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RESEARCH ARTICLE

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Special Section:

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Key Points:

- Fluorescent dissolved organic matter (fDOM) high frequency sensing in a catchment underlain by discontinuous permafrost revealed dissolved organic carbon (DOC) export seasonality and captured flood events
- Spring floods dominate annual export, but autumn floods, coinciding with watershed refreezing are most intense for carbon export
- Nearly chemostatic DOC behavior suggests an important contribution of peatlands to the annual DOC flux (5.2–5.5 g C m⁻² yr⁻¹)

Supporting Information:

Supporting Information may be found in the online version of this article.

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Seasonality of DOC Export From a Russian Subarctic Catchment Underlain by Discontinuous Permafrost, Highlighted by High-Frequency Monitoring

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Abstract Intense climate change and permafrost degradation impact northern watersheds and ultimately organic carbon transfer from terrestrial to aquatic ecosystems. We investigated the contemporary dissolved organic carbon (DOC) dynamics in a northern catchment underlain by discontinuous permafrost (Graviyka River, northern Siberia), where historical meteorological and hydrological data are available since 1936. Mean annual air temperature (MAAT), in contrast to precipitation and discharge was found to show a significant increasing trend since 1950. Using *in situ* sensing of fluorescent dissolved organic matter (fDOM), we estimated DOC concentrations at a high temporal frequency (1h) during 3 years (2015–2018), and calculated annual specific fluxes of 5.2–5.5 g C m² yr⁻¹. High DOC concentrations (above 10 mg L⁻¹) are sustained all year, exhibiting nearly chemostatic behavior. Nevertheless, the high-frequency survey of DOC and other water parameters revealed the seasonality of DOC origin and pathways in the watershed. The spring freshet dominates the annual export (up to 80%), but summer and autumn floods can also contribute up to 9% and 8% respectively. The high-frequency sampling was able to capture the specific dynamic of DOC concentration during spring flood (DOC peak preceding discharge, dilution during the spring freshet) and summer and autumn floods (contribution of DOC-rich, low conductivity water). These observations suggest a significant contribution of organic-rich water originating in peatlands, potentially from degrading palsas. The study demonstrates both that high-frequency sampling is essential to capture key events for DOC export, and that more long-term monitoring is urgently needed in these rapidly evolving watersheds.

Plain Language Summary Carbon transported by rivers forms a large part of the planetary carbon budget. In a changing climate, it is important to know how much carbon is transported to rivers, especially in the Arctic, where soils are rich in organic carbon and are experiencing permafrost thaw. We installed *in situ* equipment for long-term high-frequency observations in a river in northern Siberia in order to track changes in water quality and carbon content. The climate has been becoming warmer in this region since 1950, but there has been no increase in the precipitation or water volume in the river. The waters of the studied river are rich in dissolved organic carbon throughout the year. Spring floods transport the majority of carbon, owing to high water discharge. In summer and autumn, there is less water flowing, but the carbon content in the water is still high. This water and carbon originate in peatlands. Today, these peatlands are partially frozen, but are expected to thaw in the near future. This process can increase the amount of carbon in the water, whereas the increased thawing soil depth can reduce carbon export. Therefore, more long-term studies are needed to forecast future carbon export from northern watersheds.

1. Introduction

Northern latitude soils represent approximately 50% of the global soil organic carbon pool, or 1,300 ± 200 Pg C, of which ~800 Pg C are perennially frozen in permafrost (Hugelius et al., 2014; Strauss et al., 2017; Tarnocai et al., 2009). In this context, northern catchments contribute significantly to organic carbon transfer from terrestrial to aquatic ecosystems, and the Arctic Ocean receives the largest amount of organic carbon on a volume basis (Opsahl et al., 1999). The dissolved organic carbon (DOC) fluxes reaching the Arctic Ocean from the six largest Arctic rivers range from 18.3 Tg C yr⁻¹ (Amon et al., 2012; Holmes et al., 2012) to

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21.6 Tg C (Mu et al., 2019), while the pan-Arctic fluxes reach 33 Tg C yr⁻¹ (McGuire et al., 2009). However, the actual fluvial organic carbon transfers from northern terrestrial to aquatic ecosystems are expected to be even higher. A significant fraction of the DOC fluxes to surface waters is subject to microbial mineralization and photodegradation in first-order streams or immobilized in soils and sediments before reaching the Arctic Ocean (Abbott et al., 2016; Mann et al., 2015; McGuire et al., 2009; Wild et al., 2019). Quantifying fluvial organic carbon export at smaller scales is crucial, in order to establish accurate carbon budgets from northern ecosystems (Lundin et al., 2016; Olefeldt et al., 2013).

Northern watersheds are facing climate change and permafrost degradation. Vegetation shifts and disruption to hydrological connectivity alter biogeochemical cycles (Frey & McClelland, 2009; Lafrenière & Lamoureaux, 2019; Stieglitz et al., 2003). In contrast to the consistent increase in availability of inorganic nutrients in the Arctic's aquatic ecosystems, organic carbon's response to thaw is much more variable with respect to local topographic, geologic and permafrost status (Frey & McClelland, 2009; Tank et al., 2012, 2020). In addition, the diversity of soil and ecosystem types within a watershed strongly controls fluvial organic carbon fluxes. For instance, peatlands coverage directly drives the intensity of organic carbon transfer to streams (Laudon et al., 2004; Olefeldt et al., 2013). Permafrost degradation is expected to further increase organic carbon transfer from peatlands by deepening the active layer (Frey & Smith, 2005), and it may release DOM with higher biodegradation potential (Selvam et al., 2017). Alternatively, increased fire frequency, as observed in recent years in the Arctic (Hu et al., 2015) may reduce organic transfer from terrestrial to aquatic ecosystem (Parham et al., 2013; Rodríguez-Cardona et al., 2020). With regard to this complexity, the scarce (Laudon et al., 2017) long-term records of fluvial organic exports from northern watersheds report contrasting trends (Frey & McClelland, 2009). In the Yukon River, organic carbon fluxes decreased during summer and autumn from 1978–1980 to 2001–2003 (Striegl et al., 2005), whereas fluxes have remained steady since the 1930s in the Severnaya River (Chupakov et al., 2020) and in small watersheds of Northern Sweden since the early 1980s (Giesler et al., 2014). Meanwhile, organic carbon fluxes to rivers have increased in the Central Siberian Plateau since the 1960s (Prokushkin et al., 2011), and in the McKenzie River and its sub-catchments over a survey period of nearly 40 years (Tank et al., 2016).

In northern watersheds, water and DOC fluxes are highly seasonal (Giesler et al., 2014; Holmes et al., 2012; Townsend-Small et al., 2011). A key characteristic of these watersheds is the dominance of the spring freshet. Most (50%–90%) of the fluvial organic carbon export occurs during a short period, ranging from a few days to a few weeks in June (Amon et al., 2012; Carey, 2003; Finlay et al., 2006; Holmes et al., 2012; Johnston et al., 2018). Recent observations from the high Arctic suggest that northern watersheds could shift from this nival regime to a multimodal one, with an increased influence of summer rains (Beel et al., 2021; Lamoureaux & Lafrenière, 2017). This renders it necessary to monitor rivers year-round and to include “shoulder seasons” in surveys of organic carbon transfer (Shogren et al., 2020; Song et al., 2019). The origin and composition of exported dissolved organic matter (DOM) is also highly seasonal (Fouché et al., 2017; O'Donnell et al., 2012; Shatilla & Carey, 2019). During the spring freshet, mostly modern carbon, originating in shallow organic soil layers, is exported, whereas the contribution of deeper soil layers and, potentially, thawed permafrost carbon is higher under autumn and winter base-flow conditions (Amon et al., 2012; Johnston et al., 2018; Raymond et al., 2007). The composition of DOM depends on the relative contribution of sources and DOM lability may be higher in permafrost layers (Fouché et al., 2020; Selvam et al., 2017). This has important implications, because DOM origin (i.e., thawing permafrost or recently fixed carbon from the atmosphere) and lability control the potential ecosystem feedback on climate change of its transfer from terrestrial to aquatic ecosystems (Estop-Aragonés et al., 2020; Gandois et al., 2019; O'Donnell et al., 2020).

In northern watersheds, remoteness, harsh conditions and the prevalence of the spring freshet on annual budgets have let to focus sampling on this period, with a higher sampling frequency (up to daily) (Carey, 2003; Chupakov et al., 2020; Finlay et al., 2006; Holmes et al., 2008; Juhls et al., 2020). In the past decade, optical properties of DOM (both absorbance and fluorescence) have been used to develop *in situ* sensors able to quantify DOC concentrations (Downing et al., 2012; Grayson and Holden, 2012; Ruhala & Zarnetske, 2017) at a much higher resolution (hours to minutes). The use of these *in situ* sensors has revealed an unexpected variability of DOC concentrations, at various time scales (Pellerin et al., 2012; Rosset et al., 2019; Shultz et al., 2018; Tunaley et al., 2018). The high-frequency analysis of DOC, combined with other hydrochemical tracers, makes it possible to track DOC origin and export processes during high flow

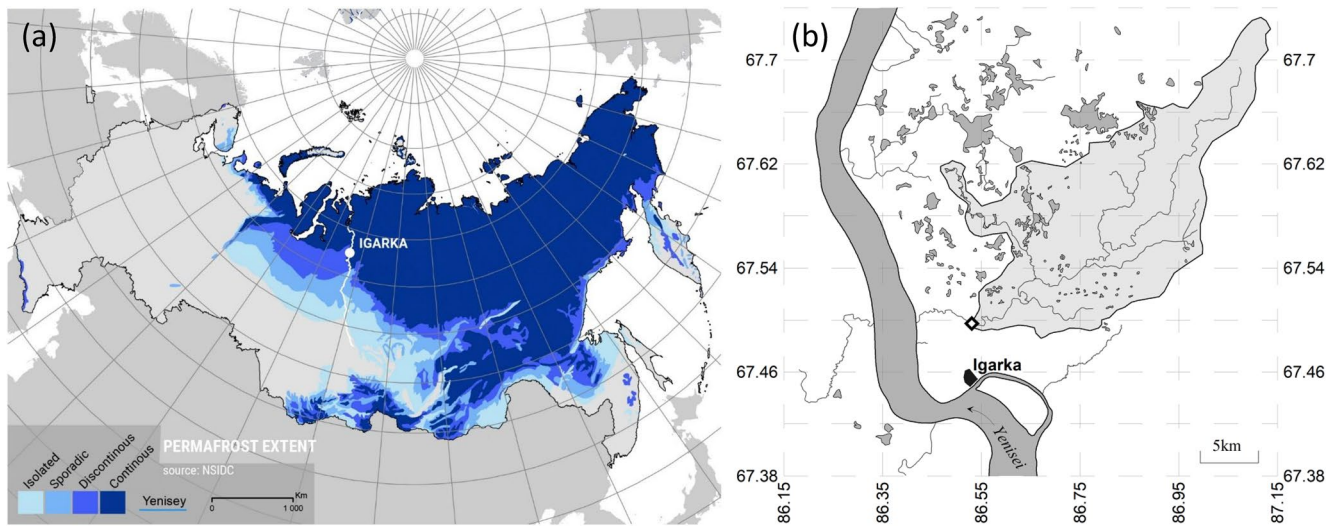


Figure 1. (a) Location of study area and permafrost status (data: NASA) (b) In gray: Graviyka catchment adapted from Tananaev (2016). The diamond indicates the location of the gauging station and the multiparameter probe.

events (Fovet et al., 2018; Pellerin et al., 2012; Rosset et al., 2020; Shogren et al., 2021; Tunaley et al., 2016; Vaughan et al., 2017).

This article focuses on a northern watershed located in Siberia underlain by discontinuous permafrost. Climate change has already impacted this region, and induced permafrost degradation (Streletskiy et al., 2015). We hypothesize that this may have affected organic carbon fluvial export, through modifying hydrological pathways within the watershed. In this perspective, we combine high-frequency hydrochemical data with historical records, for a long-term hydrological perspective. The objectives of the article are to: (a) describe the DOC concentration and export dynamics using high-frequency sensing, (b) outline the seasonality and potential shifts in hydrological and organic carbon export (c) identify the DOC export processes and origin for different hydrological events.

2. Materials and Methods

2.1. Study Site

The Graviyka River is a medium-sized subarctic river and one of the northernmost tributaries of the Yenisey River. The river outlet is located near the city of Igarka, Krasnoyarsk Krai (Figure 1). The catchment, with an area of 320 km², is underlain by discontinuous permafrost (Figure 1a), and is characterized by a forest-tundra ecotone, dominated by larch (*Larix sibirica*), birch (*Betula pendula*), and Siberian pine (*Pinus sibirica*), and by palsa (frozen peat mounds) landscapes (Streletskiy et al., 2015; Tananaev, 2016). Palsas are covered by lichens, Labrador tea (*Rhododendron spp*), mosses and dwarf birch (*B. nana*). Permafrost thaw promotes the development of thermokarst depressions and ponds of various sizes, where *Sphagnum spp.* and *Eriophorum spp.* are abundant. The vegetation in the area is an indicator of the permafrost status. Forested areas cover drained silty soils developed on Pleistocene permafrost with an active layer ranging from one to several meters deep, while palsa-dominated areas are indicative of Holocene permafrost with a shallow active layer (<1m). Peatland accumulation in the region started around 9,500 yr BP (Peteet et al., 1998, and references therein). Permafrost degradation has been observed in the past 30 years in the Igarka region, evidenced both by ground temperature records and the evolution of permafrost landscapes (Streletskiy et al., 2015).

2.2. Historical Hydrological and Meteorological Data

Meteorological data have been collected since 1936 at the Igarka meteorological station. Data are available on the RIHMI-WDC web-portal (<http://aisori-m.meteo.ru/waisori/>). In the 1940 and 1950s, new rain gauges

were deployed in the USSR, and precipitation records are known to be non-homogeneous (Groisman & Rankova, 2001). Precipitation data corrected for rain gauge bias, available at RIHMI-WDC, were used for trend analysis for the 1936–2015 period. Uncorrected data from 2015 to 2018 were used for descriptive purposes.

The Russian Hydrometeorological Service (Roshydromet) has maintained the gauging station on the Graviyka River since 1936, although observations ceased in 1993. Hydrological data for this period (water stage and daily flow) were obtained from the official hydrological yearbooks published by the Roshydromet. The gauging station was revisited in 2014 for this study. Water level was measured hourly, and a historical rating curve (Figure S1) along with systematic gauge leveling was used to reconstitute hourly water stage and discharge values.

2.3. Instrumentation

In June 2015, an EXO2 multiparameter probe (YSI, Xylem Inc., USA) was installed at the historical gauging station location, its observations spanned the period from June 2015 to September 2018. The probe recorded water level, temperature, conductivity, pH, turbidity, dissolved oxygen (DO), and fluorescent dissolved organic matter (fDOM) values hourly. The fDOM signal, with a single excitation (365 ± 5 nm) and emission (480 ± 40 nm) wavelength couple acted as a proxy for DOC concentration (Downing et al., 2012).

2.4. Water Sampling and Analysis

Water was sampled regularly during the ice-free period at the outlet of the Graviyka catchment. Bulk samples were stored in sealed 10 ml plastic or glass vials for water stable isotopes, and kept refrigerated prior to analysis. Water was filtered using pre-combusted glass fiber filters (GF/F, Whatman) for DOC, dissolved inorganic carbon (DIC), major element concentrations and ultraviolet-visible (UVvis) spectra. UVvis spectra were measured using a Cary 100 spectrometer (Agilent, USA). Non-purgeable organic carbon (hereafter DOC) was analyzed on filtered samples after acidification to pH 2 (HCl) by TOC Vario Cube (Elementar, Germany). DIC concentrations measured using the same instrument without the catalytic combustion step. The quantification limit for the determination of DOC and DIC was <0.5 mgC L⁻¹. The specific UV absorbance at 254 nm (SUVA, L mg C⁻¹m⁻¹) was calculated as follows: $SUVA = A_{254}/(b \times [DOC])$ (L mg⁻¹ m⁻¹), where A_{254} is the sample absorbance at 254 nm (nondimensional), b is the optical path length (m), and DOC the concentration in milligrams per liter. SUVA is a proxy for DOM aromaticity (Weishaar et al., 2003). Major elements (Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, K⁺) were analyzed by ion chromatography (Dionex ICS-1100, Thermo Fischer Sci., USA). The precision of measurement was 0.2 mg L⁻¹. Certified material (ion 915, Environment and Climate Change Canada, Canada) was included in the analytical loop and recovery was >90% of the certified value. Flow injection analysis (QuikChem 8500 Series 2; Lachat Instruments, USA) was used for low levels of NO₃⁻ and PO₄³⁻. Water isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was measured using cavity ring-down spectroscopy (Picarro L-2120-i, Picarro Inc., USA). Both water isotopes were determined for the same water sample. The values are given relative to the Vienna Standard Mean Ocean Water (VSMOW). The accuracy of the method is $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for $\delta^2\text{H}$.

On three occasions, water was sampled for ¹⁴C analysis of DOC. Water was filtered using combusted GF/F filters, stored in acid washed and burned glass bottles, and freeze-dried. The radiocarbon content of DOM was measured at “Laboratoire des sciences du climat et l’environnement” (LSCE, Gif-sur-Yvette, France) on the ECHOMICADAS compact Accelerator Mass Spectrometry (AMS) system, through elemental analyzer gas interface system (EA-GIS) coupling (Tisnerat-Laborde et al., 2015). The $\delta^{13}\text{C}$ value of the freeze-dried powder was compared to the direct analysis of $\delta^{13}\text{C}$ -DOM on the liquid sample after acidification, to evaluate the need for removal of inorganic carbon. Typically, 0.5 mg of sample material was prepared in a tin capsule and acidified with 3 μL of HCl 1 M. Samples were duplicated, and the reproducibility of duplicates was checked (Chi-squared test). Blanks and standard materials (C7 and OXA2 oxalic acid) were included in the analysis sequence. All ¹⁴C results were corrected for isotopic fractionation according to the conventions of Stuiver and Polach (1977) and reported as F¹⁴C following the recommendation of Reimer et al. (2004).

2.5. Data Treatment and Flux Calculations

The pH, conductivity, DO and turbidity sensors of the YSI EXO2 probe were calibrated using commercial solutions. The raw fDOM data were corrected following the sequential correction procedure described by De Oliveira et al. (2018). The correction was limited to temperature and turbidity correction, as the absorbance at 254 nm (A_{254}) was always <0.6 . The corrected signal was on average $8 \pm 4\%$ different from the raw signal. The corrected fDOM signal was calibrated using grab sample DOC concentrations. A linear model ($\text{DOC} = 0.217 \cdot \text{fDOM}$, $n = 58$, $r^2 = 0.27$, $p < 0.001$) was established between DOC concentrations and corrected fDOM values. The relatively low r^2 can be related local heterogeneity between the probe location (ballasted in the river) and the sampling point (surface water), as well as potential evolution of DOM composition with hydrological conditions (Saraceno et al., 2009). The fDOM sensor mostly records terrestrial DOC signal, and may be affected by the contribution of non-fluorescent DOM. This was the case during the dry summer 2016, when a lack of response of the fDOM sensors was observed. Nevertheless, the slope between DOC concentrations and the fDOM signal was very close to the one established in the Yenisei River close to the Graviyka outlet over a larger range of DOC concentrations ($1.8\text{--}19 \text{ mg L}^{-1}$) ($a = 0.225$, $r^2 = 0.93$, $p < 0.0001$, $n = 100$) (Figure S2).

The water level recorded by the probe was linked to a gauge datum by leveling, and converted to water discharge using the historical rating curve (Figure S1). The hourly DOC fluxes were calculated as described in Equation 1.

$$F_{\text{DOC}} = \int Q * [\text{DOC}] * dt \approx \Delta t * \sum_0^N \frac{(Q_i * [\text{DOC}]_i + Q_{i-1} * [\text{DOC}]_{i-1})}{2} \quad (1)$$

The observation period ranged from June 18, 2015 to September 28, 2018. However, logistical constraints and vandalism led to a loss of data. Indeed, from August 9 to September 21, 2017, no data could be recorded, because the probe was vandalized. On June 19, 2018, the water level probe became dysfunctional, so no fluxes could be calculated after this date. In summer 2016, owing to the extremely low water level, the fDOM records showed no response to the evolution of DOC concentrations and were discarded. For DOC flux calculations, the mean grab sample DOC concentration for the period ($11.7 \pm 0.4 \text{ mg L}^{-1}$, $n = 15$) was used. This has a negligible influence on the flux calculation because the water discharge was very low during this period.

The hydrograph was divided into four hydrological periods. (a) the spring freshet from the end of May to mid-July; (b) the pronounced summer low-flow from mid-July until early September; (c) the autumn flood period from mid-September to late October; and (d) the winter base flow period, from November to May.

Flood events were identified (via visual identification of the inflexion point and checking for a 10% increase in discharge) in spring, summer, and autumn. The flood hysteresis were characterized following the methodology described by Godsey et al. (2019); Koenig et al. (2017); Shogren et al. (2021) and Vaughan et al. (2017). The direction (clockwise, anticlockwise) of the hysteresis was identified. The slope of the logarithmic C-Q relationship (β) was calculated as an indicator of transport limitation ($\beta > 0$), source limitation ($\beta < 0$), or chemostatic behavior ($\beta = 0$) in the watershed. The flushing index ($\text{FI} = C_{\text{Qpeak, norm}} - C_{\text{initial, norm}}$), was calculated as an indicator of the flushing or diluting effect of the rising limb.

2.6. Statistical Analysis

Statistical analysis was performed using R (R Core Team, 2019) and the RStudio software (Version 1.2.1335), using the ggplot (Wickham, 2016), tidyverse (Wickham, 2017), dplyr (Wickham et al., 2019), dunn.test (Dinno, 2017), and trend (Pohlert, 2020) packages. Significant differences ($p < 0.05$) between groups were evaluated using the Kruskal-Wallis and Dunn's post hoc multiple tests. The Mann-Kendall test was used to assess the presence and the significance of linear trends in data, and the Pettitt test to detect breakpoint changes in the time series.

Table 1
Mean Annual Air Temperature (MAAT), Annual Precipitation and Hydrological Data for 1938–1992 and the Study Period

	1938–1992 (mean ± SD)	2016	2017
MAAT (°C)	-7.8 ± 1.5	−5.5	−5.8
Annual precipitation (mm)	647 ± 99	452	706
Annual water flux (km ³ yr ^{−1})	0.160 ± 0.032	0.169	0.158
Water specific Flux (m ³ m ² yr ^{−1})	0.496 ± 0.01	0.524	0.489
DOC flux (T)	/	1,770	1,690
DOC specific flux (g m ² yr ^{−1})	/	5.5	5.2

Note. Annual DOC Fluxes Estimated for the Study Period (2016 and 2017).

3. Results

3.1. Meteorology and Hydrology: Historical and Contemporary Data

Over the long-term period (1936–2019), Igarka's climate was continental subarctic, or “Dfc,” using the Köppen climate classification (Peel et al., 2007), with a mean annual air temperature (MAAT) of $-7.8^{\circ}\text{C} \pm 1.5^{\circ}\text{C}$, and mean annual precipitation (P) of 647 ± 99 mm (Table 1). Since 1936, MAAT has presented a significant ($p < 0.05$) increasing trend. No monotonic trend existed for annual precipitation (Figure S3). MAAT and P fluctuations could be separated into different periods: (a) from the 1930s to the late 1950s, with decreasing MAAT and increasing P (counterphase); (b) from the late 1950s to the late 1970s, cold and mostly humid; (c) from the late 1970s to the late 1990s, moderate and dry; and (d) since the early 2000s, increasing MAAT and P (synphase).

During the observation years with full high-frequency records, 2016 and 2017, MAAT (-5.5°C and -5.8°C) was above the long-term average of -7.8°C (Table 1). The climate for the first observation year, 2015, was close to the average, except for intense July rains. In 2016, the region experienced a rare drought period. No rain was recorded for 30 days, from June 29 to July 28, 2016, the longest dry period on record (Figure S4a). The mean annual water flux for the historical record (1938–1992) was 0.160 ± 0.032 km³ yr^{−1}. This corresponded to a daily flow of 5.08 ± 1.02 m³ s^{−1} and a specific water flux of 0.496 ± 0.01 m³ m² yr^{−1}. No trend appeared for mean annual daily flow (Figure 2). The spring peak flow (black dot on Figure 2) showed cyclic behavior. The variation in peak flow timing was associated with a negative trend in May runoff, $p < 0.05$, and the mean May air temperature, which reached a pronounced minimum in the 1960 and 1970s. Subsequently, an insignificant runoff increase was observed in June and July, $p > 0.05$, followed by a decrease from August to October, $p > 0.1$.

Water fluxes for the studied period were comparable to historical means (Table 1). Monthly flows differed from historical trends in relation with the extremely variable climate and hydrology during the observation years. The observed June runoff was 15%–30% above the average (2016–2017). The July runoff was 200% higher than the average in 2015%, and 6% above the previously observed maximum (1968), but 25%–75% lower than the average in 2016–2017. The September 2015 discharge was twice the historical average value, but both the September and the October discharge were 40%–60% lower than average in 2016–2017.

3.2. Grab Water Sample Characteristics

The grab sample chemistry is summarized in Table 2.

The ranges of selected parameters for the different periods considered are presented in Figure 3. The Graviyka River's water chemistry was characterized by a relatively high pH and high DOC concentrations. The Graviyka River's composition showed a strong seasonal pattern. High values of specific conductivity, associated with high values of DIC and Ca, were measured during winter, with a consistent drop in spring. Positive correlations were found between conductivity and DIC concentrations ($r^2 = 0.51$, $p < 0.001$, $n = 74$), and between DIC and Ca concentrations ($r^2 = 0.53$, $p < 0.001$, $n = 30$). Relatively high DOC concentrations

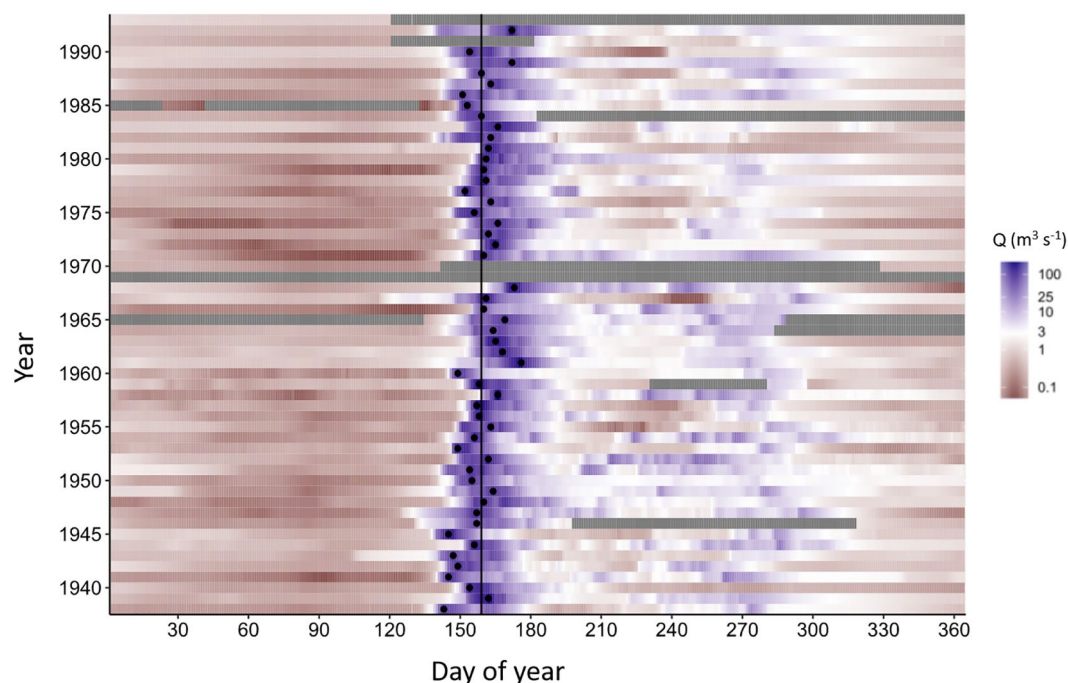


Figure 2. (a) Annual variation of discharge at the outlet of the Graviyka River from 1936 to 1992. Black dots indicate the freshet discharge peak. The black line is the average date for the freshet discharge peak.

were measured all year round ($\text{DOC} = 11.1 \pm 1.5 \text{ mg L}^{-1}$), with significantly lower concentrations recorded in winter ($9.9 \pm 1.0 \text{ mg L}^{-1}$), and higher concentrations during spring ($12.1 \pm 1.8 \text{ mg L}^{-1}$). The SUVA values showed a slight increase from winter to autumn, indicating a higher proportion of aromatic DOM in autumn. The highest SO_4 values were reported in autumn ($2.00 \pm 0.88 \text{ mg L}^{-1}$). Water isotopes also showed clear seasonal patterns (Figure S5). Winter and spring were characterized by depleted values, indicating the snow signature, whereas autumn showed the highest values. During summer, the lowest d-excesses were measured, reflecting highly evaporated sources (Streletskiy et al., 2015).

The ^{14}C values of DOC (Table 3) were highly depleted. Values of $F^{14}\text{C}$ of 0.963 ± 0.005 and 0.956 ± 0.005 (corresponding to $300 \pm 40 \text{ yr BP}$ and $355 \pm 40 \text{ yr BP}$, respectively) were measured on the July 2 and August 17, 2015. On August 2, 2016, a value of $F^{14}\text{C}$ of 0.873 ± 0.009 ($1120 \pm 80 \text{ yr BP}$) was measured.

3.3. High-Frequency *in situ* Data

3.3.1. Hydrochemical Annual Trends

The timelines of the meteorological, hydrological and water chemistry parameters (water discharge, conductivity, pH, turbidity, DOC and dissolved oxygen concentrations) acquired at the gauging station of the Graviyka River are presented in Figure S4. Figure 4 presents the annual dynamics of daily means of water

Table 2

Mean and Standard Deviation for pH, Conductivity, Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC) Concentrations, SUVA Index, and Major Element (Cl, SO_4 , Ca, and Mg) Concentrations in Grab Samples, for Each of the Periods Considered

Period	Conductivity ($\mu\text{S cm}^{-1}$)	pH	DIC (mg L^{-1})	DOC (mg L^{-1})	SUVA ($\text{L mgC}^{-1} \text{ m}^{-1}$)	SO_4 (mg L^{-1})	Ca (mg L^{-1})	Mg (mg L^{-1})
Winter	195.3 ± 48.4	7.3 ± 0.4	15.1 ± 6.4	9.90 ± 0.98	3.26 ± 0.35	1.56 ± 0.35	14.07 ± 4.56	3.89 ± 1.19
Spring	75.3 ± 24.9	6.8 ± 0.4	4.2 ± 2.6	12.10 ± 1.83	3.48 ± 0.36	1.31 ± 0.55	6.27 ± 1.76	1.85 ± 0.51
Summer	137.9 ± 37.0	7.7 ± 0.5	10.5 ± 4.5	11.46 ± 1.41	3.44 ± 0.38	1.27 ± 1.16	13.68 ± 2.57	4.07 ± 1.48
Autumn	135.5 ± 20.7	7.5 ± 0.7	11.5 ± 3.8	11.51 ± 1.23	3.53 ± 0.33	2.00 ± 0.88	9.67 ± 2.06	3.14 ± 1.21

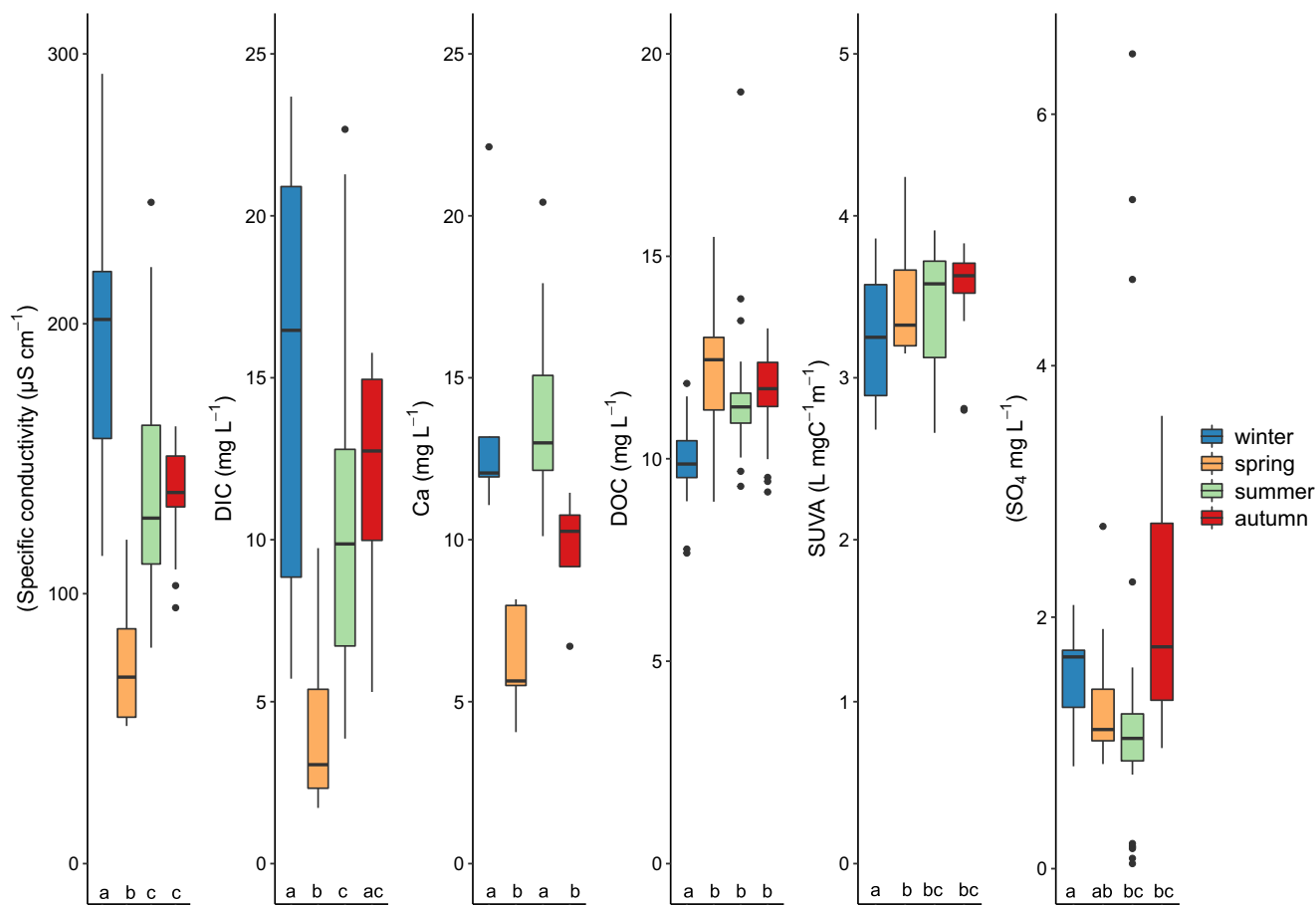


Figure 3. Ranges of several water characteristics (specific conductivity, dissolved inorganic carbon (DIC), Ca, dissolved organic carbon (DOC) concentrations, SUVA, and SO_4 concentrations) in grab samples for each sampling season. The black line is the median. The lower and upper levels of the box represent the 25% and 75% quartiles, respectively. The lower whisker is the smallest observation greater than or equal to the lower hinge $-1.5 * \text{IQR}$ (inter-quartile range), the upper whisker is the largest observation less than or equal to the upper hinge $+1.5 * \text{IQR}$. Letters represent significantly different groups (Kruskall-Wallis and Dunn's post hoc multiple tests [$p < 0.05$]).

discharge, dissolved oxygen, conductivity, pH, turbidity and DOC concentration. The physico-chemical composition of the Graviyka River water showed consistent patterns during observation period. The river presented a neutral to basic pH ($\text{pH} = 7.06 \pm 0.86$) throughout the year. A sharp decrease in pH values occurred during the spring freshet, while the highest pH values were observed during summer. Conductivity values varied widely over the year (from 37 to $298 \mu\text{S}\cdot\text{cm}^{-1}$). The highest values were measured at the end of the winter period (increasing from 100 to $250 \mu\text{S cm}^{-1}$ during winter). Conductivity values then sharply declined (up to fivefold) during the spring freshet. The values rose again during summer and autumn, with occasional drops during rainstorm floods. With very few exceptions, turbidity remained low throughout the year ($<10 \text{ FNU}$). The main peak almost coincided with the spring freshet peak. The Graviyka River waters were under-saturated in oxygen during winter. The values rose during summer and oscillated between 90% and full saturation during summer and autumn. The calculated DOC concentrations ranged from 8.0 to

Table 3
Sampling Date, Sample Codes, $\delta^{13}\text{C}$ -DOC and $F^{14}\text{C}$ of Graviyka River Samples Investigated for Radiocarbon Content

Sampling date	Sample ID GifA-	Sample ID ECHO-	$\delta^{13}\text{C}$ -DOC (‰)	$F^{14}\text{C}$	Age (conv cal BP)
02/07/2015	GifA16508	ECHO-1287	-28.4	0.963 ± 0.005	300 ± 40
17/08/2015	GifA16519	ECHO-1298	-28.9	0.956 ± 0.005	355 ± 40
02/08/2016	GifA17335	ECHO-1900	-29.0	0.870 ± 0.009	$1,120 \pm 80$

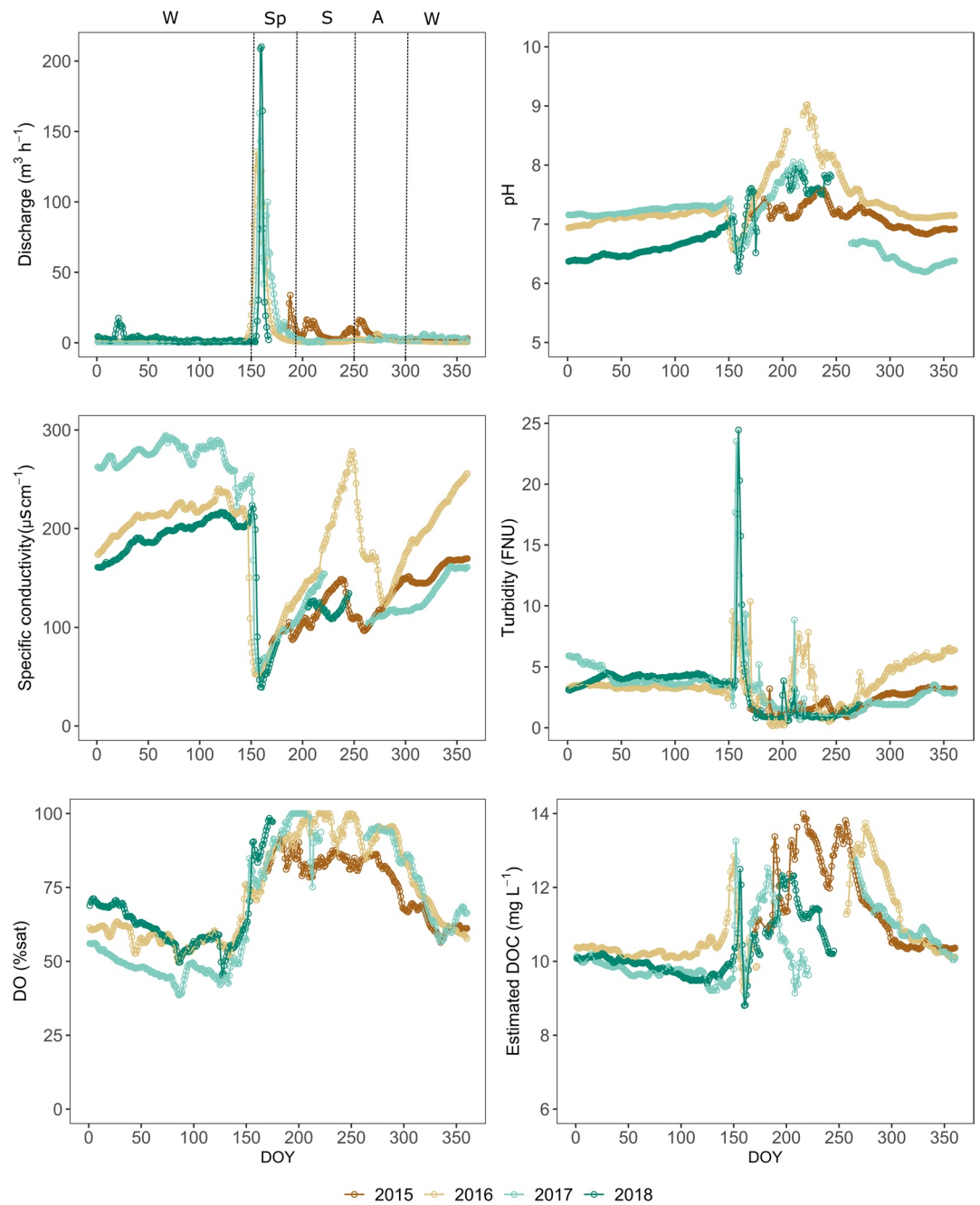


Figure 4. Evolution of daily means of water physico-chemical parameters of the Graviyka river water depending on day of year (DOY) for the studied period. The different periods are indicated by dotted lines. W=Winter, Sp = Spring, S=Summer, A = Autumn.

14.9 mg L⁻¹, with a mean annual average of 10.8 ± 1.0 mg L⁻¹ in 2016 and 10.3 ± 0.9 mg L⁻¹ in 2017. A sharp increase in DOC preceded the water level rise of the spring freshet. At the discharge peak, DOC concentrations dropped. During summer and autumn, DOC concentrations varied in relation to hydrological conditions: intense peaks were observed during autumn floods in 2015, while low values were measured during the dry summer of 2016.

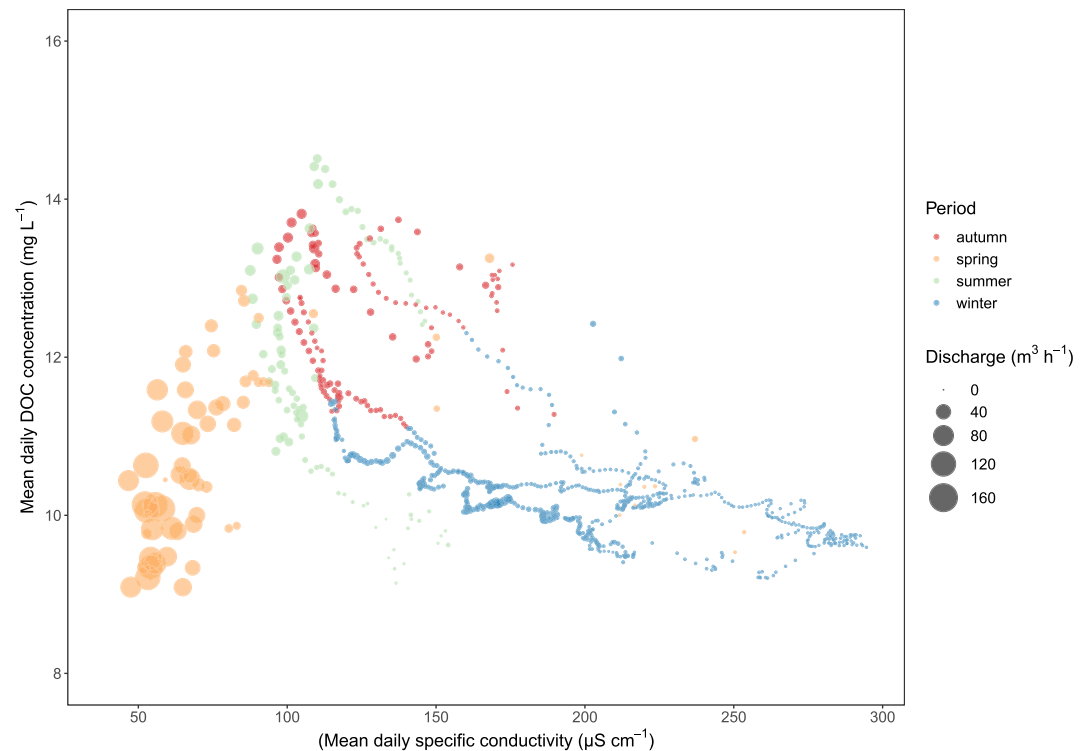


Figure 5. Evolution of daily dissolved organic carbon (DOC) concentrations depending on conductivity, for the different seasons considered, including the discharge values.

3.3.2. Seasonality of DOC Dynamics

The combined evolution of DOC concentrations and conductivity evidences the seasonality of water and organic carbon origin (Figure 5). During the spring freshet, the discharge peak induced a dilution of river water and both DOC concentration and conductivity decreased sharply. Dilution was much greater for conductivity compared to DOC. During the summer and autumn high-discharge periods, the highest DOC concentrations were measured and were associated with relatively low conductivity values. During winter, the lowest DOC concentrations but the highest conductivity values characterized the baseflow conditions in the Graviyka River.

The contrasted dynamics of DOC during high flows in spring, summer and autumn are highlighted in the normalized C-Q plots in Figure 6. In the three years studied, spring floods showed a consistent pattern in two steps (Figure 6a): an increase in DOC concentration before the Q peak, followed by a decrease of DOC concentration due to dilution by snow-melt. The C-Q is a clockwise hysteresis, and dilution is the dominant pathway (overall $\beta = [-0.055; 0.005]$, $FI = [-0.24; -2.4]$). During storm events in summer (Figure 6b), a quick increase in DOC concentration was observed and the DOC concentration peak was simultaneous with the Q peak. Subsequently, DOC concentrations decreased slower than discharge. The hysteresis patterns were anticlockwise, with positive values of β [0.015; 0.05] and FI [0.95; 0.99], typical of subsurface flows with no source limitation. Autumn floods (Figure 6c), ending with the freezing of the watershed showed specific patterns, with DOC concentration rising and falling in line with discharge, inducing a quasi-linear form to the hysteresis loop ($\beta = [0.04; 0.11]$, and $FI = [0.43; 1.05]$).

3.4. DOC Exports

The annual DOC exports were calculated for 2016 and 2017. Consistent values of 1,770 and 1,690 tons of carbon were exported at the outlet of the Graviyka River. This corresponded to specific fluxes of 5.5 and $5.2 \text{ g m}^2 \text{ yr}^{-1}$. Most of the DOC export, up to 85%, occurred during the spring freshet, while the summer and autumn periods accounted up to 9% and 8% respectively. In 2015, the DOC flux was 1,070 t for the period of

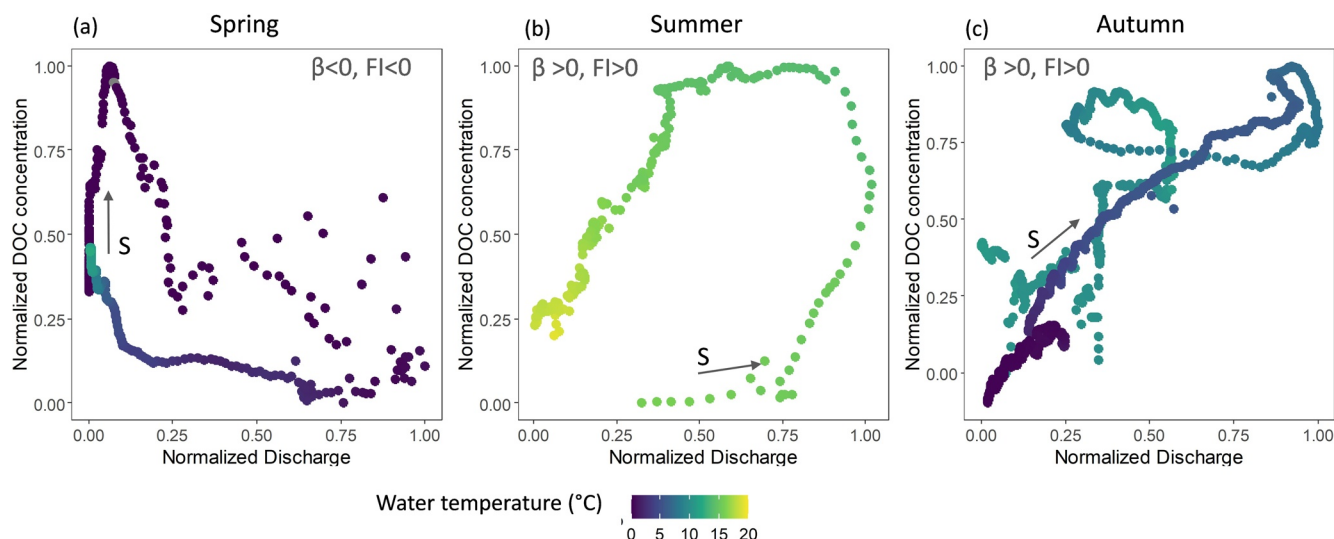


Figure 6. Hysteresis plots of normalized dissolved organic carbon (DOC) with normalized discharge during the Spring freshet (a), Summer flood (b) and Autumn flood (c). The color scale is the water temperature. S and the arrow represent the starting point of the flood.

record, starting after the spring freshet. Using the average annual export, summer and autumn flood would represent 30% and 23% of the annual organic carbon export, respectively for this year.

Discharge was the main driver of DOC fluxes. The strong linear relationship between hourly water and DOC fluxes was seasonal (Table 4). Autumn floods showed the highest slope. These events, although minor in terms of discharge, proved very intense in terms of organic carbon export.

4. Discussion

4.1. High-Frequency Hydrochemical Surveys in High-Latitudes Watersheds

This study has reported the results of a long-term (three years), year-round, high-frequency (1h) hydro-chemical monitoring in a subarctic catchment north of the Arctic Circle. In northern watersheds, stream and river sampling strategies vary from monthly to weekly sampling, depending on the season, with a higher sampling frequency during the spring freshet (Carey, 2003; Chupakov et al., 2020; Finlay et al., 2006). In northern Eurasia, recent studies have reported efforts for year-round high-frequency sampling, ranging from weekly to daily sampling for the Severnaya Dvina River (Chupakov et al., 2020), as well as a systematic four-day sampling for the Lena River (Juhls et al., 2020). These studies have shown that higher frequency surveys improve annual flux calculations, for instance by revealing seasonal relationships between discharge and DOC concentrations (Juhls et al., 2020), or by improving discharge measurements during low flow periods (Chupakov et al., 2020). In addition to improving the quantification of annual fluxes, high-frequency surveys are highly relevant in the context of permafrost-affected watershed, as it can track both immediate and delayed impacts on stream hydrology and biogeochemistry of permafrost

Table 4
DOC Exports (F_{DOC}) for the Different Periods Considered and Models of F_{DOC} Versus Water Fluxes (Q) for the Different Periods

	F_{DOC} (kg h ⁻¹)			F_{DOC} (kg h ⁻¹) versus Q (m ³ h ⁻¹)			
	Mean	Min	Max	a	b	r ²	p
Spring	1,900 ± 1,795	17	9,401	0.0098	67.5	0.98	<2.10 ⁻¹⁶
Summer	197 ± 254	2.43	1,724	0.0127	-5.95	0.99	<2.10 ⁻¹⁶
Autumn	192 ± 158	42	795	0.0134	-9.53	0.99	<2.10 ⁻¹⁶
Winter	59 ± 59	4	657	0.0106	-0.08	0.99	<2.10 ⁻¹⁶

degradation and subsequent catchment disturbance (Beel et al., 2021; Bowden et al., 2008; Lafrenière & Lamoureux, 2019). At our site, the systematic high-frequency sensing revealed seasonality in water and DOC origin. The year-round survey, including during winter baseflow revealed sustained high DOC concentrations. The *in situ* high-resolution sensing could capture flood events (Figure 6), and allowed the use of a normalized methodology to track the origin of water and carbon (Shogren et al., 2021). As a result, it revealed the specific behavior of northern watersheds during spring and autumn floods, in relation to snowmelt and the refreezing of the watershed.

4.2. Climatic Control on Hydrology and Recent Evolution in the Graviyka Watershed

In the Igarka region, the weather has been extremely unstable over the past decade. Within a few months, both the highest daily temperature (+34.0°C, July 22, 2013) and the lowest monthly temperature (−44.7°C, January 2014) were recorded, along with the highest annual precipitation (717 mm in 2018). For the first time on record, June was the warmest month of the year in 2011, and this reoccurred in 2018. These facts illustrate a climatic system in distress and out of balance, and are most likely related to the recent climate warming (Diffenbaugh et al., 2017).

In Igarka, no trend in precipitation has appeared since 1936. In the Arctic, precipitation observations are deemed uncertain and a global increasing trend is considered with low confidence (Meredith et al., 2019). The Graviyka River annual runoff did not show any trend. This contrasted with the discharge increase reported for large Siberian rivers (Makarieva et al., 2019; Tananaev et al., 2016), and the projections for the area (Bring et al., 2017). This stresses the need for regional and lower scale studies to assess climate change and permafrost degradation effect on northern catchments hydrology (Laudon et al., 2017). The study period covered a highly peculiar climatic context, making it difficult to infer any conclusions on contemporary links between annual precipitation and discharge. In addition to this inter-annual variability, permafrost degradation observed in the 1970 and 1980s (Streletskiy et al., 2015) potentially alters the links between precipitations and discharge in the Graviyka catchment. First, the deepening of the seasonally thawed layer increases water retention capacity, especially in organic soils. In 2017, in spite of extremely high precipitations, over 700 mm, water runoff was only 0.158 km³, close to the historical average. Intense precipitations might have replenished storage compartments that had been exhausted by the 2016 drought. Increased ground-water flow for a similar total discharge has been reported in other subarctic watersheds (Lapp et al., 2017). The ultimate impact of permafrost degradation on outlet discharge is related to water connectivity in the watershed (Lafrenière & Lamoureux, 2019). Permafrost degradation (ground ice thaw and related cryogenic processes) promotes thermokarst pond inception and development. These small ponds evolve with time into larger thermokarst lakes or wetlands, depending on their initial pond position within the catchment, that is, close to the river valley or at the water divide. They can therefore constitute a transitory buffer for water circulation in the watershed, and explain the lack of response of discharge to changes in precipitations.

4.3. Seasonality of DOC Exports in the Graviyka Watershed

At the outlet of the Graviyka catchment, DOC concentrations varied in a narrow range, exhibiting a nearly chemostatic behavior (Godsey et al., 2009; Koenig et al., 2017). Despite this relative stability, DOC origin and DOC export were highly seasonal. The spring freshet represented from 76% to 80% of the annual DOC export. This is typical of northern catchments, where the spring freshet largely dominates organic carbon export (Amon et al., 2012; Laudon et al., 2004, 2011; Olefeldt et al., 2013; Prokushkin et al., 2011). Just before snow melt, an increase of DOC concentration indicated the contribution of water flowing through shallow organic-rich layers from forest soils or some thermokarst ponds and lakes from the watershed. This later origin was suggested by punctual negative *d*-excess values measured during early spring freshet (Streletskiy et al., 2015), reflecting inputs from thermokarst lakes or other evaporated sources. But snowmelt was of course by far the dominant water source in the Graviyka River throughout the spring freshet, as evidenced by the overall dilution of all major elements (conductivity DIC, Ca) at the flood peak. The DOC concentration decrease was not as drastic, suggesting an important storage of DOC in shallow organic layer, only partially diluted by snowmelt. Summer and autumn floods accounted for up to 9% and 8% respectively of the annual DOC export. Summer floods hysteresis, with a positive flushing index, and anticlockwise

hysteresis, were typical of subsurface flows from organic-rich soils (no limitation by DOC source) (Godsey et al., 2019; Shogren et al., 2021; Vaughan et al., 2017). This is close to the behavior described for tundra watersheds in Alaska (Shogren et al., 2021) and may represent peatland contribution to the Graviyka river. Autumn floods, coinciding with re-freezing of the watershed, were characterized by synchronous DOC and discharge dynamics. Autumn was the most intense period in terms of DOC exports, as revealed by the highest $F_{\text{DOC}} = f(Q)$ relationship (Table 4). This appeared as a specific feature for permafrost affected watershed. This role of watershed freezing on riverine DOC has been highlighted for the Tibetan Plateau (Song et al., 2019). The relative contributions of summer and autumn floods to annual runoff depend on the timing of precipitations, and the rain/snow ratio. This ratio is expected to increase with the potential evolution of the precipitation regime and an increase in the rain/snow ratio (Beel et al., 2021; Makarieva et al., 2019). During winter, the conductivity of the Graviyka River water rised, with an important contribution of DIC. This suggested the input of water draining supra- and intra-permafrost groundwater. Part of the Yenisei catchment includes carbonated rocks (Beeskow & Rachold, 2003), and high winter DIC concentrations have been recorded in the Nizhnyaya Tunguska River, a contributor to the Yenisei, whose watershed is dominated by carbonate rocks in its southernmost portion (Prokushkin et al., 2011). The Graviyka catchment develops over silty fluvial-glacial sediments (Rodionov et al., 2007). The existence of winter water pathways, partially related to permafrost degradation in recent decades has already been revealed before in the area (Streletskiy et al., 2015). Interestingly, this water sustains relatively high DOC concentrations (winter mean DOC concentration of $9.9 \pm 0.9 \text{ mg L}^{-1}$). This is higher than what has been reported in the Yukon River Basin during winter (O'Donnell et al., 2012), and in the Central Siberian Plateau (Prokushkin et al., 2011), but in the lower end of values reported for western Siberian rivers (Pokrovsky et al., 2015). This may indicate that supra-permafrost and sub-permafrost water drains organic-rich soil layers during winter in the Graviyka catchment.

4.4. Leading Role of Peatlands in DOC Exports

The annual DOC fluxes estimated in this study, 5.5 and 5.2 $\text{g m}^2 \text{ yr}^{-1}$, are in the range of the TOC (total organic carbon) exports recorded in northern latitude catchments of various sizes. It was not possible to estimate TOC export in our study, but it is plausible that the particulate organic carbon fluxes were low compared to DOC ones, since turbidity values remained low all year round (Figure S3). Moreover, in the context of a significant contribution of peatlands, it has been largely shown that DOC dominates annual TOC fluxes (Dinsmore et al., 2010; Laudon et al., 2011; Rosset et al., 2019). In northern Sweden, Laudon et al. (2004) reported fluxes from 3.5 to 7.6 $\text{g m}^2 \text{ yr}^{-1}$ and Giesler et al. (2014) and Olefeldt et al. (2013) reported fluxes from 0.8 to 2.3 $\text{g m}^2 \text{ yr}^{-1}$ for catchments from 0.3 to 61 km^2 . In Alaska, small catchments of a few km^2 export from 4.34 to 8.34 $\text{g m}^2 \text{ yr}^{-1}$ (Petroni et al., 2006), when in Siberia, larger subcatchments of the Yenisei export from 4.3 to 7.3 $\text{g m}^2 \text{ yr}^{-1}$ (Prokushkin et al., 2011). DOC specific fluxes relate not to catchment size but rather to the wetland proportion in the watershed (Olefeldt et al., 2013). In the Graviyka catchment, peatlands cover 27% of the watershed surface (Streletskiy et al., 2015), and show the highest carbon densities (Rodionov et al., 2007). A typical pattern for large Arctic rivers is a DOC peak almost synchronous with the discharge peak (Amon et al., 2012; Juhls et al., 2020). Here, we have reported a different dynamic: A DOC peak preceding the discharge peak, an almost twofold dilution of DOC concentration at the discharge maximum, and an overall nearly chemostatic behavior of DOC. This pattern is typical of peatland-dominated watersheds (Finlay et al., 2006; Laudon et al., 2004), sustaining a high DOC concentrations throughout the year, diluted during snowmelt. DOM aromaticity (as indicated by the SUVA index) increased in summer and autumn. In the Graviyka catchment, potential contributors to summer and autumn floods were large degraded permafrost peatland complexes, which produce highly aromatic DOM (Gandois et al., 2019). The depleted ^{14}C values of DOM measured during summer low flows, suggest that previously frozen permafrost layers including permafrost peatlands may export old carbon (Gandois et al., 2019; Streletskiy et al., 2015) and that this DOM is not consumed before reaching the main stream. This contrasts with observation from the context of Yedoma, where only modern carbon has been detected in the Kolyma River and its tributaries, old carbon originating from degrading permafrost being preferentially consumed upstream (Mann et al., 2015; Rogers et al., 2021). In large Arctic rivers, mostly modern carbon is exported in the form of DOC, with the exception of a few measurements during summer and autumn (Amon et al., 2012; Estop-Aragonés et al., 2020). But increase of the export of old carbon has recently been reported in the MacKenzie River

Basin in the context of warm years, this dynamic could be amplified in the future (Schwab et al., 2020). This is in line with our results suggesting a higher contribution of permafrost carbon during the 2016 drought.

4.5. Potential Implication of Permafrost Degradation for DOC Export

The future evolution of fluvial organic carbon export from northern watersheds is crucial for the global carbon budget. The observed seasonality of DOC export and changes in hydrological cycles allow us to formulate hypotheses regarding the evolution of DOC export in the coming years and decades. In the Graviyka catchment, no significant discharge increase has been observed since 1936. With the hypothesis of a stable discharge, and given that DOC fluxes are mainly driven by discharge, they should not evolve greatly. In the Graviyka catchment, palsa degradation and forest expansion have been reported since the mid-80s (Streletskiy et al., 2015). Forest expansion could lead to an increase of DOC concentration in surface waters (Škerlep et al., 2020). In addition, the degradation of permafrost peatlands has been shown to potentially increase DOC export to surface water in western Siberia (Frey & Smith, 2005). In Scandinavia, permafrost peatland degradation and transition from intact palsa to flow through fens has been shown to increase DOC specific fluxes (Olefeldt & Roulet, 2012). Following these hypotheses, it can be surmised that the extensive palsa degradation observed in the watershed may lead to an increase in DOC exports in the future. On the other hand, the increase in the active layer thickness across the catchment, largely underlain by mineral soils, will increase adsorption to mineral phases and lead to a decrease in DOC export to surface waters. Such competing effects occurring at the same time in northern watersheds may explain the lack of significant evolution of DOC export reported for Swedish catchments (Giesler et al., 2014), and for the Severnaya Dvina River (Chupakov et al., 2020).

5. Conclusions

This study combined 3 years of high-frequency hydrochemistry data and historical climatic and hydrological data in a northern catchment underlain by discontinuous permafrost. The long-term increase in mean annual temperature and unstable climatic observations evidence recent climate evolution in the region. The year-round high-frequency *in situ* sensing of a proxy of DOC concentration (fDOM) revealed the key features of fluvial organic carbon export in this watershed. Relatively high DOC concentrations were sustained throughout year, including during winter base-flow, leading to specific fluxes of 5.2–5.5 g.m⁻² yr⁻¹. The Spring freshet dominated the annual export, but high flow events during summer and autumn were particularly effective for DOC export. High frequency sensing proved essential in capturing these high flow events, and characterizing export processes, that are specific of each hydrological conditions. In autumn, the freezing of the watershed and the flushing of organic-rich layers and lakes led to intense DOC export. The degrading peatlands of the watersheds appeared to be potentially important contributors at the catchment scale to DOC export, including from previously frozen layers. Although the climate is clearly evolving in the region, the future of organic fluvial export is uncertain, in relation to complex processes at the watershed scale. This article highlighted the temporal and spatial complexity of terrestrial-aquatic linkages in the Arctic and calls for more long-term monitoring of Northern watersheds.

Data Availability Statement

Data are available at Gandois, Laure (2021): Hourly record of water level, temperature, pH, specific conductivity, turbidity, fDOM and dissolved oxygen at the outlet of the Graviyka River (Siberia), from 2015 to 2018. PANGAEA, <https://doi.pangaea.de/10.1594/PANGAEA.927871>.

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