Biogeochemical Processes in the Soil-Groundwater System of a Forest-Peatland Complex, North Coast British Columbia, Canada

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Abstract

There is a limited understanding of the distribution and transport of solutes in the coastal forest-peatland systems of northern British Columbia, Canada. The purpose of this research was to evaluate the sources, concentration and flux of major ions and dissolved organic carbon (DOC) in the soil-groundwater system of a forest-peatland complex in the coastal western hemlock (CWH) forest zone. DOC dominated the groundwater flux, with most of it exported during high flow conditions. Inorganic ion concentration increased and DOC decreased with ground surface slope and community type from open peatland to bog woodland, bog forest, swamp forest and upland forest. Base cations, HCO_3^- and DOC in the peatland forest communities differed significantly ($P < 0.05$) from concentrations in the upland forest. The greatest concentrations of ions derived from mineral weathering were found in the upland forest where the absence of peat, deep mineral soil (85-465 cm) and steep surface slope (26%) combined to increase dissolution by recharging groundwater. NO_3^-, SO_4^{2-} and PO_4^{3-} were at or below detection limits. Concentrations of DOC, metals and HCO_3^- decreased from summer to spring with dilution by rainfall and decreasing decomposition. In addition to providing novel data in a data-sparse region, this study provides an analysis of the processes controlling runoff production and the transport and transformation of biogeochemical elements impacting stream water quality.

Keywords: biogeochemistry, dissolved organic carbon, peatland, wetland hydrology

Introduction

In the coastal western hemlock (CWH) forests of north coast British Columbia, Canada, forest-peatland complexes represent a contemporaneous view of historical succession from upland forest to open peatland (Asada et al. 2003, Turunen and Turunen 2003). The close spatial proximity of mature forest and transitional peatland communities provide an opportunity to study several forest community types under similar climatological conditions, thus providing a way to relate site characteristics such as topography and hydrology with susceptibility to biogeochemical changes resulting from land use and climate change.

These forest-peatland ecosystems are characterized by slow decomposition, resulting in the significant accumulation of organic matter (Banner et al. 1993). A predominant biogeochemical feature of these peatland systems is the high level of acidity, attributed to the production of organic acids from incomplete decomposition and H^+ ion release by invading bryophytes (Vitt et al. 1990). The large cation exchange capacity of humic and fulvic acids (75-90% of total capacity) removes base cations from soil-water suspensions (Prescott et al. 1995). Therefore, although the nutrient capital in the organic-soil horizon is considerable, nutrient availability is relatively low and forest stands are considered of low productivity (Banner et al. 2005).

Understanding the timing and magnitude of hydrochemical processes is important because changes in hydrology may alter how nutrients are produced, retained and flushed from the organic-soil horizons of forest-peatland systems (Sebestyen et al. 2009). In these systems, storm runoff response is dominated by shallow subsurface flow processes (Emili and Price 2006) and topography is a significant control on the spatial variability of sources, pathways and rates of hydrochemical flow (Emili et al. 2006). The prevalence of topographic lows (i.e. areas with thicker

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organic-soil horizons, water tables near the surface and higher soil moisture contents) increases the potential for solute export following harvesting activities or changes in climate that increase the amount of water entering the soil-groundwater system (Emili et al. 2006). Forest harvesting operations in the poorly drained portions of CWH forests (British Columbia Ministry of Forests, Lands and Natural Resource Operations 2000) may interrupt surface and subsurface flowpaths and biogeochemical dynamics with consequences for downstream aquatic and terrestrial environments (Banner et al. 2005).

The hydrochemistry of forest-peatland systems has been well-studied in Europe (e.g. Boatman et al. 1975, Christophersen et al. 1982, Mulder et al. 1991) and continental North America (e.g. Verry and Timmons 1982, Glaser et al. 1990, Devito and Dillon 1993, Vitt et al. 1995). However, comparatively few studies address the hydrochemistry of forest-peatland systems in coastal hillslope environments in North America (Gibson et al. 2000, Fellman et al. 2009, D'Amore et al. 2010). These latter studies have focused on the sources and transport of dissolved organic matter (DOM) in stream water (Gibson et al. 2000, Fellman et al. 2009) and soil pore water (D'Amore et al. 2010). Even fewer studies have examined the hydrologic controls on water flowpath, major ion chemistry and stream quality in British Columbia (Hudson and Golding 1997).

Gibson et al. (2000) and Fitzgerald et al. (2003) examined dissolved organic carbon (DOC) dynamics measured at basin and sub-basin outlets within the study area, but did not examine internal catchment source fluxes and pathways. Knowledge of the integration of soil physical properties and soil-groundwater chemistry with hydrologic flux is needed to fully understand the storage, flow paths and export of major ions and DOC in coastal forest-peatland ecosystems (D'Amore et al. 2010).

Our paper provides novel information regarding the distribution and transport of inorganic and organic solutes in ground and stream water in a complex sloping forest-peatland system. The main goal of this study was to characterize the natural biogeochemical functioning of this system. To achieve this overall objective, we established the hypothesis that forest community biogeochemistry is linked to its hydrologic regime by the interaction between soil aeration and drainage and the availability of major ions and DOC within the soil-groundwater system. To test this hypothesis, we set the following specific objectives:

(i) to determine the influence of slope, season and water table elevation on the concentration of major ions and DOC in groundwater and stream water, and
(ii) to estimate the flux and pathways of major ions and DOC in groundwater and stream water.
(iii) to develop a conceptual model of the hydrochemical processes controlling the composition of groundwater.

Methods

Study Area

As part of a larger multi-disciplinary study (Pattern, Process, and Productivity in Hypermaritime Forests of Coastal British Columbia-HyP^3, Banner et al. 2005), a study site was established within the very wet hypermaritime (vh2) region of the CWH zone (Banner et al. 2005). The study site is located within Diana Lake Provincial Park (54° 09' N, 130° 15' W), 14 km to the Hecate Strait, 178 km to open ocean (Pacific) and 26 km southeast of the town of Prince Rupert, British Columbia (Figure 1).

This site contains a typical CWHvh2 cross-section of ecosystems, including lower-productivity forests on gentle slopes, bog forests, bog woodlands, blanket bogs, swamps and productive forests on steeper slopes. A 500-m transect was established along a forest-peatland complex comprising these representative forest communities (Figures 2 and 3). The transect rises from an elevation of 150-185 meters above sea level (masl), with slopes ranging from 1% in the open peatland to 26% in the upland forest.

The study area is characterized by cool (average annual temperature of 6.9 °C), and hypermaritime conditions with little snow (0.06% of annual precipitation) and frequent periods of fog. The

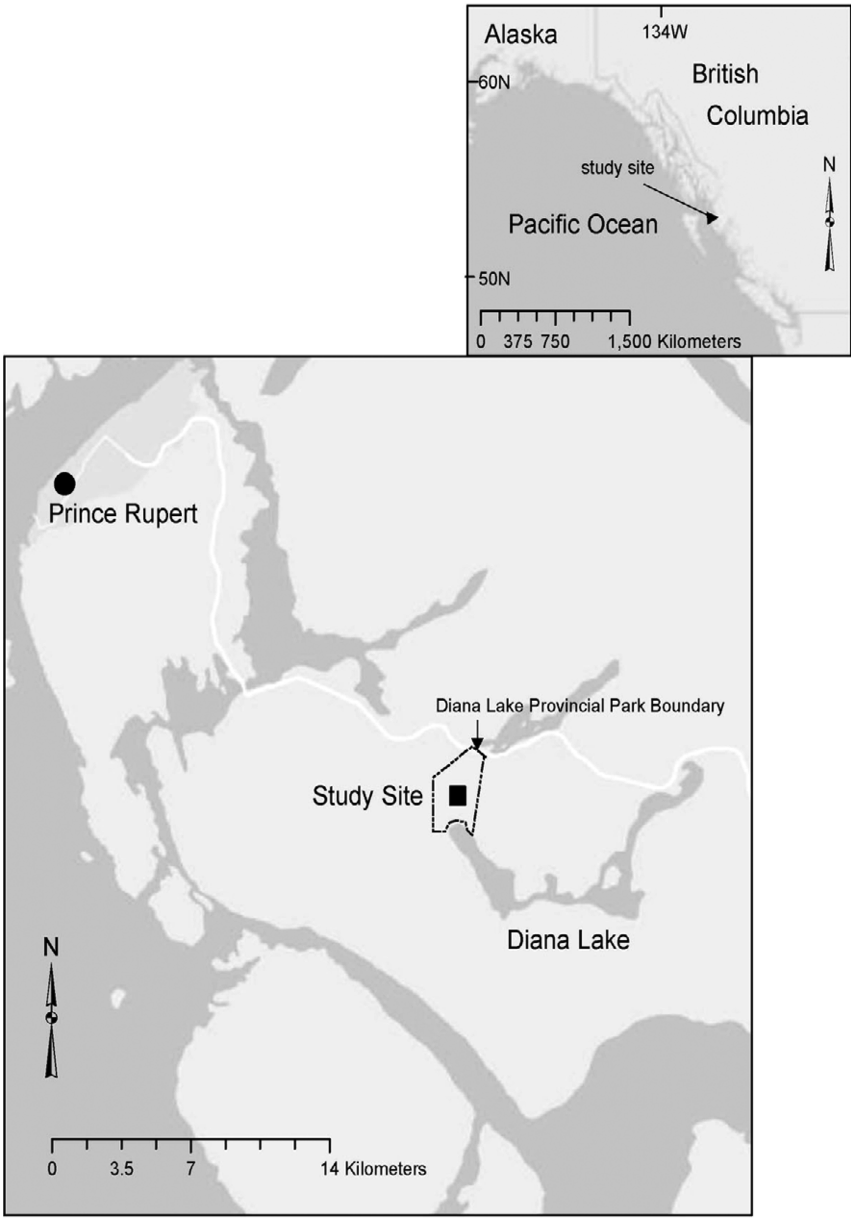

Figure 1. Study site and transect location at Diana Lake Provincial Park, British Columbia, Canada.

long-term (1971-2000) mean annual rainfall at Prince Rupert is 2469 ± 79 SD mm, with summer being the driest season and autumn the wettest (Environment Canada 2002).

The bedrock geology is a complex mixture of rock types, geological structures and stratigraphic sequences. The study area is underlain by amphibolite schist and gneiss (Banner et al. 2005). Colluvial processes have resulted in rockfalls and granular disintegration in upland areas. Peat has developed on gentler slopes, ranging from thicknesses of approximately 40 cm on mid-elevation forested slopes to 300 cm in open blanket bog in local depressions or benches. The underlying fine to medium sandy mineral-soil horizon thickness is variable, ranging in thickness from 85-465 cm in

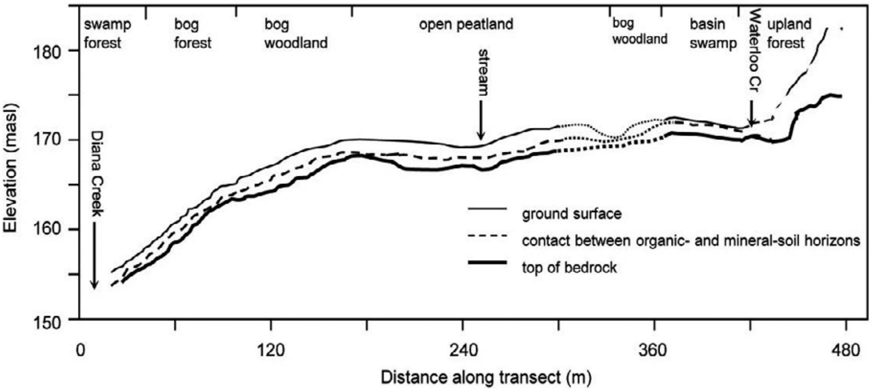

Figure 2. Stratigraphic profile of the forest-peatland complex along the transect at Diana Lake, British Columbia, Canada. Dashed lines at a transect distance between about 300 and 360 m represent interpolated surfaces.

the upland forest to less than 150 cm in swamp forest, bog forest, bog woodland and open peatland communities (Emili et al. 2006).

Forest vegetation is grouped into community types characterized by similar climax plant communities. The forest community types in the study area comprise swamp forest, bog forest, bog woodland, open peatland, basin swamp and upland forest (Figure 2). The tree canopy in the swamp forest is not completely closed and shrub layers are well developed. In the bog forest, the canopy is more open than the swamp forest and tree height rarely exceeds 20 m (Asada 2002). The bog woodland is characterized by an abundance of scrubby trees. The canopy height in the upland forest is higher than 20 m (Asada 2002), and its shrub layer has lower cover than the swamp and bog forests. Forest vegetation is dominated by conifer stands of *Tsuga heterophylla* (Raf.) Sarg., *Thuja plicata* Donn ex D. Don- ; *Pinus contorta* Dougl. Ex Loud. var. *contorta* and *Chamaecyparis nootkatensis* (D. Don) Spach are abundant on organic soils. The understory is composed primarily of shrubs (*Vaccinium* spp.), *Pleurozium* spp. (Brid.) Mitt. and *Sphagnum* mosses (Lindb.), *Oplopanax horridus* (Sm.) Miq. and *Lysichiton americanum* (Hultén &

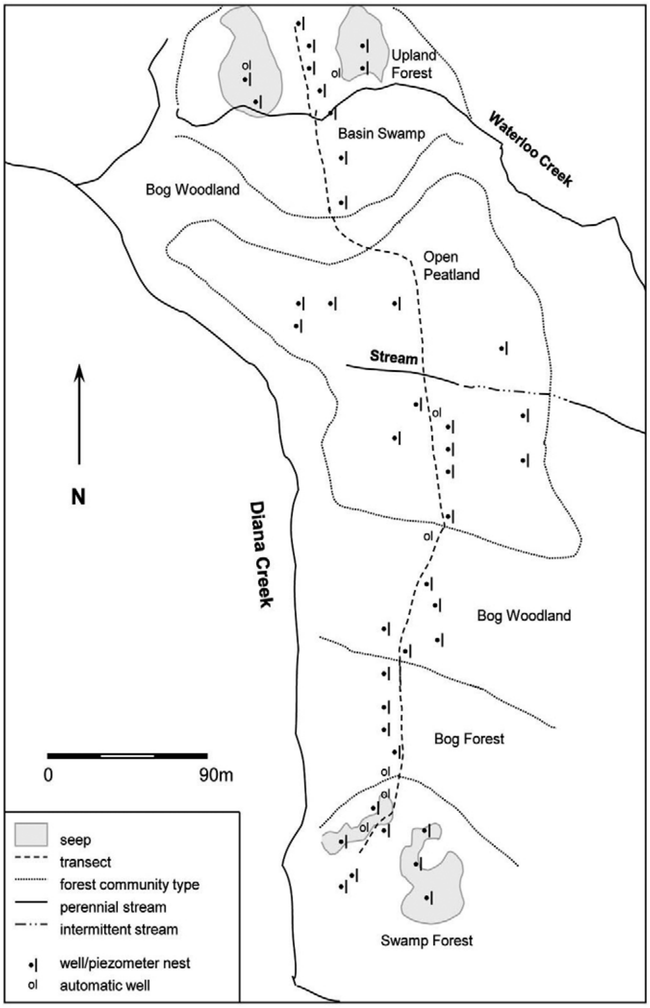

Figure 3. Network of wells and piezometers within each forest community type along the transect at Diana Lake.

H. St. John) in wetter areas. The open peatland comprises hummock, hollow, pool and lawn communities dominated by *Sphagnum (*Sull and Schimp.) mosses and dwarf shrubs.

Sample Collection and Laboratory Analyses

Major anions (HCO_3^-, Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), metals (Fe^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}) and DOC concentrations in rainfall, throughfall, fog drip, groundwater, and stream water were measured from July 1997 through July 2000. Stem water was not sampled for chemical analyses as it was negligible, accounting for only 0.31% and 0.84% of total rainfall in the two years (1998 and 1999) it was measured (Maloney et al. 1999). Rainfall was collected on an event basis in a storage rain gauge, with an aperture of 41.5 cm^2, placed 45 cm above the ground surface in the open peatland. A rainfall event was defined as a minimum one hour period of rain (water depth > 0.03 mm) separated by at least four rain-free hours until the next event. There were 133 rain events with rainfall occurring on 62% of the days. The gauge was rinsed with distilled water following each collection. From May -September, throughfall was collected every 48 hours. From October to April, throughfall was collected monthly. Throughfall was collected from six plastic troughs positioned beneath the open canopy, closed canopy and partially open canopy within the swamp and upland forests. Troughs were scrubbed and flushed with distilled water twice a week from May through September and monthly from October through April to remove leaf debris. The troughs were 10.5 cm wide and 5.2 cm deep and 7 m long, angled at 10^o from the horizontal, and set 1.5 m above the ground surface. Troughs emptied through a screened polyethylene funnel, into a 4-L polyethylene collection bottle. Fog drip was accompanied by rain on 125 out of the 126 days that rainfall occurred. Fog drip alone was measured on 12 days. Due to the low amount (5.3 mm) of fog drip, it was collected when the minimum volume of sample for analysis (60 ml) was obtained in the open peatland with a rectangular harp (1.2 m x 0.9 m), constructed of 3.8 cm (outside diameter) ABS pipe strung with vertically oriented monofilament nylon line spaced 0.5 cm apart (Price 1992). The collector was positioned over a funnel that was directed into a 4-L polyethylene collection bottle.

Groundwater was sampled from stand-pipe wells (n = 41) and piezometers (n = 66) of 2.5 cm (inside diameter) PVC pipe, slotted along the entire length for wells and the bottom 20 cm for piezometers (Figure 3). Wells and piezometer slots were screened with 40 µm Nitex (Thermo Fisher Scientific, Burlington, Canada) mesh. Wells were generally 1.2 m deep, although 0.6 m wells were installed in the swamp forest and bog forest in areas with perched water tables. Piezometers of 2.5 cm (inside diameter) PVC, slotted along the bottom 20 cm and screened with 250 µm Nitex -mesh, were nested at depths determined by the depth of the organic-soil, to the organic-mineral soil transition and to mineral-soil. All piezometer nests were in locations representative of the physiognomy ascribed by Banner et al. (1993) to that particular forest community. Samples were collected using an Easy-Load hand pump with 0.63 cm (outside diameter) Masterflex tubing (Cole–Palmer Instrument Company, Montreal, Canada). Wells and piezometers were purged 24 hours and 48 hours, respectively in advance of sampling. Groundwater was collected in a 250 ml Nalgene (Thermo Fisher Scientific, Burlington, Canada) polyethylene bottle and transferred into 30 ml bottles. Water samples were taken from the entire network of wells and piezometers along the study transect in August 1997 (Figure 3). Samples were collected from 39 sampling stations consisting of one well and one nest of piezometers (each nest had 2-3 piezometers) in each vegetation community along the transect in October 1997, January 1998 and May 1998. In the summer of 1998 and 1999, samples were collected on a rain-event basis.

Remote Data System (Wilmington, USA) WL40 automatic recording wells were used to monitor water table fluctuation at 12-hour intervals in 1998 at one station per forest community type. Stand-pipe wells and piezometers were measured weekly from May to September 1998.

Above ground flow zones (seeps) were instrumented in the swamp forest and upland forest with 15 cm (outside diameter), 120 cm length PVC pipe, laid downslope and partially imbedded lengthwise into the organic soil so as to capture shallow subsurface and overland flow. Samples were collected during rain events in 30 ml Nalgene bottles. Stream samples were collected in Diana Creek and the upland forest stream (Waterloo Creek) in the summer and fall of 1998 and 1999 on a daily basis, with more intensive hourly sampling during the largest rain event in summer 1998 (Figure 3). These samples were grab sampled in 500 ml Nalgene bottles, and then decanted into 30 ml Nalgene bottles. Seep water samples were collected during summer rain events (1998).

Stream discharge (computed from water velocities obtained using an OSS stream gauging meter) and stage heights recorded hourly with a Unidata Hydrostatic water depth probe were correlated to produce a stage-discharge curve. The equation for the curve was used to calculate total hourly discharge from stage height data (Maloney et al. 1999). Runoff depth was determined by dividing the discharge volume (m^3) by the watershed area (m^2).

All samples were collected in Nalgene bottles that were cleaned with a solution of Sparkleen detergent and tap water. Bottles were acid-washed with 20% H_2SO_4 and then triple rinsed with distilled water. Collected samples were stored on ice for transport to the laboratory where samples were filtered (within four hours of collection) through 0.45 mm cellulose nitrate filters and stored in 30 ml Nalgene bottles at 4 °C until analysis. Dissolved metal samples were acidified with 0.1 ml of concentrated HNO_3 to prevent microbial degradation. Samples for DOC analysis were preserved with 0.1 ml of a solution of 20% H_2SO_4 and then subsampled into 10 ml glass test tubes with rubber stoppers. Any trapped air bubbles were removed with a syringe through the rubber stopper. The samples were refrigerated at 4 °C until analysis.

The analysis of water for major cations, anions, metals and reactive silica was performed according to Standard Methods for the Examination of Water and Wastewater, 18th Edition (Clesceri et al. 1995) by Philip Analytical Services Corporation, Burnaby, British Columbia. Method blanks and laboratory spiked samples were analyzed for each sample batch. The mean recovery for laboratory spikes ranged from 83-106%. Method blanks (25% of samples) were prepared using the same procedure as for the sample analyses. The level of analytes found in method blanks was equal to or below method detection limits. Five samples of water were collected at the end of washing and rinsing procedures and were treated as an analytical sample to verify that collection procedures were not sources of contamination. Limited sample volumes precluded the analysis of duplicate field samples. DOC concentration was measured by high temperature combustion using a Dohrmann DC-190 high temperature total carbon analyzer (0.5 mg L^{-1} standard error of measure) at the University of Waterloo, Ontario, Canada.

Groundwater Flux Determination

Vertical hydraulic gradients (dh/dz) were expressed as a ratio of the change in piezometric head between two piezometers at the same location to the vertical distance between the open intervals of these piezometers. The soil-groundwater system was considered isotropic with hydraulic conductivity as each soil horizon was homogenous in porosity (Emili et al. 2006). Saturated hydraulic conductivity (K_{sat}) of the soils was determined at each well and piezometer in seeps and along the Diana Lake transect in August 1997 and 1998 using the Hvorslev water level recovery method (Freeze and Cherry1979). Water-level recovery was 90% for wells and 80% for piezometers. The elapsed time between well and piezometer purging to recovery ranged from about 1 hour to almost 55 hours and from less than 1 minute to about 100 hours, respectively.

Groundwater flux was determined in each forest community along the transect from June-August 1998. Groundwater flux, Q, was determined between successive downslope pairs of piezometers as

$$Q = K_{sat}\frac{dh}{dl}bw \qquad (1)$$

where K_{sat} (m s^{-1}) is the mean value of the saturated hydraulic conductivity measured at two piezometers and d*h/dl* is the difference in hydraulic head over the horizontal distance between the piezometers. The flux through a cross-section of slope was defined for the organic-soil horizon and the mineral-soil horizon, where *b* represents the saturated thickness (m) of the particular soil horizon and *w* is the width (m) of the cross-section. Fluxes in each soil horizon were summed to determine total flux and expressed as a per a unit width of 1 m (m^3 s^{-1} m^{-1}).

DOC and Inorganic Ion Flux Determination

To provide a relative comparison of solute flux in each flowpath, estimates of inorganic ion and DOC instantaneous fluxes in rainfall, throughfall, groundwater and stream water on a unit area basis were determined for the October 1997 sampling date. This was the only date for which a full suite of analyses were available. The hydrologic conditions for 1997 were comparable and representative of the other years of data collection, with the exception of 1999 which was a relatively wet year with an annual rainfall 1362 mm greater than the 1997 total rainfall (Emili and Price 2006). Flux was calculated from the concentration, saturated hydraulic conductivity and horizontal hydraulic gradient as

$$F = [i * K_{sat} * m]/A \qquad (2)$$

where F is the flux of an individual ion (kg ha^{-1}s^{-1}), *i* is the individual ion, *m* is the land-surface slope and A is the unit area of land-surface slope (1 m^2). Ionic data for groundwater was available for the period 1997 to 1998 and was therefore expressed as an annual flux of ions (kg ha^{-1}y^{-1}). For comparative purposes, the Fall (October 1997) flux of DOC was also expressed as an annual flux.

Statistical Analyses

Multi-variate analyses of variance (MANOVA) were performed with an unbalanced design using Hotelling's Trace (SPSS Inc. 1999) to compare mean concentration of major ions in groundwater with forest community type, season, groundwater flux, depth to water table and depth to mineral soil. A post-hoc two-way least squares means test (SAS Institute Inc. 1990) was used to investigate forest community type and seasonal interactions. Univariate analysis of variance (ANOVA) of an unbalanced design was used to compare the concentration of DOC in groundwater with the same set of environmental variables as used in the MANOVA of major ions (SPSS Inc. 1999). Since the DOC data for atmospheric water, groundwater, seep water and stream water were not normally distributed, variations in DOC concentrations were analyzed with the non-parametric Mann-Whitney test for equality.

Results

Atmospheric Water, Groundwater and Surface Water Chemistry

DOC Analyses—DOC concentrations differed between soil strata, forest community type and season (Table 1). Overall, there were higher concentrations of DOC in groundwater from organic- than mineral-soil horizons. DOC in organic-soil groundwater ranged from 5.2-33.7 mg L^{-1}. The range of concentrations for groundwater flowing through mineral-soil was 3.0-22.6 mg L^{-1}. While the mean DOC concentration of seep water (13.7 ± 0.6 mg L^{-1}) and stream water (13.1 ± 0.1 mg L^{-1}) were similar, the range of DOC concentrations (5.7-26.1 mg L^{-1}) and coefficient of variation (53%) of seep water were larger. The largest DOC concentrations were found in groundwater of the swamp forest and open peatland (Table 1). Mean DOC concentrations also exhibited seasonal variation (Table 1), with mean DOC concentrations generally decreasing from summer through winter. The mean DOC concentration in organic-soil groundwater decreased (53%) from an average of 19.9 ± 7.3 mg L^{-1} in the summer to 9.4 ± 5.2 mg L^{-1} in the spring. The relatively small difference in mean DOC concentration in groundwater in the organic-soil horizon in the fall and winter may be a reflection of the small sample size (n = 6 and n = 3, respectively). The average DOC concentration in mineral-soil groundwater in the spring was elevated by two unusually high values (21.8 and 22.7 mg L^{-1}) measured at one station in the swamp forest. The average DOC concentra-

TABLE 1. Mean pH, soluble reactive silica (SiO_2) and dissolved organic carbon (DOC) in organic- and mineral-soil horizon groundwater by forest community type, and mean DOC by season, Diana Lake, British Columbia, Canada, 1997-99. Standard deviations are shown in parentheses.

	Organic Horizon			Mineral Horizon		
	pH standard units	SiO_2 μmol L^{-1}	DOC mg L^{-1}	pH standard units	SiO_2 μmol L^{-1}	DOC mg L^{-1}
Forest Community Type						
Swamp forest	5.04(0.52)	39(40)	17.6(7.0)	5.52(0.49)	69(48)	11.1(6.0)
Bog Forest	5.75(0.17)	45(42)	†	5.19(0.89)	56(40)	4.9(1.1)
Bog Woodland	4.89(0.57)	44(15)	12.6(5.1)	5.44(0.62)	162(129)	7.5(2.3)
Open Peatland	4.85(0.77)	41(27)	16.6(8.3)	5.62(0.99)	266(135)	10.2(4.0)
Upland Forest	---	---	---	6.03(0.99)	129(42)	8.2(2.9)
Season						
Summer			19.9(7.3)			10.9(4.5)
Fall			12.8(5.0)			8.5(0.6)
Winter			12.3(4.9)			4.8(0.2)
Spring			9.4(5.2)			10.3(7.4)

†Due to low sample volumes in the bog forest, values were combined with those of the bog woodland.

tion in rainfall (4.3 ± 2.3 mg L^{-1}) was much less than the average for throughfall (19.8 ± 10.8 mg L^{-1}).

The DOC concentration in Diana Creek measured during the largest summer storm event of 1998 (Julian Day 217-224, Figure 4) increased from 8.7 mg L^{-1} during baseflow conditions on Julian Day 217 to a maximum of 19.2 mg L^{-1} on Julian Day 220. Regression analysis showed a significant ($r^2 = 0.88$, $\alpha = 0.01$) positive linear relationship between stage height and DOC concentration for the storm event.

The Mann-Whitney test for the equality of medians demonstrated that DOC concentration in rainfall, throughfall, organic-soil groundwater, mineral-soil groundwater, seep water and stream water (Figure 5) was significantly

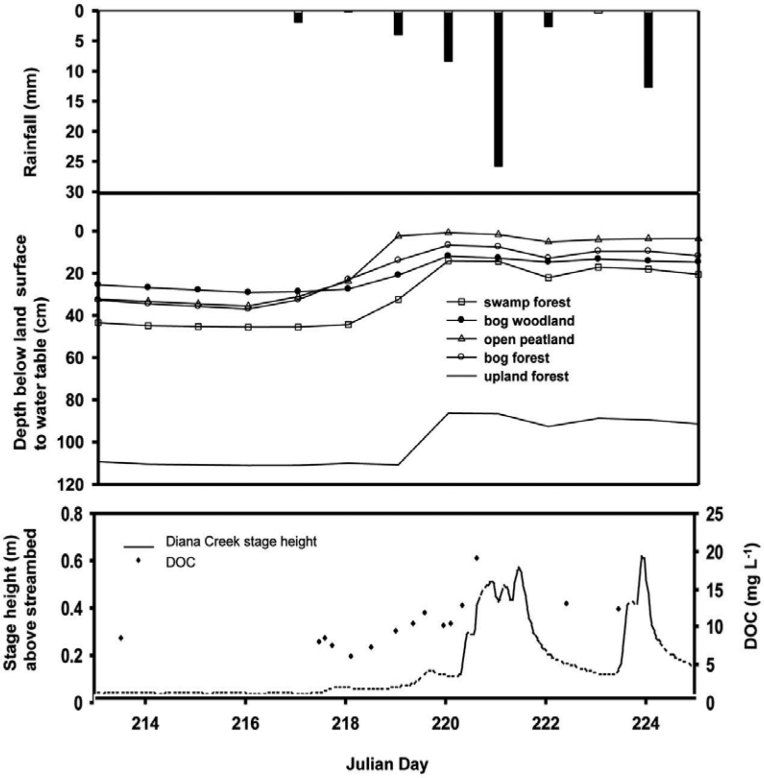

Figure 4. Dissolved Organic Carbon (DOC) in relation to daily rainfall, depth to water table and stage height of Diana Creek for the largest summer storm event of 1998.

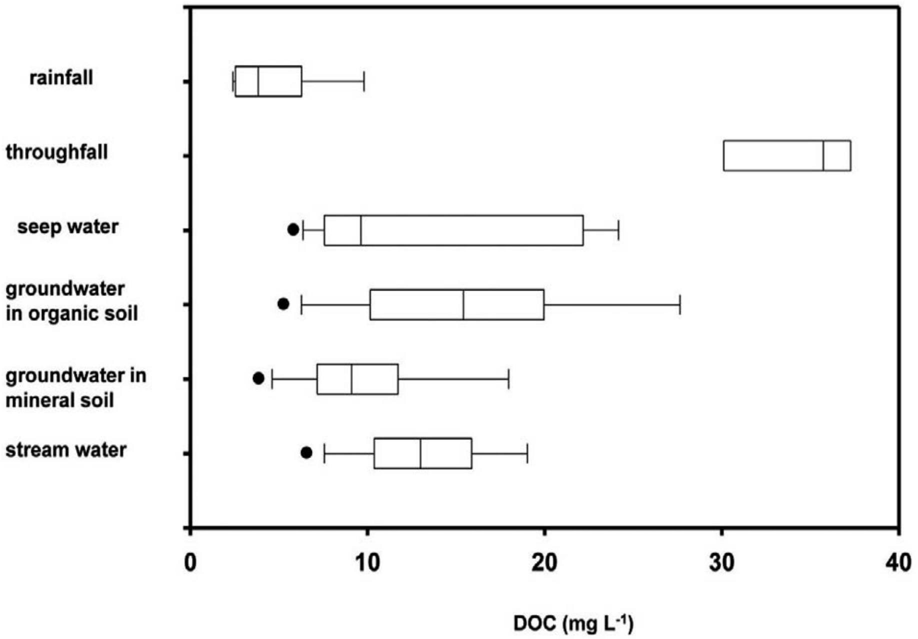

Figure 5. Simple box plots of dissolved organic carbon (DOC) concentration in rainfall, throughfall, seep water, groundwater and stream water along the Diana Lake transect, British Columbia, Canada, July 1997-July 1999. Each box represents the interquartile range of the data and shows the median value. The whiskers illustrate the 25th and 75th percentiles of the data set. The whiskers for throughfall data were too short to be visible. The black dots represent outliers.

different at $\alpha = 0.05$. A paired Mann-Whitney analysis demonstrated that median DOC concentration could be ranked according to the following: rainfall < groundwater in mineral soil < seep water < stream water < groundwater in organic soil << throughfall.

Inorganic Analyses—The number of rainfall, fog drip and throughfall samples for which a full suite of inorganic ion analyses was performed was limited (n = 5, n = 2 and n = 1, respectively). Therefore, charge balance analysis was used to develop a general chemical characterization of inorganic solutes in atmospheric, ground and surface water. The charge balance for selected samples is shown in Table 2. The principle of electroneutrality (EN) was applied according to the equation

$$EN = 100\frac{\Sigma cations - \Sigma anions}{\Sigma cations + \Sigma anions} \tag{3}$$

where EN represents the electroneutrality of the solution, and Σ is the sum of the cations or anions (μeq L^{-1}). The ionic balances for rainfall were good (*EN* = 0.8%), but the balances for fog drip (*EN* = 17%), throughfall (*EN* = 23%), groundwater (*EN* = 0.9-74%) and stream water (*EN* = 12%) were poor (Σ cations > Σ anions). The poor EN balances indicate that anions such as organic acids may be missing from the analysis (Vance and David 1991) that may be accounted for by considering the charge contribution of DOC (Oliver et al. 1983). White and Shannon (1997) found that the anion charge deficit in peatland soil water was strongly correlated with DOC concentration in soil water and that the missing or unmeasured charge deficit was due to organic anions associated with the DOC pool. Thus, the DOC concentration can be used as a predictor of charge deficit. However, we did not find a strong correlation ($r = 0.48$, $\alpha = 0.05$), nor a statistically significant correlation between anion deficit and DOC concentration, which may have been a function of the low sample number (n = 11).

The mean pH of rainfall, fog drip and throughfall (± standard error) was 5.53 ± 0.07, 5.02 ± 0.02 and 5.33 ± 0.02, respectively. Groundwater

TABLE 2. Ionic concentration and charge balance of selected samples of rain, fog drip, throughfall and stream water at Diana Lake, British Columbia Canada, 1997-98.

	Rainfall μeq L^{-1}	Fog Drip μeq L^{-1}	Throughfall μeq L^{-1}	Stream Water μeq L^{-1}
Anions				
HCO_3^-	36	---	---	92
Cl^-	<28	87	34	46
NO_3^-	<0.3	0.6	<0.3	<0.3
NO_2^-	<0.1	<0.1	<0.1	<0.1
SO_4^{2-}	<22	<22	<22	44
PO_4^{3-}	<0.1	<0.1	0.3	<0.1
Σ anions	36	87.6	34.3	182
Base Cations				
Na^+	17	85	25	110
K^+	10	<10	<10	<10
Ca^{2+}	6	7	17	75
Mg^{2+}	3	20	7	26
Metals				
Fe^{2+}	<0.1	11	0.3	3
Mn^{2+}	<0.07	<0.07	1	<0.07
Zn^{2+}	0.6	0.5	4	7
Al^{3+}	<2	<2	<2	12
Σ cations	36.6	123.5	54.3	233
Σ cations-Σ anions	0.6	35.9	20	51
Electroneutrality(EN)	0.8%	17%	23%	12%

< indicates concentration less than specified detection limit
--- indicates no data

in the organic-soil horizon was more acidic than rainfall and had a pH within the pH range of fog drip and throughfall. Groundwater pH generally increased with depth, i.e., from the organic- to the mineral-soil horizon (Table 1). The pH of organic-soil horizon groundwater increased along the gradient of open peatland-bog woodland-bog/swamp forest-upland forest as a function of slope, drainage and depth of the organic soil. On gentler slopes (1-7%) with poor drainage, and accumulation of organic matter (peat thicknesses of 65-180 cm) groundwater was more acidic. pH in groundwater increased with depth and on steeper slopes (23-30%) due to contact with mineral-soil sources of alkalinity (Ca^{2+}, Mg^{2+} and HCO_3^-). The mean pH of Diana Creek water (6.52 ± 0.02) was higher than that of rainfall and organic- and mineral-soil groundwater and much higher than that of runoff from the open peatland (4.75 ± 0.03) and shallow subsurface flow in the swamp forest (4.50 ± 0.03).

Groundwater from the organic- and mineral-soil horizons at the study site was dilute with mean total dissolved solids (TDS) of 39.84 ± 0.05 mg L^{-1}. The large range (4.38-217.37 mg L^{-1}) in TDS was skewed by 27 (out of 253) samples with TDS in excess of 110 mg L^{-1}. These high values were found at depths of 209 to 215 cm in the open peatland where the low K_{sat} (10^{-4}-10^{-5} m s^{-1}) of the organic-soil and low hydraulic gradients decreased groundwater flow and increased the length of time that groundwater was in contact with mineral-soil. TDS was also high in the eastern margin of the open peatland and in the upland forest, where mineral-soil horizon groundwater was discharging.

Mean concentrations of soluble reactive silica (SiO_2) increased from organic- to mineral-soil horizons with the greatest mean concentrations in the mineral-soil in the bog woodland and open peatland (Table 1). In Diana Creek water, the SiO_2 concentration was 81 μmol L^{-1} and the mean electrical conductivity (23.66 ± 0.41 μS cm^{-1}) was much lower than that of groundwater (51.31 ± 0.06 μS cm^{-1}). Electrical conductivity of Diana Creek water measured during the largest summer storm event of 1998 (161 mm, 33% of the rainfall received for the season) decreased from 27.20 μS cm^{-1} to 18.01 μS cm^{-1}.

Sodium (Na^+) was the dominant ion in stream water and of secondary importance in rainfall, fog drip and throughfall (Table 2). Concentrations of Na^+ and Cl^- occurred in fog drip and throughfall in an almost 1:1 and 1:1.4 ratio, respectively. With the exception of Mn^{2+}, concentrations of cations were greater in groundwater (Table 3) than in precipitation and throughfall (Table 2). The dominant cation in groundwater was Na^+, accounting for 52% of the total base cation concentration. With the exception of K^+ and Fe^{2+}, cation concentration increased with depth (Table 3). Iron and Al^{3+} concentrations decreased from dry (summer) to wet conditions (fall through winter), with mean concentrations of 25 μeq L^{-1} and 32 μeq L^{-1}, respectively. Mn^{2+} and Zn^{2+} were present in comparable concentrations (Table 3). With the exception of K^+ (below detection limits), concentrations in the stream water decreased in the same order as the mean concentration of all groundwater samples ($Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+} > Fe^{2+}$). Base cations and metals in stream water were present in generally much smaller concentrations than in groundwater.

The concentrations of anions were generally greater in groundwater than in precipitation and throughfall. HCO_3^-, accounting for 67% of the mean anion concentration, was the dominant anion in groundwater (Table 3). Chloride and SO_4^{2-} were also relatively important, contributing 27 and 31%, respectively, to the mean anion concentration in groundwater. Bicarbonate, Cl^- and SO_4^{2-} were the dominant anions in stream water (92, 46 and 44 μeq L^{-1}, respectively). Bicarbonate concentrations in stream water were dilute in comparison with mean ground water concentrations (102-573 μeq L^{-1}). Chloride was at the lower end of the range of values for groundwater (Tables 2 and 3). The SO_4^{2-} concentration in stream water was comparable to groundwater. Nitrate, NO_2^- and PO_4^{3-} were below detection limits.

Concentrations of HCO_3^-, Cl^- and the metals Fe^{2+}, Al^{3+} and Zn^{2+} varied significantly (MANOVA, $P < 0.05$ for HCO_3^-, Cl^-, Al^{3+}, Zn^{2+} and $P = 0.05$ for Fe^{2+}) by season (Table 3). With the exception of Cl^-, these concentrations were greatest in the summer. Nitrite (NO_2^-) and PO_4^{3-} concentrations in groundwater varied significantly (MANOVA, $P < 0.05$) with water table elevation. Nitrite (NO_2^-) and PO_4^{3-} concentration decreased with higher water table elevation and increased with lower water table elevation. Phosphate (PO_4^{3-}) increased with depth to mineral soil (MANOVA, $P < 0.05$). The examination of replicate forest community types at Diana Lake and in other CWH forests will be necessary to determine the generality of these results.

DOC and Inorganic Ion Fluxes in Rainfall, Groundwater, and Stream Water

The flux of DOC in the organic-soil horizon was greater than inorganic fluxes of HCO_3^-, Na^+, Ca^{2+}, and Cl^- for the fall season (Table 4). For all seasons, the fluxes of metals, K^+ and Mg^{2+} were less important than the preceding ions and fluxes of NO_3^-, NO_2^- and PO_4^{3-} were negligible. In the mineral-soil horizon, inorganic fluxes were dominated by HCO_3^-, Ca^{2+}, Na^+, Cl^-, and to a lesser extent, Fe^{2+}, Al^{3+}, K^+ and Mg^{2+}. Metal fluxes were greater in the mineral- than organic-soil horizon.

The instantaneous flux of major ions entering the forest-peatland system through atmospheric water was small relative to the internal fluxes (throughfall and groundwater). Base cations in rainfall were the largest relative input ($4.0x10^{-8}$ kg $ha^{-1}s^{-1}$) to the forest-peatland system. Inorganic anions were below detection limits in rainfall. DOC was a comparatively large input ($2.2x10^{-7}$ kg $ha^{-1}s^{-1}$). There was an increase in DOC (from $2.2x10^{-7}$ to $4.8x10^{-7}$ kg $ha^{-1}s^{-1}$) as rainfall passed through the forest canopy. Stream water was dominated by DOC ($7.9x10^{-7}$ kg $ha^{-1}s^{-1}$) and lesser contributions of SO_4^{2-}, HCO_3^- and Cl^-. Sodium and Ca^{2+} were the dominant cations in stream water. The concentration of DOC in seep flow and runoff from the open peatland was not measured during the same sampling event for which the atmospheric water, groundwater and stream water fluxes were estimated. Instantaneous flux estimates based on 1998 data showed a DOC flux of $1.6x10^{-7}$ $kgha^{-1}s^{-1}$

TABLE 3. Mean (standard deviation) ionic concentration of groundwater in organic- and mineral-soil horizons, by forest community type and season, Diana Lake, British Columbia, Canada, 1997-98.

	HCO_3^- μeq L^{-1}	Cl^- μeq L^{-1}	NO_3^- μeq L^{-1}	NO_2^- μeq L^{-1}	PO_4^{3-} μeq L^{-1}	SO_4^{2-} μeq L^{-1}	Ca^{2+} μeq L^{-1}	Mg^{2+} μeq L^{-1}	Na^+ μeq L^{-1}	K^+ μeq L^{-1}	Fe^{2+} μeq L^{-1}	Mn^{2+} μeq L^{-1}	Al^{3+} μeq L^{-1}	Zn^{2+} μeq L^{-1}
Organic Horizon	219.0(20)	61.9(11)	0.7*	0.2(0)	0.6(1)	39.6*	99.0(33)	28.0(5)	154.0(59)	28.0(25)	25.0(0.5)	0.7(0.2)	25.0(0.5)	5.0(0.2)
Mineral Horizon	262.0(58)	58.0(7)	1.2(1)	0.2(0)	0.5(0)	68.0(68)	127.7(25)	31.1(4)	166.6(38)	19.9(6)	22.4(0.5)	1.2(0.0)	33.7(0.5)	8.5(3.0)
MANOVA														
p value	<.001	.067	.957	.819	.584	<.001	<.001	<.001	.001	.031	.624	.212	.692	.370
Swamp Forest	172(62)*b*	59(7)	0.8(1)	0.2(0)	0.7(0)	60(124)*b*	76(12)*b*	26(4)*b*	114(25)*b*	25(25)*b*	20(0.5)	1(0.0)	39(0.7)	6(0.2)
Bog Forest	148(62)*b*	70(37)	0.7(1)	0.2(0)	0.2(0)	<21.82	73(37)*b*	73(37)*b*	100(25)*b*	30(161)*b*	27(2)	2(0.1)	36(1)	6(0.5)
Bog Woodland	224(148)*b*	47(12)	<0.32	0.2(0)	0.2(0)	<21.82	134(111)*b*	26(11)*b*	83(25)*b*	14(25)*a*	34(2)	0.5(0.03)	16(1)	8(0.7)
Open Peatland	456(495)*b*	42(9)	<0.32	0.2(0)	0.6(3)	40*	188(148)*b*	39(25)*b*	101(37)*b*	15(4)*a*	38(3)	0.6(0.04)	14(0.9)	21(3)
Upland Forest	573(458)*a*	91(62)	2(10)	0.6(6)	1(6)	75(148)*a*	509(730)*a*	98(148)*a*	168(210)*a*	27(49)*b*	1(0.2)	1(0.6)	8(1)	0.2(0.0)
MANOVA														
p value	.001	.001	.789	.966	.110	.295	.078	.427	.444	.853	.050	.654	.006	.025
Summer	340(87)*b*	70(12)*b*	2(25)	0.3(0)	0.7(0)	48(173)	143(62)	46(10)	157(25)	23(12)	59(2)*b*	1(0.07)	53(2)*b*	26(1)*a*
Fall	—	42(5)*a*	<0.32	0.2(0)	0.7(1.2)	70(111)	163(49)	33(7)	56(10)	18(2)	18(0.5)*a*	1(0.06)	26(0.6)*c*	2(0.2)*b*
Winter	198(148)*a*	91(25)*a*	7(0.5)	0.2(0)	0.3(0)	<21.82	67(37)	19(5)	125(49)	24(6)	14(0.8)*a*	1(0.1)	14(1)*a*	6(0.4)*c*
Spring	102(74)*b*	41(74)*c*	8(3)	0.2(0)	0.4(0)	76(322)	65(62)	21(10)	117(25)	33(5)	8(0.3)*c*	0.6(0.04)	23(1)*c*	2(0.2)*b*

* denotes one sample below detection limits, < indicates all samples had a concentration less than specified detection limit

[a,b,c] Means within a column followed by a different letter are significantly different according to least squares analysis at $P<0.05$

Sample size is 153 for each ion

TABLE 4. Flux of dissolved organic carbon (DOC) and inorganic ions in groundwater at Diana Lake, British Columbia, Canada 1997-98.

	DOC kg ha^{-1} y^{-1}	HCO_3^- kg ha^{-1} y^{-1}	Cl^- kg ha^{-1} y^{-1}	NO_3^- kg ha^{-1} y^{-1}	NO_2^- kg ha^{-1} y^{-1}	PO_4^{3-} kg ha^{-1} y^{-1}	SO_4^{2-} kg ha^{-1} y^{-1}	Ca^{2+} kg ha^{-1} y^{-1}	Mg^{2+} kg ha^{-1} y^{-1}	Na^+ kg ha^{-1} y^{-1}	K^+ kg ha^{-1} y^{-1}	Fe^{2+} kg ha^{-1} y^{-1}	Mn^{2+} kg ha^{-1} y^{-1}	Al^{3+} kg ha^{-1} y^{-1}	Zn^{2+} kg ha^{-1} y^{-1}
Summer 1997															
Organic soil	—	1.460	2.560	0.002	0.004	0.007	0.329	0.146	0.037	0.256	0.029	0.073	<	0.037	<
Mineral soil	—	56.675	5.110	0.007	0.007	0.015	0.073	1.825	0.365	3.205	0.730	1.825	0.073	1.095	0.010
Fall 1997															
Organic soil	10.001	—	0.004	<	<	<	<	0.037	0.004	0.036	<	<	<	<	<
Mineral soil	0.003	—	0.007	<	<	<	<	4.745	0.730	2.190	0.183	0.730	0.073	0.365	0.006
Winter 1998															
Organic soil	—	1.460	2.190	0.002	0.001	0.010	<	0.730	1.460	0.329	0.015	0.029	<	0.018	<
Mineral soil	—	106.580	2.190	0.015	<	0.001	<	7.665	2.555	19.345	1.095	16.425	0.110	2.555	0.001
Spring 1998															
Organic soil	—	1.095	0.730	<	<	<	<	0.146	0.022	0.329	0.073	0.018	<	0.007	<
Mineral soil	—	29.200	3.285	<	<	<	<	6.935	1.095	8.030	0.730	0.365	0.037	0.730	<

< indicates concentration less than the detection limit

for runoff from the open peatland and fluxes of 1.9×10^{-7} kg ha^{-1}s^{-1} to 1.5×10^{-6} kg ha^{-1}s^{-1} from the upland forest and swamp forest seeps.

Hydraulic Gradients, Groundwater Recharge/Discharge

Vertical hydraulic gradients at Diana Lake varied both spatially and temporally (Figures 6 to 10). The gradients were greatest in the open peatland (-0.76 to 0.05, where a negative value indicates that groundwater flow is in the direction of decreasing hydraulic head) and upland forest seeps (-0.59 to 0.09). Vertical hydraulic gradients in the swamp forest, bog forest and bog woodland were in the range -0.51 to 0.15. The range in vertical hydraulic gradient was lowest in the upland forest along the transect (-0.05 to 0.05).

Groundwater recharge/discharge was plotted as piezometric head relative to water table depth (Figures 6 to 10). Piezometric head in the open peatland along the main transect and at stations

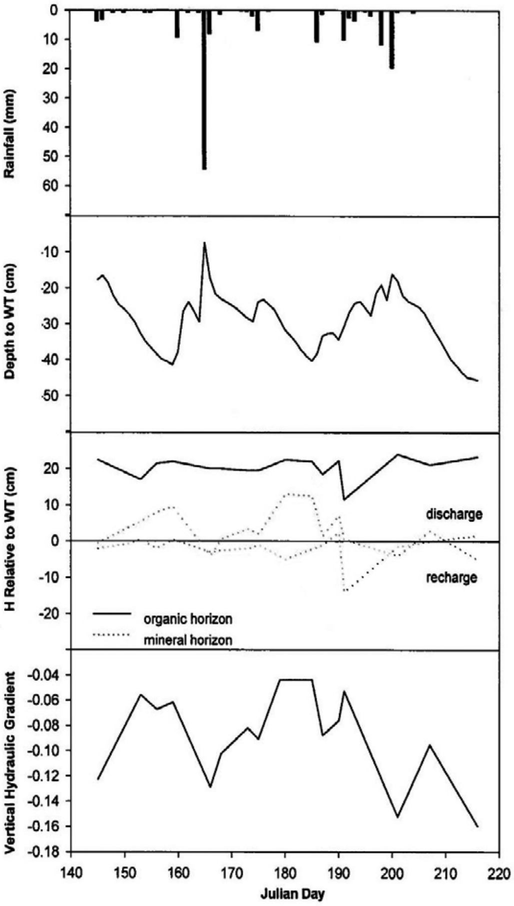

Figure 6. Daily rainfall, depth to water table (WT), piezometric head (h) relative to water table and vertical hydraulic gradient for a piezometer nest (3 piezometers, 1 well) in the swamp forest, Diana Lake, British Columbia, Canada (May-August 1998). Negative vertical hydraulic gradients are defined as downward gradients and positive vertical hydraulic gradients are defined as upward gradients.

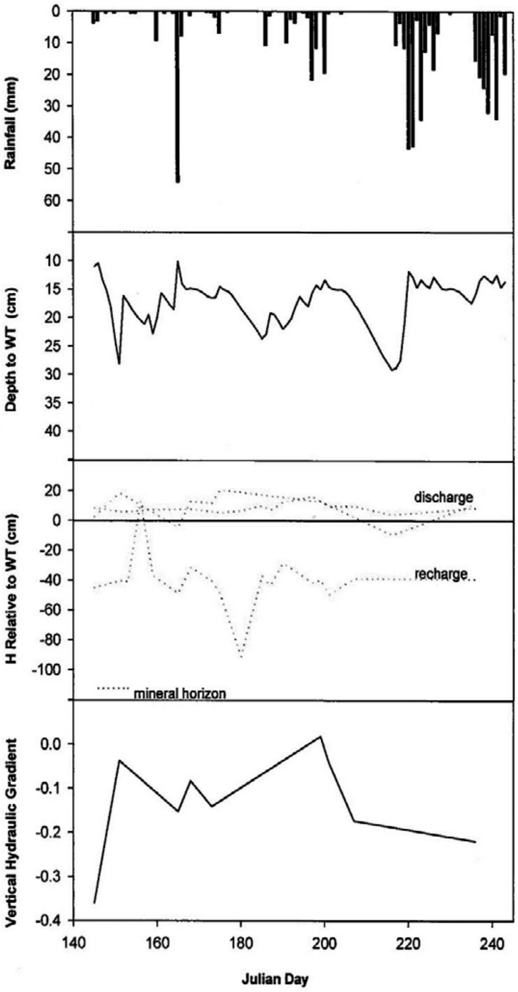

Figure 7. Daily rainfall, water table depth, piezometric head (h) relative to water table (WT) for 3 stations (1 piezometer, 1 well per station) and vertical hydraulic gradient for one station in the bog forest, Diana Lake, British Columbia, Canada (May-August 1998).

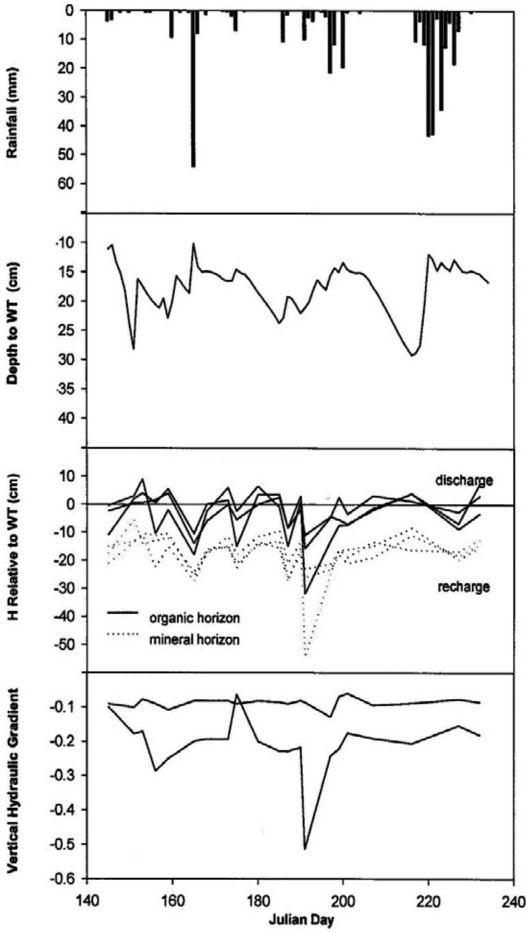

Figure 8. Daily rainfall, water table depth, piezometric head (h) relative to water table (WT) for 3 piezometer nests (2 piezometers, 1 well per nest) and vertical hydraulic gradient for two stations in the bog woodland, Diana Lake, British Columbia, Canada (May-August 1998).

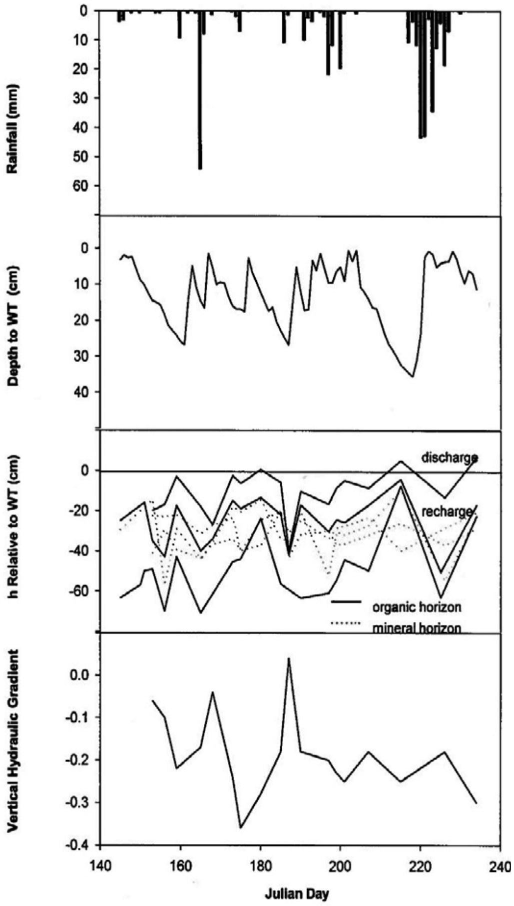

Figure 9. Daily rainfall, water table depth, piezometric head (h) relative to water table (WT) for 3 stations (1 piezometer, 1 well per station) and vertical hydraulic gradient for one station in the open peatland, Diana Lake, British Columbia, Canada (May-August 1998).

west of the transect (Figures 3 and 9) and in the upland forest (Figures 3 and 10) indicated that these areas were consistent regions of recharge. East of the transect in the open peatland, organic soil was discharging groundwater. Along the transect in the swamp and bog forests and in seeps (Figures 3, 6 and 7), the organic-soil horizon was discharging groundwater. Seep discharge from the organic-soil horizon in the west portion of the swamp and upland forest was intermittent. With the exception of sampling stations located at the base of steep slopes (zones of discharge), the mineral-soil horizon in the swamp forest, bog forest and seeps were zones of recharge. In the bog woodland, flow direction in the organic- and mineral-soil horizons changed between wet and dry periods, with groundwater recharge during rainfall events. Along the transect in the upland forest, mineral-soil horizon recharge occurred for the entire sampling period.

Groundwater flux varied between organic- and mineral-soil horizons and was a function of variations in K_{sat} (Emili et al. 2006). In general, K_{sat} was lower in the organic-soil horizon (10^{-4} to 10^{-5} m s^{-1}) compared with the mineral-soil horizon (10^{-2} to 10^{-3} m s^{-1}). Exceptions to this trend occurred

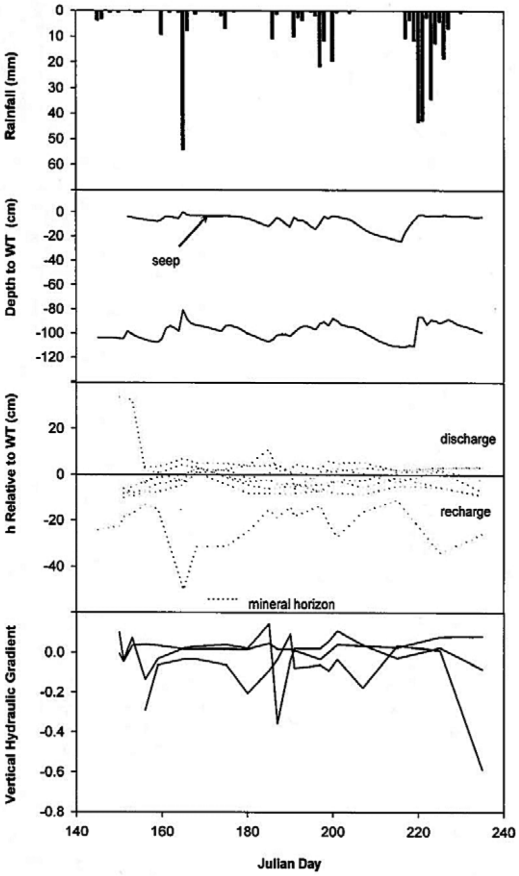

Figure 10. Daily rainfall, water table depth, piezometric head (h) relative to water table (WT) for 3 stations (2 piezometers, 1 well per station) and vertical hydraulic gradients in the upland forest, Diana Lake, British Columbia (May-August 1998).

in the open peatland, where K_{sat} was comparable in the organic- and mineral-soil horizons (10^{-4} to 10^{-5} m s^{-1}) and in zones of discharge located at the base of steep slopes in the swamp and upland forests where K_{sat} was greater in the organic-soil horizon (10^{-2} to 10^{-3} m s^{-1}) than the mineral-soil horizon (10^{-4} to 10^{-6} m s^{-1}). The mean daily groundwater flux along the transect was 0.005 ± 0.006 m^3 day^{-1} m^{-1} and 0.032 ± 0.072 m^3 day^{-1} m^{-1} in the organic-soil horizon and mineral-soil horizon, respectively.

Discussion

At the outset of our study, we hypothesized that forest community biogeochemistry in the sloping forest-peatland complexes of north coast British Columbia was a function of the hydrologic regime and its relationship to soil aeration, drainage and the availability of major ions and DOC. We used water table elevation as a proxy for soil aeration, whereby the oxic (non- saturated) zone was the area above the highest water table and the anoxic (saturated) zone was the area below the lowest water table (Asada and Warner 2005). D'Amore et al. (2010) have applied Ingram's (1978) diplotelmic model of an aerobic surface layer (acrotelm) and a permanently saturated subsurface (catotelm) defined by distinct differences in saturation duration, K_{sat} and redox potential in sloping forested peatlands in southeast Alaska. However, it is only the open peatland at the Diana Lake study site that would truly fit into the diplotelmic model of Ingram (1978).The peatland occupies a distinct hydrogeologic setting (concave bedrock morphology), with an organic soil-horizon of 0.31-3.15 m thickness comprising well-decomposed peat of low K_{sat} overlying a mineral-soil horizon of much greater K_{sat}. Water tables in the open peatland were within 25 cm of the surface for 90% of the study period. It is only within the open peatland, where vertical hydraulic gradients were greater than horizontal hydraulic gradients, that this distinctly stratified model applies and where changes in redox condition driven by the vertical movement of the water table control biochemical reactions, the mineralization of nutrient cations and the concentration of dissolved organic matter available for cycling and export (D'Amore et al. 2010).

Hydrologic flow paths in the forest communities at Diana Lake are a function of complex topography (Emili et al. 2006) and differences in K_{sat}, affecting both the pattern of discharge/recharge areas and the groundwater flux in the organic-soil and mineral-soil horizons. Discharge occurred where groundwater flow was directed up towards the water table. Recharge occurred where groundwater flow was directed away from the water table. Discharge from the organic-soil horizon at Diana Lake was important for the transport and flushing of DOC from this horizon during storm events, whereas discharge from the mineral-soil horizon was responsible for the upward distribution of inorganic ions.

The persistent vertical stratification of acidity (as indicated by changes in pH) and DOC within the soil profile along the forest-peatland complex reflects a common set of physical and biogeochemical processes. The decrease in groundwater DOC from organic- to mineral-soil horizon at Diana Lake is common in other forest and peatland systems and is a function of microbial and mineral-soil adsorption processes (Moore 1989, Schiff et al. 1990, Dalva and Moore 1991). The higher organic matter content in the organic-soil horizon compared to the mineral-soil horizon may also reduce the number of sites available for adsorption of DOC resulting in an increase in DOC available for runoff (Vance and David, 1992) from the soil horizon.

Marked seasonality in DOC concentration in groundwater has been observed in other studies and was found to be a function of temperature, redox condition, degree of decomposition and the frequency and rate of leaching of organic materials (see review in Moore et al. 2008). At Diana Lake, the higher summer temperatures, lower water table elevations and extended oxic conditions in the organic-soil horizon contributed to the increased production of DOC through microbial activity and decomposition (Creed et al. 2008) and hence the amount of DOC available for runoff during rainfall events.

DOC in the enriched organic-soil horizon was flushed from the system via shallow subsurface flow and seeps during rainfall events. While flushing behavior has been well studied (Worrall et al. 2002, Inamdar and Mitchell 2007, Creed et al. 2008), the sources of DOC are less understood (McGlynn and McDonnell, 2003). At Diana Lake during rainfall events, the water table rose in seeps and into the shallow organic-soil horizon. When the water table exceeded a threshold elevation, surface ponding occurred (Emili and Price 2006). When the depression storage was exceeded, cumulative overland flow from the hillslope to the stream caused a steady increase of DOC concentration in stream water. Topographic lows, with higher organic matter accumulations and potentially higher acidity and DOC, act as identifiable source areas for runoff along the Diana Lake transect (Emili et al. 2006). These source areas have been identified and the spatial distribution along the Diana Lake transect characterized by means of topographic (slope) indices (Emili et al. 2006).

Significant changes in the DOC concentration in Diana Creek water occurred over the course of storm events. Pre-event stream water concentrations were similar to concentrations in streams in watersheds with considerable peatland cover (Schiff et al. 1997). In contrast to stream water concentrations of major ions (represented by electrical conductivity) that exhibit dilution with increased flow, DOC concentrations in Diana Creek increased with increased storm flow. Fitzgerald et al. (2003) and Gibson et al. (2000) found similar results for the upland forest stream at Diana Lake and a small creek 6 km southwest of Diana Creek, respectively. This increase in DOC concentrations was consistent with abundant contributions from DOC-rich sources in organic soils and lesser contributions from DOC-poor deep groundwater sources. As an event progressed and water tables rose closer to land surface, shallow subsurface flow and overland flow predominated. This flow moved rapidly through upper soil horizons allowing DOC-rich water to circumvent adsorption processes in the underlying mineral soil (Fellman et al. 2009), leading to the input of relatively DOC-rich water on the rising limb of the storm hydrograph and decreasing DOC concentration on the falling limb as the upper organic-soil horizon was exhausted of DOC (Worrall et al. 2002). This flushing of DOC has been observed in other forest-wetland watersheds (Worrall et al. 2002, Creed et al. 2008).

The two primary controls on the ionic composition of groundwater at Diana Lake were forest community type and season. Bicarbonate, SO_4^{2-} and base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) varied significantly with forest community type (Table 3). With the exception of K^+, the concentration of each of these ions was significantly greater in the upland forest than other forest communities. Damman (1986) reported that lower K^+ concentrations in peatland communities compared to forest communities are due to preferential adsorption onto peat colloids and/or uptake by *Sphagnum*. During dry periods and on well-drained slopes and topographic highs, water tables were lower, extending the aerobic (oxic) zone. Under more aerobic conditions, decomposing soil organic matter releases nitrogen, sulphur and phosphorus which are oxidized to NO_3^-, SO_4^{2-} and PO_4^{3-}, respectively (Devito and Dillon 1993). Warmer temperatures also accelerate microbial degradation of organic matter that results in the release of inorganic ions, HCO_3^- and DOC into solution (Mulholland et al. 1990).

During wetter periods or on less well-drained slopes and in topographic lows, higher water tables resulted in less storage capacity in the soils, a shallower aerobic zone and prevention of the oxidation of nutrients to available forms. Research in cedar-hemlock forests in south coastal British Columbia has shown low to negligible concentrations of NO_3^- and PO_4^{3-} in forest groundwater to be the result of competing processes of uptake by nutrient limited cedar and cypress trees, assimilatory reduction by DOC and adsorption by organic oxides (Prescott et al. 1995). The reductive dissolution of Fe and Al oxides under anaerobic conditions can also lead to the release of DOC that was previously adsorbed on the oxides (Tipping 1981).

We performed an analysis of the flux of major ions and DOC as a means of understanding the flowpaths and processes controlling the export of ions and DOC from the Diana Lake transect. The dominance of Na^+ and Cl^- and the range of cations in rainfall, fog drip and throughfall was comparable to results for study areas 35-50 km inland of the ocean (Christophersen et al. 1982, 1990; Edmonds et al. 1995). In coastal environments, 2- to 5- fold higher concentrations of sea salt ions have been observed in fog drip (Reynolds and Pomeroy 1988, Price 1992). While Na^+ and Cl^- concentrations in fog drip at Diana Lake were almost 3 times greater than in rainfall, the comparatively small water flux (5.3 mm compared to 613 mm) limits input to the system. The relatively high concentration of HCO_3^- in rainfall may have been the by-product of conifer pollen (deposited on the gauge) broken down by precipitation ($C_m (H_2O)_n \rightarrow CO_2 + H_2O \rightarrow H^+ + HCO_3^-$, Stanley and Linskens 1974). The pH of rainfall and fog drip at Diana Lake was within the range of values for relatively pristine sites (Christophersen et al. 1990, Edmonds et al. 1995). The greater acidity of fog drip compared to rainfall at Diana Lake may have been due to the relative increase in inorganic acid anions, such as Cl^- and NO_3^- (Heath et al. 1992). The DOC concentration in rainfall (range of 2.33 to 5.44 mg L^{-1}) was high compared to results (range of 1 to 2 mg L^{-1}) reported elsewhere (McDowell and Likens 1988, Moore 1989, Koprivnjak and Moore 1992). The higher concentration in rainfall at Diana Lake may have been the result of algal contamination. Sample collection bottles were scrubbed then rinsed with distilled water between collections, but they were not acid-washed. Leaching of organic acids from foliage contributed a large amount of DOC (4.8×10^{-7} kg ha^{-1} s^{-1}) to the soil system at Diana Lake.

Throughfall DOC concentrations were in the upper range of reported values (Cronan and Aiken 1985, McDowell and Likens 1988, Koprivnjak and Moore 1992). There were insufficient samples to characterize temporal changes in throughfall DOC concentration. There was dilution of DOC in throughfall water once it entered the soil-groundwater system. Inamdar et al. (2011) found a decline in DOC concentration in groundwater with increasing depth in the soil profile and along hydrologic flow paths that had greater contact with soil. They attributed this decline to the sorption of dissolved organic matter as water percolated through the soil profile. Substantial decreases in DOC concentration as water moves through soil may also be caused by dilution with groundwater of lower DOC concentration (Bengston and Bengtsson 2007). Emili and Price (2006) found isotopic evidence of mixing of groundwater during recharge rain events at Diana Lake.

A high rate of DOC production in the organic-soil at Diana Lake, coupled with high water tables, resulted in a significant lateral flux of DOC from the shallow subsurface horizon (10 kg $ha^{-1}y^{-1}$) and seeps (6-48 kg $ha^{-1}y^{-1}$) to Diana Creek. The range in stream water concentration fell at the lower end of the range of concentrations reported in the literature for watersheds with a large proportion of peatland (Eackhardt and Moore 1990, Marin et al. 1990). A similar range (3-20 mg L^{-1}) has been reported in a rainforest in New Zealand (Moore 1989). In comparison to forested peatland systems in the literature (see review in Dalva and Moore 1991, 1-50 mg L^{-1} DOC), the degree of variability in stream water DOC concentrations is relatively low, reflecting a consistent source of DOC.

Stream water pH and inorganic chemistry were within the range found in other coastal forests (Vitt et al. 1990, Edmonds et al. 1995). The dissolved reactive silica concentration in stream water (0.1 mmol L^{-1}) indicated that active weathering was occurring (Edmonds et al. 1995). The lower concentration of base cations and metals in stream water relative to groundwater was due to retention in the watershed by nutrient uptake, cation exchange and adsorption mechanisms. Chloride as a conservative element passed through the hillslope. Nitrate and PO_4^{3-} were consumed by direct plant uptake in the soil-groundwater system. The export of SO_4^{2-} may have been due to lower plant uptake by non-sulphur-limited cedar and cypress trees and/or due to competition with DOC for soil exchange sites (Prescott et al. 1995).

Figure 11 presents the conceptual model that illustrates the specific hydrological and biogeochemical processes operating from upland forest to open peatland along the forest-peatland complex at Diana Lake. Solute inputs in rainfall and fog drip to the soil-groundwater system were dominated by Na^+ and Cl^-. Leaching from the forest canopy contributed a significant amount of DOC to the system. The chemical composition of the groundwater system was dominated by Na^+, Cl^-, DOC and HCO_3^-. The former two ions reflected sea salt inputs and the DOC and HCO_3^- reflected the importance of organic matter decomposition to acidity and nutrient cycling. The influence of mineral-soil sources of inorganic ions (HCO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) increased as the depth of organic-soil decreased as a function of increasing land-surface slope and dissolution by recharging groundwater. As hydraulic gradients decreased,

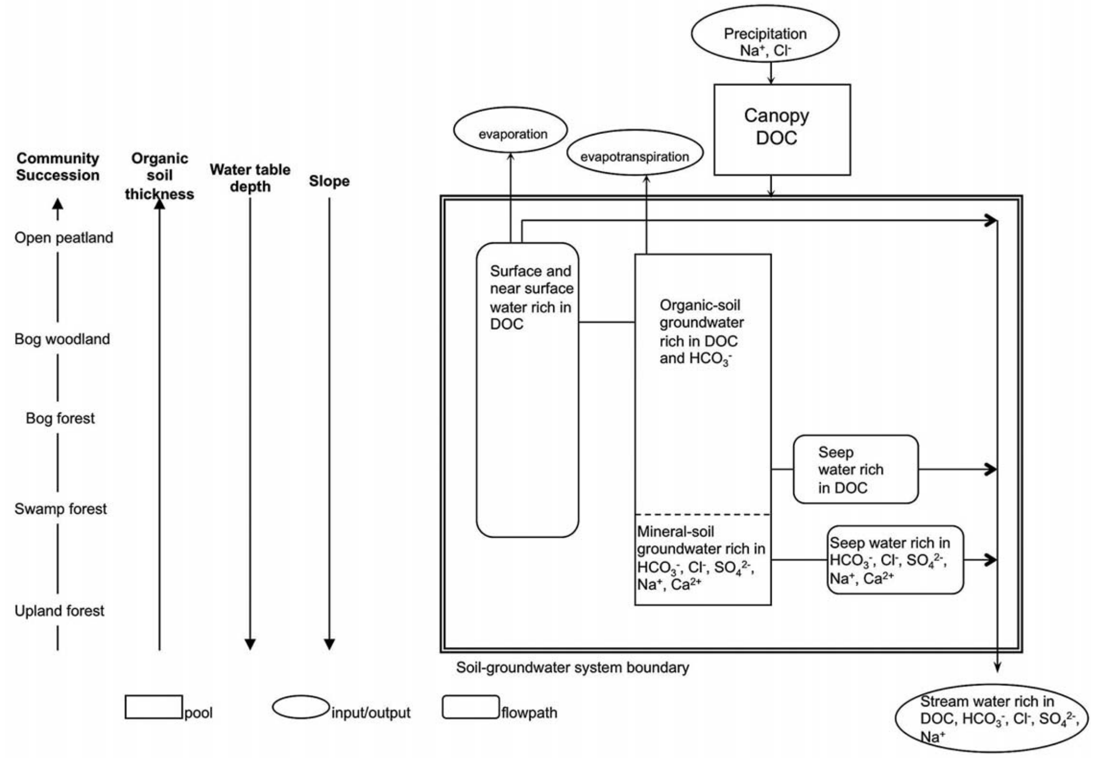

Figure 11. Conceptual model of hydrochemical dynamics along the forest-peatland complex at Diana Lake, British Columbia, Canada.

poor drainage and elevated water tables slowed decomposition and contributed to the accumulation of organic matter. Changes in water table elevation impacted redox sensitive species (Al^{3+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, NO_3^-, SO_4^{2-}, PO_4^{3-}). The concentration of oxidized ions was greater during dry periods and on better-drained slopes where lower water tables extended the oxic zone. In forest communities with shallow water tables and during wetter periods, these ions were absent. The hillslope was a sink for NO_3^-, PO_4^{3-} and K^+ and an exporter of SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^- and DOC. The flux of inorganic ions in mineral-soil horizon groundwater was large compared to the flux in the organic-soil horizon groundwater. During storm events, however, the shallow organic soil groundwater flux dominated runoff (Emili and Price 2006), thus increasing the relative importance of DOC exports.

Conclusions

Currently, less is known about the soil and water resources of British Columbia than about the timber resources (British Columbia Ministry of Forests, Mines and Lands 2010). The potential impacts of forest harvesting on the hydrological regimes of forest soils and nutrient loss into groundwater is a topic with relevance for significant land areas in British Columbia (Banner et al. 2005). This study contributes important data on the groundwater chemistry and biogeochemical functioning of a sloping forest-peatland complex. Hydrological and biogeochemical processes combine in space and time along the forest-peatland complex at Diana Lake. Major ions and DOC entering the stream are derived from multiple, spatially distinct groundwater sources whose relative inputs change as a result of inter- and intra- storm event, i.e. wet versus dry conditions. Hydrologic flowpaths change to near- surface soil horizons and DOC source pools become linked. As a rainfall event progresses, differences in DOC concentration associated with source waters control the temporal variation in DOC dynamics observed at the watershed outlet. Information on temporal patterns of ground and stream water chemistry is needed not only in developing models of discharge and solute concentration, but for computing solute flux budgets for watersheds (Inamdar et al. 2006). Further, the characterization of the relative contribution of topographic units in controlling watershed hydrology and solute export is the first step in scaling-up hillslope level research results to the landscape context (McGlynn and McDonnell 2003).

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