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Seasonal variability in particulate organic carbon degradation in the Kolyma River, Siberia

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Abstract

Major Arctic rivers are undergoing changes due to climate warming with higher discharge and increased amounts of solutes and organic carbon (OC) draining into rivers and coastal seas. Permafrost thaw mobilizes previously frozen OC to the fluvial network where it can be degraded into greenhouse gases and emitted to the atmosphere. Degradation of OC during downstream transport, especially of the particulate OC (POC), is however poorly characterized. Here, we quantified POC degradation in the Kolyma River, the largest river system underlain with continuous permafrost, during 9-15 day whole-water incubations (containing POC and dissolved OC - DOC) during two seasons: spring freshet (early June) and late summer (end of July). Furthermore, we examined interactions between dissolved and particulate phases using parallel incubations of filtered water (only DOC). We measured OC concentrations and carbon isotopes ($\delta^{13}C$, $\Delta^{14}C$) to define carbon losses and to characterize OC composition, respectively. We found that both POC composition and biodegradability differs greatly between seasons. During summer, POC was predominantly autochthonous (47-95 %) and degraded rapidly (~33 %) whereas freshet POC was largely of allochthonous origin (77-96 %) and less degradable. Gains in POC concentrations (up to 31 %) were observed in freshet waters that could be attributed to flocculation and adsorption of DOC to particles. The demonstrated DOC flocculation and adsorption to POC indicates that the fate and dynamics of the substantially-sized DOC pool may shift from degradation to settling, depending on season and POC concentrations - the latter potentially acting to attenuate greenhouse gas emissions from fluvial systems. We finally note that DOC incubations without POC present may yield degradation estimates that do not reflect degradation in the *in situ* river conditions, and that interaction between dissolved and particulate phases may be important to consider when determining fluvial carbon dynamics and feedbacks under a changing climate.

Keywords: permafrost, Arctic, degradation rate, carbon isotopes, adsorption, flocculation

1. Introduction

Ground temperatures in permafrost (i.e., perennially frozen ground) have increased globally over the last decades [1-2]. This causes thaw of all types of terrestrial permafrost which, in turn, releases previously frozen organic carbon (OC) into fluvial networks [3]. Old permafrost-OC can be released into the modern carbon cycle through gradual or abrupt thaw processes. Gradual thaw occurs from top-down as active layer horizons thaw over summer leaching largely dissolved OC (DOC) to inland waters [4-5]. By contrast, abrupt permafrost thaw such as river bank erosion and thaw slumping, mobilize mainly particulate OC (POC) [6-7]. During fluvial transport, permafrost-DOC can be rapidly degraded acting as a positive feedback to climate change [8-10]. However, the fate and biological availability of POC in fluvial systems is still largely unknown, despite the increasing potential for future abrupt thaw processes to deliver large quantities of permafrost-derived OC to aquatic ecosystems with a cascade of downstream effects [7,11-12].

Major Arctic rivers are extensive conduits of freshwater carrying and modifying terrestrial materials from land-to-ocean. Ongoing climate change is causing freshwater runoff and river constituent loads such as Ca, Mg and SO_4 to increase [13-15]. Warmer permafrost temperatures are likely to intensify thaw processes, releasing greater quantities of OC into the fluvial network in the future [16-17]. So far, the majority of OC degradation studies have focused on DOC [18-21]. Therefore, constraining POC degradation during downstream transport is critical, to assess if future changes may result in enhanced climate feedbacks.

In this study, we focus on the Kolyma River, one of the six major Arctic rivers delivering freshwater and OC loads to the Arctic Ocean [22], with an annual average POC flux of 123 ± 19 Gg [23]. The POC pool transports a greater proportion of permafrost and peat-derived OC relative to the DOC pool [24]. The hydrograph of the Kolyma River shows sharp seasonal differences with the highest annual discharge peak occurring during spring freshet, while summers are characterized with deeper thaw depths of permafrost [25]. Here, we constrain degradation rates and track compositional changes in fluvial POC and DOC in the Kolyma River over two of its distinct hydrologic seasons (spring freshet vs. late summer) using 9-15 day incubations. Alongside OC concentrations, we measure stable and radioisotopes of carbon (δ^{13}C-OC, δ^{13}C of dissolved inorganic carbon - DIC and Δ^{14}C-POC) to constrain POC sources and degradation pathways.

2. Materials and methods

2.1 Study area and field sampling

The Kolyma watershed is underlain by continuous permafrost and spans over 640,000 km^2 [22]. It is covered by tundra and boreal forests, and characterized by wetlands, floodplains and mountainous regions [8]. The regional climate is continental with distinct seasonality [8,26]. The oldest permafrost (Yedoma) in the area is OC-rich (2-5 % [27]), high in ground ice content (up to 75 % of volume [28]) and dates back to the Last Glacial period [29-30]. The mean annual discharge of the Kolyma is 132 km^3 with the highest discharge peak (~20,000 m^3 s^{-1}) during the spring freshet (May-June [31]), and lower values (~5,000 m^3 s^{-1}) during summer (July-August).

Surface water samples (water depth of ~20 cm) were collected to sterile polyethylene bags (10-20 L) from the middle of the river channel during two field campaigns: late summer at the end of July 2018, and the high-runoff spring freshet period in early June 2019 (figure 1, supplementary table 1). One deeper water sample (KOL2-D) was collected in summer at a depth of ~10 m, near the riverbed. At each sampling location pH, water temperature, electrical conductivity (EC) and dissolved oxygen (DO) were measured using a multi-parameter sonde (Eijkelkamp Aquaread AP-800 in 2018, YSI Professional Plus in 2019). We also collected water samples for stable water isotopes (δ^{18}O, δH), which were filtered and stored cool (+5 °C) without headspace. See more details about sampling methods in supplementary methods.

2.2 Incubation experiments

Within 12 h of sampling, water samples were prepared for the whole-water and filtered incubations (for schematic depiction see supplementary figure S1). Prior to filtering, all water samples were vigorously shaken to ensure thorough mixing of the sample. Part of the sample was immediately filtered through pre-weighed and combusted glass-fiber filters (GF/F, Whatman, 0.7 µm) to act as the initial, non-incubated time point (T0). Filters were subsequently frozen at -20 ºC, while the collected 30 ml of filtrate was treated with 30 µl of HCl (37 %) and stored cool (+5 ºC). To collect DIC samples, in 2018, 4 ml of water was filtered into a pre-evacuated 12 ml exetainer (Labco, UK) containing 100 µl of H_3PO_4. In 2019, DIC samples were filtered into 12 ml exetainers containing ~100 µL of saturated KI solution and filled to the rim.

The remaining whole-water sample (including both DOC and POC) was mixed thoroughly and distributed to pre-furnaced 100 ml glass bottles (Wheaton) and filled to the rim with no headspace (three replicate bottles per timepoint in 2018 and four in 2019). Samples were then incubated on a custom-made rotating device (supplementary figure S2) for a period of 9 to 15 days in dark and oxic (DO > 7 mg L^{-1}) conditions. The rotating device, similar to those used in previous studies [32-33], keeps bottles in a constant rotation

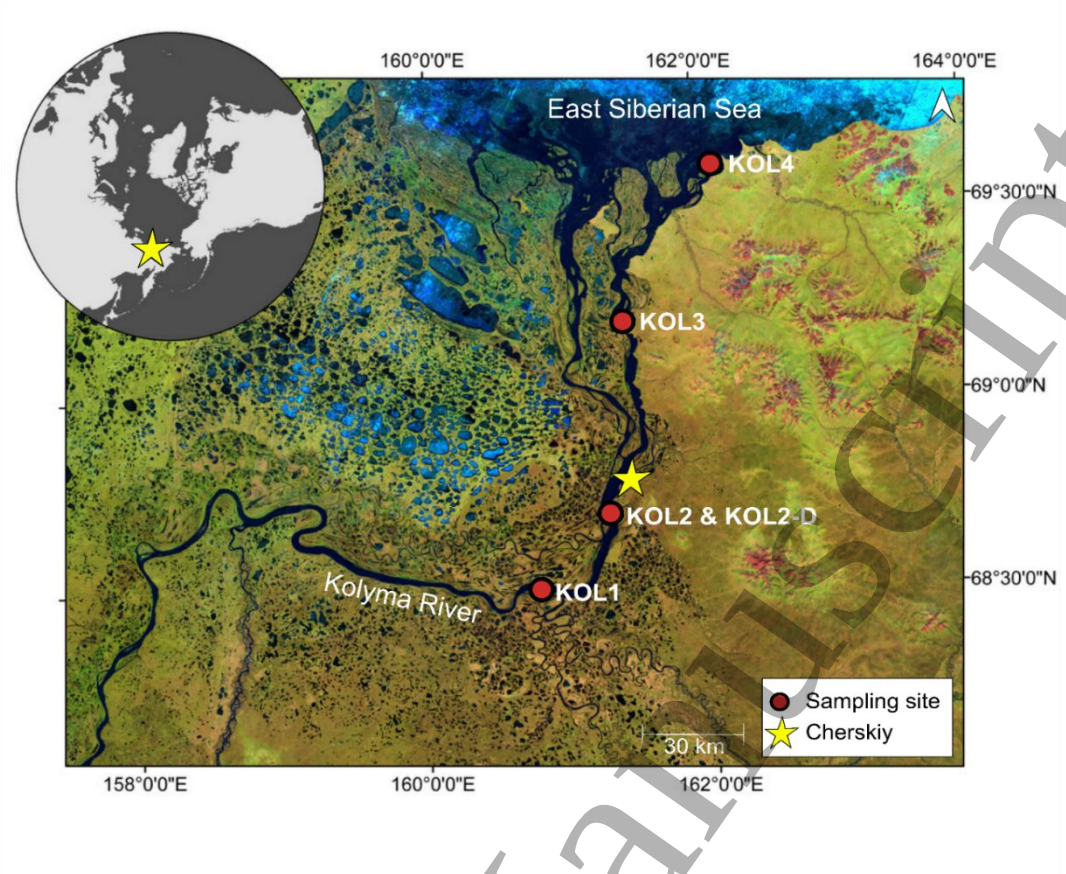

Figure 1. Map of the study area showing sampling sites KOL1, KOL2, KOL2-D, KOL3 and KOL4. Sites KOL1, KOL2, KOL3 were sampled both during freshet and summer, while KOL2-D was sampled only during summer and KOL4 only during freshet. All the samples were of surface water (sampled ~20 cm below surface) except KOL2-D, which was sampled at the depth of ~10 m (near the riverbed) at the same location as KOL2. The map is adapted according to reference 8.

preventing particles from settling and mimicking the river hydrodynamic conditions. As a temperature-controlled room was not available at the field station, we incubated at ambient air temperatures which were 15 ± 4 °C in 2018 and 21 ± 2 °C in 2019. To address this temperature disrepancy, we corrected the calculated degradation constants (*k*) afterwards to reflect OC degradation in the *in situ* river temperatures (see 2.3 and supplementary methods).

Three sampling time points (T1, T2 and T3) were taken every three to six days. At each time point, replicate bottles (three in 2018 and four in 2019) were removed from the rotator, and waters filtered as described above and separated for POC, DOC and DIC (supplementary figure S1). Parallel to the whole-water incubations, a separate filtered incubation (three replicates per time point) was carried out to assess DOC dynamics without the presence of particles (for the protocol see [34] and supplementary methods). All details on analytical analyzes are available on supplementary methods.

2.3 Degradation losses, rates and half-life

We quantified degradation of POC and DOC during the incubations by measuring the change in the OC pool (in %) over time with the following equation:

$$OC_{change} = [(OC_{init} - OC_t)/OC_{init}] \times 100 \quad \text{(Eq. 1)}$$

where OC_{change} is the percent OC (DOC or POC) loss or gain during the defined incubation period t, OC_t is the residual OC concentration at time t and OC_{init} is the initial OC concentration (see supplementary methods).

The degradation rates (*k*, day^{-1}) for POC and DOC were calculated using a first-degree exponential degradation model [32, 35]. Temperature corrections of the constant for *in situ* river temperatures were calculated using the Arrhenius equation assuming Q10=2 [36-37]. All results are reported as averages ± standard deviation. Further details are provided in the supplementary methods.

2.4 Source apportionment and statistical analysis

For the source apportionment of POC, we used a Monte Carlo Markov Chain (MCMC) model. The two $\delta^{13}C$ endmembers used were: -32.0 ± 3.4 ‰ for autochthonous (i.e., within-river production) POC and -27.1 ± 1.1 ‰ for allochthonous (i.e., from terrestrial sources) POC [24, 38-39].

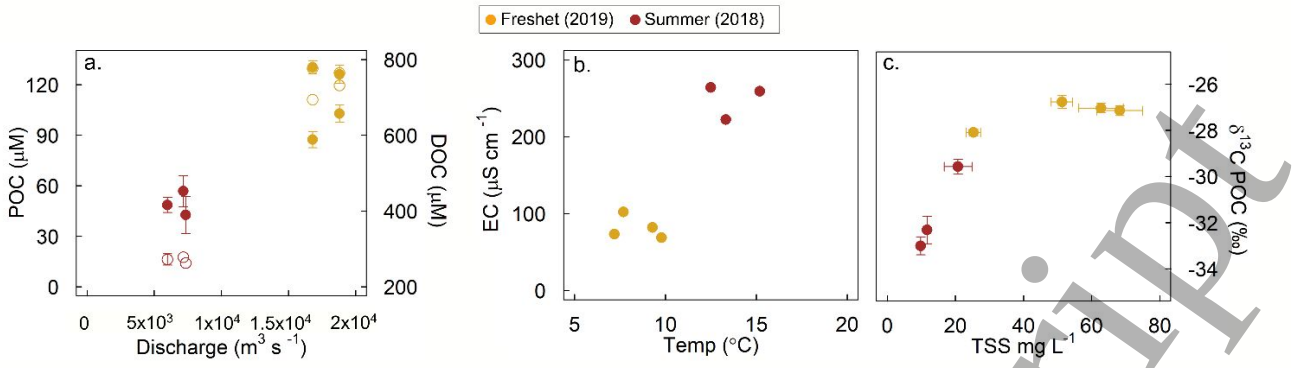

Figure 2. (a) Particulate and dissolved organic carbon (POC and DOC) concentrations and Kolyma River discharge measured at Kolymskoye (Roshydromet, Federal Service for Hydrometeorology and Environmental Monitoring, Ministry of Natural Resources and Environment, Russian Federation). Concentrations of DOC are marked with open symbols (note the different axes). (b) Surface water temperature (Temp) and electrical conductivity (EC). (c) Total suspended solids (TSS) and δ^{13}C-POC. All panels show surface water samples from freshet (yellow circles) and summer (red circles). On panels a and c, standard deviations are derived from replicate samples (not shown if smaller than the symbol).

Table 1. Concentrations of total suspended solids (TSS), particulate and dissolved organic carbon (POC and DOC) with δ^{13}C of POC, DOC and dissolved inorganic carbon (DIC), and Δ^{14}C-POC in the Kolyma River during freshet and summer, along with total particulate nitrogen (TPN), molar ratio between POC and TPN (POC/TPN) and water isotopes (δ^{18}O, δH). All the samples (KOL1-KOL4) were of surface water except KOL2-D, which was sampled at ~10 m depth. The results are reported as averages and standard deviations between replicates. For $_d$^{13}C-DIC (during freshet) and Δ^{14}C-POC the standard deviation includes analytical uncertainty of repeated measurements. For δ^{13}C-DIC during summer and for all the water isotope data (δ^{18}O, δH), only the analytical uncertainty is shown (no sample replicates).

Freshet	Sampling date (dd/mm/yyyy)	TSS (mg L^{-1})	POC (µM)	δ^{13}C-POC (‰)	Δ^{14}C (‰)	TPN (µM)	POC/TPN	DOC (µM)	δ^{13}C-DOC (‰)	δ^{13}C-DIC (‰)	δ^{18}O (‰)	δH (‰)
KOL1	07/06/2019	51±2	103±5	-26.77±0.2	-353±32	9.0±0.5	9.8±0.3	731±8	-26.36±0.2	-12.19±0.3	-22.89±0.09	-178.4±0.6
KOL2	07/06/2019	63±3	126±5	-27.04±0.2	-340±32	11±0.4	9.9±0.3	764±7	-26.42±0.2	-13.77±0.3	-22.88±0.22	-176.4±1.4
KOL3	11/06/2019	68±5	130±4	-27.15±0.2	-69±20	11±0.6	10.1±0.3	694±11	-27.11±0.2	-13.81±0.3	-22.65±0.05	-174.5±0.2
KOL4	11/06/2019	25±2	87±5	-28.10±0.2	-302±29	8.1±0.5	9.2±0.3	776±11	-26.89±0.1	-13.62±0.2	-22.99±0.05	-177.1±0.4
Summer												
KOL1	23/07/2018	10	43±3	-33.01±0.4	-217±37	5.3±0.2	7.4±0.2	262±5	-29.37±0.2	-9.36±0.02	-22.14±0.03	-171.7±0.5
KOL2	25/07/2018	12±1	49±2	-32.32±0.6	-222±33	6.2±0.3	6.7±0.1	272±15	-29.31±0.3	-9.46±0.04	-22.10±0.04	-171.5±0.3
KOL2-D	25/07/2018	21±2	68±7	-30.93±0.2	-286±27	7.5±0.4	8±0.3	264±7	-28.68±0.4	-9.18±0.02	-22.17±0.01	-171.7±0.8
KOL3	28/07/2018	21±4	57±11	-29.57±0.3	-306±20	5.6±0.6	8.7±0.5	278±5	-29.46±0.6	-9.08±0.02	-21.36±0.03	-165.5±0.1

The model was run in R [40] with a package *MixSiar* [41]. We report results as a mean ± standard deviation. See supplementary methods for details.

We tested whether the difference of POC and DOC losses over time were significantly different from the initial concentrations with (one-way) analysis of variance (ANOVA) in R [40]. See supplementary methods for details.

3. Results

3.1 Initial river conditions during freshet and summer

Water chemistry differed between the freshet and summer sampling periods. During freshet, surface water temperatures (8.5 ± 1.2 °C), pH (6.9 ± 0.2) and EC (81 ± 14 µS cm^{-1}) were lower than during summer (13.7 ± 1.4 °C, 7.5 ± 0.1 and 248 ± 23 µS cm^{-1}, respectively; figure 2, supplementary table S2). Water isotopes (δ^{18}O, δH) showed a more depleted signal during freshet (-22.85 ± 0.14 ‰ and -176.6 ± 1.64 ‰, respectively) than summer (-21.87 ± 0.44 ‰ and -169.6 ± 3.50 ‰, respectively; table 1).

Both DOC and POC concentrations (surface water) were higher during freshet (from 694 to 776 µM for DOC and from 87 to 130 µM for POC) than those during summer (between 262 and 278 µM for DOC and between 43 and 57 µM for POC; figure 2, table 1). The highest POC concentration during summer was at KOL2-D (68 µM) near the riverbed. The molar ratio of POC/TPN of suspended particulate matter was higher during freshet (9.2-10) than summer (6.7-8.7, table 1). Total suspended solids (TSS) during freshet ranged from 25 to 68 mg L^{-1}, while those in the summer varied between 9.8 and 21 mg L^{-1} (table 1).

The δ^{13}C signatures of DOC and POC were less depleted during freshet than summer, while the δ^{13}C-DIC showed the

opposite between the seasons. The δ^{13}C-DOC ranged from -27.11 ‰ to -26.36 ‰ during freshet and from -29.46 ‰ to -29.31 ‰ during summer (surface water), and δ^{13}C-POC between -28.10 ‰ to 26.77 ‰ during freshet and between -33.01 ‰ and -29.57 ‰ during summer (table 1). At KOL2-D (summer), the δ^{13}C-DOC was -28.68 ‰ and δ^{13}C-POC -30.93 ‰. The δ^{13}C-DIC varied between -13.81 ‰ and -12.19 ‰ during freshet and from -9.36 ‰ to -9.08 ‰ during summer (table 1). The Δ^{14}C-POC was more depleted (i.e., older) during freshet on the upstream sites KOL1 and KOL2 (-353 ± 32 ‰ and -340 ± 32 ‰) than during summer (-217 ± 37 ‰ and -222 ± 33‰; table 1, supplementary table S3). Downstream, at KOL3, the Δ^{14}C signal was more enriched during freshet, (-69 ± 20 ‰) than summer (-306 ± 20 ‰). During freshet, at the Kolyma River mouth (KOL4) the Δ^{14}C-POC was -302 ± 29 ‰ while the deep sample (KOL2-D) showed a Δ^{14}C-POC of -286 ± 27 ‰ during summer.

3.2 Changes in organic carbon concentrations and isotopic values during incubation

Residual POC concentrations increased during incubations of freshet waters at all sites (+23.5 % to +31.3 %, figure 3, supplementary tables S4 and S5). In contrast, concentrations of residual POC consistently declined during incubations of summer waters (-0.8 % to -34 %; figure 3, supplementary table S4 and S5). On the contrary, residual DOC concentrations (in the whole-water incubations) showed consistent losses both with freshet (-8.5 % to -17.9 %) and summer waters (-3.3 % to -10.9 %; figure 3, supplementary tables S4 and S5). The POC/TPN ratios increased both during freshet and summer incubations (table 2). During the filtered incubation (without particles), DOC losses ranged between -4.7 % and -8.6 % during freshet, and between -4.8 % and -14.2 % during summer (figure 4, table 2), while the KOL2 showed a gain of +2.7 % during summer.

Degradation constants (k), derived from whole-water incubations, showed that POC increased during freshet incubations at a rate of 0.023 ± 0.006 day^{-1}, while DOC decreased at a rate of -0.014 ± 0.006 day^{-1} (supplementary table S6). During summer incubations, the degradation constants were -0.029 ± 0.001 day^{-1} for POC and -0.006 ± 0.002 day^{-1} for DOC. The filtered incubations showed a degradation constant of -0.008 ± 0.003 day^{-1} for DOC during freshet and -0.010 ± 0.01 day^{-1} for DOC during summer (supplementary table S6).

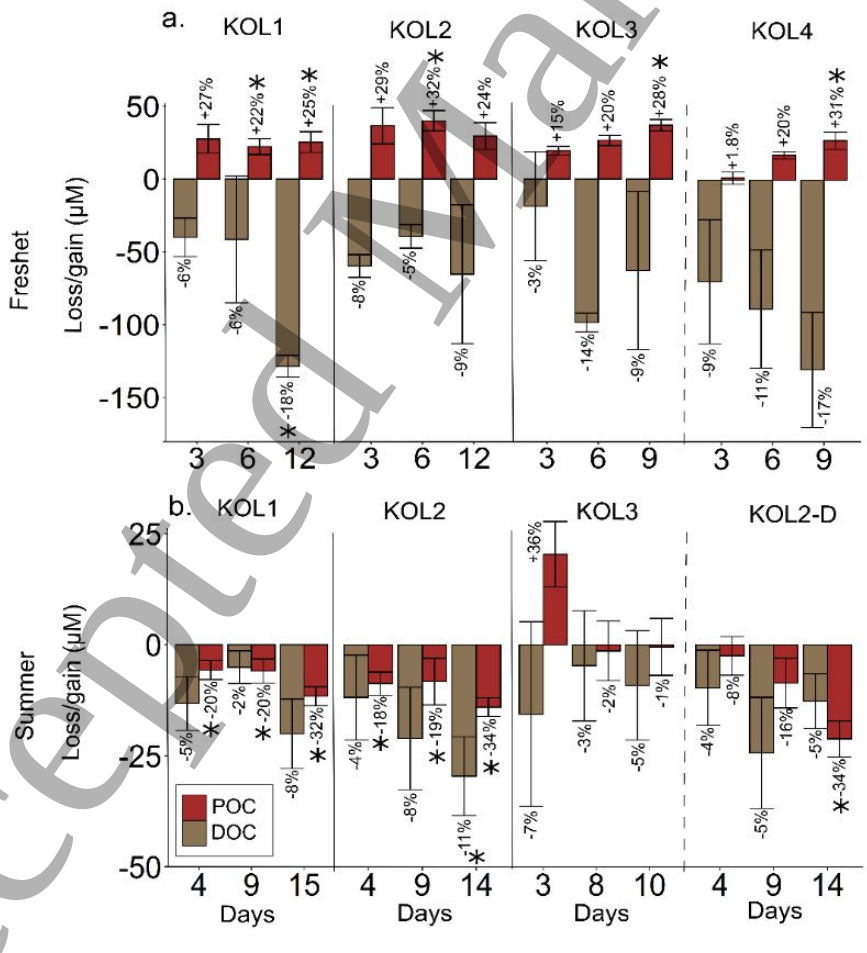

Figure 3. Changes in particulate and dissolved organic carbon (POC and DOC) concentrations during the 9 to 15 day whole-water incubations during (a) freshet and (b) summer (note that the scale of y-axes differ). The bars show averages ± standard error between replicate samples (n=4 during freshet and n=3 during summer) and are all relative to the initial OC concentrations. Relative changes (%) are indicated under/over the bars on both panels. The ambient incubation temperature during freshet was ~6 °C warmer than during summer. The bars marked with an asterisk are significantly different from the initial OC concentration ($p<0.05$, see supplementary table S3 and S4).

Table 2. Changes (average ± standard deviation) in particulate and dissolved organic carbon (POC and DOC), in total particulate nitrogen (TPN), in ratio between POC and TPN (POC/TPN), Δ^{14}C-POC, δ^{13}C-POC, δ^{13}C-DOC and δ^{13}C of dissolved inorganic carbon (DIC) during 9 to 15 day whole-water (i.e., POC+DOC) incubations of Kolyma River water during freshet (i.e., spring ice break-up) and summer. Changes in DOC and δ^{13}C-DOC during filtered incubations (without particles) are also shown. The %-loss of POC and DOC of the total OC were not calculated during freshet due to both gains (POC) and losses (DOC) to the OC pool.

		POC						Whole-water DOC			Total OC			DIC	Filtered incubation DOC		
Freshet	Days	µM	%	δ^{13}C (‰)	Δ^{14}C (‰)	TPN (µM)	POC/TPN	µM	%	δ^{13}C (‰)	µM	POC (%)	DOC (%)	δ^{13}C (‰)	µM	%	δ^{13}C (‰)
KOL1	12	+25.4±14	+24.7	+0.37±0.2		+1.2±1.9	+1.1±1.4	-129±14	-17.6	-0.25±0.3	-103	n/a	n/a	-1.21±0.4	-47.6±30	-6.52	-0.37±0.2
KOL2	12	+29.6±17	+23.5	+0.30±0.5	+40±22	-2.1±6.2	+1.5±2.4	-65.3±95	-8.54	-1.60±1.8	-35.7	n/a	n/a	-1.12±0.3	-59.7±32	-7.81	+0.35±0.7
KOL3	9	+37.0±7.1	+28.4	+0.06±0.4		+1.7±2.4	+0.2±1.8	-62.8±94	-9.05	-1.41±2.3	-25.8	n/a	n/a	-1.72±0.3	-32.9±26	-4.74	+0.50±0.3
KOL4	9	+27.2±12	+31.1	-1.33±0.2		+1.5±1.2	+1±1.7	-130±79	-16.8	-0.48±1.6	-103	n/a	n/a	-2.92±0.3	-66.3±12	-8.55	+0.18±0.2
Summer																	
KOL1	15	-11.6±3.7	-32.4	+3.72±0.8		-2.8±0.4	+3.3±0.8	-20.1±14	-7.66	+0.27±0.3	-31.7	12	13	-1.19±0.2	-37.1±31	-14.2	+0.35±0.5
KOL2	14	-14.1±3.7	-33.7	+3.46±0.7	-92±19	-3.6±0.3	+4±0.8	-29.61±5.3	-10.9	+0.68±0.4	-43.6	14	18	-1.09±0.2	+7.27±24	2.67	+0.39±1.6
KOL2-D	14	-21.2±7.1	-34.0	+2.22±0.5		-4.5±0.4	+4.9±1.1	-12.7±11	-4.80	+0.07±0.6	-33.9	21	7.6	-1.45±0.1	-18.8±32	-7.10	-0.58±0.8
KOL3	10	-0.5±9.2	-0.84	+1.62±0.6		-2.0±0.7	+4.6±1.2	-9.1±21	-3.28	+0.70±0.7	-9.6	0.5	6.0	-1.60±0.1	-34.3±40	-12.3	+0.28±1.5

The δ^{13}C signature of POC became more enriched over the course of the incubation both during freshet (+0.5 ± 0.6 ‰) and summer (+2.75 ± 1 ‰; figure 5(a), table 2). The δ^{13}C-DOC showed depletion at the end of the whole-water incubations by -0.9 ± 0.7 ‰ during freshet, but enrichment during summer by +0.4 ± 0.3 ‰ (table 2). The filtered incubation showed enrichment of δ^{13}C-DOC during both freshet (+0.34 ± 0.2 ‰) and summer (+0.34 ± 0.1 ‰; table 2), except at KOL1 (freshet) and at KOL2-D (summer), which both showed depletion of δ^{13}C (-0.37 ± 0.2 ‰ and -0.58 ± 0.8 ‰, respectively). The δ^{13}C-DIC showed depletion during both freshet (-1.74 ± 0.83 ‰) and summer (-1.29 ± 0.27 ‰; figure 5(b), table 2). At the end of the incubation, the Δ^{14}C-POC at site KOL2 (the only site measured for Δ^{14}C during the incubation) showed an enrichment by +40 ± 22 ‰ during freshet and depletion by -92 ± 19 ‰ during summer (table 2).

3.3 Source apportionment of particulate organic carbon before and after incubation

The source apportionment of POC showed that most of the POC during freshet consisted of allochthonous POC (77-96 %), whilst during summer only 4-52 % of the POC was from an allochthonous source (figure 6, supplementary table S7). After incubations, residual POC pools contained higher proportions of allochthonous OC, both during freshet (93% to 98 %) and summer incubations (58 % to 80 %).

4. Discussion

4.1 Seasonal variability in river OC composition and source

4.1.1 River conditions of freshet and summer

The strong seasonality in northeastern Siberia drives the water chemistry of the Kolyma River. Concentrations of TSS were nearly four times greater during freshet versus summer months (table 1) reflecting the high discharge conditions during this period (average for freshet 17,800 ± 160 m^3 s^{-1} and for summer 6,700 ± 210 m^3 s^{-1} during sampling [42]). Lower EC (by ~170 µm cm^{-1}) and pH values (by 0.6) during freshet compared to summer are likely caused by dilution or due to fewer solutes draining to the river from the soil, as permafrost thaw has not yet reached deeper soil layers [23]. Additionally, the higher rate of primary production in the summer may increase pH [43]. These trends agree with seasonal variations observed in previous studies [8,44]. The water isotopes, especially δH (table 1), showed a more depleted signal during freshet, suggesting a higher contribution of snow than of rain compared to summer [44-45].

4.1.2 OC sources of freshet and summer

The POC and DOC concentrations in the Kolyma River follow seasonal discharge patterns [22] with higher concentrations during freshet than summer (figure 2, table 1). During freshet, the high runoff mobilizes OC mainly from surface scouring, litter and surface soil horizons [46-47], while during summer higher air temperatures contribute to active layer deepening and initiation of thermokarst, releasing OC from deeper permafrost sources [23, 48].

The role of primary production in fluvial OC dynamics of major Arctic rivers has not received a lot of attention, partly because, the autochthonous OC in these systems likely consists mainly of recycled allochthonous OC [24]. In our study, between 71 % to 96 % of POC during freshet originated from allochthonous sources, while during summer, only 4 % to 52 % of POC was allochthonous, suggesting a high riverine

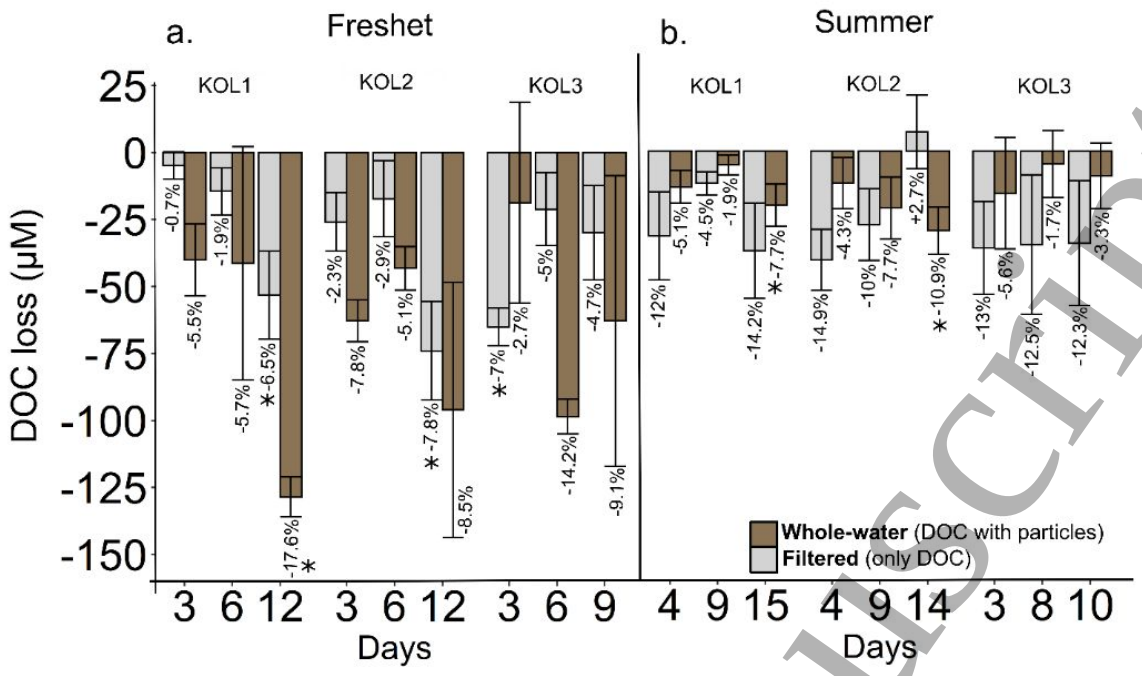

Figure 4. Dissolved organic carbon (DOC) losses (average ± standard error of replicate samples) during 9 to 15 day incubations during (a) freshet and (b) summer. Brown bars indicate DOC loss during whole-water incubations (with particles) and grey bars during filtered incubations (without particles). All losses are relative to the initial DOC concentrations. The percentages under the bars show relative losses (%) from the initial concentrations. The ambient incubation temperature during freshet was ~6 °C warmer than during summer. The asterisks indicate a significant difference ($p<0.05$) from the initial DOC concentration, see supplementary table S3 and S4 for details.

primary production during summer (figure 6). Similarly, higher POC/TPN ratios during freshet indicate a larger contribution of allochthonous OC, while lower ratios during summer suggest a higher contribution of autochthonous OC, more degraded OC and/or terrestrial OC originating from deeper thaw depths that dominate during summer [23, 49-50]. Similar to POC, freshet DOC is mainly allochthonous (δ^{13}C-DOC -26.69 ± 0.37 ‰), while during summer the more depleted δ^{13}C signature (-29.38 ± 0.08 ‰) suggests higher contribution of autochthonous DOC [51]. While most of this autochthonous production in summer may derive from allochthonous sources, the eventual fate and lability of this OC may change (see 4.2) upon incorporation into fluvial organisms.

The δ^{13}C-DIC signature varies little within a season, but shows more depleted signatures during freshet than summer (table 2, figure 5(b)). The enriched δ^{13}C-DIC during summer may suggest higher primary production [52-53] supporting the findings from δ^{13}C-DOC and δ^{13}C-POC.

The Δ^{14}C-POC varies within and between seasons with no apparent trends (table 2). These seasonal differences in Δ^{14}C may be due to yearly fluctuations of the river as seen in previous studies [44] that likely depend on variation in air temperatures, precipitation and thus different permafrost thaw patterns [54].

4.2 Seasonal variability in OC losses during whole-water incubations

4.2.1 Autochthonous POC is preferentially degraded during summer

During summer, the relative losses of POC were approximately -33 % over 14 to 15 days at all sites, except at KOL3 with a loss of -1 % over 10 days. The relatively small losses at KOL3 are likely due to its more allochtonous POC composition compared to the other sites, which may cause stronger flocculation and adsorption of DOC into the POC pool, thus slowing down POC degradation (see 4.2.2). Losses of DOC were on average lower (ranging between -4 % and -10 %), suggesting that POC is susceptible for degradation, likely partly via leaching to the DOC pool followed by microbial degradation (figure 3(b)). The concentrations of POC were lower than those of DOC in summer (table 1), thus relatively greater quantities of DOC were lost (table 2, figure 3). Of the total OC losses (DOC and POC combined; supplementary figure S3), 6-18 % was DOC, while only at the deeper site KOL2-D the POC pool showed higher losses (21 % of total OC, table 2) than DOC. This contrast could be explained by a different composition of the near river bed POC

and/or DOC combined with differing microbial communities on the river surface [55]. While our study focused on surface water samples (not depth-integrated sampling), the reactivity of POC near the riverbed (KOL2-D) was comparable to the surface sample at the same site (KOL2), even though the absolute losses were greater near the riverbed as initial POC concentrations were higher (table 1). The overall degradation patterns are supported by the changes in the δ^{13}C-DIC during incubations as its depletion indicates microbial respiration (figure 5(b); [56]). Furthermore, both δ^{13}C-POC and δ^{13}C-DOC enrich during the incubation (table 2).

Our source apportionment results show that most of the POC degraded during summer is of autochthtonous origin (figure 6), indicating preferential degradation of autochthonous POC. Similarly, the increase in POC/TPN ratios (table 2) indicates a shift to more allochthonous POC over time, suggesting degradation of the autochthonous POC pool [35]. Furthermore, the Δ^{14}C-POC shows a more depleted signature (-92 ± 19 ‰) at the end of the incubation than during initial conditions, suggesting that modern POC was degraded during summer (table 2). It has been demonstrated in previous studies that old permafrost OC can be preferentially degraded from the DOC fraction, but that most microbial respiration in the Kolyma River (~99 %) is subsidized by modern allochthonous and autochthonous carbon [21]. In addition, our results indicate that a more depleted initial δ^{13}C-POC signature (i.e., a more autochthonous POC pool), caused a larger shift in δ^{13}C during incubations and higher POC losses over time (supplementary figure S4), supporting the high biolability of the autochthonous POC pool, either directly or as a shift to the DOC pool.

The high relative losses of summer POC (figure 3) agree with the results from a previous incubation study [35] based on fresh water samples (late summer) from three Swedish rivers, Ljusnån, Hedströmmen and Fyrisån, suggesting higher losses for POC (average -24.7 ± 3.1 % over seven days) than for DOC (-0.72 ± 0.14 % over seven days, all data are re-calculated to include only rivers). In another POC degradation study, based on flume experiments [57], POC losses were relatively low, and divided between petrogenic POC (-10.1 ± 4.1 %, Posidonia shale and lignite) and biospheric POC (-9.4 ± 4.1 %, Lookout Creek, Oregon, US and Rio Bermejo, Argentina), while DOC showed both losses and increases. Our calculated degradation constant (k) for summer POC (-0.029 ± 0.001 day^{-1}) was comparable to those in the Swedish rivers with -0.036 ± 0.03 day^{-1} [35]. However, for whole-water DOC in the same study [35], the degradation constant was lower, -0.001 ± 0.0004 day^{-1}, than in our study, -0.006 ± 0.002 day^{-1}. It is notable that *in situ* temperatures in the Swedish rivers were 15 ± 0.2 °C and the incubation lasted only for seven days, making the comparison not straightforward. Our incubation temperatures were close to the *in situ* river temperatures, but when corrected for the offset (i.e., difference between incubation and *in situ* river temperatures), degradation rate constants became slightly lower both for POC (-0.026 ± 0.003 day^{-1}) and DOC (-0.005 ± 0.002 day^{-1}) than uncorrected. A modeling study (box-model) in a sub-arctic estuary in the Bothnian Bay [58], reports higher degradation constants both for POC (-0.38 day^{-1}) and DOC (-0.03 day^{-1}). This disrepancy could be due to difference in methods (modeling vs. experimental) and study systems (estuary vs. river). Overall, summer POC losses in northern rivers are greater than those of DOC. However, our whole-water incubations suggest that when these two OC pools are together *in situ*, POC likely breaks down to DOC, and thus 'slows' DOC degradation rates as the DOC pool is constantly replenished (figure 7).

4.2.2 Allochthonous POC dominates during freshet, showing no degradation

During freshet incubations, constant gains of POC (+15 % to +32 % over 9 to 12 days; figure 3) indicate that the allochthtonous POC that makes up the majority of the POC in this season, is not easily biodegradable (or converted into

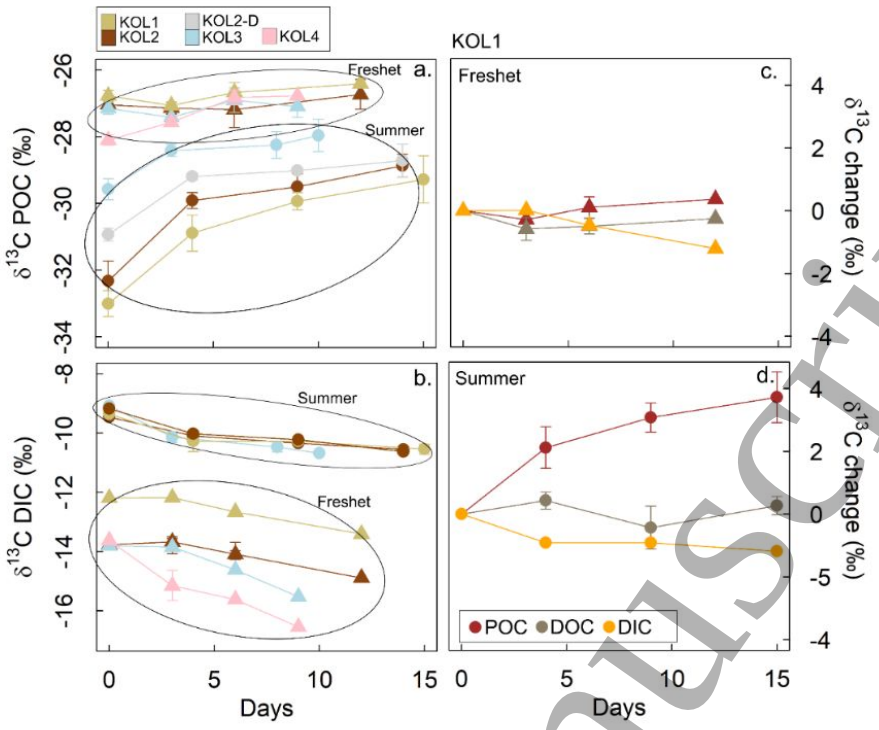

Figure 5. Changes in $\delta^{13}C$ of (a) particulate organic carbon (POC) and (b) dissolved inorganic carbon (DIC) during the whole-water incubations (between 9 to 15 days) during freshet and summer for sites KOL1, KOL2 and KOL3, and KOL2-D (only summer) and KOL4 (only freshet). The $\delta^{13}C$-POC changes are significantly different from the initial conditions at all sites and time points during summer (except at KOL3), and during freshet at KOL4 (except at time point T1). Panels c-d show relative changes in $\delta^{13}C$ of POC, dissolved organic carbon (DOC) and DIC at location KOL1 during (c) freshet and (d) summer. The error bars indicate standard deviation between replicate samples and include the analytical uncertainty for DIC. The T0 time points for DIC only show analytical uncertainties during summer (no replicates available). Only the error bars larger than the symbol are shown.

DOC). Processes that can explain gains in the POC fraction during the incubation are i) primary production fuelled by aqueous inorganic carbon species, ii) increase in bacterial detritus or biomass following bacterial consumption of organic carbon species, and/or iii) adsorption and/or flocculation of DOC. As photosynthesis uses light as an energy source [59], dark incubation conditions should inhibit photosynthetic growth. Other energy conversion pathways, such as chemosynthesis, can produce organic compounds in the dark [60], however, these processes are mainly restricted to deep-sea ecosystems and stratified waterbodies [61-62]. A study on the Canadian Peel Plateau [33], suggested that chemolithoautotrophs potentially contribute to OC mineralization in slump thaw streams, yet these environments have extremely high OC concentrations thus differ greatly from our study system. We deem the first process (primary production) unlikely to cause POC gains in river surface waters with relatively low POC concentrations. Second, bacterial detritus and biomass as a POC source has been shown to be negligible based on lake data [63], however, most of the allochthonous lake DOC is used for bacterial biomass building rather than for respiration [51], making option (ii) a more likely explanation. Third, both adsorption and flocculation of dissolved organic matter transfer OC from the dissolved to the particulate OC pool, e.g., [64-67]. The largely allochthonous POC during freshet likely comprises of mineral particles that offer adsorption surfaces for DOC [68-69]. Furthermore, the river conditions during freshet with higher DOC concentrations and on average lower EC and pH values promote adsorption to particles, while river turbulence and higher particulate concentrations enhance flocculation of DOC [64, 70]. We therefore consider adsorption and/or flocculation of DOC the most likely cause for POC gains, yet contribution of bacterial biomass/detritus might also play a role.

The ^{13}C signature of POC barely changes during freshet incubations, suggesting only a minimal increase in the proportion of allochthonous POC at the end of the incubation (figure 6). This mild shift may suggest that regardless of the apparent gains of POC, some degradation of autochthonous POC occurs, yet these losses would be masked by the addition of DOC to the POC pool via adsorption and flocculation. Alternatively, the increase in allochthonous POC is solely due to addition of allochthonous DOC. Nevertheless, the

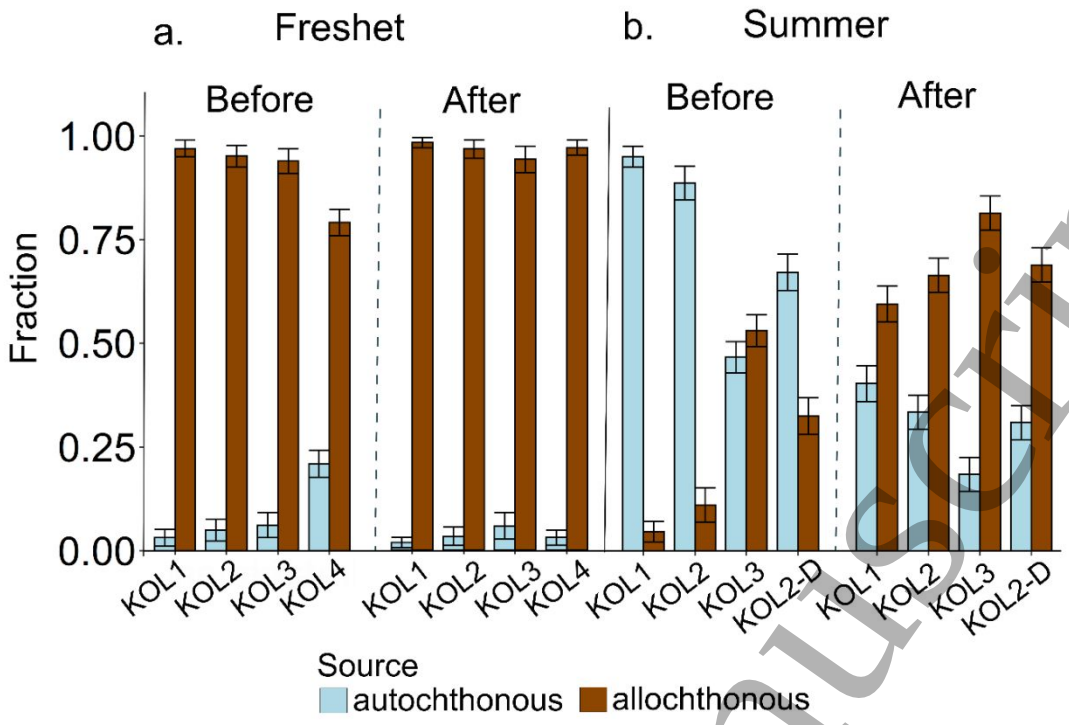

Figure 6. Source apportionment of particulate organic carbon (POC, mean ± standard deviation) during (a) freshet (n=4 per site) and (b) summer (n=3 per site) based on δ^{13}C-POC for sites KOL1, KOL2, KOL3, KOL4 (only freshet) and KOL2-D (only summer). The source apportionment was conducted before and after 9 to 15 days of incubation. Endmember used for autochthonous POC was -32.0 ± 3.4 ‰ [24, 38-39] and for allochthonous POC -27.1 ± 1.1 ‰ [24] (see supplementary methods and supplementary table S7 for details).

enrichment in the Δ^{14}C-POC during the incubation (+40 ± 22 ‰) shows that the residual POC at the end of the incubation is more modern than in the beginning (table 2), implying that modern OC was either adsorbed, flocculated or preferentially preserved. Similar to summer, the POC/TPN ratio increases, however, during freshet the increase is caused by a slower increase of TPN than POC (except at KOL2 the TPN decreases), in contrast to the TPN decreasing at a faster rate than POC during summer (table 2). Given that nitrogen is an important nutrient, e.g., [71], and the losses of DOC during summer are high, this may suggest that nitrogen is used by microbes also during freshet.

During freshet, DOC degrades at a rate -0.014 ± 0.01 day^{-1}, however, these estimates for the freshet are not solely informative of degradation given that flocculation and adsorption likely diminish the DOC pool too. In contrast to summer, the δ^{13}C-DOC signature in freshet becomes slightly more depleted over time (table 2), potentially due to preferential sorption of carboxyl groups of DOC to particles, known to decrease the δ^{13}C-DOC of the residual DOC [60]. We accounted for the difference between freshet incubation temperature (21 ± 2 °C) and *in situ* river temperatures (8.5 ± 1.2 °C, supplementary table S2) and temperature corrected the degradation constants (*k*) for DOC (supplementary table S6). The corrected decay constant for freshet DOC was lower (-0.006 ± 0.003 day^{-1}) than uncorrected, and similar to the temperature corrected decay constant for summer DOC (-0.005 ± 0.002 day^{-1}). However, even though the reaction rates depend on temperature, the correction does not factor in environmental conditions such as differing microbial communities that might affect degradation rates [72].

The transfer of DOC into the POC pool, may implicate that the fate of this DOC pool differs from the DOC that remains dissolved. A study based on lake data has suggested that allochthonous DOC is more likely to flocculate and settle than be degraded [67]. Similar results regarding preferential settling of mineral POC have been shown in the East Siberian Sea [73]. If the DOC-derived POC behaves similarly in the fluvial system, i.e., protects its OC from degradation, it may have an attenuating effect on the climate impact of the fluvial DOC. While many studies have shown the opposite – indicating that old permafrost DOC is highly labile, e.g., [9, 18,21,56], none of these studies has included particles in their incubations so the potential impact of DOC flocculation and/or sorption to particles has not yet been assessed.

4.3 Particles change DOC dynamics

4.3.1 DOC from filtered incubations differs from whole-water DOC

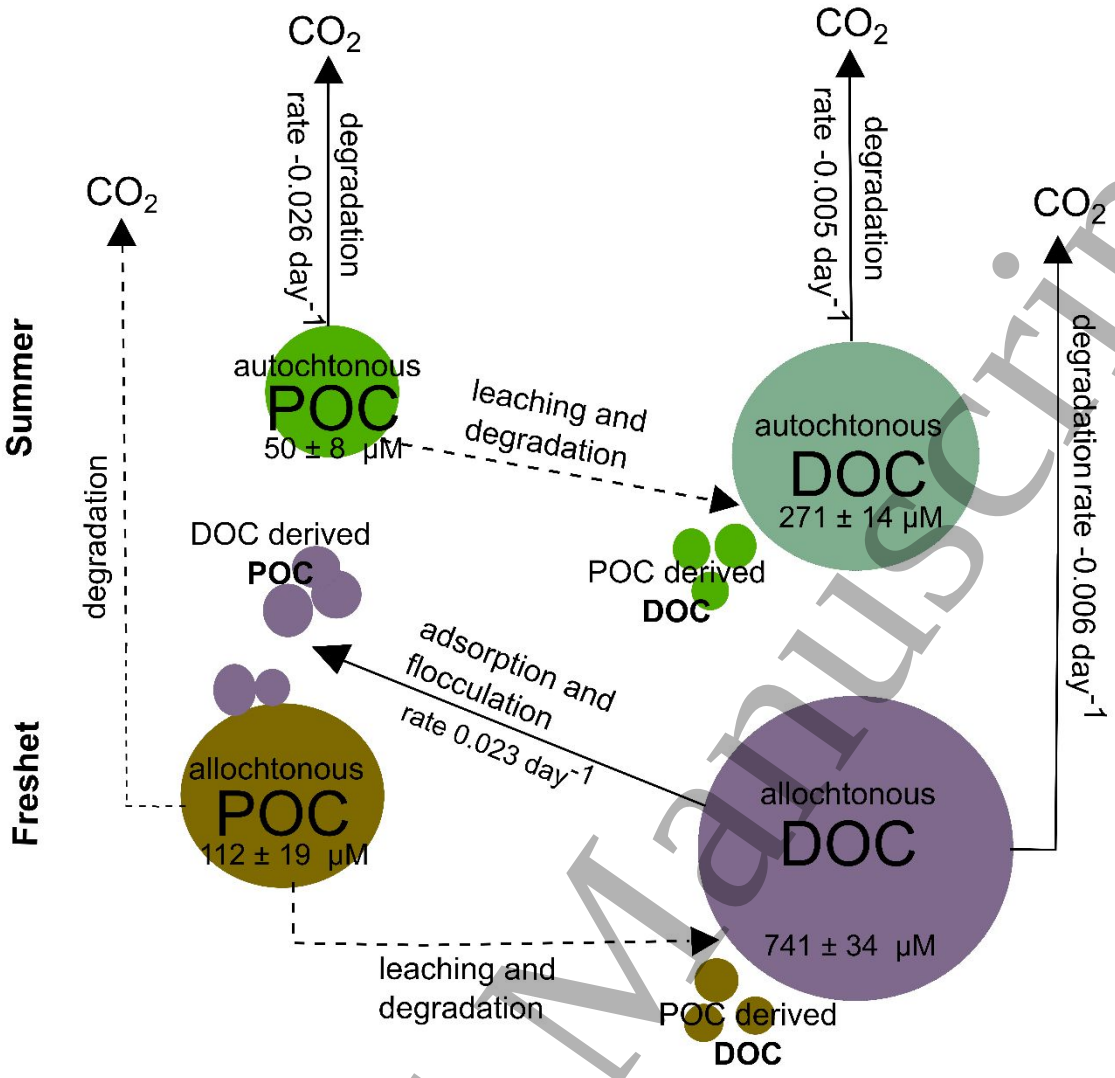

Figure 7. Conceptual figure of the dominating pathways of particulate and dissolved organic carbon (POC and DOC) loss and interactions of POC and DOC during freshet and summer conditions. Note that the term 'degradation rate' is used for the combined losses from microbial and mechanical breakdown and is temperature-corrected for *in situ* river temperatures (see supplementary table S2). During summer, both POC (green circle) and DOC (turquoise circle) are mostly autochthonous, and degrade over time. Breaking down of POC likely replenishes the DOC pool, thus slowing down DOC degradation, in addition to ongoing leaching. During freshet, both POC (brown circle) and DOC (purple circle) are mostly of allochthonous origin. The POC pool is replenished via DOC adsorption and/or flocculation (this may also happen during summer to a lower extent) while part of the DOC pool degrades. Breakdown of POC may happen, but would be likely masked by addition of DOC-derived POC. The concentrations (mean ± standard deviation) in the circles are at time point T0 before the incubation. The dashed lines show processes likely happening that we were not able to quantify; these processes are therefore currently indirectly accounted for in other rates that are reported in the figure. Size of the circles is indicative of the size of the organic carbon pool, but not to scale.

The default method to assess DOC degradation in inland waters, e.g., [8, 19-20, 34], is based on filtered (0.2-0.7 µm) DOC incubations (without particles). In our study, we performed both whole-water (unfiltered, see 4.2) and filtered incubations in an attempt to disentangle DOC and POC dynamics. We have shown that DOC interactions with POC affect the (i) relative and absolute losses of DOC over time (figure 4) and (ii) estimates of DOC degradation rate and fate (figure 7). The DOC degradation rates for filtered incubations (without particles) were slightly lower during freshet (-0.009 ± 0.003 day^{-1}, temperature corrected -0.004 ± 0.002 day^{-1}) than during summer (-0.012 ± 0.002 day^{-1}, temperature corrected -0.011 ± 0.001day^{-1}), suggesting faster DOC loss during summer months. These results differ from the DOC in the whole-water incubation, which showed higher losses during freshet and lower during summer compared to the respective filtered incubations (figure 4). During freshet, the whole-water DOC degradation constant is higher than the filtered, likely

due to losses of DOC to flocculation/adsorption, while during summer, breakdown of POC to DOC replenishes the DOC pool and thereby essentially slows down net degradation. Alternatively, filtration may change (i) the composition of the microbial pool through exclusion of predators of bacteria and/or (ii) the composition of the DOC pool (e.g., through lysis) thus enhancing degradation of DOC in the filtered incubations relative to whole-water incubations [74].

4.3.2 Seasonal variability of the OC dynamics in the Kolyma River

Our study shows that loss of POC in the Kolyma River is strongly seasonally dependent, and tightly linked to DOC dynamics, especially during the freshet period when both POC and DOC are largely comprised of allochthonous materials. As allochthonous POC appears not readily degradable, the climate impact (i.e., generation of greenhouse gases) of POC during freshet may be minimal. The DOC on the other hand is labile, yet interaction with particle surfaces may attenuate the climate impact of DOC as part of the DOC transitions into the POC pool through adsoprtion and/or flocculation (figure 7), and may be more prone to settling. During summer, autochthonous POC is preferably lost, faster than DOC. However, (mechanical) degradation of POC (e.g., leaching) likely produces DOC, which replenishes the DOC pool, artificially 'slowing down' the degradation of DOC.

When we combine our summer POC incubation results (loss of ~33 %) with summer POC flux estimates (0.049 Tg [23]), we estimated that each year during July-October potentially 0.016 Tg of POC degrades. For DOC, we combined our summer whole-water DOC incubation results (loss of ~8 %) and the filtered incubation DOC (loss of ~11 %) with summer DOC fluxes (0.329 Tg [22]) giving degradation estimates of 0.026 Tg and 0.036 Tg, respectively. The estimate with the filtered incubation is remarkably comparable to the one, 0.034 Tg, reported previously for the Kolyma River [20]. The whole-water DOC is lower likely due to addition of POC to the DOC pool slowing down the degradation. Additionally, it is notable that while POC concentrations during summer are more than five times lower than those of DOC (table 1), the POC degradation estimate is roughly half of that of DOC, suggesting that the role of river POC is quite important.

Our findings suggest that using filtered incubations to estimate DOC degradation may be misleading as these estimates are likely either over- or underestimating DOC breakdown depending on the season. Laboratory incubations operationally separate DOC and POC fractions while *in situ* they cannot be treated as separate pools. Incubation studies should therefore consider including particles when estimating DOC degradation, and future studies should focus on interactions of POC and DOC in fluvial and estuarine systems. Lastly, we recommend further investigation on the fate of DOC-derived POC in fluvial and marine environments as this may be an underappreciated mechanism to attenuate fluvial DOC breakdown.

5. Conclusions

• Our results indicate total OC losses both in freshet (-3 % to -12 %) and summer (-3 % to -14 %), but the relative importance of DOC and POC and their interactions are distinctly different between seasons.

• In summer, loss of POC (mostly autochtonous) is faster (-0.029 day^{-1}) than whole-water DOC (-0.006 day^{-1}), while during freshet, POC (mostly allochthonous) does not show losses, but instead gains (+15 % to +32 %) that are likely mostly driven by flocculation/adsorption of allochthonous DOC .

• Adsorption/flocculation of fluvial DOC to POC may change the ultimate fate of this DOC. If it settles rather than degrades, these processes may have an attenuating effect on breakdown of fluvial DOC, a process that mostly seems to occur during freshet.

• We estimated that each year during summer months (July-October) roughly 0.016 Tg of POC is lost in the Kolyma River, compared to roughly 0.026 Tg of DOC in whole-water conditions.

• Given our results, we recommend future DOC incubation experiments to consider POC, because these carbon pools are interlinked regarding degradation and their fate in the fluvial system.

Data availability

Any data that support the findings of this study are included within the article or in the supplement.

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References

1. Biskaborn B K, Smith S L, Noetzli J, Matthes H, Vieira G, Streletskiy D A, Schoeneich P, Romanovsk, V E, Lewkowicz A

G, Abramov A, Allard M, Boike J, Cable W L, Christiansen H H, Delaloye R, Diekmann B, Drozdov D, Etzelmüller B, Grosse G, Guglielmin M, Ingeman-Nielsen T, Isaksen, K, Ishikawa M, Johansson M, Johannsson H, Joo A, Kaverin D, Kholodov A, Konstantinov P, Kröger T, Lambiel C, Lanckman J -P, Luo D, Malkova G, Meiklejohn I, Moskalenko N, Oliva M, Phillips M, Ramos M, Sannel A B K, Sergeev D, Seybold C, Skryabin P, Vasiliev A, Wu Q, Yoshikawa K, Zheleznyak M and Lantuit H 2019 Permafrost is warming at a global scale *Nat. Commun.* 10 264, doi:10 1038/s41467-018-08240-4

2. Post E, Alley R B, Christensen T R, Macias-Fauria M, Forbes B C, Gooseff M N, Iler A, Kerby J T, Laidre K L, Mann M E, Olofsson J, Stroeve J C, Ulmer F, Virginia R A and Wang M 2019 The polar regions in a 2°C warmer world *Sci. Adv.* 5 doi:101126/sciadvaaw9883

3.Schuur E A G, Vogel J G, Crummer K G, Lee H, Sickman J O and Osterkamp T E 2009 The effect of permafrost thaw on old carbon release and net carbon exchange from tundra *Nat. Lett.* 459 556-559 doi:101038/nature08031

4.Bonnaventure P P and Lamoureux S F 2013 The active layer: A conceptual review of monitoring, modelling techniques and changes in a warming climate *Prog. Phys. Geogr.* 37 352-376 doi:10.1177/0309133313478314

5. Schuur E A G, McGuire A D, Schädel C, Grosse G, Harden J W, Hayes D J, Hugelius G, Koven C D, Kuhry P, Lawrence D M, Natali S M, Olefeldt D, Romanovsky V E, Schaefer K, Turetsky M R, Treat C C and Vonk J E 2015 Climate change and the permafrost carbon feedback *Nature* 520 171-179 doi:101038/nature14338

6. Kokelj S V and Jorgenson M T 2013 Advances in Thermokarst Research *Permafr. Perigracial Process.* 24 108-119 doi:101002/ppp1779

7. Turetsky M R, Abbott B W, Jones M C, Anthony K W, Olefeldt D, Schuur E A G, Grosse G, Kuhry P, Hugelius G, Koven C, Lawrence D M, Gibson C, Sannel A B K and McGuire A D 2020 Carbon release through abrupt permafrost thaw *Nat. Geosci.* 13 138-143 doi:101038/s41561-019-0526-0

8. Mann P J, Davydova A, Zimov N, Spencer R G M, Davydov S, Bulygina E, Zimov S and Holmes R M 2012 Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin *J. Geophys. Res. Biogeosciences* 117 1-15 doi:101029/2011JG001798

9. Spencer R G M, Mann P J, Dittmar T, Eglinton T I, Mcintyre C, Holmes R M, Zimov N and Stubbins A 2015 Detecting the signature of permafrost thaw in Arctic rivers *Geophys. Res. Lett.* 42 2830-2835 doi:101002/2015GL063498Received

10. Vonk J E, Mann P J, Dowdy K L, Davydova A, Davydov S P, Zimov N, Spencer R G M, Bulygina E G, Eglinton T I and Holmes R E 2013 Dissolved organic carbon loss from Yedoma permafrost amplified by ice wedge thaw *Environ. Res. Lett.* 8 035023 doi:101088/1748-9326/8/3/035023

11. Lantuit H and Pollard W H 2008 Fifty years of coastal erosion and retrogressive thaw slump activity on Herschel Island, southern Beaufort Sea, Yukon Territory, Canada *Geomorphology* 95 84-102 doi:101016/jgeomorph200607040

12. Kokelj S V, Kokoszka J, van der Sluijs J, Rudy A C A, Tunnicliffe J, Shakil S, Tank S E and Zolkos S 2021 Thaw-driven mass wasting couples slopes with downstream systems and effects propagate through Arctic drainage networks *Cryosph.* 15 3059-3081 doi:105194/tc-15-3059-2021

13. Peterson B J, Holmes R M, Mcclelland J W, Vörösmarty C J, Lammers R B, Shiklomanov A I, Shiklomanov I A and Rahmstorf S 2002 Increasing River Discharge to the Arctic Ocean *Science* 298 2171-2174

14. Tank S E, Striegl R G, McClelland J W and Kokelj S V 2016 Multi-decadal increases in dissolved organic carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic Ocean *Environ. Res. Lett.* 11 054015 doi:10.1088/1748-9326/11/5/054015

15. Zhang X, He J, Zhang J, Polyakov I, Gerdes R, Inoue J and Wu P 2013 Enhanced poleward moisture transport and amplified northern high-latitude wetting trend *Nat. Clim. Chang.* 3 47-51 doi:101038/nclimate1631

16. Kokelj S V, Lacelle D, Lantz T C, Tunnicliffe J, Malone L, Clark I D and Chin K S 2013 Thawing of massive ground ice in mega slumps drives increases in stream sediment and solute flux across a range of watershed scales *J. Geophys. Res. Earth Surf.* 118 681-692 doi:101002/jgrf20063

17. Olefeldt D, Goswami S, Grosse G, Hayes D, Hugelius G, Kuhry P, McGuire A D, Romanovsky V E, Sannel A B K, Schuur E A G and Turetsky M R 2016 Circumpolar distribution and carbon storage of thermokarst landscapes *Nat. Commun.* 7 13043 doi:101038/ncomms13043

18. Vonk J E, Mann P J, Davydov S, Davydova A, Spencer R G M, Schade J, Sobczak W V, Zimov N, Zimov S, Bulygina E, Eglinton T I and Holmes R M 2013 High biolability of ancient permafrost carbon upon thaw *Geophys. Res. Lett.* 40 2689-2693 doi:101002/grl50348

19. Holmes R M, McClelland J W, Raymond P A, Frazer B B, Peterson B J and Stieglitz M 2008 Lability of DOC transported by Alaskan rivers to the Arctic Ocean *Geophys. Res. Lett.* 35 3-7 doi:101029/2007GL032837

20. Wickland K P, Aiken G R, Butler K, Dornblaser M M, Spencer R G M and Striegl R G 2012 Biodegradability of dissolved organic carbon in the Yukon River and its tributaries : Seasonality and importance of inorganic nitrogen *Global Biochem. Cycles* 26 1-14 doi:101029/2012GB004342

21. Mann P J, Eglinton T I, Mcintyre C P, Zimov N, Davydova A, Vonk J E, Holmes R M and Spencer R G M 2015 Utilization of ancient permafrost carbon in headwaters of Arctic fluvial networks *Nat. Commun.* 6 1-7 doi:101038/ncomms8856

22. Holmes R M, McClelland J W, Peterson B J, Tank S E, Bulygina E, Eglinton T I, Gordeev V V, Gurtovaya T Y, Raymond P A, Repeta D J, Staples R, Striegl R G, Zhulidov A V and Zimov S

A 2012 Seasonal and Annual Fluxes of Nutrients and Organic Matter from Large Rivers to the Arctic Ocean and Surrounding Seas *Estuaries and Coasts* 35 369-382 doi:101007/s12237-011-9386-6

23. McClelland J W, Holmes R M, Peterson B J, Raymond P A, Striegl R G, Zhulidov A V, Zimov S A, Zimov N, Tank S E, Spencer R G M, Staples R, Gurtovaya T Y and Griffin C G 2016 Particulate organic carbon and nitrogen export from major Arctic rivers *Global Biogeochem. Cycles* 30 629-643 doi:101002/2015GB005351

24. Wild B, Andersson A, Bröder L, Vonk J. Hugelius G, McClelland J W, Song W, Raymond P A and Gustafsson Ö 2019 Rivers across the Siberian Arctic unearth the patterns of carbon release from thawing permafrost *Proc. Natl. Acad. Sci.* 116 10280–10285 doi:101073/pnas1811797116

25. Frey K E and McClelland J W 2009 Impacts of permafrost degradation on arctic river biogeochemistry *Hydrol. Process.* 23 169-182 https://doi.org/10.1002/hyp.7196

26. Dutta K, Schuur E A G, Neff J C and Zimov S A 2006 Potential carbon release from permafrost soils of Northeastern Siberia *Glob. Chang. Biol. 12* 2336-2351 doi:101111/j1365-2486200601259x

27. Zimov S A, Schuur E A G and Stuart Chapin III F 2006 Permafrost and the global carbon budget *Science* 312 1612-1613 doi:101126/science1128908

28. Strauss J, Schirrmeister L, Wetterich S, Borchers A and Davydov S P 2012 Grain-size properties and organic-carbon stock of Yedoma Ice Complex permafrost from the Kolyma lowland northeastern Siberia *Global Biogeochem. Cycles* 26 1-12 doi:101029/2011GB004104

29. Lindgren A, Hugelius G, Kuhry P, Christensen T R and Vandenberghe J 2016 GIS-based Maps and Area Estimates of Northern Hemisphere Permafrost Extent during the Last Glacial Maximum *Permafr. Periglac. Process.* 27 6-16 doi:101002/ppp1851

30. Strauss J, Schirrmeister L, Grosse G, Fortier D, Hugelius G, Knoblauch C, Romanovsky V, Schädel C, Schneider T, Deimling V, Schuur E A G, Shmelev D, Ulrich M and Veremeeva A 2017 Deep Yedoma permafrost : A synthesis of depositional characteristics and carbon vulnerability *Earth-Science Rev.* 172 75-86 doi:101016/jearscirev201707007

31. Griffin C G ,Frey K E, Rogan J and Holmes R M 2011 Spatial and interannual variability of dissolved organic matter in the Kolyma River East Siberia observed using satellite imagery *J. Geophys. Res. Biogeosciences* 116 1-12 doi:101029/2010JG001634

32. Richardson D C, Newbold J D, Aufdenkampe A K, Taylor P G and Kaplan L A 2013 Measuring heterotrophic respiration rates of suspended particulate organic carbon from stream ecosystems *Limnol. Oceanogr. Methods* 11 247-261 doi:104319/lom201311247

33. Shakil S, Tank S, Vonk J and Zolkos S 2021 Low biodegradability of particulate organic carbon mobilized from thaw slumps on the Peel Plateau, NT, and possible chemosynthesis and sorption effects *Biogeosciences Discuss.* [Preprint] https://doi.org/10.5194/bg-2021-150

34. Vonk J E, Tank S E, Mann P J, Spencer R G M, Treat C C, Striegl R G, Abbott B W and Wickland K P 2015 Biodegradability of dissolved organic carbon in permafrost soils and aquatic systems : a meta-analysis *Biogeosciences* 12 6915-6930 doi:105194/bg-12-6915-2015

35. Attermeyer K, Catalán N, Einarsdottir K, Freixa A, Groeneveld M, Hawkes J A, Bergquist J and Tranvik L J 2018 Organic Carbon Processing During Transport Through Boreal Inland Waters: Particles as Important Sites *J. Geophys. Res. Biogeosciences* 123 2412-2428 doi:10.1029/2018JG004500

36. Catalán N, Marcé R, Kothawala D N and Tranvik L J 2016 Organic carbon decomposition rates controlled by water retention time across inland waters *Nat. Geosci.* 9 501-504 doi:101038/ngeo2720

37. Stets E G, Striegl R G and Aiken G R 2010 Dissolved organic carbon export and internal cycling in small headwater lakes *Global Biogeochem. Cycles* 24 1-12 doi:101029/2010GB003815

38. Winterfeld M, Laepple, T and Mollenhauer G 2015 Characterization of particulate organic matter in the Lena River delta and adjacent nearshore zone, NE Siberia - Part I: Radiocarbon inventories *Biogeosciences* 123769–3788 https://doi.org/10.5194/bg-12-3769-2015

39. Shakil S, Tank S E, Kokelj S V, Vonk J E and Zolkos S 2020 Particulate dominance of organic carbon mobilization from thaw slumps on the Peel Plateau, NT: Quantification and implications for stream systems and permafrost carbon release *Environ. Res. Lett.* 15 114019 doi:10.1088/1748-9326/abac36.

40. R Core Team 2020 R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.

41. Stock B C and Semmens B X 2016 MixSIAR GUI User Manual. Version 3.1. (available at: https://github.com/brianstock/MixSIAR/) doi:10.5281/zenodo.47719.

42. Roshydromet, Federal Service for Hydrometeorology and Environmental Monitoring, Ministry of Natural Resources and Environment, Russian Federation.

43. Maberly S C 1996 Diel episodic and seasonal changes in pH and concentrations of inorganic carbon in a productive lake *Freshw. Biol. 35* 579-598 doi:101111/j1365-24271996tb01770x

44. Bröder L, Davydova A, Davydov S, Zimov N, Haghipour N, Eglinton T I and Vonk J E 2020 Particulate Organic Matter Dynamics in a Permafrost Headwater Stream and the Kolyma River Mainstem *J. Geophys. Res. Biogeosciences* 125 1-16 doi:10.1029/2019JG005511

45. Welp L R, Randerson J T, Finlay J C, Davydov S P, Zimova G M, Davydova A I and Zimov S A 2005 A high-resolution time series of oxygen isotopes from the Kolyma River: Implications for the seasonal dynamics of discharge and basin-scale water use *Geophys. Res. Lett.* 32 1-5 doi:101029/2005GL022857

46. Kaiser K, Canedo-Oropeza M, McMahon R and Amon R M W 2017 Origins and transformations of dissolved organic matter in large Arctic rivers *Sci. Rep.* 7 1-11 doi:101038/s41598-017-12729-1

47. Neff J C, Finlay J C, Zimov S A, Davydov S P, Carrasco J J, Schuur E A G and Davydova A I 2006 Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams *Geophys. Res. Lett.* 33 1-5 doi:101029/2006GL028222

48. Lewkowicz A G and Way R G 2019 Extremes of summer climate trigger thousands of thermokarst landslides in a High Arctic environment *Nat. Commun.* 10 1-11 doi:101038/s41467-019-09314-7

49. Meyers P A 1994 Preservation of elemental and isotopic source identification of sedimentary organic matter *Chem. Geol.* 114 289-302 doi:101016/0009-2541(94)90059-0

50. Schmidt M W, I Knicker H and Kögel-Knabner I 2000 Organic matter accumulating in Aeh and Bh horizons of a Podzol - Chemical characterization in primary organo-mineral associations *Org. Geochem.* 31 727-734 doi:101016/S0146-6380(00)00045-0

51. Guillemette F, Leigh Mccallister S and Del Giorgio P A 2016 Selective consumption and metabolic allocation of terrestrial and algal carbon determine allochthony in lake bacteria *ISME J* 10 1373-1382 doi:101038/ismej2015215

52. Campeau A, Wallin M B, Giesler R, Löfgren S, Mörth C M, Schiff S, Venkiteswaran J J and Bishop K 2017 Multiple sources and sinks of dissolved inorganic carbon across Swedish streams refocusing the lens of stable C isotopes *Sci. Rep.* 7 1-14 doi:10.1038/s41598-017-09049-9

53. Waldron S, Scott E M and Soulsby C 2007 Stable isotope analysis reveals lower-order river dissolved inorganic carbon pools are highly dynamic *Environ. Sci. Technol.* 41 6156-6162 doi:101021/es0706089

54. Segal R A, Lantz T C and Kokelj S V 2016 Acceleration of thaw slump activity in glaciated landscapes of the Western Canadian Arctic *Environ. Res. Lett.* 11 034025 doi:doi:101088/1748-9326/11/3/034025

55. Simon M, Grossart H P, Schweitzer B and Ploug H 2002 Microbial ecology of organic aggregates in aquatic ecosystems *Aquat. Microb. Ecol.* 28 175-211 doi:103354/ame028175

56. Drake T W, Guillemette F and Hemingway J D 2018 The Ephemeral Signature of Permafrost Carbon in an Arctic Fluvial Network *J. Geophys. Res. Biogeosciences* 123 1475-1485 doi:101029/2017JG004311

57. Scheingross J S, Hovius N, Dellinger M, Hilton R G, Repasch M, Sachse D, Gröcke D R, Vieth-Hillebrand A and Turowski J M 2019 Preservation of organic carbon during active fluvial transport and particle abrasion *Geology* 47 958-962 doi:101130/G464421

58. van Dongen B E, Zencak Z and Gustafsson Ö 2008 Differential transport and degradation of bulk organic carbon and specific terrestrial biomarkers in the surface waters of a sub-arctic brackish bay mixing zone *Mar. Chem.* 112 203-214 doi:101016/jmarchem200808002

59. Johnson M P 2016 Photosynthesis *Essays Biochem.* 60 255-273 doi:101042/EBC20160016

60. Howarth R W 1984 The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments *Biogeochemistry* 1 5-27 doi:101007/BF02181118

61. Middelburg J J 2011 Chemoautotrophy in the ocean *Geophys. Res. Lett.* 38 94-97 doi:101029/2011GL049725

62. Morana C, Roland F A E, Crowe S A, Llirós M, Borges A V, Darchambeau F and Bouillon S 2016 Chemoautotrophy and anoxygenic photosynthesis within the water column of a large meromictic tropical lake (Lake Kivu East Africa) *Limnol. Oceanogr.* 61 1424-1437 doi:101002/lno10304

63. von Wachenfeldt E, Bastviken D and Tranvik L J 2009 Microbially induced flocculation of allochthonous dissolved organic carbon in lakes *Limno.l Oceanogr.* 54 1811-1818 doi:104319/lo20095451811

64. Groeneveld M, Catalán N, Attermeyer K, Hawkes J, Einarsdóttir K, Kothawala D, Bergquist J and Tranvik L 2020 Selective Adsorption of Terrestrial Dissolved Organic Matter to Inorganic Surfaces Along a Boreal Inland Water Continuum *J. Geophys. Res. Biogeosciences* 125 1-22 doi:101029/2019JG005236

65. Kaiser K, Guggenberger G and Zech W 2001 Isotopic fractionation of dissolved organic carbon in shallow forest soils as affected by sorption *Eur. J. Soil. Sci.* 52 585-597 doi:101046/j1365-2389200100407x

66. Kothawala D N, Roehm C, Blodau C and Moore T R 2012 Selective adsorption of dissolved organic matter to mineral soils *Geoderma* 189-190 334-342 doi:101016/jgeoderma201207001

67. von Wachenfeldt E and Tranvik L J 2008 Sedimentation in boreal lakes - The role of flocculation of allochthonous dissolved organic matter in the water column *Ecosystems* 11 803-814 doi:101007/s10021-008-9162-z

68. Kleber M, Bourg I C, Coward E K, Hansel C M, Myneni S C B and Nunan N 2021 Dynamic interactions at the mineral-organic matter interface *Nat. Rev. Earth Environ.* 2 402-421 doi:101038/s43017-021-00162-y

69. Opfergelt S 2020 The next generation of climate model should account for the evolution of mineral-organic interactions with permafrost thaw *Environ. Res. Lett.* 15 091003 doi:101088/1748-9326/ab9a6d

70. Kepkay P E 1994 Reactivity of Colloids *Mar. Ecol. Prog. Ser.* 109 293-304

71. Xia X, Zhang S, Li S, Zhang L, Wang G, Zhang L, Wang J and Li Z 2018 The cycle of nitrogen in river systems: Sources transformation and flux *Environ. Sci. Process. Impacts* 20 863–891 doi:101039/c8em00042e

72. Davidson E A and Janssens I A 2006 Temperature sensitivity of soil carbon decomposition and feedbacks to climate change *Nat. Rev.* 440 doi:10.1038/nature04514

73. Vonk J E, Sánchez-García L, Semiletov I, Dudarev O, Eglinton T, Andersson A and Gustafsson O 2010 Molecular and radiocarbon constraints on sources and degradation of terrestrial organic carbon along the Kolyma paleoriver transect East Siberian Sea *Biogeosciences* 7 3153-3166 doi:105194/bg-7-3153-2010

74. Dean J F, Van Hal J R, Dolman A J, Aerts R and Weedon J T 2018 Filtration artefacts in bacterial community composition can affect the outcome of dissolved organic matter biolability assays *Biogeosciences* 15 7141-7154 doi:105194/bg-15-7141-2018