Dissolved organic and inorganic carbon dynamics in glacial river systems of the Canadian Arctic

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Research at Lake Hazen

The sensitivity of northern freshwater and marine ecosystems to climate change is of keen interest to the scientific community. Research has been designed to better describe vectors of this change, but the dynamic nature of Arctic environments has challenged process-based studies and future projections. Glacier mass loss of the Canadian Arctic Archipelago has been bolstered over past decades resulting in increased fluxes from networks of glacial meltwater to receiving aquatic environments. The unique physical and chemical characteristics of these glacial meltwaters and their transformation via processes taking place along glacial river continua could impact the global carbon cycle by affecting dissolved organic and inorganic carbon (DOC and DIC). The hydrologic mass budget of Lake Hazen, located on northern Ellesmere Island, is dominated by runoff from glacial meltwaters and has been selected as a sentinel for change in the Canadian high Arctic as part of a multiyear collaborative project.

Rationale and Objectives

DOC plays major biogeochemical roles in aquatic environments serving as a) a key source of nutrients, b) a ligand for heavy metal binding/transport, and c) a chemical constituent responsible for absorbing solar radiation and influencing the extent of the photic zone.

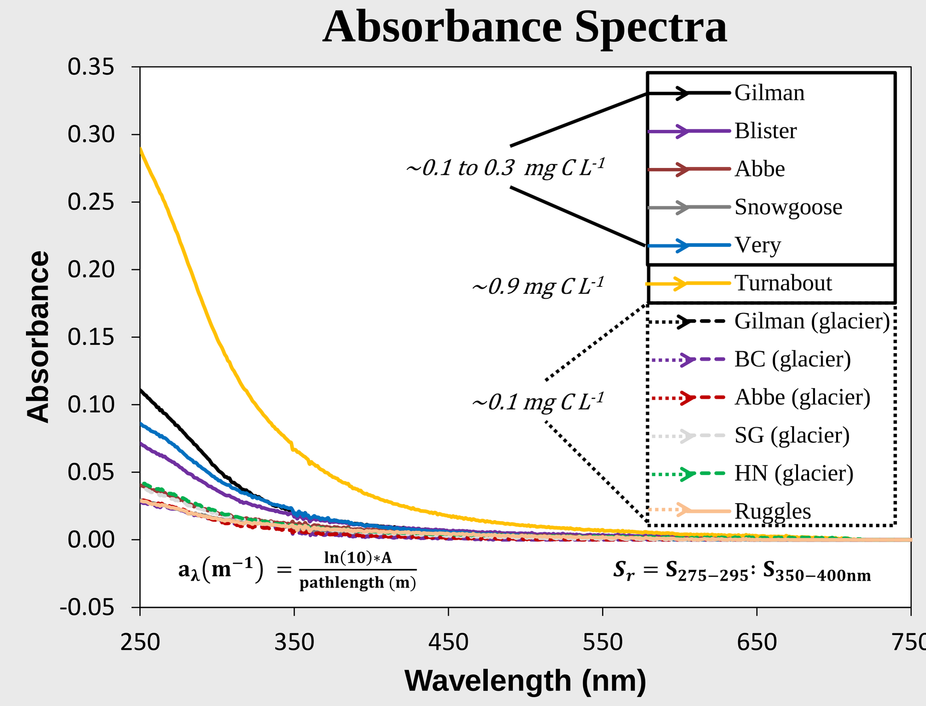
1) Assess DOC quantity and compositon amongst glacial river systems emptying into Lake Hazen to provide insight into implications of increased glacial melt water fluxes

DIC speciation is intrinsic to chemical and ecological processes that define aquatic systems such as atmospheric exchange, mineral interactions, and biological activity.

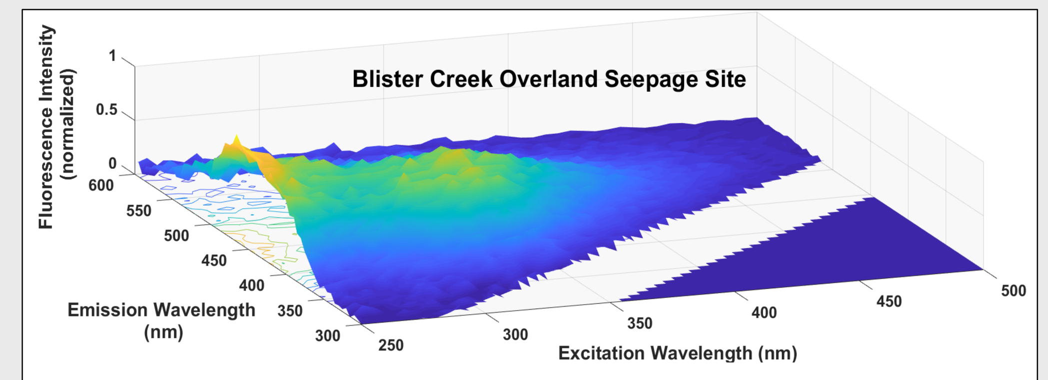
2) Evaluate processes that are influential with respect to DIC speciation and isotopic ($\delta^{13}C$) fractionation in glacial river systems of the Lake Hazen watershed

Dissolved Organic Carbon (DOC) in Glacial River Systems

Absorbance Spectra



Excitation Emission Matrix Spectra (EEMs)



Humic-like

A peak – Ex. 260 / Em. 450 nm (UV)

C peak – Ex. 340 / Em. 440 nm (UV-vis)

M peak – Ex. 300 / Em. 390 nm

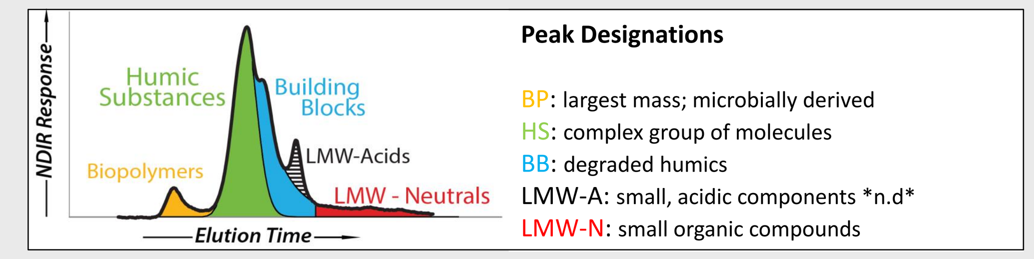
Humification Index = **HIX** = $\frac{\text{Ex. 254 Em. 435} \rightarrow \text{480 nm}}{\text{Ex. 254 Em. 300} \rightarrow \text{345 nm}}$

(Zsolnay et al. 1999; Ohno et al. 2002)

Protein-like

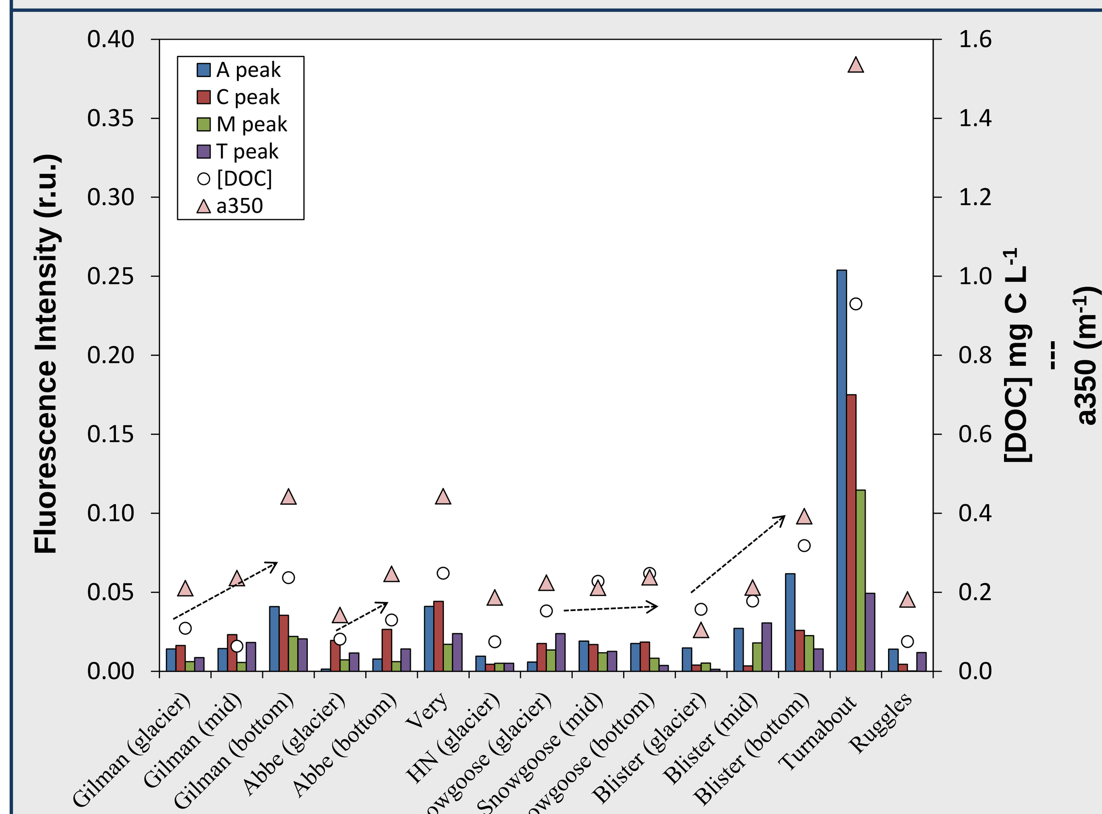
T peak – Ex. 275 / Em. 340 nm

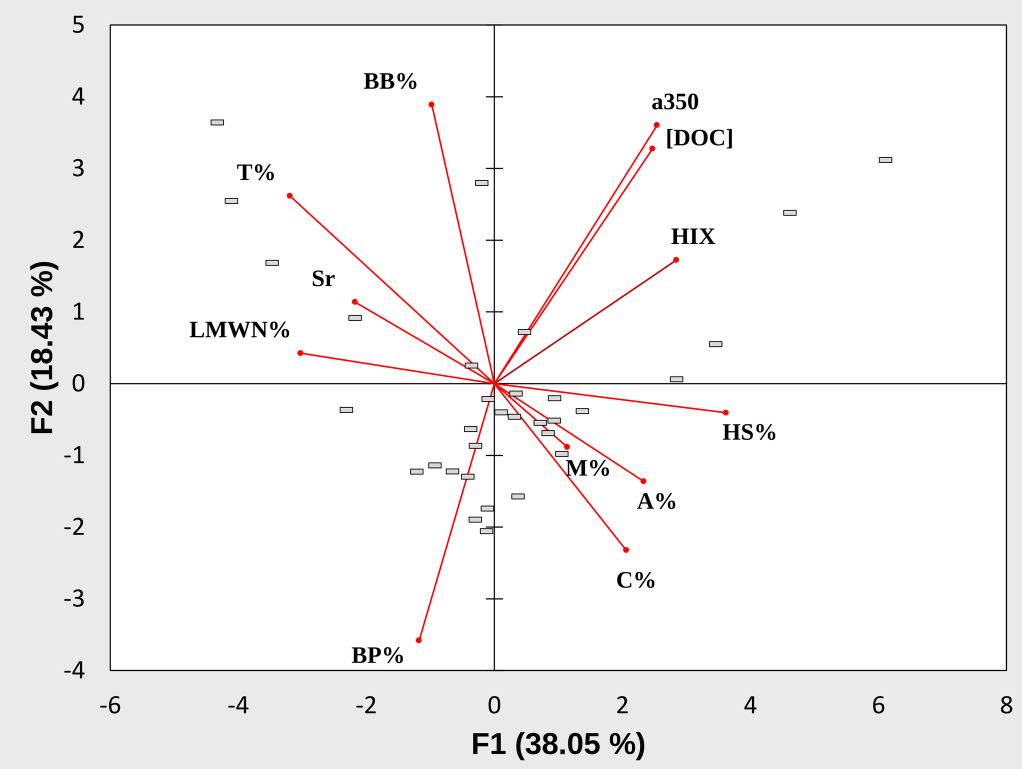
Size Exclusion Chromatography (SEC)

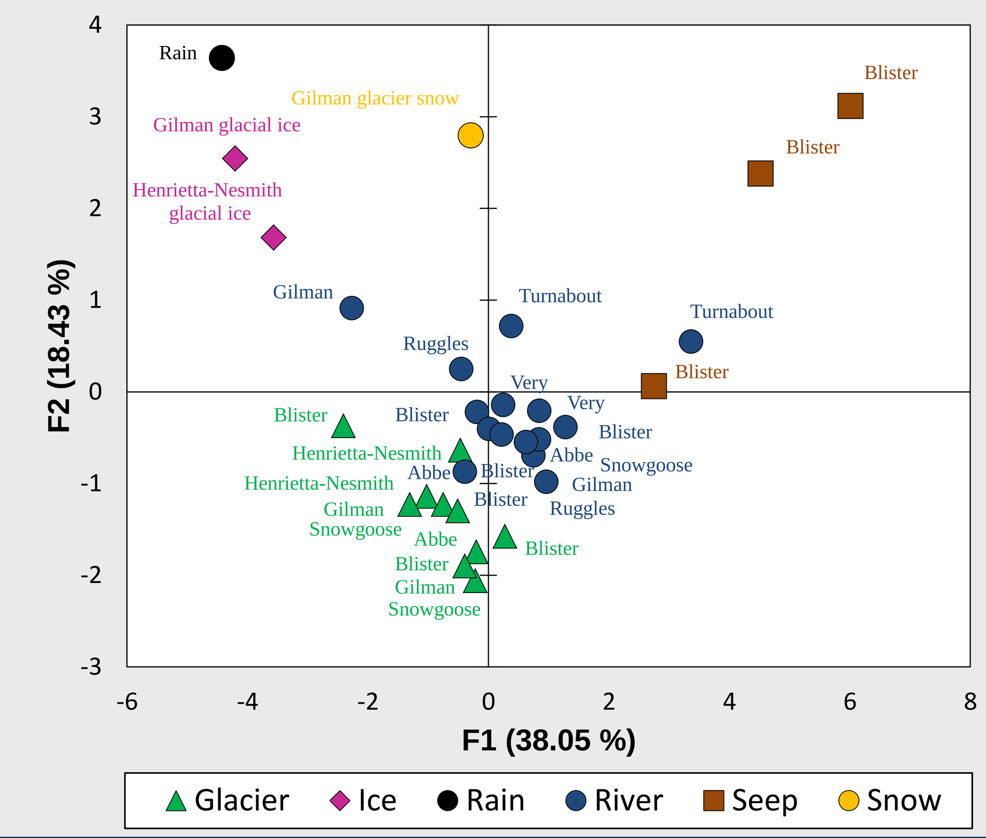


Stable Carbon Isotopes ($\delta^{13}C$-DOC)

Sample Type	Sample ID	$\delta^{13}C$-DOC ‰	BP%	HS%	BB%	LMW-N%	S_r	HIX
Glacier	Gilman	-23.93	26.0	39.2	7.0	27.8	1.98	0.46
	Snowgoose	-23.96	20.1	38.7	6.5	34.7	1.19	0.88
	Henrietta-Nesmith	-23.87	18.0	35.0	16.9	30.1	1.41	0.46
	Blister	-24.44	19.5	35.3	11.2	34.0	1.09	0.56
Delta	Abbe	-25.51	10.0	45.6	9.4	35.0	1.90	0.48
	Gilman	-26.09	5.5	41.6	9.9	43.0	1.42	2.60
	Snowgoose	-24.62	4.6	46.6	13.5	35.3	1.51	2.12
	Blister	-25.72	3.6	62.8	11.7	21.9	1.49	2.11
	Very	-26.16	2.5	52.1	12.0	32.4	1.18	3.55
	Turnabout	-26.32	2.3	75.0	10.6	12.1	1.11	9.43
Overland Seepage	Blister	-28.80	1.4	79.2	13.1	6.3	0.94	16.63







Dissolved Inorganic Carbon (DIC) Dynamics

$$\boldsymbol{DIC} = \sum CO_2^{\ *} + HCO_3^{\ -} + CO_3^{\ 2-}$$

$$\boldsymbol{K_{CO_2}} = \frac{[H_2CO_3]}{pCO_2 * H_2O}$$

$$\boldsymbol{K_1} = \frac{[H^+][HCO_3^-]}{H_2CO_3}$$

$$\boldsymbol{K_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

(*Calculated using* pCO_2 *and* $[DIC]$)

Isotopic fractionation factors $(\boldsymbol{\alpha})$

$$H_2CO_{3(aq)} - CO_{2(g)} \rightarrow 1000 \ln \boldsymbol{\alpha} = -0.91 + 0.0063 * 10^6/T^2$$

$$HCO_{3\ (aq)}^- - CO_{2(g)} \rightarrow 1000 \ln \boldsymbol{\alpha} = -4.54 + 1.099 * 10^6/T^2$$

$$CO_{3\ (aq)}^{2-} - CO_{2(g)} \rightarrow 1000 \ln \boldsymbol{\alpha} = -3.4 + 0.87 * 10^6/T^2$$

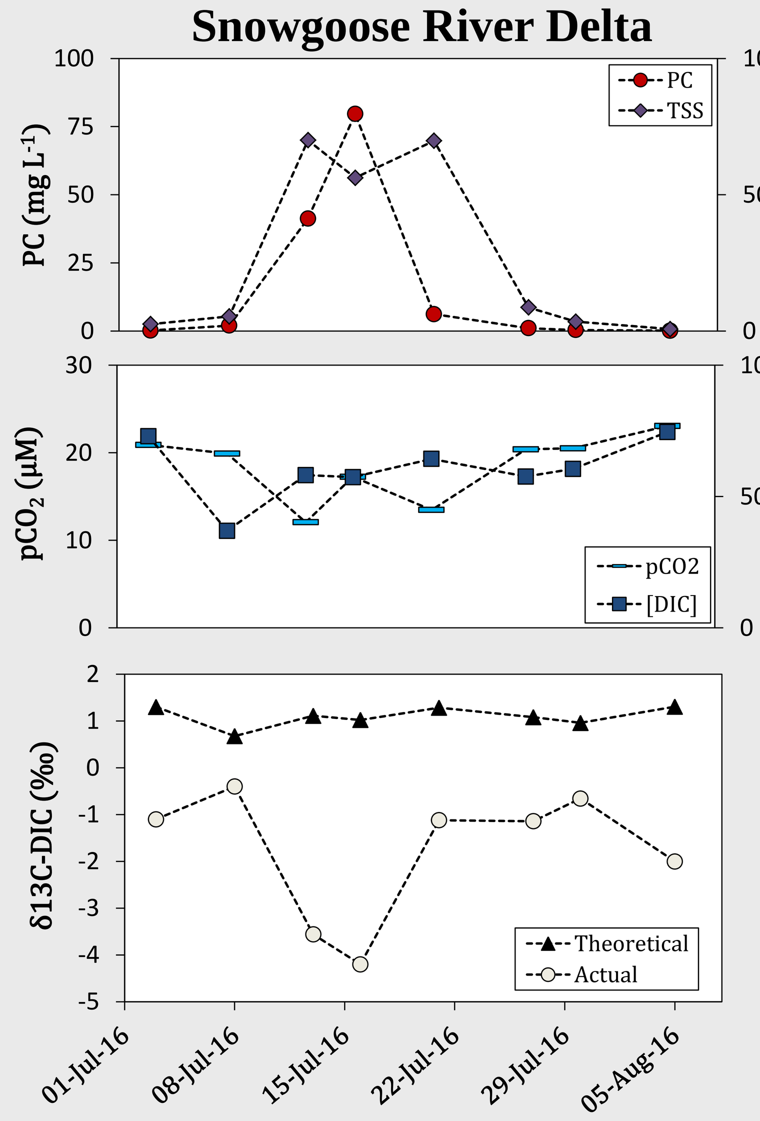
i.e. $\boldsymbol{\delta 13C - HCO_3^-} = \alpha * (\boldsymbol{-8} + 1000) - 1000$ *in per mille* (‰)

$\boldsymbol{Atmospheric\ CO_2} \approx \boldsymbol{-8‰}$

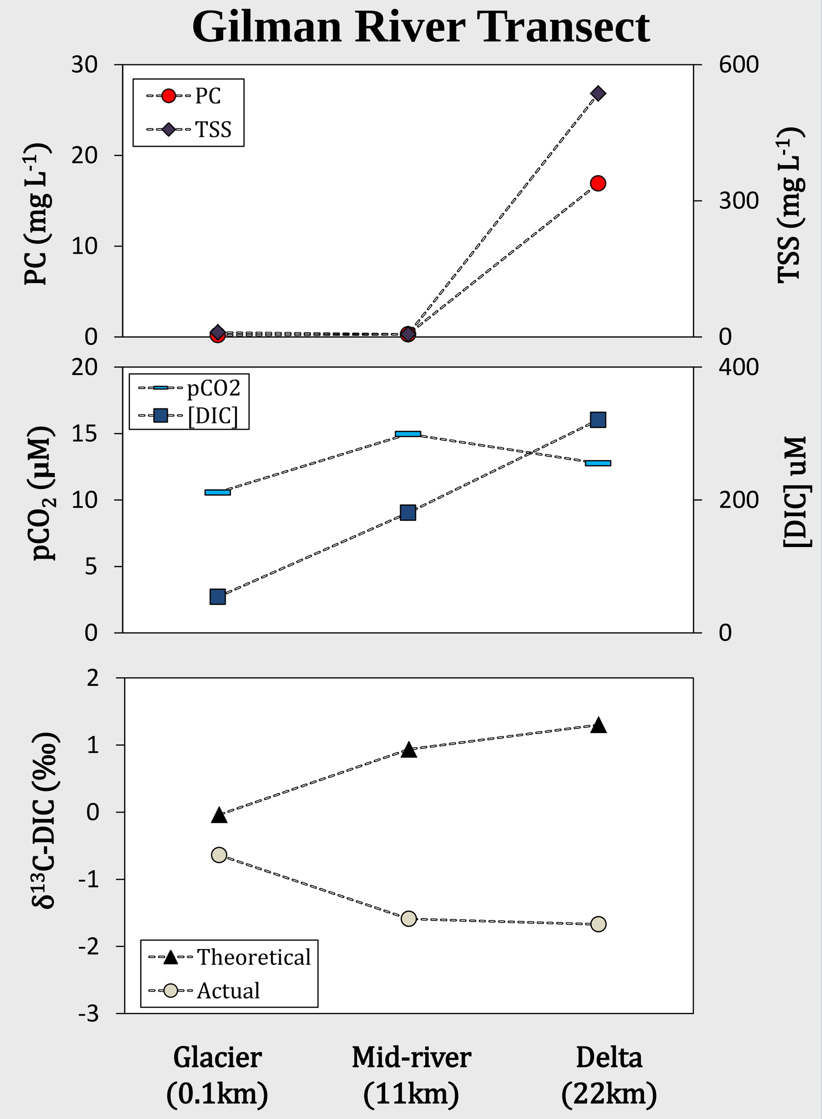
$$f\ H_2CO_3^{\ *} + f\ HCO_3^- + f\ CO_3^{2-} = 1$$

$\boldsymbol{Theoretical\ 'open'\ system\ \delta^{13}C - DIC}$
$$= (f\ H_2CO_3^{\ *} *\ \delta\ H_2CO_3^{\ *}) + (f\ HCO_3^- * \delta\ HCO_3^-) + (f\ CO_3^{2-} * \delta\ CO_3^{2-})$$

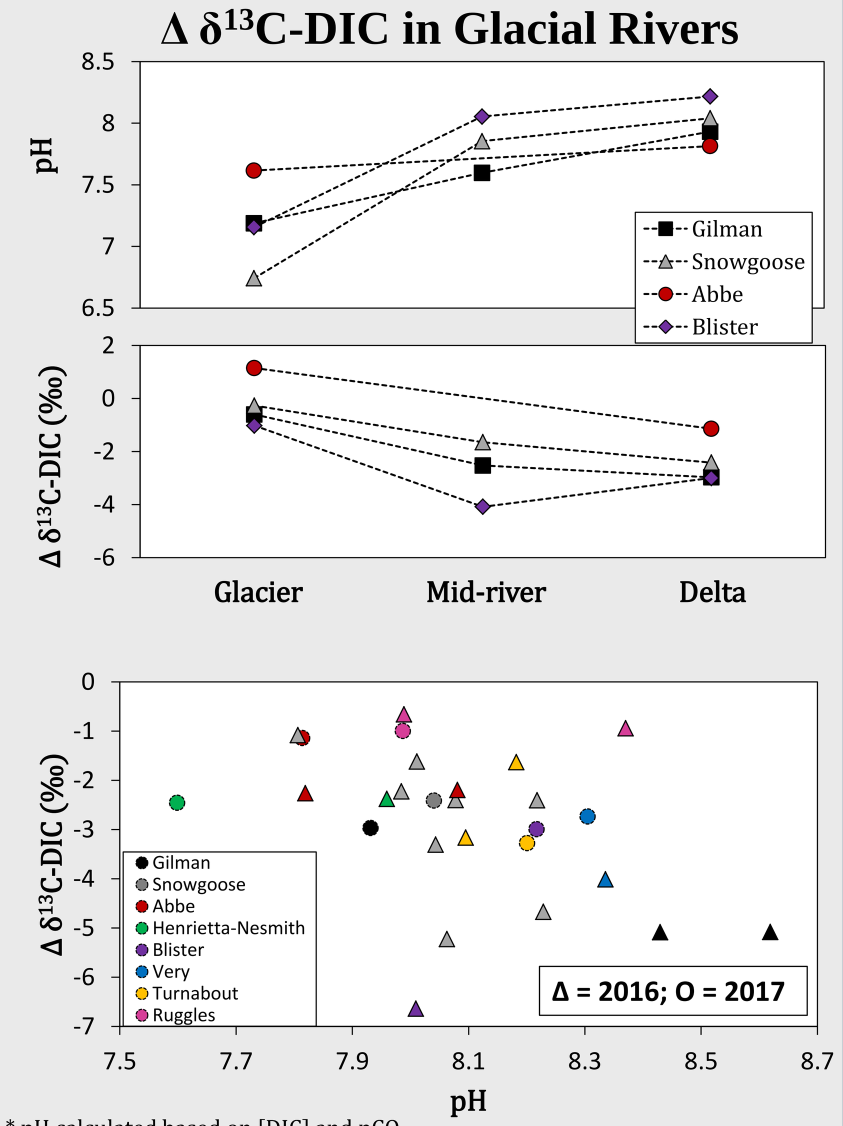
Snowgoose River Delta



Gilman River Transect



Δ $\delta^{13}C$-DIC in Glacial Rivers



* pH calculated based on [DIC] and pCO_2

Summation

DOC

1) There is a marked increase in DOC quantity along glacial river transects suggesting addition of organic material during transit
2) From glacier to delta sites DOC composition shifts to favour more extensively conjugated humic-like chemical structures
3) DOC released in glacier meltwater, additions by overland seepage/streams, and dissolution from suspended solids are expected to be the main sources of DOC in glacial rivers

DIC

1) Increased glacial meltwater flux inferred from TSS and PC loading, and downriver processes, both appeared to be associated with more negative $\delta^{13}C$-DIC values
2) Glacial rivers are variable intermediaries between ideal 'open' and 'closed' systems
3) Mineral/particle interactions are a likely factor when explaining the departure of measured $\delta^{13}C$-DIC from theoretical

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