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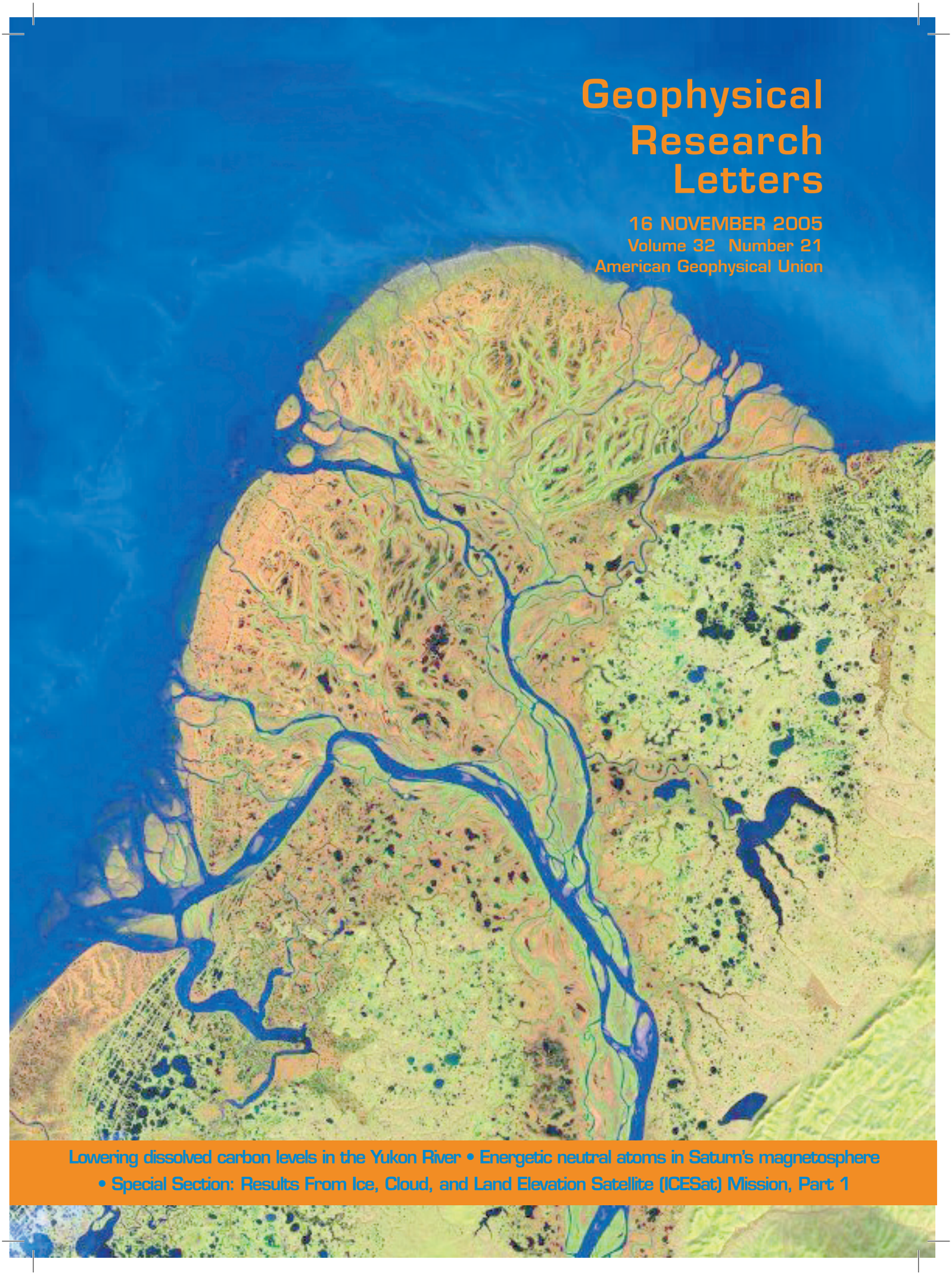

Lowering dissolved carbon levels in the Yukon River • Energetic neutral atoms in Saturn's magnetosphere
• Special Section: Results From Ice, Cloud, and Land Elevation Satellite (ICESat) Mission, Part 1

A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn

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[1] Climate warming is having a dramatic effect on the vegetation distribution and carbon cycling of terrestrial subarctic and arctic ecosystems. Here, we present hydrologic evidence that warming is also affecting the export of dissolved organic carbon and bicarbonate (DOC and HCO_3^-) at the large basin scale. In the 831,400 km^2 Yukon River basin, water discharge (Q) corrected DOC export significantly decreased during the growing season from 1978–80 to 2001–03, indicating a major shift in terrestrial to aquatic C transfer. We conclude that decreased DOC export, relative to total summer through autumn Q, results from increased flow path, residence time, and microbial mineralization of DOC in the soil active layer and groundwater. Counter to current predictions, we argue that continued warming could result in decreased DOC export to the Bering Sea and Arctic Ocean by major subarctic and arctic rivers, due to increased respiration of organic C on land. **Citation:** Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland (2005), A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn, *Geophys. Res. Lett.*, *32*, L21413, doi:10.1029/2005GL024413.

1. Introduction

[2] Arctic and subarctic river basins yield disproportionately large amounts of water and terrigenous DOC to northern seas and the Arctic Ocean [*Opsahl et al.*, 1999; *Hansell et al.*, 2004] when compared to other major river basins. As northern latitudes warm, the amount and chemical nature of DOC exported from these basins are expected to change [*Dittmar and Kattner*, 2003]. There is direct evidence that Q from the Arctic's major rivers is increasing [*Peterson et al.*, 2002] and air temperature increases of $\sim$0.05 $^oC\ a^{-1}$ over the past three decades are having measurable effects on terrestrial ecosystems [*Serreze et al.*, 2000; *Sturm et al.*, 2005]. However, reliable historical water chemistry data are lacking, so it is impossible to verify circumpolar trends in riverine chemical export. Because DOC concentrations have increased in some northern European [*Freeman et al.*, 2001; *Worrall and Burt*, 2004; *Tranvik and Jansson*, 2002] and North American [*Findlay*, 2005] rivers in recent decades and release of DOC from northern peatlands has been predicted to increase with warming [*Frey and Smith*, 2005], it is commonly presumed that DOC export to the Arctic Ocean will respond positively to climate warming.

[3] Climate warming effects on the terrestrial C cycle are extensively measured and modeled for northern high latitudes [*Serreze et al.*, 2000]. Warming effects on the transfer of C from land to water and on freshwater C export are not as well known, especially for large arctic and subarctic river basins [*Dittmar and Kattner*, 2003; *Guo et al.*, 2004]. This creates a gap in our understanding of feedbacks among climate warming and C cycling. The response of frozen soils to climate warming is key to understanding potential change in C export by these rivers. High hydraulic conductivity, low mineral content, and low DOC sorption capacity of the soil active layer overlying impermeable permafrost lead to quick DOC transport to streams and rivers with limited microbial transformation (Figure 1a), especially during spring. As the depth, temperature and seasonal duration of the active layer increase with climate warming, new inputs of DOC may derive from thawed permafrost and/or vegetation changes [*Sturm et al.*, 2005]. If the newly mobilized DOC is biologically recalcitrant within its hydraulic transport time, then riverine DOC export to the ocean will increase (Warming I, Figure 1b). Conversely, if the DOC is bioactive on time scales shorter than its hydraulic residence, most of it will be respired in upland areas instead of being exported to streams [*Carey*, 2003]. DOC respiration will be partly stimulated by increased temperature [*Meentemeyer*, 1978]. More importantly, permafrost melting will result in increased hydraulic residence of soil water DOC and in rerouting of DOC into shallow groundwater, allowing for increased microbial mineralization and decreased riverine export of the terrestrially derived DOC (Warming II, Figure 1c). Although the extent of permafrost melting is not well documented throughout the Yukon basin, localized areas of melting are common and permafrost temperatures are increasing [*Osterkamp and Romanovsky*, 1999]. Increased respiration of soil and groundwater DOC results in increased CO_2 and HCO_3^- production, increased CO_2 efflux from soil, and increased HCO_3^- transport to streams and rivers. Permafrost melting may also result in increased groundwater contribution to annual river discharge [*Walvoord and Striegl*, 2005]. Relatively labile [*Michaelson et al.*, 1998] and modern [*Benner et al.*, 2004] arctic soil DOC, increased arctic CO_2 flux [*Oechel et al.*, 1995], and increased HCO_3^- in arctic surface water (Arctic Climate Impact Assessment (ACIA), available at http://www.acia.uaf.edu) also support Warming II.

[4] To examine the effects of warmer temperatures on chemical export from a large permafrost-dominated watershed, the United States Geological Survey (USGS) began measuring Q and inorganic and organic chemical composi-

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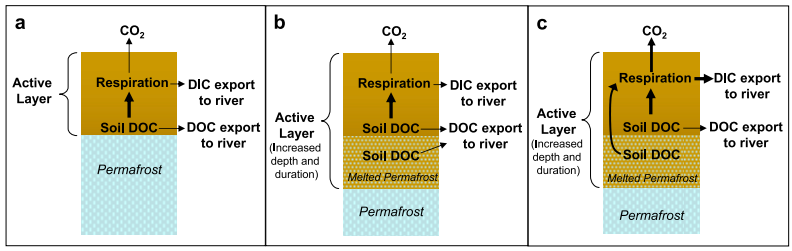

Figure 1. Carbon cycling in permafrost soils. (a) Initial condition – Biogeochemical processes in the soil active layer contribute DOC and DIC to streams and rivers and CO_2 to the atmosphere; (b) Warming I - DOC in melting permafrost is mostly recalcitrant, DOC transport to rivers increases; (c) Warming II - DOC in melting permafrost is mostly labile, increased respiration leads to decreased DOC and increased DIC transport to rivers.

tion of river water 6–8 times a^{-1} at Yukon River at Pilot Station (YRP), the most downstream location before Yukon Delta, and at four other locations in the Yukon basin in 2001 [*Schuster*, 2003] (Figure 2). During 1978–80, USGS used similar methods to measure continuous Q and seasonal DOC and HCO_3^- concentration at YRP (USGS National Water Information System (NWIS): Web Data for the Nation, available at http://waterdata.usgs.gov/nwis). With these data, we applied the LOADEST program [*Runkel et al.*, 2004] to calculate daily DOC and HCO_3^- fluxes at YRP during 1978–80 and 2001–03. LOADEST centers Q and chemical concentration data to eliminate colinearity and applies the method of adjusted maximum likelihood estimation [*Cohn et al.*, 1992] to calculate chemical loads.

[5] Here, we describe the C chemistry of the Yukon River during 2001–03, and compare changes in seasonal DOC and HCO_3^- export vs. Q at YRP between 1978–80 and 2001–03.

2. Results and Discussion

[6] Based on seasonal patterns of Q and the chemical characteristics of DOC, we divided annual hydrographs into spring flood (May 1–June 30), summer through autumn (July 1–October 31) and winter (November 1–April 30) flow periods. DOC concentration and specific ultraviolet absorbance at 254 nm (SUVA), an indicator of DOC aromaticity [*Weishaar et al.*, 2003], were strongly seasonal, ranging from 2.4–14 mg C L^{-1} (Figure 3a) and from 2.0 to 4.0 L mg C^{-1} m^{-1} at YRP (Figure 3b). River pH was also seasonal, ranging from 6.6 to 8.3, with lowest pH in winter under ice and highest pH during summer and autumn. DOC concentration and SUVA were greatest during the spring flood, suggesting high contribution of minimally altered terrestrial plant material. Values were intermediate during summer through autumn, and lowest during winter low flow. DOC collected downstream of YRP during summer 2003 was primarily of recent terrestrial plant origin ($\Delta^{14}C$ = +20‰; $\delta^{13}C$ = −28‰). Hydrophobic organic acid (HPOA), hydrophobic neutral (HPON), transphilic acid (TPIA), and hydrophilic (HPI) fractions of the DOC [*Aiken et al.*, 1992] are also seasonal (Figure 3c), with HPOA dominating. The HPOA fraction of the June 13 2003 sample was very aromatic, SUVA = 4.3 L mg C^{-1} m^{-1}, and had C:N = 71.4, indicative of terrestrial plant sources, short hydraulic residence, and little microbial processing [*McKnight and*

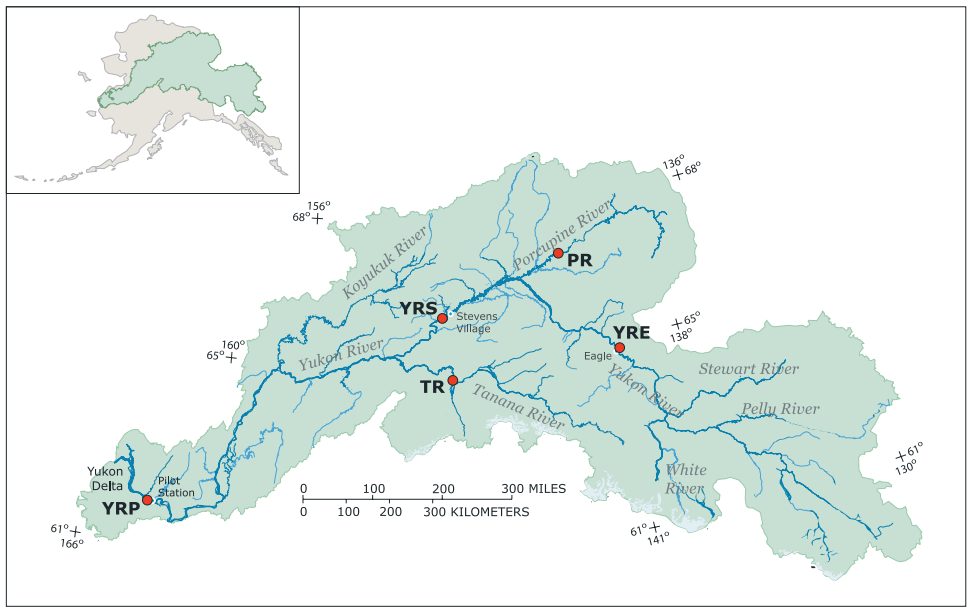

Figure 2. Map of the Yukon River Basin. Yukon River at Eagle – YRE, Yukon River at Stevens Village – YRS, Yukon River at Pilot Station – YRP, Porcupine River – PR, Tanana River – TR.

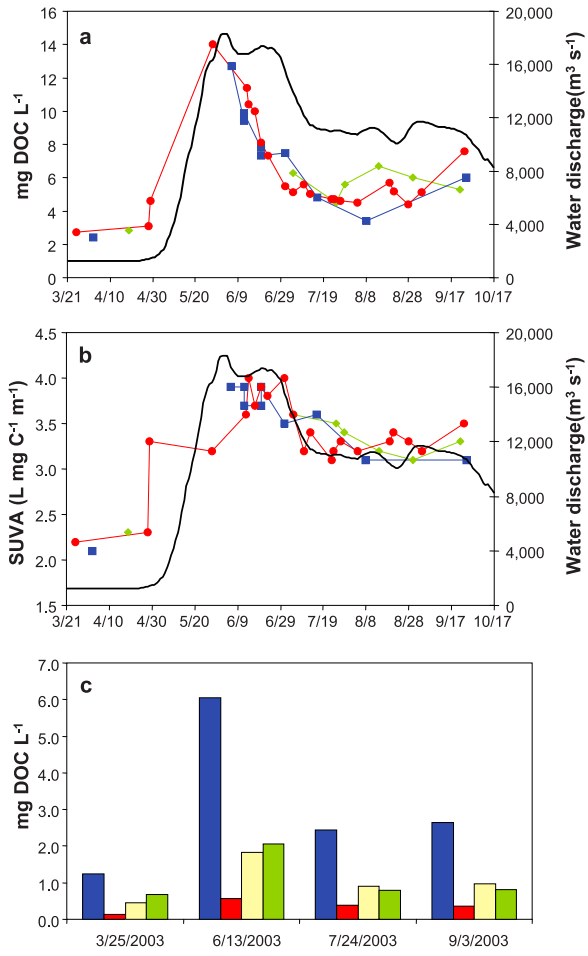

Figure 3. DOC and Q at YRP, 2001–2003. (a) DOC and Q vs. day of year. DOC 2001 = green diamonds; DOC 2002 = blue squares; DOC 2003 = red circles; 2001–03 mean Q = black line. (b) SUVA at YRP, 2001–03; legend same as in panel A. (c) Concentration of HPOA (blue), HPON (red), TPIA (yellow), HPI (green) on four sampling dates in 2003.

Aiken, 1998]. The March 25 2003 sample collected through the ice in late winter was less aromatic (SUVA = 2.9 L mg C^{-1} m^{-1}) with lower HPOA concentration and C:N = 55.6. Winter base flow is largely groundwater having DOC chemistry consistent with increased water residence and microbial degradation. Summer through autumn DOC had intermediate HPOA concentration, but was relatively aromatic (SUVA = 3.8 L mg C^{-1} m^{-1}). Chemistry and C-isotope composition of organic C in the Arctic Ocean [*Benner et al.*, 2004] also suggest modern terrestrial plant sources consistent with the YRP DOC chemistry.

[7] Annual Q averaged 193 ± 24 km^3 a^{-1} during 1978–80 and 212 ± 21 km^3 a^{-1} during 2001–03. To control for inter-annual variability in Q, linear regressions of C flux vs. total Q were calculated for each flow period and the 1978–80 and 2001–03 results were compared by Analysis of Covariance (Figure 4). Figures 4c and 4d indicate that DOC export decreased from ~0.88 Tg C in 1978–80 to ~0.53 Tg C in 2001–03, at total growing season Q = 100 km^3, while HCO_3^- export increased from ~1.80 Tg C to ~1.86 Tg C. This period coincides with high soil biological activity and possible basin-wide increase in the depth and duration of the soil active layer over the past several decades [*Serreze et al.*, 2000]. About 17% of the calculated decrease in DOC flux is compensated by an increase in HCO_3^- flux, supporting Warming II. The remainder is probably emitted across the soil-air interface as CO_2 and CH_4 or cycled to biomass or solute storage. No significant change in DOC export vs. Q occurred during winter when river discharge is dominated by groundwater or during the spring flood when DOC is flushed from the watershed with minimal biogeochemical alteration.

[8] Besides a decrease in the quantity of DOC exported relative to Q during summer through autumn, the chemical quality of exported DOC is probably also changing. As soils warm and permafrost melts, the residence time of DOC in contact with subsurface microbes increases and the chemical character of the DOC can be expected to shift from DOC having little microbial processing (spring flood), towards more microbially degraded DOC (winter). Respiration of DOC in soil also releases inorganic nutrients, which can affect long term terrestrial productivity [*Sturm et al.*, 2005] and nutrient export. Warming may also lead to a change in the relative proportion of HCO_3^- vs. DOC exported from the basin. LOADEST calculations of HCO_3^- and DOC flux from the Porcupine River (PR) and Tanana River (TR) sub-basins (Figure 2) during 2001–03 indicate a HCO_3^-:DOC molar ratio of ~1:1 in the PR, ~4:1 in the TR and ~3:1 in the Yukon River. The Porcupine basin is almost entirely underlain by permafrost and DOC delivery from the

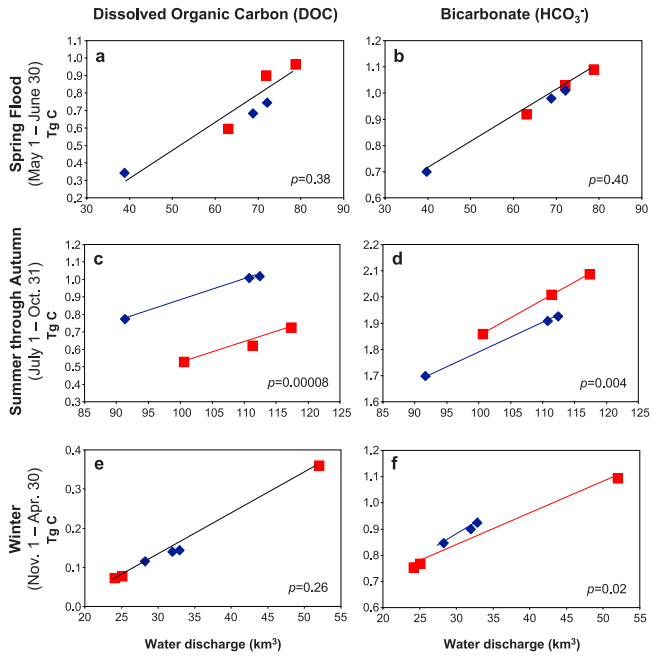

Figure 4. DOC and HCO_3^- flux vs. water discharge per flow period at YRP during 1978–80 (blue diamonds) and 2001–03 (red squares). The Analysis of Covariance *p*-value for testing the equality of intercepts of linear regression lines determined for 1978–80 and 2001–03 data is in the lower right-hand corner of each panel. Where $p > 0.05$ a single linear regression line representing all data is shown, indicating no change in C flux vs. Q over the 23 year period. Where $p < 0.05$, the 1978–80 and 2001–03 regression lines are shown separately.

land surface to streams is fast, whereas the Tanana basin is underlain by patchy or discontinuous permafrost [*Brabets et al.*, 2000]. Groundwater in annual river Q is also increasing in portions of the basin. At Yukon River at Eagle (Figure 2), groundwater has increased from ~15% of annual flow in the early 1950's to >20% today [*Walvoord and Striegl*, 2005]. Groundwater had an average of ~2.5 mg C L^{-1} DOC and 50 mg C L^{-1} DIC at YRP during 2001–03, while mean annual river water concentrations were ~8 mg C L^{-1} DOC and 24 mg C L^{-1} DIC. Consequently, increased groundwater flow leads to decreased DOC export and increased HCO_3^- export, if Q is held constant. As climate warming progresses in the Yukon basin, we hypothesize that HCO_3^-:DOC will increase.

[9] Reduced summer through autumn DOC export contrasts with observations of increased DOC concentration in northern Europe [*Forsberg*, 1992; *Freeman et al.*, 2001; *Tranvik and Jansson*, 2002; *Worrall and Burt*, 2004] and north-eastern USA [*Findlay*, 2005] and contradicts suggestions that rising temperature in northern latitudes will result in a significant increase of DOC flux to the marine system. Recent changes in temperature alone cannot explain observed increases in DOC concentration in the other rivers or the decrease in summer through autumn DOC export vs. Q at YRP. Hydrology, scale, and complex DOC interactions associated with vegetation change and soil microbiology [*Neff and Hooper*, 2002; *Sturm et al.*, 2005] must also be considered. Compared to the Yukon River basin, watersheds studied in Europe and north-eastern USA are warmer, wetter, have little or no permafrost, and are orders of magnitude smaller. Warming of unfrozen soil by a degree or two may result in increased DOC production/decomposition and increased export of DOC, especially if coupled with increased precipitation runoff [*Tranvik and Jansson*, 2002]. Widespread melting of permafrost soil has a more profound effect on DOC dynamics. A large fraction of DOC leached from soil and peat no longer runs off to streams and rivers, but infiltrates and decomposes in the soil active layer or in groundwater, reducing riverine DOC export. The reduction in DOC export occurs during summer through autumn when the active layer is most active. This effect is masked during the spring flood when soil is frozen, Q is high, and surface runoff dominates. We suggest that similar decreases in the summer through autumn DOC export vs. Q are occurring in other large permafrost-dominated river basins throughout the north.

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