Multidecadal increases in the Yukon River Basin of chemical fluxes as indicators of changing flowpaths, groundwater, and permafrost

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Abstract The Yukon River Basin, underlain by discontinuous permafrost, has experienced a warming climate over the last century that has altered air temperature, precipitation, and permafrost. We investigated a water chemistry database from 1982 to 2014 for the Yukon River and its major tributary, the Tanana River. Significant increases of Ca, Mg, and Na annual flux were found in both rivers. Additionally, SO_4 and P annual flux increased in the Yukon River. No annual trends were observed for dissolved organic carbon (DOC) from 2001 to 2014. In the Yukon River, Mg and SO_4 flux increased throughout the year, while some of the most positive trends for Ca, Mg, Na, SO_4, and P flux occurred during the fall and winter months. Both rivers exhibited positive monthly DOC flux trends for summer (Yukon River) and winter (Tanana River). These trends suggest increased active layer expansion, weathering, and sulfide oxidation due to permafrost degradation throughout the Yukon River Basin.

1. Introduction

Arctic and boreal regions have experienced rapid rates of warming and thawing of permafrost over the past 30 years [*Hinzman et al.*, 2005; *Osterkamp*, 2007; *Romanovsky et al.*, 2010; *Jorgenson et al.*, 2013]. General circulation models suggest a positive trend for the intensification of the hydrological cycle with increased precipitation, evapotranspiration, and river discharge throughout the Pan-Arctic [*Rawlins et al.*, 2010]. The state-wide average warming of Alaskan temperatures relative to the Pacific Decadal Oscillation has increased by approximately 1°C since 1920. If these trends continue, the Yukon River Basin (YRB) is expected to become one of the hot spots of enhanced warming in Alaska [*Bieniek et al.*, 2014]. Environmental changes such as these may alter the biogeochemistry of the YRB, its carbon cycle, fish and wildlife habitat, and rural communities that depend on subsistence resources [*Chapin et al.*, 2008; 2014; *Herman-Mercer et al.*, 2011; *Wilson*, 2014].

Surface water quantity and quality changes within the YRB may have important global implications. The Yukon River, along with Ob, Yenisey, Lena, Kolyma, and Mackenzie Rivers, transport more than 11% of global river discharge into the Arctic Ocean [*Holmes et al.*, 2012; *McClelland et al.*, 2012]. Both the chemistry and quantity of these rivers' freshwater discharge play an important role in the circulation and composition of the Arctic Ocean [*Menard and Smith*, 1966; *Aagard and Carmack*, 1989]. Many Arctic rivers are experiencing altered discharge [*McClelland et al.*, 2006]. However, since the 1950s, annual flow has remained relatively unchanged within the YRB, while other seasonal hydrographical trends indicate increases in groundwater contributions [*Walvoord and Striegl*, 2007; *Brabets and Walvoord*, 2009; *Ge et al.*, 2013]. *Muskett and Romanovsky* [2011], between 2002 and 2008, also found decreasing groundwater storage within the YRB. Several studies have hypothesized that expansion of existing and new taliks may be a critical flow pathway contributing to these hydrological changes [*Zhang et al.*, 2005; *Muskett and Romanovsky*, 2011; *Walvoord et al.*, 2012]. A talik is defined as unfrozen soil within permafrost. Taliks can be vertical, horizontal, bound by permafrost (closed), or connected to other unfrozen zones (open) [*Walvoord and Kurylyk*, 2016].

Throughout YRB and the Arctic, observed spatial and temporal patterns in aquatic chemistry have been linked to different permafrost conditions (i.e., continuous versus discontinuous) [*Striegl et al.*, 2007] and increasing active layer depths [*Guo*, 2004; *Keller et al.*, 2010; *Guo et al.*, 2012; *O'Donnell et al.*, 2012; *Douglas et al.*, 2013]. While northern boreal soils are spatially heterogeneous, many of these soils include a surface organic layer over finer mineral soils [*Carey and Woo*, 2002; *Koch et al.*, 2014; *Pastick et al.*, 2014b]. Runoff

and subsurface shallow flow is constrained within the upper organic layer by the depth of the seasonal thaw front during the early open water season. As thaw occurs over the summer, water infiltrates to deeper mineral soils [*Bolton et al.*, 2004; *Petrone et al.*, 2007; *Koch et al.*, 2013]. Preferential pathways and locations of infiltration may develop during the summer, increasing hydraulic gradients and groundwater recharge [*Sloan and van Everdingen*, 1988; *Muskett and Romanovsky*, 2011; *Koch et al.*, 2014; *Walvoord and Kurylyk*, 2016].

The temporal scale of boreal and Arctic aquatic chemistry studies are often limited to multiyear or decadal data sets. Investigating dissolved organic carbon (DOC), and to a lesser extent nutrients, over longer periods has been rare due to the lack of continuous historical data collection of these parameters in these areas [*Tank et al.*, 2016]. At multidecadal time scales, it is speculated that permafrost degradation may lead to increased weathering of mineral soils, bedrock, and permafrost that in turn leads to long-term trends of changing aquatic chemistry [*Keller et al.*, 2010; *Frey and McClelland*, 2009; *Vonk et al.*, 2015b; *Tank et al.*, 2016]. Warming climate may enhance subsurface flow into deeper mineral soils while ultimately percolating to groundwater with an increased mineral signature. At longer temporal scales, relatively conservative major ion (Ca, Mg, and Na) concentrations are expected to dramatically increase throughout Pan-Arctic rivers as the result of chemical weathering of minerals [*Frey and McClelland*, 2009; *Vonk et al.*, 2015b]. Nutrient and DOC dynamics can be more complex with associated microbial processes acting as another control on release to aquatic systems [*Striegl et al.*, 2005; *Walvoord and Striegl*, 2007; *Harms and Jones*, 2012; *Koch et al.*, 2013]. Deep flowpaths can thaw near-surface permafrost and deliver the products of weathering and thaw to surface water and groundwater. These processes alter aquatic biogeochemistry as suggested by data from the Yukon River [*Striegl et al.*, 2005]. Throughout Alaska and western Canada, near-surface permafrost has been found to be rich with carbon, major ions, and nutrients [*Kokel et al.*, 2002; *Kokel and Burn*, 2005; *Keller et al.*, 2007].

In this study, we hypothesized that major ions and nutrients should be increasing as the result of changing flowpaths due to permafrost degradation. To investigate this hypothesis, we analyzed a 32 year (1982 to 2014) river discharge and water chemistry database from the Yukon River and one of its major tributaries, the Tanana River. More specifically we asked the following. (1) Are annual fluxes of major ions, nutrients, and DOC changing over time?; (2) Are certain months experiencing long-term trends of major ions, nutrients, and DOC flux? (3) Are these trends consistent with permafrost degradation and altered flowpaths? While a number of studies have investigated the YRB historical record using a variety of techniques, we were able to investigate additional hypotheses about mineral soil exposure, groundwater, and active layer expansion. Our results are discussed within the context of previous research within the YRB and their relationship to permafrost degradation.

2. Methods

2.1. Study Area

The Yukon River originates in northwestern British Columbia, Canada, then flows northwest through Yukon, across the interior of Alaska to its delta in western Alaska where it discharges into the Bering Sea (Figure S1 in the supporting information). The Yukon River is an important source of freshwater, sediments, and solutes to the Bering Sea [*Lisitsyn*, 1969]. The Yukon River is unique among the Arctic Great Rivers in that it runs east to west through a predominantly discontinuous permafrost watershed that encompasses nearly 30% of Alaska's land area (853,300 km^2) [*Brabets et al.*, 2000; *Holmes et al.*, 2012]. Peak precipitation occurs in August, while many of the basin tributaries also receive flow from glacial melt during July and August with groundwater as the primary source of base flow during the winter months [*Walvoord and Striegl*, 2007; *Brabets and Walvoord*, 2009; *Ge et al.*, 2013]. Roughly 23% of the YRB is underlain by continuous permafrost while discontinuous and sporadic permafrost underlie approximately 76% of the basin [*Holmes et al.*, 2013]. Permafrost thickness is estimated to be ≤ 15 m in the tundra and lowland portions of western Alaska, growing to a thickness of approximately 180 m in the northeastern part of the basin [*Brabets et al.*, 2000]. Over 146,000 people live in the basin (0.18 people km^{-2}) [*Holmes et al.*, 2013] with one hydroelectric dam near Whitehorse, Yukon [*Nilsson et al.*, 2005].

The Tanana River is one of the major tributaries of the Yukon River draining close to 13.7% of the YRB area and providing approximately 20% of Yukon River discharge at Pilot Station [*Brabets et al.*, 2000]. Peak discharge in the Yukon River occurs in May or June with freshet, whereas peak discharge in the Tanana River occurs in July due to both maximum glacial melt and summer precipitation within the watershed [*Bennett et al.*, 2015]. A large portion of the Tanana Basin is underlain by discontinuous or continuous permafrost [*Bennett et al.*, 2015; *Pastick et al.*, 2014a]. Discontinuous permafrost, coarse subsurface alluvial material, and steep hydraulic

gradients allow for significant groundwater contributions (>25% of annual flow) to Tanana River discharge [*Walvoord and Striegl*, 2007].

2.2. Water Chemistry, Discharge, and Precipitation

The locations of the two U.S. Geological Survey (USGS) gaging stations used in this study are shown in Figure S1. The USGS gaging station located on the Yukon River at Pilot Station, Alaska (15565447), is considered the operational outlet of the Yukon River, representing the integration of upstream major tributaries before it is tidally influenced. The USGS gaging station that is located at Nenana, Alaska (15515500), drains approximately two thirds of the Tanana watershed. Both stations were selected based on location and length of data record.

Water chemistry and discharge data were obtained through the National Water Information System (NWIS) (U.S. Geological Survey, USGS Water Data for the Nation, 2015, http://waterdata.usgs.gov/nwis/ (Accessed 1 June 2015)), Open File Reports [*Schuster et al.*, 2010], and the Yukon River Water Quality website [*Herman-Mercer*, 2016]. This last source includes data collected by Yukon River Inter-Tribal Watershed Council staff and YRB communities as part of the Indigenous Observation Network (ION). The ION data fill important USGS gaps in data collection for these Alaska sentinel discharge and water quality data sites most notably from 2006 to 2007 on the Yukon and 2006 to 2014 on the Tanana. Water chemistry and quantity data gaps exist for the Yukon (1996–1999) and Tanana (1997–2000) Rivers. Wet deposition and precipitation data were obtained from the Denali National Park (AK03), 1986 to 2014, and Poker Creek (AK01), 1993 to 2014, from the National Atmospheric Deposition Program (2015, http://nadp.sws.uiuc.edu/ (Accessed 10 January 2016)) (Figure S1).

2.3. Statistical Methods

Annual and monthly flux of Ca, Mg, Na, P, SO_4 (1982 to 2014), and DOC (2001 to 2014) for both sites (Yukon and Tanana Rivers) were calculated using NWIS discharge, the combined USGS/YRITWC water quality database, LoadRunner (G. Booth and P. A. Raymond, LoadRunner, software and website. Yale University, New Haven, Conn., 2007, https://environment.yale.edu/loadrunner/, (Accessed 1 February 2016)), and LOADEST [*Runkel et al.*, 2004]. LoadRunner provides a graphical user interface to automate LOADEST. LOADEST pairs streamflow and concentration data to build a calibration regression. This regression is then applied to the historical daily discharge record to calculate flux (mass d^{-1}). To account for some models within LOADEST using a linear time function to parameterize the model, we divided runs into 3–5 year periods to minimize this effect. Trend analyses were then completed on the entire compiled data record. Chemical fluxes were not calculated for the previously mentioned data gaps due to lack of discharge and water chemistry data. In addition, P flux was not calculated on the Tanana River due to lack of data from 2006 to 2014. The Akaike information criterion was used to select the model of best fit for the calibration equation for each parameter and site [*Burnham and Anderson*, 2002].

Nonparametric statistics were used with all time series data because they are considered conservative and robust with nonnormal distributions, missing data, and outliers [*Helsel and Hirsch*, 2002; *Yue et al.*, 2002; *Kaushal et al.*, 2013]. All data sets were evaluated for serial correlation using the prewhitening technique developed by *Yue et al.* [2002] in the R zyp. Package (D. Bronaugh and A. Werner, zyp: Zhang and Yue-Pilon trends package, 2015, http://cran.r-project.org/). This package was also used to calculate Sen-Thiel slopes with confidence intervals (95%). P values < 0.05 were used to determine significance. The rank-based correlation test of Kendall's tau was calculated to determine the probabilities of positive or negative flux trends in time (range: -1 to 1). We used Sen-Thiel slopes, a nonparametric regression line related to Kendall's Tau, to estimate the magnitude of chemical trends over time. Mann-Kendall tests on annual wet deposition, precipitation, chemical fluxes, and discharge were used for trend analysis and comparisons. Mann-Kendall tests were also conducted on chemical fluxes and discharge for each month for the period of record to determine additional intra-annual trends that were more informative of specific seasonal hydrological flowpaths. We also used the Mann-Kendall test to determine any discharge trend at the two USGS gaging stations that exactly overlapped the water quality data. Discharge analyses were conducted on monthly and annual discharge for both time periods 1982 to 2014 and 2001 to 2014 (DOC).

3. Results and Discussion

### 3.1. Major Ions

Precipitation ($p = 0.33$) or wet deposition of Ca ($p = 0.86$), Mg ($p = 0.68$), Na ($p = 0.07$), and SO_4 ($p = 0.22$) did not exhibit any trends at site AK03 from 1986 to 2014 (Figure 1). While the data record was somewhat shorter
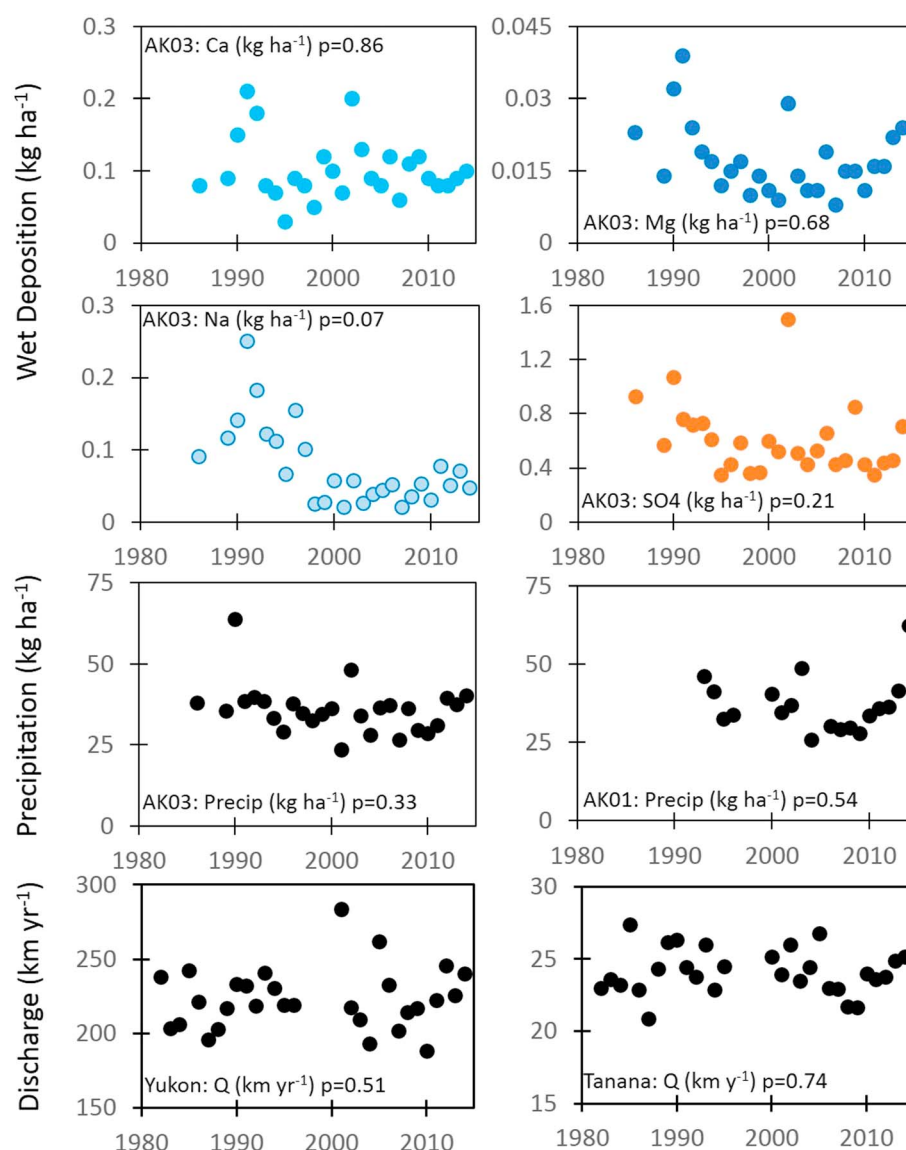
Figure 1. Annual wet deposition (kg/ha), precipitation, and discharge (Q) with no observed trends.

(1993 to 2014), no trends were detected at site AK01 for precipitation ($p = 0.54$) or wet deposition of Na ($p = 0.90$) and SO_4 ($p = 1.0$) (Table S1). Increases were detected for wet deposition of Mg and Ca at AK01; however, these trends were not significant due to confidence intervals that contained zero. Therefore, from this limited data, increasing trends in precipitation or wet deposition do not appear to be influencing surface water chemistry.

Multidecadal increases in Ca, Mg, and Na annual flux were observed in both the Tanana and Yukon Rivers (Figure 2). The Tanana River exhibited increases of annual flux for Ca ($13\% \pm 8\%$), Mg ($26\% \pm 8\%$), and Na ($38\% \pm 12\%$) from 1982 to 2014. In the Yukon River, annual flux of Ca ($21\% \pm 16\%$), Mg ($36\% \pm 13\%$), and Na ($25\% \pm 16\%$) increased over the same period (Figure 2). Increasing discharge did not contribute to these increases as no trend for annual discharge was observed in either river (Figure 1 and Table S1). Many studies have suggested that an overall warming trend in the YRB in recent decades may be contributing to permafrost degradation and increasing groundwater contributions [*Walvoord and Striegl*, 2007; *Brabets and Walvoord*, 2009; *Muskett and Romanovsky*, 2011; *Ge et al.*, 2013]. As the active layer increases, soil water from the shallow organic layer descends earlier in the summer to the mineral part of the soil profile where these ions are more prevalent. From the mineral part of the soil, soil water then reaches surface water through
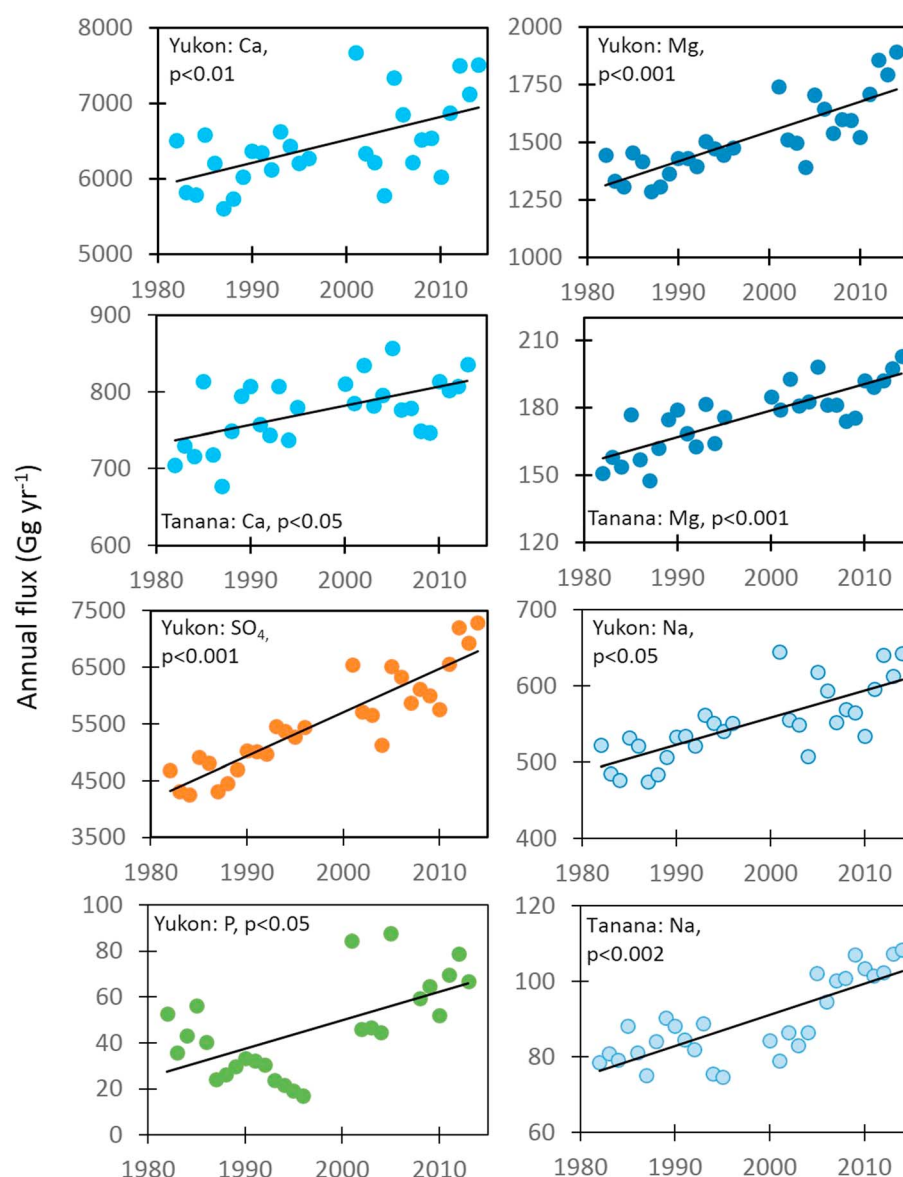
Figure 2. Annual flux increases in the Yukon and Tanana Rivers with Thiel-Sen trend lines.

lateral subsurface flow and groundwater exchange. Increased exposure of carbonate through active layer expansion may be another source of Ca and Mg contributing to these positive fluxes. *Brabets et al.* [2000] concluded that throughout the YRB the major ion composition of surface water is consistent with the dissolution of carbonate minerals. Weathering of carbonate by carbonic acid also releases Ca and Mg as products of this reaction similar to observations in the Mackenzie River and at the Toolik Lake Inlet Stream [*Keller et al.*, 2010; *Beaulieu et al.*, 2011; *Tank et al.*, 2016]. Much of the current Ca and Mg present in groundwater is derived from this weathering process. In the YRB, *Muskett and Romanovsky* [2011] suggested that permafrost degradation was occurring with increasing groundwater discharge through active layer expansion and development of new taliks. Taliks can connect surface water to suprapermafrost and subpermafrost aquifers that then supply groundwater to river discharge as a base flow component [*Walvoord et al.*, 2012].

The Yukon River exhibited monthly increases in Ca, Mg, and Na flux, while the Tanana River had monthly flux increases of only Mg and Na. For the Tanana River, Mg and Na fluxes increased every month from April to September (Figure 3 and Table S1). The greatest increases for Mg flux on the Tanana River occurred during June ($2.7 \, \text{Gg decade}^{-1} \pm 1.4$) and August ($2.7 \, \text{Gg decade}^{-1} \pm 1.5$) most likely due to a combination of
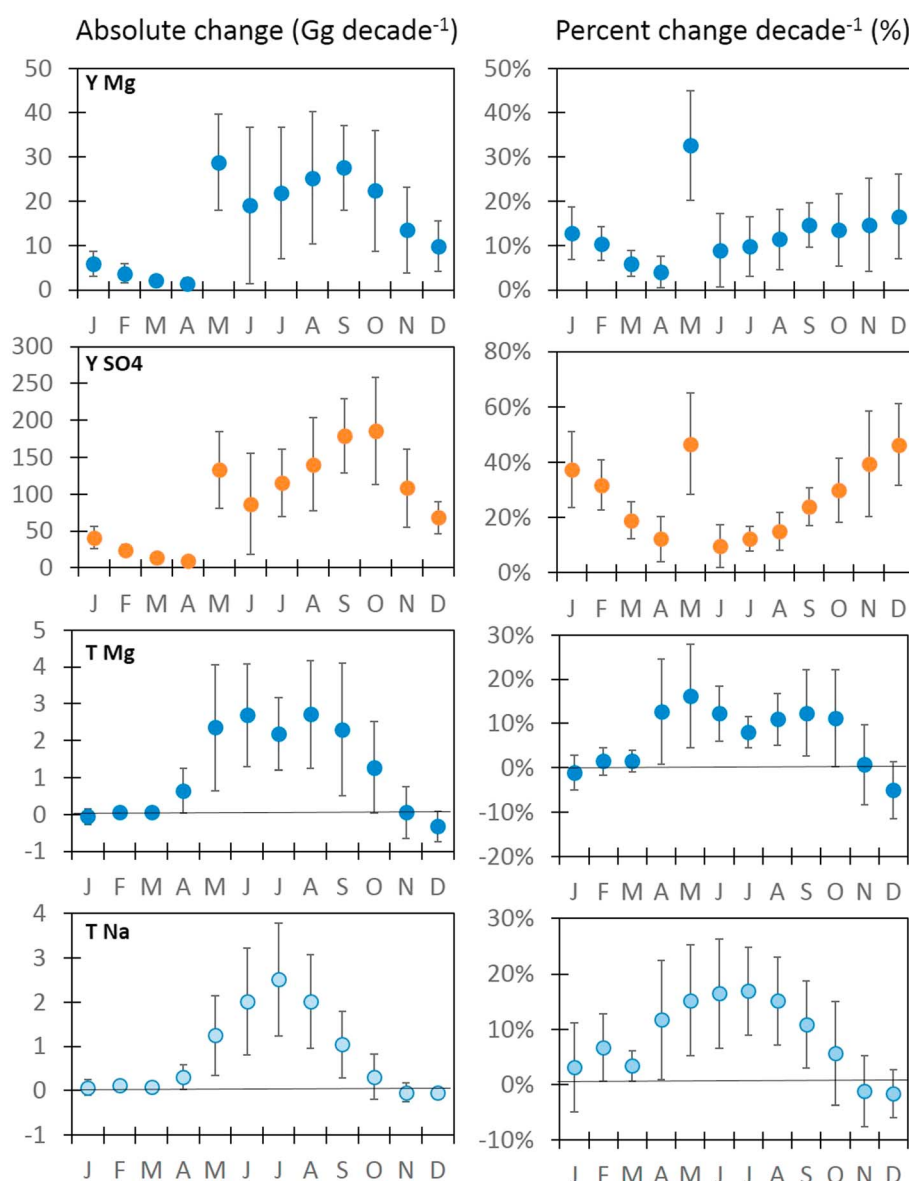
Figure 3. Monthly flux trend in absolute and percent change in the Yukon River (Y) and Tanana River (T) for 1982 to 2014.

seasonal thaw front progression into the mineral soil (June) and maximum precipitation (August). In May, the Yukon River exhibited the only positive trend ($p < 0.05$) for discharge that accounted for a change of 34% $\pm$ 26% km decade^{-1} (Table S1). For May, the Yukon River had similar percent (Gg decade^{-1}) increases for both Na (28% $\pm$ 16%), Ca (30% $\pm$ 16%), and Mg (33% $\pm$12%) (Figure 3 and Table S1). The Ca flux (Gg decade^{-1}) also increased in the Yukon River for September (8% $\pm$ 5%) and December (13% $\pm$ 8%). The Yukon River had positive trends for Na flux in August, September, and December. Positive monthly trends were observed for Mg flux in the Yukon during every month except April ($p = 0.05$, Figure 3 and Table S1). Therefore, positive trends in fall and winter ion fluxes appear to be enriching fall and winter flows in the Yukon River. The northern part of the Yukon River Basin (i.e., the Koyukuk and Porcupine Basins) are largely continuous permafrost [*Brabets et al.*, 2000]. Degradation of permafrost within these northern basins and its associated increased weathering may be one explanation for why these specific ions are increasing only in the Yukon River. Thermokarst features may provide another mechanism for delivery of these ions as thermoerosion gullies have also been observed to supply high concentrations of Mg and Ca even after stabilization [*Abbott et al.*, 2015]. Thermokarst rates have increased at least within the Tanana Basin between 1949 and 2009 [*Lara et al.*, 2016].
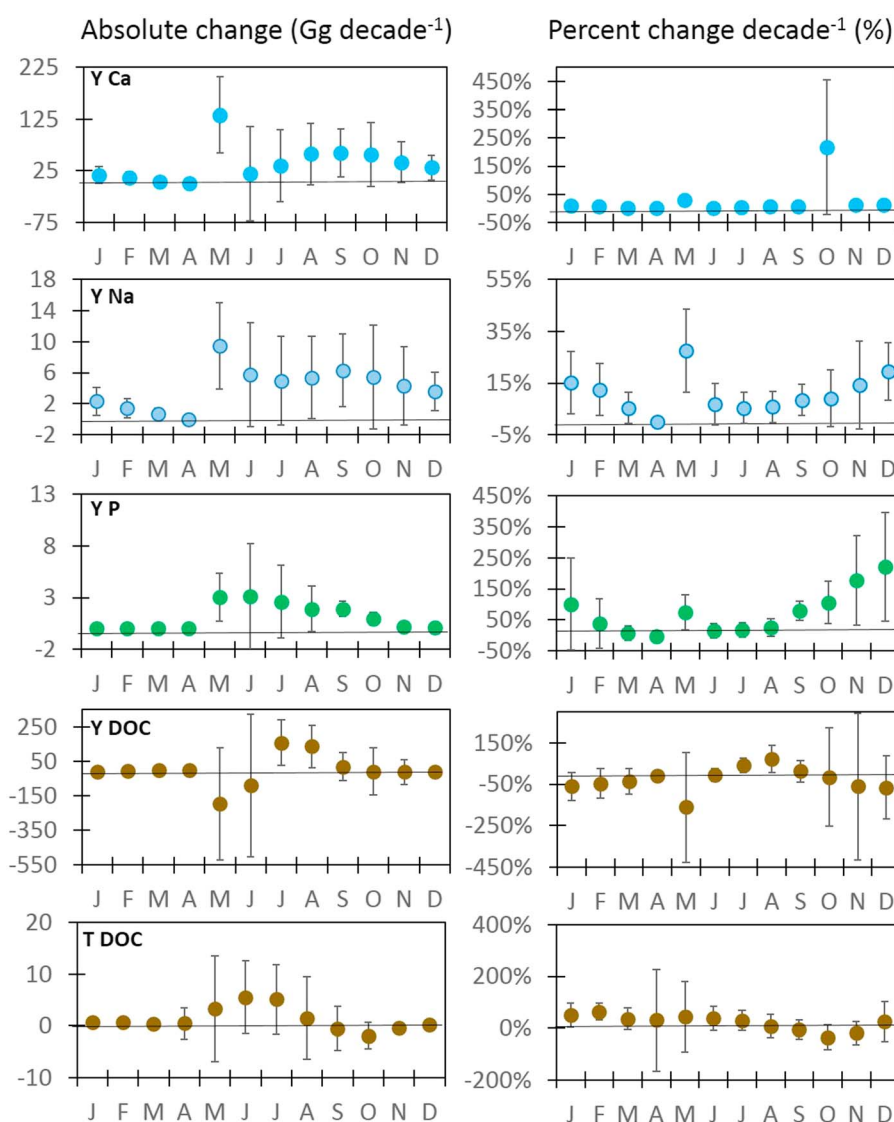
Figure 4. Monthly flux trends in absolute and percent change in the Yukon River (Y) and Tanana River (T).

In the Yukon River, annual SO_4 flux increased by 1076 Gg decade^{-1} $\pm$ 291.8 (21% $\pm$ 6%) (Figure 2). The greatest monthly percentage increase of SO_4 flux in the Yukon River occurred during May (47% decade^{-1} $\pm$ 18%) with the previously mentioned increasing May monthly discharge contributing to this trend. However, absolute change of SO_4 flux from May to October was similar and ranged from 86.8 to 185.9 Gg decade^{-1} (Figure 3). The combination of the higher percentage change and the similar magnitude of the open water period absolute changes in SO_4 flux to May values suggests that the pathway for SO_4 flux is opening approximately 1 month earlier than previously observed. Part of these early open water increases may be due to increased April and May temperatures and precipitation resulting in earlier breakups in May [*Brabets and Walvoord*, 2009; *Bieniek et al.*, 2011, 2014] and/or anaerobic conditions in the near surface, wetlands, or thermokarst that are flushed during snowmelt [*Abbott et al.*, 2015; *Lewis et al.*, 2015].

Significant positive percent changes in SO_4 occurred during late summer and into winter suggesting that as base flow starts to dominate the Yukon River hydrograph, groundwater has been enriched with SO_4 along with the other major ions (Figures 3 and 4). Surprisingly, no trend was observed for annual or monthly SO_4 flux in the Tanana River. The subpermafrost aquifers in alluvial deposits within the ecoregion of the Boreal Mountains and Plateaus of the YRB have gypsum geology that is most likely a significant source of SO_4 for the Yukon River [*Sloan and van Everdingen*, 1988; *Brabets et al.*, 2000]. Sulfuric acid, from either anthropogenic

disturbance or sulfide oxidation, can also contribute to weathering reactions releasing Ca and SO_4 to aquatic systems [*Tank et al.*, 2016]. Sulfide oxidation has been observed by several studies within the YRB [*Marsh et al.*, 2003; *Verplanck et al.*, 2008]. Increased sulfate flux may also be related to thermokarst activity throughout the watershed as significant SO_4 concentrations downstream of thermokarst slumps, gullies, and slides have been found throughout the Arctic [*Malone et al.*, 2013; *Abbott et al.*, 2015].

3.2. Phosphorous

Increasing annual flux of P in the Yukon River may indicate several processes occurring within the YRB. Annual flux of P increased by 14.5 Gg decade^{-1} ± 13.8 (Figure 2 and Table S1). May provided the greatest absolute increase (3.03 Gg decade^{-1} ± 2.34) for P flux in the Yukon River (Figure 4) which may be the result of earlier breakups being observed throughout the YRB. During the open water season, *Dornblaser and Striegl* [2007] found that particulate phosphorous (PP) was prevalent and highly correlated with suspended sediment yield from 2001 to 2005 suggesting surface runoff and bank erosion as additional major sources. In this study, the greatest percent change in Yukon River monthly P flux occurred from September to December (Figure 4 and Table S1). These increases represent significant positive increases per decade of 79% ± 30 (September), 106% ± 69 (October), 178% ± 145 (November), and 221% ± 175 (December) (Figure 4 and Table S1). Most of the P within the YRB is likely the result of chemical and physical rock weathering [*Gardner*, 1990; *Dornblaser and Striegl*, 2007; *Schlesinger and Bernhardt*, 2013]. Water saturation, and hence anoxic conditions, at deeper soil levels may also facilitate dissociation of iron-phosphate complexes with inorganic phosphates released as the product [*Patrick and Khalid*, 1974; *Lewis et al.*, 2015]. Increases of P during the fall and winter may also be indicative of later and/or interrupted river freezing that could also contribute to surface runoff and bank erosion [*Janowicz*, 2010; *Wilson*, 2012]. Considering PP is mostly unreactive [*Lobbes et al.*, 2000; *Dittmar and Kattner*, 2003], it is unlikely that that this source of P would contribute to increased levels of bioavailable phosphorous [*Dornblaser and Striegl*, 2007].

3.3. DOC

There was no trend for annual DOC flux in either river from 2001 to 2014 (Table S1). While the time frame is shorter than other studies [*Tank et al.*, 2016], the lack of DOC flux trend within the Yukon River is fairly unique among the arctic rivers. *Striegl et al.* [2005] reported a significant decrease in summer to autumn discharge-normalized DOC export between 1978 and 2003 that they attributed to increased microbial mineralization, flow path, and residence time of DOC in the soil active layer. Dissolved organic carbon dynamics involve a variety of complex mechanisms that involve permafrost degradation, peat hydrochemical processes, decomposition, leaching, and production with more indirect effects occurring through increased shrub abundance [*Sturm et al.*, 2005] and microbial mineralization [*Wickland et al.*, 2007; *Vonk et al.*, 2015a]. The Yukon River did have two positive DOC trends in July (41% decade^{-1} ± 34%) and August (73% decade^{-1} ± 65%) (Figure 4 and Table S1). The Tanana exhibited positive trends during January (51% decade^{-1} ± 46) and February (64% decade^{-1} ± 32). These increasing DOC trends may be indicative of active layer expansion with resulting DOC enrichment of groundwater as the result of permafrost thaw. For the Yukon River, these increasing DOC flux trends may also be related to glacial melt. Ultimately, more research is needed on hydrological and biological processes of DOC flux that may best explain these mechanisms. While the DOC data set is limited in longevity (2001 to 2014), the longer-term trends of increased major ions and nutrients do suggest that the Yukon and Tanana River geochemical signatures are experiencing deeper flow paths, increased groundwater discharge, near-surface permafrost thaw, and most likely increased weathering throughout the YRB.

3.4. Fall and Winter Chemical Fluxes

While Mg and Na flux in the Tanana River generally increased during the open water season, the Yukon River Ca, Mg, Na SO_4, and P had some of the greatest increases in terms of percent change from September to December (Figures 3 and 4). For example, while the absolute change in Yukon River P flux is low, these changes reflect increases between 79 and 221% decade^{-1} (Figure 4) at a time when particulate phosphorous should be low. Increased monthly SO_4 flux during the winter ranges between 12 and 46% decade^{-1}. These increasing fluxes are most likely the result of either a lag effect of soil water mineral exposure that continues to percolate to groundwater or continuous weathering even after the majority of surface water within the basin has frozen. Annual discharge changed very little within the YRB from 1945 to 2005 [*Brabets and Walvoord*, 2009]. However, *Walvoord and Striegl* [2007] observed a positive trend of 0.7–0.9% per year in

groundwater contribution to total streamflow within the YRB. This increasing flux of ions, nutrients, and DOC agree with the hydroclimatological studies that suggest increasing winter, spring, and groundwater flows [*Walvoord and Striegl*, 2007; *Brabets and Walvoord*, 2009; *Ge et al.*, 2013]. The changing groundwater signature is most likely the result of increased weathering and hydrological connectivity to groundwater sources. Increasing P and DOC during this season maybe an additional indicator of active layer expansion throughout the watershed [*Hobbie et al.*, 1999; *Keller et al.*, 2010], or the result of percolation from mineral soils earlier in the year to the groundwater sources of Yukon River base flow. Finally, *Spence et al.* [2015] also describe a conceptual model that may explain these results by incorporating a wetter autumn season with freezeup that has similar patterns in seasonal aquatic chemistry to breakup.

4. Conclusions

The Yukon River Basin (YRB), underlain primarily by discontinuous permafrost, has experienced a warming climate over the last three decades that has led to permafrost degradation. Positive trends in surface water chemical fluxes of the Yukon and Tanana Rivers provides strong evidence that suggests altered hydrological flowpaths and increased weathering due to widespread permafrost degradation. Annual flux of Ca, Mg, Na, SO_4, and P has significantly increased over the last three decades within the Yukon River Basin. While part of this annual flux increase occurred during the open water season, positive trends of these parameters have also significantly increased in fall and winter river flow over the past three decades. These positive trends suggest expanding active layers, increased weathering, and sulfide oxidation. Changing geochemistry of the YRB may have important implications for the carbon cycle and aquatic ecosystems.

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