



**Figure S1:** Mean daily discharge for the Mackenzie mainstem site, showing mean (dark blue line) and 5<sup>th</sup> and 95<sup>th</sup> percentiles (dashed lines) for the 1973 – 2012 period. Vertical black lines demarcate the spring (May – June), summer (July – August), autumn (September – November) and winter (December – April) periods used for concentration analyses.

**Table S1:** Characteristics of the Mackenzie River Basin upstream of the mainstem site, and related sub-catchments. Data for permafrost, soil organic carbon, and basin lithologies are derived from the information presented in Figure 1.

Basin name	Basin size (at gauge)	Mean annual discharge (2003-2012)	Mean annual water yield (2003-2012)	Continuous permafrost % cover	Discontinuous permafrost % cover	Isolated + sporadic permafrost % cover	Average soil organic carbon (1 m depth) mg m <sup>-2</sup>	Sedimentary % cover	Metamorphic + Basement % cover	Magmatic % cover
Mackenzie	1679	305	182	13	29	39	27.0	73	20	3
Great Bear	146	18.6	127	28	50	0	26.8	51	27	1
Liard	275	85.3	310	1	33	66	15.7	82	11	8
Hay	49	3.78	77	0	0	91	24.0	100	0	0
Slave	606	101	166	0	4	53	14.1	82	15	3

**Table S2:** Output parameters from the LOADEST models run for the Mackenzie mainstem and subcatchment sites. For each parameter, the parameter value is given with standard deviation in parentheses. The base model is as follows:

$$\text{InLoad} = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi d\text{time}) + a_4 \cos(2\pi d\text{time}) + a_5 d\text{time} + a_6 d\text{time}^2$$

Station	Constituent	r <sup>2</sup>	Model	a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	a <sub>5</sub>	a <sub>6</sub>
Mackenzie	DOC	95.77	9	15.002 (0.029)	1.408 (0.039)	0.135 (0.040)	-0.128 (0.030)	-0.174 (0.034)	0.006 (0.002)	-0.0002 (0.0002)
	Alkalinity	99.35	7	17.969 (0.004)	0.895 (0.009)	--	0.015 (0.009)	-0.039 (0.007)	0.001 (0.000)	--
	Calcium	99.18	9	16.982 (0.008)	0.884 (0.011)	0.005 (0.011)	-0.010 (0.011)	0.043 (0.007)	0.002 (0.000)	0.0001 (0)
	Magnesium	98.87	9	15.609 (0.009)	0.831 (0.013)	-0.013 (0.013)	0.072 (0.011)	-0.017 (0.011)	0.004 (0.001)	0.0001 (0)
	Sulfate	94.91	8	16.985 (0.017)	0.829 (0.025)	-0.039 (0.026)	-0.054 (0.022)	0.048 (0.021)	0.010 (0.001)	--
Liard	DOC	92.98	9	13.520 (0.060)	1.595 (0.057)	-0.078 (0.036)	-0.101 (0.055)	0.457 (0.089)	0.009 (0.003)	-0.0005 (0.0004)
	Alkalinity	98.12	9	16.706 (0.015)	0.759 (0.015)	0.034 (0.010)	-0.044 (0.023)	-0.084 (0.015)	0.002 (0.001)	-0.0001 (0.0001)
	Sulfate	96.90	7	15.497 (0.011)	0.736 (0.020)	--	0.132 (0.027)	-0.061 (0.021)	0.013 (0.001)	--
Great Bear	DOC	38.89	3	11.435 (0.022)	0.806 (0.205)	--	--	--	0.013 (0.003)	--
	Alkalinity	72.68	7	14.765 (0.006)	1.022 (0.057)	--	-0.033 (0.008)	-0.080 (0.009)	0.001 (0.001)	--
	Sulfate	62.59	7	13.409 (0.007)	0.944 (0.072)	--	-0.086 (0.011)	0.011 (0.010)	0.002 (0.001)	--
Hay	DOC	99.09	7	11.483 (0.016)	1.017 (0.012)	--	0.095 (0.019)	-0.124 (0.030)	0.003 (0.002)	--
	Alkalinity	98.25	4	12.981 (0.014)	0.762 (0.012)	--	0.069 (0.020)	-0.062 (0.030)	--	--
	Sulfate	95.93	5	12.346 (0.040)	0.852 (0.015)	0.016 (0.010)	--	--	-0.009 (0.004)	--
Slave	DOC	84.71	8	14.198 (0.027)	1.695 (0.077)	0.440 (0.124)	0.072 (0.030)	0.117 (0.043)	0.005 (0.002)	--
	Alkalinity	95.52	9	16.807 (0.009)	0.986 (0.018)	0.160 (0.023)	0.017 (0.012)	-0.011 (0.009)	0.001 (0.0004)	-0.0001 (0)
	Sulfate	87.72	8	15.267 (0.014)	0.986 (0.033)	0.202 (0.041)	-0.020 (0.019)	-0.069 (0.019)	0.002 (0.001)	--

As illustrated in the table, model fits for DOC, alkalinity, and ion flux at the Mackenzie mainstem site were strong. Model fits were also strong for all sub-catchment analyses except for the Great Bear DOC results. As discussed in the main text, DOC fluxes at this site were driven by clear increases in DOC concentration during most months, and thus despite the low r<sup>2</sup> value for this result, the trends described appear to be robust. The challenge in modeling constituent flux from the Great Bear site may be caused by issues related to the effect of using discharge measurements from a site immediately downstream of the outflow of a large lake.

**Table S3:** Statistical outputs for Mann-Kendall trend analyses, and associated Theil-Sen lines, for changes in yearly flux over time. Shown are the Kendall's p-value, Kendall's tau, and Sen's slope, as positive or negative per decade trend with associated 95% confidence limits. Constituent units are Gmol (DOC, SO<sub>4</sub>, Ca, and Mg), Geq (alkalinity), and km<sup>3</sup> (discharge). See main body text for additional methodological details.

	<b>p</b>	<b>tau</b>	<b>Trend slope (decade<sup>-1</sup>)</b>	<b>95% confidence (±)</b>
<b><i>Mackenzie mainstem flux</i></b>				
DOC, full record	0.001	0.394	11.40	5.80
DOC, discharge-accompanied	<0.001	0.471	17.41	7.17
Alkalinity	0.008	0.311	15.77	15.42
Discharge	0.105	0.190	5.31	9.90
SO <sub>4</sub>	<0.001	0.689	12.42	2.75
Ca	<0.001	0.432	11.07	9.01
Mg	<0.001	0.505	6.37	3.28
(Ca+Mg)	<0.001	0.448	17.47	10.90
<b><i>Subcatchment flux</i></b>				
Liard DOC	<0.001	0.447	6.63	3.18
Liard alkalinity	0.018	0.266	6.77	4.60
Liard SO <sub>4</sub>	<0.001	0.456	3.72	0.82
Liard discharge	0.217	0.139	2.29	3.42
Great Bear DOC	<0.001	0.865	0.54	0.04
Great Bear alkalinity	<0.001	0.622	1.00	0.50
Great Bear SO <sub>4</sub>	<0.001	0.632	0.12	0.05
Great Bear discharge	<0.001	0.460	0.44	0.32
Hay DOC	0.385	0.130	0.75	2.56
Hay alkalinity	0.503	0.101	0.30	1.53
Hay SO <sub>4</sub>	0.940	0.014	-0.07	0.60
Hay discharge	0.568	0.087	0.17	1.08
Slave DOC	0.518	0.084	1.78	3.40
Slave alkalinity	0.026	-0.221	-5.36	3.45
Slave SO <sub>4</sub>	0.052	-0.192	-0.59	0.46
Slave discharge	0.019	-0.233	-3.05	1.87

**Table S4:** Statistical outputs for Generalized Least Squares (gls) analysis of change in point measurements of concentration (as  $\mu\text{mol L}^{-1}$  or  $\mu\text{eq L}^{-1}$ ) and equivalent ratios (unitless) over time. See main body text for additional methodological details.

	p	Trend slope (decade <sup>-1</sup> )	95% confidence ( $\pm$ )
<b><i>Concentration trends</i></b>			
DOC winter	0.024	16.84	14.53
DOC spring	0.321	37.88	76.42
DOC summer	<0.001	44.46	21.40
DOC autumn	0.009	31.54	23.30
Alkalinity winter	0.255	-16.17	28.09
Alkalinity spring	0.376	16.16	36.49
Alkalinity summer	0.001	51.18	29.21
Alkalinity autumn	0.545	6.90	22.64
<b><i>Ion ratio trends</i></b>			
Alkt:(Ca+Mg)	0.006	-0.0106	0.0075
Alkt:(Ca+Mg); discharge-accompanied	0.001	-0.0172	0.0105
(Alkt+SO4):(Ca+Mg)	0.759	0.0015	0.0094
(Alkt+SO4):(Ca+Mg); discharge-accompanied	0.603	0.0041	0.0154