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Supporting Information for

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[Hillslopes in Headwaters of Qinghai-Tibetan Plateau as Hotspots for Subsurface Dissolved Organic Carbon Processing during Permafrost Thaw]

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[Yuqin Sun[1,2,3], Kale Clauson[4], Min Zhou[1], Ziyong Sun[5], Chunmiao Zheng[2,3] and Yan Zheng[2,3*]]

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[[1] College of Engineering, Peking University, Beijing, 100871, China.

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[2] State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, 518055, China.

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[3] Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, 518055, China.

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[4] School of Earth and Environmental Sciences, Queens College, City University of New York, Flushing, NY 11367, USA.

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[5] School of Environmental Studies, China University of Geosciences, Wuhan 430074, China.]

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Introduction

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Supporting information contains descriptions of sampling protocols, field and laboratory measurement details (Text S1), soil incubation experimental procedure (Text S2) and results (Text S3). Figures S1 and S6 illustrates the variations of $SUVA_{254}$ FI and BIX. Figure S2 depicts the soil incubation experiment set up. Figures S3 – S5 show fluorescent characteristics of the DOM samples and PARAFAC modeling results. Tables S1 reports uncertainties of endmember compositions and analysis. Table S3 and Figure S7 report soil incubation experimental data. Dataset S1 to S2 (separate electronic files) are original data of field and laboratory measurements of water chemistry parameters for all samples.

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Text S1. Sampling and Measurements.

Temperature (T), electrical conductivity (EC) and pH were measured in the field using WTW-COND-3301 instrument in 2012 and 2013, and Thermo 520M-01A instrument in 2018. Alkalinity was measured using titration method in the field [*Gran*, 1952]. All samples were stored on ice at 4°C for shipment to laboratory.

Stable isotopes (δD and δ^{18}O) were measured for samples collected in July 2013, and September of 2013 and 2018 on a water isotope spectrometer analyzer (Model PICARRO L2130-I) at Pri-ecoco, Beijing, China. Three standard solutions (GBW58, GBW59, and GBW60) were employed as daily QA/QC. Each sample was analyzed 6 times and the result was calculated as the average of the last three injections. The relative standard deviation (RSD) for duplicate analysis was < 0.8%. The isotope compositions are expressed as the δ-notation related to Vienna Standard Mean Ocean Water (VSMOW) in ‰.

DOC concentrations for samples collected in 2012 and 2013 were measured on a TOC-5000 Analyzer (Shimadzu) at both the Environmental Engineering Laboratory, Peking University and Queens College, CUNY according to a Non Purgeable Organic Carbon (NPOC) method. Samples collected in 2018 were analyzed by a TOC-L Analyzer (Shimadzu) at Southern University of Science and Technology following the same protocol. Samples were analyzed in triplicate with the RSD less than 3% as a threshold for accepting the result.

Measurement of cations was performed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) at Peking University for samples collected in 2012 and 2013. Anions of nitrate (NO_3), sulfate (SO_4) and chloride (Cl) were measured using ion chromatography (IC) at Peking University. Major anions and cations concentrations were measured using IC at Southern University of Science and Technology for samples collected in 2018.

Text S2. Experimental Procedure of Soil Incubation.

At the start of the second incubation in the reactor, 100 g of wet soil was weighed and added to a glass reactor and filled with 5L CO_2-free MQ water without headspace at room temperature. The reactor was kept in dark for 80 hours, with a peristaltic pump running at 29 ml/min to ensure mixing. The inlet and outlet of the reactor were connected with 6M NaOH solution to maintain CO_2-free headspace (Fig. S1). A total of 29 samples were collected at an interval of 30 min in the initial 4.6 hours, at an interval of 60 min till 12 hours, and at an interval of 180 min until the end of incubation that lasted 80 hours. At each sampling time, approximately 75 ml of water was removed. Water volume and pH were measured immediately before filtering with 0.22 μm SPE filters. Filtered samples were analyzed for DOC concentrations, UV-vis and fluorescence as in section 2.2 of the main text.

Text S3. Soil Incubation Results.

During the 80-hours dark incubation of the frost soil in the reactor, the carbon mass of DOC decreases from 30 mg to 12 mg in the initial 12 hours (Fig. S6a). The utilization of aromatic DOC is supported by the doubling of $SUVA_{254}$ values concurrent with a 60% decrease in DOC mass in the system between 0 to 12 hours (Fig. S6). From 12 hours to 80 hours, $SUVA_{254}$ values instead decreased with an increase of DOC mass from 12 mg to 18 mg (Fig. S6c). The EEMs of all incubation samples show the main fluorescent peak at excitation of 230 nm and emission of 240 nm, suggesting that protein-like fluorophores are significant.

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78   The first-order kinetic equation was applied to fit the SOC degradation curves for the
79   decrease in DOC mass in the first 12 hrs (Fig. S6c). The half-time of soil derived DOC degradation
80   is estimated to be 5 hours, and the degradation constant is calculated as dividing -ln (0.5) by half-
81   time. Therefore, the degradation constant following first-order kinetics of DOC derived from
82   permafrost soil is estimated to be 0.32 d^{-1} at $20^{o}C$, and is corrected to 0.11 d^{-1} for $5^{o}C$.
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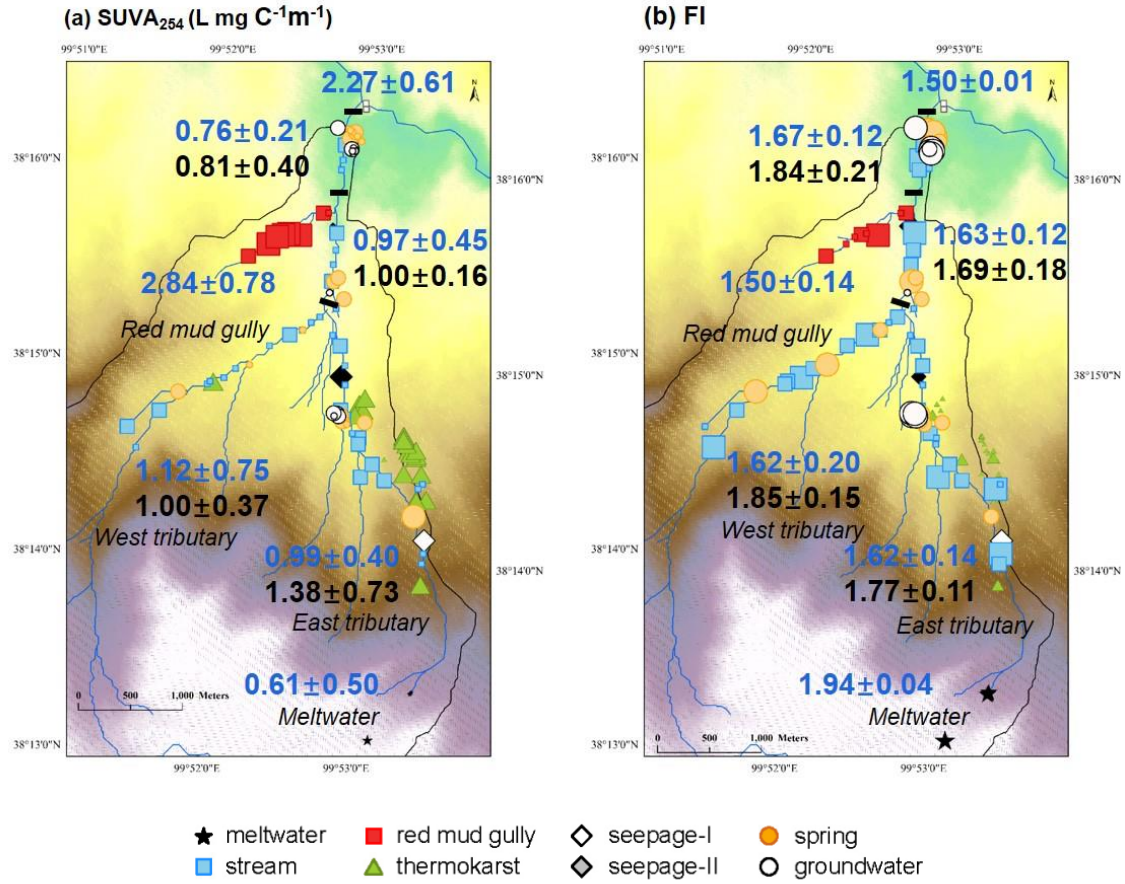
Figure S1. (a) $SUVA_{254}$ for eight types of water in HLGW, Qinghai-Tibetan Plateau. Small, medium and large symbol sizes indicate low (< 0.91 L mg C^{-1} m^{-1}), medium (0.91–2.46 L mg C^{-1} m^{-1}) and high (>2.46 L mg C^{-1} m^{-1}) $SUVA_{254}$ according to tertile values of the entire dataset. Numbers are mean value ± one standard deviation for $SUVA_{254}$ in stream (blue) and subsurface water (black). (b) FI with small, medium and large symbol sizes indicate low (<1.59), medium (1.59–1.69) and high (>1.69) according to tertile values. Numbers are mean value ± one standard deviation for FI in stream (blue) and subsurface water (black).

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(a) Preparation of CO₂-free MQ water
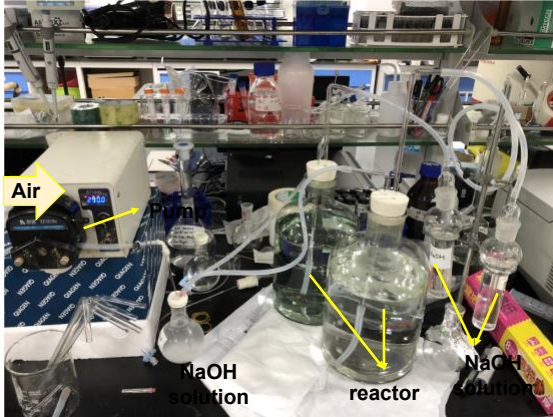
(b) Incubation reactor setting up and sampling

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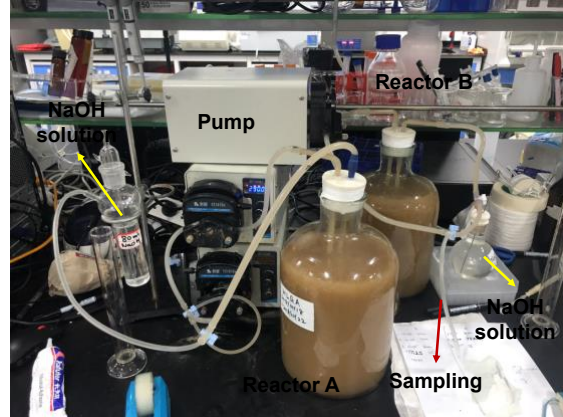
Figure S2. Figure S1. Experimental set up of frost soil reactor incubation. Left photo shows the preparation of CO_2-free water for the two reactors. Right photo shows ongoing experiment with sampling port location during incubation. The reactors used 5-L glass containers with inlet and outlet ports. Continuous mixing is ensured by pumping water at a rate of 29 mL min^{-1} from the reactors by a peristaltic pump through a CO2-free chamber. Samples were collected by a syringe at the sampling port with a three-way valve.

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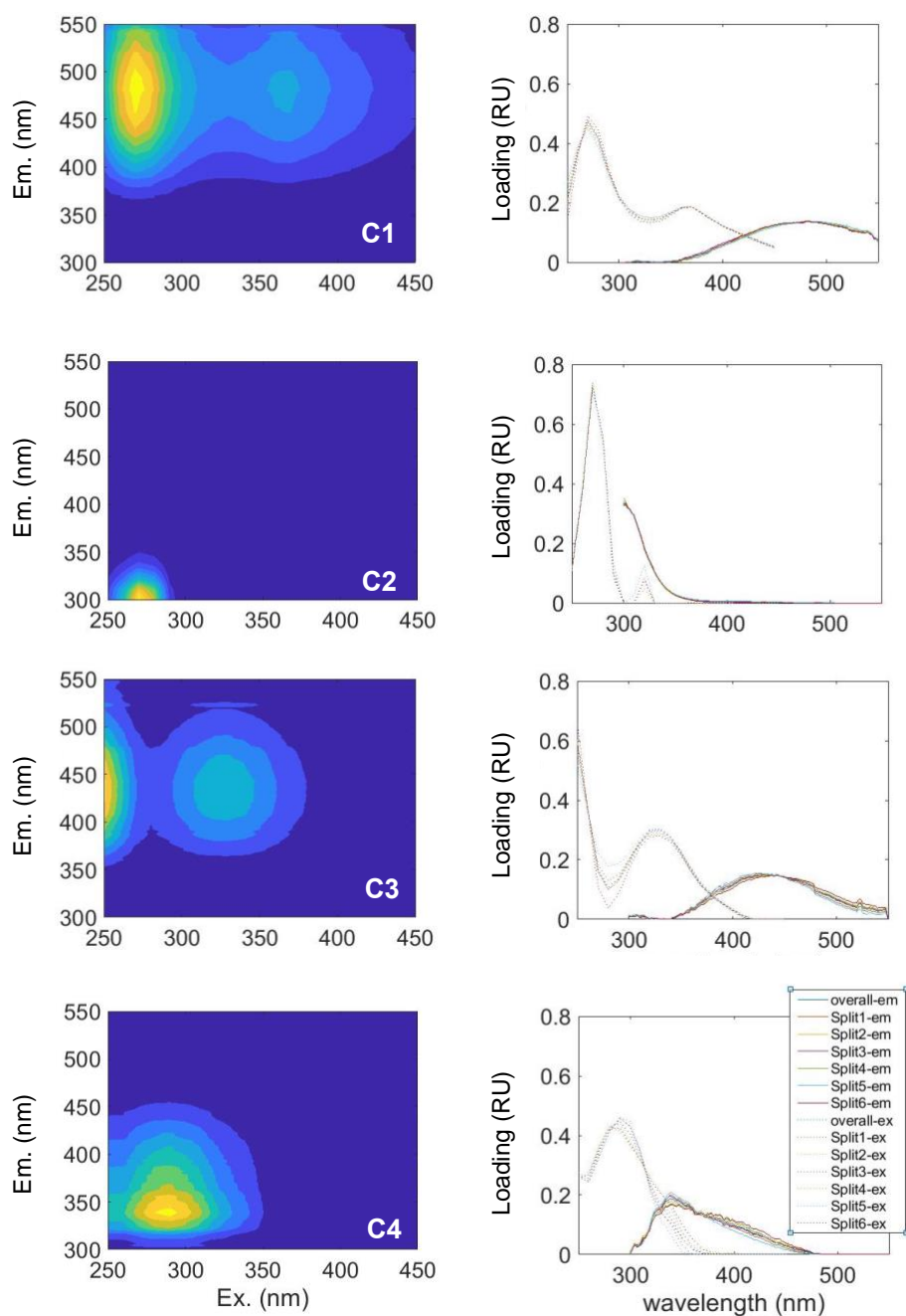
Figure S3. Fluorescence matrixes of the four identified components (left) and loadings of excitation (the dot lines) and emission (the solid lines) wavelength (right), respectively. Component 1 (ex: 270/370 nm, em: 470 nm) and component 3 (ex: <250/330 nm, em:420 nm) represent two humic-like components. Fluorescence characteristic of C2 (ex: 270 nm, em: 304 nm) represents tyrosine-like material [*D'Andrilli et al.*, 2019] (20), and C4 (ex: 290 nm, em: 338 nm) represents amino-acids, free or bound in proteins compounds [*Catala et al.*, 2015; *Murphy et al.*, 2008].

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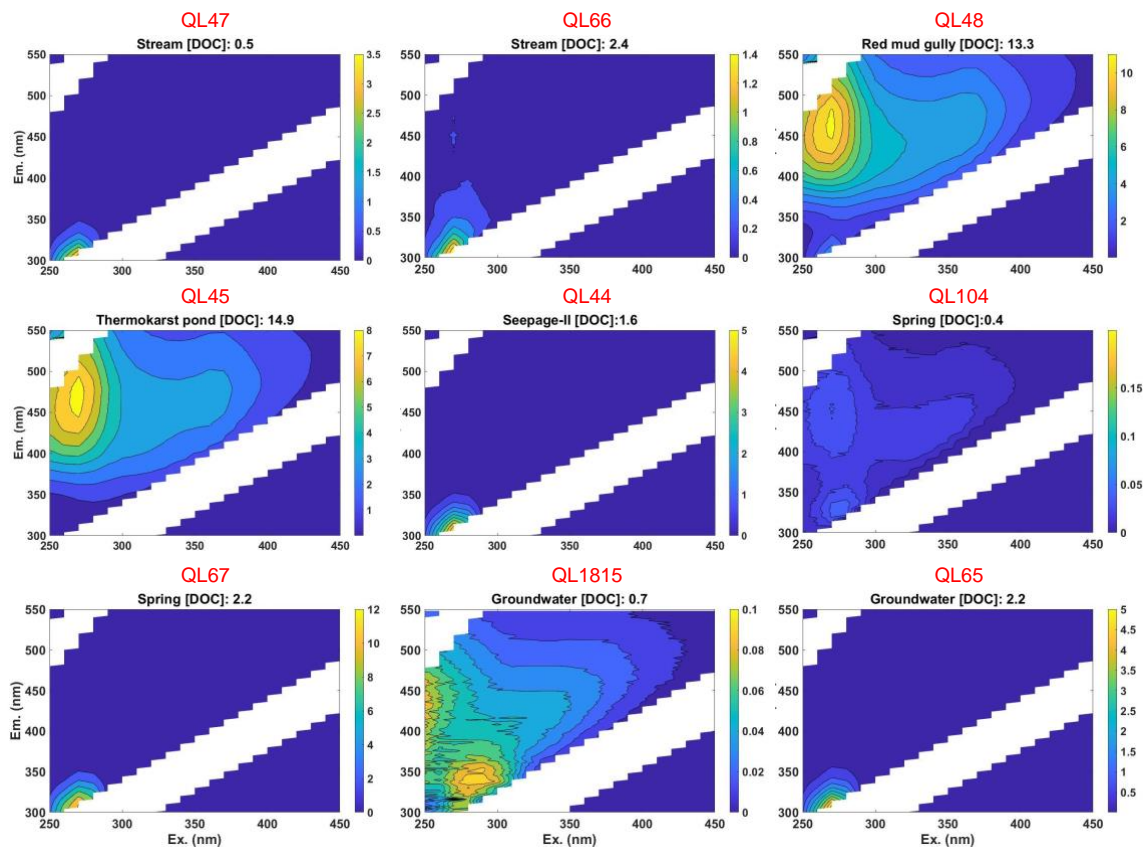
Figure S4. EEMs plots of typical stream, red mud gully, thermokarst pond, seepage-II, spring and groundwater samples in HLGW. Sample ID is written in red (see Data set S1 for details), and the DOC concentration (mg L^{-1}) is written in black above each EEMs. Color bar represents the fluorescence intensity.

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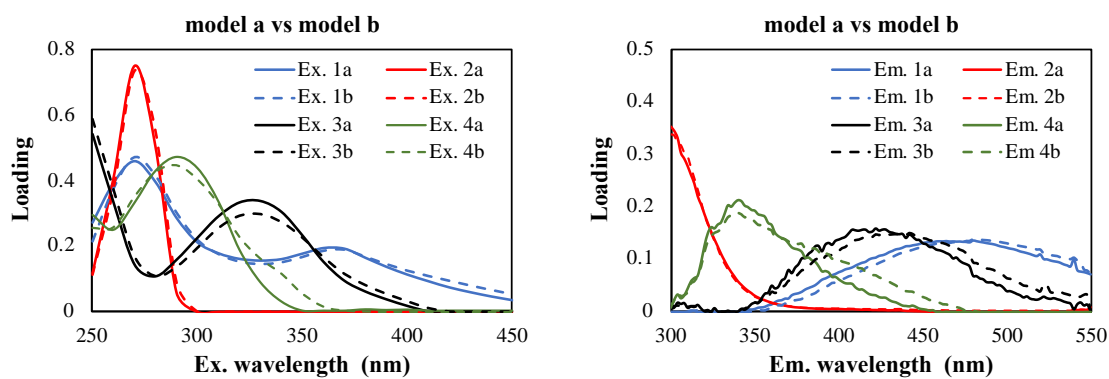
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119 **Figure S5.** Comparison of excitation (Ex.) and emission (Em.) loadings of the four-components
120 models.

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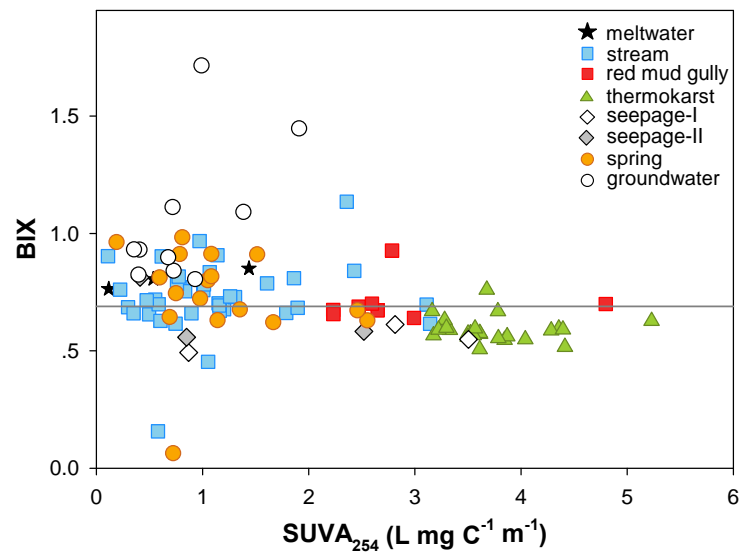
Figure S6. SUVA$_{254}$ vs BIX for eight types of water samples with gray line indicating the median value of BIX for entire dataset.

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(a)

(b)

(c)

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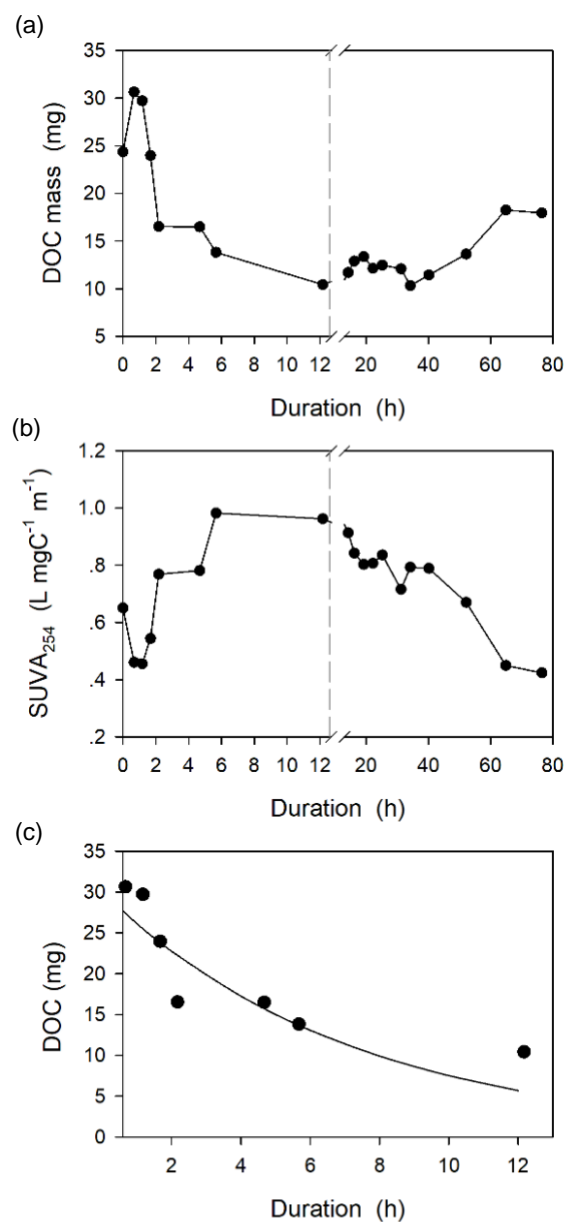
Figure S7. Changes of (a) DOC expressed as carbon mass in supernatant and (b) SUVA$_{254}$ values
over 80 hrs for the reactor soil incubation experiment in dark. The first-order kinetics fit to the
soil carbon derived DOC degradation data in the first 12 hrs is shown in (c).

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Sample ID	Type	f_G	f_P	f_S	W_G	W_P	W_S
QL41	stream	0.20	0.73	0.08	0.48	0.46	0.02
QL42	stream	0.26	0.68	0.06	0.35	0.34	0.02
QL43	stream	0.31	0.65	0.04	0.49	0.47	0.02
QL47	stream	0.26	0.68	0.06	0.42	0.41	0.02
QL58	stream	0.22	0.73	0.05	0.38	0.36	0.02
QL61	stream	0.24	0.73	0.04	0.40	0.38	0.02
QL64	stream	0.23	0.72	0.05	0.39	0.37	0.02
QL66	stream	0.24	0.66	0.10	0.39	0.38	0.02
QL68	stream	0.21	0.72	0.07	0.37	0.35	0.02
QL73	stream	0.23	0.59	0.18	0.37	0.36	0.03
QL83	stream	0.27	0.59	0.13	0.43	0.42	0.02
QL84	stream	0.25	0.64	0.11	0.40	0.39	0.02
QL85	stream	0.27	0.60	0.13	0.42	0.41	0.02
QL86	stream	0.26	0.61	0.13	0.42	0.40	0.02
QL87	stream	0.22	0.62	0.16	0.36	0.35	0.02
QL90	stream	0.30	0.54	0.16	0.47	0.45	0.03
QL92	stream	0.29	0.55	0.16	0.44	0.43	0.03
QL99	stream	0.26	0.66	0.08	0.42	0.40	0.02
QL100	stream	0.26	0.65	0.09	0.42	0.40	0.02
QL101	stream	0.25	0.66	0.09	0.41	0.40	0.02
QL102	stream	0.25	0.66	0.09	0.40	0.39	0.02
QL103	stream	0.25	0.66	0.09	0.40	0.39	0.02
QL106	stream	0.22	0.67	0.12	0.36	0.35	0.02
QL1814	stream	0.29	0.57	0.14	0.44	0.43	0.03
QL1816	stream	0.27	0.59	0.14	0.43	0.42	0.03
QL1817	stream	0.26	0.59	0.15	0.42	0.40	0.03
QL1829	stream	0.29	0.66	0.05	0.46	0.44	0.02
QL1832	stream	0.32	0.61	0.08	0.49	0.47	0.02
QL1833	stream	0.31	0.61	0.08	0.48	0.46	0.02
QL1834	stream	0.25	0.60	0.15	0.40	0.39	0.03
QL1836	stream	0.45	0.50	0.04	0.68	0.66	0.03
QL1837	stream	0.38	0.50	0.12	0.58	0.56	0.03
QL1838	stream	0.23	0.68	0.09	0.38	0.37	0.02
QL1839	stream	0.35	0.50	0.15	0.54	0.52	0.03
QL1844	stream	0.50	0.46	0.04	0.75	0.72	0.03

Sample ID	Type	f_G	f_P	f_S	W_G	W_P	W_S
QL67	spring	0.23	0.61	0.17	0.37	0.36	0.03
QL71	spring	0.23	0.71	0.06	0.36	0.35	0.03
QL72	spring	0.29	0.66	0.05	0.39	0.38	0.02
QL88	spring	0.27	0.56	0.17	0.42	0.41	0.03
QL104	spring	0.30	0.53	0.18	0.45	0.44	0.03
QL1812	spring	0.22	0.61	0.17	0.36	0.35	0.03
QL1813	spring	0.18	0.66	0.16	0.32	0.31	0.03
QL1818	spring	0.23	0.58	0.19	0.37	0.36	0.03
QL1819	spring	0.22	0.59	0.19	0.36	0.35	0.03
QL1820	spring	0.21	0.61	0.18	0.35	0.34	0.03
QL1821	spring	0.22	0.61	0.16	0.37	0.36	0.03
QL1830	spring	0.31	0.64	0.05	0.48	0.46	0.02
QL1831	spring	0.22	0.61	0.17	0.46	0.45	0.02
QL65	groundwater	0.21	0.62	0.17	0.35	0.34	0.03
QL94	groundwater	0.27	0.59	0.14	0.42	0.41	0.03
QL95	groundwater	0.27	0.58	0.14	0.43	0.42	0.03
QL98	groundwater	0.11	0.74	0.15	0.27	0.26	0.02
QL1808	groundwater	0.17	0.66	0.17	0.31	0.31	0.03
QL1809	groundwater	0.17	0.67	0.17	0.31	0.30	0.03
QL1810	groundwater	0.21	0.59	0.20	0.34	0.33	0.03
QL1811	groundwater	0.17	0.69	0.14	0.32	0.31	0.02
QL1815	groundwater	0.20	0.60	0.20	0.34	0.33	0.03
QL1840	groundwater	0.22	0.63	0.15	0.37	0.35	0.03
QL1841	groundwater	0.22	0.63	0.15	0.36	0.35	0.03
QL1842	groundwater	0.21	0.64	0.15	0.35	0.34	0.03

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Table S1. Unmixed fractions of glacier-snow (f_G), precipitation (f_P) and soil (f_S) endmember contributions and the associated uncertainties for glacier-snow (W_G), precipitation (W_P) and soil (W_S). For isotopic and EC "conservative" tracer concentrations and other chemical data of each sample, see Dataset S1 and S2.

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Depth b.s.l	Time (d)	DOC (mg/ L solution)	DOC (mg/g wet soil)	SUVA$_{254}$ (L mg C^{-1} m^{-1})	Protein-like percent	FI	BIX	Protein-like intensity (RU)

Depth b.s.l	Time (d)	DOC (mg/ L solution)	DOC (mg/g wet soil)	SUVA$_{254}$ (L mg C^{-1} m^{-1})	Protein-like percent	FI	BIX	Protein-like intensity (RU)
profile 1: thawed soil in seasonal permafrost zone near red mud gully (38.2630N, 99.8777E, 2850 m a.s.l)								
5 cm	3	13.1	0.05	3.48		1.33	0.48	
	40	282.8	1.10	0.88		1.41	0.47	
15 cm	3	10.0	0.04	3.53	22%	1.29	0.52	0.12
	40	125.4	0.35	0.98	11%	1.53	0.52	0.10
30 cm	3	13.6	0.02	3.79	29%	1.38	0.60	0.25
	40	16.1		3.87	13%	1.50	0.52	0.12
50 cm	3	27.8	0.05	1.71	42%	1.54	0.69	0.45
	40	33.1	0.06	1.88	13%	1.50	0.52	0.12
profile 2: dried thermokarst sediment (38.2423N, 99.8859 E, 3500 m a.s.l)								
10 cm	3	15.4	0.24	4.07	22%	1.33	0.53	0.22
	40	34.4	0.13	6.13	7%	1.41	0.48	0.17
30 cm	3	15.6	0.03	2.92	33%	1.51	0.60	0.34
	40	23.6	0.05	4.27	19%	1.43	0.54	0.13
80 cm	3	16.6	0.03	2.83	33%	1.47	0.58	0.39
	40	34.0	0.05	2.98	22%	1.35	0.53	0.18
profile 3: wet thermokarst sediment (38.2443N, 99.8879 E, 3500 m a.s.l)								
10 cm	1	18.7	0.06	1.48	20%	1.43	0.48	0.13
	3	44.8	0.14	1.33	10%	1.38	0.46	0.05
	40	46.8	0.16	4.18	6%	1.42	0.49	0.07
20 cm	1	28.0	0.07	2.08	19%	1.43	0.50	0.17
	3	53.3	0.14	1.93	9%	1.31	0.44	0.06
	40	42.5	0.12	4.40	9%	1.34	0.50	0.10
30 cm	1	23.1	0.06	2.51	19%	1.45	0.49	0.20
	3	63.5	0.16	1.80	9%	1.41	0.50	0.09
	40	38.9	0.11	4.44	7%	1.36	0.47	0.10
profile 4: permafrost zone (38.2414N, 99.8862E, elevation: 3600 m)								
5 cm	1	12.4	0.09	3.64	18%	1.29	0.42	0.11
	3	24.4	0.20	2.91	61%	1.35	0.48	1.17
	40	129.5	0.80	1.29	40%	1.45	0.55	0.58
15 cm	1	13.4	0.06	3.80	17%	1.30	0.42	0.11
	3	15.3	0.06	4.45	15%	1.29	0.48	0.14
	40	55.4	0.27	2.42	13%	1.40	0.50	0.11
25 cm	1	15.8	0.08	2.92	21%	1.27	0.43	0.13
	3	18.0	0.09	3.20	13%	1.30	0.45	0.11
	40	99.2	0.57	1.64	20%	1.38	0.55	0.21
35 cm	1	11.6	0.05	5.05	20%	1.32	0.43	0.15
	3	18.9	0.07	4.30	19%	1.27	0.48	0.20
	40	32.5	0.11	3.38	23%	1.38	0.56	0.15

Table S2. DOC concentrations and fluorescence properties for four soil profiles in soil batch incubation experiment after 1, 3 and 40 extraction days.

144　**Dataset S1.** Detailed sampling information including water types, sampling date
145　(year/month/date), locations (Lat., Long, and Elev.), electrical conductivity (EC, μS/cm).
146　Calculations including proportions of glacier-snow meltwater, precipitation, and frozen soil
147　meltwater end members (G, P, S) based on stable isotopes and EC, the expected initial DOC (DOC_0)
148　and utilized DOC (ΔDOC). DOC concentrations (mg L^{-1}) and DOM optical parameters including
149　$SUVA_{254}$ (L mg $C^{-1}m^{-1}$), fluorescence index (FI), freshness index (BIX), percentage proportions of
150　protein-like component (%) derived from PARAFAC.

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152　[*] Only DOC concentrations were available for samples collected in Apr 2012. One thermokarst
153　sample collected near the west tributary was excluded in the data analysis.
154　[‡] The 7 groundwater samples were collected from the same monitoring well screened at 30 m at
155　the outlet (see MW in Fig.1d and Fig 3).
156　[†] The four groundwater samples were collected from the WW3 well (see WW3 in Fig.1d) located
157　in piedmont sloping plain dominated by seasonal frost, with screened intervals being 5, 10, 20
158　and 30 m underground, respectively.
159　[§] The groundwater/well water was collected from the WW4 with depth at 1m without pumping.
160　[†] The groundwater sample was collected from the WW1 well screened at 25 m (WW1 in Fig.1d).

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163　**Dataset S2.** Additional field measurements including water temperature, pH, alkalinity (Alk, meq
164　L^{-1}), dissolved oxygen (DO, mg L^{-1}). Concentrations of major ions and total nitrogen (TN, mg L^{-1}).
165　The intensity loadings of the four components derived from PARAFAC (C1 to C4).

166
167 **Reference**
168
169 Catala, T. S., et al. (2015), Turnover time of fluorescent dissolved organic matter in the
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