Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005

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[1] Loads and yields of dissolved and particulate organic and inorganic carbon (DOC, POC, DIC, PIC) were measured and modeled at three locations on the Yukon River (YR) and on the Tanana and Porcupine rivers (TR, PR) in Alaska during 2001–2005. Total YR carbon export averaged 7.8 Tg C yr^{-1}, 30% as OC and 70% as IC. Total C yields (0.39–1.03 mol C m^{-2} yr^{-1}) were proportional to water yields (139–356 mm yr^{-1}; $r^2 = 0.84$) at all locations. Summer DOC had an aged component (fraction modern (FM) = 0.94–0.97), except in the permafrost wetland-dominated PR, where DOC was modern. POC had FM = 0.63–0.70. DOC had high concentration, high aromaticity, and high hydrophobic content in spring and low concentration, low aromaticity, and high hydrophilic content in winter. About half of annual DOC export occurred during spring. DIC concentration and isotopic composition were strongly affected by dissolution of suspended carbonates in glacial meltwater during summer.

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1. Introduction

[2] Hydrology is changing across subarctic and arctic regions. Permafrost degradation, construction of hydroelectric dams, and changing climate have resulted in changed amount and/or timing of water discharge (Q) in recent decades [*Peterson et al.*, 2002; *Ye et al.*, 2003; *McClelland et al.*, 2004, 2006; *Dery and Wood*, 2005]. Coincident changes in the ecology and biogeochemistry of northern watersheds [*Serreze et al.*, 2000; *Chapin et al.*, 2005; *Hinzman et al.*, 2005] have altered the relationship between Q and carbon (C) transport in the Yukon [*Striegl et al.*, 2005] and possibly in other northern river basins. However, there are few historical water chemistry data to confirm this. Until 2001, data on flow and C chemistry of the Yukon River (YR) and its tributaries were mostly of a short term and sporadic nature [*Kempe*, 1982; *Telang et al.*, 1991; *Brabets et al.*, 2000; U.S. Geological Survey National Water Information System, Water Data for the Nation, http://waterdata.usgs.gov/nwis]. During 2001–2005, the National Stream Quality Accounting Network, the Alaska Water Science Center, and the National Research Program of the United States Geological Survey (USGS) combined efforts to conduct a systematic study of Q and water chemistry at three locations on the YR and two of its major tributaries, the Tanana River (TR) and the Porcupine River (PR) [*Schuster*, 2003; http://ak.water.usgs.gov/yukon/]. This paper focuses on dissolved and particulate C measurements made during the Yukon basin study. It documents Q and C concentration, export, and yield and C composition at the five locations. Additionally, the three YR sites allow for interpretation of the relative importance of within-river cycling of organic and inorganic C (OC, IC). Although such interpretations are limited by the large size of the basin and the long distances between sampling locations, they provide a platform for hypothesis formulation and for more detailed biogeochemical assessment of the largest unregulated river in the United States.

2. Study Area

[3] The 3340 km Yukon River drains 853,300 km^2 of northwest Canada and Alaska, United States, discharging to Norton Sound on the Bering Sea (Figure 1). The basin is mostly wilderness, with ~115,000 of its <130,000 inhabitants residing in or near Fairbanks, AK and Whitehorse, Yukon Territory (YT). Precipitation varies across the basin, ranging from ~250 mm yr^{-1} in the upper Porcupine basin, to ~280 mm yr^{-1} in other areas of interior AK and YT, ~400 mm yr^{-1} near the Yukon Delta and the Bering Sea, and >1500 mm yr^{-1} in headwater areas of the St. Elias and Coast Mountains. Permafrost underlies much of the basin and thawing of permafrost is widespread, causing deepening of the soil active layer, slope and bank erosion, and thermokarst formation [*Osterkamp and Romanovsky*, 1999; *Jorgenson et al.*, 2001]. Basin lowlands include black spruce forest, extensive areas of wetlands and lakes known as ''flats'', shrublands, and tundra. Vegetated uplands include spruce, pine, aspen, and birch forest, shrublands and tundra. There are extensive ice and snow fields in headwater areas of Alaska Range and the Wrangell, St. Elias, and Coast Mountains [*Brabets et al.*, 2000].

[4] Tributaries to the YR can be categorized into three general types with respect to C. Meltwater-dominated

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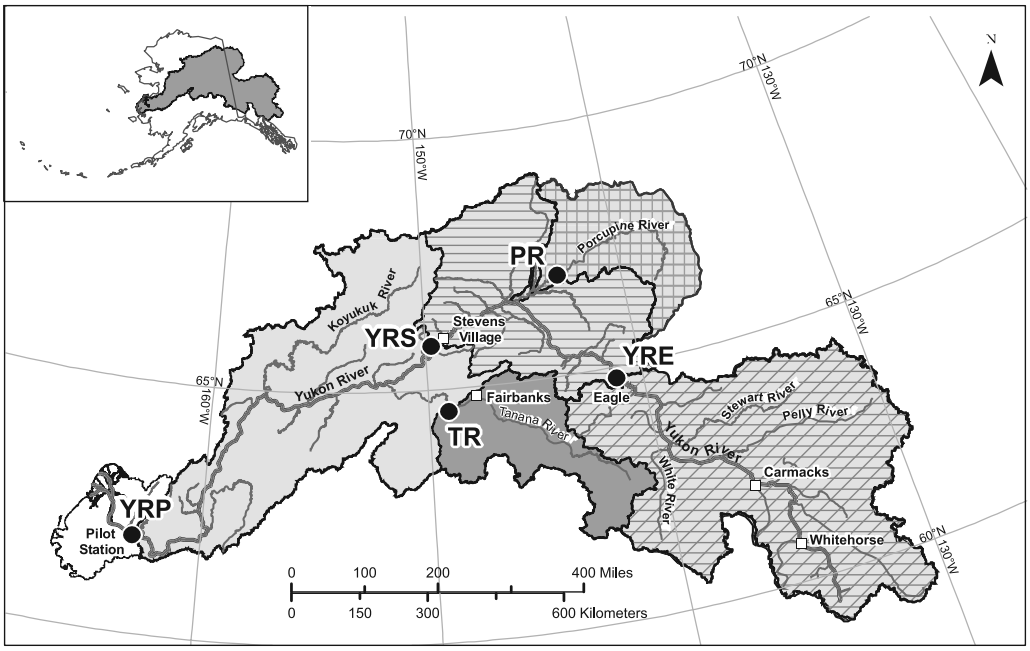

Figure 1. Map of the Yukon River basin showing measurement station locations and watershed boundaries. YRE, Yukon River at Eagle; PR, Porcupine River; YRS, Yukon River near Stevens Village; TR, Tanana River at Nenana; YRP, Yukon River at Pilot Station.

rivers, including the TR, have high sediment load, potentially high particulate and dissolved IC (PIC, DIC), and low dissolved OC (DOC). They originate from perennial ice and snow fields and alpine glaciers and may carry large amounts of unweathered glacial flour, including carbonates. Blackwater-dominated rivers, including the PR, are highly colored with DOC and originate from permafrost wetlands and other peat-dominated lands. They typically have high DOC, low DIC and low sediment concentration. Clear water rivers typically originate from zones of groundwater discharge, have low DOC and sediment concentration and can have high DIC concentration. Although clear water streams exhibit a unique C chemistry, they tend to be smaller than, and drain to, the other tributary types.

[5] The Tanana and Porcupine watersheds are thought to be particularly sensitive to climate warming, but for different reasons. The Tanana and similar watersheds originating in mountainous terrain in the south central and southeastern portions of the Yukon basin are experiencing extensive melting of alpine glaciers and perennial snow fields. The Porcupine and many other low-lying watersheds in the Yukon basin are experiencing progressive permafrost degradation, thermokarst formation, and drying in locations where surface waters perched on thawing permafrost have drained [*Jorgenson et al.*, 2001; *Yoshikawa and Hinzman*, 2003; *Riordan et al.*, 2006].

[6] The YR integrates drainage from throughout the basin, receiving a mix of water from all tributary types. It flows clear (Secchi transparency > 1 m) from its headwaters in British Columbia to its confluence with the White River (WR; km 815), after which it is sediment laden, having a transparency of ~0.02 m. Mean cross-sectional velocities can range from <0.12 m s^{-1} under ice to >3.0 m s^{-1} during high flow. Ice cover is usually from November into May, averaging ~200 days yr^{-1}. Late summer water temperature can reach 20°C. The river is a major waterway for salmon migration from the Bering Sea, but provides limited habitat for benthic or primary production in AK portions of the river.

3. Methods

3.1. Data Collection

[7] USGS established five fixed stations in the Yukon basin, AK to continuously measure Q and to systematically measure water and sediment chemistry during 2001–2005 (Figure 1 and Table 1). Yukon River at Eagle (YRE; km 1043) receives a mix of waters from snow and ice fields, headwater lakes, and boreal forest. Porcupine River near Fort Yukon (PR), located 201 km upstream of the confluence with YR (km 1450), is a high DOC river receiving black water drainage. Yukon River near Stevens Village (YRS; km 1744) includes drainage from PR and from the 35,000 km^2 Yukon Flats. The Tanana River near Nenana (TR), 286 km upstream of the confluence with YR (km 1973), receives sediment-laden meltwater from the Alaska Range and drainage from extensive boreal forest and the Fairbanks area. Yukon River at Pilot Station (YRP; km 3137) receives drainage from the entire Yukon basin above the Yukon Delta and is the furthest downstream location where the river is contained in a single channel and is unaffected by tidal fluctuation. Station descriptions and water quantity and quality data for the five fixed stations are accessible at http://waterdata.usgs.gov/NWIS and http://ak.water.usgs.gov/yukon.

[8] The sampling objective was to characterize all flow conditions at all sites over the 5-year sampling period using USGS equal discharge increment (EDI) sampling protocol (http://pubs.usgs.gov/twri/). Samples were collected at approximately 3 week intervals from ice melt through

Table 1. Station Name, Location, and Water Discharge at the Five Measurement Stations for 2001–2005 and Mean Annual, Peak, and Low Q for the Period of River Flow Record

Station Name	USGS Station Number	Latitude, °N, Longitude, °W (NAD 83)	Drainage Area, km^2	Elevation, m	Annual Q, km^3 yr^{-1}					Period of Record	Mean Annual Q, km^3 yr^{-1}	Peak Q, m^3 s^{-1}	Low Q, m^3 s^{-1}
					2001	2002	2003	2004	2005				
Yukon River at Eagle	15356000	64°47′22″, 141°47′22″	294,000	259	91.1	74.5	65.4	71.0	79.1	1951–2005	75.1	15,400 (12 Jun 1964)	204 (Feb 1951)
Porcupine River near Fort Yukon	15389000	66°59′26″, 143°08′16″	76,400	158	10.8	12.1	11.1	9.30	9.52	1965–1978, 2001–2005	12.4	8,470 (24 May 1973)	0 (Mar 1966, Mar 1967)
Yukon River near Stevens Village	15453500	65°52′32″, 149°43′04″	508,400	73	123	108	98.9	96.6	108	1977–2005	106	26,500 (15 Jun 1964)	396 (Apr 1997)
Tanana River at Nenana	15515500	64°33′55″, 149°05′30″	66,300	103	23.3	23.8	22.4	24.1	24.7	1963–2005	21.8	5,270 (18 Aug 1967)	113 (Mar 1974)
Yukon River at Pilot Station	15565447	61°56′04″, 162°52′50″	831,400	6	223	188	225	190	227	1976–1995, 2001–2005	205	35,100 (16 May 2005)	991 (Feb–Mar 1984)

September. One sample was collected each year in March to characterize winter base flow. Water discharge measurements were made before each EDI sample was collected. Additional samples to characterize DOC chemistry and specific ultraviolet absorbance (SUVA), dissolved carbon dioxide [CO_2], [DIC], and $\delta^{13}C$ and fraction modern (FM) of ^{14}C in carbon species were collected from just beneath the water surface at the center of flow [*Schuster*, 2003; *Striegl et al.*, 2005]. During the summers of 2003 (YRS) and 2004 (YRE, YRP, and YR at Carmacks, YT), more frequent samples were collected to characterize temporal variability of DIC, and $\delta^{13}C$-DIC. Carmacks is upstream of the White River, the major source of PIC to the YR.

[9] DOC was chromatographically fractionated using XAD resins into hydrophobic organic acid (HPOA), transphilic acid (TPIA) and hydrophilic fractions (HPI) [*Aiken et al.*, 1992]. The carbonate content of suspended sediment was determined by X-ray diffraction of aliquots of suspended sediment [*Eberl*, 2004]. PIC was calculated as the product of the EDI sediment concentration and measured carbonate content of the suspended sediment. Aliquots of DOC were incubated for four weeks in the laboratory at 20°C to estimate potential within-river DOC mineralization [*Kalbitz et al.*, 2003].

3.2. Loads and Yields

[10] River C loads (mass C t^{-1}) were calculated from continuous Q data and water and suspended sediment chemistry measurements using the FORTRAN Load Estimator (LOADEST) program [*Runkel et al.*, 2004]. The model requires at least 12 direct measurements of chemistry over a wide range of flow conditions to calculate loads by applying the method of adjusted maximum likelihood estimation (AMLE). We used 53 measurements at YRE, 34 at PR, 41 at YRS, 38 at TR, and 43 at YRP, collected during October 2000 to September 2005. LOADEST centers Q and chemical concentration data to eliminate colinearity and automatically selects one of nine predefined regression models to fit the data. Model output lists the coefficient of variation of calculated loads for the modeled flow period, the r^2 of the AMLE, residuals data, and the serial correlation of residuals to quantify estimation error and to confirm normal distribution of the data.

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

4. Results

4.1. Water Discharge (Q)

[12] Water discharge is highly seasonal in the Yukon basin, with peak Q on the YR and PR occurring mid to late June, tapering through fall and reaching low flow in late winter (Figure 2). Smaller streams and rivers within subbasins may freeze solid in winter, depending on local groundwater conditions. For YR and PR, 34–51% of annual Q occurred during spring. The TR and streams dominated by glacial meltwater and overflow of alpine lakes typically peak during summer, usually in mid to late July (Figure 2) [*Brabets et al.*, 2000]. Average annual Q at YRP during 2001–2005 was 211 km^3, within 3% of the mean for 25 years of record. Average annual Q at PR was ~15% less

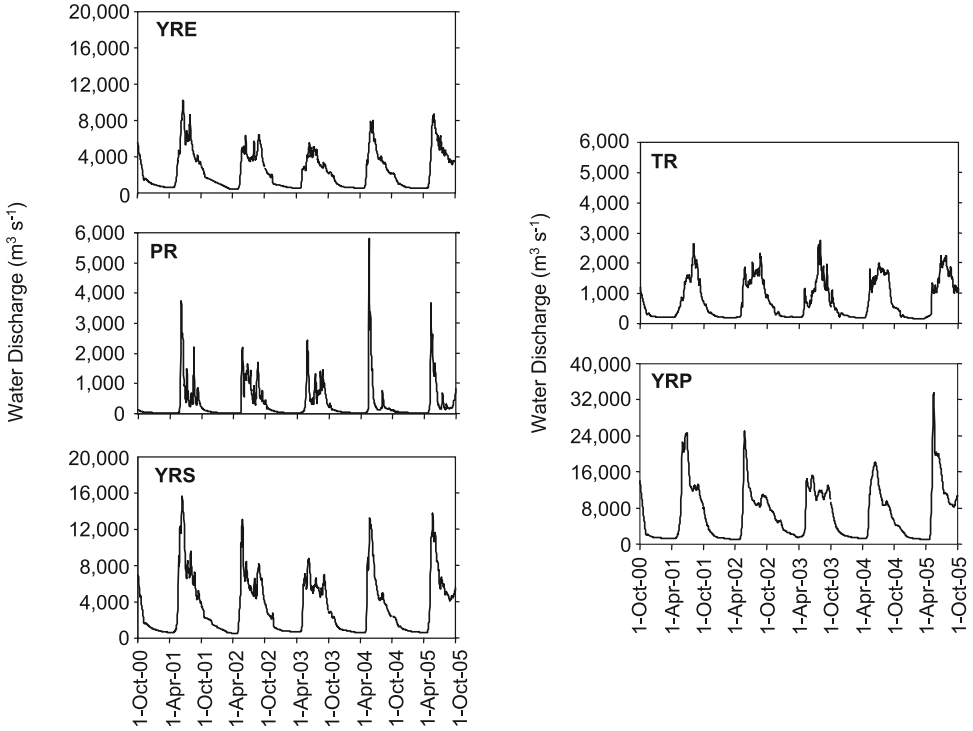

Figure 2. Water discharge hydrographs for the five measurement stations, water years 2001–2005.

than the 19 year average, and Q at TR was ~8.5% greater than the 43-year average (Table 1). There is some indication that annual Q may be trending downward at PR (Sen-Theil-Kendall trend line; P = 0.19) and slightly upward at TR (P = 0.19). Long-term data were insufficient to determine trends in annual Q at YRS or YRP.

4.2. Carbon

4.2.1. Total Carbon Export

[13] An average of 7.8 Tg C yr^{-1} discharged past YRP during 2001–2005; 30% as organic C and 70% as inorganic C (Table 2). Following *Striegl et al.* [2005], annual flow was divided into three seasonal flow periods based on hydrology and on the chemical character and concentration of C (Table 3). Total C loads generally follow Q, with peak daily C export occurring during spring, except at TR which peaks during summer (Figure 2 and Table 3).

4.2.2. Organic Carbon

[14] Organic carbon comprised 26–42% of total C flux, with highest DOC loads occurring during spring at all stations except TR (Table 3). SUVA, a measure of DOC aromatic carbon content [*Weishaar et al.*, 2003], and DOC concentration were greatest during spring and least during low flow in winter (Table 4). Within the YR, average DOC concentration and SUVA increased from YRE to YRP.

[15] HPOA, TPIA and HPI fractions comprised >79% of the DOC in all samples, with HPOA being the most abundant fraction (Table 5). HPOA was the most aromatic fraction, followed by TPIA and HPI. Like DOC, HPOA concentration and aromaticity were greatest during spring and increased from YRE to YRP. HPI comprised a larger percentage of DOC during winter than during other flow periods. Incubation results indicated that DOC half life (20°C) was 12 ± 6 d for winter samples and 48 ± 20 d for all other samples.

[16] The δ^{13}C-DOC values were −27.3, −26.6, −24.1, and −26.4‰ for PR, TR, YRE, and YRP, respectively. The respective FM of ^{14}C-DOC was 1.07, 0.97, 0.94, and 0.96, corresponding to radiocarbon ages of modern, 244, 497, and 327 years before present (B.P.). This indicates the presence of some aged DOC in all the rivers, except the Porcupine.

[17] POC loads were variable and mostly associated with high flows (Table 3). POC was mostly composed of terrestrial plant debris, having δ^{13}C-POC values of −29.9, −25.7, and −26.4 ‰ at YR above WR, YR above PR, and

Table 2. Average Annual DOC, POC, DIC, PIC, and Total C Loads for the Five Measurement Stations for Water Years 2001–2005, With Estimation Error for Each Calculated Load[a]

Station Name	DOC, 10^6 kg yr^{-1}	DOC Error, %	POC, 10^6 kg yr^{-1}	POC Error, %	DIC, 10^6 kg yr^{-1}	DIC Error, %	PIC, 10^6 kg yr^{-1}	PIC Error, %	Total C, 10^6 kg yr^{-1}
Yukon River at Eagle	408	7.4	314	22.7	1639	2.3	457	12.9	2818
Porcupine River near Fort Yukon	124	8.4	27	10.2	187	4.5	18	13.0	356
Yukon River near Stevens Village	781	6.0	382	10.2	2296	3.7	433	9.9	3892
Tanana River at Nenana	80	10.9	88	8.7	578	3.8	76	14.3	822
Yukon River at Pilot Station	1585	6.0	751	7.2	4963	3.1	506	10.9	7805

[a]Water year is 1 October to 30 September.

Table 3. Seasonal and Annual DOC, POC, DIC, and PIC Loads and 5-year Means for the Five Measurement Stations, 2001–2005[a]

	2001				2002				2003				2004				2005[b]				5-year Means			
Station	DOC	POC	DIC	PIC	DOC	POC	DIC	PIC	DOC	POC	DIC	PIC	DOC	POC	DIC	PIC	DOC	POC	DIC	PIC	DOC	POC	DIC	PIC
Yukon River at Eagle																								
Spring	191	246	591	170	149	101	380	95.4	148	89.5	353	101	225	199	489	187	257	225	545	215	194	172	472	153
Summer–autumn	186	221	1060	312	168	136	882	271	129	104	709	250	115	93.9	675	264	159	142	834	358	151	139	832	291
Winter	74.6	1.29	380	9.12	85.5	1.13	340	11.7	52.1	1.23	300	12.1	34.7	0.945	278	13.8	26.8	0.840	272	15.0	54.7	1.09	314	12.3
Total	451	468	2030	491	403	238	1600	378	329	195	1360	363	374	294	1440	465	443	368	1650	588	400	313	1620	457
Porcupine River near Fort Yukon																								
Spring	83.3	20.2	46.6	5.91	63.2	13.1	63.3	7.62	40.7	9.81	54.2	5.98	94.3	37.1	66.9	6.96	109	25.1	88.7	8.73	78.0	21.1	63.9	7.04
Summer–autumn	54.9	6.69	85.2	10.2	63.5	9.54	107	12.4	62.9	10.1	111	12.4	11.4	1.01	50.8	4.82	25.6	2.06	72.0	6.74	43.7	5.88	85.3	9.30
Winter	2.19	0.036	32.5	1.58	1.98	0.047	33.0	1.57	2.78	0.090	43.1	2.07	3.03	0.101	48.4	2.22	1.93	0.053	35.6	1.49	2.38	0.065	38.5	1.79
Total	140	26.9	164	17.6	129	22.7	203	21.6	106	20.0	209	20.5	109	38.2	166	14.0	136	27.3	196	17.0	124	27.0	188	18.1
Yukon River near Stevens Village																								
Spring	397	252	823	195	381	172	671	159	330	132	600	145	480	228	785	185	566	255	841	196	430	208	744	176
Summer–autumn	297	217	1250	268	289	188	1190	242	244	158	1100	229	143	90.7	888	182	235	147	1070	223	242	160	1100	229
Winter	91.0	7.66	436	25.4	146	11.8	459	26.8	100	9.82	446	26.9	72.0	6.78	425	24.1	55.0	4.93	412	23.7	92.7	8.19	436	25.4
Total	785	477	2510	488	815	371	2320	428	674	301	2150	401	695	326	2100	392	856	407	2330	443	765	376	2280	431
Tanana River at Nenana																								
Spring	17.5	18.2	98.2	11.2	30.5	33.9	123	19.5	16.6	11.6	98.6	9.50	36.6	41.8	150	17.3	36.6	42.8	159	10.2	27.6	29.7	126	13.5
Summer–autumn	38.4	58.5	275	64.9	45.6	57.5	299	74.2	40.1	55.5	302	70.4	32.6	46.2	294	39.5	43.3	59.7	339	26.5	40.0	55.5	302	55.1
Winter	11.1	1.52	135	5.73	8.55	1.16	137	9.07	18.0	3.02	159	8.97	13.4	2.05	161	7.55	7.38	1.92	156	5.20	11.7	1.93	150	7.31
Total	67.1	78.2	508	81.8	84.7	92.5	560	103	74.7	70.2	560	88.9	82.5	90.0	606	64.3	87.2	104	655	41.9	79.2	87.1	578	75.9
Yukon River at Pilot Station																								
Spring	651	357	1480	152	732	250	1300	86.2	659	174	1080	65.4	819	290	1320	117	1270	655	1980	305	826	345	1430	145
Summer–autumn	646	465	2680	318	574	315	2280	220	599	433	2460	288	392	290	1940	271	538	422	2260	457	550	385	2320	311
Winter	79.1	10.1	1130	48.0	89.1	12.1	1150	44.2	569	30.1	1300	29.0	131	16.5	1150	45.0	114	17.9	1160	71.3	197	17.3	1180	47.5
Total	1380	831	5300	518	1390	577	4740	350	1830	637	4840	382	1340	596	4410	433	1920	1100	5410	833	1570	748	4940	503

[a]Spring is 1 May to 30 June; summer–autumn is 1 July to 31 October; winter is 1 November to 30 April. All loads are in 10^6 kg C.
[b]Summer–autumn 2005 uses estimated flow for 1–31 October 2005.

YRP, respectively. FM ^{14}C-POC was 0.70, 0.63, and 0.67 at those locations, with corresponding radiocarbon ages of 2840, 3710, and 3250 years B.P.

4.2.3. Inorganic Carbon

[18] DIC comprised 52–70% of total C flux at all stations (Table 3). With pH ranging from 6.2 to 8.4 for all stations and times, most DIC was [HCO_3^-]. DIC concentrations were greatest during base flow in winter and were diluted by spring runoff (Table 4). Partial pressure of CO_2 ($pCO2$) was generally greater than equilibrium with the atmosphere throughout the year, indicating CO_2 flux to the atmosphere during the ice free period. The exception was during the summer of 2001, when subatmospheric pCO_2 was measured in the YR [*Schuster*, 2003]. High [CO_2] in ground water, within-river respiration, and lack of atmospheric exchange during winter result in build up of $pCO2$ under ice (Table 4).

[19] Yukon River DIC concentrations were influenced by inflow of suspended particulate carbonates from the White River [*Eberl*, 2004]. Peak PIC loads coincided with the glacial meltwater peak, with ~75% of annual PIC load

Table 4. Mean Measured DOC, SUVA, DIC, and pCO_2, ± Percent Variance for the Five Measurement Stations, 2001–2005[a]

	Yukon River at Eagle	Porcupine River Near Fort Yukon	Yukon River Near Stevens Village	Tanana River at Nenana	Yukon River at Pilot Station
DOC, μmol L^{-1}					
Spring	640 ± 10.5 (12)	1000 ± 10.7 (12)	890 ± 14.0 (11)	420 ± 14.7 (13)	900 ± 7.0 (11)
Summer–autumn	340 ± 17.3 (16)	670 ± 11.0 (17)	360 ± 11.9 (17)	220 ± 16.3 (18)	430 ± 10.0 (19)
Winter	140 ± 3.5 (4)	160 ± 3.2 (4)	180 ± 6.7 (5)	120 ± 2.9 (5)	220 ± 2.7 (5)
Annual	460 ± 12.7 (32)	760 ± 8.8 (33)	510 ± 11.5 (33)	280 ± 11.8 (36)	560 ± 9.0 (35)
SUVA, L mg C^{-1} m^{-1}					
Spring	3.3 ± 4.2 (12)	3.5 ± 1.4 (12)	3.4 ± 1.5 (11)	3.0 ± 4.7 (13)	3.5 ± 2.3 (11)
Summer–autumn	2.8 ± 10.4 (16)	3.1 ± 4.8 (17)	2.9 ± 4.8 (17)	2.6 ± 8.5 (18)	3.1 ± 4.2 (19)
Winter	1.9 ± 4.2 (4)	2.1 ± 8.1 (4)	2.1 ± 6.2 (5)	2.0 ± 11.0 (5)	2.3 ± 3.5 (5)
Annual	2.9 ± 3.4 (32)	3.1 ± 3.2 (33)	3.0 ± 3.3 (33)	2.7 ± 3.7 (36)	3.1 ± 3.2 (35)
DIC, μmol L^{-1}					
Spring	1530 ± 3.5 (10)	1070 ± 70 (12)	1530 ± 6.9 (10)	1770 ± 6.3 (13)	1480 ± 4.2 (10)
Summer–autumn	1860 ± 3.2 (16)	1730 ± 5.9 (17)	1900 ± 3.8 (17)	1840 ± 4.1 (17)	1890 ± 3.0 (19)
Winter	2580 ± 2.1 (7)	4270 ± 1.6 (8)	2930 ± 2.5 (6)	3410 ± 1.1 (6)	4100 ± 1.9 (8)
Annual	1910 ± 3.9 (33)	2070 ± 10.1 (37)	2020 ± 5.1 (33)	2080 ± 5.5 (36)	2250 ± 7.4 (37)
pCO_2, μatm					
Spring	1280 ± 20.2 (10)	1610 ± 12.1 (12)	957 ± 15.0 (10)	1390 ± 11.4 (13)	1530 ± 9.5 (9)
Summer–autumn	908 ± 11.3 (16)	1240 ± 7.8 (17)	989 ± 13.3 (17)	1580 ± 23.2 (18)	1650 ± 24.0 (19)
Winter	1820 ± 4.5 (7)	3720 ± 6.0 (8)	2340 ± 3.8 (6)	3480 ± 6.7 (5)	8280 ± 3.6 (8)
Annual	1220 ± 9.1 (33)	1890 ± 9.9 (37)	1270 ± 10.1 (33)	1830 ± 12.4 (36)	3090 ± 16.5 (36)

[a]Errors are in percent variance. The values given in parentheses are the number of samples.

Table 5. Five-Year Average DOC Fractions, as Percent HPOA, TPIA, and HPI of Total DOC Concentration

Season	DOC Fraction	Yukon River at Eagle	Porcupine River Near Fort Yukon	Yukon River Near Stevens Village	Tanana River at Nenana	Yukon River at Pilot Station
Spring	HPOA	52.6	52.8	47.8	50.4	49.5
Spring	TPIA	16.7	16.5	14.7	17.1	14.8
Spring	HPI	17.0	17.3	16.9	21.5	16.5
Spring	total recovery	86.4	86.6	79.4	89.0	80.8
Summer–autumn	HPOA	50.7	50.1	50.9	56.0	48.9
Summer–autumn	TPIA	22.3	17.4	20.4	23.4	18.1
Summer–autumn	HPI	23.0	16.8	19.8	25.6	17.5
Summer–autumn	total recovery	96.1	84.3	91.1	105	84.5
Winter	HPOA	48.6	40.8	42.4	40.7	45.4
Winter	TPIA	22.0	20.2	21.9	22.9	19.2
Winter	HPI	30.6	27.5	38.6	40.0	29.6
Winter	total recovery	101	88.4	103	104	94.2

passing YRE during summer-autumn (Table 3). WR had δ^{13}C-PIC = −0.1‰ and FM ^{14}C-PIC = 0. During 2001, passing of the PIC peak at YRS corresponded with enrichment of δ^{13}C-DIC from −12.7‰ in early June to −5.2‰ in mid-August, depletion of ^{14}C-DIC from FM 0.69 to 0.57, and depletion of [CO2] to below atmospheric equilibrium. Input and dissolution of WR carbonates also had a dramatic effect on δ^{13}C-DIC versus [DIC] along the YR (Figure 3).

5. Discussion

5.1. Carbon Cycling

[20] The chemistry and amount of C exported by rivers results from interactions among geologic and atmospheric inorganic C, terrestrial and aquatic organic C, climate, and hydrology. With vast stores of aged OC in permafrost and soils, it is important to understand current sources, ages, and proportions of C species so that future climate change effects can be assessed [*Raymond and Bauer*, 2001a].

[21] The chemical character and ^{13}C composition of DOC suggest terrestrial origin with little down river biogeochemical alteration. Half-lives of DOC determined by incubations also suggest that most DOC is exported from the basin before it is mineralized. Increased HPI fraction and low DOC concentration in winter are consistent with groundwater input, as hydrophobic DOC is preferentially sorbed on mineral soil [*Kaiser and Zech*, 1997] and the increased flow path allows for DOC consumption in soil and groundwater [*Striegl et al.*, 2005]. The HPI fraction is relatively labile [*Qualls and Haines*, 1992]; resulting in shorter DOC half lives during winter.

[22] During August–September 2004, YRP DOC averaged FM ^{14}C-DOC = 0.96, indicating a radiocarbon age of 330 yrs B.P. Previous studies have recorded modern DOC in arctic rivers [*Benner et al.*, 2004]. Although YR samples are not dominated by old DOC, there is an aged component consistent with mixing of a large pool of modern DOC with a small pool of old DOC of unknown origin [*Raymond and Bauer*, 2001b]. It is possible that this aged DOC component exists in other arctic rivers. In addition to the >3000 years old POC measured by this study, others have also measured aged POC in the Yukon [*Guo and MacDonald*, 2006] and other high latitude rivers [*Goni et al.*, 2005]. Annual floods erode deeply into YR river banks, dropping trees and other vegetation, roots, and old soil organic matter into the river. The ^{14}C-depleted POC we measured is consistent with significant contribution from these old carbon pools.

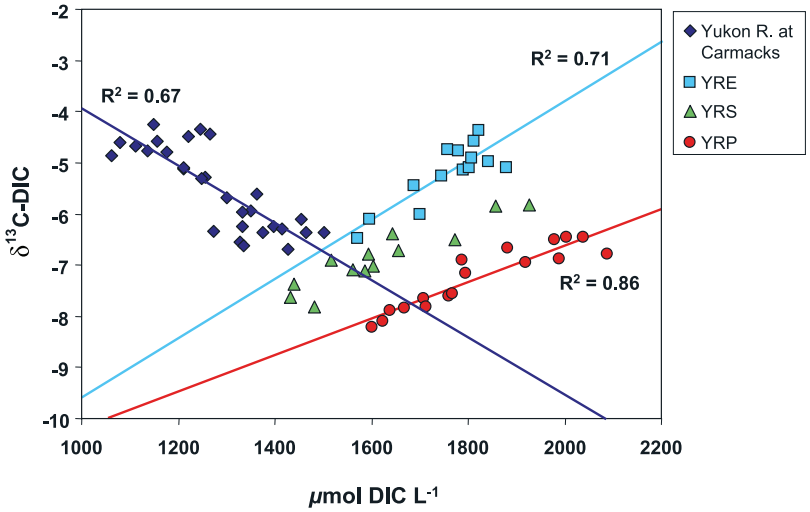

Figure 3. Plot of δ^{13}C-DIC versus DIC in the Yukon River. Unit for δ^{13}C is per mil, relative to Peedee belemnite. YRS is from June–August 2001; all other stations are from June–August 2004. Yukon R. at Carmacks is upstream of the confluence of the Yukon and White rivers.

Table 6. Seasonal and Annual DIC, DOC, PIC, POC, and Water Yields for the Five Measurement Stations, 2001–2005

Station	DIC, mmol/m^2	DOC, mmol/m^2	PIC, mmol/m^2	POC, mmol/m^2	Water, mm
Yukon River at Eagle					
Spring	134	55.0	43.5	48.7	86
Summer–autumn	235	42.9	82.5	39.5	128
Winter	88.9	15.5	3.5	0.30	42
Annual	464	116	130	89.0	256
Porcupine River near Fort Yukon					
Spring	69.7	85.0	7.7	23.0	71
Summer–autumn	93.0	47.6	10.1	6.40	59
Winter	42.0	2.60	1.9	0.10	9
Annual	203	135	20.0	29.0	139
Yukon River near Stevens Village					
Spring	122	70.5	28.9	34.0	81
Summer–autumn	180	39.6	37.5	26.2	97
Winter	71.3	15.2	4.2	1.3	30
Annual	376	128	71	62.0	208
Tanana River at Nenana					
Spring	158	34.6	17	37.3	93
Summer–autumn	379	50.2	69.2	69.7	206
Winter	188	14.7	9.2	2.4	57
Annual	726	101	95	110	356
Yukon River at Pilot Station					
Spring	144	82.6	14.5	34.6	93
Summer–autumn	233	55.1	31.1	38.5	121
Winter	118	19.7	4.8	1.7	37
Annual	497	159	51	75	251

[23] PIC load decreased from YRE to YRS, probably due to particle settling and PIC dissolution [*Eberl*, 2004]. Weathering consumes ~30% of PIC during transport, has substantial effect on the isotopic composition of DIC (Figure 3), and occasionally consumes [CO_2] to below atmospheric equilibrium, but has small effect on the overall DIC mass balance. Given PIC export of 500 × 10^6 kg C yr^{-1} (Table 3) and assuming this represents 2/3 of PIC input, weathering only contributes ~5% of total DIC export at YRP. Mass balance calculations of silicate and nonsilicate weathering at YRP suggest that ~54% of C-DIC originates from the atmosphere or OC respiration [*Blum et al.*, 1998;

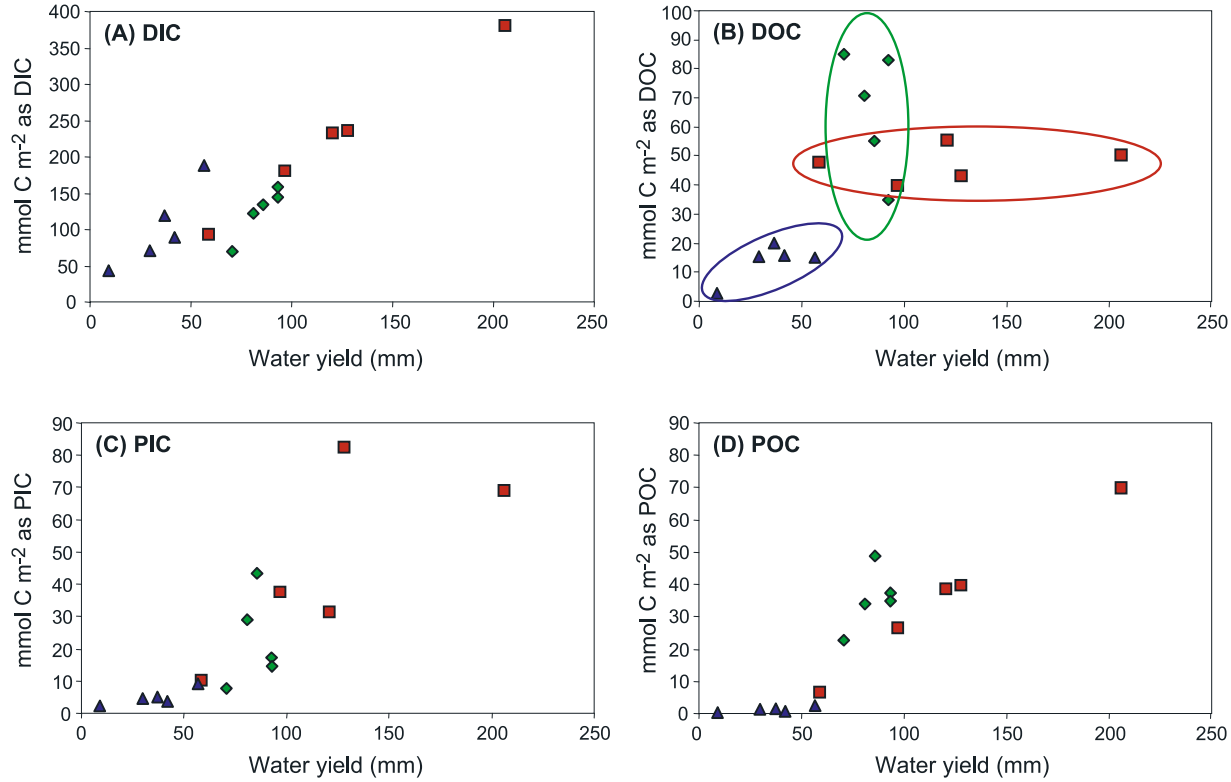

Figure 4. Mean seasonal (a) DIC, (b) DOC, (c) PIC, and (d) POC yield versus water yield for the five measurement stations, 2001–2005. Blue triangles, winter; green diamonds, spring; red squares, summer–autumn.

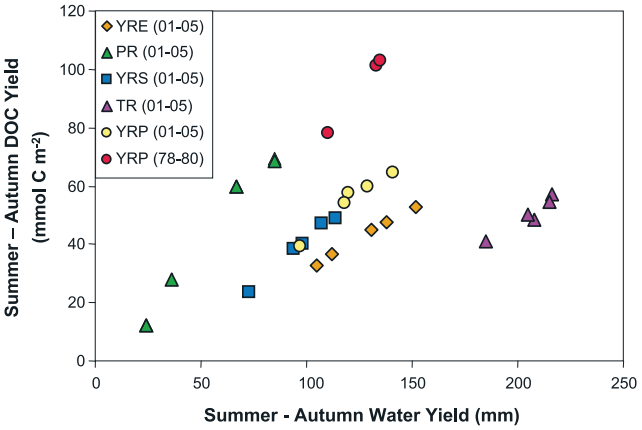

Figure 5. Summer–autumn DOC yields for the five measurement stations, 2001–2005, and for YRP, 1978–1980.

Anderson et al., 2000]. Decreased δ^{13}C-DIC with increased [DIC] in YR at Carmacks suggests a respiration source (Figure 3). However, PIC dissolution masks the respiration signal downstream of the White River, and is only marginally perceptible at YRP.

5.2. Watershed Carbon Yield

[24] Carbon yield (mmol C m^{-2} watershed area t^{-1}) with respect to water yield (mm water t^{-1}) provides valuable comparative information on C source and export from watersheds within a basin. Five-year averages of seasonal C species yields versus water yields at the five stations are listed in Table 6 and shown in Figure 4. Total C yield at YRP averaged 0.73 mol m^{-2} yr^{-1} and was highest at TR (1.03 mol m^{-2} yr^{-1}) where DIC dominated C flux. DIC yield increased linearly with water yield among YR subbasins for all seasons and all stations ($r^2 = 0.95$, $n = 75$, $p < 0.001$). Although the slope of DIC versus water yield (Figure 4a) was steepest during winter due to high base flow DIC concentrations, it was generally similar for all seasons throughout the basin.

[25] DOC chemistry and export group into three distinct seasons at YRP [*Striegl et al.*, 2005] and throughout the basin (Tables 5 and 6 and Figure 4b). Winter DOC concentrations were fairly constant at all stations, averaging 161 ± 35 μmol C L^{-1} ($n = 21$). This resulted in a linear relation between DOC and water yields during winter, with DOC yield proportional to areal groundwater discharge. During spring, water yield was fairly constant across the basin, while DOC yield was variable, with highest DOC yield at PR and lowest yield at TR. Much of the land surface remains frozen in early spring and new DOC runs off with melt water. Annual DOC yield was greatest from wetland influenced portions of the basin (PR and YRP) and least from subbasins having a higher proportion of bare rock, ice and snow, and forested uplands (TR and YRE) [*Brabets*, 2000]. Highest annual DOC yield (0.16 mol C m^{-2} yr^{-1}) was at YRP (Table 6). This suggests that our fixed station measurements missed at least one major DOC source, most likely the remote Koyukuk River (Figure 1). Although the Koyukuk basin has flats and wetlands similar to the PR basin, it is wetter and likely yields more OC.

[26] In contrast to the spring pattern, DOC yields during summer-autumn were fairly constant across the basin, while water yields varied. At first appearance, this suggests limited DOC sources available for hydrologic export. However, closer inspection suggests that DOC export was water limited, not C limited (Figure 5). Coincident occurrence of low runoff in the PR watershed, where DOC source is relatively high, and high runoff in the TR watershed, where DOC source is relatively low, resulted in similar yields at all stations. The slope of DOC yield versus water yield at PR was about twice as steep as at TR and slopes for the YR stations were intermediate.

[27] The only historical DOC export data available for the Yukon River were collected at YRP during 1978–1980 [*Striegl et al.*, 2005] and those yields fall more in line with 2001–2005 PR yields than with 2001–2005 YRP yields (Figure 5). There is weak suggestion of an increased trend in summer–autumn Q at TR (Sen-Theil-Kendall trend line, $P = 0.16$), which could contribute to shifting the YRP DOC versus water yield relation to the right, but no trends in summer–autumn Q were observed at other stations. However, winter Q has increased significantly at PR ($P < 0.001$), TR ($P = 0.004$) and YRE ($P < 0.001$). This increase in base flow supports the argument that change in water flow path, and not change in water quantity, has produced a downward shift in the relation between summer–autumn DOC export and water export from the Yukon basin in recent decades [*Striegl et al.*, 2005].

[28] PIC yield (Figure 4c) was directly related to the export of suspended sediment having high carbonate content from the White River basin [*Eberl*, 2004]. Therefore fixed station yields were greatest at YRE and decreased downstream to YRS and YRP because of sediment dilution and PIC dissolution. Yields were intermediate at TR, due to high suspended sediment concentration and low carbonate content, and were lowest at PR, which had low suspended sediment concentration and presumably low carbonate content.

[29] POC yields (Figure 4d) reflected their primary source from bank erosion and generally increased with water yield. Yields were greatest in the upper Yukon basin during spring, reflecting the tremendous bank scour by ice that occurs during spring melt. POC yields were smallest at PR and were negligible during winter at all stations.

5.3. Carbon and Climate Change

[30] Net primary production (NPP) in the Yukon River basin is currently about 110 Tg C yr^{-1} (10.8 mol C m^{-2} yr^{-1} (D. Kicklighter, unpublished data, 2006)). About 6% of this is exported from the basin annually as DOC and DIC. NPP is expected to change in response to climate warming and interactions among ecology, hydrology, and C export can also be expected to change [*Serreze et al.*, 2000; *Hinzman et al.*, 2005; Arctic Climate Impact Assessment, http://www.acia.uaf.edu]. Thawing of permafrost will initially result in higher DOC concentrations in melt water [*Michaelson et al.*, 1998; *Kawahigashi et al.*, 2004] and possibly in increased DOC yield [*Frey and Smith*, 2005]. However, as flow paths deepen and more DOC is consumed in soil and groundwater, DOC yield may decrease coincident with increased respiration and DIC yield [*Striegl et al.*, 2005]. Carbon yield is proportional to water yield in all settings, therefore understanding of change in C export in

response to climate change will be directly linked to understanding of change in hydrology from the small watershed to the basin scale.

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