Supplementary Materials

S1 Detailed sample analysis

Hg and MeHg analyses were conducted at the Biogeochemical Analytical Service Laboratory (BASL) at the University of Alberta, Edmonton, Canada. This laboratory is certified and accredited with the Canadian Association for Laboratory Accreditation (CALA). THg samples were analyzed using the EPA Method 1631 via cold vapour atomic fluorescence spectroscopy using a Tekran 2600 Automated Total Mercury Analyzer (Tekran Instruments Corporation, USA). Following field collection and preservation, samples were analyzed within three months of collection. Bromine monochloride (BrCl) was added directly to the samples to oxidize all the forms of Hg in the sample to the Hg(II) oxidative state for a minimum duration of 12 hours before analysis. The concentration of BrCl needed to be added to oxidize the samples varies depending on many factors, including but not limited to turbidity or DOM content. Samples for this research were brominated a minimum of 0.5% and up to 2%. This BrCl was then neutralized by the addition of hydroxylamine hydrochloride ($NH_2OH*HCl$). After the BrCl was neutralized, stannous chloride ($SnCl_2$) was added to the sample to then reduce the Hg from the Hg(II) oxidative state to the Hg(0) oxidative state. The present Hg(0) was detected via the aforementioned cold vapour atomic fluorescence spectroscopy by purging and desorbing the Hg vapour onto two different gold traps. This detection was performed against a 9-point standard curve (0 – 40 ng L^{-1}; $r^2 > 0.999$) that was recreated daily. Quality control standards were run at 1 ng L^{-1} and 10 ng L^{-1} Additionally, sample duplicates and spikes (with a known concentration of $HgCl_2$ standard) were run every 20 samples in case of instrument drift. Spike recoveries ranged from 90% - 110%, and duplicate percent differences fell within a range of ±10%. The detection limit for THg was 0.06 ng L^{-1}.

TMeHg samples were analyzed using the EPA Method 1630. Samples were distilled at 127 ºC using a Tekran 2750 Methyl Mercury Distillation System for up to 4 hours (Tekran Instruments Corporation, USA). The water samples were spiked with a known volume of ^{201}MeHg as an internal standard for a minimum detection concentration, with the addition of ammonium 1-pyrrolidinecarbodithioate (APDC) and hydrochloric acid (HCl) that removed matrices that can complicate the ethylation processes later during analysis. Following the removal of the samples from the distiller and the distillation process, ascorbic acid was added immediately to the distillate to remove any free chlorine. A known mass of distillate was transferred to a glass vial and was buffered to adjust the pH to 4.9 using an acetate buffer. Subsequently, sodium tetraethyl borate (NaTEB) was added to the glass vial to complete the ethylation process of MeHg to the volatile form, MeHgEt. These ethylated samples were then analyzed using a Tekran 2700 Methyl Mercury Analyzer coupled with an Agilent 7900 ICP-Mass Spectrometer (ICP-MS) (Tekran Instruments Corporation, USA; Agilent Technologies, USA). The ethylated mercury compounds were stripped, trapped, desorbed, separated by mercury species, and broken down pyrolytically to the oxidized Hg(0) form on the Tekran 2700 Methyl Mercury Analyzer. This elemental form of mercury was then introduced to the ICP-MS for detection. The detection limit for TMeHg was 0.01 ng L^{-1}.

Absorbance was measured using a Shimadzu UV-1280 Spectrophotometer from 200 nm – 700 nm at a 1 nm interval within one week of collection (Shimadzu Corporation, Japan) at the Catchment and Wetland Sciences Research Group Laboratory at the University of Alberta, Edmonton, Canada. The samples were run using a 1 cm quartz cuvette. No samples were diluted as the absorbance value was consistently below the limit of 0.4 cm^{-1}. Ultrapure water blanks were run every 10 samples, and the blank measurements were subtracted from the absorbance measurements. This absorbance analysis was used to extract absorbance at 254 nm (A_{254}) as an indicator of the quantity of aromatic DOC (Weishaar et al., 2003). Additionally, the A_{254} value was used to calculate specific UV absorbance at 254 nm ($SUVA_{254}$), commonly used as a measure of DOC aromaticity with the following formula (Weishaar et al., 2003):

$$SUVA_{254} = \frac{Absorbance\ at\ 254\ nm\ (m^2)}{DOC\ (mg\ L^{-1})}\ x\ 100$$

Finally, the remaining water chemistry analyses were completed by the Natural Resources Analytical Laboratory (NRAL) at the University of Alberta, Edmonton, Canada. DOC and TDN were measured by combustion catalytic oxidation using a Shimadzu TOC-L CPH Model Total Organic Carbon Analyzer with an ASI-L and TNM-L (Shimadzu Corporation, Japan). DOC was measured as non-purgeable organic carbon (NPOC) by acidifying the sample with 1M HCl, followed by sparging the sample to strip any purgeable carbon ahead of instrument injection. TDN was analyzed by combusting the nitrogen to NO, followed by NO_2, this is then reacted to form NO_2 in an excited state and was measured by a chemiluminescence detector. The following dissolved metals (plus S and P) were measured by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Thermo iCAP6300 Duo (N. America) ICP-OES: Ca, Fe, and Mg (Thermo Fisher Scientific, USA). These elements were measured from the same sample. The samples were aspirated by a nebulizer into an argon plasma to produce characteristic emission patterns unique to each element of interest; these emission spectra are detected by a spectrometer and corrected by yttrium (Y).

The determination of dissolved ions by colourimetric ion analysis was completed by NRAL with the frozen and non-acidified 60 mL sample using a Thermo Gallery Plus Beermaster Autoanalyzer (Thermo Fisher Scientific, USA). The target analytes of this analysis include: SO_4-

S, NO_3-N, NO_2-N, SRP (PO_4-P), and NH_4-N. These analytes were measured using well-known colour reactions by injecting samples and method reagents into reaction cuvettes, which generated coloured complexes once the reaction of the two together are complete. The intensity of colour change was measured by light absorbance at a specific wavelength as this was dependent on the concentration of the analyte in the sample and how the final concentration is determined. Finally, alkalinity as carbonate was performed using a Schott Instruments Titronic Universal automatic titrator. The automatic titrator performed a titration using Bromocresol Green-Methyl Red (equivalence point pH 4.5) or methyl orange (equivalence point pH 3.7) as an indicator. The results were then converted from HCO_3 mg L^{-1} to $CaCO_3$ by a calculation.

Table S1. Percentage of ICP-OES and colorimetry analyses that were below the LOQ and LOD, as well as the percentage of values <LOD and substituted with the LOD as no measured value was provided.

Analyte	**LOD / LOQ**	**% < LOD**	**% LOD Value Used**	**% < LOQ**
Ca	0.004 / 0.012 mg L^{-1}	0.00	0.00	0.00
Fe	0.001 / 0.005 mg L^{-1}	0.27	0.27	0.54
Mg	0.005 / 0.018 mg L^{-1}	0.00	0.00	0.00
TDP	0.012 / 0.035 mg L^{-1}	37.0	12.8	72.6
S	0.009 / 0.012 mg L^{-1}	0.00	0.00	0.00
SO_4-S	0.4 / 1 mg L^{-1}	15.1	6.45	20.2
NO_2-N	0.5 / 2.5 ug L^{-1}	69.1	46.0	88.2
NO_3-N	4.3 / 13 ug L^{-1}	48.4	15.9	67.2
SRP (PO_4-P)	7 / 18 ug L^{-1}	72.3	0.00	95.4
NH_4-N	2.2 / 5 ug L^{-1}	0.00	0.00	0.00

A small number of ion and nutrient analyses completed produced values below either the level of quantification (LOQ) or level of detection (LOD). If concentrations were provided by the lab despite being below LOQ or LOD, these concentrations were used. If there was no concentration provided, we used the value equal to the LOQ. The percentage of < LOQ and LOD values, as well as the percentage of values substituted with the LOD can be found in the Supplementary Materials (Table S.1.1).

S2 Detailed flow percentile calculation

If a stream sampled had a hydrometric station collecting discharge data, then the ranked discharge data of that stream was the only data used in the calculation. This was the case for nine out of the twenty-seven streams in this project. However, for the remaining eighteen streams that did not have a station, we used a station that was in closest proximity to the stream of interest. If the streams were both of a similar size (within 50%), then only that station was used to calculate the flow percentile during that sampling day, unless data limitations (i.e., missing or incomplete datasets) required the use of additional nearby stations. However, there were several streams where the closest station was either significantly larger or smaller than its proximal station. In this case, an average flow percentile of the closest station plus the closest station of similar size was used to make the most accurate estimation. At most, an average of three stations were used.

Table S2. The ten streams used to calculate flow percentile using Water Survey of Canada (WSC) data.

ID	Site Name	WSC ID	Long	Lat	Area (km^2)
H002	Hay River in Hay River	07OB001	60.75	-115.82	52,000
H011	Hay River at 60th Parallel	07OB008	60.00	-116.97	46,200
H022	Lutose Creek	07OB006	59.41	-117.28	296
H023	Hay River near Meander River	07OB003	59.15	-117.64	37,500
H050	East Sousa Creek	07OA001	58.59	-118.49	836
H051	Chinchaga River via HWY 58	07OC001	58.60	-118.33	10,600
L06	Scotty Creek	10ED009	61.42	-121.46	130
L12	Birch Creek	10ED003	61.33	-122.01	551
M064	Jean Marie River	10FB005	61.44	-121.24	1260
M076	Sambaa Deh (Trout River)	07OB004	61.14	-119.85	9060
H020	Steen River*	07OB004	59.58	-117.19	2647
L13	Blackstone River*	10ED007	61.06	-122.90	1409

Table S3. The twenty-seven streams sampled for this project (gauged and ungauged by the Water Survey of Canada) with information on the streams that were used in order to best estimate flow conditions and calculate flow percentile. Up to three gauged streams were used to best estimate flow.

ID	Site Name	Long	Lat	Area (km^2)	Site #1 Used	Site #2 Used	Site #3 Used
H002	Hay River in Hay River	60.75	-115.82	52,000	H002		
H003	Escarpment Creek	60.53	-116.22	215	H020	H022	
H004	Mink Creek	60.44	-116.34	187	H020	H022	
H006	Swede Creek	60.27	-116.57	526	H020	H022	
H011	Hay River at 60th Parallel	60.00	-116.97	46,200	H011		
H013	Camp Creek	59.84	-117.04	193	H020	H022	
H022	Lutose Creek	59.41	-117.28	296	H022		
H023	Hay River near Meander River	59.15	-117.64	37,500	H023		
H034	Hay-Zama Wetland Outflow	58.81	-118.62	21,200	H051		
H043	White Muskrat Creek	58.39	-119.49	243	H022	H050	H051
H044	Unnamed River on HWY 58	58.35	-119.51	1340	H022	H050	H051
H045	Hay River Inflow on HWY 58	58.35	-119.58	983	H022	H050	H051
H049	West Sousa Creek	58.60	-118.67	984	H022	H050	H051
H050	East Sousa Creek	58.59	-118.49	836	H050		
H051	Chinchaga River via HWY 58	58.60	-118.33	10,600	H051		
H052	Unnamed Creek via HWY 58	58.61	-118.28	278	H022	H050	H051
H059	Hutch Creek	58.81	-117.42	124	H022		
L06	Scotty Creek	61.42	-121.46	130	L06		
L07	Poplar River	61.34	-121.80	1650	L07	M064	
L12	Birch Creek	61.33	-122.01	551	L12		
M064	Jean Marie River	61.44	-121.24	1260	M064		
M076	Sambaa Deh (Trout River)	61.14	-119.85	9060	M076		
M079	Red Knife River	61.15	-119.34	1850	M064	M076	
M083	Axe Handle Creek	61.09	-118.72	529	L06	M076	
M087	Kakisa River	60.98	-117.24	15,800	M076		
M100	Buffalo River	60.72	-114.91	18,000	H002		
M105	Little Buffalo River	60.05	-112.77	3340	H002		

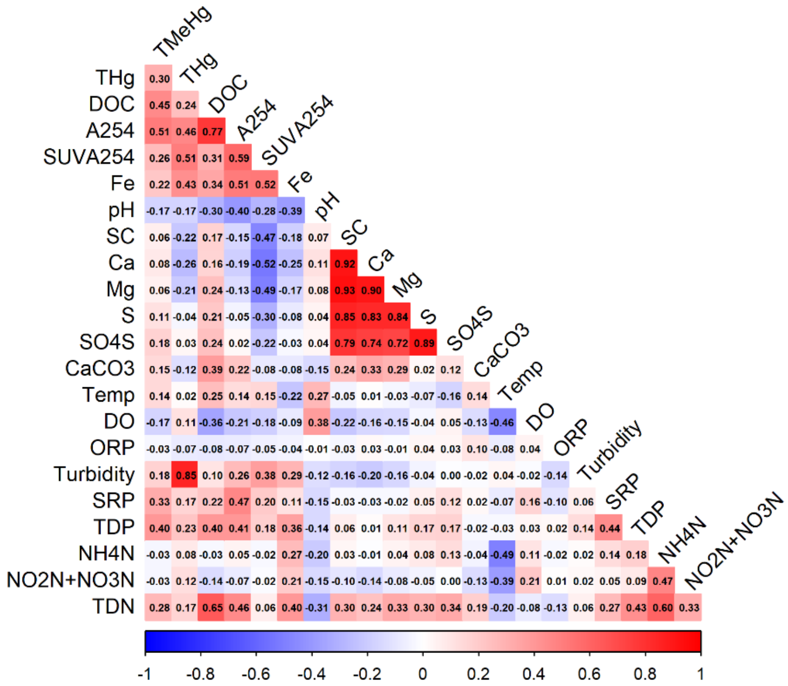
S3. Candidate models for LMMs

The LMMs were used to both determine the type of C-Q relationship that existed, as well as determining the interactive effects of discharge and various key catchment characteristics that have been determined to potentially drive water quality in the region: permafrost condition (using MAT), catchment size, peatland extent, and the presence or absence of wildfire within the catchment. Twelve models of a combination of these different predictor variables were run to determine which inputs yielded the best prediction of changes in concentration over a range of hydrological conditions (flow percentile). Models were ran for the following 11 variables: TMeHg, DOC, A254, SUVA254, THg, Turbidity, TDP, SRP, TDN, NO2- + NO3-, NH4+, and SC. Below are the twelve models:

1) Parameter ~ (1 | ID)
2) Parameter ~ FP + (1 | ID)
3) Parameter ~ FP + MAT + (1 | ID)
4) Parameter ~ MAT + (1 | ID)
5) Parameter ~ FP + FP:MAT + (1 | ID)
6) Parameter ~ FP + MAT + FP:MAT + (1 | ID)
7) Parameter ~ FP + MAT + Area + FP:MAT + FP:Area + (1 | ID)
8) Parameter ~ FP + FP:MAT + FP:Area (1 | ID)
9) Parameter ~ FP + FP:MAT + Peat (1 | ID)
10) Parameter ~ FP + MAT + Peat + FP:MAT + Peat:FP + (1 | ID)
11) Parameter ~ FP + MAT + Area + Peat + FP:MAT + Area:FP + Peat:FP + (1 | ID)
12) Parameter ~ FP + MAT + Area + Peat + WF + FP:MAT + Area:FP + Peat:FP + FP:WF + (1 | ID)

S4. Supplemental results

THg and TMeHg were moderately correlated with other parameters (e.g., TMeHg vs. A_{254}: r = 0.51; Figure A.3.1). DOC showed stronger correlations with A_{254} (r = 0.77), $SUVA_{254}$ (r = 0.59), and TDN (r = 0.65). A_{254} also correlated moderately with $SUVA_{254}$ (r = 0.52) and TDN (r = 0.46). SC was strongly correlated with major ions, including Ca (r = 0.92), Mg (r = 0.90), and S (r = 0.84), reinforcing its use as a proxy for groundwater. SC also showed strong correlations with SO_4S (r = 0.74) and weak with $CaCO_3$ (r = 0.24). TDN was strongly correlated TDP (r = 0.60). Several weaker negative correlations were observed, most notably between DO and DOC (r = -0.36), A_{254} (r = -0.40), and $SUVA_{254}$ (r = -0.28).



	TMeHg	THg	DOC	A254	SUVA254	Fe	pH	SC	Ca	Mg	S	SO4S	CaCO3	Temp	DO	ORP	Turbidity	SRP	TDP	NH4N	NO2N+NO3N
THg	0.30																				
DOC	0.45	0.24																			
A254	0.51	0.46	0.77																		
SUVA254	0.26	0.51	0.31	0.59																	
Fe	0.22	0.43	0.34	0.51	0.52																
pH	-0.17	-0.17	-0.30	-0.40	-0.28	-0.39															
SC	0.06	-0.22	0.17	-0.15	-0.47	-0.18	0.07														
Ca	0.08	-0.26	0.16	-0.19	-0.52	-0.25	0.11	0.92													
Mg	0.06	-0.21	0.24	-0.13	-0.49	-0.17	0.08	0.93	0.90												
S	0.11	-0.04	0.21	-0.05	-0.30	-0.08	0.04	0.85	0.83	0.84											
SO4S	0.18	0.03	0.24	0.02	-0.22	-0.03	0.04	0.79	0.74	0.72	0.89										
CaCO3	0.15	-0.12	0.39	0.22	-0.08	-0.08	-0.15	0.24	0.33	0.29	0.02	0.12									
Temp	0.14	0.02	0.25	0.14	0.15	-0.22	0.27	-0.05	0.01	-0.03	-0.07	-0.16	0.14								
DO	-0.17	0.11	-0.36	-0.21	-0.18	-0.09	0.38	-0.22	-0.16	-0.15	-0.04	0.05	-0.13	-0.46							
ORP	-0.03	-0.07	-0.08	-0.07	-0.05	-0.04	-0.01	-0.03	0.03	-0.01	0.04	0.03	0.10	-0.08	0.04						
Turbidity	0.18	0.85	0.10	0.26	0.38	0.29	-0.12	-0.16	-0.20	-0.16	-0.04	0.00	-0.02	0.04	-0.02	-0.14					
SRP	0.33	0.17	0.22	0.47	0.20	0.11	-0.15	-0.03	-0.03	-0.02	0.05	0.12	0.02	-0.07	0.16	-0.10	0.06				
TDP	0.40	0.23	0.40	0.41	0.18	0.36	-0.14	0.06	0.01	0.11	0.17	0.17	-0.02	-0.03	0.03	0.02	0.14	0.44			
NH4N	-0.03	0.08	-0.03	0.05	-0.02	0.27	-0.20	0.03	-0.01	0.04	0.08	0.13	-0.04	-0.49	0.11	-0.02	0.02	0.14	0.18		
NO2N+NO3N	-0.03	0.12	-0.14	-0.07	-0.02	0.21	-0.15	-0.10	-0.14	-0.08	-0.05	0.00	-0.13	-0.39	0.21	0.01	0.02	0.05	0.09	0.47	
TDN	0.28	0.17	0.65	0.46	0.06	0.40	-0.31	0.30	0.24	0.33	0.30	0.34	0.19	-0.20	-0.08	-0.13	0.06	0.27	0.43	0.60	0.33

Figure S1. Pearson correlation matrix of various water chemistry parameters. Values range from -1 (blue) to +1 (red), with darker colours indicating stronger correlations.

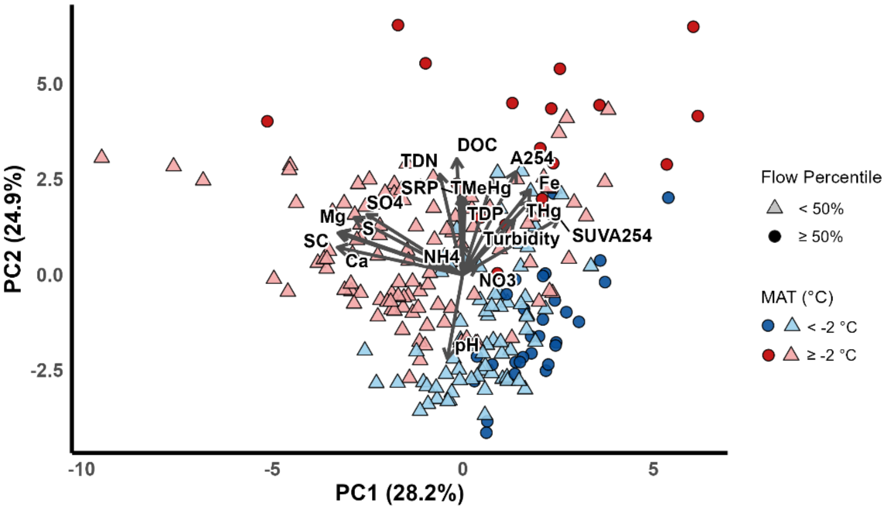


Figure S2. A similar PCA of water chemistry to Figure 4 in the main paper, but this includes turbidity. Points represent individual samples, and arrows indicate the loadings of water chemistry variables on the first two principal components. Shapes represent high (circle) and low (triangle) flow conditions, with flow percentiles greater than 50% being high and lower than 50% being low flow. Colours represent the MAT, where blue indicates a temperature less than -2°C, and red indicates warmer, permafrost absent regions with MATs greater than or equal to -2°C. Shade of colour is used to additionally indicate flow conditions for clarity, with light blue and pink triangles being indicative of low flow conditions, and dark blue and red circles indicating higher flow conditions. Note: NO_2 contributed < 5% of oxidized N and is therefore reported as NO_3 for clarity.