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Nutrient (N, P) loads and yields at multiple scales and subbasin types in the Yukon River basin, Alaska

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[1] Loads and yields of dissolved and particulate nitrogen (N) and phosphorus (P) were measured and modeled at three locations on the Yukon River (YR) and on the Tanana and Porcupine Rivers in Alaska during 2001–2005. Total export of N and P upstream of Yukon Delta averaged 120 Gg N a^{-1} and 56 Gg P a^{-1}, respectively, with 43.5% of total N (TN) as dissolved organic N, and 98% of total P (TP) as particulate phosphorus. Approximately half of the annual export of TN and TP occurred during spring. Hydrologic yields of TN (5.6–13.3 mmol N m^{-2} a^{-1}) and TP (0.8–9.0 mmol P m^{-2} a^{-1}) were least in the Porcupine basin and greatest in the Tanana basin and were proportional to water yield. Comparison of current and historical dissolved organic matter (DOM) export from the basin indicates decreased DON export with respect to total water discharge during summer and autumn in recent decades. Any possible climate-related change in annual water discharge will result in proportional changes in N and P export.

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1. Introduction

[2] Global climate change is altering hydrology across the arctic/subarctic regions. The magnitude and timing of water discharge (Q) in arctic and subarctic watersheds has changed in recent decades [*Peterson et al.*, 2002; *Yang et al.*, 2002; *McClelland et al.*, 2006] owing to thawing permafrost, changes in precipitation patterns, and warmer temperatures. In the Yukon basin, hydrologic change in recent decades appears to be limited mostly to change in the timing and source of water discharge and not to change in total annual Q [*Walvoord and Striegl*, 2007]. The relationship between Q and carbon export in the Yukon basin appears to be changing [*Striegl et al.*, 2005, 2007], suggesting that Q-nutrient relationships may also be changing. Thawing permafrost releases stored nutrients, which become available for metabolism by terrestrial and freshwater organisms or for export downstream. The effect of these releases on within-river cycling and net export of N and P to receiving waters is not accurately quantified because, as with most northern rivers, Q and nutrient data for the Yukon River are limited [*Kempe*, 1982; *Leenheer*, 1982; *Telang et al.*, 1991; *Brabets et al.*, 2000; *Striegl et al.*, 2005, 2007] (see also NWIS, U.S. Geological Survey National Water Information System, Web Data for the Nation, http://waterdata.usgs.gov/nwis, hereinafter referred to as NWIS web data). In order to help rectify this situation, the United States Geological Survey (USGS) conducted a comprehensive study of river flow and water chemistry of the Yukon River and two of its major tributaries, the Porcupine and Tanana Rivers, during 2001–2005 [*Schuster*, 2003] (http://ak.water.usgs.gov/yukon; http://www.usgs.gov/nasqan/). This paper focuses on the N and P aspects of that larger study, quantifying source and seasonality of nutrient export over a wide range of flow conditions at the 66,000 to 831,000 km^2 scale and establishing a benchmark against which future changes can be compared. Where possible, current conditions are compared with historical record to evaluate possible responses to recent climatic warming in the basin.

2. Study Area

[3] The Yukon River flows approximately 3340 km from British Columbia through Yukon Territory and Alaska to the Bering Sea, draining approximately 853,300 km^2 (Figure 1), and annually depositing 18 billion kg of sediment in floodplains and delivering 55 billion kilograms of sediment to Norton Sound [*Brabets et al.*, 2000]. It supplies the Arctic Ocean with ~8% of its freshwater inputs [*Aagaard and Carmack*, 1989] and is of prime importance to the ecology of the Bering Sea, contributing most of its freshwater runoff, sediment load, and dissolved solutes [*Lisitsysn*, 1969]. Approximately 126,000 people live within the basin and depend on the Yukon River and its tributaries for drinking water, commerce, and recreational and subsistence fish and game resources. The Yukon basin is diverse, encompassing twenty different ecoregions and having large variability in topography, climate, soils, geology, permafrost, land cover, and water quality [*Brabets et al.*, 2000].

[4] Air temperature records between 1961 and 1990 indicate a warming trend of about 0.75°C per decade at latitudes of the Yukon River [*Chapman and Walsh*, 1993].

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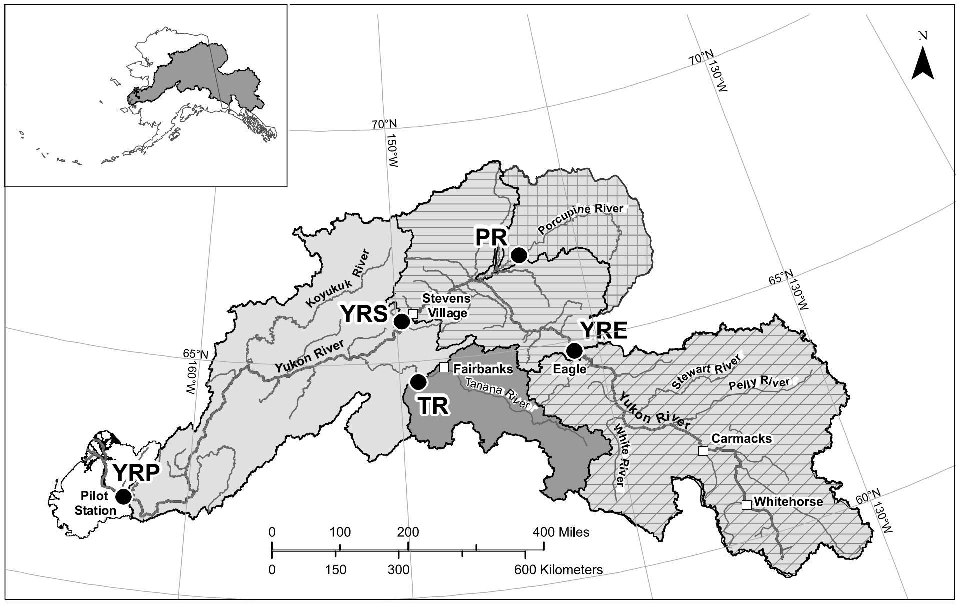

Figure 1. Map of the Yukon River basin showing measurement station locations and watershed boundaries. Yukon River at Pilot Station (YRP), Yukon River near Stevens Village (YRS), Tanana River at Nenana (TR), Porcupine River near Fort Yukon (PR), and Yukon River at Eagle (YRE).

Recent research suggests that much of this change is occurring during the summer [*Clein et al.*, 2007]. The basin, which is underlain by areas of permafrost containing vast amounts of carbon and nutrients, has already undergone changes as a result of this recent warming. There is evidence of thawing permafrost, thermokarst expansion, lengthening of the growing season, deepening of the soil active layer, drying of upland soils, and shrinking of wetlands [*Hinzman et al.*, 2005; *Jorgenson et al.*, 2006]. These mostly terrestrial effects also affect the hydrology of the basin, changing the timing, magnitude, and fate of water and dissolved and particulate materials delivery to the Yukon River and the Bering Sea.

[5] The hydrograph of the Yukon River (YR) is characterized by a peak in discharge occurring in late May or early June due to snowmelt. In many years a much smaller secondary peak in discharge is evident in mid to late August as a result of melting of perennial snowpack and alpine glaciers and/or rain events in headwater areas. During 2001–2005, annual discharge at Pilot Station, the furthest downstream station before the Yukon River enters the Bering Sea, ranged from 188–227 $km^3\ a^{-1}$ (ave. = 211 $km^3\ a^{-1}$) (Table 1). Peak discharge at Pilot Station can reach 35,000 $m^3\ s^{-1}$, while winter base flow discharge is typically ~1300 $m^3\ s^{-1}$.

3. Methods

3.1. Data Collection and Sample Analyses

[6] From 2001 to 2005, the USGS measured water discharge and water and suspended sediment chemistry at five fixed stations in the YR basin in Alaska (Figure 1 and Table 1). Relevant station descriptions, river discharge, and water chemistry data are archived in the National Water Quality Information System (NWIS web data). Flow characteristics are also summarized by *Striegl et al.* [2007]. Yukon River at Eagle (YRE) represents flow from all headwater areas in Canada. Yukon River near Stevens Village (YRS), ~700 km down river from Eagle, is just downstream of the 34,000 km^2 Yukon Flats, an area of extensive bogs and wetlands. Yukon River at Pilot Station (YRP) is the farthest downstream location where the Yukon

Table 1. Station Name, Location, and Annual Water Discharge for 2001–2005 and Flow Statistics for the Period of Record

Station Name	Station Abbreviation.	USGS Station Number	Latitude (N): Longitude (W) (NAD 83)	Drainage Area, km^2	Elevation, m	Annual Q, $km^3\ yr^{-1}$ 2001	2002	2003	2004	2005	2001–2005 Mean Annual Q, $km^3\ yr^{-1}$
Yukon River at Eagle	YRE	15356000	64°47′22″: 141°47′22″	294,000	259	91.1	74.5	65.4	71	79.1	75.1
Porcupine River near Fort Yukon	PR	15389000	66°59′26″: 143°08′16″	76,400	158	10.8	12.1	11.1	9.3	9.52	12
Yukon River near Stevens Village	YRS	15453500	65°52′32″: 149°43′04″	508,400	73	123	108	98.9	96.6	108	106
Tanana River at Nenana	TR	15515500	64°33′55″: 149°05′30″	66,300	103	23.3	23.8	22.4	24.1	24.7	22
Yukon River at Pilot Station	YRP	15565447	61°56′04″: 162°52′50″	831,400	6	223	188	225	190	227	211

River can be gaged and sampled before it enters the Yukon Delta and Norton Sound. The Porcupine River (PR) station was located 201 km upstream of its confluence with the Yukon River and represents a large tributary draining permafrost-dominated wetlands. The Tanana River at Nenana (TR) has a high sediment load. It headwaters are in the Alaska Range and its watershed includes the city of Fairbanks.

[7] Samples were collected at each station 6–8 times a^{-1} using the USGS Equal Discharge Increment (EDI) sampling protocol [*Edwards and Glysson*, 1988] (http://pubs.usgs.gov/twri). One sample was collected each year under ice to characterize late winter base flow conditions, while the remainder of the samples were collected approximately every 3 weeks during the ice-free season between May and September. Samples were composited and processed according to established USGS protocols (U.S. Geological Survey, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, 1997–1999, http://water.usgs.gov/owq/FieldManual/(site includes updates)). All N and P samples were analyzed at the USGS National Water Quality Laboratory (NWQL, http://nwql.usgs.gov/) in Denver, Colorado, except for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$ of suspended sediment, which were analyzed at the USGS Isotope Tracers Laboratory in Menlo Park, California, and NO_3^-, which was analyzed at the USGS laboratories in Boulder, Colorado. In addition, replicate samples collected in 2005 for total particulate N (PN) and particulate inorganic N (PIN) were analyzed at the University of Maryland Chesapeake Biological Laboratory (CBL, http://www.cbl.umces.edu/nasl/). Ammonium (NH_4^+), ammonium plus dissolved organic nitrogen (NH_4^+ + DON), nitrate (NO_3^-), nitrite plus nitrate (NO_2^-+ NO_3^-), PN, PIN, total dissolved phosphorus (TDP), phosphate (PO_4^{3-}), total P (TP), and $\delta^{15}N$ of suspended sediment were analyzed following methods cited by *Schuster* [2003]. The $\delta^{15}N\text{-} NO_3^-$ was analyzed according to methods described by *Sigman et al.* [2001]. DON was determined by difference, [DON] = [NH_4^+ + DON] − [NH_4^+]. Particulate P (PP) was also determined by difference, [PP] = [TP] − [TDP], as was PON, [PON] = [PN] − [PIN].

3.2. Concentrations, Loads, and Yields

[8] Average seasonal concentrations were calculated using 2001–2005 data. On certain sampling dates, some constituent concentrations were below analytical detection. In these instances, below detection values were set to half the detection limit for the purpose of calculating seasonal concentrations, and are noted in the results. Analytical values that were reported as estimates by NWQL were treated as actual values. For the calculation of DOC/DON, POC/PN, and TDN/TDP ratios, constituent concentrations below detection were set to half the detection limit.

[9] Daily river constituent loads (mass d^{-1}) were calculated from continuous discharge (Q) data and water chemistry measurements using the FORTRAN Load Estimator (LOADEST) program [*Runkel et al.*, 2004]. The model requires at least 12 direct measurements of flow and chemistry over a wide range of flow conditions in order to calculate loads by applying the statistical method of Adjusted Maximum Likelihood Estimation (AMLE). We used approximately 30 measurements of each constituent at each site collected during October 2001 to September 2005 to calculate loads. In addition, as LOADEST requires at least 12 noncensored (above detection) values, it was necessary to set below-detection values equal to half the detection limit for NH_4^+, NO_2^-, and TDP when there were <12 noncensored values. When running LOADEST for PN, values reported by CBL were included with the data set from NWQL.

[10] LOADEST centers the Q and chemical concentration data to eliminate colinearity and automatically selects one of nine predefined regression models to fit the data, based on the Akaike Information Criterion. Model output presents the estimation error as the coefficient of variation (CV) of loads calculated for the modeled flow period. In addition, r^2 of the AMLE, residuals data, and the serial correlation of residuals are output to verify the validity of the model and to confirm that the data are normally distributed.

[11] Yields were calculated by dividing total Q (m^3 t^{-1}) or constituent load (mass t^{-1}) for a flow period by watershed area (m^2). Water yield is presented as mm water t^{-1} for each basin, and constituent yield is presented as mmol m^{-2} t^{-1}.

4. Results

4.1. Nutrient Concentrations

[12] Water discharge is highly seasonal in the Yukon basin, with peak flow on the YR and PR occurring mid to late June. For YR and PR during 2001–2005, 34–51% of annual Q occurred during spring. Discharge decreases through summer into fall, and reaches base flow in late winter. On the basis of this hydrology, the following seasonal flow periods were assigned: spring (May 1 to June 30), summer-autumn (July 1 to October 31), and winter (November 1 to April 30). Average seasonal concentrations of [NH_4^+ + DON], [NO_2^-+ NO_3^-], [PN], and [TP] from 2001–2005 are listed in Table 2. Estimated concentrations were treated as actual values for these calculations, resulting in some average concentrations that were below detection limits. [NH_4^+] is not included in Table 2, as it was below detection for most of the year at all stations. Thus [NH_4^+ + DON] is essentially [DON] in most cases.

[13] [NH_4^+ + DON] ranged from below detection (<0.10 mg N L^{-1}) to 0.66 mg N L^{-1}, with the greatest concentration at PR. The greatest seasonal concentrations for all stations occurred in the spring, while the lowest concentrations occurred in winter (except at YRP). In all seasons, [NH_4^+ + DON] increased going down river. [NO_2^-] was mainly below or near detection levels (<0.002 mg N L^{-1}) for all stations and seasons, with no seasonal or longitudinal pattern. [NO_2^- + NO_3^-] ranged from below detection (<0.022 mg N L^{-1}) to 0.217 mg N L^{-1}, with the highest concentration found at PR. Greatest [NO_2^- + NO_3^-] were measured at all stations in winter. Spring and summer-autumn concentrations of [NO_2^- + NO_3^-] were similar among the sites, and were approximately 2–7 times lower than those found under ice. The greatest spring and summer-autumn concentrations were found in the TR. [NO_2^-+ NO_3^-] increased going down river in all seasons.

[14] PN concentrations ranged from below detection (<0.02 mg N L^{-1}) to 0.820 mg N L^{-1}, with the greatest

Table 2. Average Measured Seasonal Concentrations, 2001–05, ± Standard Error

Season	NH_4^+ + DON mg N L^{-1}	n	NO_2^- + NO_3^- mg N L^{-1}	n	PN mg N L^{-1}	n	Total P mg P L^{-1}	n
Yukon River at Eagle								
Spring	0.20 ± 0.04	12	0.034 ± 0.003	12	0.28 ± 0.05	12	0.593 ± 0.111	12
Summer-Autumn	(0.12 ± 0.01)[a]	18	0.033 ± 0.003	18	0.19 ± 0.03	17	0.559 ± 0.092	17
Winter	(0.06 ± 0.03)[a]	5	0.091 ± 0.004	5	<0.02	5	0.004 ± 0.000	5
Porcupine River Near Fort Yukon								
Spring	0.36 ± .03	12	(0.027 ± 0.003)[a]	12	0.21 ± 0.03	12	0.105 ± 0.016	12
Summer-Autumn	0.23 ± .01	17	(0.025 ± 0.004)[b]	17	(0.07 ± 0.01)[b]	16	0.027 ± 0.005	17
Winter	(0.06 ± .01)[a]	5	0.210 ± 0.003	5	<0.02	5	0.003 ± 0.000	5
Yukon River Near Stevens Village								
Spring	0.29 ± 0.04	12	0.038 ± 0.004	12	0.35 ± 0.05	16	0.449 ± 0.045	12
Summer-Autumn	0.14 ± 0.01	18	0.042 ± 0.003	18	0.17 ± 0.02	18	0.359 ± 0.029	18
Winter	0.07 ± 0.01	5	0.098 ± 0.005	4	<0.02	5	0.012 ± 0.003	5
Tanana River at Nenana								
Spring	(0.15 ± 0.02)[b]	13	0.103 ± 0.011	13	0.29 ± 0.03	16	0.829 ± 0.142	13
Summer-Autumn	(0.013 ± 0.03)[c]	17	0.099 ± 0.007	17	0.29 ± 0.05	17	0.933 ± 0.124	17
Winter	0.10 ± 0.01	5	0.176 ± 0.005	5	<0.02	5	0.028 ± 0.001	5
Yukon River at Pilot Station								
Spring	0.32 ± 0.03	10	0.073 ± 0.007	10	0.34 ± 0.04	18	0.359 ± 0.045	10
Summer-Autumn	0.15 ± 0.01	18	0.081 ± 0.004	18	0.24 ± 0.02	18	0.298 ± 0.028	19
Winter	0.18 ± 0.01	5	0.188 ± 0.009	4	(0.03 ± 0.01)[a]	5	0.024 ± 0.001	5

[a]Average includes one sample below detection that was set to half the detection limit.
[b]Average includes two samples below detection that were set to half the detection limit.
[c]Average includes four samples below detection that were set to half the detection limit.

concentration at YRS. The greatest concentrations were in spring, except for TR, where spring and summer-autumn had similar values. The lowest concentrations were in winter. There was little change in PN concentration moving down river.

[15] TP concentrations ranged from 0.003 to 2.13 mg P L^{-1}, with the greatest concentration found at TR. Lowest concentrations were in winter and greatest concentrations were in spring, except at TR, where greater values occurred during summer-autumn. The PR had the lowest TP. In spring through summer-autumn, TP decreased moving down river, but it increased during winter. TDP concentrations ranged from below detection (typically <0.006 mg P L^{-1}) to 0.018 mg P L^{-1}. The highest values occurred in spring at all stations.

[16] It was not always possible to calculate PP (TP – TDP), owing to the values for TDP that were below detection. Where calculated, PP ranged from 0 to 2.12 mg P L^{-1}. The lowest values occurred in winter, when the suspended sediment load was low. Winter PP at YRP was 0.020 ± 0.001 (SE) mg P L^{-1}, n = 4. The highest concentrations were in spring and summer-autumn; in spring, PP at YRP was 0.348 ± 0.044 (SE) mg P L^{-1}, n = 10, and in summer-autumn, PP at YRP was 0.288 ± 0.030 (SE) mg P L^{-1}, n = 18.

[17] Ninety-three percent of samples from all stations had PO_4^{3-} concentrations below detection (<0.007 mg P L^{-1}), suggestive of the relatively pristine nature of the Yukon River basin.

4.2. Loads

4.2.1. Nitrogen

[18] An average of 120 Gg N a^{-1} discharged past YRP during 2001–2005 (Table 3). TDN comprised 50–62% of the TN load at all stations. Of the TDN load, the majority was DON, comprising 70–85% of TDN at all stations except TR, where DON comprised only 43% of TDN. $NH4^+$ loads were minor, contributing only 1–4% of the TN load. Seasonal and annual loads for each species at each station for 2001–2005 are listed in Table 4. Total N loads generally follow Q, with peak TN export occurring during spring, except at TR (Table 4). The same is true for NH_4^+ + DON and PN, although at YRP, the summer-autumn season has a slightly higher PN load than spring. For NO_2^-+ NO_3^-, summer-autumn loads were greatest at all stations except PR. The smallest loads of NH_4^+ + DON, PN, and TN occurred at all stations during low flow in winter.

4.2.2. Phosphorus

[19] An average of 56.3 Gg P a^{-1} discharged past YRP during 2001–2005 (Table 3). Nearly this entire load was PP, comprising >99% of the TP load at YRE, YRS, TR, and YRP, and 75% at PR. Assuming PO_4^{3-} concentrations to be one half the detection limit, LOADEST calculations confirmed that PO_4^{3-} could contribute no more than 1% of the TP load. As most of the TP was in the particulate fraction, it follows that most of the load occurred during spring, when sediment loads were highest (Table 4). The exceptions were YRE, where TP load was slightly higher in summer-autumn, and TR, which has substantial sediment loads during summer-autumn. Winter low-flow conditions, having low sediment load, produce very low TP loads at all stations.

4.3. Yields

4.3.1. Nitrogen

[20] Seasonal and annual nitrogen yields for 2001–2005 are shown in Table 5. Total N yield at YRP averaged 10.2 mmol m^{-2} a^{-1}, although the highest yield was at TR

Table 3. Mean Annual Loads for Water Years 2001–2005, With Coefficients of Variation (CV) of the LOADEST Results[a]

Site Name	NH_4^+, 10^9g a^{-1}	CV	NH_4^+ + DON, 10^9g a^{-1}	CV	NO_2^-, 10^9g a^{-1}	CV
Yukon River at Eagle	0.67	16.3%	12.0	12.1%	0.12	14.6%
Porcupine River near Fort Yukon	0.06	12.6%	3.2	5.9%	0.02	9.0%
Yukon River near Stevens Village	0.80	12.7%	21.6	8.1%	0.14	7.9%
Tanana River at Nenana	0.54	26.2%	3.2	13.7%	0.04	7.4%
Yukon River at Pilot Station	2.79	10.1%	54.8	7.1%	0.50	23.4%
Site Name	**NO_2^- + NO_3^-, 10^9g a^{-1}**	**CV**	**PN, 10^9g a^{-1}**	**CV**	**Total N, 10^9g a^{-1}**	
Yukon River at Eagle	3.2	8.8%	14.5	11.3%	29.7	
Porcupine River near Fort Yukon	0.5	23.9%	2.3	17.6%	6.0	
Yukon River near Stevens Village	5.2	20.2%	21.2	8.1%	48.0	
Tanana River at Nenana	3.0	7.0%	6.1	8.5%	12.3	
Yukon River at Pilot Station	19.6	6.0%	45.2	6.6%	119.6	
Site Name	**TDP, 10^9g a^{-1}**	**CV**	**PP, 10^9g a^{-1}**	**CV**	**TP, 10^9g a^{-1}**	**CV**
Yukon River at Eagle	0.30	9.5%	34.9	11.2%	34.6	10.8%
Porcupine River near Fort Yukon	0.12	10.5%	1.5	20.3%	2.0	20.8%
Yukon River near Stevens Village	0.52	7.1%	35.7	8.4%	35.4	6.9%
Tanana River at Nenana	0.16	20.4%	18.5	7.3%	18.5	7.1%
Yukon River at Pilot Station	2.01	8.2%	55.2	11.0%	56.3	9.6%

[a]Total N is the sum of NH_4^+ + DON, NO_2^- + NO_3^-, and PN.

(13.3 mmol m^{-2} a^{-1}), where the PN yield is substantially higher than any other station. Within the YR, annual yields of NH_4^+, NO_2^-, NO_2^- + NO_3^-, PN, and TN decreased between YRE and YRS, but increased between YRS and YRP. This suggests dilution by the PR, which was relatively N-poor for all N species except DON. In contrast, the TR was relatively N-rich, averaging not only the highest annual TN yield, but also the highest PN, NO_2^- + NO_3^-, and NH_4^+ yields (Table 5). Further, for each of these species, the seasonal yields at TR were almost always higher than every other station. For every station except TR, the greatest TN yields occurred in spring.

4.3.2. Phosphorus

[21] Total P yield at YRP averaged 2.18 mmol m^{-2} a^{-1}, smaller than the TP yield at every other station except PR (Table 5). The TR averaged the greatest annual TP yield

Table 4. Average Seasonal Loads, 2001–2005[a]

Season	NH_4^+	NH_4^+ + DON	NO_2^-	NO_2^- + NO_3^-	PN	TN	TDP	PP	TP
Yukon River at Eagle									
Spring	0.23	5.1	0.04	0.9	7.6	13.6	0.13	15.7	15.9
Summer-Autumn	0.27	4.5	0.05	1.2	6.5	12.2	0.11	19.0	18.4
Winter	0.17	2.2	0.03	1.0	0.2	3.4	0.05	0.05	0.08
Annual	0.67	11.8	0.12	3.1	14.3	29.2	0.29	34.8	34.4
Porcupine River Near Fort Yukon									
Spring	0.032	2.0	0.0097	0.22	1.9	4.1	0.089	1.3	1.7
Summer-Autumn	0.027	1.1	0.0068	0.13	0.4	1.6	0.028	0.2	0.2
Winter	0.006	0.09	0.0007	0.18	0.006	0.28	0.002	0.0006	0.003
Annual	0.065	3.19	0.0172	0.53	2.3	6.0	0.119	1.5	1.9
Yukon River Near Stevens Village									
Spring	0.36	11.6	0.059	1.7	13.0	26.3	0.32	18.7	18.7
Summer-Autumn	0.34	7.2	0.057	2.5	7.7	17.4	0.14	16.4	16.1
Winter	0.10	2.4	0.022	1.0	0.4	3.8	0.04	0.2	0.2
Annual	0.80	21.2	0.138	5.2	21.1	47.5	0.50	35.3	35.0
Tanana River at Nenana									
Spring	0.05	0.91	0.0097	0.62	2.17	3.7	0.049	5.7	5.7
Summer-Autumn	0.20	1.59	0.0210	1.44	3.90	6.9	0.094	12.4	12.4
Winter	0.30	0.68	0.0075	0.98	0.07	1.7	0.016	0.2	0.3
Annual	0.55	3.18	0.0382	3.04	6.14	12.4	0.159	18.3	18.4
Yukon River at Pilot Station									
Spring	1.04	27.3	0.20	5.7	21.4	54.4	1.0	27.5	28
Summer-Autumn	0.57	16.2	0.15	8.6	22.3	47.1	0.7	26.9	27.3
Winter	1.17	10.8	0.14	5.3	1.3	17.4	0.3	0.7	0.8
Annual	2.78	54.3	0.49	19.6	45.0	118.9	2.0	55.1	56.1

[a]Unit is gigagrams. TN is the sum of NH_4^+ + DON, NO_2^- + NO_3^-, and PN. Seasons are as follows: spring, 1 May to 30 June; summer-autumn, 1 July to 31 October; winter, 1 November to 30 April. Summer-autumn 2005 uses estimated flow for 1–31 October 2005.

Table 5. Average Seasonal and Annual Yields, 2001–2005[a]

Season	NH_4^+	NH_4^+ + DON	NO_2^-	NO_2^- + NO_3^-	PN	TN	TDP	PP	TP	Water Yield
					Yukon River at Eagle					
Spring	0.06	1.24	0.010	0.22	1.84	3.30	0.014	1.73	1.75	86
Summer-Autumn	0.06	1.10	0.011	0.30	1.59	2.99	0.012	2.09	2.02	128
Winter	0.04	0.52	0.008	0.24	0.06	0.82	0.006	0.01	0.01	42
Annual	0.16	2.86	0.029	0.76	3.49	7.11	0.032	3.83	3.78	256
					Porcupine River Near Fort Yukon					
Spring	0.03	1.85	0.009	0.21	1.74	3.80	0.038	0.53	0.74	71
Summer-Autumn	0.02	1.07	0.006	0.12	0.38	1.57	0.012	0.09	0.10	59
Winter	0.01	0.08	0.001	0.17	0.01	0.26	0.001	0.00	0.001	9
Annual	0.06	3.00	0.016	0.50	2.13	5.63	0.051	0.62	0.84	139
					Yukon River Near Stevens Village					
Spring	0.05	1.63	0.008	0.24	1.82	3.69	0.021	1.19	1.19	81
Summer-Autumn	0.05	1.01	0.008	0.36	1.08	2.45	0.009	1.04	1.02	97
Winter	0.01	0.34	0.003	0.14	0.06	0.54	0.003	0.01	0.02	30
Annual	0.11	2.98	0.019	0.74	2.96	6.68	0.033	2.24	2.23	208
					Tanana River at Nenana					
Spring	0.06	0.98	0.010	0.66	2.34	3.98	0.024	2.80	2.78	93
Summer-Autumn	0.17	1.71	0.023	1.55	4.19	7.45	0.046	6.04	6.06	206
Winter	0.37	0.73	0.008	1.06	0.08	1.87	0.008	0.12	0.13	57
Annual	0.60	3.42	0.041	3.27	6.61	13.30	0.078	8.96	8.97	356
					Yukon River at Pilot Station					
Spring	0.09	2.34	0.017	0.49	1.84	4.67	0.040	1.07	1.09	93
Summer-Autumn	0.05	1.39	0.013	0.74	1.92	4.05	0.030	1.04	1.06	121
Winter	0.10	0.92	0.012	0.45	0.12	1.49	0.010	0.03	0.03	37
Annual	0.24	4.65	0.042	1.68	3.88	10.21	0.080	2.14	2.18	251

[a]Constituent yields are in mmol m^{-2}. Water yield is in millimeters. Seasons are as follows: spring, 1 May to 30 June; summer-autumn, 1 July to 31 October; winter, 1 November to 30 April. Summer-autumn 2005 uses estimated flow for 1–31 October 2005.

(8.97 mmol m^{-2} a^{-1}), more than fourfold greater than the yield at YRP. This is consistent with the high sediment load in TR. Despite the high yield in TR, TP and PP yields decreased moving down river from YRE to YRP. The TDP yield, while a small fraction of TP, increased moving down river from YRE to YRP. The smallest annual TP yield was at PR, although the TDP yield at PR was greater than both YRE and YRS. Seasonally, the TP yields between spring and summer-autumn were similar at YRE, YRS, and YRP.

4.4. Nitrogen Isotopes

[22] The $\delta^{15}N$ of suspended sediment ranged from −4.1 to +9.4‰ during 2001–2005 [*Schuster*, 2003] (http://ak.water.usgs.gov/yukon/). There was no significant difference in values between stations. The $\delta^{15}N$-NO_3^- values in 2005 ranged from +0.44 to +6.09‰ across all stations (data not shown). There was a trend of ^{15}N depletion moving down river, with $\delta^{15}N$- NO_3^- values at YRE ranging from 3.70 to 6.09‰ and $\delta^{15}N$- NO_3^-values at YRP ranging from 0.44 to 2.24‰.

5. Discussion

5.1. N Yields Versus Water Yield

[23] Valuable information on nutrient source areas and export may be gained by comparing nutrient yields to water yield. By normalizing constituent yield to water yield, differences in the export of nutrients from the subbasins can be evaluated within a common hydrologic framework. Five-annum seasonal average DIN, DON, PN, and TN yields are shown in Figure 2. DIN yield increased linearly with water yield among the YR subbasins (spring: r^2 = 0.69; summer-autumn: r^2 = 0.87; winter: r^2 = 0.60) (Figure 2a). While the slope of DIN yield versus water yield was steepest during winter owing to high DIN concentration in base flow, DIN yield versus water yield was generally similar throughout the basin, during all seasons.

[24] Winter base flow DON concentrations were fairly constant at all stations, resulting in a nearly linear relationship between DON yield and water yield during winter (Figure 2b). This suggests that DON yield was proportional to areal groundwater discharge to the rivers. Water yield was fairly consistent throughout the basin during spring, while DON was highly variable, with the highest yields occurring at YRP and PR and the lowest at TR. This pattern was similar to that of DOC [*Striegl et al.*, 2007]. DON yields were greatest from the wetland-influenced portions of the basin (YRP and PR), and least from the subbasins having a higher proportion of bare rock, ice and snowfields, and forested uplands (TR and YRE) [*Brabets et al.*, 2000].

[25] Contrary to spring, summer-autumn DON yields had a fairly small range, while water yield was highly variable among subbasins (Figure 2b). This might suggest that sources of DON available for hydrologic export were limited throughout the basin during summer-autumn. However, when the summer-autumn data are plotted for years 2001–2005 (Figure 3), it was evident that DON export was primarily water limited, not N limited. Similar DON yields among stations resulted from low water yields at PR, where DON concentrations were relatively high, and high water yields at TR, where DON concentrations were relatively low. Figure 3 indicates that, with the possible exception of TR, any changes in water yield that may occur in the YR

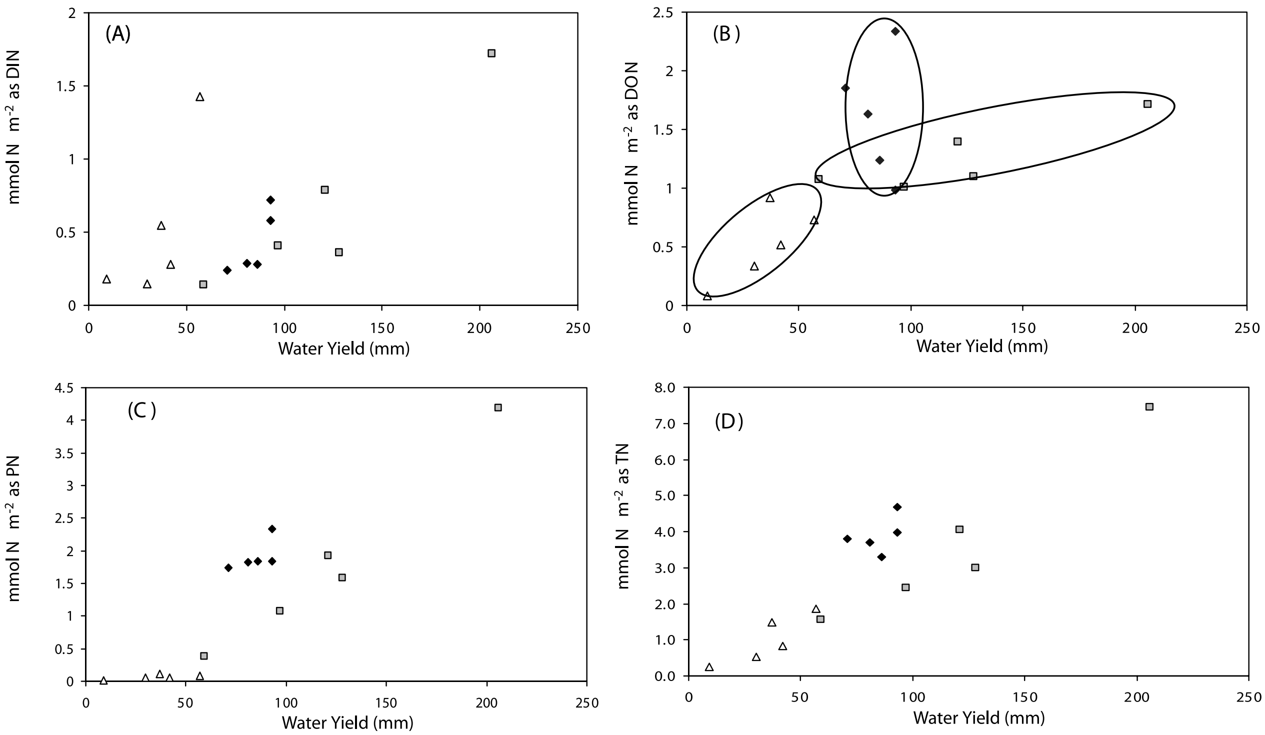

Figure 2. Seasonal N yield versus seasonal water yield, 2001–2005 mean, for the five measurement stations. (a) DIN, (b) DON, (c) PN, and (d) TN. Black diamonds, spring; gray squares, summer-autumn; white triangles, winter.

basin will likely result in proportional changes in DON yield.

[26] PN yields (Figure 2c) generally increased with water yield during summer-autumn, reflecting bank erosion as the primary source in most basins. The highest PN yields occurred in the TR basin (Table 5), coincident with large suspended sediment concentrations (NWIS web data). PN yields were smallest at PR throughout the year and were negligible during winter at all stations.

[27] TN yields (Figure 2d) generally increased with water yield for all seasons across all stations. This relationship is consistent with that of *Lewis* [2002], who found a strong correlation between TN yields and water yield for 19 minimally disturbed watersheds across the US, as well as for 25 undisturbed watersheds in the tropics [*Lewis et al.*, 1999]. Our data extend this relationship to undisturbed subarctic watersheds. The slope (0.89, r^2 = 0.70) of the log-log relationship between TN (kg ha^{-1} a^{-1}) and water yield (mm a^{-1}) is nearly identical to that determined by *Lewis* [2002] for the temperate watersheds (slope = 0.87, r^2 = 0.91).

5.2. P Yields Versus Water Yield

[28] Five-annum averages of seasonal P yields of TDP, PP, and TP are shown in Figure 4. TDP yield increased linearly with water yield during summer-autumn and winter (Figure 4a). Although water yield is similar from all watersheds during spring, TDP yield is greatest from wetland influenced watersheds (PR and YRP) and least from TR. Spring values for 2001–2005 (Figure 5) support this observation with slopes of TDP yield versus water yield increasing from watersheds influenced by glaciers and mountains to watersheds influenced by wetlands.

[29] PP and TP yields also increased linearly with water yield for spring and summer-autumn for all stations and were almost identical because of the predominance of PP in the overall phosphorus budget (Figures 4b and 4c). As with PN, this reflects erosion as the primary source of PP, and therefore TP, in the basin. Winter particulate yields did not increase with water yield, because of low suspended solids concentrations.

5.3. Nutrient Cycling

[30] While a number of studies of nutrients in large arctic/subarctic rivers have been published [*Brunskill et al.*, 1975;

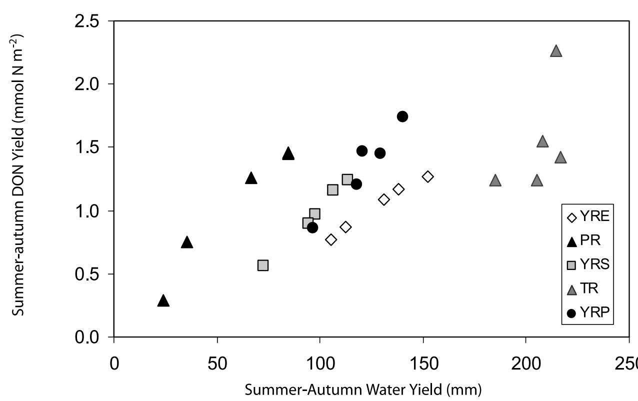

Figure 3. Summer-autumn DON yield versus summer-autumn water yield, 2001–2005, for the five measurement stations.

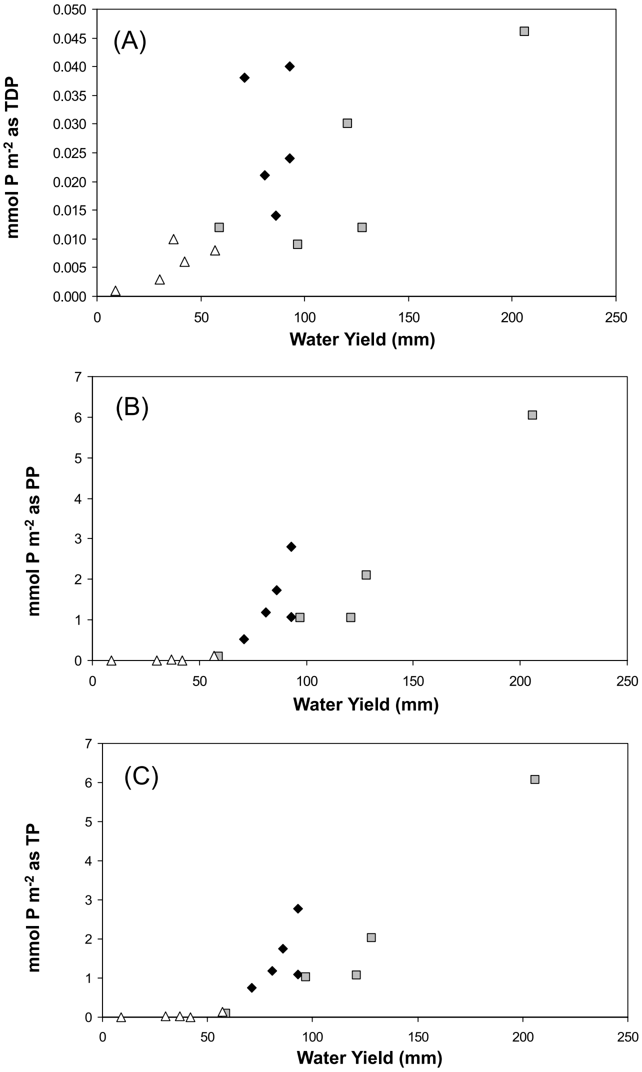

Figure 4. Seasonal P yield versus seasonal water yield, 2001–2005 mean, for the five measurement stations. (a) TDP, (b) PP, and (c) TP. Black diamonds, spring; gray squares, summer-autumn; white triangles, winter.

Telang et al., 1982; *Smirnov*, 1994; *Gordeev and Tsirkunov*, 1998; *Lara et al.*, 1998; *Gordeev*, 2000; *Lobbes et al.*, 2000; *Holmes et al.*, 2001; *Guo et al.*, 2004; *Gebhardt et al.*, 2004], none of these characterize multiple years of seasonal concentration, load, and yield data at multiple locations in a large river basin. Further, uncertainties in the early Russian data have been called into question [*Holmes et al.*, 2000], placing increased importance on comprehensive, long-term, large-scale studies, particularly if we are to adequately assess impacts of climate change.

5.3.1. Nitrogen

[31] The source of most N in the Yukon River, be it DON, DIN, or PN, is terrestrial. DON comes largely from runoff, with a minor contribution from groundwater (~7.5% at YRP, assuming winter base flow is essentially groundwater). This terrestrial linkage is in agreement with others [*Lara et al.*, 1998; *Lobbes et al.*, 2000; *Dittmar and Kattner*, 2003], who conclude that DOM is largely recalcitrant, and not derived from autochthonous sources. C/N ratios support this. DOC/DON ratios ranged from 28 to 42 (Table 6), with little change seasonally or longitudinally. These values are consistent with soil-derived OM and are similar to values found in other northern watersheds [*Telang et al.*, 1991; *Lara et al.*, 1998; *Lobbes et al.*, 2000]. DON yield was highly correlated with DOC yield across all subbasins and seasons (r^2 = 0.96, n = 20, data not shown). As with DOC [*Striegl et al.*, 2005, 2007], DON appears to undergo little within-river biological alteration. Arctic rivers tend to have low primary production [*Dittmar and Kattner*, 2003; *Cauwet and Sidorov*, 1996; *Sorokin and Sorokin*, 1996] and negligible phytoplankton and living bacterial biomass, with most organic matter composed of soil-derived material [*Dittmar and Kattner*, 2003]. Low light conditions limit primary production in the Yukon River downstream of the White River (secchi depths ~0.02 m).

[32] Particulate N is largely organic in the YR. In 2005, PON averaged 85% of the PN pool at YRE, YRS, and YRP (data not shown). This pool consisted mostly of terrestrial detritus, although some PN could be in the form of ammonium adsorbed to clay minerals [*Ittekkot and Zhang*, 1989]. POC/PN ratios (Table 6) showed very little longitudinal or seasonal change among the YR stations, averaging 17.7 annually and ranging from 11 to 21. This average was slightly higher than the average POC/PON ratios of 11.1 in Russian rivers [*Lobbes et al.*, 2000], and 10.5 for world rivers [*Ittekkot and Zhang*, 1989], but again indicates limited biogeochemical alteration of the terrestrial OM source [*Guo and Macdonald*, 2006; *Gebhardt et al.*, 2004; *Dittmar and Kattner*, 2003].

[33] Nitrate also has largely terrestrial sources, including mineralized soil OM and groundwater, which is estimated to contribute 37% of the annual NO_3^- load at YRP. The δ^{15}N-NO_3^- becomes depleted by about 3.9‰ from YRE to YRP. Although this suggests within-river nitrification as another possible source of NO_3^-, long distances between sampling sites and lack of process-based information preclude drawing such conclusions. The TR basin was the largest source of NO_3^- to the YR, with concentrations during spring and summer-autumn roughly three times greater than those of the other subbasins except YRP, and yields that were higher than all other locations in all seasons (Tables 2 and 5).

[34] Terrestrial sources of N change seasonally. In the spring flush, N is derived from a combination of plant

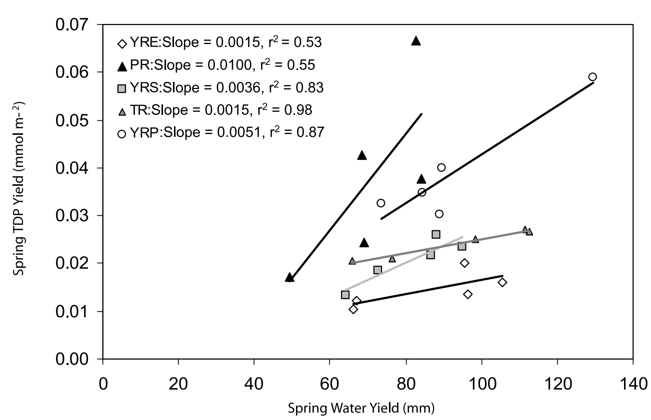

Figure 5. Spring TDP yield versus spring water yield, 2001–2005, for the five measurement stations.

Table 6. Seasonal and Annual C/N and N/P Ratios for the Five Measurement Stations, 2001–2005

Season	DOC/DON	POC/PN	TDN/TDP
Yukon River at Eagle			
Spring	42.3	19.5	47.9
Summer-Autumn	35.9	18.6	58.3
Winter	(32.7)[a]	11.0	70.3
Annual	(37.8)[a]	17.8	56.4
Porcupine River Near Fort Yukon			
Spring	36.4	12.2	39.3
Summer-Autumn	36.4	14.5	64.2
Winter	36.2	5.0	100.1
Annual	36.4	12.2	60.6
Yukon River Near Stevens Village			
Spring	36.6	16.0	42.7
Summer-Autumn	34.6	20.5	70.7
Winter	29.6	19.7	62.0
Annual	34.6	18.8	59.1
Tanana River at Nenana			
Spring	35.1	13.8	43.6
Summer-Autumn	30.6	15.6	63.1
Winter	27.9	28.0	120.3
Annual	31.9	16.7	64.6
Yukon River at Pilot Station			
Spring	35.1	15.1	34.7
Summer-Autumn	36.9	17.9	34.4
Winter	36.1	17.1	151.5
Annual	36.2	16.6	49.1

[a]Excludes DOC/DON value of 425.0 on 23 March 2001.

material on the land surface and erosion of the riverbanks. In summer-autumn, as the soil active layer deepens, more N is likely received from a leaching of these deeper soil horizons. In winter, with the freezing of the land and headwater streams, groundwater becomes an important source. Despite the changing sources, there appears to be little cycling of N within the YR, at least during the open water season. This is in agreement with the conclusions of *Green et al.* [2004], who estimated a 60–80% TN transport efficiency for the Yukon basin.

5.3.2. Phosphorus

[35] Unlike N, which has no major mineral source, most P is derived from chemical and physical rock weathering [*Gardner*, 1990; *Schlesinger*, 1991]. PP yield is very highly correlated with suspended sediment yield across all subbasins for 2001–2005 ($r^2 = 0.94$, n = 25, data not shown) and most P in the YR is particulate during the open water season (Table 2). Most of this PP is probably derived from surface runoff and bank erosion. In winter, TDP was a larger fraction of TP, but PO_4^{-3} was below detection (<0.007 mg P L^{-1}) for virtually all samples at all sites. PP and TP yields were greatest at TR, followed by YRE (Table 5). This was expected, given the weathering source and the higher percentage of these subbasins that are in mountainous areas covered by rock and ice.

[36] TDN/TDP ratios (Table 6) were far above the Redfield ratio of 16:1, indicating that the YR is P-limited. The TDN/TDP ratio did not appreciably change going down river, suggesting little within river transformation. Winter had the highest TDN/TDP at all sites except YRS, most likely the result of high [NO_3^-] in groundwater inflow (Table 2).

[37] There appears to be little turnover of P in the YR, compared to the size of the TP pool. The vast majority of P was particulate, which is mostly unreactive in transport. This agrees with other studies of arctic/subarctic rivers [*Lobbes et al.*, 2000; *Dittmar and Kattner*, 2003], and indicates that most P appears to be exported from the Yukon basin with little chemical or biological alteration. P yields correlated with water yield. This is in agreement with *Behrendt and Opitz* [2000], who found that water yield explained 80% of the variance in P retention in 100 river basins in Europe.

5.4. Climate Change Implications

[38] There is already evidence of thawing permafrost in the Yukon basin [*Hinzman et al.*, 2005; *Jorgenson et al.*, 2006]. If predicted temperature increases of >5°C in arctic regions are correct [*Symon et al.*, 2005], this can only continue. Thawing of the vast stores of permafrost in the basin will likely mobilize nutrients to new biomass and/or to downstream export. Consequently, terrestrial to aquatic fluxes of nutrients may increase with climate warming [*Hobbie et al.*, 1999; *Guo et al.*, 2004]. However, a downward shift in the relationship between DOC yield and water yield during summer through autumn at YRP has occurred in recent decades [*Striegl et al.*, 2005, 2007]. A similar shift has likely occurred between DON yield and water yield at YRP and at other locations in the basin. Recent warming of the basin has yet to result in significant change in annual water discharge from Yukon River subbasins, but has resulted in shifts in the timing and source of water discharge that may ultimately increase DIN and DIC export and decrease DON and DOC export [*Walvoord and Striegl*, 2007]. Regardless of how total annual discharge may change in the subbasins, positive relationships between nutrient yield and water yield over the current range of basin hydrologic conditions suggest that any climate related changes in water discharge will lead to proportional changes in nutrient export.

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