Surface Water and Groundwater Contributions to Streamflow in the James Bay Lowland, Canada

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Abstract

Climate and land-use changes are going to leave an indelible mark on the hydrology and globally significant peatlands of the Hudson Bay Lowlands (HBL), Canada. With forecasts for warmer and drier conditions over the next century, the relative contribution of water from surface and subsurface sources affecting both water quantity and quality will undoubtedly shift. Unfortunately, no empirical data exist for any streams or rivers of the HBL on the relative contributions of surface water and groundwater to streamflow, making assessment of future change difficult. Here we report the first data on sources of water to streams and rivers across a range of catchment sizes in the James Bay Lowland (JBL) ecoregion of the HBL. Solute chemistry was determined for a range of potential end members, and a chemical mixing model approach was used to determine the relative end-member contributions to streamflow across a range of catchment sizes (~30–2000 km²). The relative contributions of bedrock-derived groundwater to streamflow increased with catchment area from <20 to >40% under dry conditions, and were ~50% lower under wet conditions across all catchments. Runoff contributions from peatlands were relatively constant over space and time (53–67%), but the fraction of streamflow composed of rain and snowmelt varied dramatically between wet and dry periods, and among catchments. Given the importance of peatland-derived surface waters, future changes in precipitation and temperature could have significant implications for streamflow in the JBL, particularly during summer base-flow conditions. Moreover, the definition of reference catchments for baseline/impact monitoring must be carefully considered, given the potential for variation in hydrochemistry across physiographically similar catchments.

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Introduction

Northern catchments are among the first to be affected by global climate change and will exhibit a complex range of responses in different and often interacting biotic and abiotic components (Prowse et al., 2009). According to the current projections of large-scale climate models, Canada’s North, and the Hudson Bay region in particular, will be among the most severely affected areas. The projections for northeastern Canada, including the Hudson and James Bay area, indicate one of the largest increases in annual average air temperature (+4.3 °C) and precipitation (+15%), with the maximum changes expected in winter months: +5.9 °C and +26%, respectively (IPCC, 2007).

Northern peatlands are highly sensitive to climate variations that may shift a subtle balance between water input and output. Wetland distribution, extent, and sustainability in the future will depend on the quantity and seasonality of precipitation (Clair, 1998). The projected higher temperatures will lead to increased water loss through evapotranspiration, changes in vegetation composition, and potentially a loss of peat depth through decomposition (Moore, 2002), all of which may affect the timing and magnitude of river flows. In addition to changes in precipitation and evapotranspiration, climate change is linked to reduced intensity of seasonal ground freezing and, as a result, increased subsurface flow contributions to streamflow derived from enhanced groundwater connectivity (Frey et al., 2007), leading to higher minimum flows (Smith et al., 2007), and changes in stream water chemistry and primary productivity in freshwater and marine ecosystems (Frey et al., 2007). Certainly in regions where the catchment land cover is dominated by peatlands, these changes will be strongly felt. The surface streams and rivers draining the Hudson Bay Lowlands (HBL), the second largest contiguous peatland in the world (474,000 km²) (Rouse, 1991), will undoubtedly reflect changes in temperature and precipitation in both water quality and quantity.

The freshwater streams and rivers of the HBL are a source of drinking water and fish for residents of northern communities and freshwater to James Bay and Hudson Bay. Recognizing the importance of hydrological dynamics of rivers in the HBL for the environment, northern communities, and development, several studies have investigated the annual and seasonal fluxes of water in the HBL catchment. The existing evidence of changes in hydrology of northern watersheds suggests earlier spring peak discharge and decreased magnitude of hydrologic events (Westmacott and Burn, 1997; Déry et al., 2005), decreased mean annual and monthly flows, except for the snowmelt period (McClelland et al., 2006). The Churchill, Severn, Winisk, Ekwan, and Attawapiskat Rivers exhibited a statistically significant negative trend in annual discharge, while the Moose and Albany Rivers had no trend (Déry et al., 2005). A change in the river flows affects salinity of James Bay, and the upper layer of the Arctic and northwestern Atlantic Oceans (Déry et al., 2005), which alters the ice regime, climatic parameters, and hence the duration of the growing season, evaporation, and species distribution in the coastal areas (Rouse et al., 1992). The results of the diminished river flows and increased regional temperature are consistent with the observed earlier ice breakup in James Bay and southern parts of Hudson Bay (Gagnon...
a total catchment area of ~2100 km². The hydrology and water connectivity to shallow bedrock groundwater aquifers that underlie the Nayshkootayaow River and its downstream tributaries as a result of channel incision driven by in-channel processes and base-level adjustment due to isostatic rebound. Geology of the study area is further complicated by the presence of bioherms protruding above the peatland terrain within the Attawapiskat Formation (Canadian Environmental Assessment Agency, 2005), and karst developed on or around the reef knolls as a result of acidic peatland groundwater dissolving bioclastic rock (Cowell, 1983).

### Methods

Field work was undertaken in April–November 2010 in conjunction with streamflow gauging and sampling associated with the environmental monitoring of DeBeers Canada Inc. for their Victor Diamond Mine located just to the northeast of the study watersheds. Streamflow discharge data were provided by DeBeers Canada, and was collected as part of their environmental monitoring program. Their water level data were collected at eight streamflow monitoring locations accessible only by helicopter at the confluences of tributaries and upstream-downstream stations on the Nayshkootayaow River (Fig. 1). Daily mean stage values were calculated from 15-minute measurements of submersible pressure transducers. Discharge has been measured manually every month during the open-water season since 2005 at stations Trib 3, Trib 5, and Trib 7, 2006 at the Nayshkootayaow River, and 2007 at Trib 5A with a SonTek FlowTracker Acoustic Doppler Velocimeter. Daily discharge data were calculated from the derived stage-discharge relationship (rating curve). Winter under-ice daily flows were estimated between manual flow measurements using a recession curve method (D. Ott, DeBeers Canada, personal communication).

Precipitation data were obtained with a rain gauge, located at the research weather station 2 km northwest of the De Beers Victor Mine. Ten minute data were converted to daily precipitation values. Due to a technical problem, rain data for the 2010 study period are available only until mid-September.

### WATER CHEMISTRY

#### General Sampling Approach

Samples of stream water, ponds, pore water, peatland groundwater, bedrock and overburden groundwater, and precipitation were collected in April–November 2010 and February 2011 for chemical and isotopic analyses. Stream water sampling was conducted regularly at each flow station, usually biweekly from the end of April until August. Several samples were also collected in the fall and in February 2011. Water samples for ion and dissolved organic carbon (DOC) analyses were filtered with a 0.45-μm nylon filter, collected in high-density polyethylene (HDPE) 30-mL bottles, and stored frozen until analyses. Water samples for analyses of...
stable isotopes were collected unfiltered in 20-mL polyethylene scintillation vials and stored at 4 °C until analysis. Field duplicates and blanks were taken periodically for quality control.

PRECIPITATION

The field season started when the winter snowpack was almost gone, and only four snow samples were obtained representing “old” snow and “new” snow collected immediately after the snowfalls. The snow samples were collected in sterile 250-mL HDPE bottles and thawed at room temperature in the field laboratory. Rain samples were collected with a rain sampler that consisted of a large Teflon funnel attached to a sterile 500-mL HDPE bottle installed in the vicinity of the mine camp.

Stream Water Sampling

Stream water sampling was conducted regularly at each flow station, usually biweekly from the end of April until August 2010. Four samples were collected in September and October from the Nayshkootayaow River, all streams were sampled again in November, and then six streams (except Trib 3 and Trib 7) were sampled in February 2011.

Surface Water Sampling

The term surface water in this work refers to water collected from peatland ponds and shallow peat pore water throughout the 2010 field season at the research transects and at some of the De Beers Victor Mine monitoring locations. Overall, 25 samples were collected from the ponds ranging in size, including seasonal ponds, and 5 pore water samples were collected in the summer from the depth of 0–10 cm relative to the water table in the hollows.

Groundwater Sampling

Groundwater samples were collected from the peatland, overburden, and bedrock aquifers across the watershed. Most wells and piezometers are a part of the De Beers Victor Mine network for annual compliance monitoring. Peatland wells are about 2–3 m deep in the peat. Piezometers installed in the overburden have depths of 3–5 m. Bedrock piezometers were usually installed in the bioherms and screen the Upper Attawapiskat Formation between 4 and 66 m below the ground surface. Prior to each sampling event, all wells and piezometers were purged with a peristaltic pump to remove standing water. Samples of peatland groundwater were also collected at the three research transects from wells and piezometers of 0.9 to 2.5 m deep.

CHEMICAL AND ISOTOPIC ANALYSES

Field measurements of pH and specific conductance (SC) were taken with a YSI 6600 Multiparameter Sonde. The instrument was calibrated prior to sampling sessions: a three-point calibration (4, 7, and 10 pH solutions) of the pH probe, and a one-point (100 μS cm⁻¹) calibration of the conductivity probe, in accordance with manufacturer’s instructions.

All water samples were analyzed for major ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻) with the Dionex ICS-1600 ion chromatography system at the University of Toronto in Mississauga, and later Dionex ICS-3000 for anions and Dionex
TABLE 1
Watershed and flow characteristics of the four gauging stations of the Nayshkootayaow River and four study tributaries.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Watershed area* (km²)</th>
<th>Mean discharge in 2010* (m³/s)</th>
<th>Total annual discharge in 2010* (km³)</th>
<th>Shreve stream order</th>
<th># of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-001</td>
<td>702.5</td>
<td>4.1</td>
<td>0.128</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>NR-002</td>
<td>1069</td>
<td>7.2</td>
<td>0.226</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>NR Exploration Camp</td>
<td>1721.8</td>
<td>10.2</td>
<td>0.322</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>NR-003</td>
<td>1958.4</td>
<td>12.8</td>
<td>0.404</td>
<td>29</td>
<td>19</td>
</tr>
<tr>
<td>Trib 3</td>
<td>126.5</td>
<td>0.82</td>
<td>0.026</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Trib 5A</td>
<td>29.9</td>
<td>0.25</td>
<td>0.006</td>
<td>1</td>
<td>32</td>
</tr>
<tr>
<td>Trib 5</td>
<td>203.4</td>
<td>1.62</td>
<td>0.050</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Trib 7</td>
<td>51.4</td>
<td>0.49</td>
<td>0.011</td>
<td>1</td>
<td>13</td>
</tr>
</tbody>
</table>

* Data courtesy of De Beers Canada, Inc.

ICS-1600 for cations in the Biotron Analytical Services Laboratory at the University of Western Ontario. Several samples with very low concentrations were analyzed for Ca and Mg on the Perkin Elmer Optima 300DV ICP-OES in the Biotron.

Dissolved organic carbon was determined by high-temperature catalytic oxidation at the University of Toronto (Lachat IL-550 TOC/TN Analyzer, MDL 0.05 mg L⁻¹) and the University of Western Ontario (Shimadzu TOC-VCSSH, MDL 0.004 mg L⁻¹).

The isotopes of water δ²H and δ¹⁸O were measured on a Los Gatos Research DT-100 Liquid-Water Stable Isotope Analyzer at the University of Western Ontario. Results are reported relative to the Vienna-Standard Mean Ocean Water (VSMOW) standard using the δ-notation. Precision of the analyses is 2‰ for δ²H and 0.3‰ for δ¹⁸O.

MIXING MODEL

Our approach was based on the End-Member Mixing Analysis approach (EMMA) (Christophersen and Hooper, 1992) to define contributing areas controlling stream water chemistry, and a three-component hydrograph separation model (Ogunkoya and Jenkins, 1993) to estimate the component contributions to streamflow. Mixing diagrams (biplots of solutes or other measured parameters plotted against each other) were constructed for stream data using all pairs of tracers to check the data for outliers and analyze the curvature. Some solutes (K, Na, Ca, and SO₄) were not included in the mixing model analyses because of evident or expected (based on other studies) nonconservative behavior. In this study, Ca was rejected for all sites based on the curvature in the mixing diagrams (i.e., stream water Ca concentrations fell unpredictably outside of the bounds of bivariate solute plots bounded by expected end members). The saturation index (SI) of calcite computed using the geochemical program PHREEQC predicted concentrations of CaCO₃ in stream water close to saturation (SI = 0) in July, thus suggesting favorable conditions for in-stream precipitation. Also, based on their behavior in the mixing diagrams, K, Na, and SO₄ behaved nonconservatively at stations NR-001, Trib 3, and Trib 5A. Na and K concentrations may have been affected by ion exchange in the silt or deep peat, as well as vegetative uptake. SO₄ is nonconservative with regard to peatland pore water groundwater because of microbial reduction that lowers the concentrations to below the method detection limit.

Results

CLIMATE AND STREAMFLOW

The 2010 field season was warmer and drier than the long-term average. The annual average temperature at the nearest meteorological stations located 250 km southeast (Moosonee) and 300 km west-southwest (Lansdowne House) was about 3 °C higher than the norm. The total precipitation amounted to only 425 mm at Moosonee (the long-term average was 682 mm) and 580 mm at Lansdowne House (700 mm) (Environment
The winter of 2009/2010 was mild, and fast, early snowmelt ended before the end of April, when the field season started. Little precipitation occurred between April and late July, with the months of May and June 2010 receiving only 21 and 36 mm of rain, respectively. The average water table was well below the peat surface, the surface mosses were visibly desiccated, and most small shallow surface ponds dried up. The landscape was generally rewetted after a 57-mm rainfall on July 28 and subsequent rain events.

The annual hydrograph in 2010 was characterized by an early and relatively low snowmelt peak, very low summer and winter flows, and a flood in the end of July produced by the end-of-July heavy rainfall that exceeded spring high flows (Figs. 2 and 3). The average runoff in 2010 was about one-third of that in 2009 (Fig. 4) (Richardson et al., 2012). The hydrographs reveal distinct periods of high flows (March to May and August to November) and low flows (June to July and December to February).

WATER CHEMISTRY

The summary data for water chemistry from all sites are presented in Table 2. Water chemistry data are not presented as a function of time or discharge here; however, general tendencies with respect to each are discussed below.

Stream Water

Stream water chemistry showed seasonality in as well as differences in water chemistry among the streams. Stream waters were slightly acidic to alkaline, with pH varying from stream to stream from 6.1 to 8.1. The lowest pH was measured at station Trib 5A (mean of 6.8), whereas other streams had mean pH values of 7.2 to 7.6.

The concentrations of Ca, Na, Cl, and SO4 and SC were generally inversely correlated with discharge. Stations NR-001, Trib 3, and Trib 5A had lower concentrations of Na, Cl, and SO4, and lower SC. Concentrations of SO4 in Trib 5A were below the method detection limit most of the time. Using the above solutes and Piper plots (data not shown), stream waters were generally of the Ca-HCO3 type, and the samples collected in February 2011 from the Nayshkootayaow River stations and Trib 5 were Ca-Cl facies.

The relationship between discharge and DOC in stream water was complex. DOC increased steadily from ~9 ppm in most streams in April, reached maximum values (~16–20 ppm) in mid-August, and then declined throughout the fall. Trib 3 had the highest DOC concentrations over the year, with concentrations higher than in other streams by 3 to 8 ppm.

Stream δ2H and δ18O generally became more enriched with increasing discharge at all stations and generally plotted slightly below the global meteoric water line (GMWL). Some Trib 5A δ2H and δ18O had high d-excess values, suggesting the stream water contained precipitation water that was recycled through evaporation (Gat et al., 1994).

Surface Water and Groundwater

Peatland shallow groundwater and surface-water chemistry varied temporally and spatially. Solute concentrations in peatland groundwater ubiquitously increased with depth and in some deep (>1.5 m) peatland piezometers was comparable to that in bedrock groundwater. Field measurements at the MS-15 and Trib 5A research transects in the end of June showed SC values of 50–180 μS cm–1 at 0.9 m, 100–400 μS cm–1 at 1.5 m, and 500–800 μS cm–1 below 2.0 m; pH increased from 4.5 in the wells to >6 in the deep (>1.5 m) piezometers. Peatland groundwater chemistry was dominated by carbonate mineral dissolution, although at several locations it contained high concentrations of Na and Cl. Concentrations of SO4 in peatland surface and groundwater usually exhibited concentrations below the limit of quantitation. Most bedrock and overburden groundwaters were Ca-HCO3 facies as well, with only a few samples having relatively high Cl and SO4 content.

DOC concentrations in peatland surface water and shallow groundwater varied greatly. Peatland pore water and shallow groundwater had the highest DOC content, and DOC in the peatland ponds was lower in the spring (range from 7 to 23 ppm) and increasing over the summer (14–41 ppm). Overburden groundwater and bedrock groundwater had relatively high DOC concentrations (mean of 15 and 10 ppm, respectively).

Bedrock and overburden groundwater δ2H and δ18O were almost indistinguishable from precipitation, plotting close to the Global Meteoric Water Line (GMWL). Evaporatively enriched
pond water samples plot below the GMWL along a local evaporation line (LEL) and cover a large range of compositions. δ²H and δ¹⁸O signatures of ponds and pore waters were changing throughout the field season, reaching maximum (less negative) values in July and August. Both δ²H and δ¹⁸O quickly decreased from the surface down the peat column, and peatland groundwater in deep piezometers was as depleted in the heavier isotopes as bedrock groundwater.

MIXING MODEL
PCA and End-Member Definition

In PCA, six original variables (Mg, Cl, SC, DOC, δ²H, δ¹⁸O) were reduced to two principal components with an eigenvalue >1. Together the components explain 83% of total variance. The first principal component (PC1) is negatively correlated with all original variables, and the second principal component (PC2) has high loadings of Mg, Cl, and SC, and low loadings of δ²H, δ¹⁸O, and DOC.

Represented in a two-dimensional space, these data revealed two distinct trends, the first being associated with a change in the concentrations of Cl, Mg, and SC (Fig. 5). This trend is clearly observed in the Nayshkootayaow River water chemistry data as an increase in scores on PC2 and a decrease in scores on PC1 in subsequently downstream stations. Stations Trib 5 and Trib 7 behaved similarly to the downstream station on the Nayshkootayaow River. The scores on PC2 increased during low-flow periods and reach maximum values in the end of June and in February. Stations Trib 3, Trib 5A, and NR-001 showed minimal variation along this trend, suggesting that Cl, Mg, and SC are not as important in controlling water chemistry for these streams as they are for other streams. The second trend is characterized by increasing scores on both principal components and reflects a decrease in loadings of δ²H, δ¹⁸O, and DOC. Trib 5A exhibits a maximum variation along this trend.

The potential end members were projected onto the U-space defined by the stream water data (Christophersen and Hooper, 1992). These end members were as follows: precipitation, representing 10 snow and rain samples; pore water (5 pore waters from the top 0–10

![FIGURE 3. 2010 mean daily instantaneous discharge hydrographs for upstream to downstream gauging stations (NR-001 to NR-003) of the main Nayshkootayaow River. Data courtesy of DeBeers Canada Inc.](https://bioone.org/journals/Arctic,-Antarctic,-and-Alpine-Research)

### TABLE 2

Median, minimum and maximum concentrations of solutes and tracers found in the study streams, precipitation, surface waters, and groundwaters of the study basin.

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Unit</th>
<th>NR–001</th>
<th>NR–002</th>
<th>NR Expl. Camp</th>
<th>Trib 3</th>
<th>Trib 5A</th>
<th>Trib 5</th>
<th>Trib 7</th>
<th>Precip.</th>
<th>Ponds</th>
<th>Muskeg g.w.</th>
<th>Overburden g.w.</th>
<th>Bedrock g.w.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>mEq/L</td>
<td>0.109</td>
<td>0.197</td>
<td>0.190</td>
<td>0.266</td>
<td>0.137</td>
<td>0.095</td>
<td>0.266</td>
<td>0.342</td>
<td>0.067</td>
<td>0.028</td>
<td>0.043 (0.008–0.045)</td>
<td>0.185</td>
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<td>(0.094–0.220)</td>
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<td></td>
<td>(0.027–0.262)</td>
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<tr>
<td>K</td>
<td>mEq/L</td>
<td>0.008</td>
<td>0.010</td>
<td>0.010</td>
<td>0.014</td>
<td>0.007</td>
<td>0.013</td>
<td>0.015</td>
<td>0.015</td>
<td>0.002</td>
<td>0.003</td>
<td>0.006 (0.004–0.018)</td>
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<td></td>
<td>(0.003–0.14)</td>
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<tr>
<td>Mg</td>
<td>mEq/L</td>
<td>0.249</td>
<td>0.233</td>
<td>0.198</td>
<td>0.229</td>
<td>0.127</td>
<td>0.181</td>
<td>0.237</td>
<td>0.166</td>
<td>0.008</td>
<td>0.025</td>
<td>0.091 (0.027–0.140)</td>
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<td>(0.003–0.14)</td>
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<tr>
<td>Ca</td>
<td>mEq/L</td>
<td>1.07</td>
<td>1.10</td>
<td>0.92</td>
<td>1.03</td>
<td>0.53</td>
<td>0.65</td>
<td>0.93</td>
<td>0.61</td>
<td>0.15</td>
<td>0.61 (0.163)</td>
<td>3.39 (0.233–3.127)</td>
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<tr>
<td>Cl</td>
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<td>0.121</td>
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<td>0.201</td>
<td>0.051</td>
<td>0.044</td>
<td>0.19</td>
<td>0.257</td>
<td>0.010</td>
<td>0.018</td>
<td>0.025 (0.034–0.053)</td>
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<td>(0.017–1.334)</td>
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<tr>
<td>SO₄²⁻</td>
<td>mEq/L</td>
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<td>0.026</td>
<td>0.033</td>
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<td>0.007</td>
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<td>0.000 (0.002–0.017)</td>
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<td>(0.010–2.290)</td>
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<td>HCO₃⁻</td>
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surface water (18 isotopically enriched peatland water samples from ponds and 5 shallow pore waters sampled in June–August); peatland groundwater (38 groundwater samples from wells and piezometers installed in peat, sampled during summer and fall); and bedrock and overburden groundwater (18 groundwater samples from DeBeers Victor Mine compliance groundwater monitoring piezometers 3 to 60 m deep installed in limestone and marine sediment). In addition, 3 samples with relatively high Cl content were projected onto the plot: WS15 (5-m-deep overburden piezometer located ~20 km southwest of the mine); NS8 (29.4-m-deep bedrock piezometer located ~3.5 km northwest of the mine); ES2 (15-m-deep bedrock piezometer located ~7 km east of the mine). Precipitation, surface water, and deep groundwater bound the stream data fairly well. The pore-water and surface-water end members plot close to each other. The peatland groundwater end member plots within the stream data cloud. Individual bedrock and overburden groundwater samples reveal large variability in deep groundwater chemistry; they plot far from the mixing space (NS8) or poorly bound the stream chemistry data (WS15) (Fig. 5).

In the mixing diagram of $\delta^{2}H$ versus Cl, the bedrock/overburden groundwater end member, represented by a median value, does not explain variability in Cl concentrations observed in the streams (Fig. 6). The large streams evolve toward bedrock groundwater rich in Cl and SO$_4$ from NS8. The water samples collected from ice-covered streams in February plot relatively close to NS8, suggesting that it is a good approximation of the contributing deep groundwater end member for large streams. Stations Trib 3, Trib 5A, and NR-001 had relatively low Cl content and do not exhibit any distinct trend toward NS8.

The relative contribution of the three end members—precipitation, surface water, and bedrock/overburden groundwater—is estimated from the mixing diagram of SC vs. $\delta^{2}H$ (Fig. 7). These tracers are selected to represent the two observed trends in the data based on the highest loadings. The mean end-member concentrations effectively bound the points defined by the stream water chemistry, particularly when the variability about the mean end-member concentrations is taken into consideration (Fig. 7).

Estimation of End-Member Contributions

Mass-balance calculations using Equations 1–3 were performed for selected end members using SC and $\delta^{2}H$ as tracers to determine seasonal contributions of each end member (Figs. 8 and 9). Infrequent stream sampling did not allow for continuous hydrograph separation. Instead, data were further aggregated into two groups reflecting two hydrological periods—wet and dry. The wet periods corresponded to high flows observed from April until mid-June, and from August until November. The dry periods included summer baseflow (mid-June to late-July) and February 2011 winter flow samples. The compartmentalization of flow data is supported by the results of the PCA, precipitation, discharge, and stream water chemistry data. The proportions of precipitation, surface water, and deep groundwater in

![Figure 5](https://bioone.org/journals/Arctic,-Antarctic,-and-Alpine-Research)
streamflow were estimated for each sampling date and averaged over the respective hydrologic period.

The results indicate seasonal changes in end-member contributions, as well as differences among the streams (Figs. 8 and 9). The proportion of groundwater was greater at the Nayshkootayaow River stations and station Trib 5: 17–20% during wet period and 33–45% during dry period. The proportions were slightly lower at station Trib 7 (12 and 30%, respectively), and the lowest at stations Trib 3 (10 and 20%) and Trib 5A (8 and 12%).

Surface water was a major source of water to the streams. For all streams other than Trib 5A, the stream chemical mixing models indicate that the relative contribution did not change significantly between the wet and dry periods. The surface-water end member provides 53–57% of water to the streams during high flows, and 52–67% during low flows. In contrast, the percentage is smaller at station Trib 5A, amounting to only around 40%.

Precipitation was a significant contributor to streamflow during wet periods, accounting for about 25% of flow in the Nayshkootayaow River, and slightly more in the tributaries. The maximum estimated contribution was almost 50% at station Trib 5A. The precipitation end-member contribution was significantly less (<10%) during dry season in most streams, except for stations Trib 3 (21%) and Trib 5A (42%).

The relationship between relative groundwater contribution and watershed area approximates a logarithmic trend (Fig. 10). The rate of change rapidly increases for stations Trib 5A, Trib 7, and Trib 5, and then levels out for the Nayshkootayaow River stations. Only Trib 3 with significantly lower proportion of groundwater stands out.

Discussion

CLIMATE AND STREAMFLOW

This study was conducted during an extremely dry year. The dry first half of the year resulted not only in relatively low spring and summer flows, but also in lower stream discharges later in the season compared to the previous years. Because of the extraordinary dry conditions, the results of the analysis might not be indicative of the average functioning of the hydrologic system, but instead, may be more generally relevant to future, drier climate scenarios.

WATER CHEMISTRY

Stream Water Chemistry

The observed spatial and temporal variations in stream water composition can be explained by varying contributions of sources of water and physical processes. Isotopic enrichment of the surface water throughout the summer due to evaporation was evident in the stream water isotope data, and decreases in stream-water solute concentrations with increases in flow were attributable to dilution by solute-depleted precipitation and surface waters.

River morphology was another factor controlling solute content in stream water. The channel of the Nayshkootayaow River in the lower reaches and tributaries Trib 5 and Trib 7 are down-cut into bedrock. Stream water chemistry at these stations exhibited elevated concentrations of Cl, SO4, and Na. The channels of the Nayshkootayaow River at NR-001, Trib 3, and Trib 5A sit in the organic layer on top of marine sediments and were characterized by lower concentrations of these solutes in stream water due to a dominance of surface water.

Surface Water and Groundwater Chemistry

Peatland and bedrock groundwater chemistry was highly variable. The sparse sampling network was insufficient to characterize what appears to be significant heterogeneity in groundwater chemical composition in the study basin.

The chemical composition of surface water and shallow peatland groundwater changed over time. Water in the ponds evolved from precipitation as the residence time increased. Solute content and SC were low in the beginning of the field season due to dilution by meltwater. As the summer progressed, the concentrations of major ions and DOC slightly increased, and variability in the peatland surface and pore water chemistry became more pronounced.

Peatland groundwater quality varies both with depth and peatland type. Peat pore-water chemistry is controlled by transport of solutes from the underlying calcareous mineral substrate (Reeve et al., 1996). An increase of solute concentrations with depth is a result of molecular diffusion and groundwater advection that distribute solutes up the peat column from underlying mineral
Price and Woo (1988) explained high concentrations of Na and Cl in peat by invoking relict salts from entrapped sea water in marine sediments. The only overburden groundwater sample with high concentrations of Na, Cl, and SO₄ (6.2, 1.1, and 0.5 mEq L⁻¹, respectively) was collected from the depth of 5 m at WS15. We assumed the groundwater chemistry was sufficiently invariant over the period of study to consider groundwater a static end member. The samples collected in 2010 agreed well with historical compliance monitoring data and the results of hydrogeological investigations from 1999 to 2003 that roughly defined two hydrogeological zones, representing the Upper (0 to 75 m) and Lower (75 to 220 m) Attawapiskat Formations (Canadian Environmental Assessment Agency, 2005). All bedrock groundwater samples collected in 2010 fall into the “shallow dilute waters with low Cl concentration” category presented in the aforementioned report (Canadian Environmental Assessment Agency, 2005).

A previous survey of deep groundwater in the Victor Mine area showed greater salinity (up to 100 mEq L⁻¹ of Cl) groundwater in the zone adjacent to the Nayshkootayaow River, suggesting advection and discharge of high-salinity groundwater to the river (DeBeers Canada, unpub. data). Most bedrock piezometers sampled in this study are installed in the bioherms, which are considered a zone of recharge of bedrock aquifer by surface water and peatland groundwater (Whittington and Price, 2012), and the depths of these piezometers are relatively shallow. This may explain low concentrations of Na, Cl and SO₄, as well as elevated DOC content. Bedrock groundwater with relatively high Cl and SO₄ concentrations was found in only one well sample (NS8) taken from the depth of 30 m.

The observed variability in isotopic enrichment of the potential water sources was the result of phase changes (evaporation/condensation) and water mixing. The isotopic composition of rainwater varied significantly between summer rain storms. Studies have shown that precipitation becomes isotopically heavier, and intrastorm variability can be especially large for high magnitude and duration rainfalls (Genereux and Hooper, 1998). Due to a limited number of rain water samples, we could not account for temporal variability in rain water chemistry; therefore, a median value is used to define the precipitation end member instead of a volume- or depth-weighted average. The bedrock aquifer is primarily recharged by precipitation and has an isotopic signature of local mean annual precipitation, which is supported by our data. The large seasonal variations in δ²H and δ¹⁸O values in surface waters are due to dilution with isotopically depleted precipitation water during snowmelt and storm events and evaporation (hence the enrichment).

**MIXING MODEL**

**PCA and End-Member Definition**

PCA has been widely used in hydrological studies to explore large datasets, summarize the relationships, and define controls on water chemistry (e.g., Worrall et al., 2003). However, there is some uncertainty associated with this approach. First, the results of the PCA depend on the size of the dataset. Generally, the larger the sample size, the more reliable the results of the PCA are. In this study, the total number of stream water samples was less than 160, with the number of samples for individual streams ranging between 13 (Trib 7) and 32 (Trib 5A), because sites were accessible by helicopter only. In comparison, studies of other more accessible watersheds used hundreds or thousands of water samples analyzed over several years of continuous observations (e.g., Hooper et al., 1990; James and Roulet, 2006).

With a relatively small number of samples for individual streams, the principal components could not be determined with confidence for each stream. To increase sample size and reliability of the correlations, the stream data were lumped and analyzed together.

![Mixing diagram of specific conductance (SC) vs. δ²H. End members are represented by median values with the error bars bracketing the range of reported concentrations for each end member.](https://bioone.org/journals/Arctic,-Antarctic,-and-Alpine-Research)
Examination of the structure of the principal components allows us to define the controls on stream water chemistry. The original variables highly correlated with the component reflect the nature of the principal components and emphasize the distinction from other components better than other variables.

The variables Mg, Cl, and SC have high loadings on PC1, suggesting they have the same origin. The main source of solutes to the system was bedrock. Upper bedrock formations consist of limestone, which was likely the source of Ca, while deeper formations contain dolomite, gypsum, and clays that are the source of other dissolution products. Strong correlation with major ions suggests that PC1 is responsible for the groundwater end member rich in Cl, SO4, and Na. PC2, on the other hand, is related to the isotopically enriched water with high content of organic matter, corresponding to peatland surface water inputs. Dissolved organic carbon has a lower loading than the isotopes of water in PC2, likely due to nonconservative behavior, despite the fact that other chemical mixing studies found DOC a useful indicator of shallow subsurface flow (e.g., Brown et al., 1999).

Based on the importance of the original variables in the structure of retained components, the end-members’ composition at stations Trib 3 and Trib 5A varies. The differences in composition between the streams can be attributed to their connection to the overburden and bedrock aquifers. While large streams are cut through to bedrock and are possibly directly fed by bedrock groundwater, the small tributaries have no direct connection to the deep groundwater aquifer.

The seasonality in the stream chemistry is seen as distinct trends along the two axes in the mixing space. In the plot of PC1 vs. PC2, stations Trib 5 and Trib 7 behave similarly to the downstream Nayshkootayaow stations, even though both tributaries are significantly smaller than the Nayshkootayaow River. The samples that are most evolved along the PC1 axis were collected in the driest summer period. As water contribution to the streams from the dry peatland dropped, the proportion of bedrock groundwater (and the scores on PC1) increase. Precipitation has a diluting effect on stream water and pulls the data points to the area of lower scores on both components. Low scores on both principal components are observed in the spring, when stream water is diluted with melt water. A shift from one cluster of points with low scores on PC1 to the other cluster with high (positive) scores on PC1 is a shift between the two distinct hydrological periods.

**Mixing Diagrams**

Specific conductivity (SC) and δ^2H selected are appropriate tracers for the mixing model as they strongly differentiate mineral-rich (SC) bedrock groundwater and isotopically enriched (δ^2H) surface water. Based on the results of the PCA and the mixing diagrams, the end members are precipitation, surface peatland water, and deep groundwater. The same sources have been identified in other mixing studies (e.g., Ogunkoya and Jenkins, 1993). In others, throughfall (Brown et al., 1999; James and Roulet, 2006)
and O-horizon soil water (Brown et al., 1999) end members have been found to be more applicable than precipitation and surface water. Moreover, several runoff generation studies observed mixing of two types of groundwater with different residence time (James and Roulet, 2006; Uhlenbrook et al., 2002; Uhlenbrook and Hoag, 2000). Clearly, end-member definition is context and basin specific and is dependent on catchment physiography and surface water–groundwater connectivity.

The precipitation and surface water end members sufficiently bound the stream water data, given the variability in our measurements. An even better fit might be achieved if we could better account for temporal and spatial variability in these end members. The chemistry of precipitation certainly varies over the season and within a melt or rain event (Taylor et al., 2002; Worrall et al., 2003). In this study location, there could even be a potential for marine-influenced air masses to deliver significantly higher concentrations of solutes (e.g., Cl, Na, Mg, SO4) in rain and snow than the continental systems that seemed to prevail during our measurements given the relatively low concentrations. In addition, the surface water quality would evolve over the year as well due to fresh precipitation inputs and evaporative effects on both solute concentrations and isotope fractionation. So, as with precipitation, all available pond and pore water samples from the summer and fall were considered together.

The chemical parameters that defined the end member for groundwater in the bedrock and overburden did not bound the stream water data well in the mixing diagrams, although there was a clear tendency in stream water chemistry of large streams toward the chemistry of the bedrock/overburden groundwater. The bedrock/overburden groundwater end member also has a different chemical composition between small and large streams. This difference can be attributed to the intersection of different stream channels with differing scales of groundwater systems (Töth, 1962), as well as inherent variability in the groundwater chemistry. Considering the large variations in size and geologic settings among the study catchments, the variability in groundwater flow path length and flow rates can be significant. Moreover, the extent of subsurface watersheds is harder to define than surface watersheds (Winter et al., 2003), especially in a low-gradient environment with a nonuniform geology, like the HBL.

**Estimation of End-Member Contributions**

In this study, we aggregate stream data into wet and dry periods that are clearly evident in the hydrographic record. The end-member contributions were estimated for these two periods. We do not attempt a continuous or a daily/monthly hydrograph separation because there are insufficient data to extrapolate the separation results and analyze individual events. The aggregation of data into these two periods affords a confident interpretation of differences.

The surface water end member is the dominant component during both wet and dry periods. Although the relative contribution of the surface water end member to streamflow does not change significantly between the periods, the absolute contribution of water from the peatland is significantly greater during the wet period due to high water tables and high hydrologic connectivity. This being said, the peatland is not hydrologically decoupled during lower flow periods (Richardson et al., 2012) and continues to influence stream chemistry despite lower volumetric contributions.

The large contribution of the precipitation end member during wet seasons is not unexpected. Overland runoff during snowmelt and spring rains, when the soil is still frozen, is a major contributor to water draining from peatlands (Winter, 2000). The proportion of precipitation during the drought period is negligible (except for station Trib 5A) compared to the overall uncertainty of the mixing analysis. Taking into account seasonal evolution of the surface water end member would result in changes in proportions of precipitation vs. surface water end member.

When the frost table is near the surface, or when the water table is close to the surface, a small rain event is enough for saturation overland flow (St Amour et al., 2005), which results in high precipitation and surface water contribution. During very wet periods the streams are connected to the peatland through overland flow and throughflow. During the dry season the water table draws down, and the dry peat absorbs most of the rainfall (Boudreau and Rouse, 1995). Worrall et al. (2003) suggested that runoff generation in a small upland peat catchment is driven by percolation excess and that it exists as shallow throughflow at the catotelm-acrotelm boundary, but because of the small storage capacity of the acrotelm the process could quickly turn into infiltration-excess.
The mixing model results confirm our hypothesis of an increase in deep groundwater contribution to the streams with an increase in catchment area. A downstream increase in deep groundwater input to the Nayshkootayaw River during both wet and dry seasons is an illustration of this pattern. Only station Trib 3 shows inconsistent behavior. Deep groundwater is a minor contributor of water to the streams (~20%) compared to surface runoff during wet periods but is comparable during dry seasons, providing ~40% of flow.

The results are consistent with observations in other regions. For example, groundwater was the most significant component of streamflow in wetland-dominated catchments in the Liard River basin, contributing 54-79% during the freshest, and on average 7% more than this during the baseflow. Surface waters from wetlands and lakes contributed to runoff during summer and fall, whereas snowmelt input through overland and shallow subsurface flow was important in the spring (St Amour et al., 2005).

Singer and Cheng (2002) separated the flow of the two upper tributaries of the Attawapiskat, the KAWingonas and Pineimuta, located in the Canadian Shield, into surface and baseflow components. The long-term groundwater contribution to the annual runoff of these rivers was 26.9% and 23.4%, respectively, with the maximum contribution occurring in May–July and the minimum in November–April. The authors conclude that groundwater recharge to the larger basins would be much smaller because of the low infiltration capacity of the materials, covering the watersheds. The same work reports the results of Wang and Chin (1978), who estimated groundwater discharge to the Attawapiskat and Albany Rivers of 8 and 27%, respectively, using the 95% exceedance probability levels on the flow duration curves (Singer and Cheng, 2002).

The mechanism of groundwater discharge to the small streams, such as Trib 5A, Trib 3, and NR-001 with the channel beds directly on top of the silt sediment, is not clear. The groundwater can be discharging directly into the streams through the low-conductivity overburden. In contrast, seeps may exist where the sediment material is coarse, or where the thickness of the overburden is small. Exposed and buried beach ridges consisting of coarser sediment could provide additional flow paths for groundwater (Canadian Environmental Assessment Agency, 2005).

Lateral flow through the peat may be another mechanism of groundwater discharge to the small streams. Rapid subsurface flow in peatlands can be provided by macrochannels, or pipes—the systems of connected macropores (Quinton, 1997). Woo and DiCenzo (1988) showed the importance of pipes, found along the banks of the streams and in marine sediment, in a coastal wetland of James Bay. Pipe flow varied with water table position and contributed 10% of stormflow.

There is scant evidence in the literature of a thin layer of sand at the peatland/overburden interface (Cowell, 1983). Although no sand deposits were observed on site in the peat cores, this layer could potentially transfer groundwater from the peatland to the streams and bioherms due to higher hydraulic conductivity. This groundwater would then become enriched in solutes from the contact with marine sediment.

A variety of factors need to be considered to understand the differences in streamflow generation in the study catchments. It has been shown that the distribution and organization of bogs and fen control flow pathways and water storage (e.g., Hayashi et al., 2004; Quinton and Roulet, 1998), vegetation cover affects energy balance (e.g., Boudreau and Rouse, 1995) and snow distribution (Woo and Young, 2006), and topographic gradient influences snowmelt response (St Amour et al., 2005). An overriding control on groundwater discharge to the streams is the surficial geology of the basin. For example, the relatively small Trib 7 joins the Nayshkootayaw River in the lower reaches, and thus its channel is incised in bedrock and receives saline bedrock groundwater similar to the large river.

Conclusion

In this study we present the first model of surface water and groundwater contributions to stream and river waters of the JBL. Through this work, we found that there was considerable spatial and temporal variability associated with the fraction of precipitation, and groundwater in particular. The relative proportions of these contributions are generally related to watershed size and stream order, which seem to generally control the degree of connection with underlying geology and need to be considered in the studies of runoff generation and water chemistry in this region. This is particularly salient when efforts are being made to define a “reference” catchment in this hydrologically diverse region.

Climate models predict a rise in temperatures and precipitation across the HBL, with most work suggesting that the increased precipitation will be more than offset by higher evapotranspiration, resulting in a generally drier environment. This will reduce water availability in the peatland and potentially decrease contributions from both precipitation and surface waters, thus lowering total flows and increasing the groundwater fraction.

These groundwater-dominated low flows are very sensitive to climate warming in northern regions, and increases in groundwater contribution have been used as an indicator of climate change (Smith et al., 2007). In addition, greater winter precipitation combined with winter thaws and an earlier snowmelt could also contribute to higher flows in winter and early spring and generally lower flows later in the spring/summer, as was observed in the relatively warm, dry year of this study. As such, the data presented here may foreshadow future hydrological regimes in this region.

Acknowledgments

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