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Analyzing peatland discharge to streams in an Alaskan watershed: An integration of end-member mixing analysis and a water balance approach

Michael B. Gracz [a,b,1], Mary F. Moffett [c], Donald I. Siegel [d], Paul H. Glaser [b,*]

[a] Conservation Biology Program, University of Minnesota, Saint Paul, MN 55108, United States
[b] Department of Earth Sciences, University of Minnesota, Minneapolis, MN 55455, United States
[c] Mid-Continent Ecology Division, United States Environmental Protection Agency, 6201 Congdon Blvd., Duluth, MN 55804, United States
[d] Department of Earth Sciences, 204 Heroy Geologic Laboratory, Syracuse University, Syracuse, NY 13244, United States

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S U M M A R Y

Peatlands are the dominant landscape element in many northern watersheds where they can have an important influence on the hydrology of streams. However, the capacity of peatlands to moderate stream flow during critical dry periods remains uncertain partly due to the difficulty of estimating discharge from extensive peat deposits. We therefore used two different approaches to quantify diffuse pore water contributions from peatlands to a creek within a small watershed in Southcentral Alaska. A sensitivity analysis of a water budget for a representative peatland within this watershed showed that a substantial surplus of pore water may remain available for subsequent discharge during a dry period after accounting for water losses to evapotranspiration. These findings were supported by end member mixing analysis (EMMA), which indicated that 55% of the stream flow during a dry period originated from the near-surface layers of peatlands within the watershed. Contributions from peatlands to stream flow in northern coastal regions may therefore provide an important buffer against the potentially harmful effects of changing climatic conditions on commercially important fish species.

1. Introduction

The IPCC (2013) predicts a global warming trend that began in the late 19th century will continue to warm northerly regions by as much as 2–6 °C by 2100. Rising air temperatures will probably perturb stream ecosystems particularly during droughts when low flow rates are less capable of buffering stream temperatures (Cowx et al., 1984; Jones and Petreman, 2013). In Southcentral Alaska, stream temperatures have already exceeded the threshold for spawning king salmon (*Oncorhynchus tshawytscha*) during the yearly dry season (Mauger, 2005), and this type of environmental stress may be pervasive elsewhere. Since dry-season flow is dependent on groundwater inputs from different landscape elements, identifying the relative contributions from different elements is critical to understanding stream ecology.

Peatlands cover approximately 25% of the land surface in northern regions above 45°N latitude but are especially prominent in coastal areas and continental lowlands (Kivinen and Pakarinen, 1981; Wieder et al., 2006; Rydin and Jeglum, 2006). Despite their abundance and the high water-holding capacity of peat (e.g. Clymo, 1983), the evidence for peatland contributions to stream flow remains equivocal. Two thirds of the studies reviewed by Bullock and Acreman (2003) concluded that wetlands are associated with reduced stream flow during dry seasons within a wide range of physiographic settings. Although these studies were largely based in Europe and North America they are supported by overwhelming evidence that evapotranspiration rates are higher in wetlands than in non-wetlands in the same watershed (Bullock and Acreman, 2003).

Other explanations for the relationship between peatlands and lower stream flows during dry seasons are (a) insufficient water storage in the relatively porous upper layers of peat deposits (Bay, 1969; Ingram, 1983; Evans et al., 1999) and (b) poor drainage related to the low hydraulic gradient and permeability of peat deposits (Boelter and Verry, 1977; Siegel, 1988a; Burt, 1995). In contrast, Panu (1988) reported higher dry-season flows in streams

* Corresponding author at: Department of Earth Sciences, 310 Pillsbury Drive, University of Minnesota, Minneapolis, MN 55455, United States.

E-mail addresses: gracz016@umn.edu (M.B. Gracz), moffett.mary@epa.gov (M.F. Moffett), dsiegel@syr.edu (D.I. Siegel), glase001@umn.edu (P.H. Glaser).

[1] Present address: Kenai Watershed Forum, Box 15301, Fritz Creek, AK 99603, United States.

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from Newfoundland in which the watersheds contained a high cover of relatively pristine peatlands. Other studies of peatlands in paired watersheds from Minnesota, Great Britain, and Sweden associate a high cover of peatlands with relatively high stream flows during droughts (Ackroyd et al., 1967; Newson, 1980; Brandesten, 1988).

One reason for the absence of a consensus among these studies may be the varied hydrogeologic settings of the peatland watersheds (Siegel, 1988a; Johansson and Seuna, 1994; Burt, 1995; Spence and Woo, 2006). Boelter and Verry (1977), for example, suggest that while flow may be straightforward to quantify from peatlands in small depressions that have a single outlet, these small peatlands may be poor contributors to streamflow because they lack sufficient storage or comprise only a small portion of a watershed. In contrast, a more common setting for peatlands in many boreal watersheds are broad lowlands overlying gently sloping deposits of glacio-lacustrine sediment or glacial till (Gore, 1983; Rydin and Jeglum, 2006). The extensive peatlands that spread over these deposits commonly lack well-defined outlet streams and may only produce diffuse discharge from pore waters.

Quantifying peatland contributions to streamflow presents an array of challenges. Studies based solely on water budgets are prone to compounding measurement and estimation errors particularly when terms are calculated as residuals (Winter, 1981). Although advances in instrumentation have permitted more precise estimates of ET using tower based instruments (e.g. energy balance and eddy covariance) sources of error still remain (e.g. Twine et al., 2000; Wilson et al., 2002; Drexler et al., 2004). Holden et al. (2004) therefore identified a need for process-based investigations to understand the dynamics of peatland contributions to stream flow. An alternative approach is provided by end member mixing analysis (EMMA), which has been used to assess end-member contributions to event flows in a range of watersheds (Christophersen et al., 1990; Christophersen and Hooper, 1992; Hooper et al., 1990; Liu et al., 2008). EMMA uses the chemical signature of water originating from potential end-members within a watershed to determine the percent that each contributes to a final mixture. We therefore compared an end member mixing analysis with a water budget approach to quantify peatland-stream interactions in a small watershed from Southcentral Alaska. This watershed is typical of many in Southcentral Alaska and serves as a useful template to characterize the climatic sensitivity of these ecologically important streams, which provide spawning habitat for salmon.

2. Study region

The 1516 ha Limpopo Creek watershed lies in the Cook Inlet Basin of Southcentral Alaska. The two tributaries of this 17.3 km-long creek flow down a gradient of 5–7% from their headwaters near tree line at an elevation of 250 m through alder (*Alnus viridis* (Chaix) DC.) and open meadows overlying weakly-lithified sedimentary deposits. The tributaries then flow at a gradient of 1–2% through a landscape of lutz spruce forest (*Picea* X *lutzii* Little) and peatlands that developed on glacial deposits. The tributaries eventually join about 2.4 km above the creek's confluence with the Anchor River. Both tributaries are confined to a single channel along most of their length except for a reach of a few hundred meters where the northern tributary anastomoses as unchannelized flow over peat (Fig. 1). Peatlands cover about 22% of the watershed and consist of fens or poor fens supporting either a lutz spruce woodland, or non-forested assemblages dominated by ericaceous shrubs and sedges interspersed with pools.

The upper third of the watershed generally lacks glacial deposits, and is primarily underlain by alluvial sedimentary deposits, carbonaceous shale, and lignite beds of the thick Sterling Formation (Flores et al., 1997). These deposits were eroded from the surrounding mountains that support diverse rock lithologies, including: sandstone, arkose, argillite, greywacke, slate, granodiorite, breccia, and intermediate-to-felsic volcanic rocks (Beikman, 1994). The lower watershed is underlain by glacio-lacustrine and poorly-sorted till deposits of the last glacial advances (Reger et al., 2007; Petrik, 1993). Peatlands are primarily restricted to these low-permeability, surficial materials. In addition, the entire watershed has frequently been blanketed by volcanic ash for at least 10.5 ma (Fournelle et al., 1994). Ash deposition has created tephra layers whose composition ranges from high-silica andesite through low-silica dacite to calc-alkaline glass (Riehle, 1985). Mineral soils are generally entisols where wet, and andisols and humicryods where mesic to well-drained (Van Patten, 2005). Two gravel roads cross the watershed, which is inhabited by fewer than a dozen families.

The cool temperate climate of the watershed is moderated by its proximity to the Gulf of Alaska. Annual precipitation averages 625 mm at the nearest station with a long record (Homer), although a station near the headwaters of the Limpopo watershed reports an average of 748 mm (Utah Climate Center, 2013). More than half of the precipitation falls late in the year (August–December), whereas less than 20% falls during the yearly dry-period (April–July). Average annual temperature is 3.1 °C, and the average July maximum is 16.0 °C. The ratio of precipitation to potential evapotranspiration is 1.27 by the Thornthwaite method.

3. Methods

Two independent methods were used to estimate peatland contributions to streamflow in the Limpopo watershed during dry periods in order to assess the reliability of their results. Water budget surpluses were first calculated for a representative peatland within this watershed using a sensitivity analysis and these results were then compared to EMMA calculations. The water budget was based on the drawdown of an observation well within this peatland during a well-defined dry period, whereas the EMMA provides a snapshot of geochemical mixing of end-members in the stream during conditions of low flow.

3.1. Water budget

Stream flow was measured three times in Limpopo Creek in order to compare these values with the results of a water budget for a shrub-dominated peatland during a dry season. The first measurement was made on July 13, 2010 at the end of the normal-summer dry period and two days prior to the stream sampling for water chemistry. Flow was re-measured a week later on July 22 following a storm, and also on September 23, 2010, at the end of an unseasonable late-summer dry period. Measurements were made with a Pygmy current meter along a 14-point transect across the 3 meter-wide channel 400 m above the confluence with the Anchor River.

To evaluate changes in peatland water storage during a dry period, an observation well was installed to a depth of 98 cm just above the base of a representative peatland in the watershed and instrumented with a U20-series water-level logger in 2005 (Fig. 1). The observation well was calibrated upon installation and changes in barometric pressure were compensated for by an additional logger suspended in the wellhead. The drawdown of water levels in this well during the longest rainless period (August 5–12, 2005) of the study was used to estimate the quantity of water potentially available for streamflow using the following water budget:

$$Q = P + GW_i - GW_o + SW_i \pm \Delta S - ET \tag{1}$$

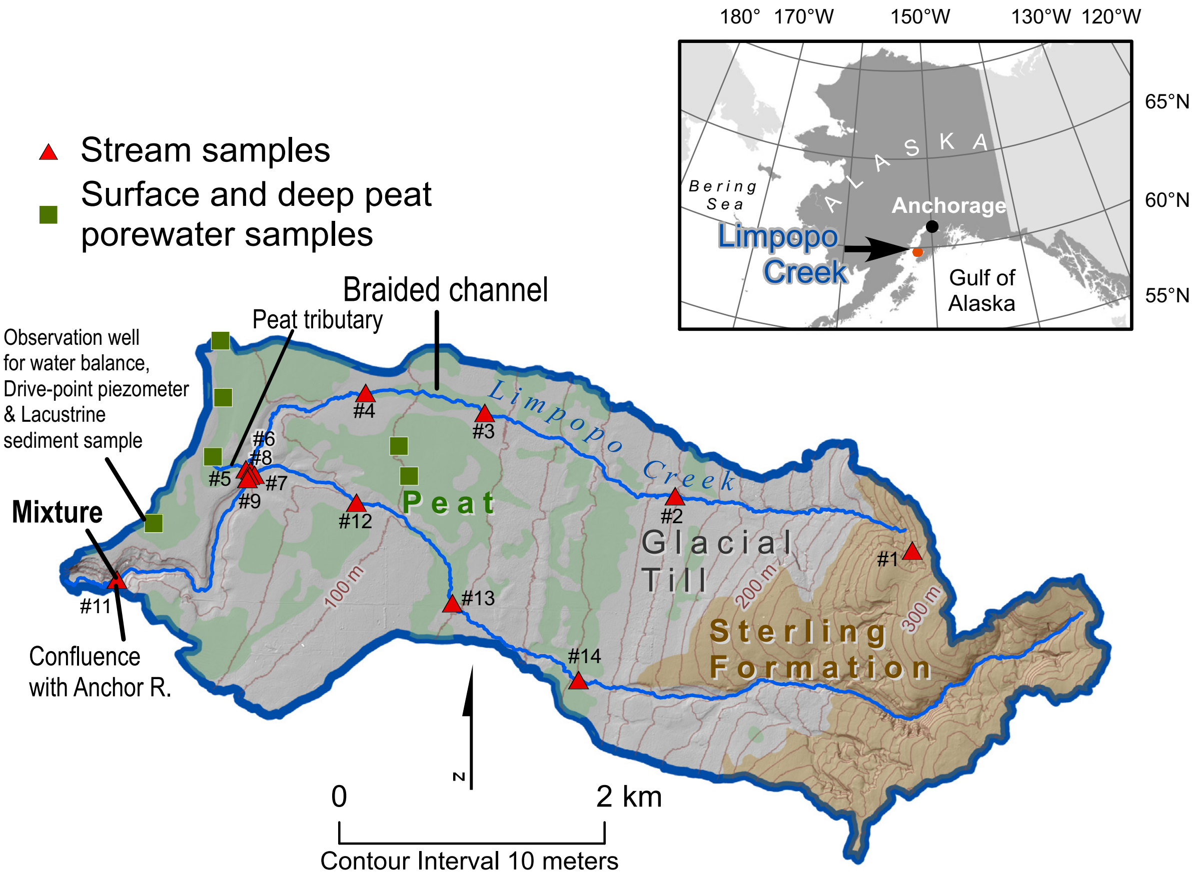

Fig. 1. The Limpopo Creek Watershed in Southcentral Alaska. The steeper eastern third of the watershed is underlain by the Sterling Formation (tan), whereas the western two-thirds is composed of glacial till (gray) and lacustrine deposits overlain by peatlands (green). Sample locations are numbered and marked by triangles for stream samples and squares for EMMA end-members. The northern tributary of Limpopo Creek flows as a braided channel across peat where indicated.

where Q is discharge from peatland porewater, P is precipitation, GW_i is input from deeper groundwater, GW_o is output to deeper groundwater, SW_i is surface water input, ΔS is the change in storage, and ET is evapotranspiration. All the components of Eq. (1) are considered in units of $m^3\,s^{-1}$ to facilitate the comparison to actual flows measured in Limpopo Creek. P was set to 0 for calculating the peatland water budget during a dry period marked by no precipitation. We assumed that $GW_i = GW_o$ and $SW_i = 0$. These assumptions are reasonable given: the topographically high setting of the peatland, the low permeability of the underlying lacustrine sediments, the absence of streams flowing into or out of this peatland, and the form of the water level hydrograph during the dry period, which suggested only discharge from porewater (Laine, 1984). The hydrograph indicates a steeper decline during the day than at night (Fig. 2). Eq. (1) thus simplifies to:

$$Q = \Delta S - \mathrm{ET} \quad (2)$$

The effect of ET on storage was estimated by two methods. First, the Thornthwaite method (Thornthwaite, 1948) was calculated using an MS Excel spreadsheet (Lehre, 1994). The Thornthwaite method has been widely used as a complementary method to estimate Potential Evapotranspiration (PET) from peatlands in both Europe and North America (e.g. Bay, 1968; Ingram, 1983; Bridgham et al., 1999; Brooks et al., 2011). Although this method tends to overestimate PET at upland sites (e.g. Shaw and Riha, 2011) by not considering the effects of changing vegetation, soil, or hydrogeologic setting, PET may still provide a reasonable estimate for peatlands, in which the peat mass moderates water table fluctuations. To calculate fluxes by this method (Eq. (2)), the

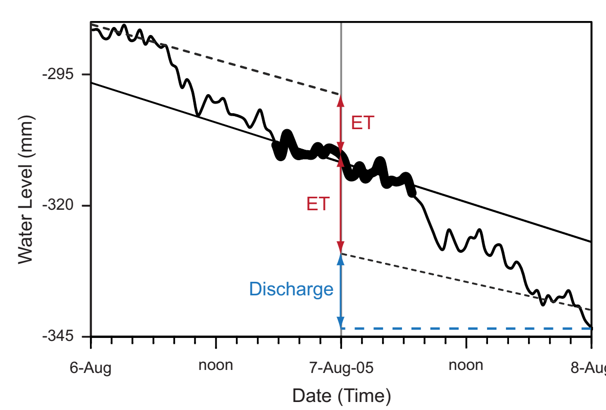

Fig. 2. Estimation of ET using the diurnal variation of a declining water-level hydrograph in the absence of recharge. Linear regressions (straight sloping lines) are fitted to the slower rate of decline during the evening and morning when only discharge is active (thicker black line crossing at midnight on day 2) and then extended to predict the water level at midnight on both the previous and following day. The average difference between the predicted water level and the actual water level is attributed to ET (red arrows), which is multiplied by S_y to obtain the actual amount available for discharge (blue arrows). The partial regression lines from day 1 and day 3 are also shown (dotted sloping lines). Data shown are from the observation well between 6 and 8 August 2005. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

change in water level is first multiplied by specific yield (S_y) after accounting for recharge (White, 1932; Laine, 1984; Mitsch and Gosselink, 2007). S_y is the proportion of water in a saturated soil column that freely drains between 0 and ∼−0.1 atm (Freeze and Cherry, 1979). This method of calculation produces a reliable estimate for the proportion of drawdown that is actually available in wetlands where water levels are close to the surface, or where recharge is sufficient to raise the water level each night. However, because the water level was falling steadily from deeper in the peat profile in the absence of recharge, a significant amount of vadose water (stored between field capacity and the wilting point) is available to meet ET demands. It is possible that all of the ET demand could be supplied from the vadose zone as it is for plants in non-wetland ecosystems (White, 1932). In recognition of this possibility, ET was subtracted from the total drawdown (accounting for porosity) before multiplying by S_y. In order to obtain the flow produced by similar peatlands in the Limpopo watershed the following equation was used:

$$Q = ((\Phi \Delta W) - \mathrm{ET}) S_y A t^{-1} \quad (3)$$

where Φ is porosity (dimensionless proportion), ΔW is the water level decline (m), ET is evapotranspiration (m), S_y is a dimensionless proportion, A is the area of similar peatlands in the watershed (m^2), t is the time period of water level decline (s), and Q is in $m^3\,s^{-1}$.

The second method uses the diurnal pattern in the water table hydrograph to estimate the portion of ΔS due to ET. During the dry period, the hydrograph from the well was characterized by a lower slope at night that steepened during the day. The slopes differ because only discharge is assumed to be active at night, while both ET and discharge occur during the day. To quantify the difference, the nighttime drawdown rate is projected by linear regression to midnight on the following and preceding days. The average difference between the actual water level at midnight and the level predicted by the regression (multiplied by S_y) is attributed to ET (Fig. 2). The two estimates for each day are averaged to account for an inconstant rate of drawdown (Laine, 1984).

We evaluated the sensitivity of Q in Eq. (3) by varying ET, S_y, and Φ. For the Thornthwaite method S_y was set to 0.05, 0.14, 0.25, and 0.45 with porosity equal to both 0.8 and 0.9 while Q was allowed to vary. We then set Q equal to 0 and allowed porosity to vary to estimate the porosity value necessary for the total measured decline in the water level to be due to Thornthwaite Potential Evapotranspiration (PET). We then set Q equal to 0.06 and porosity to 0.8 (following Boelter, 1972) to determine the value for S_y that would produce all of the lowest flow measured in Limpopo Creek. For the diurnal method we set S_y = 0.05, 0.1, 0.14, and 0.45 and allowed Q to vary. We then set Q = 0.06 and 0.03 to determine if a reasonable value for S_y could produce all or half the lowest streamflow measured in the creek.

3.2. Antecedent moisture

Antecedent moisture conditions were evaluated by installing a shallow drive-point piezometer near the observation well from 16 June until 9 October 2010. The shallow drive-point piezometer was installed at depth of 30 cm and instrumented with a water-level logger as above except that it was calibrated monthly against an arbitrary datum driven into the underlying lacustrine sediments. The elevation of the datum was estimated from 1.23-m resolution bare-earth LiDAR data collected in 2009.

3.3. EMMA sampling

Water samples were collected from Limpopo Creek for the EMMA snapshot on July 15, 2010 at 12 points distributed downgradient from the headwaters to just above the confluence with the Anchor River where the streamflow was measured. This date was selected as the most likely time to sample the lowest stream flow of the summer based on observations from past years. The extreme–downstream sampling point was located just above the confluence with the Anchor River and represented the final mixture in the EMMA. On the same day, surface water samples were collected from other potential end-members. These samples were collected from (a) near the headwaters of the stream where only groundwater from the Sterling Formation could contribute to stream flow, (b) a spring originating in the glacial till just above the creek, and (c) a short rivulet originating from within a peatland. During July and August in 2010, samples were also collected from two additional end-members (the deep peat and the glaciolacustrine sediment) from seven piezometers installed in the watershed (Fig. 1). The peatland piezometers were installed near the base of the peat profile (at depths of 98–210 cm) or into the underlying lacustrine sediment (140 cm). Pointed inserts facilitated pounding the piezometers to depth (Chason and Siegel, 1986). All piezometers were bailed until they produced clear water and then were left to equilibrate overnight before being sampled the next day. The piezometer in the lacustrine sediment required five days of equilibration to produce an adequate sample volume. Water from an additional end-member, the peat surface, was also collected near the piezometers. All samples were filtered through a 0.45μ capsule filter using a peristaltic pump and kept cool until analysis.

Samples were analyzed for $\delta^{18}O$ vs. VSMOW at the Stable Isotope Laboratory at University of Alaska, Anchorage (UAA) using a Picarro L-1102i WS-CRDS analyzer. The samples were then acidified and analyzed on an Agilent inductively-coupled plasma mass-spectrometer at the Applied Science Engineering & Technology lab at UAA for cation concentrations. Samples collected in separate bottles were analyzed at the Mid-Continent Ecology Division lab of the United States Environmental Protection Agency (EPA) for chloride and sulfate using EPA method 300.0 with NaOH eluent on a Dionex-DX-600 ion chromatograph using Chromeleon v6.6 software.

3.4. EMMA calculations

EMMA was used to estimate the percent contribution from each end-member to the ultimate geochemical mixture at the mouth of the stream. An end-member is defined as the waters originating from a discrete watershed element, which ideally could be distinguished by a distinct geochemical signature (Fig. 1). Samples collected along the length of the creek would be expected to show the shifting chemistry of the stream in response to inputs from different end-members. In EMMA, the shifting chemistry of the stream samples is analyzed by Principal Components Analysis (PCA) to determine the appropriate tracers, the concentrations of which are used to project stream sample points onto PCA axes. Residual analysis guides the evaluation of conservative mixing and the number of principal components identifies the number of end-members responsible for the variance in the chemistry of the stream samples. The contributing end-members are identified by plotting end-members and stream samples on a mixing diagram using the prediction equation for the stream samples. Percent contribution is then solved for each contributing end-member by using matrix algebra to solve the simultaneous equations of complex mixing. The conceptual model was that water originating in the Sterling Formation at the headwaters mixed with other end-members to form the final mixture in the sample collected near the confluence with the Anchor River.

A series of centered PCAs were performed on the correlation matrix of stream samples (rows) by tracer concentrations (columns), in the software PC-ORD™ 6 (McCune and Mefford, 2011) to find the combination of tracers that explained the most variance in the stream samples with the fewest principal components.

Residual plots (which are in units of concentration) were examined for non-linearity and deviation from errors greater than laboratory detection limits, both of which are diagnostic of non-conservative mixing (Hooper, 2003).

Once the criteria in the residual analysis were satisfied, the mixing diagram was constructed. On an adequate mixing diagram, the points representing the end-members should define a convex mixing space that completely encloses the stream sample points. Missing end-members are indicated if any stream values lay far outside the mixing space (Hooper, 2003). After an adequate mixing space was defined, the percentage contribution of each end-member to the mixture was calculated by post-multiplying the inverse matrix of PCA scores for the end-members by the column vector of the mixture scores:

$$\mathbf{S_e^{-1} S_m} = \mathbf{f_e} \tag{4}$$

where $\mathbf{S_e}$ is the 3 × 1 matrix of principal component scores (rows) for each end-member (columns), with the first row vector consisting of 1 s (ones); $\mathbf{S_m}$ is the 1 × 3 matrix (column vector) of mixture scores, with the first row element = 1; and $\mathbf{f_e}$ is the 1 × 3 vector of the fractional contribution of each end-member (multiplied by 100 to obtain percentages). Values of unity were used in the first row of each matrix to force 100% contribution from the end-members (Hooper et al., 1990; Liu et al., 2008). For comparison with the values for peatland discharge produced in the water budget analysis, the percentage contribution from peatland end-member (s) was multiplied by the flow measured in the creek two days prior to EMMA sampling.

4. Results

4.1. Water budget

The peatland observation well provided an estimate for water losses driven by ET in the dry year of 2005. From August 5–12, 2005 the water level in the well fell by 228 mm, from a depth of 256 to 484 mm. Total Thornthwaite PET was estimated at 29.29 mm for this eight-day period. Using this Thornthwaite estimate, contributions from peatlands to Limpopo Creek varied widely when different values for S_y were used, whereas different values for Φ had a smaller effect (Fig. 3). The lowest values for S_y (0.05) and Φ (0.8) presented by Eggelsmann (1971) (as cited by Ingram, 1983 and Siegel, 1988a) produced a surplus equal to 48% of the lowest stream flow measured in the creek. When the highest values for S_y (0.45) and Φ (0.9), reported by Boelter (1972) were used, the surplus equaled approximately two times the highest flow measured in the creek. An unrealistically low Φ (0.131) was required for the Thornthwaite PET method to explain all of the drawdown observed in the peatland well in August, 2005. However, sufficient surplus remained to support all of the lowest flow measured in Limpopo Creek when $\Phi = 0.8$ and $S_y = 0.10$.

Using the diurnal method for ET estimation, a higher value for S_y was needed to produce the same flow as the Thornthwaite method (Fig. 3). When S_y is equal to 0.132, all of the lowest stream flow (0.06 $m^3\ s^{-1}$) could be produced, and with S_y equal to 0.066 about half of the low flow could be produced. The diurnal method could not attribute all of the observed drawdown to ET alone, however, because discharge was evident at night, in the presumed absence of ET (Fig. 2).

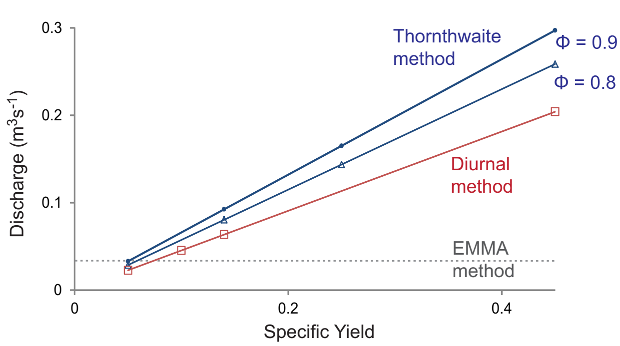

Fig. 3. Sensitivity analysis of the water surplus (Q) in the Limpopo peatlands that is available for stream flow. The uppermost two lines (blue) show surplus calculated with the Thornthwaite method using different estimates of porosity (Φ). The lower line (red) shows the amount calculated using the diurnal method, which does not depend on porosity. For comparison, the lower horizontal dashed line shows the amount of streamflow predicted by the EMMA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.2. Stream flow and antecedent moisture

The lowest flow in the creek (0.06 $m^3\ s^{-1}$) was measured at the beginning of a minor rain event on July 13, 2010 that appeared to have little effect on stream flow by the time of the EMMA sampling, on July 15, 2010 (Fig. 4). The highest flow (0.144 $m^3\ s^{-1}$) was measured a week later on July 22 following a rain event that was observed to produce even greater rainfall at the creek than at the nearby Homer climate station. Another low flow (0.07 $m^3\ s^{-1}$) was measured near the end of an unseasonably long dry-period (23 September 2010).

4.3. EMMA

The final PCA in the EMMA used five tracers (^{18}O, SO_4^{2-}, K, Ni, and Ba) to explain 95.8% of the variance with two principal components. Plots of the residuals revealed random errors that were smaller in magnitude than laboratory detection limits, supporting the assumption that the tracers mixed conservatively (Fig. 5). Because two principal components were retained, a model with three end-members is required to solve the mixing equation (Eq. (4)). The three end-members that enclose the mixing space were waters from the Sterling Formation, the surface peat, and the glacial till. These end members enclose all the water samples with the exception of two stream samples that lie somewhat outside the mixing space (Fig. 6). However, the shape of the convex mixing space (Renner, 1993) is affected by sampling and lab errors (Christophersen and Hooper, 1992). As a result it would be reasonable to assume that all of the points lie within a suitably convex mixing space, although we consider the effects on the analysis if two of the points (#4 and #6) in Fig. 6 were to lie outside of it. In addition, the coordinates of samples representing potential end-members from the deep peat (−10.9, 5.8) and the lacustrine sediments (113.6, 76.5) plotted far from the stream values.

The EMMA calculations show that the end member represented by the peat surface contributed 54.7% to the composition of the final mixture, the Sterling Formation contributed 40.8% and the glacial till contributed 4.5%. In contrast, the potential contributing volume of peatlands comprises 0.5% of the watershed, whereas the potential contributing volume of the Sterling Formation is 35%, and the till 65%. Contributing volumes are defined as the volume of each potential end-member within a 3D conceptual model of the watershed. The volumes were determined by multiplying the surface area of each end-member by its depth relative to the level of the Limpopo Creek outlet, which is the lowest point in the watershed. The percentage contribution from the peatland surface multiplied by the flow in the stream two days before the EMMA sampling gives a value of 0.03 m^3s^{-1}, which equals the estimate produced by the diurnal water budget when S_y equals 0.072 (Fig. 3).

5. Discussion

Peatlands are typically confined to topographic depressions or poorly-drained lowlands where saturated soils favor the accumulation of organic matter (Rydin and Jeglum, 2006). However, in northern maritime regions peatlands have also spread over sloping terrain creating many challenges for quantifying peatland contributions to streams that may be important for spawning fish populations. These sloping peatlands usually lack a well-defined discharge point that can be monitored for hydrological responses to climatic fluctuations. The peatlands in Limpopo Creek watershed, for example, lack visible outlet pipes that characterize the blanket bogs of the British Isles (Gilman and Newson, 1980; Holden and Burt, 2002; Evans and Warburton, 2007) and similar peatlands in the Maritime provinces of Canada (Glaser and Janssens, 1986). In addition, an extensive peat cover obscures the underlying topography of the mineral substratum that can be responsible for routing subsurface runoff into discrete discharge zones (Allan and Roulet, 1994). In these complex settings end-member mixing analysis provides an alternate means to estimate peatland contributions to stream flow. This approach appears to be well suited to the Limpopo Creek watershed, which is composed of five principal watershed elements, which are distinguishable on the basis of the chemical composition of their waters. The results of the mixing analysis can then be compared to a sensitivity analysis of a water budget in order to independently assess the potential of peatland storage to contribute to stream flow during dry periods.

Estimates from the sensitivity analysis of the water budget indicate that evapotranspiration is sufficiently low and storage capacity and yield is sufficiently high for peatlands to support approximately half the flow measured in Limpopo Creek during dry periods. For example, if streamflow during the EMMA sampling was set to 0.06 $m^3\,s^{-1}$, then S_y would need to equal 0.072 (diurnal method) or 0.057 or 0.049 (Thornthwatie method) for the water budget to produce an equivalent flow (Fig. 3). These estimates of S_y generally agree with Ingram's (1983) suggestion for using Eggelsmann's (1971) values of between 0.03 and 0.10. However, they are lower than the range of values (0.26–0.125) that Letts et al. (2000) applied for more humidified layers of peat. Although these findings are supported by studies of paired-watersheds from other regions (Ackroyd et al., 1967; Newson, 1980; Brandesten, 1988; Panu, 1988), they differ from the conclusions of Bullock and Acreman (2003) that peatlands have minimal effect on flow during dry periods. The contrast between these concepts of peatland-stream interaction may be due to differences in methodology, hydrogeologic setting, or antecedent conditions.

5.1. Differences in methodology

EMMA provides an alternative approach for estimating contributions to streamflow from different landscape components that avoids the sources of error related to a water budget approach such as the estimation of recharge, ET, and groundwater flow. Mixing analysis should yield a reliable estimate of peatland contributions to stream flow so long as four fundamental assumptions are met: (1) distinct composition; (2) hydrologic feasibility; (3) conservative mixing; (4) fixed composition.

The first two assumptions are satisfied because the composition of the end member is sufficiently distinct in the Limpopo watershed to bound the stream samples on the mixing diagram and the mixing diagram reproduces the down-gradient locations of the sample points along the stream tributaries showing that mixing is hydrologically feasible (Fig. 6). The third assumption is at least partially satisfied because three of the five tracers (barium, nickel, and $\delta^{18}O$) should mix conservatively at the concentrations measured. Barium and nickel will not form precipitates at the observed concentrations (Stumm and Morgan, 1996; Snodgrass, 1980). Complexation of these two elements with larger organic molecules is possible but was not likely to be a major control because their respective stability constants differ by orders of magnitude (Stumm and Morgan, 1996) yet their concentrations behaved similarly in the stream (Fig. 5). Complexes with smaller organic molecules and with inorganic ligands would have remained soluble. Furthermore, since kinetic considerations favor the formation of Ba and Ni complexes at much higher rates than their dissociation, any complexes should have formed rapidly near the headwaters, where the concentrations of these two elements was highest, with little effect on mixing further downstream. The stable oxygen isotope (^{18}O) is not fractionated during transpiration (Clark and Fritz, 1997). However, the other two tracers (potassium and sulfate) may mix non-conservatively. Potassium is an essential nutrient for plants and other organisms, whereas sulfur can degas as hydrogen sulfide under anaerobic conditions. The fourth assumption of fixed composition may have been violated by the

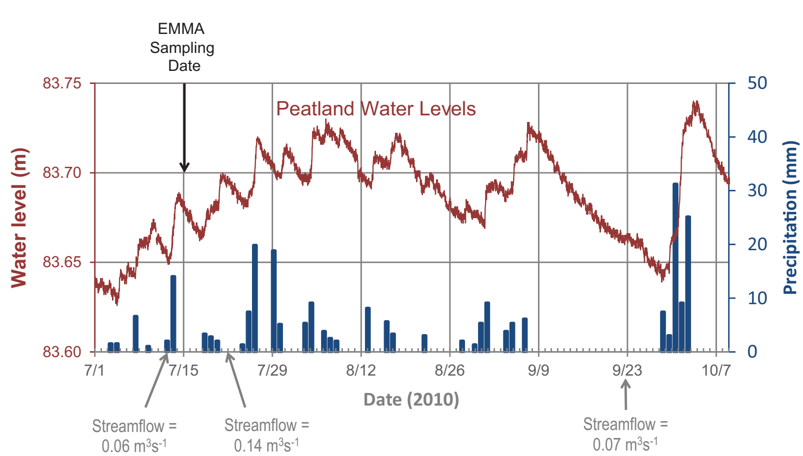

Fig. 4. Peatland hydrograph from the Limpopo watershed with respect to other measurements from 2010. Peatland water levels recorded in the shallow drive-point piezometer (red line) are compared to precipitation (blue bars), stream flow and sample times (gray arrows); and the EMMA sampling period (black arrow). The precipitation data are from the Homer Airport, 20 km to the southeast. The peat surface elevation was 83.73 m according to a LiDAR survey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

end-member represented by the pore waters at the peat surface. Therefore, only the non-fixed composition of the peatland end-member and the potential non-conservative mixing of potassium and sulfate may depart from the fundamental assumptions of mixing analysis. Below, we consider the effects that these departures may have had on the EMMA calculations.

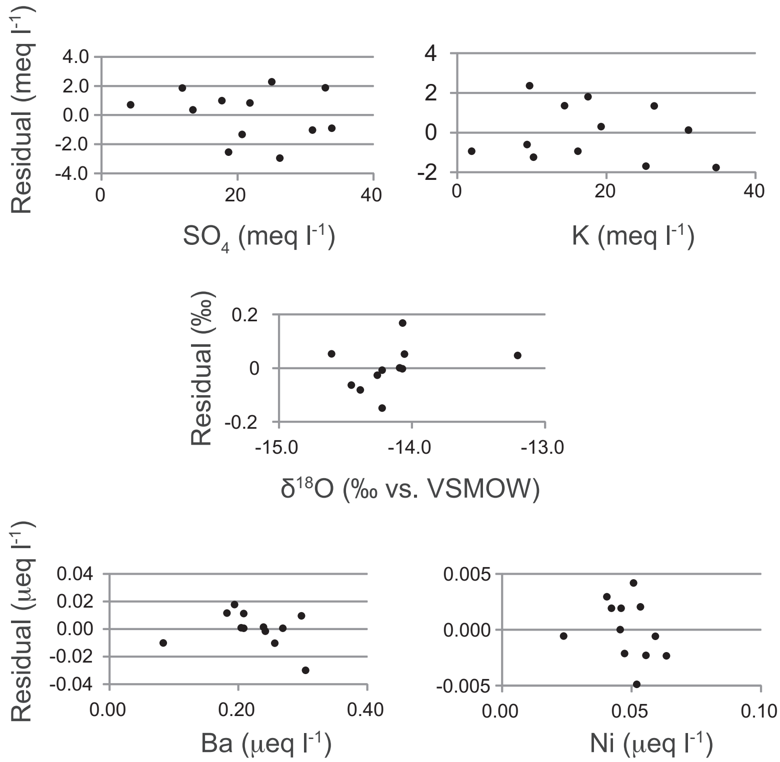

Fig. 5. Residual plots of observed versus predicted concentration values for the tracers used in the EMMA. The absence of pattern and the low values of the residuals (within the detection limits of the laboratory analyses) is an indication of conservative mixing.

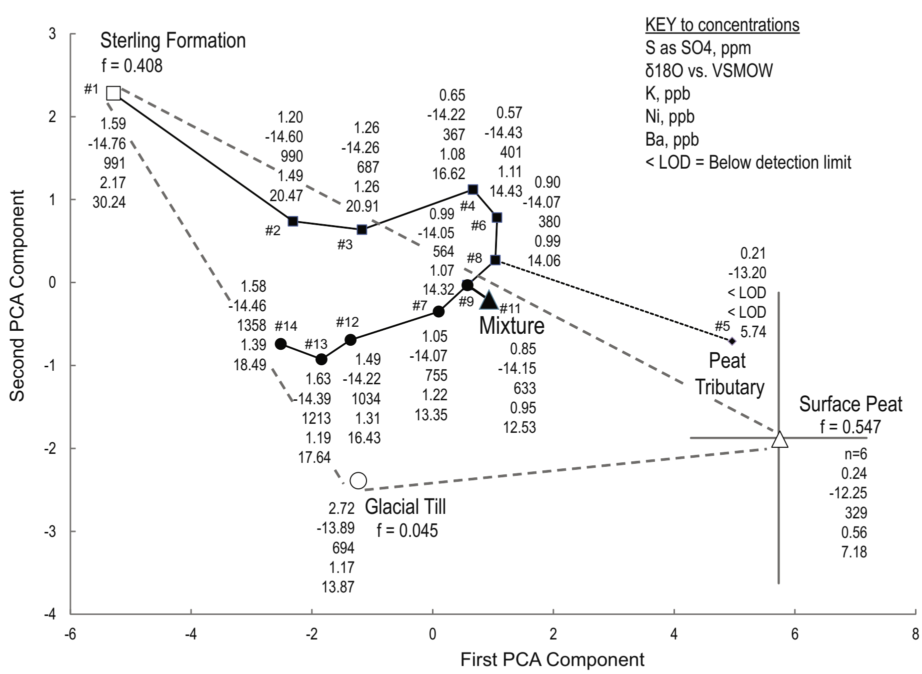

Fig. 6. EMMA mixing diagram from the Limpopo watershed on July 15, 2010. A convex mixing space (approximated by the dashed lines) is defined by three end-members (hollow squares) enclosing stream samples (solid squares), which are numbered according to their location along Limpopo Creek (Fig. 1) and connected in downstream order. Concentrations of the tracers at each point are given in the order shown in the key. The point labeled "peat tributary" represents a sample taken from a small tributary flowing into the creek from a peatland just above the confluence of the two tributaries. The peat surface end-member is depicted with one standard deviation in its projected values (large cross). The *f*-value listed under each end-member is the fractional proportion that the end-member contributed to the final mixture located at the mouth of the stream. The EMMA samples were collected toward the end of the early-season dry period.

Potassium was apparently present at concentrations that exceeded the limiting values in local ecosystems, which are limited by nitrogen and/or phosphorus (Shaftel et al., 2012). Furthermore, when potassium is excluded from the EMMA analysis, there was little change in the final proportions of contributing end-members (Sterling Formation 44%, surface peat 57%, till 0%). The small amount of uptake of potassium compared to its concentration likely did not measurably affect the EMMA.

Eliminating sulfate as a tracer in the EMMA also produces little change in the contributing proportions from the original end-members (Sterling Formation 42%, surface peat 58%, till 0%). Non-conservative mixing could only be a problem with sulfate if it excluded the two end-members that were sampled under anaerobic conditions (glacial-lacustrine sediment and deep peat). However, the concentrations of other tracers in the lacustrine sediment and deep peat were incompatible with the composition of the final mixture. With respect to the lacustrine sediment end-member, $\delta^{18}O$ was substantially more depleted (−15.98‰) and the concentration of barium was higher (373 ppb) than that of samples from both the headwaters (−14.76‰ and 30.2 ppb respectively) and the final mixture (−14.15‰ and 7.2 ppb respectively). In the deep peat porewater, the barium concentration was also too high (47.8 ppb) for this end-member to be a significant contributor to the stream due to the excessive dilution that would be required from other end-members. Non-conservative mixing from the anaerobic samples likely did not affect the EMMA.

Two sample points lying outside of the mixing space suggest that the peatland end-member may not be of fixed composition (Fig. 6). Points lying outside of the convex mixing space (e.g. points #4 and #6 in Fig. 6) indicate that additional end-members may be unaccounted for in an EMMA (Hooper, 2003). On the Limpopo mixing diagram, however, a small shift in the coordinates of the peatland end-member within one standard deviation of its range of variability (e.g. to the coordinates of the peat tributary) could create a triangular space encompassing all of the stream samples (Fig. 6). Alternatively, the range of variation of the peat surface water might indicate that it is actually composed of two different end-members, e.g. fens and poor fens. Splitting the peatland end-member might produce a three-dimensional mixing space with four end-members completely bounding the stream samples, yet would not alter the conclusion that peatlands, whether from two types or one, contribute substantially to baseflow.

5.2. Hydrogeologic setting

Three major characteristics of the hydrogeologic setting of the Limpopo Creek watershed are most likely responsible for enhancing peatland contributions to streamflow during dry periods. (1) moderate annual precipitation and a relatively high P/ET ratio, (2) extensive peat cover over sloping terrain, and (3) restriction of peatlands to relatively impermeable glacial deposits. In contrast, studies that determined peatlands were not substantial contributors to downgradient streams were largely based in watersheds with (1) relatively high summer rainfall (Ingram, 1983; Evans et al., 1999), (2) a small area of peatlands (Siegel, 1988a,b), or (3) peatlands confined to small topographic depressions with a single outlet stream (Boelter and Verry, 1977).

The large volume of relatively impermeable glacial till in the Limpopo Creek watershed may be especially important for determining the relative contributions of each landscape component to stream flow (Fig. 1). The low conductivity of this till deposit precludes substantial contributions from this end-member to streamflow. For example, if the area of till traversed by the stream (14,438 m long × 2 m wide) is multiplied by a mean value of hydraulic conductivity for till (10^{-8} m/s) (Freeze and Cherry, 1979) a flow rate of 0.0029 $m^3\,s^{-1}$ would result. A comparison of this value to the flow measured in the creek (0.06 $m^3\,s^{-1}$) suggests that the saturated till in the Limpopo watershed could directly produce only 4.8% of the lowest stream flow measured. This low contribution to stream flow is consistent with the value from the mixing analysis (4.5%) and other reports. Ackroyd et al. (1967), for example compared watersheds across Minnesota, USA and found that watersheds with a greater proportion of glacial till produced less runoff during dry periods. In addition, Brandesten (1988) compared eight catchments with different proportions of either bogs or glacial till in Sweden. Bog catchments provided stream flow during a drought, whereas in the till catchments stream flow sometimes ceased altogether.

5.3. Antecedent moisture conditions

Different antecedent conditions could alter the contributing proportions of the end-members to stream flow in the Limpopo watershed. Rain fell two days previous to the EMMA sampling period in 2010 although the previous 2.5 months experienced lower-than-average precipitation (56 vs. 69 mm) (Utah Climate Center, 2013). With even drier antecedent conditions the proportion of contributions from the peat end-member to stream flow may decrease as pore water storage within the peatlands becomes depleted. However, the lowest water-levels measured in the drive-point piezometer at the peatland study site suggest that ample storage remains in the peat during dry periods. Furthermore, the long, steady drawdown in September 2010 along with the measurements of stream flow at this time shows that discharge from peat at this site continues during even longer dry periods (Fig. 4). In other regions, however, discharge from peat may dry up during a severe drought, as Newson (1980) reported in Wales.

5.4. Remaining challenges

The variability of natural landscapes in space and time poses a persistent challenge for estimating diffuse discharge from peatlands to nearby streams. This fundamental property of all landscapes introduces an element of uncertainty for determining water budgets for watersheds, particularly with respect to evapotranspiration and the validity of using solutes to determine sources of stream flow.

This study relied on two different methods to estimate ET, which represents one of the more problematic values in most hydrological water budgets. The relative simplicity of the Thornthwaite method for estimating potential ET has facilitated its application to a wide range of peatlands (Ingram, 1983) including those in regions subject to dry periods (e.g. Bay, 1968; Bridgham et al., 1999; Brooks et al., 2011). The diurnal method, in contrast, has also been widely used but provides an estimate of actual ET on the basis of water level fluctuations in wells (Todd, 1980; Mitsch and Gosselink, 2007; Lautz, 2008). This method was originally developed by White (1932) and Troxell (1936) but later applied to peatlands by Heikurainen (1971) and Laine (1984). Both the Thornthwaite and diurnal methods lack the precision of more rigorous methods (e.g. energy balance and eddy covariance) that require intensive instrumentation. However, even these instrumental approaches are not free from errors that can propagate when scaled beyond the footprint of the instruments (e.g. Twine et al., 2000; Wilson et al., 2002; Field et al., 1992; Drexler et al., 2004). As a result we relied on a sensitivity analysis of both the Thornwaite and diurnal methods to provide a probable upper and lower range of values for ET from the Limpopo peatland during a dry period.

We then used EMMA to estimate the proportional contribution of peatlands to streamflow in the Limpopo watershed during a dry period. However, a series of studies in Canada and Wales have raised a serious challenge to the theoretical foundations of end-member mixing analysis. James and Roulet (2006) for example noted variable results from their EMMA analysis of a watershed in southern Quebec that were probably caused by temporal changes in the partitioning of water and solute fluxes from different portions of the watershed to a nearby stream. Kirchner and Neal (2013) and Kirchner et al. (2000, 2001) have reported spurious trends in stream chemistry over time from the Plynlimon watershed of upland Wales that are related to the complexity of solute transport across a sloping landscape. Non-linear trends in the time series of stream chemistry were probably related to the time-dependent variation in flow paths, localized residence times of individual solutes, and relative importance of advection and dispersion as solute transport mechanisms. The complexity of these interactions acted as "fractal filters" producing constantly increasing variance (1/*f* noise) in the time series of stream chemistry. Our sampling plan was designed to avoid this problem by substituting spatial sampling at one point in time for the temporal sampling at one point in the stream that is traditionally used in EMMA. Therefore, rather than showing shifting stream chemistry in response to mixing from different storm events over the course of several years, our mixing diagram provides a snapshot of the shifting chemistry of the stream along its length, as waters from different end-members mix on a single day during a dry period.

6. Conclusions

Peatlands represent an important source for stream flow in the Limpopo Creek watershed of Southcentral Alaska probably accounting for more than half of the flow during dry seasons. Most of the remaining dry-season flow probably originates in the bedrock of the Sterling Formation, whereas little additional discharge was contributed from the poorly-sorted glacial till. Peatlands may also be important contributors to streamflow in other northern watersheds that have similar hydrogeologic settings. The key features are (1) an extensive peat cover over sloping terrain, (2) an underlying mineral substratum composed of impermeable till or other unconsolidated deposits, and (3) a moist regional climate with a pronounced dry period. The disruption of this sensitive linkage between peatlands and streams by drainage or reclamation operations could therefore magnify the effects of global warming on the ecohydrology of streams, which provide important spawning habitats for salmon in Southcentral Alaska.

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