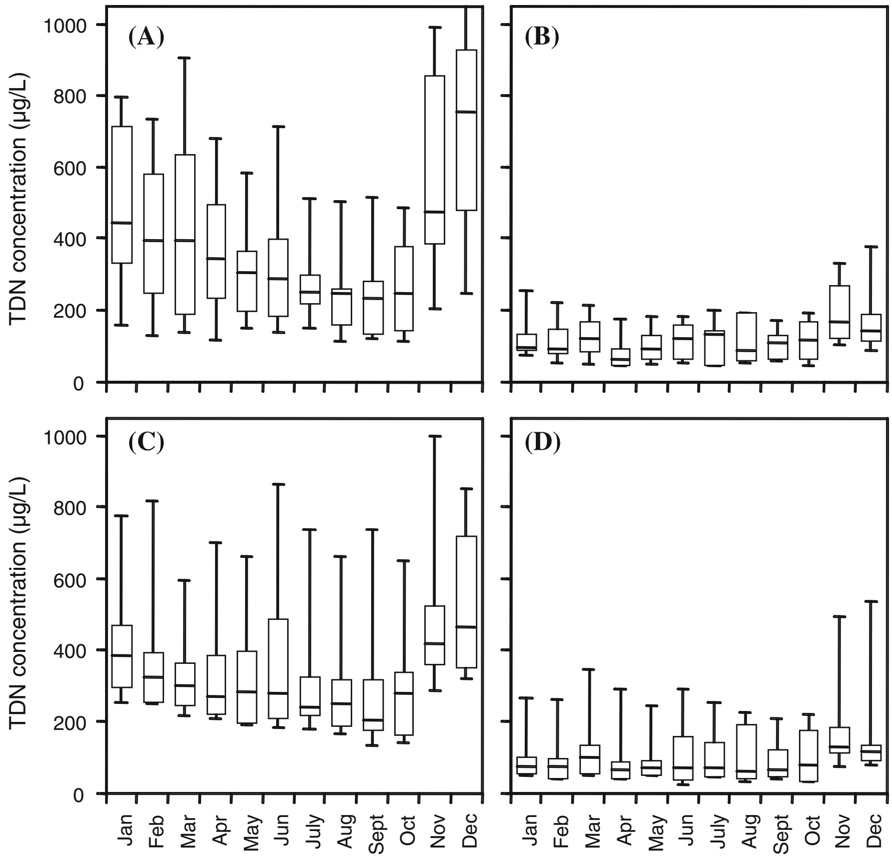
	AIC weight	R^2
Concentration (μg l^{-1})		
NO_3 = 7.46 × (deciduous mixed forest) + 3.37 × (pop density) + 23.8	0.49	0.42
NO_3 = 1.95 × (till) + 6.90 × (deciduous mixed forest) + 0.608	0.47	0.42
DIN = 7.25 × (deciduous mixed forest) + 3.46 × (pop density) + 42.6	0.63	0.40
DIN = 1.83 × (till) + 6.81 × (deciduous mixed forest) + 24.1	0.31	0.38
TDN = 9.34 × (deciduous mixed forest) + 3.47 × (pop density) + 60.9	0.48	0.46
TDN = 2.01 × (till) + 8.77 × (deciduous mixed forest) + 37.2	0.46	0.45
DON = 33.4 × log(hydric soils) + 22.1	0.94	0.35
PN = 11.6 × log(hydric soils) + 28.3	0.98	0.30
TON = 35.2 × log(hydric soils) + 1.30 × (deciduous mixed forest) + 38.0	0.77	0.53
TON = 45.0 × log(hydric soils) + 50.4	0.23	0.48
TN = 9.94 × (deciduous mixed forest) + 3.57 × (pop density) + 88.6	0.51	0.47
TN = 2.02 × (till) + 9.38 × (deciduous mixed forest) + 65.4	0.42	0.46
Areal loading (kg ha^{-1} $year^{-1}$)		
NO_3 = 0.0265 × (deciduous mixed forest) + 0.0235 × (pop density) + 0.728	0.71	0.27
NO_3 = 0.0267 × (pop density) + 1.12	0.21	0.19
DIN = 0.0260 × (pop density) + 1.28	0.87	0.17
DIN = 0.0289 × (deciduous mixed forest) + 1.20	0.13	0.09
TDN = 0.0251 × (pop density) + 1.75	0.75	0.15
TDN = 0.0313 × (deciduous mixed forest) + 1.62	0.25	0.10
DON = 0.179 × log(hydric soils) + 0.0110 × (slope) + 0.0414	0.99	0.41
PN = 0.0104 × (slope) + 0.191	1.00	0.14
TON = 0.320 × log(hydric soils) + 0.0239 × (slope) + 0.0452	0.99	0.42

Terms with the lowest *p* values are listed first

Hydric soils and deciduous mixed forest were expressed as watershed area percentages (numbers between zero and 100). Population density was expressed as people km^{-2}, and slope was dimensionless

Hood Canal estuary, and the Monte Carlo simulations based on our regression models to apportion this loading between the putative sources identified in our statistical analyses. For example, our most probable TDN model is TDN concentration (μg l^{-1}) in any stream = DMF × 9.3 + pop density × 3.5 + 61 (Table 5). For a hypothetical stream with average attributes for all streams (i.e., 16 people km^2 and 14% DMF) and an overall observed TDN export of 20 MT, our regression model would predict 61 μg TDN l^{-1} is naturally occurring (3.5 × 16 =) 56 μg l^{-1} is associated with humans, and

Fig. 4 **a** Average monthly TDN concentrations in the ten catchments with the highest proportion deciduous mixed forest (using the site codes provided in Fig. 1, these streams are 1, 2, 3, 22, 31, 32, 37, 41, 42 and 43). **b** TDN concentrations in the ten catchments with the most mature coniferous forest (i.e., 4, 7, 8, 10, 11, 12, 13, 27, 28 and 36). **c** Average TDN concentrations in the 10 most densely populated catchments (i.e., 24, 25, 28, 32, 33, 34, 35, 41, 42 and 43). **d** TDN concentrations in the 10 least densely populated catchments (i.e., 1, 5, 6, 7, 8, 9, 12, 13, 19 and 20)



(9.3 × 14 =) 102 µg l^{-1} is associated with DMF. In relative terms, these values equate to 28, 26 and 47% of the TDN coming from natural sources, humans and deciduous vegetation, respectively. When adjusted for the observed load, this suggests 5.6, 5.1 and 9.5 MT, respectively, of TDN in this hypothetical stream originated from the three sources indicated above. When also taking into account uncertainty associated with the coefficients of the multiple regression model, the Monte Carlo simulations for both models predicted deciduous mixed forest was associated with 51 ± 15% of the annual TDN load to Hood Canal (Table 6), or 354 ± 202 MT $year^{-1}$. The same simulations suggested 13.6 ± 6.5% of the annual TDN load was associated with population density (Table 6), or 95 ± 45 MT $year^{-1}$. These Monte Carlo simulations were also run for just Lynch Cove, and for this region 56 ± 11% of the TDN load could be attributed to deciduous mixed forest, and 31 ± 10% was associated with population density (Table 6).

Box model of N inputs to Hood Canal and Lynch Cove

The surface mixed layer salinities were only slightly lower than salinities at depth, so in both Hood Canal and Lynch Cove, the calculated the upwelling flows were much larger than freshwater inflows to the euphotic zone (Fig. 5). Similarly, upwelling was the major N source to the surface mixed layer, where it constituted 88% and 98% of the N load to the euphotic zone of Lynch Cove and the mainstem Hood Canal, respectively. Upwelling was a larger proportion of the N load to the surface layer of the mainstem Hood Canal because the relative difference between salinities at the surface and at depth is smaller in the mainstem Hood Canal, and the watershed N concentration is lower for the mainstem Hood Canal (143 µg TDN l^{-1}) than for the Lynch Cove tributaries (448 µg TN l^{-1}). In both Lynch Cove and the mainstem Hood Canal, the N concentration of upwelling water was high (388 and 405 µg TDN l^{-1},

Table 6 Models for TDN concentration reconstructed from original variables and analyzed in a Monte Carlo simulation

Reconstructed models (with coefficient standard deviations)

TDN (μg l^{-1}) = 2.0 (±0.8) × Till + 8.8 (±2.1) × Mixed deciduous forest + 37.2 (±48.6)

TDN (μg l^{-1}) = 3.5 (±1.4) × Population density + 9.4 (±2.0) × Mixed deciduous forest + 60.9 (±44.7)

	Percentage (±1 SD) of TDN load attributed to each term
Monte Carlo simulation results for Hood Canal[a]	
Mixed deciduous forest/till model	
Mixed deciduous forest	51.0 (±14.5)
Till	25.1 (±10.3)
Intercept (background)	23.8 (±18.0)
Mixed deciduous forest/population density model	
Mixed deciduous forest	50 9 (±14 8)
Population density	13.6 (±6.5)
Intercept (background)	36.1 (±17.5)
Monte Carlo simulation results for Lynch Cove[a]	
Mixed deciduous forest/till model	
Mixed deciduous forest	60.2 (±11.7)
Till	27.1 (±9.7)
Intercept (background)	12.7 (±10.8)
Mixed deciduous forest/population density model	
Mixed deciduous forest	52.2 (±10.7)
Population density	30.9 (±10.2)
Intercept (background)	15.8 (±9.7)

[a] A total of four Monte Carlo simulations were run by applying each of the two models to the 43 sampled catchments and to the unsampled area of Hood Canal and then by applying each model to the 12 catchments and unsampled area draining to Lynch Cove. Based on the intercepts and coefficients and their standard deviations, a random normal distribution (n = 50,000) was created term in each model. These distributions were applied to the observed catchment characteristics (i.e. vegetation, population density, and soil type) to predict the expected contribution of each model component to TDN concentrations in each catchment. All terms were constrained to be positive so that negative predicted concentrations could be avoided. These values were then multiplied by the observed average annual flow from each catchment and summed for the entire Hood Canal watershed (or Lynch Cove watershed) to derive 50,000 estimates of the partial contributions of vegetation, population density, and glacial till to terrestrial TDN export to the Hood Canal

respectively). A sensitivity analysis showed estimates of the upwelling flow and the related marine N loading calculations depended to some extent on the choice of the surface depth assumed in the Hood Canal box model. Reducing the assumed pycnocline depth from 9 to 7 m decreased the estimated upwelling flow by 1%, whereas increasing the assumed pycnocline to 11 m increased the estimated upwelling flow by 24%. The direct rainwater N load to the surface of Hood Canal was relatively small because the watershed area is much larger than the estuary's surface, and the rainwater DIN concentration was low (68 DIN μg l^{-1}) (Fig. 5). However, across the entire watershed rainwater DIN was more than sufficient to account for the baseline streamwater DIN concentrations (i.e., $\approx$70 μg l^{-1}).

Discussion

Terrestrial controls on stream N export

Watershed nitrogen export to Hood Canal was strongly correlated with deciduous mixed forest and population density. High dissolved N concentrations were to a lesser extent statistically associated with the presence of glacial till, while organic N export was higher in catchments with a high prevalence of hydric

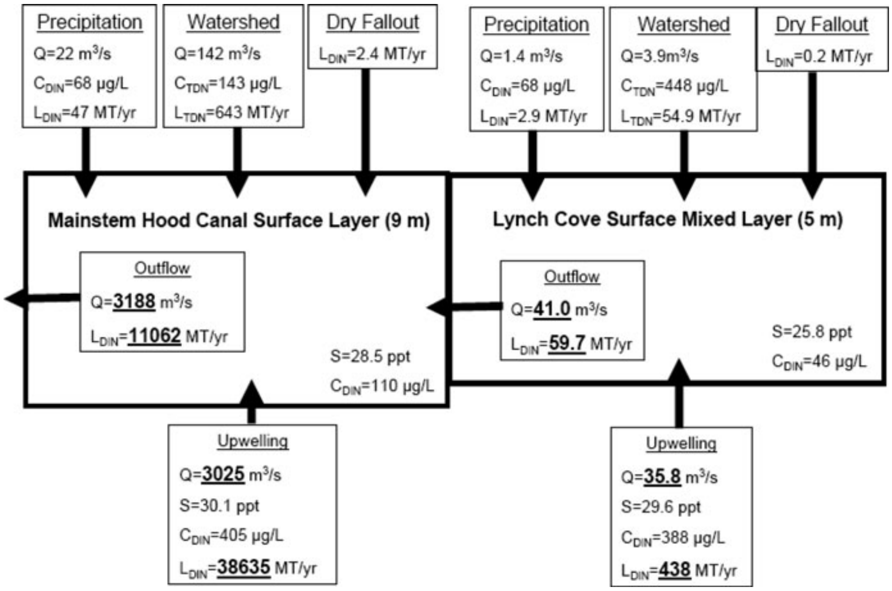


Fig. 5 Salinity balance box models are depicted, showing N concentrations (*C*), N loads (*L*), salinities (*S*), and flows (*Q*). Flows and loads calculated based on salinity balance model are shown with enlarged, underlined numbers

and wetlands soils. Seasonal patterns of stream water dissolved N concentrations were shaped largely by the timing of hydrologic and biological processes, such as plant uptake during the summer, and leaf and root senescence and hydrologic flushing during the late fall. A large majority of the N export from this watershed occurred during the late fall/early winter (November–January).

Vegetation effects

The presence of deciduous mixed forest in both of the best-fit TDN models suggests a strong effect of red alder on stream water N concentrations. This result is similar to the findings of Compton et al. (2003), who studied red alder effects on TDN concentrations in Oregon coastal streams. Red alders are a classic early successional species and are a natural component of highly dynamic or distributed areas, such as riparian zones, in the Pacific northwest of North America (Van Pelt et al. 2006). Red alders are also strongly favored by anthropogenic disturbances such as forest harvest and land clearing. Therefore, alders contribute to both the natural and the anthropogenic N cycle of the Hood Canal watershed.

Population

Our regression models indicate population density was a predictor of nitrogen concentrations and yields in most cases. Based on the Monte Carlo simulation of the reconstructed deciduous mixed forest and population density model, 13.6 ± 6.5% of the annual TDN load was associated with population density (Table 6), which is equivalent to 50–141 MT year^{-1}. The low stream water NH_4^+ concentrations indicate septic system dissolved N (which is discharged from the drainfield as >90% NH_4^+) is completely nitrified before reaching the streams we sampled. This is consistent with the literature on N transformations in OSS drainfields (McCray et al. 2005), and field sampling of OSS drainfields in the Hood Canal watershed (Brett et al., unpubl. data).

By assuming the statistical association between stream water concentrations and population density primarily represents OSS discharges, we could use the likely loading of N to OSSs to estimate how much of this N source is removed before it reaches Hood Canal. To estimate the percentage removal of N from the OSS discharges, we used a hybrid Bootstrap/Monte Carlo simulation, where we combined the distribution of reported per capita N inputs to septic systems multiplied by the total population of the Hood Canal watershed with the Monte Carlo simulation's predicted human N inputs to Hood Canal streams. For this we used estimates of the mean per capita N input to septic systems, which ranged from 4.1 to 5.0 kg year^{-1} (Valiela et al. 1997; Crites and Tchobanoglous 1998; EPA 2002; Tchobanoglous et al. 2003). Based on the difference between probable N input to septic systems and the N output to streams from this source suggested by our models, we calculated 56 ± 20% of the N loaded to OSSs was removed by denitrification in subsurface flows prior to reaching the Hood Canal. However, N removal from OSS effluents in areas we have not sampled may be lower than in areas we have sampled because much of the population lives in very close proximity (i.e., <50 m) to the marine shoreline and subsurface flow distances to surface water in these areas are much shorter than in the sampled catchments. Thus, the assumption that the unsampled areas' N concentrations and yields are similar to those of the most populated sampled catchments should be supported by further field sampling.

Soils

Shallow water tables maximize the exposure of groundwater to soil C, and are often associated with enhanced denitrification (Hedin et al. 1998; Hill 1996). However, in this study the presence of a compacted glacial till layer was positively correlated with stream water TDN concentrations. Although the reasons for this correlation cannot be determined from the current study, we speculate the cause may be shallow routing through soils which could short-circuit the groundwater removal processes where most denitrification probably occurs in the coarse-textured soils of this watershed.

Hydric, histic and wetland soils occurred in the best-fit DON and TON models. Higher dissolved organic matter concentrations due to riparian wetlands have been found in several other studies (e.g., Wetzel 1992; Gergel et al. 1999). The effect of wetland soils on organic N is most obvious in the catchment with the largest percentage of its area in wetland/organic soils. In this catchment (Skabob Creek) TON was 92% of TN, while in the other catchments TON averaged 46% of TN. These relationships are similar to those observed in a survey of TON yields in 850 streams across the conterminous US (Scott et al. 2007).

Biological versus physical drivers

Co-occurrence of seasonal senescence of deciduous vegetation and the onset of autumn rains makes it difficult to distinguish between biological and physical drivers of N flushing (Bechtold et al. 2003). Biological influences on N concentration can be inferred from large differences between the seasonal cycles of TDN concentrations in catchments with high and low proportions of deciduous mixed forest (Fig. 4). In catchments with high population density, average concentrations were high but seasonal cycles were more muted (Fig. 4). In order to better differentiate influences on the seasonal responses for these two stream types, we separated our entire dataset into streams with above and below median proportions of deciduous mixed forest and population density. This isolated six catchments with high population density/low deciduous mixed forest, and five streams with low population density/high deciduous mixed forest. These two sets of streams had nearly identical average annual TDN concentrations (i.e., ≈420 μg l^{-1}), but the high deciduous mixed forest streams had substantially more variation between annual minimum and maximum values (i.e., 252–859 μg l^{-1}, respectively) than did the high population density streams (i.e., 375 and 561 μg l^{-1}, respectively). This suggests OSS discharges impart a higher baseline TDN concentration, but less seasonal variation than does N export associated with red alders.

The importance of hydrology is suggested by the positive correlation between TDN concentrations and monthly mean flow ($r = 0.49$). In both years, the highest TDN concentrations were in the early part of the wet season (November and December), indicating that by the second half of the wet season (January to February) soil labile N had been largely flushed out of the soils. Our findings parallel those of other studies from Ontario and Washington State's Olympic Peninsula, which showed the importance of hydrologic flushing as a control on N discharge (Creed et al. 1996; Bechtold et al. 2003).

At global (e.g., Caraco and Cole 1999) and continental (e.g., Scott et al. 2007) scales, runoff is a good predictor of terrestrial N yield, leading some to conclude that high discharges lead to less processing and removal of anthropogenic and atmospheric N loads and therefore greater streamwater N yields (Jaworski et al. 1992). In general we have not found this to be the case in the Hood Canal watershed. Among the 43 catchments' 2 year mean TDN yields, areal runoff was not correlated with areal TDN yield ($r = 0.19$, $p = 0.23$). One exception is the

Skokomish River, which had the highest runoff rate and a high N yield despite low N concentrations (Table 2). Several studies have found inter-annual variations in N load are of the same scale (Salvia-Castellvi et al. 2005) or greater than (Riggan et al. 1985; Jaworski et al. 1992) inter-annual variations in discharge. In contrast, we found that total TDN export to the Hood Canal estuary was almost identical between dry and wet years when streamflows differed by 29%. These results suggest that there was a steady amount of dissolved N available to be leached on an annual basis, and greater precipitation did not increase watershed TDN yield.

A box model of watershed TDN contributions to Hood Canal

Terrestrial N loading to the surface layer (i.e., the euphotic zone) was more important in Lynch Cove, where it accounted for 11.1% of total N load, than in the mainstem Hood Canal, where it only accounted for 1.6% of the N load (Fig. 5). Part of this difference can be attributed to higher TDN concentrations in watershed inputs to Lynch Cove (448 $\mu g\ l^{-1}$) than the mainstem Hood Canal (143 $\mu g\ l^{-1}$). Further, the surface salinity of Lynch Cove (25.7 ppt) was substantially lower than that of the mainstem Hood Canal (28.5 ppt), which indicates Lynch Cove received proportionally more riverine and groundwater inputs.

To estimate what portion of the load to Lynch Cove was due to anthropogenic sources, we repeated the deciduous mixed forest and population density Monte Carlo simulation while only using tributaries and groundwater inputs to Lynch Cove (Table 6). This showed 52 ± 11% of the terrestrial N export was associated with deciduous mixed forest and 31 ± 10% of the watershed load was associated with population density. Combining this model with the salinity balance showed 5.8 ± 1.2 and 3.4 ± 1.1%, respectively, of the overall N load to the Lynch Cove surface mixed layer can be statistically associated with indirect (i.e., red alder) and direct (OSS discharges) anthropogenic inputs. In both Lynch Cove and the mainstem Hood Canal, direct DIN inputs to the surface of the estuary via rainwater and dry fallout were very minor sources. However, because NADP data for the western Washington State region indicate rainwater DIN concentrations were $\approx$70 $\mu g\ l^{-1}$ (NADP 2008), and the overall watershed average TDN concentration was 152 $\mu g\ l^{-1}$, atmospheric loading cannot be dismissed as an insignificant N source to the actual watershed. It is also noteworthy that these rainwater DIN concentrations were a factor $\approx$20 less than what is commonly encountered in the eastern seaboard of the United States where rainwater DIN concentrations range between 500 and 2,500 $\mu g\ l^{-1}$ (Whitall et al. 2003; Kelly et al. 2009). Low rainwater DIN concentrations may also be one of the reasons why streams and rivers draining to Hood Canal have much lower DIN concentrations (213 ± 208 $\mu g\ l^{-1}$) than do streams draining to Lake Washington (875 ± 324 $\mu g\ l^{-1}$) in the metropolitan Seattle area only 40–70 km to the west (Brett et al. 2005).

The salinity mass balance model also allowed us to estimate the mean hydraulic residence time (HRT) of the surface mixed layer. For the mainstem Hood Canal the estimated steady state HRT was 12 days. This short HRT indicates much of the wet season watershed TDN load should be advected out of the estuary before the peak phytoplankton growing season in late spring and summer (HCDOP 2008). However, it is notable that during the uncommonly dry February weather in both 2005 and 2006, phytoplankton N uptake reduced DIN in the surface mixed layer to <10 $\mu g\ l^{-1}$. This suggests that although the most important watershed N loads for promoting phytoplankton productivity are those that occur during the peak phytoplankton months in the spring and summer, watershed N export during November–January could be important during sunny (i.e., high algal productivity) periods during the winter. During the spring and summer peak phytoplankton growth, the TDN load associated with humans may be especially important, since population density and OSS effluents are associated with a higher baseline N concentration and less seasonal variability. Thus, during low flow months, population density may contribute a higher proportion of the N load to Lynch Cove than indicated by the 3.4% estimate above.

In this study we have placed the greatest emphasis on TDN loading to Hood Canal because TDN is representative of the N which stimulates phytoplankton production, and it is this phytoplankton production which exerts an oxygen demand in the bottom waters of the estuary as senescent cells or zooplankton fecal pellets settle to the sediments. Field research on Hood Canal has shown that during the peak phytoplankton growth period of April to October, DIN concentrations in the surface layer are drawn down to very low levels (i.e., <10 μg l^{-1}) (HCDOP 2008). This indicates that nearly all of the N loaded to the euphotic zone during this time of year is taken up by phytoplankton and used to generate new growth. Due to the Redfield ratio of marine phytoplankton (i.e., C:N molar ratio ≈7) and the stoichiometry of nitrification, the complete oxidation of 1 mol of phytoplankton biomass requires approximately 9 mol of oxygen (O_2). Thus during peak phytoplankton growth periods each mole of TDN loaded from watershed sources to the euphotic zone of Hood Canal will consume approximately 21 times its mass in dissolved oxygen when it decomposes.

Based on the salinity mass balance values presented above, it is unlikely that watershed TDN export (and in particular that TDN associated with anthropogenic activities) will result in a substantial additional oxygen debt in the mainstem Hood Canal because the watershed only contributed 2% of the N loading to the surface layer of overall estuary. Our salinity mass balance calculations indicate the loading of marine derived TDN to the surface layer of the mainstem Hood Canal is 39,000 MT $year^{-1}$ (Fig. 5). As previously noted, this estimate is high (relative to terrestrial loading) because the salinity data indicate the surface layer of this estuary is 95% marine and the marine water entrained into the surface layer has nearly three times the nitrogen content of freshwater inputs (Fig. 5). Our 39,000 MT $year^{-1}$ marine contribution estimate agrees moderately well with Paulson et al.'s (2006) 10,100–34,000 MT $year^{-1}$ estimate. Paulson et al.'s estimate assumed similar marine upwelling TDN concentrations, but calculated the flux of marine water into Hood Canal based on the net flow of currents into this estuary. If we assume a population of 45,300 individuals (Table 1) each contributing 4.5 ± 0.5 kg N $year^{-1}$ to the estuary with zero N removal, we can consider a worst case scenario for N inputs to this estuary. In this hypothetical case, the flux of OSS N would be equivalent to $29 \pm 4\%$ of watershed export to Hood Canal, but only $0.5 \pm 0.1\%$ of marine loading.

In the Lynch Cove sub-basin inferring the magnitude of anthropogenic N inputs is complicated by the fact that our stream monitoring program does not capture the immediate shoreline areas were most water flows directly to the estuary via subsurface flow paths, and where many people reside. We have accounted for these "unsampled inputs" in our watershed nitrogen budget by applying the same areal hydrologic yields and runoff TDN concentrations as observed in several densely populated catchments that were sampled (see Tables 1, 2). Our statistical approach estimates total watershed export contributes 11% of nitrogen loading to the euphotic zone of Lynch Cove, and most of this nitrogen was statistically associated with indirect (red alder) and direct (OSS) anthropogenic N sources, i.e., 5.8 ± 1.2 and $3.5 \pm 1.1\%$ of total loading, respectively. If we consider a worst-case-scenario for OSS N inputs to Lynch Cove from the unsampled shoreline areas, i.e., 4,500–5,000 people (HCDOP, unpublished data) times 4–5 kg N $year^{-1}$, then it is conceivable that an additional 21 ± 3 MT $year^{-1}$ could come from this source which would amount to an additional $4 \pm 1\%$ of total loading.

While estuarine hypoxia can have natural causes, it is often the result of anthropogenic nutrient sources (Diaz and Rosenberg 2008). Several classic case studies of eastern North American estuaries have concluded human wastewaters and agricultural runoff played major or even the main role in worsening hypoxia, e.g., Waquoit Bay in Massachusetts (Valiela et al. 1997), Narragansett Bay in Rhode Island (Nixon 1997), Chesapeake Bay in Maryland/Virginia (Kemp et al. 2005) and the Neuse River Estuary in North Carolina (Paerl 2006). Hood Canal differs from these better known systems in that its watershed is much less densely populated and its estuarine circulation is very dominated by marine inflows with quite high DIN concentrations (Mackas and Harrison 1997) compared to the low marine DIN concentrations of the mid-Atlantic shelf (Dafner et al. 2007). Furthermore, the DO dynamics of Hood Canal may have been influenced by recent strong incursions of low DO water onto the continental shelf off of the Pacific Northwest of North America (Chan et al. 2008; Connolly et al. 2010).

Conclusions

We present two multiple regression models to predict TDN concentration in streams of the Hood Canal watershed ($R^2 \approx 0.50$). Both models show strong effects of deciduous mixed forest (ca. 50%, red alder) and suggest $51 \pm 15\%$ of the annual TDN load from the watershed can be attributed to deciduous mixed forest. One model includes population density as a factor and suggests direct anthropogenic N inputs (septic system effluents) contribute between 7.1 and 20.1% of the annual watershed TDN load to Hood Canal. In the Lynch Cove area our data indicate humans directly contributed 21 to 41% of the terrestrial N export. A salinity balance model indicated ≈98% of N loading to the surface layer of the mainstem Hood Canal is from marine upwelling. However, our calculations suggest watershed export accounts for 11% of the total N load to Lynch Cove's surface mixed layer. Overall our results suggest OSS N discharges are not an important contributor to hypoxia in the mainstem Hood Canal, but this source may contribute to oxygen depletion with the Lynch Cove sub-basin.

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