Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

The Molecular Diversity of Dissolved Organic Matter in Forest Streams Across Central Canadian Boreal Watersheds

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Table S1: Water chemistry variables including pH, electrical conductivity, DO%, water temperature, and DOC concentrations of the 13 sampled locations in the spring of 2019. Landscape classifications are based on pH in the spring.

Site	Landscape Classification	Collection Date	pH	Conductivity (uS cm-1)	DO (%)	Water Temperature (°C)	[DOC] (mg L^{-1})
DWR1	Peatland/Plain	2019-05-30	4.40	129	72	5.7	14.6±0.02
CF2	Sandy Soils	2019-06-04	5.02	13.4	73	6.3	13.9±0.06
CFR1	Sandy Soils	2019-06-11	5.44	20.2	55	3.7	28.6±0.25
DE3	Acidic Shallow Soil	2019-06-02	5.71	320	51	10.6	14.2±0.09
DE2	Acidic Shallow Soil	2019-05-31	6.15	27	82	13.3	16.4±0.28
DE1	Acidic Shallow Soil	2019-06-05	6.28	39.9	77	18.1	14.6±0.22
CF3	Sandy Soils	2019-06-04	6.46	32.9	91	8.4	14.4±0.32
DER1	Acidic Shallow Soil	2019-06-05	6.68	45.6	45	6.6	10.2±0.09
CF1	Sandy Soils	2019-06-06	6.69	67.6	95	4.3	18.6±0.18
SN1	Neutral Soil	2019-06-10	6.79	66.8	81	19.1	6.46±0.09
SN2U	Neutral Soil	2019-06-02	6.85	188.4	45	13.6	5.08±0.28
SN2	Neutral Soil	2019-05-31	6.97	217.3	69	11.3	7.200.16
DW1	Basic Soil	2019-06-03	7.15	75	84	8.3	$3.80\pm4.00\times10^{-3}$

Table S2: DOC concentrations and water chemistry variables including pH, conductivity, DO% and water temperature of the 13 sampled locations in the fall of 2019. Landscape classifications are absent for fall sampling as they are based on pH of watersheds in the spring.

Site	Collection Date	pH	Conductivity (uS cm^{-1})	DO (%)	Water Temperature (°C)	[DOC] (mg L^{-1})
CF1	2019-10-14	7.03	66.8	69	5.40	16.9±0.29
CF2	2019-10-10	6.54	15.1	72	8.30	25.6±0.62
CF3	2019-10-10	7.50	31.8	68	8.40	17.0±0.23
CFR1	2019-10-14	6.71	22.5	60	4.80	27.0±0.27
DE1	2019-10-13	N/A	N/A	N/A	N/A	16.2±0.25
DE2	2019-10-16	7.12	25.3	67	5.80	25.1±0.31
DE3	2019-10-12	7.76	28	61	6.60	24.1±0.27
DER1	2019-09-26	7.86	42.1	60	5.90	29.8±0.27
DW1	2019-10-15	6.91	10.8	65	5.80	6.73±0.39
DWR1	2019-10-15	6.67	16.6	52	6.30	23.7±0.27
SN1	2019-10-12	7.44	43.9	86	9.00	15.3±0.12
SN2	2019-10-11	7.29	157	47	10.8	7.58±1.96
SN2U	2019-10-11	7.11	0.8	75	12.0	7.58±0.14

Table S3: Optical properties of the 14 sampled locations during Spring 2019.

Site	Collection Date	a254nm	a300nm	E2:E3 Ratio	S275-295nm	S350-400nm	Slope Ratio
CF1	06-Jun	51.8	33.3	4.73	0.01	0.02	0.82
CF2	04-Jun	1.65×10^2	65.3	4.40	0.01	0.02	0.72
CF3	04-Jun	94.7	57.0	4.41	0.01	0.02	0.72
CFR1	11-Jun	1.04×10^2	59.6	5.01	0.01	0.02	0.73
DE1	05-Jun	50.3	30.3	4.12	0.01	0.01	0.84
DE2	31-May	92.5	58.3	4.70	0.01	0.02	0.79
DE3	02-Jun	87.3	52.4	4.98	0.01	0.02	0.77
DER1	05-Jun	50.5	27.9	5.30	0.01	0.02	0.81
DW1	03-Jun	28.5	15.2	5.79	0.02	0.02	0.86
DWR1	30-May	77.6	48.2	3.97	0.01	0.02	0.75
SN1	10-Jun	62.1	36.9	4.79	0.01	0.02	0.94
SN2	31-May	30.8	16.3	6.08	0.02	0.02	0.78
SN2U	02-Jun	39.7	20.9	5.84	0.02	0.02	0.86

Table S4: Optical properties of the 14 sampled locations during Fall 2019.

Site	**Collection Date**	a254nm	a300nm	E2:E3 Ratio	S275-295nm	S350-400nm	Slope Ratio
CF1	14-Oct	77.0	44.49	4.87	0.01	0.02	0.74
CF2	10-Oct	1.27×10^2	75.95	4.49	0.01	0.02	0.71
CF3	10-Oct	1.02×10^2	61.18	4.43	0.01	0.02	0.70
CFR1	14-Oct	1.41×10^2	82.99	4.73	0.01	0.02	0.71
DE1	13-Oct	50.8	28.02	5.41	0.01	0.02	0.78
DE2	16-Oct	1.20×10^2	71.09	4.63	0.01	0.02	0.72
DE3	12-Oct	1.21×10^2	70.17	4.91	0.01	0.02	0.72
DER1	07-Oct	1.36×10^2	79.45	4.84	0.01	0.02	0.72
DW1	15-Oct	38.0	20.75	5.57	0.01	0.02	0.78
DWR1	15-Oct	1.50×10^2	91.32	4.40	0.01	0.02	0.68
SN1	12-Oct	77.2	43.05	5.27	0.01	0.02	0.78
SN2	11-Oct	46.6	25.44	5.81	0.01	0.02	0.73
SN2U	11-Oct	49.3	27.13	5.55	0.01	0.02	0.75

Table S5: Intensity weighted average bulk FT-ICR-MS molecular properties including *m/z*, atomic ratios, elemental percentage contributions, aromaticity proxies and oxidation states of carbon during spring collections.

Site	Collection Date	m/z_{wa}	O/C_{wa}	H/C_{wa}	N/C_{wa}	S/C_{wa}	$\%C_{wa}$	$\%H_{wa}$	$\%O_{wa}$	$\%N_{wa}$	$\%S_{wa}$	DBE_{wa}	$DBE\text{-}O_{wa}$	AI_{wa}	$AImod_{wa}$	$NOSC_{wa}$
CF1	2019-06-06	493.894	0.49	1.36	2.57×10^{-2}	2.37×10^{-2}	54.4	6.26	34.6	1.51	3.22	7.68	-2.63	-0.50	0.25	-0.30
CF2	2019-06-04	500.822	0.45	1.28	2.88×10^{-2}	2.86×10^{-2}	54.7	5.88	33.6	1.75	4.10	8.01	-1.36	-0.36	0.35	-0.25
CF3	2019-06-04	466.152	0.46	1.20	2.60×10^{-2}	2.19×10^{-2}	56.6	5.73	32.8	1.67	3.24	9.64	0.70	-0.43	0.37	-0.21
CFR1	2019-06-11	308.660	0.48	1.15	5.44×10^{-3}	2.55×10^{-3}	58.3	5.75	35.2	0.36	0.36	7.31	0.45	-0.07	0.65	-0.18
DE1	2019-06-05	321.410	0.51	1.10	6.04×10^{-3}	2.49×10^{-3}	57.0	5.37	36.9	0.37	0.31	7.84	0.33	-0.12	0.67	-0.07
DE2	2019-05-31	339.773	0.50	1.14	7.55×10^{-3}	5.58×10^{-3}	57.0	5.58	36.3	0.43	0.69	7.95	0.14	-0.17	0.63	-0.12
DE3	2019-06-02	316.206	0.50	1.13	7.03×10^{-3}	2.99×10^{-3}	57.3	5.55	36.4	0.43	0.33	7.47	0.18	-0.17	0.63	-0.11
DER1	2019-06-05	323.137	0.47	1.11	4.69×10^{-3}	1.91×10^{-2}	57.3	5.44	34.0	0.30	2.99	7.81	0.92	-0.12	0.62	-0.16
DW1	2019-06-03	366.160	0.48	1.13	1.19×10^{-2}	2.63×10^{-2}	55.8	5.37	34.3	0.74	3.77	8.46	0.60	-0.25	0.51	-0.14
DWR1	2019-05-30	293.105	0.37	1.24	3.26×10^{-2}	2.24×10^{-2}	60.1	6.30	27.8	2.31	3.55	6.70	1.74	0.07	0.44	-0.44
SN1	2019-06-10	285.579	0.52	1.10	4.10×10^{-3}	1.13×10^{-3}	56.7	5.28	37.6	0.22	0.14	6.18	0.31	-0.08	0.66	-0.06
SN2	2019-05-31	297.367	0.38	1.28	1.65×10^{-3}	1.04×10^{-2}	61.5	6.67	30.2	0.07	1.61	6.40	0.78	0.05	0.41	-0.52
SN2U	2019-06-02	294.240	0.44	1.27	1.66×10^{-2}	3.98×10^{-3}	58.4	6.22	33.7	1.03	0.65	6.11	-0.03	-0.07	0.43	-0.33

Table S6: Intensity weighted average bulk FT-ICR-MS molecular properties including *m/z*, atomic ratios, elemental percentage contributions, aromaticity proxies and oxidation states of carbon during fall collections.

Site	Collection Date	m/z_{wa}	O/C_{wa}	H/C_{wa}	N/C_{wa}	S/C_{wa}	$\%C_{wa}$	$\%H_{wa}$	$\%O_{wa}$	$\%N_{wa}$	$\%S_{wa}$	DBE_{wa}	$DBE\text{-}O_{wa}$	AI_{wa}	$AImod_{wa}$	$NOSC_{wa}$
CF1	2019-10-14	308.290	0.45	1.15	1.54×10^{-2}	8.84×10^{-3}	58.2	5.66	33.7	0.99	1.44	7.39	0.88	5.47×10^{-2}	0.57	-0.21
CF2	2019-10-10	344.468	0.44	1.09	1.78×10^{-2}	1.63×10^{-2}	58.0	5.39	32.8	1.20	2.56	8.53	1.52	7.15×10^{-2}	0.62	-0.16
CF3	2019-10-10	333.148	0.46	1.10	1.59×10^{-3}	1.36×10^{-2}	57.5	5.40	34.8	0.11	2.22	8.03	0.79	3.77×10^{-2}	0.56	-0.18
CFR1	2019-10-14	314.360	0.44	1.16	1.50×10^{-2}	1.65×10^{-2}	58.0	5.72	32.7	1.00	2.62	7.25	0.89	3.16×10^{-2}	0.55	-0.25
DE1	2019-10-13	302.807	0.42	1.29	1.35×10^{-2}	9.03×10^{-3}	58.9	6.41	32.3	0.85	1.42	6.20	0.11	-5.72×10^{-2}	0.40	-0.41
DE2	2019-10-16	304.098	0.44	1.16	1.50×10^{-2}	1.65×10^{-2}	58.0	5.72	32.7	1.00	2.62	7.25	0.89	3.16×10^{-2}	0.56	-0.25
DE3	2019-10-12	308.329	0.43	1.21	1.65×10^{-3}	9.06×10^{-3}	59.3	6.05	33.2	0.10	1.42	6.94	0.53	-3.18×10^{-3}	0.47	-0.34
DER1	2019-10-07	295.689	0.36	1.19	2.52×10^{-2}	3.03×10^{-2}	59.8	6.00	27.5	1.85	4.86	7.17	2.21	1.29×10^{-1}	0.51	-0.40
DW1	2019-10-15	303.818	0.40	1.22	4.13×10^{-4}	1.43×10^{-2}	59.9	6.19	31.5	0.03	2.29	6.82	0.83	5.45×10^{-2}	0.45	-0.41
DWR1	2019-10-15	295.144	0.41	1.19	3.77×10^{-3}	1.89×10^{-2}	59.3	5.99	31.4	0.28	3.05	6.82	1.04	5.31×10^{-2}	0.49	-0.37
SN1	2019-10-12	302.365	0.42	1.20	1.32×10^{-3}	6.79×10^{-3}	60.1	6.11	32.6	0.10	1.11	7.02	0.84	7.17×10^{-2}	0.49	-0.36
SN2	2019-10-11	329.806	0.38	1.24	5.85×10^{-3}	1.54×10^{-3}	60.9	6.37	29.9	0.35	2.40	7.61	1.50	5.50×10^{-2}	0.45	-0.46
SN2U	2019-10-11	293.320	0.42	1.18	3.37×10^{-4}	7.35×10^{-2}	59.8	5.98	33.0	0.02	1.17	6.93	0.87	6.29×10^{-2}	0.49	-0.34

Figure S1: Total precipitation data (obtained from Environment Canada) for the Dryden area for May (A), June (B) and October (C) 2019.

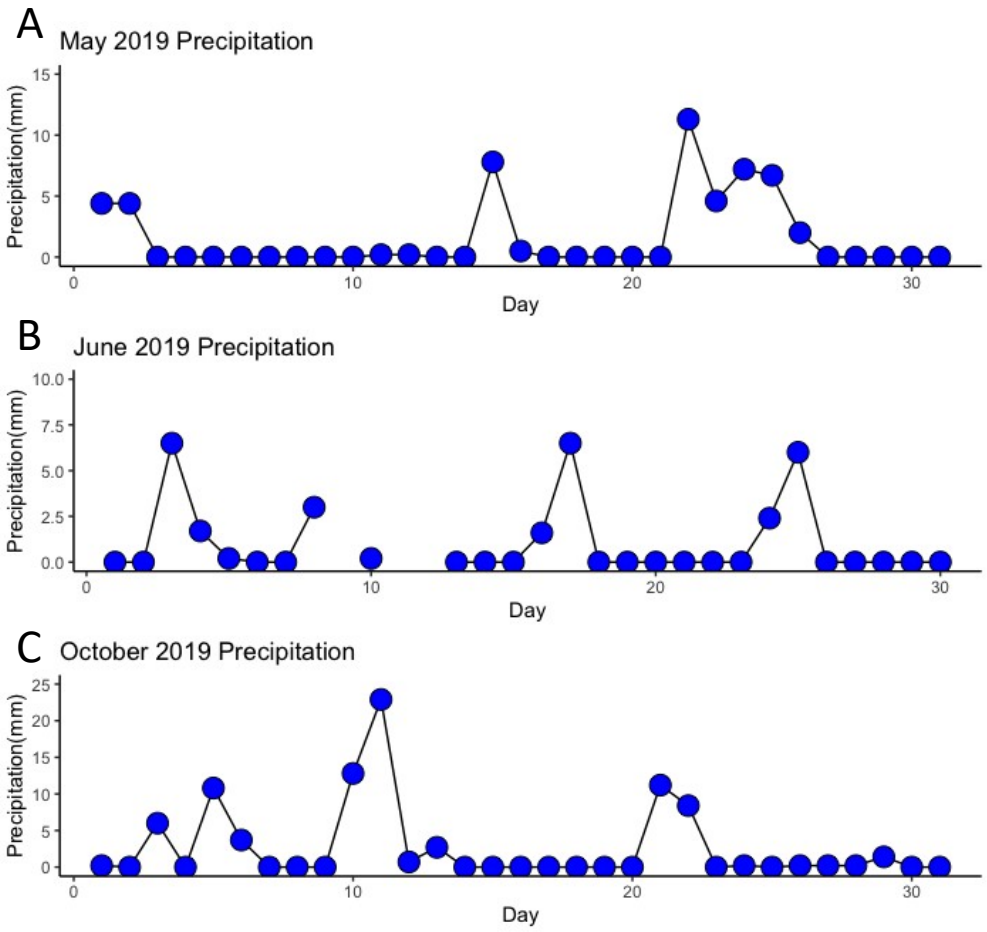

Figure S2: Air temperature data (obtained from Environment Canada) for the Dryden area for May (A), June (B) and October (C) 2019.

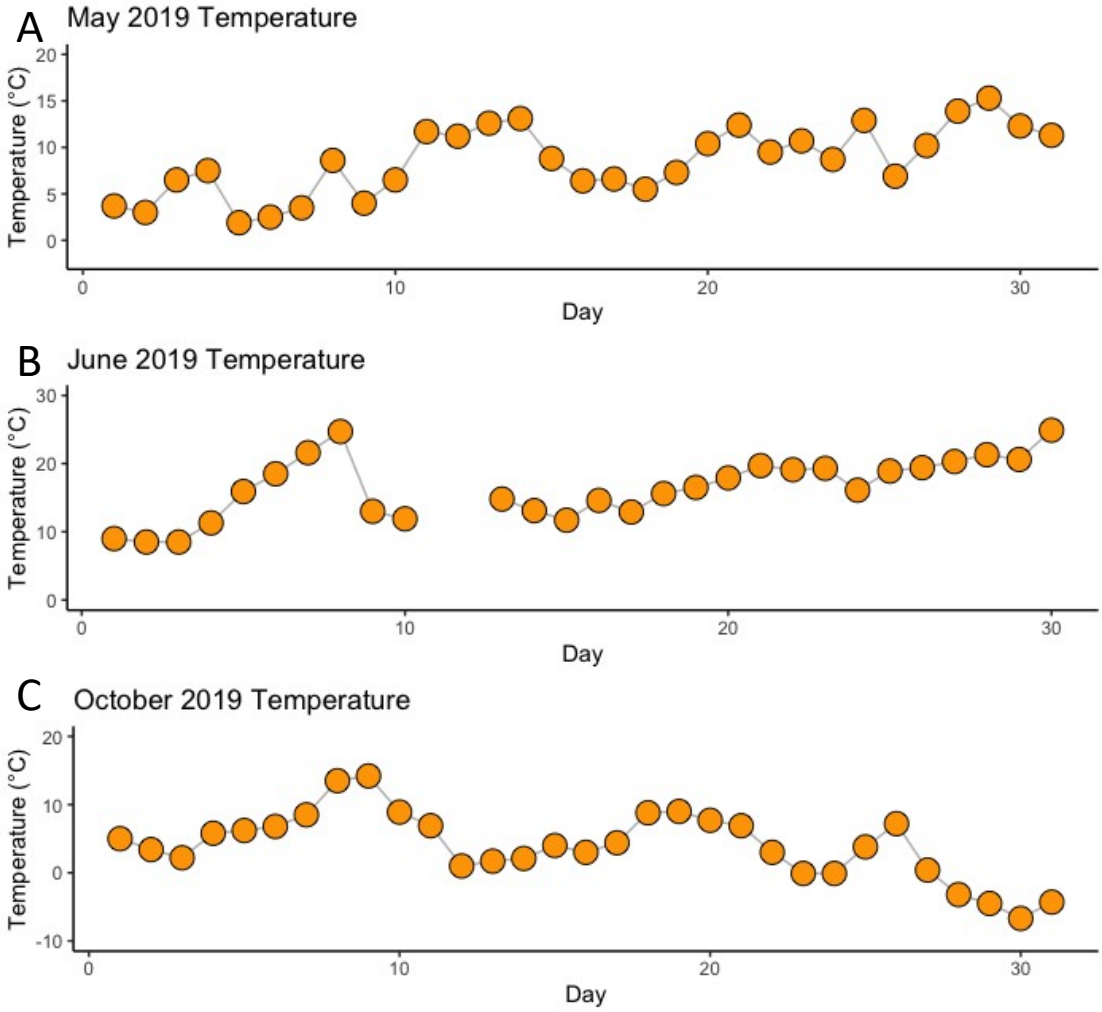

Figure S3: FT-ICR-MS spectra of center fire sandy soil sites CF1 (A, E), CF2 (B, F), CF3 (C, G) and CFR1 (D, H) collected during spring (A-D) and fall (E-H).

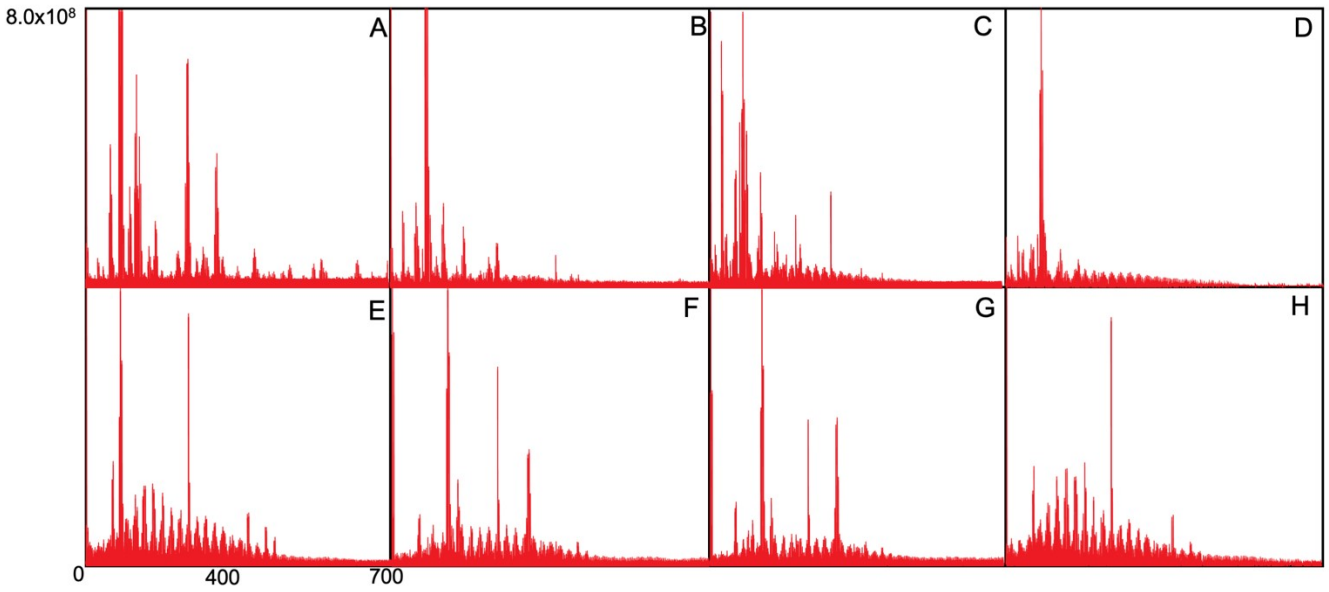

Figure S4: FT-ICR-MS spectra of acidic shallow soil site Deserre DE1 (A, E), DE2 (B, F), DE3 (C, G) and DER1 (D, H) collected during spring (A-D) and fall (E-H).

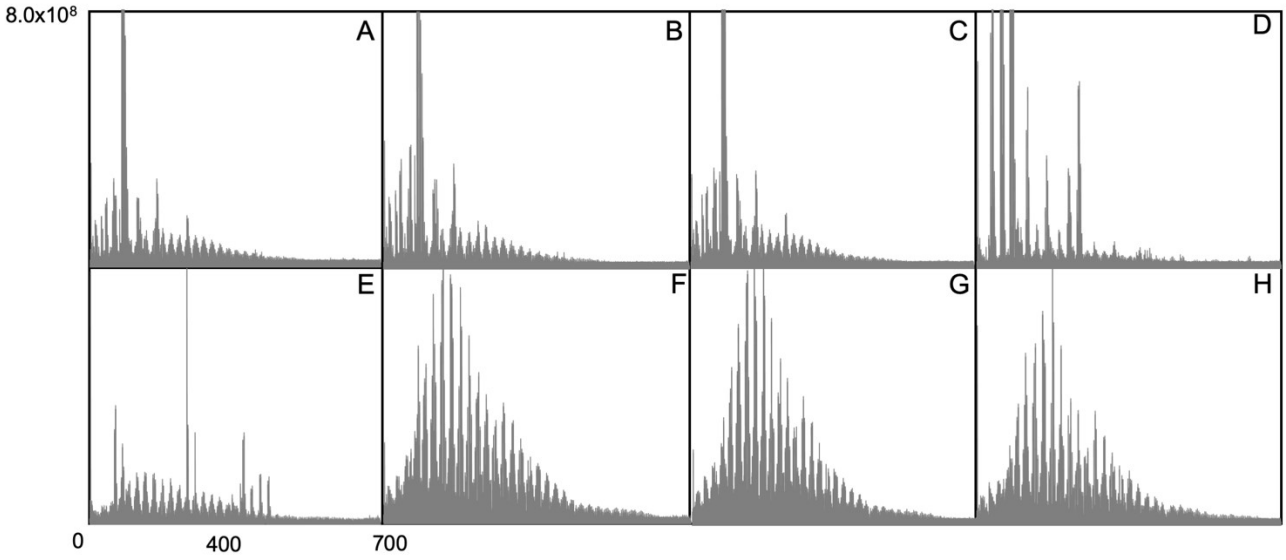

Figure S5: FT-ICR-MS spectra of basic shallow soil Dinorwic site DW1 (A, C), and peatland/plain site DWR1 (B, D), during spring (A, B) and fall (C, D).

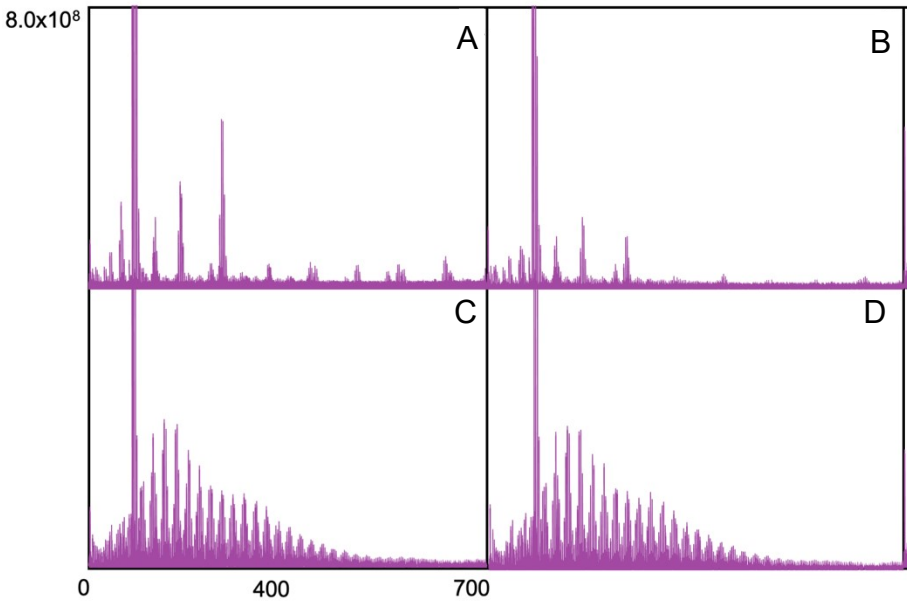

Figure S6: FT-ICR-MS spectra of Snowfall mixed sites SN1 (A, E), SN2 (B, F), SN2U (C, G) and collected during spring (A-C) and fall (E-G).

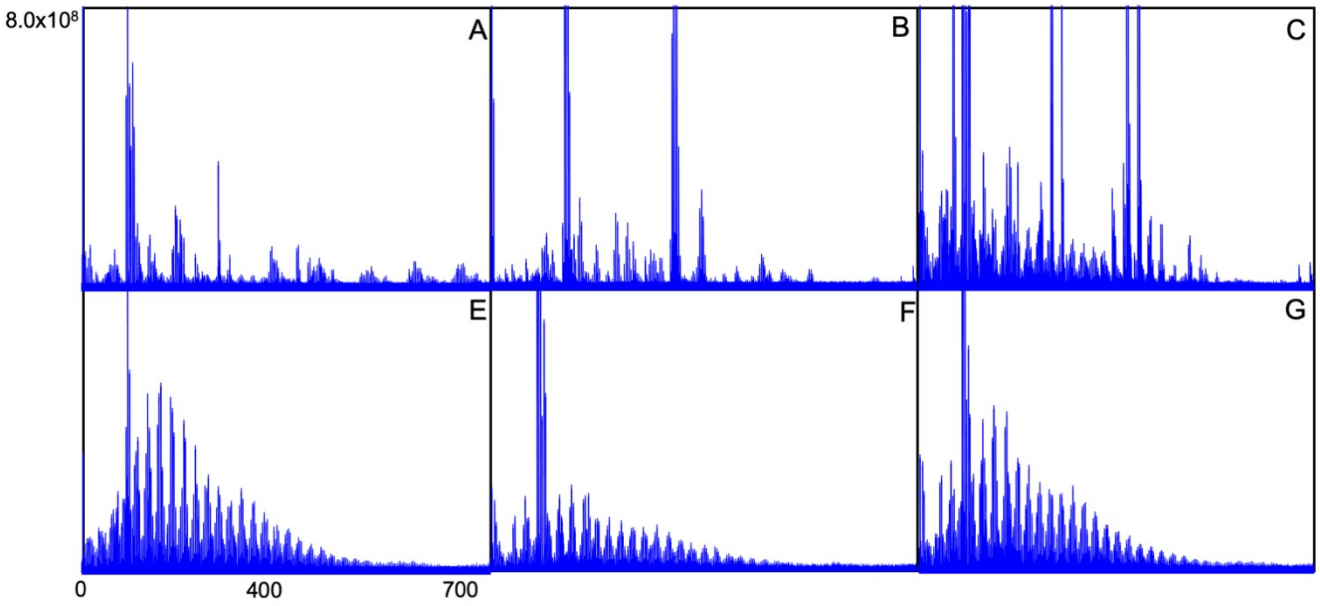

Figure S7: Observed (A) and theoretical (B) observations of ^{13}C and ^{18}O isotopes that reinforce accurate formula assignment of spectra.

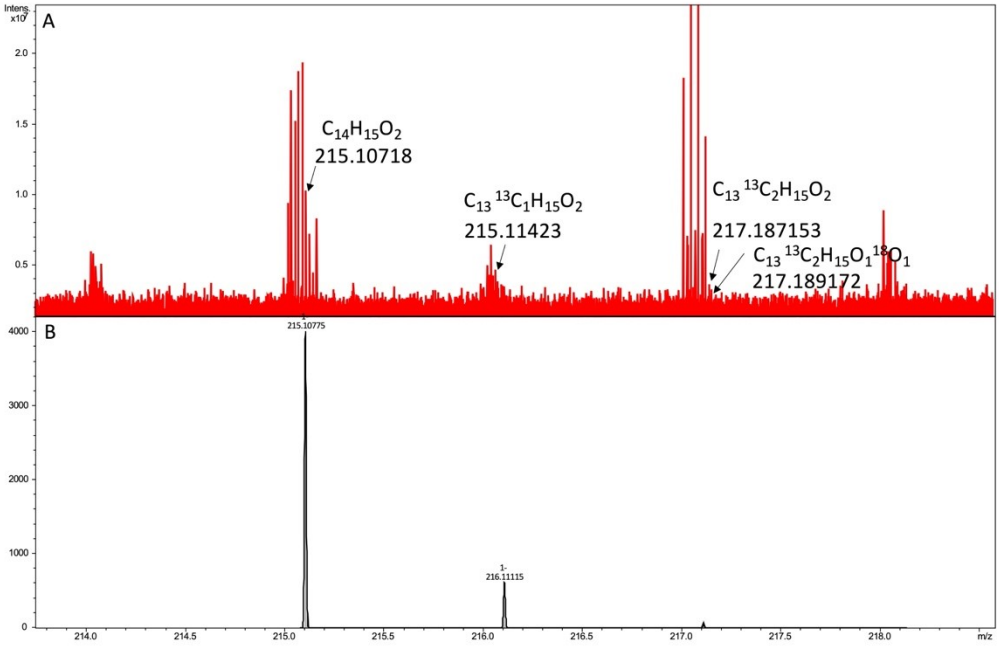

Figure S8: Mean DOC concentrations (A) and mean monthly runoff(B) for each boreal watershed sampled in late spring (May/June; blue) and fall (October; orange) in 2019. Error bars represent standard errors based on triplicate measurements across watersheds. Dashed lines in the DOC concentration graph separate watersheds of a similar landscape classification. Precipitation during the sampling period in the late spring and fall were 47 mm and 82 mm, respectively, with a 23 mm rainfall event on October 11th, 2019.

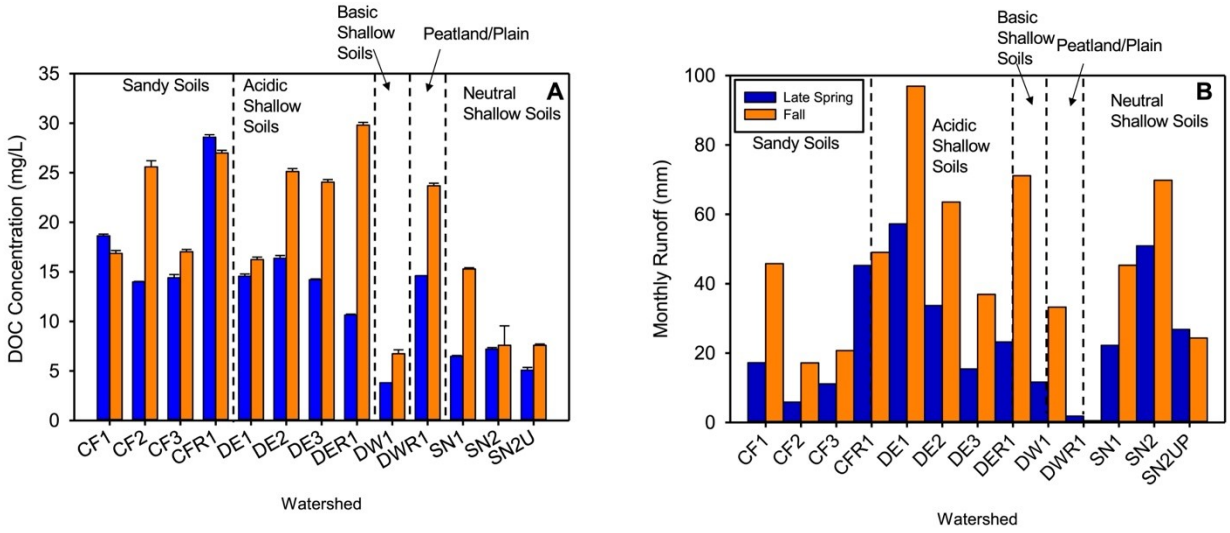

Figure S9: Monthly mean runoff calculated by dividing stream discharge by watershed area during the fall (blue) and spring (orange).

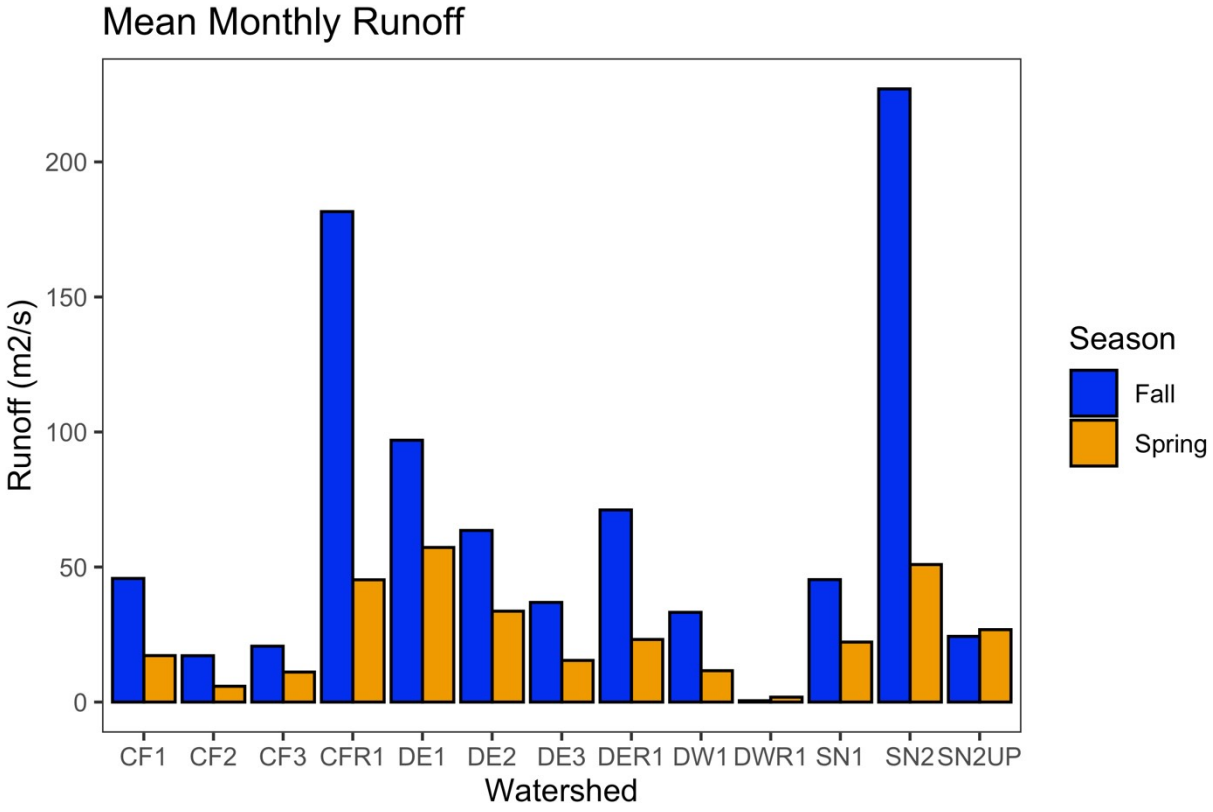

Figure S10: Van Krevelen diagram (A) of all molecules found in the spring (blue) and fall (orange), along with a pie chart highlighting up to 86 % of common molecules found across both seasons, but 14 % unique compounds found in the spring.

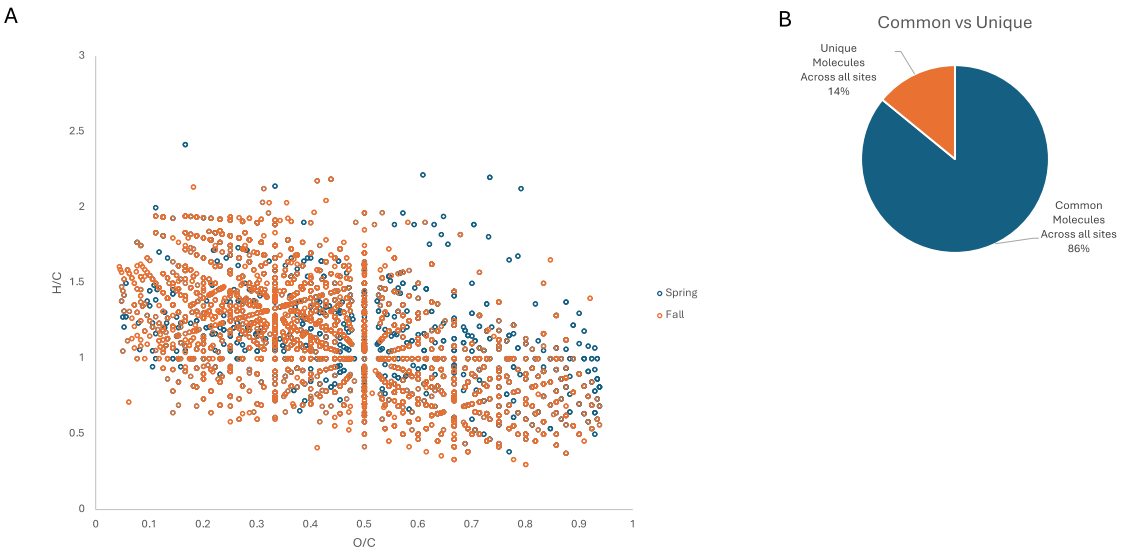

Figure S11: Spearman rank correlation of DOM molecules significantly ($p < 0.05$) correlating with wet forest coverage % (A), dry forest coverage % (B), and mixed forest coverage % (C). Molecules positively correlating with each landscape characteristic are found in green whereas molecules negatively correlating with the respective landscape characteristic is found in purple.