



Photodegraded dissolved organic matter from peak freshet river discharge as a substrate for bacterial production in a lake-rich great Arctic delta

Jolie A.L. Gareis and Lance F.W. Lesack

Abstract: Lake-rich Arctic river deltas are recharged with terrigenous dissolved organic matter (DOM) during the yearly peak water period corresponding with the solstice (24 h day⁻¹ solar irradiance). Bacteria-free DOM collected during peak Mackenzie River discharge was exposed to sunlight for up to 14 days in June 2010. As solar exposure increased, carbon and lignin concentrations declined (10% and 42%, respectively, after 14 days), as did DOM absorptivity (62% after 14 days), aromaticity, and molecular weight. Photochemical changes were on par with those normally observed in Mackenzie Delta lakes over the entire open-water season. When irradiated freshet DOM was provided as a substrate, no significant differences were observed in community-level metabolism among five bacterial communities from representative delta habitats. However, bacterial abundance was significantly greater when nonirradiated (0 day) rather than irradiated DOM (7 or 14 days) was provided, while cell-specific metabolic measures revealed that per-cell bacterial production and growth efficiency were significantly greater when communities were provided irradiated substrate. This complex response to rapid DOM photodegradation may result from the production of inhibitory reactive oxygen species (ROS), along with shifts in bacterial community composition to species that are better able to tolerate ROS, or metabolize the labile photodegraded DOM.

Key words: circumpolar river delta, photodegradation, dissolved organic matter, bacterial metabolism, Mackenzie River.

Résumé : Les deltas arctiques riches en lacs sont rechargés en matière organique dissoute (MOD) terrigène pendant la période annuelle de crue maximale correspondant au solstice (irradiance solaire 24 h jour⁻¹). De la MOD sans bactéries collectée durant la pointe de crue du fleuve Mackenzie a été exposée à la lumière du soleil pendant 14 jours en juin 2010. À mesure que l'exposition solaire se prolongeait, les concentrations de carbone et lignine diminuaient (10 % et 42 % respectivement, après 14 jours), tout comme le pouvoir d'absorption de la MOD (62 % après 14 jours), son aromaticité et son poids moléculaire. Les changements photochimiques correspondaient à ceux normalement observés dans les lacs du delta du Mackenzie sur l'ensemble de la saison des eaux libres. Lorsque de la MOD de crue irradiée fut utilisée comme substrat, aucune différence significative n'a été observée quant au métabolisme au niveau de la communauté en comparant cinq communautés bactériennes issues d'habitats représentatifs du delta. Néanmoins, l'abondance de bactéries était considérablement plus grande lorsque de la

Received 7 December 2017. Accepted 8 March 2018.

J.A.L. Gareis. Department of Geography, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.
L.F.W. Lesack. Departments of Geography and Biological Sciences, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.
Corresponding author: Jolie Gareis (e-mail: jolieg@sfu.ca).
 This article is open access. This work is licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0). http://creativecommons.org/licenses/by/4.0/deed.en_GB.

MOD non irradiée (0 jour) a été fournie au lieu de la MOD irradiée (7 ou 14 jours), tandis que les mesures de l'activité métabolique spécifique aux cellules ont révélé que la production bactérienne par cellule et le rendement de croissance étaient considérablement plus élevés lorsque les communautés avaient accès au substrat irradié. Cette réaction complexe à la photodégradation rapide de la MOD pourrait découler de la production de dérivés réactifs de l'oxygène (DRO) inhibiteurs, ainsi que des glissements dans la composition des communautés bactériennes vers des espèces capables de mieux tolérer les DRO, ou de métaboliser la MOD photodégradée labile. [Traduit par la Rédaction]

Mots-clés : delta circumpolaire, photodégradation, matière organique dissoute, métabolisme bactérien, fleuve Mackenzie.

Introduction

The Mackenzie River Delta, located in northwest Canada where the Mackenzie River empties into the Beaufort Sea basin of the Arctic Ocean, is both lake-rich and ecologically diverse. High levels of productivity are sustained by the annual spring flood, when discharge in the north-flowing Mackenzie peaks due to melting snow in the large subarctic watershed, and water levels peak in the delta due to restricted flows as channels become clogged with fractured ice cover and rubble. As water levels exceed channel bank heights, sediment-, nutrient-, and organic-rich floodwater (Gareis and Lesack 2017) spreads out over the delta floodplain in a thin layer covering an average of 11 000 km² (Emmerton et al. 2007). The timing of the annual flood corresponds with the Arctic summer solstice, when solar exposure is continuous and there is high potential for dissolved organic matter (DOM) photodegradation. Direct sampling of floodwater is difficult, however, since unstable ice cover and moving debris in river channels means that the only safe method of accessing sampling sites is by helicopter. The spring freshet is therefore a relatively understudied part of the annual hydrograph, and at present Mackenzie River freshet DOM is poorly characterized, and its photoreactivity and suitability as a bacterial substrate are not well understood.

Dissolved organic matter is a heterogeneous pool of organic compounds that are present in all natural waters. Sources include both in situ production by phytoplankton, aquatic plants, and benthic algae (autochthonous DOM), and detrital sources from terrestrial plants and soils in the surrounding watershed (allochthonous DOM). Collectively, DOM represents a large source of potential energy for heterotrophic bacterioplankton communities (hereafter referred to as bacteria), although allochthonous DOM is generally more recalcitrant due to the structural complexity of terrestrially-derived molecules and microbial preprocessing in soils during passage through watersheds. Once present in the water column and exposed to sunlight, however, allochthonous DOM can be photodegraded via the absorption of high-energy ultraviolet (UV) wavelengths (280–400 nm). Absorbed UV breaks down aromatic carbon rings, producing smaller, less aromatic DOM molecules (Bertilsson and Tranvik 2000; Osburn et al. 2001; Sulzberger and Durisch-Kaiser 2009) that have lower molecular weights and are more bioavailable for bacterial consumption and decomposition (Wetzel et al. 1995; Moran and Zepp 1997; Bertilsson and Tranvik 1998; Obernosterer and Benner 2004). Heterotrophic grazers subsequently consume bacteria, which shunts otherwise unavailable carbon, organic matter, and energy back into the aquatic food web via the microbial loop (Azam et al. 1983). This is a critical process that mobilizes otherwise unavailable DOM molecules in high-latitude aquatic environments (Cole 1999; Cory et al. 2014) via bacteria, contributing to overall food web production in Mackenzie Delta lakes (Spears and Lesack 2006; Tank et al. 2011), the Mackenzie River (Vallières et al. 2008), and

the nearshore Beaufort Sea (Garneau et al. 2008; Bell et al. 2016). Because DOM is an important component of carbon budgets in aquatic ecosystems, an understanding of how photodegradation alters DOM bioavailability is critical to understand carbon fluxes through the landscape. In contrast to the positive effects of increased substrate availability on bacterial metabolism, photodegradation also exerts indirect negative effects on aquatic bacteria through the production of free radicals and reactive oxygen species (ROS) (e.g., singlet oxygen, peroxides, and superoxides) (Scully et al. 1996). These by-products of the photodegradation process are short-lived, but nevertheless inhibit bacterial growth and production (Lund and Hongve 1994; Henle and Linn 1997; Anesio et al. 2005). To some extent, therefore, irradiation of DOM by sunlight simultaneously stimulates and inhibits heterotrophic bacterial production (BP) (Scully et al. 2003; Ruiz-Gonzalez et al. 2013), leading to complex interactions that can result in enhanced, negative, mixed, or no effect on bacterial community metabolism (Lonborg et al. 2016). In addition, the bacterial community composition may be altered either by exposure to ROS (Glaeser et al. 2010; Glaeser et al. 2014) or in response to the increased lability of the pool of DOM substrate (Judd et al. 2007; Piccini et al. 2009; Paul et al. 2012; Ward et al. 2017), giving rise to a species assemblage that is better suited to the ambient conditions.

Although prior work in Mackenzie River Delta lakes has shown an increase in DOM bioavailability (using proxy measurements of DOM bioavailability; Gareis 2007) and the production of high levels of ROS (hydrogen peroxide; Febria et al. 2006) even after short periods of exposure to ambient sunlight around the time of the summer solstice, the direct effects of photodegraded DOM substrate on the growth and metabolism of delta bacterial communities have not yet been directly examined. We therefore initiated a study in 2010 to assess the potential for DOM photodegradation on the Mackenzie Delta floodplain, and to evaluate the growth and metabolism of various bacterial communities when provided photodegraded DOM as a substrate. A large volume of Mackenzie River floodwater was incubated under ambient solar conditions for 0, 7, and 14 days, and then fed to five communities of bacteria from different delta habitats. Several growth parameters were monitored throughout 48 h bioassay periods to examine differences in bacterial metabolism resulting from changes in DOM lability, as well as any differential use of DOM among communities. We hypothesized that (1) the bioavailability of freshet DOM would continually increase throughout the irradiation period, (2) increased duration of solar exposure would support higher rates of bacterial growth and metabolism, and (3) the greatest increases in growth and metabolic rates would be found in bacterial communities from habitats that frequently receive subsidies of photodegraded DOM.

Methods

The ecology and hydrology of the Mackenzie Delta

The Mackenzie is the second largest delta in the circumpolar Arctic and contains more than 45 000 shallow floodplain lakes (Emmerton et al. 2007). The delta is fed by the Mackenzie River, one of the world's great circumpolar rivers that flows northward, draining a 1.8 million km² basin in northwest Canada before discharging to the Beaufort Sea (Fig. 1). Average annual Mackenzie discharge is 289 km³ a⁻¹ (1973–2015; HYDAT 2015), with an uneven flow distribution among seasons (Fig. 2). Winter is characterized by ice cover and low flows. Discharge and water levels increase rapidly at the start of the freshet, driven by melting of the basin snowpack which generates a flood wave that moves north towards still-frozen regions nearer the Arctic coastline. Water levels, already elevated by melting snow and ice, are further amplified when ice jams form in delta channels and block the downstream flow of water. The resulting rise in water levels can overtop levees and

Fig. 1. Map of sampling locations in the Mackenzie River Delta and Beaufort Sea coastal zone, western Canadian Arctic. The area enclosed by the purple square is enlarged in the insert, and shows sampling locations near the town of Inuvik (CON, connected, MAC, macrophyte, and TK, thermokarst lakes, RIV sampling site). The two Water Survey of Canada gauging stations referenced herein are located immediately upstream of the delta near the hamlet of Tsiigehtchic (Mackenzie at Arctic Red, station ID 10LC014) and near the RIV sampling site upstream of Inuvik (East Channel at Inuvik, station ID 10LC002).

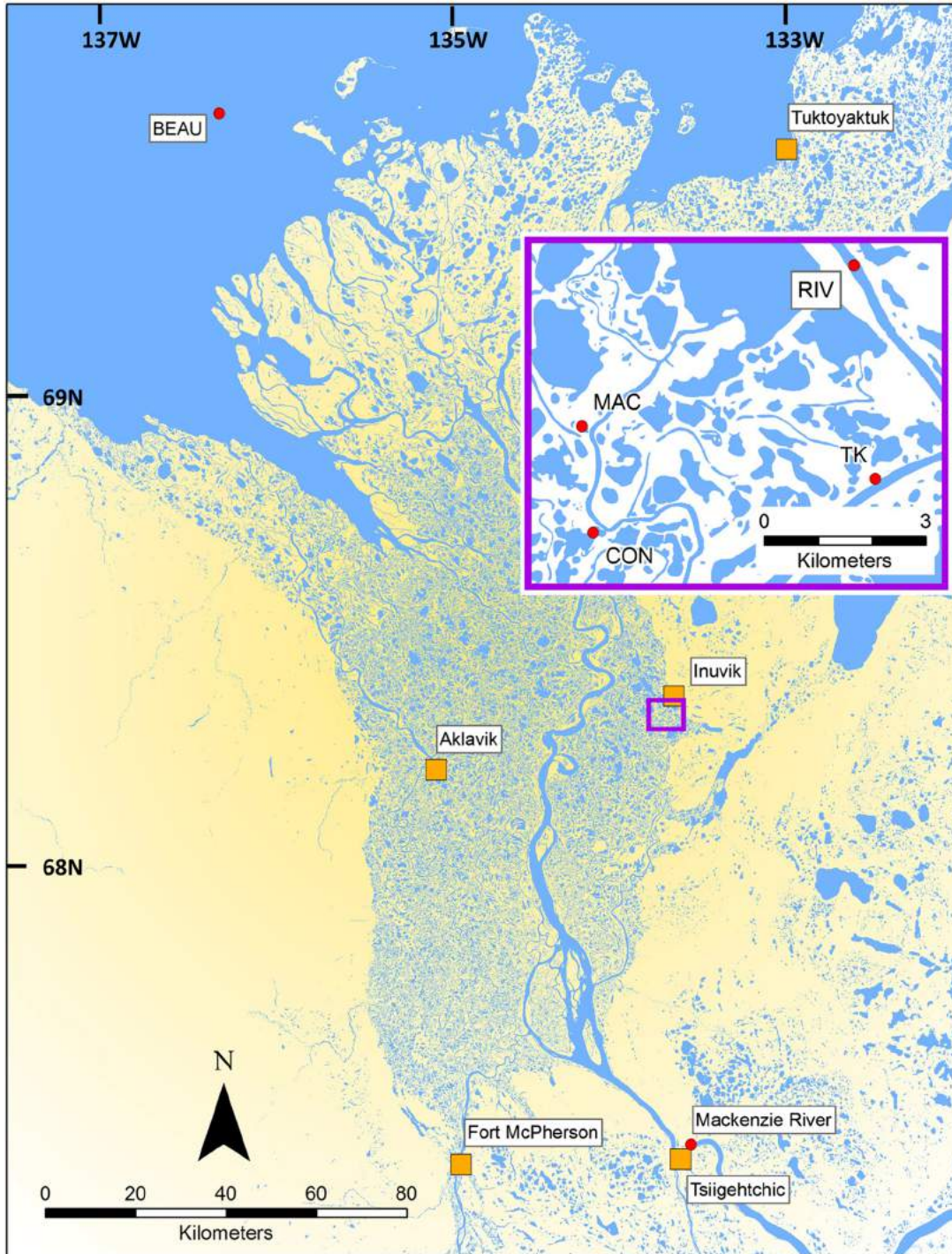


Table 1. Physical and flood frequency characteristics of three Mackenzie Delta lakes from which bacterial communities were isolated in June 2010.

	Lake number ^a	Surface area (ha)	Mean depth (m)	Spring sill height (m)	Summer sill height (m)	Mean connection time \pm SD (d yr ⁻¹) ^b	Connection time, 2010 (d) ^c	River water renewal coefficient, 2010 ^c	Macrophyte biomass (g m ⁻²) ^d	Thermokarst extent (%) ^e
CON	129	37.8	1.29	2.363	1.272	159.4 \pm 25.7	172	0.830	15.9	0
MAC	56	3.1	1.08	4.623	4.210	9.3 \pm 5.3	8	0.409	87.9	0
TK	520	0.2	2.23	4.913	4.587	6.5 \pm 4.7	6	0.111	2446	100

^aLake numbers that have been used to designate individual lakes in many prior studies of the Mackenzie River Delta.

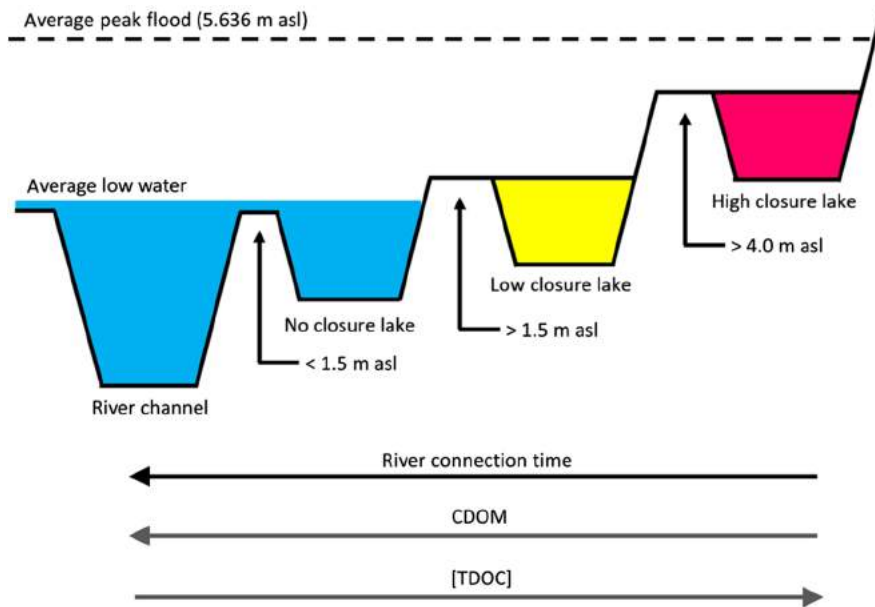
^bFrom [Lesack and Marsh \(2010\)](#).

^cDetermined following the methods of [Lesack and Marsh \(2010\)](#).

^dFrom [Squires et al. \(2002\)](#).

^eFrom [Tank et al. \(2009\)](#).

Fig. 3. Flood frequency gradient of lakes in the Mackenzie River Delta. Average river-to-lake connection time is determined by the elevation of an individual lake relative to the river channel (Lesack and Marsh 2010), while differences in connection times drive gradients in C quantity (e.g., total dissolved organic carbon (TDOC) concentrations) and quality (e.g., chromophoric dissolved organic matter (CDOM)) across the floodplain (Squires and Lesack 2003b).



Experimental design and rationale

The purpose of this experiment was to explore how bacterial communities from different Mackenzie Delta habitats respond to the availability of progressively photodegraded freshet DOM as a metabolic substrate. The experiment consisted of three parts. In the first, bacterial communities were isolated from five representative delta habitats that have widely differing DOM compositions. In the second, a single sample of floodwater, retrieved from the Mackenzie River on the day of peak flood, was irradiated under ambient conditions in Inuvik, NT (68.3607°N, 133.7230°W) for 0, 7, and 14 days, to simulate photodegradation that would occur during floodplain storage at the time of the annual peak flood. In the third, the photodegraded floodwater was mixed with bacterial communities in a total of 15 different experimental treatments (bacterial community \times length of solar exposure), and bacterial metabolism was assessed.

Step 1 – sampling and processing of bacterial communities

Bacterial use of DOM differs among delta habitats based on the dominant character of the local DOM pool (Tank 2009), and therefore, likely reflects variations in community composition. We collected bacteria from five habitats with divergent DOM compositions (Fig. 1) to assess the response of the different communities to progressively photodegraded freshet DOM substrate:

1. *Connected (CON) community*: CON lakes remain connected to delta channels throughout the open-water season (Table 1, Fig. 3). They are continually flushed with river water, which has high sediment loads and a DOM pool that is primarily terrigenous in origin (Tank et al. 2011). High sediment levels limit light penetration in CON lakes (Gareis et al. 2010),

which in turn limits in situ primary production (Squires et al. 2002). The CON bacterial community was collected from Lake 129.

2. *Macrophyte (MAC) community*: MAC lakes are perched at higher elevations relative to delta channels and therefore have lower rates of water renewal. The short period of river flooding during the spring freshet introduces a pulse of organic nutrients and sediment. When water levels fall after the freshet, sediment rapidly settles out of the water column and light penetration increases. This creates ideal conditions for abundant MAC growth, which may reach 350 g m^{-2} (dry weight; Squires et al. 2002; Table 1). MAC-derived DOM generally supports much higher levels of BP and C cycling than terrestrially-derived DOM (Tank et al. 2011). The MAC bacterial community was collected from Lake 56.
3. *Thermokarst (TK) community*: TK lakes are a subset of the high closure lake class that have been deepened by ground subsidence resulting from permafrost thawing and slumping along their lake beds (Table 1, Fig. 3). The DOM pool in TK lakes tends to increase throughout the open-water season due to leaching from thawed permafrost and evaporative concentration. Unaltered TK DOM is a poor bacterial substrate (Tank et al. 2011). The TK bacterial community was collected from Lake 520.
4. *RIV community*: DOM carried in Mackenzie River water passing through delta channels is strongly terrigenous in origin, with quantity driven by within-basin processes (i.e., rainfall events) throughout the open-water season. As river water passes through the delta, the DOM pool is modified to some degree by inputs of water that have been incubated (and therefore modified) on the delta floodplain or in delta lakes. The RIV bacterial community was collected from the East Channel of the Mackenzie Delta, upstream of the town of Inuvik.
5. *BEAU community*: Freshwater discharged from the Mackenzie Delta mixes with seawater in the Beaufort basin, altering the DOM composition and reducing C concentrations offshore (Emmerton et al. 2008; Vallières et al. 2008). The BEAU bacterial community was collected from the nearshore Beaufort shortly before ice out, and had a salinity of 0.95 ppt, suggesting that mixing with ocean water was restricted by ice cover and that the community largely originated in the Mackenzie River plume.

The CON, MAC, TK, and RIV communities were isolated four times during June 2010. Dip samples were collected from the mid-point of each lake or channel using 5 L high-density polyethylene containers that had been acid-cleaned and rinsed with ultrapure water. Delta lakes are shallow, well-mixed by wind, and do not stratify, so surface dip samples are representative of the average bacterial community. Samples were transported to the Inuvik Research Centre in cool ($4 \text{ }^{\circ}\text{C}$), dark conditions, where they were processed within 3 h of collection. The BEAU community was isolated from a single water sample taken from the nearshore Beaufort Sea (Fig. 1). Due to the logistical difficulties of accessing this sampling site once the ice cover began to thaw, a single 20 L sample was taken on 30 May 2010 using an integrated sampler deployed through an augered hole.

Several 60 mL aliquots were filtered through precombusted (16 h at $450 \text{ }^{\circ}\text{C}$) GF/C filters ($0.7 \text{ }\mu\text{m}$ nominal pore size) for analysis of dissolved nitrogen (total, nitrate, and ammonium) and phosphorus (total and dissolved inorganic). Another 60 mL subsample was filtered through a $0.2 \text{ }\mu\text{m}$ polyethersulfone filter (GSPW, Millipore Corporation) for analysis of dissolved organic carbon (DOC) concentration and DOM absorbency. The remaining sample water was then filtered using Whatman GF/D filters ($2.7 \text{ }\mu\text{m}$ nominal pore size) to remove grazers and isolate the bacterial community (Roland and Cole 1999; Tank 2009). Triplicate samples were preserved with glutaraldehyde (final concentration 2.5%) for counts of in situ BA. Bacterial community isolates were then stored overnight at $4 \text{ }^{\circ}\text{C}$ in the dark. Four hours before bioassays were scheduled to begin, isolates were moved into dark cupboards to slowly warm to room temperature.

Step 2 – freshet DOM photodegradation incubation

A 60 L water sample was taken from the Mackenzie River upstream of the delta on the day of peak flood (19 May 2010). Water was collected from the float struts of a helicopter that landed mid-channel, and was stored in dark, cool (4 °C) conditions for 3 h before processing at the Inuvik Research Centre in Inuvik, NT, Canada, where it was sequentially filtered through several capsule filters with progressively smaller pore sizes to remove particulates. The final filter was a sterile 0.2 µm in-line capsule filter (Pall Life Sciences) that removed bacteria. The DOM filtrate was then stored in cool (4 °C), dark conditions until the incubation began.

On 15 June 2010, 15 L of DOM filtrate was subsampled and set aside as the 0 day photodegradation treatment (unaltered freshet DOM that was not irradiated). The remaining DOM filtrate was divided between two clear, shallow polyethylene (PET) incubator trays on the roof of the Inuvik Research Centre to simulate solar exposure during floodplain storage. The flat roof was covered with a layer of black shingles, which prevented any reflection of sunlight back into the incubators. Each incubator was filled with 15 L of DOM filtrate (~15 cm in depth), covered with a piece of PET sheeting that was secured using bungee cords, and placed in unobstructed sunlight. Incubator covers permitted the transmission of 87% of incident visible light from 400 to 700 nm, and 84% of incident UV radiation from 280 to 400 nm (Gareis 2007). The incubators were checked daily to ensure that the covers remained transparent and in good condition; they were replaced as needed (i.e., if dust had accumulated on the surface). The incubators were continually irradiated under ambient light and temperature conditions, with one incubator removed after 7 days and the second after 14 days.

Two black-and-white pyranometers (Eppley model 8–48) were located near the incubators in unobstructed sunlight. The pyranometers measured global radiation ($W m^{-2}$) from 280 to 2800 nm every 5 s, with average values recorded at 15 min intervals. The aperture of one pyranometer was completely covered by a disk of Acrylite® OP-2 plastic, which removed over 99% of the incident UV radiation (Gareis 2007) and therefore gave measurements of UV-excluded radiation. UV levels were determined by difference (global – UV-excluded radiation).

At the end of each incubation, the irradiated DOM filtrate was immediately refiltered through 0.2 µm polyethersulfone filters (GSWP, Millipore Corporation) and subsampled for DOC, DOM, and lignin analyses. The balance of the DOM filtrate was then mixed with the five bacterial communities to create the treatments for the bacteria-DOM bioassay, which began no more than 2 h after each incubation ended.

Step 3 – bacteria-DOM bioassays

A series of three bioassays were conducted during June 2010 to assess the growth and metabolism of five bacterial communities (BEAU, RIV, CON, MAC, and TK) when provided progressively photodegraded freshet DOM (0, 7, and 14 days) as a substrate, giving a total of 15 experimental treatments (bacterial community × length of solar exposure).

During each bioassay, the five treatments were run in duplicate by combining 1.2 L of bacterial isolate with 2.8 L of irradiated DOM (a 30:70 ratio), then splitting the water between two 1 L amber glass bottles and two 1 L cubitainers. A replicate consisted of one bottle and one cubitainer which were sealed using tubing and stoppers configured to make a sampling port (as in Tank 2009). This allowed repeated subsampling of each replicate without introducing air to the microcosm. Replicates were incubated in the dark at ambient lab temperatures (~23 °C) by submerging bottles and cubitainers to the neck in a water bath.

Samples to assess bacterial growth and metabolism were taken at the beginning of each bioassay, and again after 24 and 48 h. Samples for BA were taken in triplicate, and immediately preserved using glutaraldehyde added to a final concentration of 2.5%. Triplicate

bacterial respiration (BR) samples were taken in stoppered glass bottles, and measured as the decrease in dissolved oxygen (DO) from the previous sampling occasion. Samples for BP were taken in one 20 mL vial, which was immediately subdivided and assessed for BP. Samples were also taken for DOC, dissolved nitrogen (total, nitrate, and ammonium), and dissolved phosphorus (total and dissolved inorganic) analyses at the end of each bioassay.

Laboratory analyses

Dissolved organic carbon samples were measured as nonpurgeable organic carbon on a Shimadzu TOC-Vcsh analyser (Shimadzu Corporation). Samples were sparged for 5 min with 20 mmol L⁻¹ HCl (final concentration) before analysis using the high temperature catalytic oxidation method.

Dissolved organic matter absorbance was measured at 1 nm intervals from 250 to 700 nm relative to an ultrapure water blank on a Genesys 5 UV/VIS scanning spectrophotometer (Milton Roy). Napierian absorption coefficients (a_λ , m⁻¹) were calculated for each wavelength.

$$a_\lambda(\text{m}^{-1}) = A_\lambda \times 2.303/l$$

where A_λ is the raw absorbance measurement at a given wavelength (λ) and l is the cuvette pathlength in m (Whitehead et al. 2000). Absorption coefficients at 350 nm (a_{350}) are reported herein, with higher values indicating relatively higher levels of fresh terrestrial DOM. Specific UV absorbance at 254 nm (SUVA₂₅₄; L mg⁻¹ m⁻¹) was calculated using decadal measurements of absorption and is reported as a measure of DOM aromaticity, with greater values indicating higher aromaticity and less degraded DOM (Weishaar et al. 2003).

$$\text{SUVA}_{254} = A_{254}(\text{m}^{-1}) / \text{DOC} (\text{mg L}^{-1})$$

The ratio of spectral slope coefficients (S_R) from two regions of the log-transformed absorption spectra was calculated ($S_R = 275\text{--}295 \text{ nm slope} : 350\text{--}400 \text{ nm slope}$), and used to characterize the source, molecular weight, and diagenetic state of the DOM pool (Helms et al. 2008).

Lignin was measured following the methods of Louchouart et al. (2000). Between 750 and 1000 mL of 0.2 μm filtered sample water was acidified below pH 3 with H₃PO₄ and then extracted onto a column of C₁₈ Bondesil resin (Agilent Technologies). Columns were eluted using basic methanol, and extracts were evaporated to dryness at 40 °C under constant vacuum in an AES 2000 Speedvac (Savant Instruments). Dried samples were resuspended in 2 mL of 2 N NaOH and transferred to Teflon-lined acid digestion vessels (Parr Instruments). A further 11 mL of 2N NaOH was added to the sample, along with ~500 mg cupric oxide and ~50 mg ferrous ammonium sulphate, before samples were hydrolysed at 150 °C for 3 h. Trans-cinnamic acid was added as a recovery standard, and the products of the lignin oxidation were quantified using a five-point calibration curve of eight lignin phenol standards (Hernes and Benner 2003). Phenols were separated using a Varian 431-GC gas chromatograph, followed by phenol detection using a Varian 220-MS ion-trap mass spectrometer operated in the electron ionization (EI) mode using MS-MS (tandem mass spectrometer). The measured phenols included three vanillyl phenols (VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; collectively called V), three syringyl phenols (SAL, syringaldehyde, SON, acetosyringone; SAD, syringic acid; collectively called S), and two cinnamyl phenols (CAD, *p*-coumaric acid; FAD, ferulic acid; collectively called C). Total lignin mass was taken to be the sum of all eight phenols ($\Sigma_8 = V + S + C$). Lignin concentrations were standardized to the total carbon mass of the sample.

$$\Lambda_8[\text{mg} (100 \text{ mg OC}^{-1})] = 100 * [\Sigma_8(\text{mg L}^{-1}) / \text{DOC} (\text{mg L}^{-1})]$$

Phenol ratios were calculated as the ratio of total syringyl to total vanillyl phenols (*S:V*), and total cinnamyl to total vanillyl phenols (*C:V*). When considered together, *S:V* and *C:V* ratios indicate plant tissue origin (Hedges and Mann 1979; Goñi et al. 1998), while the state of oxidative degradation is indicated by the ratio of acid to aldehyde phenols in both the vanillyl [(Ad/Al)_v] and syringyl [(Ad/Al)_s] groups (Jex et al. 2014).

Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) samples were analysed via acid photo-oxidation following the methods of Stainton et al. (1977). Nitrate samples were analysed using flow injection colorimetric spectrophotometry (Anderson 1979), while ammonium samples were analysed using orthophthaldialdehyde fluorometry (Holmes et al. 1999). Dissolved inorganic nitrogen (DIN) was calculated as the sum of the ammonium and nitrate fractions, while dissolved organic nitrogen (DON) was calculated by difference (DON = TDN – DIN). Samples were analysed for dissolved inorganic phosphorus (DIP) using molybdate blue spectrophotometry (Strickland and Parsons 1972), and the dissolved organic phosphorus (DOP) fraction was found by difference (DOP = TDP – DIP). All nutrient quality ratios (DOC:DON, DON:DOP, and DIN:DIP) were calculated using molar concentrations.

Preserved samples for BA analysis were stored in the dark at 4 °C until counting, within 6 months of collection. To ensure even dispersion of bacterial cells during filtering, TWEEN was added and the sample was sonicated following the methods of Yoon and Rosson (1990). Samples were stained with 4',6-diamidino-2-phenylindole (DAPI) at a concentration of 10 mg L⁻¹, filtered onto 0.2 µm black polycarbonate filters (GE Osmonics), and counted at 1000× magnification using a Zeiss Axioplan microscope with a 50 W bulb (Osram HBO) and DAPI-specific filters.

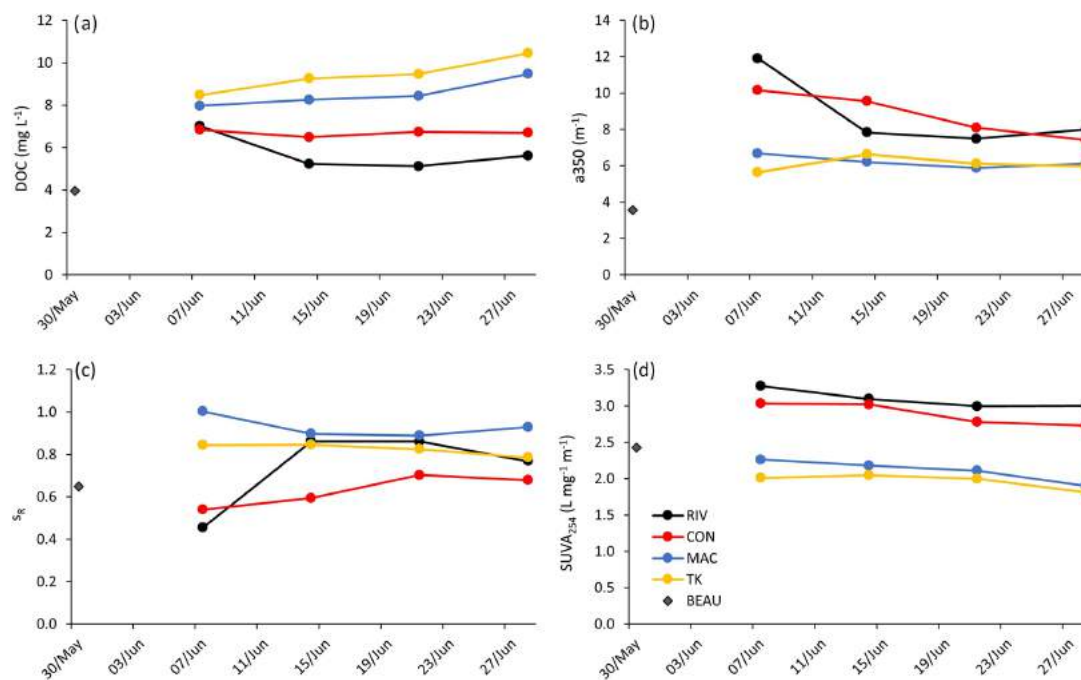
Bacterial production was determined using a modified version of the [³H] leucine (Leu) incorporation method described by Smith and Azam (1992). Incubations were conducted with four replicates plus one blank from each experimental replicate. Twenty microlitres of Leu (74 nM; saturating concentration) were added to sterile microcentrifuge tubes, and incubations began when 1.7 mL aliquots of bioassay water were added. The tubes were maintained at 20 °C for 1 h, at which point BP was halted by the addition of 89 µL of 100% (w/v) trichloroacetic acid (TCA). To remove unincorporated Leu, the samples were thoroughly mixed using a vortex, allowed to rest at room temperature for 30 min, and centrifuged (10 min at 16 000g) before the supernatant was discarded. Samples were then rinsed with 1.5 mL of 5% (w/v) TCA, mixed, centrifuged (10 min at 16 000g), and the supernatant was again discarded. Liquid scintillation cocktail (0.5 mL; BCS, GE Life Sciences) was added to each tube, followed by thorough mixing on a vortex. Samples were then read on a Triathler portable scintillation counter (Hydrex Oy), within 6 h of incubation. The isotope dilution factor was assumed to be 2, as in Roland and Cole (1999) and Simon and Azam (1989), and BP (g C L⁻¹ h⁻¹) was determined by assuming a 7.3 mol % of Leu in total bacterial protein and a carbon-to-protein ratio of 0.86, as in Simon and Azam (1989).

Bacterial respiration was measured as loss of DO in samples incubated in 60 mL stoppered glass bottles. DO concentrations were determined following the spectrophotometric method of Roland et al. (1999), and converted to CO₂ concentrations assuming a respiratory quotient of 1.

Cell-specific BP (SBP) was calculated as SBP = BP/BA, and cell-specific BR (SBR) was calculated as SBR = BR/BA. Bacterial growth efficiency (BGE) was calculated as BGE = BP/(BP + BR), whereas cell-specific BGE (SGE) was calculated as SGE = BGE/BA. Percent change in BA over the 48 h bioassay period was calculated as

$$\text{Percent change} = [(BA_{\text{end}} - BA_{\text{start}}) / BA_{\text{start}}] \times 100$$

Fig. 4. In situ measures of dissolved organic matter (DOM) quantity and quality in representative habitats in the Mackenzie Delta during the early open-water season of 2010. (a) DOM quantity was measured as dissolved organic carbon (DOC) concentration (mg L^{-1}), whereas DOM quality was evaluated using (b) absorbance (a_{350} , m^{-1}), (c) the spectral slope ratio (S_R , unitless), and (d) the specific ultraviolet absorbance of DOC (SUVA_{254} , $\text{L mg}^{-1} \text{m}^{-1}$).



Statistical analyses

Results obtained at the end of the 48 h bioassays were tested for outliers and the normality of residuals using a Shapiro–Wilk test (Shapiro and Wilk 1965). Data were analysed using a two-way analysis of variance (ANOVA), with the length of the photodegradation incubation (0, 7, and 14 days) and bacterial community (BEAU, RIV, CON, MAC, and TK) as factors. As the interaction term was not significant ($p > 0.05$) in any analysis, results were tested for main effects followed by a post-hoc Tukey's HSD to determine significant differences among treatment means.

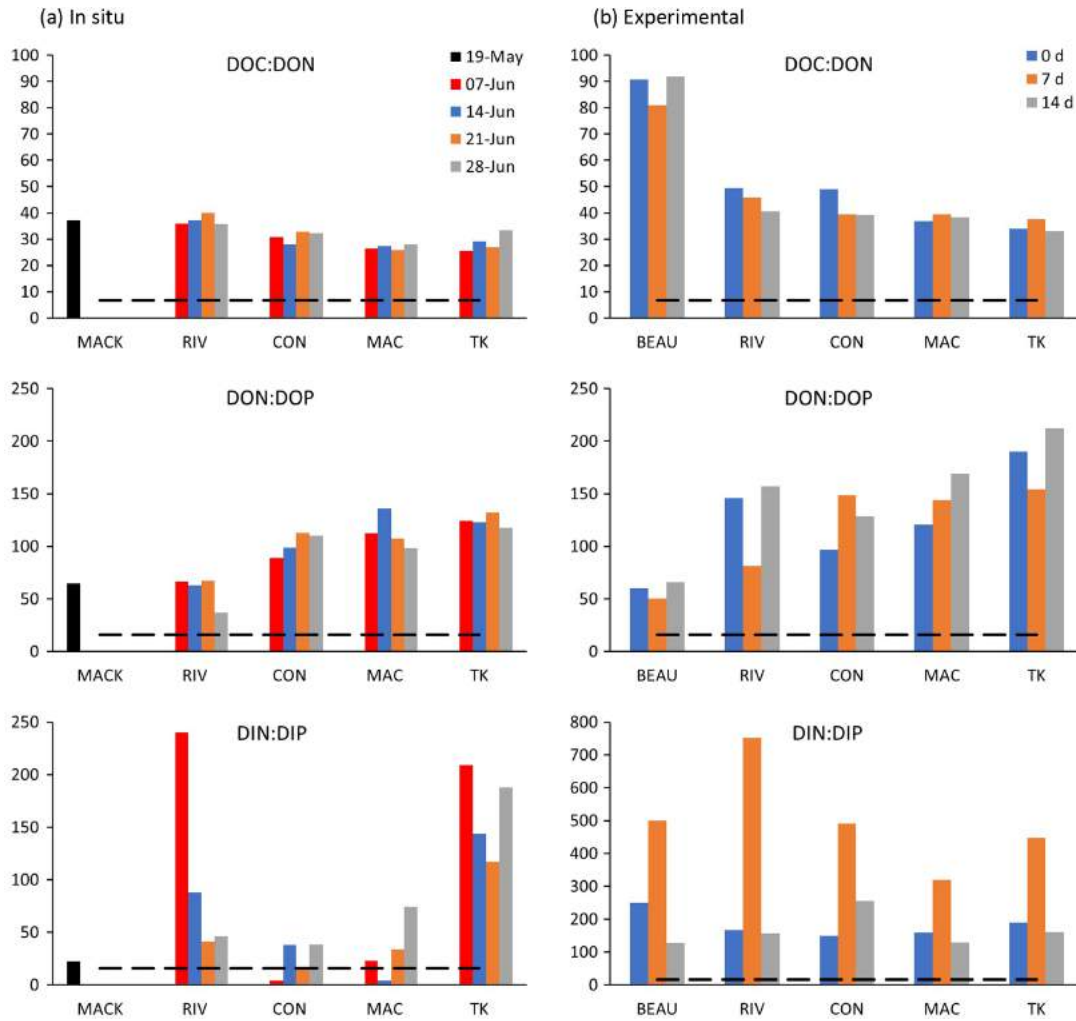
Results

Mackenzie Delta conditions during the early open-water season

In general, measures of carbon quantity (DOC concentration) and DOM quality (a_{350} , S_R , SUVA_{254}) were similar at the RIV and CON sites (Fig. 4). Both had lower DOC concentrations than did the MAC and TK lakes throughout June 2010, with proxy measurements of DOM quality that also indicated higher absorptivity, molecular weight, and aromaticity. Measurements taken at the BEAU site on 30 May show lower DOC concentrations and DOM absorptivity than were observed at any site in the Mackenzie Delta.

The initial floodwater sample taken from the Mackenzie River on 19 May (MACK) was strongly terrigenous in character (DOC:DON = 37), as were values from the RIV sampling site throughout June (Fig. 5a). Molar ratios of dissolved organic nutrients displayed little variation among delta habitats, and were also relatively similar within each site throughout the June 2010 sampling period. In all instances, ratios of DOC:DON and DON:DOP exceeded the Redfield ratio of 106C:16N:1P. Ratios of DIN:DIP were more variable among sites and

Fig. 5. Molar nutrient ratios measured (a) in situ during June 2010 and (b) at the end of the 48 h bacteria-dissolved organic matter (DOM) bioassays. The colour of the bar in (b) corresponds to that in (a) (i.e., the bacteria-DOM bioassay that used 7 days photodegraded DOM also used bacteria sampled on 21 June 2010). The dashed line in each graph represents the Redfield ratio (106C:16N:1P) specific to the nutrients being shown. DIN, dissolved inorganic nitrogen; DON, dissolved organic nitrogen; DOP, dissolved organic phosphorus.



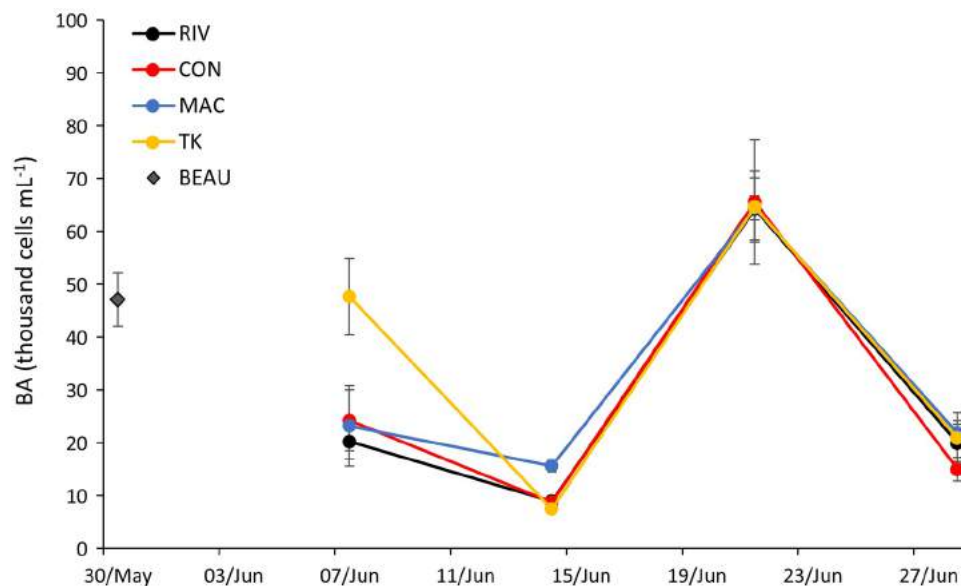
dates, and although there was a relative shortage of inorganic P on some sampling dates at the TK and RIV sites, there were also occasions when the CON and MAC lakes showed a relative shortage of inorganic N.

In situ BA was tracked weekly at all sites except BEAU, which due to sampling constraints was sampled only once (Fig. 6). The greatest variation in BA was observed immediately after ice breakup on 7 June 2010, with the highest values at TK ($47.62 \pm 10.17 \times 10^4$ cells) and lowest at RIV ($20.22 \pm 5.71 \times 10^4$ cells). During the following 3 weeks, lake and channel sites displayed similar BA values that varied following a similar pattern.

Freshet DOM photodegradation under ambient solar conditions

Incubations of freshet DOM were conducted under ambient solar conditions during the period of continuous daylight corresponding to the Arctic summer solstice. The incubation

Fig. 6. Concentrations of bacterial cells (bacterial abundance (BA), thousand cells mL⁻¹) in representative habitats in the Mackenzie Delta during the early open-water season of 2010. Error bars show one standard error of the mean.



period from 15 to 29 June 2010 was generally characterized by little cloud cover and high levels of both global and UV radiation, indicating high photochemical potential throughout most of the incubation period. Solar intensity was not uniform, however, with nighttime values dropping near 0 W m⁻² because of the very low solar angles that occur at high latitude (Fig. 7).

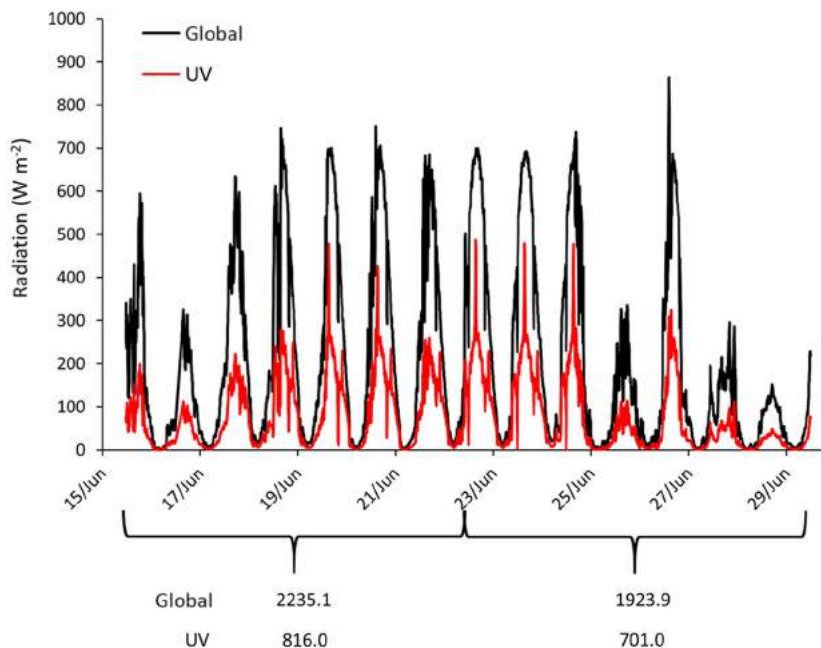
DOM indices showed evidence of substantial photodegradation with increased solar exposure (Table 2). During the first week of incubation, 8% of the initial DOC pool was lost via complete mineralization, with a further 2% lost during the second week. Chromophoric DOM (*a*₃₅₀) also decreased throughout the incubation period, whereas the slope ratio (*S_R*) increased from a strongly terrestrial value (0.38) to one more typical of estuarine or coastal samples (1.07). Decreasing values of *SUVA*₂₅₄ indicated decreasing average aromaticity of the DOM pool. Daily changes in *a*₃₅₀ and *S_R* were greatest during the first week of incubation, but were more uniform over both weeks for *SUVA*₂₅₄.

Lignin phenols showed a complex response to solar exposure (Table 2). Overall, the concentrations of two lignin phenol groups (V and S) decreased during the incubation, with the decrease occurring during the first 7 days followed by a small recovery during the second week. Ratios of S:V and C:V changed only slightly during the first week of irradiation but increased during the second week, while the response of acid:aldehyde ratios varied between the V and S phenol groups.

Bacterial metabolism using photodegraded freshet DOM as a substrate

During each bioassay, three parameters (BA, BP, and BR) were measured to evaluate the metabolic response of bacterial communities to progressively photodegraded freshet DOM. Weekly counts of in situ BA (Fig. 6) captured fluctuations in source bacterial community numbers, which clearly illustrated that initial conditions in the bioassay treatments differed and had to be properly accounted for in later analyses. To remove the effects of initial community BA numbers, a standardized measure of percent change in BA over the course

Fig. 7. Global (280–2800 nm) and ultraviolet (UV) (280–400 nm) radiation (W m^{-2}) during the freshet dissolved organic matter incubation under ambient light and temperature conditions (15–29 June 2010). Measures of global and UV radiation were taken every 5 s, with averages recorded at 5 min intervals and presented as a running 15 min average. Totals over each of the weekly incubation intervals are shown below the graph.



of the bioassays was examined (Table 3), and cell-specific rates of bacterial metabolism (SBP, SBR, and SGE) were used rather than total community-level rates (Figs. 8, 9, and Supplementary Fig. S1).¹ This allowed for a direct comparison of the relative change in BA and cell-specific rates among all treatment combinations. Although parameters were monitored at 0, 24, and 48 h, statistical comparisons were only carried out using the final data after 48 h. The results of all statistical comparisons are shown in Fig. 9, with further detail provided in Supplementary Table S1.¹

Effects on bacterial abundance

Bacterial abundance showed a complex response to the extent of photodegradation of the freshet DOM substrate (Fig. 8a). When provided raw freshet DOM (0 day irradiation), BA increased over 48 h in all communities except RIV. When provided DOM that had been irradiated for either 7 or 14 days, however, BA declined over 48 h in all communities. At the end of each bioassay, BA values were significantly higher for the raw freshet DOM treatment, as compared to values obtained in the 7 and 14 days treatments ($F = 9.437$, $p = 0.008$; Fig. 9a). This indicates that, while raw freshet DOM generally supported an increase in the number of bacteria, the presence of photodegraded DOM (or some other substance in the incubated water) caused a reduction in bacterial numbers during the 48 h bioassay period. This may also have been caused by changes in the relative abundances of dissolved

¹Supplementary material is available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/as-2017-0055>.

Table 2. Carbon, dissolved organic matter (DOM), and lignin data for a sample of Mackenzie River floodwater (collected on 19 May 2010) that was irradiated under ambient solar conditions in the town of Inuvik, NT (68.3607°N, 133.7230°W).

	Point measurement			% Change day ⁻¹		Cumulative % change
	0 day	7 days	14 days	0–7 days	7–14 days	
C quality						
DOC (mg L ⁻¹)	7.05	6.49	6.38	-1.1	-0.2	-10
C quality						
<i>a</i> ₃₅₀ (m ⁻¹)	12.68	6.77	4.78	-6.7	-4.2	-62
<i>S</i> _R	0.38	0.85	1.07	17.8	3.8	184
SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)	3.35	2.97	2.67	-1.6	-1.4	-20
Lignin parameters						
<i>V</i> (µg L ⁻¹)	28.85	12.97	13.29	-7.9	0.4	-54
<i>S</i> (µg L ⁻¹)	7.34	3.17	4.77	-8.1	7.2	-35
<i>C</i> (µg L ⁻¹)	1.36	0.98	3.80	-4.0	41.1	179
Σ ₈ (µg L ⁻¹)	37.55	17.11	21.87	-7.8	4.0	-42
Λ ₈ [mg (100 mg OC ⁻¹)]	0.53	0.26	0.34	-7.3	4.4	-36
<i>S</i> : <i>V</i>	0.25	0.24	0.36	-0.6	7.1	44
<i>C</i> : <i>V</i>	0.05	0.08	0.29	8.6	37.5	480
(Ad:Al) _v	1.14	2.67	2.07	19.2	-3.2	82
(Ad:Al) _s	0.60	0.93	1.20	7.9	4.1	100

Note: For each parameter, the percent change per day was calculated over each of the 2 wk (0–7 days and 7–14 days) of the incubation, whereas the cumulative percent change was calculated over the entire 14 days incubation period. DOC, dissolved organic carbon.

Table 3. Percent change (standard error) in bacterial abundance (BA, thousand cells mL⁻¹) observed during bacteria-dissolved organic matter (DOM) bioassays. PD duration is the length of the photodegradation period.

PD duration	Community				
	BEAU	RIV	CON	MAC	TK
0 day	234.0 (44.0)	-10.9 (4.9)	368.8 (56.9)	32.1 (10.7)	123.7 (19.2)
7 days	-62.1 (0.5)	-80.9 (4.0)	-65.3 (6.0)	-46.1 (1.7)	-71.0 (1.5)
14 days	-40.9 (12.3)	-35.7 (6.7)	-31.9 (4.7)	-76.1 (3.4)	-70.8 (4.3)

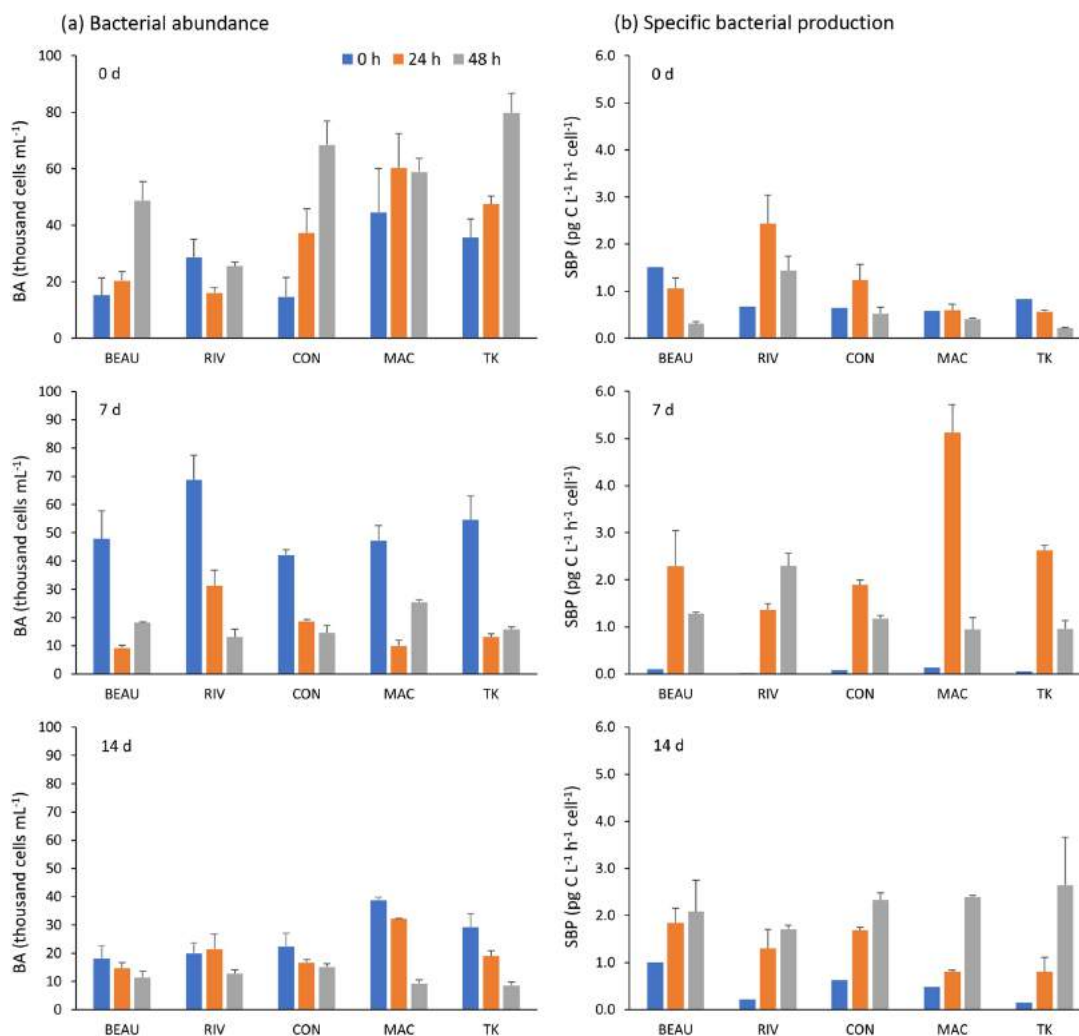
Note: The average percent change between the start (0 h) and end (48 h) of the bioassay is shown for each treatment combination (PD duration × community), with positive values indicating an increase in BA and negative values indicating a decrease. CON, connected; RIV, river; BEAU, Beaufort Sea; MAC, macrophyte; TK, thermokarst.

inorganic nutrients. While ratios of DOC:DON and DON:DOP measured at the end of each bioassay remained on par with those found in the delta habitats (generally less than double in situ values), those found for DIN:DIP at the end of each bioassay exceeded those found in situ, in some cases by a factor of 30 (Fig. 5b). This indicates that DIP was consumed during the bioassays.

Effects on bacterial metabolism

Bacterial metabolism also showed complicated responses to the extent of photodegradation of the freshet DOM substrate. Compared to the generally low rates generated using raw floodwater substrate, rates of SBP (Fig. 8b) increased rapidly during the first 24 h of incubation with DOM that had been irradiated for 7 days before declining to lower rates after 48 h. When bioassays were conducted with DOM that had been irradiated for 14 days, however, rates of SBP increased throughout the incubation, with rates after 48 h that were significantly greater than those observed at the end of the initial incubation using raw freshet DOM ($F = 46.6542$, $p = 0.0009$; Fig. 9b).

Fig. 8. (a) Bacterial abundance (BA) and (b) cell-specific measures of bacterial production (SBP) observed in five bacterial populations (BEAU, Beaufort Sea; RIV, river; CON, connected; MAC, macrophyte; and TK, thermokarst) following incubation with Mackenzie River freshet dissolved organic matter that had been continuously irradiated under ambient solar conditions for 0, 7, or 14 days. Both parameters were measured after 0, 24, and 48 h, with error bars showing one standard error of the mean.



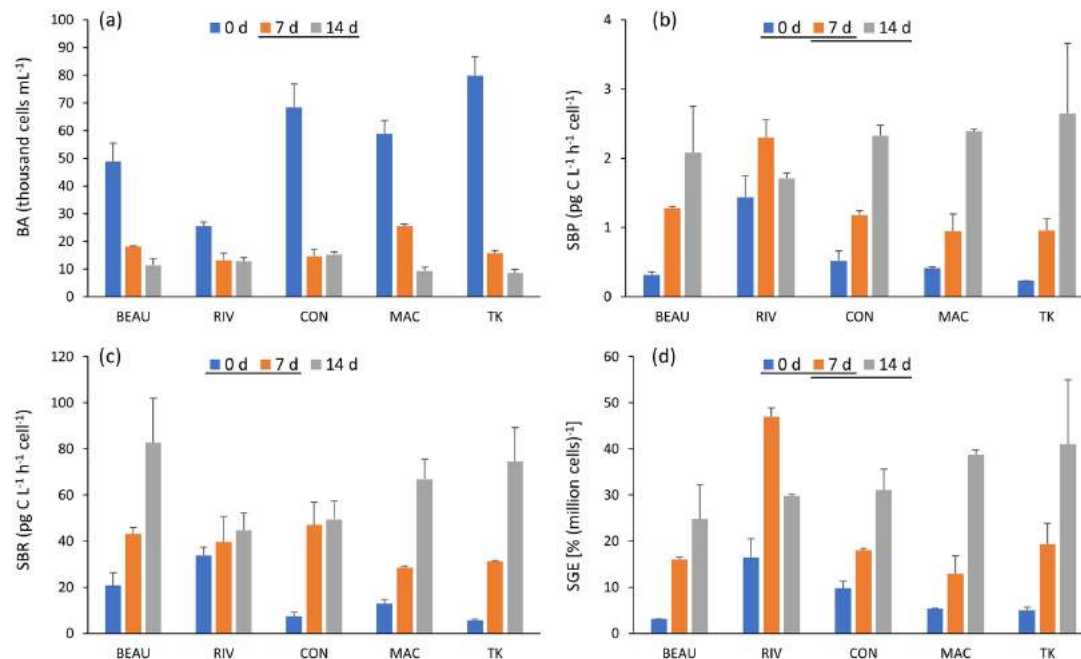
Dissolved organic matter irradiated for 14 days produced higher rates of SBR in bacterial populations than did either raw freshet DOM, or DOM that had been irradiated for 7 days ($F = 67.0534$, $p = 0.0004$; Fig. 9c). While raw freshet DOM substrate resulted in very low values of growth efficiency per cell (SGE) for all populations (Fig. 9d), rates of SGE increased with the duration of freshet DOM irradiation, with final values being significantly greater using 14 days irradiated floodwater as compared to raw substrate ($F = 17.5587$, $p = 0.0086$; Fig. 9d).

Discussion

Photoreactivity of Mackenzie River freshet DOM

Our results supported our initial hypothesis that freshet DOM bioavailability would continually increase throughout the irradiation incubation, and were consistent with prior

Fig. 9. (a) Average bacterial abundance (BA) and cell-specific bacterial metabolism ((b) SBP, cell-specific BP, (c) SBR, cell-specific BR, and (d) SGE, cell-specific BGE) observed in five source populations (BEAU, Beaufort Sea; RIV, river; CON, connected, MAC, macrophyte, and TK, thermokarst) following 48 h bioassays with Mackenzie River freshet dissolved organic matter (DOM) that had been continuously irradiated under ambient solar conditions for 0, 7, or 14 days. Error bars show one standard error of the mean. Legend entries that share a common underscore are not significantly different from one another at a significance level of $\alpha = 0.05$. Note that BA could not be directly compared amongst treatments because in situ BA (and therefore initial BA counts in the bacterial isolates that were mixed with photodegraded DOM) varied both among sites, and between sampling dates (Fig. 6). See Table 3 for the percentage changes in BA during the various bioassays that were used to conduct statistical tests.



observations of photodegradation in a range of riverine (e.g., Opsahl and Benner 1998; Moran et al. 1999; Spencer et al. 2009) and other freshwater (e.g., Bertilsson and Tranvik 2000; Osburn et al. 2001; Cory et al. 2014) environments.

In collective, our results demonstrate that Mackenzie River freshet DOM has a very high potential for photodegradation, and that it was extensively modified during a very short period of continual exposure to ambient sunlight (Table 2). Low initial values of both the S:V and C:V lignin ratios indicated that the terrigenous fraction of the freshet DOM pool largely originated from woody gymnosperms (Hedges and Mann 1979), as expected for a large subarctic basin covered by extensive boreal forest. After only a 2 weeks incubation under ambient solar conditions, we observed changes in S_R (increase of 184%) and $SUVA_{254}$ (decrease of 20%) that indicated a decrease in the average aromaticity and molecular weight of the DOM pool (Weishaar et al. 2003; Helms et al. 2008). Increases in the acid:aldehyde ratios for both the vanillyl [(Ad:Al)_V] and syringyl [(Ad:Al)_S] lignin phenol fractions also agreed with the results of previous studies of lignin photodegradation (e.g., Spencer et al. 2009), as did a negative relationship between (Ad:Al)_V (elevated) and S:V (decreased) that resulted from known differences in photodegradation rates among phenols (Opsahl and Benner 1998; Hernes and Benner 2003). In addition, decreases in DOC concentrations (−10%) and total lignin phenol concentrations (Σ_8 ; −42%) indicated that a portion of the

freshet DOM pool was completely mineralized (Moran and Zepp 1997) and evaded from the incubators as CO₂ gas. Consistent with other studies (Moran et al. 2000; Vahatalo and Wetzel 2004; Spencer et al. 2009), these C losses via mineralization were outpaced by losses of chromophoric DOM, as reflected by a greater cumulative decrease in *a*₃₅₀ (−62%) throughout the incubation period as compared to either DOC or Σ₈.

The magnitude of the observed changes in DOM absorbance parameters during our photodegradation incubation were on par with those seen over the entire open-water period in Mackenzie Delta lakes, and emphasize how rapidly photodegradation can occur during floodplain storage under prolonged Arctic solstice daylengths. For example, over a 4 month long open-water season, Cunada et al. (2018) observed declines in SUVA₂₅₄ from ~3.5 to ~2.5 L mg^{−1} m^{−1} in a set of six lakes (comprised of CON, MAC, and TK, plus three others) in the east-central Mackenzie Delta. This decline is roughly equivalent to that seen from the start (3.35 L mg^{−1} m^{−1}) to the end (2.67 L mg^{−1} m^{−1}) of our 14 days DOM incubation (Table 2). When this process is considered across the entire Mackenzie Delta, the potential ecological implications become apparent. On average, 47% of Mackenzie River freshet discharge moves off-channel into the delta, covering approximately 11 000 km² with a layer of water averaging 2.3 m in depth (Emmerton et al. 2007). This thin layer arrives on the delta floodplain at the same time that daylengths and solar exposure reach annual maximums during the Arctic summer solstice, when the sun remains above the horizon for 56 consecutive days (as observed in the town of Inuvik, on the eastern boundary of the delta). Although solar angles are low due to the high latitude of the delta (67–69°N), prior experiments on samples taken from delta lakes have found measurable declines in DOM absorption over periods as short as 8 h during the solstice (Gareis 2007). Until now, however, these experiments have only been attempted using lake water that was collected after the flooded period, due to difficult sampling conditions and restricted access to the delta during the freshet. This study is therefore the first to directly examine the photochemical potential of Mackenzie River floodwater sampled during the peak freshet.

Our results demonstrate the importance of floodplain processes taking place on circumpolar river deltas and floodplains, which are active sites of carbon and nutrient cycling in the northern landscape, but which are nevertheless frequently overlooked in studies of great circumpolar river biogeochemistry. Although DOC and lignin concentrations declined due to complete carbon photodegradation and mineralization, the changes in DOM quality, such as decreased molecular weight and aromaticity, are likely more important from an ecosystem perspective as they render freshet DOM more bioavailable for microbial consumption and bacterial metabolism (Lindell et al. 1995; Wetzel et al. 1995). These increases in bioavailable DOM occur at a critical time of year when Mackenzie Delta food web productivity is increasing rapidly due to the breakup of ice cover, warming temperatures, the delivery of nutrient-rich floodwater, and prolonged daylight hours. As a result, food web production in the Mackenzie Delta may be enhanced via the microbial loop, contributing to the high levels of productivity and biodiversity seen in this system (Squires et al. 2009). Secondary production may also be enhanced in the nearshore Beaufort when photodegraded freshet DOM is delivered in discharge.

Photodegraded freshet DOM as a substrate for bacterial metabolism

Mackenzie Delta bacterial communities displayed complex metabolic responses to the presence of photodegraded DOM. We will address each of our two hypotheses related to bacterial usage of this substrate in turn.

Initial hypothesis: Increased duration of DOM irradiation would support higher rates of bacterial growth and metabolism.

Contrary to our initial hypothesis, increases in BA were only observed during bioassays when communities were mixed with raw floodwater (Fig. 8a). When mixed with floodwater that had been irradiated for either 7 or 14 days, all bacterial communities experienced declines in BA over the 48 h bioassay period (Fig. 9a), while conversely, cell-specific growth efficiencies (SGE) were significantly greater during bioassays using floodwater that had been irradiated for 14 days (Fig. 9d). This indicated two contrasting responses to the presence of photodegraded freshet DOM; while total community populations declined, the remaining individuals experienced enhanced rates of growth.

There are several possible mechanisms that may account for these observed changes in bacterial metabolism. For instance, lysis following the death of bacterial cells can release a pool of labile nutrients that can subsequently stimulate growth in surviving bacteria (e.g., Eckert et al. 2013). We suggest, however, that our results point towards two concurrent processes with opposing effects on bacterial growth and metabolism; the simultaneous production of inhibitory ROS and stimulatory labile DOM during irradiation, both of which exert selection pressures resulting in shifts in bacterial community composition to species that are better adapted to the ambient conditions following photodegradation.

Exposure to ROS can cause oxidative damage to cellular targets in bacteria, including DNA, RNA, lipids, and proteins (Ruiz-Gonzalez et al. 2013). They are generally short-lived with half-lives ranging from less than a second to hours (Burns et al. 2012), but are not produced during dark periods so they are usually completely removed from water columns overnight. Arctic latitudes experience uninterrupted sunshine for prolonged periods (weeks to months) around the time of the summer solstice, however, which may allow for accumulation of ROS in highly absorptive (i.e., highly coloured) water columns rich in terrigenous DOM. For example, Febria et al. (2006) found that the production of hydrogen peroxide (H_2O_2) in two delta lakes that were also sampled herein (CON and TK) outpaced the rate of removal during a period of uninterrupted sunshine in 2004, leading to an accumulation of H_2O_2 within the water columns. Production of ROS during previous studies of DOM photodegradation has been observed to inhibit community-level rates of carbon production (Scully et al. 2003; Anesio et al. 2005; Glaeser et al. 2014) and result in changes in bacterial community composition (Glaeser et al. 2010, 2014). Further, in a prior study by Lund and Hongve (1994), declines in BA of up to 60% were observed after only an hour when UV-irradiated DOM was mixed with bacteria. If the irradiated DOM was instead stored for 2 weeks before mixing, no bactericidal effect was found, suggesting that short-lived ROS molecules were responsible for the observed declines. Given the prolonged periods of sunlight exposure during our irradiation incubations, the high photochemical potential of Mackenzie River floodwater, and the immediate (within 2 h) mixing of the irradiated DOM with bacterial communities at the start of each bioassay, it seems likely that ROS were produced at a high rate during the incubation period and then exerted strong inhibitory effects on BA during our bioassays (as in Fig. 8a).

Floodwater DOM that was exposed to ambient solar conditions continued to be broken down throughout the entire 14 days incubation, becoming increasingly labile as a result (Table 2). Photodegraded DOM molecules are smaller and less aromatic, and therefore more labile and easily consumed by bacteria, than are the unaltered compounds in the initial DOM pool (Wetzel et al. 1995; Moran and Zepp 1997; Bertilsson and Tranvik 1998; Obernosterer and Benner 2004). The presence of photodegraded and bioavailable DOM has been observed to fuel increases in BP in the short term, with these effects fading over longer observational periods. When bacteria from a mid-latitude alpine lake were provided irradiated DOM at the start of a 48 h incubation, Pérez and Sommaruga (2007) found that Leu incorporation increased over 24 h but subsequently declined, with no increase apparent after 48 h. A similar pattern was seen in our bioassay using 7 days irradiated floodwater

(Fig. 8b), where an initial sharp increase in SBP also suggested that the surviving bacteria were released from a relative shortage of growth substrate. Increased BP and growth have been observed in the presence of irradiated DOM in many freshwater systems (e.g., Anesio et al. 2005; Paul et al. 2012), including in the circumpolar Arctic (Cory et al. 2013; Ward et al. 2017), where photochemical oxidation of DOM accounts for the majority of C processing (Cory et al. 2014). Prior work in the Mackenzie Delta has shown that lower molecular weight DOM derived from macrophytes supports higher rates of BGE in communities isolated from a variety of habitats (including TK and CON lakes; Tank 2009). It therefore seems likely that an increase in the relative proportion of lower molecular weight, less aromatic, and more labile photodegraded DOM would also stimulate bacterial metabolism in delta lakes compared to higher molecular weight DOM. The pool of increasingly labile DOM as the photodegradation period lengthened, combined with reduced competition for resources due to decreased BA, may therefore have contributed to the higher SGE that was observed in the surviving bacteria in our irradiated bioassay treatments (both 7 and 14 days; Fig. 9d).

Collectively, our results suggest a possible shift in bacterial community composition during those bioassays that used irradiated (7 or 14 days) floodwater; for example, to species that may be more tolerant of ROS, better able to exploit the increasingly labile pool of DOM as a growth substrate, or a combination of both. The remaining, better-adapted species would have also faced less competition for resources, which may have further amplified their cell-specific metabolic rates. Further work is needed, however, to investigate the composition of Mackenzie Delta bacterial communities, variations in community structure that occur during the open-water season, and the ways that communities respond to the presence of photodegraded freshet DOM and its by-products, to further untangle this complicated set of interactions.

Initial hypothesis: The greatest increases in growth and metabolic rates would be observed in bacterial populations from habitats that frequently receive subsidies of photodegraded DOM.

Although we hypothesized that we would find the greatest rates of bacterial growth and metabolism in communities from habitats that typically receive high levels of photodegraded DOM, our observations did not support this. Instead we found that, among the five bacterial communities, there were no statistically significant differences in their metabolic rates once they were standardized to per-cell measures (SBP, SBR, or SGE). This indicates that, although bacterial communities from a range of delta habitats with divergent C and DOM characters may have had differing short-term responses after 24 h (e.g., as in Fig. 8), over the longer-term, they responded similarly to the presence of photodegraded DOM. This agrees with other studies that have observed shifts in bacterial community composition and metabolism in response to the character of the DOM substrate, regardless of the origin of the initial populations (e.g., Judd et al. 2006; Attermeyer et al. 2015). In our study, only the irradiation treatment (0, 7, or 14 days) had a significant effect on BA, as well as on all three measures of cell-specific bacterial metabolism (Fig. 9).

In situ BA at our five habitat sites varied over an order of magnitude during our sampling period, from 7.45 to 65.55×10^4 cells mL⁻¹, and varied in a similar fashion across all sites following the first sampling day (Fig. 6). These abundances were substantially lower than those reported during some prior studies in Mackenzie Delta lakes, when BA counts were up to two orders of magnitude greater [$2\text{--}20 \times 10^6$ cells mL⁻¹ in both Febria (2005) and Tank (2009)]. However, our results were comparable to those found during two other studies of BA in Mackenzie Delta lakes; Spears and Lesack (2006) found abundances of $2\text{--}12 \times 10^4$ cells mL⁻¹, whereas Chateauvert et al. (2012) found abundances of free-living bacteria in the range of $20\text{--}280 \times 10^4$ cells mL⁻¹. Although these prior results could potentially point to substantial interannual variation in BA, or in the populations of grazers feeding on bacteria, there are two other possible explanations for our lower abundances that must be

considered that both relate to the timing of our study. First, to examine the potential response of bacterial populations to irradiated floodwater, we used bacteria that had been collected very early in the open-water season (June). Other studies of BA in the Mackenzie River Delta have generally occurred later in the open-water period (July and August), once water temperatures in the river and delta lakes had warmed considerably, which may have resulted in higher BA counts. The second reason why our BA values may have been lower is that our samples may have contained a very high proportion of particle-attached bacteria relative to free-living bacteria. Particle-attached bacteria comprise, on average, 77% of the total suspended bacterial community in delta lakes, with the proportion increasing with total suspended solid (TSS) concentrations. Conversely, free-living bacteria (the fraction measured herein) account for an average of only 14% of the total suspended bacterial community in delta lakes (Chateauvert et al. 2012). In 2010, all three delta lakes received floodwater for some amount of time (between 6 and 172 days; Table 1), which would have contributed TSS to the lakes early in the open-water season, as well as particle-attached bacteria that would have been removed when samples were filtered to isolate bacteria. We found BA values in the Mackenzie River (RIV) and the Beaufort coastal zone (BEAU) to be very close to those found in the delta lakes (Fig. 6); however, our estimates in these cases were similar to those found during prior studies. For example, BA in surface water averaged 67×10^4 cells mL⁻¹ along a 300 km transect from the Mackenzie River into the Beaufort Sea (Vallières et al. 2008), and fluctuated from 10 to 100×10^4 cells mL⁻¹ in Franklin Bay (Garneau et al. 2008) and on the Mackenzie Shelf (Matsuoka et al. 2015).

Although measures of bacterial metabolism were standardized per cell, we did not standardize nutrients across the bioassays. Nutrient conditions therefore differed at the start of each bioassay due to differing nutrient compositions in each of the five bacterial isolates that were mixed in a 30:70 ratio with irradiated freshet DOM. By the end of the 48 h bioassay periods, all showed evidence of DIP utilization, with much higher ratios of DIN:DIP as compared to in situ conditions (Fig. 5). These high inorganic N:P ratios point towards P-limitation in all bioassays, similar to in situ conditions which show inorganic P-limitation on most sampling dates. This indicates that the bacterial growth and production of all communities and bioassays were likely P-limited to some extent. The RIV population was the only one that showed strong evidence of DOP being used as a substrate, as ratios of DOP:DON were up to three times greater following the bioassay as compared to ratios measured in situ.

Limitations of experimental design

Although some important insights were gained from this experimental study, we recognize that our study design did not replicate natural conditions in the Mackenzie Delta and that our results must therefore be interpreted in this context.

Polyethylene incubators were filled with floodwater to simulate photobleaching on the delta floodplain. Although this was necessary because we had limited access to the delta during the high-water freshet period, the rapid photochemical changes that were observed were likely due, in some part, to the artificial conditions in our incubator system. The incubators did not allow mixing with fresh contributions of river water, the addition of rainfall, or contributions of terrigenous DOM from the floodplain surface itself (e.g., leaching from soil surface layers or flooded vegetation). In addition, UV wavelengths penetrate the uppermost 50 cm of delta lakes on average (Gareis et al. 2010). Although the average depth of Mackenzie Delta lakes is less than 2 m, with maximum depths less than 4 m (Mackay 1963), there is still some portion of the water column that remains shielded from the effects of UV exposure. The irradiated water layer in the incubators was only ~15 cm deep, which means that the entire aliquot of flood water was continually irradiated throughout the

incubation period, with no external inputs to replenish the DOM pool. Under real-world conditions, it is therefore likely that photochemical changes to DOM on the delta floodplain are less rapid and extensive than what we observed herein. Regardless, our results emphasize the high photoreactivity of Mackenzie River freshet DOM, and the high potential for photodegradation and photomineralization during even the short periods of delta floodplain storage that occur during the high-water period corresponding to the annual flood and Arctic summer solstice.

The floodwater that was irradiated in our incubators may have also developed elevated levels of ROS compared to what would occur under natural conditions in the delta. Mackenzie Delta lakes are well-mixed by wind due to their shallow depths, and do not stratify during the ice-free season. The incubator conditions therefore differed from those in the floodplain lakes because there was no mixing of irradiated surface layers with unirradiated bottom layers, which would have distributed ROS throughout the water column and lowered concentrations. Also, under real-world conditions, Mackenzie Delta habitats experience varying degrees of water renewal and dilution, with greater rates at riverine and connected lake sites, and lower rates in delta lakes that become cut off from distributary channels following the flood. It therefore seems likely that the potential effects of ROS on our bacterial populations also differed from what would be observed under natural conditions, where the severity of these effects would differ among populations based on their rates of water renewal.

Another factor that must be considered is that our bioassays were conducted in the lab under dark conditions, which removed some direct effects of UV exposure. Wavelengths in the UV range damage bacterial DNA (Karentz et al. 1994) and inhibit BP (Jeffrey et al. 1996; Anesio et al. 2005; Ruiz-Gonzalez et al. 2013) in natural sunlit environments, and these effects may be even more pronounced at high latitudes that experience uninterrupted daylight during the summer solstice. Under natural conditions, we would likely have observed lower rates of BP and growth efficiency due to these direct UV effects.

Conclusions

This study, which to our knowledge is the first quantification of Mackenzie River freshet DOM quantity, bioavailability, and photoreactivity, fills a gap in our current knowledge of Arctic river biogeochemistry. In addition, it illustrates the importance of biogeochemical processes occurring on the world's circumpolar deltas and floodplains, which are often overlooked in studies of riverine export to the Arctic Ocean.

Photodegradation under ambient solar conditions on the large, lake-rich, and seasonally-flooded Mackenzie Delta floodplain may lead to substantial changes in DOM quality that are on par with those normally seen over the course of the entire open-water season in delta lakes. This rapid photodegradation may produce a large pool of bioavailable substrate to fuel production both within the delta itself, as well as in Beaufort Sea coastal regions, at a time of year when temperatures are warming and ice cover is rapidly lost. However, our results also suggest that some part of the DOM photodegradation process exerts selection pressures resulting in changes to bacterial community composition. Among other possibilities, ROS may reach levels that inhibit bacterial growth and metabolism, or the increasingly labile DOM pool may be exploited as a growth substrate by a subset of the bacterial population. Future work on the community composition in differing delta habitats, and how it changes in response to DOM photodegradation, is needed to fully understand these interactions.

The export of photodegraded DOM from large circumpolar rivers provides a source of readily-available energy- and nutrient-rich material to nearshore marine zones at a critical time of year, when food web production is rapidly increasing at the start of the ice-free

open-water season. An understanding of how floodplain processes alter DOM quantity and quality prior to its discharge is essential to better anticipate the potential effects of future climate change, such as thawing permafrost and shortened ice-covered seasons, on this important resource.

Conflicts of interest

The authors have no conflicts of interest to report.

Acknowledgements

The research reported in this article was conducted under NWT Scientific Research Licence #14687. This work was funded by the International Polar Year project “Study of Canadian Arctic River-delta Fluxes” and the Natural Sciences and Engineering Research Council of Canada (Discovery Grant to LL, Northern Research Internship to JG). Additional support was provided by the Polar Continental Shelf Program, the Northern Scientific Training Program, the Aurora Research Institute, and Environment Canada (Water Survey of Canada Inuvik office). Analytical support was provided by the Freshwater Institute (Fisheries and Oceans Canada) and C.L. Osburn of North Carolina State University. We thank S. Tank and J. Dixon for valuable help with methods, and L. Duma, C. Onclin, M. Russell, D. Whalen, G. Lintern, and A. McPherson for their assistance in the field and lab. We gratefully acknowledge the helpful comments received from two anonymous reviewers, and the editorial office of Arctic Science for their assistance.

References

- Anderson, L. 1979. Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. *Anal. Chim. Acta*, **110**: 123–128. doi: [10.1016/S0003-2670\(01\)83537-6](https://doi.org/10.1016/S0003-2670(01)83537-6).
- Anesio, A.M., Graneli, W., Aiken, G.R., Kieber, D.J., and Mopper, K. 2005. Effect of humic substance photodegradation on bacterial growth and respiration in lake water. *Appl. Environ. Microbiol.* **71**: 6267–6275. doi: [10.1128/AEM.71.10.6267-6275.2005](https://doi.org/10.1128/AEM.71.10.6267-6275.2005). PMID: [16204548](https://pubmed.ncbi.nlm.nih.gov/16204548/).
- Attemeyer, K., Tittel, J., Allgaier, M., Frindte, K., Wurzbacher, C., Hilt, S., Kamjunke, N., and Grossart, H.-P. 2015. Effects of light and autochthonous carbon additions on microbial turnover of allochthonous organic carbon and community composition. *Microb. Ecol.* **69**: 361–371. doi: [10.1007/s00248-014-0549-4](https://doi.org/10.1007/s00248-014-0549-4). PMID: [25515425](https://pubmed.ncbi.nlm.nih.gov/25515425/).
- Azam, F., Fenchel, T., Field, J., Gray, J., Meyerreil, L., and Thingstad, F. 1983. The ecological role of water-column microbes in the sea. *Mar. Ecol.: Prog. Ser.* **10**: 257–263. doi: [10.3354/meps010257](https://doi.org/10.3354/meps010257).
- Bell, L.E., Bluhm, B.A., and Iken, K. 2016. Influence of terrestrial organic matter in marine food webs of the Beaufort Sea shelf and slope. *Mar. Ecol.: Prog. Ser.* **550**: 1–24. doi: [10.3354/meps11725](https://doi.org/10.3354/meps11725).
- Bertilsson, S., and Tranvik, L.J. 1998. Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton. *Limnol. Oceanogr.* **43**: 885–895. doi: [10.4319/lo.1998.43.5.0885](https://doi.org/10.4319/lo.1998.43.5.0885).
- Bertilsson, S., and Tranvik, L.J. 2000. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* **45**: 753–762. doi: [10.4319/lo.2000.45.4.0753](https://doi.org/10.4319/lo.2000.45.4.0753).
- Burns, J.M., Cooper, W.J., Ferry, J.L., King, D.W., DiMento, B.P., McNeill, K., Miller, C.J., Miller, W.L., Peake, B.M., Rusak, S.A., Rose, A.L., and Waite, T.D. 2012. Methods for reactive oxygen species (ROS) detection in aqueous environments. *Aquat. Sci.* **74**: 683–734. doi: [10.1007/s00027-012-0251-x](https://doi.org/10.1007/s00027-012-0251-x).
- Chateauvert, C.A., Lesack, L.F.W., and Bothwell, M.L. 2012. Bacterial community dominance of particle-attached bacteria in lakes of the Mackenzie River Delta: transparent exopolymer particle contribution. *Aquat. Microb. Ecol.* **68**: 57–76. doi: [10.3354/ame01605](https://doi.org/10.3354/ame01605).
- Cole, J.J. 1999. Aquatic microbiology for ecosystem scientists: New and recycled paradigms in ecological microbiology. *Ecosystems*, **2**: 215–225. doi: [10.1007/s100219900069](https://doi.org/10.1007/s100219900069).
- Cory, R.M., Crump, B.C., Dobkowski, J.A., and Kling, G.W. 2013. Surface exposure to sunlight stimulates CO₂ release from permafrost soil carbon in the Arctic. *PNAS*, **110**: 3429–3434. doi: [10.1073/pnas.1214104110](https://doi.org/10.1073/pnas.1214104110). PMID: [23401500](https://pubmed.ncbi.nlm.nih.gov/23401500/).
- Cory, R.M., Ward, C.P., Crump, B.C., and Kling, G.W. 2014. Sunlight controls water column processing of carbon in arctic fresh waters. *Science*, **345**: 925–928. doi: [10.1126/science.1253119](https://doi.org/10.1126/science.1253119). PMID: [25146289](https://pubmed.ncbi.nlm.nih.gov/25146289/).
- Cunada, C.L., Lesack, L.F.W., and Tank, S.E. 2018. Seasonal dynamics of dissolved methane in lakes of the Mackenzie Delta and the role of carbon substrate quality. *J. Geophys. Res.: Biogeosci.* **123**: 591–609.
- Dunton, K.H., Weingartner, T., and Carmack, E.C. 2006. The nearshore western Beaufort Sea ecosystem: circulation and importance of terrestrial carbon in arctic coastal food webs. *Prog. Oceanogr.* **71**: 362–378. doi: [10.1016/j.pocean.2006.09.011](https://doi.org/10.1016/j.pocean.2006.09.011).

- Eckert, E.M., Baumgartner, M., Huber, I.M., and Pernthaler, J. 2013. Grazing resistant freshwater bacteria profit from chitin and cell-wall-derived organic carbon. *Environ. Microbiol.* **15**: 2019–2030. doi: [10.1111/1462-2920.12083](https://doi.org/10.1111/1462-2920.12083). PMID: [23413977](https://pubmed.ncbi.nlm.nih.gov/23413977/).
- Emmerton, C.A., Lesack, L.F.W., and Marsh, P. 2007. Lake abundance, potential water storage, and habitat distribution in the Mackenzie River Delta, western Canadian Arctic. *Water Resour. Res.* **43**: W05419. doi: [10.1029/2006WR005139](https://doi.org/10.1029/2006WR005139).
- Emmerton, C.A., Lesack, L.F.W., and Vincent, W.F. 2008. Nutrient and organic matter patterns across the Mackenzie River, estuary and shelf during the seasonal recession of sea-ice. *J. Mar. Syst.* **74**: 741–755. doi: [10.1016/j.jmarsys.2007.10.001](https://doi.org/10.1016/j.jmarsys.2007.10.001).
- Febria, C.M. 2005. Patterns of hydrogen peroxide among lakes of the Mackenzie Delta and potential effects on bacterial production. M.Sc. thesis, Simon Fraser University, Burnaby, B.C. 124 pp.
- Febria, C.M., Lesack, L.F.W., Gareis, J.A.L., and Bothwell, M.L. 2006. Patterns of hydrogen peroxide among lakes of the Mackenzie Delta, western Canadian Arctic. *Can. J. Fish. Aquat. Sci.* **63**: 2107–2118. doi: [10.1139/f06-106](https://doi.org/10.1139/f06-106).
- Gareis, J.A.L. 2007. Underwater irradiance attenuation and photobleaching of chromophoric dissolved organic matter in shallow arctic lakes of the Mackenzie Delta, NWT. M.Sc. thesis, Simon Fraser University, Burnaby, B.C. 174 pp.
- Gareis, J.A.L., and Lesack, L.F.W. 2017. Fluxes of particulates and nutrients during hydrologically defined seasonal periods in an ice-affected great Arctic river, the Mackenzie. *Water Resour. Res.* **53**: 6109–6132. doi: [10.1002/2017WR020623](https://doi.org/10.1002/2017WR020623).
- Gareis, J.A.L., Lesack, L.F.W., and Bothwell, M.L. 2010. Attenuation of in situ UV radiation in Mackenzie Delta lakes with varying dissolved organic matter compositions. *Water Resour. Res.* **46**: W09516. doi: [10.1029/2009WR008747](https://doi.org/10.1029/2009WR008747).
- Garneau, M.-E., Roy, S., Lovejoy, C., Gratton, Y., and Vincent, W.F. 2008. Seasonal dynamics of bacterial biomass and production in a coastal arctic ecosystem: Franklin Bay, western Canadian Arctic. *J. Geophys. Res.: Oceans*, **113**: C07S91. doi: [10.1029/2007JC004281](https://doi.org/10.1029/2007JC004281).
- Glaeser, S.P., Grossart, H.-P., and Glaeser, J. 2010. Singlet oxygen, a neglected but important environmental factor: short-term and long-term effects on bacterioplankton composition in a humic lake. *Environ. Microbiol.* **12**: 3124–3136. doi: [10.1111/j.1462-2920.2010.02285.x](https://doi.org/10.1111/j.1462-2920.2010.02285.x). PMID: [20636377](https://pubmed.ncbi.nlm.nih.gov/20636377/).
- Glaeser, S.P., Berghoff, B.A., Stratmann, V., Grossart, H.-P., and Glaeser, J. 2014. Contrasting effects of singlet oxygen and hydrogen peroxide on bacterial community composition in a humic lake. *PLoS ONE*, **9**: e92518. doi: [10.1371/journal.pone.0092518](https://doi.org/10.1371/journal.pone.0092518). PMID: [24667441](https://pubmed.ncbi.nlm.nih.gov/24667441/).
- Goñi, M.A., Ruttenger, K.C., and Eglinton, T.I. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim. Cosmochim. Acta*, **62**: 3055–3075. doi: [10.1016/S0016-7037\(98\)00217-8](https://doi.org/10.1016/S0016-7037(98)00217-8).
- Hedges, J., and Mann, D. 1979. Characterization of plant-tissues by their lignin oxidation-products. *Geochim. Cosmochim. Acta*, **43**: 1803–1807. doi: [10.1016/0016-7037\(79\)90028-0](https://doi.org/10.1016/0016-7037(79)90028-0).
- Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., and Mopper, K. 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* **53**: 955–969. doi: [10.4319/lo.2008.53.3.0955](https://doi.org/10.4319/lo.2008.53.3.0955).
- Henle, E.S., and Linn, S. 1997. Formation, prevention, and repair of DNA damage by iron hydrogen peroxide. *J. Biol. Chem.* **272**: 19095–19098. doi: [10.1074/jbc.272.31.19095](https://doi.org/10.1074/jbc.272.31.19095). PMID: [9235895](https://pubmed.ncbi.nlm.nih.gov/9235895/).
- Hernes, P.J., and Benner, R. 2003. Photochemical and microbial degradation of dissolved lignin phenols: implications for the fate of terrigenous dissolved organic matter in marine environments. *J. Geophys. Res.: Oceans*, **108**: 3291. doi: [10.1029/2002JC001421](https://doi.org/10.1029/2002JC001421).
- Holmes, R.M., Aminot, A., Kerouel, R., Hooker, B.A., and Peterson, B.J. 1999. A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Can. J. Fish. Aquat. Sci.* **56**: 1801–1808. doi: [10.1139/f99-128](https://doi.org/10.1139/f99-128).
- HYDAT. 2015. Water Survey of Canada real time hydrometric data. [Online]. Available from http://www.wateroffice.ec.gc.ca/index_e.html.
- Jeffrey, W.H., Aas, P., Lyons, M.M., Coffin, R.B., Pledger, R.J., and Mitchell, D.L. 1996. Ambient solar radiation-induced photodamage in marine bacterioplankton. *Photochem. Photobiol.* **64**: 419–427. doi: [10.1111/j.1751-1097.1996.tb03086.x](https://doi.org/10.1111/j.1751-1097.1996.tb03086.x).
- Jex, C.N., Pate, G.H., Blyth, A.J., Spencer, R.G.M., Hernes, P.J., Khan, S.J., and Baker, A. 2014. Lignin biogeochemistry: from modern processes to Quaternary archives. *Quat. Sci. Rev.* **87**: 46–59. doi: [10.1016/j.quascirev.2013.12.028](https://doi.org/10.1016/j.quascirev.2013.12.028).
- Judd, K.E., Crump, B.C., and Kling, G.W. 2006. Variation in dissolved organic matter controls bacterial production and community composition. *Ecology*, **87**: 2068–2079. doi: [10.1890/0012-9658\(2006\)87\[2068:VIDOMC\]2.0.CO;2](https://doi.org/10.1890/0012-9658(2006)87[2068:VIDOMC]2.0.CO;2). PMID: [16937646](https://pubmed.ncbi.nlm.nih.gov/16937646/).
- Judd, K.E., Crump, B.C., and Kling, G.W. 2007. Bacterial responses in activity and community composition to photo-oxidation of dissolved organic matter from soil and surface waters. *Aquat. Sci.* **69**: 96–107. doi: [10.1007/s00027-006-0908-4](https://doi.org/10.1007/s00027-006-0908-4).
- Karentz, D., Bothwell, M.L., Coffin, R.B., Hanson, A., Herndl, G.J., Kilham, S.S., Lesser, M.P., Lindell, M., Moeller, R.E., Morris, D.P., Neale, P.J., Sanders, R.W., Weiler, C.S., and Wetzel, R.G. 1994. Impact of UV-B radiation on pelagic freshwater ecosystems: report of working group on bacteria and phytoplankton. *Archiv für Hydrobiologie*, **43**: 31–69.
- Lesack, L.F.W., and Marsh, P. 2010. River-to-lake connectivities, water renewal, and aquatic habitat diversity in the Mackenzie River Delta. *Water Resour. Res.* **46**: W12504. doi: [10.1029/2010WR009607](https://doi.org/10.1029/2010WR009607).

- Lesack, L.F.W., Hecky, R.E., and Marsh, P. 1991. The influence of frequency and duration of flooding on the nutrient chemistry of Mackenzie Delta lakes. Pages 19–36 in P. Marsh and C.S.L. Ommanney, eds. *Northern hydrology: selected perspectives*. Environment Canada, Saskatoon, Sask.
- Lindell, M., Graneli, W., and Tranvik, L. 1995. Enhanced bacterial growth in response to photochemical transformation of dissolved organic matter. *Limnol. Oceanogr.* **40**: 195–199. doi: [10.4319/lo.1995.40.1.0195](https://doi.org/10.4319/lo.1995.40.1.0195).
- Lonborg, C., Nieto-Cid, M., Hernando-Morales, V., Hernandez-Ruiz, M., Teira, E., and Anton Alvarez-Salgado, X. 2016. Photochemical alteration of dissolved organic matter and the subsequent effects on bacterial carbon cycling and diversity. *FEMS Microbiol. Ecol.* **92**: fiw048. doi: [10.1093/femsec/fiw048](https://doi.org/10.1093/femsec/fiw048). PMID: [26940087](https://pubmed.ncbi.nlm.nih.gov/26940087/).
- Louchouart, P., Opsahl, S., and Benner, R. 2000. Isolation and quantification of dissolved lignin from natural waters using solid-phase extraction and GC/MS. *Anal. Chem.* **72**: 2780–2787. doi: [10.1021/ac9912552](https://doi.org/10.1021/ac9912552). PMID: [10905307](https://pubmed.ncbi.nlm.nih.gov/10905307/).
- Lund, V., and Hongve, D. 1994. Ultraviolet irradiated water containing humic substances inhibits bacterial metabolism. *Water Res.* **28**: 1111–1116. doi: [10.1016/0043-1354\(94\)90197-X](https://doi.org/10.1016/0043-1354(94)90197-X).
- Mackay, J.R. 1963. The Mackenzie Delta area, NWT. Geological Survey of Canada, Ottawa, Ont. Misc. Rep. 23.
- Marsh, P., and Hey, M. 1989. The flooding hydrology of Mackenzie Delta lakes near Inuvik, N.W.T., Canada. *Arctic*, **42**: 41–49. doi: [10.14430/arctic1638](https://doi.org/10.14430/arctic1638).
- Matsuoka, A., Ortega-Retuerta, E., Bricaud, A., Arrigo, K.R., and Babin, M. 2015. Characteristics of colored dissolved organic matter (CDOM) in the Western Arctic Ocean: relationships with microbial activities. *Deep Sea Res., Part II: Top. Stud. Oceanogr.* **118**: 44–52. doi: [10.1016/j.dsr2.2015.02.012](https://doi.org/10.1016/j.dsr2.2015.02.012).
- Moran, M.A., and Zepp, R.G. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnol. Oceanogr.* **42**: 1307–1316. doi: [10.4319/lo.1997.42.6.1307](https://doi.org/10.4319/lo.1997.42.6.1307).
- Moran, M.A., Sheldon, W.M., and Sheldon, J.E. 1999. Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States. *Estuaries*, **22**: 55–64. doi: [10.2307/1352927](https://doi.org/10.2307/1352927).
- Moran, M.A., Sheldon, W.M., and Zepp, R.G. 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnol. Oceanogr.* **45**: 1254–1264. doi: [10.4319/lo.2000.45.6.1254](https://doi.org/10.4319/lo.2000.45.6.1254).
- Obernosterer, I., and Benner, R. 2004. Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. *Limnol. Oceanogr.* **49**: 117–124. doi: [10.4319/lo.2004.49.1.0117](https://doi.org/10.4319/lo.2004.49.1.0117).
- Opsahl, S., and Benner, R. 1998. Photochemical reactivity of dissolved lignin in river and ocean waters. *Limnol. Oceanogr.* **43**: 1297–1304. doi: [10.4319/lo.1998.43.6.1297](https://doi.org/10.4319/lo.1998.43.6.1297).
- Osburn, C.L., Morris, D.P., Thorn, K.A., and Moeller, R.E. 2001. Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation. *Biogeochemistry*, **54**: 251–278. doi: [10.1023/A:1010657428418](https://doi.org/10.1023/A:1010657428418).
- Paul, A., Dziallas, C., Zwirnmann, E., Gjessing, E.T., and Grossart, H.-P. 2012. UV irradiation of natural organic matter (NOM): impact on organic carbon and bacteria. *Aquat. Sci.* **74**: 443–454. doi: [10.1007/s00027-011-0239-y](https://doi.org/10.1007/s00027-011-0239-y).
- Pérez, M.T., and Sommaruga, R. 2007. Interactive effects of solar radiation and dissolved organic matter on bacterial activity and community structure. *Environ. Microbiol.* **9**: 2200–2210. doi: [10.1111/j.1462-2920.2007.01334.x](https://doi.org/10.1111/j.1462-2920.2007.01334.x).
- Piccini, C., Conde, D., Perntaler, J., and Sommaruga, R. 2009. Alteration of chromophoric dissolved organic matter by solar UV radiation causes rapid changes in bacterial community composition. *Photochem. Photobiol. Sci.* **8**: 1321–1328. doi: [10.1039/b905040j](https://doi.org/10.1039/b905040j). PMID: [19707620](https://pubmed.ncbi.nlm.nih.gov/19707620/).
- Roland, F., and Cole, J.J. 1999. Regulation of bacterial growth efficiency in a large turbid estuary. *Aquat. Microb. Ecol.* **20**: 31–38. doi: [10.3354/ame020031](https://doi.org/10.3354/ame020031).
- Roland, F., Caraco, N.F., and Cole, J.J. 1999. Rapid and precise determination of dissolved oxygen by spectrophotometry: evaluation of interference from color and turbidity. *Limnol. Oceanogr.* **44**: 1148–1154. doi: [10.4319/lo.1999.44.4.1148](https://doi.org/10.4319/lo.1999.44.4.1148).
- Ruiz-Gonzalez, C., Simo, R., Sommaruga, R., and Gasol, J.M. 2013. Away from darkness: a review on the effects of solar radiation on heterotrophic bacterioplankton activity. *Front. Microbiol.* **4**: 131. doi: [10.3389/fmicb.2013.00131](https://doi.org/10.3389/fmicb.2013.00131). PMID: [23734148](https://pubmed.ncbi.nlm.nih.gov/23734148/).
- Scully, N.M., McQueen, D.J., Lean, D.R.S., and Cooper, W.J. 1996. Hydrogen peroxide formation: the interaction of ultraviolet radiation and dissolved organic carbon in lake waters along a 43–75°N gradient. *Limnol. Oceanogr.* **41**: 540–548. doi: [10.4319/lo.1996.41.3.0540](https://doi.org/10.4319/lo.1996.41.3.0540).
- Scully, N.M., Cooper, W.J., and Tranvik, L.J. 2003. Photochemical effects on microbial activity in natural waters: the interaction of reactive oxygen species and dissolved organic matter. *FEMS Microbiol. Ecol.* **46**: 353–357. doi: [10.1016/S0168-6496\(03\)00198-3](https://doi.org/10.1016/S0168-6496(03)00198-3). PMID: [19719565](https://pubmed.ncbi.nlm.nih.gov/19719565/).
- Shapiro, S., and Wilk, M. 1965. An analysis of variance test for normality (complete samples). *Biometrika*, **52**: 591–611. doi: [10.1093/biomet/52.3-4.591](https://doi.org/10.1093/biomet/52.3-4.591).
- Simon, M., and Azam, F. 1989. Protein content and protein synthesis rates of planktonic marine-bacteria. *Mar. Ecol.: Prog. Ser.* **51**: 201–213. doi: [10.3354/meps051201](https://doi.org/10.3354/meps051201).
- Smith, D.C., and Azam, F. 1992. A simple, economical method for measuring bacterial protein synthesis rates in seawater using ³H-leucine. *Mar. Microb. Food Webs*, **6**: 107–114.
- Spears, B.M., and Lesack, L.F.W. 2006. Bacterioplankton production, abundance, and nutrient limitation among lakes of the Mackenzie Delta (western Canadian arctic). *Can. J. Fish. Aquat. Sci.* **63**: 845–857. doi: [10.1139/f05-264](https://doi.org/10.1139/f05-264).
- Spencer, R.G.M., Stubbins, A., Hernes, P.J., Baker, A., Mopper, K., Aufdenkampe, A.K., Dydá, R.Y., Mwamba, V.L., Mangangu, A.M., Wabakanghanzi, J.N., and Six, J. 2009. Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. *J. Geophys. Res. -Biogeosci.* **114**: G03010.
- Squires, M.M., and Lesack, L.F.W. 2002. Water transparency and nutrients as controls on phytoplankton along a flood-frequency gradient among lakes of the Mackenzie Delta, western Canadian Arctic. *Can. J. Fish. Aquat. Sci.* **59**: 1339–1349. doi: [10.1139/f02-085](https://doi.org/10.1139/f02-085).

- Squires, M.M., and Lesack, L.F.W. 2003a. The relation between sediment nutrient content and macrophyte biomass and community structure along a water transparency gradient among lakes of the Mackenzie Delta. *Can. J. Fish. Aquat. Sci.* **60**: 333–343. doi: [10.1139/f03-027](https://doi.org/10.1139/f03-027).
- Squires, M.M., and Lesack, L.F.W. 2003b. Spatial and temporal patterns of light attenuation among lakes of the Mackenzie Delta. *Freshwater Biol.* **48**: 1–20. doi: [10.1046/j.1365-2427.2003.00960.x](https://doi.org/10.1046/j.1365-2427.2003.00960.x).
- Squires, M.M., Lesack, L.F.W., and Huebert, D. 2002. The influence of water transparency on the distribution and abundance of macrophytes among lakes of the Mackenzie Delta, Western Canadian Arctic. *Freshwater Biol.* **47**: 2123–2135. doi: [10.1046/j.1365-2427.2002.00959.x](https://doi.org/10.1046/j.1365-2427.2002.00959.x).
- Squires, M.M., Lesack, L.F.W., Hecky, R.E., Guildford, S.J., Ramlal, P., and Higgins, S.N. 2009. Primary production and carbon dioxide metabolic balance of a lake-rich arctic river floodplain: partitioning of phytoplankton, epipelton, macrophyte, and epiphyton production among lakes on the Mackenzie delta. *Ecosystems*, **12**: 853–872. doi: [10.1007/s10021-009-9263-3](https://doi.org/10.1007/s10021-009-9263-3).
- Stainton, M.P., Capel, M.J., and Armstrong, F.A.J. 1977. The chemical analysis of freshwater. 2nd ed. Canadian Fisheries and Marine Services Miscellaneous Special Publications 25. Winnipeg, Man. 166 pp.
- Strickland, J.D., and Parsons, T.R. 1972. A practical handbook of seawater analysis. Bulletin of the Fisheries Research Board of Canada, Ottawa, Ont. 310 pp.
- Sulzberger, B., and Durisch-Kaiser, E. 2009. Chemical characterization of dissolved organic matter (DOM): a prerequisite for understanding UV-induced changes of DOM absorption properties and bioavailability. *Aquat. Sci.* **71**: 104–126. doi: [10.1007/s00027-008-8082-5](https://doi.org/10.1007/s00027-008-8082-5).
- Tank, S.E. 2009. Sources and cycling of dissolved organic carbon across a landscape of arctic delta lakes. Ph.D. dissertation, Simon Fraser University, Burnaby, B.C. 217 pp.
- Tank, S.E., Lesack, L.F.W., and Hesslein, R.H. 2009. Northern delta lakes as summertime CO₂ absorbers within the arctic landscape. *Ecosystems*, **12**: 144–157. doi: [10.1007/s10021-008-9213-5](https://doi.org/10.1007/s10021-008-9213-5).
- Tank, S.E., Lesack, L.F.W., Gareis, J.A.L., Osburn, C.L., and Hesslein, R.H. 2011. Multiple tracers demonstrate distinct sources of dissolved organic matter to lakes of the Mackenzie Delta, western Canadian Arctic. *Limnol. Oceanogr.* **56**: 1297–1309. doi: [10.4319/lo.2011.56.4.1297](https://doi.org/10.4319/lo.2011.56.4.1297).
- Vahatalo, A.V., and Wetzel, R.G. 2004. Photochemical and microbial decomposition of chromophoric dissolved organic matter during long (months-years) exposures. *Mar. Chem.* **89**: 313–326. doi: [10.1016/j.marchem.2004.03.010](https://doi.org/10.1016/j.marchem.2004.03.010).
- Vallières, C., Retamal, L., Ramlal, P., Osburn, C.L., and Vincent, W.F. 2008. Bacterial production and microbial food web structure in a large arctic river and the coastal Arctic Ocean. *J. Mar. Syst.* **74**: 756–773. doi: [10.1016/j.jmarsys.2007.12.002](https://doi.org/10.1016/j.jmarsys.2007.12.002).
- Ward, C.P., Nalven, S.G., Crump, B.C., Kling, G.W., and Cory, R.M. 2017. Photochemical alteration of organic carbon draining permafrost soils shifts microbial metabolic pathways and stimulates respiration. *Nat. Commun.* **8**: 772. doi: [10.1038/s41467-017-00759-2](https://doi.org/10.1038/s41467-017-00759-2). PMID: [28974688](https://pubmed.ncbi.nlm.nih.gov/28974688/).
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**: 4702–4708. doi: [10.1021/es030360x](https://doi.org/10.1021/es030360x). PMID: [14594381](https://pubmed.ncbi.nlm.nih.gov/14594381/).
- Wetzel, R.G., Hatcher, P.G., and Bianchi, T.S. 1995. Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. *Limnol. Oceanogr.* **40**: 1369–1380. doi: [10.4319/lo.1995.40.8.1369](https://doi.org/10.4319/lo.1995.40.8.1369).
- Whitehead, R.F., de Mora, S., Demers, S., Gosselin, M., Monfort, P., and Mostajir, B. 2000. Interactions of ultraviolet-B radiation, mixing, and biological activity on photobleaching of natural chromophoric dissolved organic matter: a mesocosm study. *Limnol. Oceanogr.* **45**: 278–291. doi: [10.4319/lo.2000.45.2.0278](https://doi.org/10.4319/lo.2000.45.2.0278).
- Yoon, W.B., and Rosson, R.A. 1990. Improved method of enumeration of attached bacteria for study of fluctuation in the abundance of attached and free-living bacteria in response to diel variation in seawater turbidity. *Appl. Environ. Microbiol.* **56**: 595–600. PMID: [16348135](https://pubmed.ncbi.nlm.nih.gov/16348135/).