

Notes

1. The list of authors will be alphabetical except for the first and last authors.
- 2. Everyone should pay explicit attention to the text regarding their data to verify/confirm what I wrote.**
3. Please let me know if you think of more interesting figures to add to the paper. Keep in mind that this is not a traditional research paper; we shall not interpret the data, just present it.
4. Email us if you have any questions about making the data openly available.
5. To be submitted in [ESSD - Home](#)
6. Manuscript preparation [Submit your manuscript](#).
 - a. The maximum width of figures at 300dpi will be 17.5cm
 - b. The width should not be less than 8 cm.

Figures (figures are updated regularly, please make sure you have the latest version)

https://github.com/PMassicotte/malina_data_paper/raw/master/manuscript/essd/latex/pmassicotte_et_al_2020.pdf

The Malina oceanographic expedition: How do changes in ice cover, permafrost and UV radiation impact biodiversity and biogeochemical fluxes in the Arctic Ocean?

Philippe Massicotte, yyy, zzz and Marcel Babin

Abstract

The MALINA oceanographic campaign was conducted during summer 2009 to investigate the carbon stocks and the processes controlling the carbon fluxes in the Mackenzie River estuary and the Beaufort Sea. During the campaign, an extensive suite of physical, chemical and biological variables was measured across seven shelf-basin transects (south-north) to capture the meridional gradient between the estuary and the open ocean. Key variables such as temperature, absolute salinity, radiance, irradiance, nutrient concentrations, chlorophyll-a concentration, bacteria, phytoplankton and zooplankton abundance and taxonomy, and carbon stocks and fluxes were routinely measured onboard the Canadian research icebreaker *CCGS Amundsen* and from a barge in shallow coastal areas or for sampling within broken ice fields. Here, we present the results of a joint effort to ~~completely~~ and standardize the collected data sets that will facilitate their reuse in further studies of the changing Arctic Ocean. The dataset is available at <https://doi.org/10.17882/75345> (Massicotte2020b).

1. Introduction

The Mackenzie River is the largest source of terrestrial particles entering the Arctic Ocean (see Doxaran2015 and references therein). During the past decades, temperature rise, permafrost thawing, coastal erosion, and increasing river runoff have contributed to intensifying the export of terrestrial carbon by the Mackenzie River to the Arctic Ocean (e.g. Tank2016). Furthermore, the environmental changes currently happening in the Arctic may have profound impacts on the biogeochemical cycling of this exported carbon. On one hand, reduction in sea-ice extent and thickness expose a larger fraction of the ocean surface to higher solar radiations and increase the mineralization of this carbon into atmospheric CO₂ through photo-degradation (Miller1995, Belanger2006). On the other hand, the possible increase in nutrients brought by Arctic rivers may contribute to higher autotrophic production and sequestration of organic carbon (Tremblay2014).

Given that these production and removal processes are operating simultaneously, the fate of arctic river carbon transiting toward the Arctic Ocean is not entirely clear. Hence, detailed studies about these processes are needed to determine if the Arctic Ocean will become a biological source or a sink of atmospheric CO₂. With regard to this question, the MALINA oceanographic expedition was designed to document and get insights on the stocks and the processes controlling carbon fluxes in the Mackenzie River and the Beaufort Sea. Specifically, the main objective of the MALINA oceanographic expedition was to determine how (1) primary production, (2) bacterial activity and (3) organic matter photo-oxidation influence carbon fluxes and cycling in [the Canadian Canadian](#) Beaufort Sea. In this article, we present an overview of an extensive and comprehensive data set acquired from a

coordinated international sampling effort conducted in the Mackenzie River and in the Beaufort Sea in August 2009.

2. Study area, environmental conditions and sampling strategy

2.1 Study area and environmental conditions

The MALINA oceanographic expedition was conducted between 2009-07-30 and 2009-08-25 in the Mackenzie River and the Beaufort Sea systems (Fig. 1). [Figure 2 shows an overview of the sea ice conditions that prevailed during the expedition. In Fig. 2A, a true color image from MODIS Terra reveals how the sea ice pack was fragmented toward the end of the expedition, specially near the 200 meters isobath \(identified by the continuous red line\). On the shelf, the sea ice concentration was higher at the beginning of the expedition. During the four weeks cruise, the ice concentration gradually decreased toward the north \(Fig. 2B\).](#)

The Mackenzie River Basin is the largest in northern Canada and covers an area of approximately 1 805 000 km², which represents around 20% of the total land area of Canada (AbdulAziz2006). Between 1972 and 2016, the average monthly discharge (recorded at the Arctic Red River station) varied between 3296 and 23241 m³ s⁻¹ (shaded area in Fig. [32A](#)). The period of maximum discharge usually occurs at the end of May with decreasing discharge until December, whereas the period of low and stable discharge extends between December and May. During the MALINA oceanographic cruise, the daily discharge varied between 12600 and 15100 m³ s⁻¹ (red segment in Fig. [32A](#), see also Ehn2019). Draining a vast watershed, the Mackenzie River annually delivers on average 2100 Gg C yr⁻¹ and 1400 Gg C yr⁻¹ of particulate organic carbon (POC) and dissolved organic carbon (DOC), respectively, into the Arctic Ocean (Stein2004, Raymond2007). During the expedition conducted onboard the *CCGS Amundsen*, the air temperature recorded by the foredeck

meteorological tower varied between -2 and 11 °C (Fig. 32B). The average air temperature was 3 °C and usually remained above 0 °C.

2.2 General sampling strategy

The sampling was conducted over a network of sampling stations organized into seven transects identified with three digits: 100, 200, 300, 400, 500, 600 and 700 (Fig. 1A). Stations were sampled across the se seven shelf-basin transects (south-north) to capture the meridional gradient between the estuary and the open ocean (except for transect 100 across the mouth of the Amundsen Gulf). Within each transect, station numbers were listed in descending order from south to north. Because our goal was to sample in open waters, the order in which the transects were visited depended on the ice cover. On 2009-07-20, just before the mission, a relatively large portion of the shelf was still covered by sea ice (Fig. 2B). Soon after the beginning of the cruise, most of the shelf area was ice free. The shelf region was not ice free before mid-August. The bathymetry at the sampling stations varied between 2 and 1847 m (394 ± 512 m, mean \pm standard deviation). The stations located in the Beaufort Sea were sampled onboard the Canadian research icebreaker *CCGS Amundsen*. Biological, chemical and optical water column sampling was almost always restricted to the first 400 m of the water column during daytime. Deeper profiles for sampling the whole water column and bottom sediment were usually repeated during nighttime at the same stations. Sediment sampling for fauna and biogeochemistry was conducted at eight stations (110, 140, 235, 260, 345, 390, 680, 690). Two transects (600 and 300) were extended to very shallow waters on the shelf and sampled from either a zodiac or a barge (the bathymetry profiles are shown in Fig. 1B). In the context of this data paper, these two transects were chosen to present an overview of the principal variables measured during the

MALINA campaign. A summary of the various sampling strategies is presented below.

2.3 CTD and rosette deployment

Onboard the *CCGS Amundsen*, a General Oceanic rosette equipped with a CTD (Seabird SBE-911+) was deployed at each sampling station (Fig. 1). The rosette was equipped with twenty-four 12-L Niskin bottles. The rosette was also equipped with a transmissometer sensor (WetLabs), a PAR sensor (Biospherical), an oxygen sensor (SBE-43), a pH sensor (SBE-18), a nitrate sensor (Satlantic ISUS), a fluorometer (Sea Point) and an altimeter (Benthos). A surface PAR (Biospherical) was also installed on the roof of the rosette control laboratory. A 300 kHz, downward-looking L-ADCP (Lowered Acoustic Doppler Current Profiler) and a UVP5 (Underwater Vision Profiler, Hydroptics) were also mounted on the rosette frame providing size and abundance of particles above 200 μm and plankton above 700 μm . The Rosette data processing and quality control are described in detail in Guillot2010. Data processing included the following steps: validation of the calibration coefficients, conversion of data to physical units, alignment correction and extraction of useless data. Oxygen sensor calibration was done using Winkler titrations and salinity data were compared with water samples analyzed with a Guideline 8400B Autosol. The quality control tests were based on the International Oceanographic Commission suggested procedures and the UNESCO's algorithm standards (UNESCO1993). The recorded data were averaged every decibar. The L-ADCP data were processed according to Visbeck2002. On August 5th, the pH sensor was replaced by a chromophoric dissolved organic matter (CDOM) fluorometer (Excitation: 350-460 nm/emission 550 nm HW 40 nm; Dr. Haardt Optik Mikroelektronik). The rosette

depth range was restricted to the first 1000 m when carrying the pH, PAR and nitrates sensors because of their rating.

2.4 Sediment sampling

Surface sediments were sampled using an USNEL box corer (50 x 50 x 40 cm). Box cores with undisturbed surface were subsampled for (a) lipids (Rontani2012a), and isotopic signature of lipid biomarkers (Tolosa2013), stable isotopes (C, N) and manganese and iron oxides (Link2013a) in the 1 cm surface layer, (b) sediment pigments profiles down to 8 cm, and (c) fluxes at the sediment-water interface using on-board microcosms incubation on subcores (10 cm diameter, 20 cm deep) (Link2013a, Link2019). At three stations (140, 345, 390), microfauna abundance and diversity was determined from sieved and conserved samples (Link2019). Samples for (a)-(b) were stored frozen until analysis in the respective home labs.

3. Data quality control and data processing

Different quality control procedures were adopted to ensure the integrity of the data. First, the raw data were visually screened to eliminate errors originating from the measurement devices, including sensors (systematic or random) and errors inherent from measurement procedures and methods. Statistical summaries such as average, standard deviation and range were computed to detect and remove anomalous values in the data. Then, data were checked for duplicates and remaining outliers. The complete list of variables is presented in Table 1.

4. Data description: an overview

The following sections present an overview of a subset of selected variables from the water column. For these selected variables, a brief description of the data collection methods is presented along with general results.

4. 1 Water masses distribution (Fig. 43)

According to previous studies (Carmack1989, Macdonald1989), five main source-water types can be distinguished in the southeastern Beaufort Sea : (1) meteoric water (MW, Mackenzie River plus precipitation), (2) sea-ice meltwater (SIM), (3) winter polar mixed layer (wPML), (4) upper halocline water (UHW, modified Pacific Water with core salinity of 33.1 PSU), (5) and lower halocline water (LHW, water of Atlantic origin). In this study, we used the optimum multiparameter (OMP) algorithm to quantify the relative contributions of the different source water types to the observed data (<https://omp.geomar.de/>). We used salinity, TA, and $\delta^{18}\text{O}$ as conservative tracers as well as temperature and O_2 concentration as non-conservative tracers, to constrain the water mass analysis, following Lansard2012. Briefly, the method finds the best fitting fraction (x) of $(n+1)$ source water types that contribute to the (n) observed values of the selected tracers in a parcel of water via a solution of an overdetermined system of linear equations that minimizes the residual error. Boundary conditions were applied to the method to guarantee that all fractions calculated were positive and that the sum of all fractions was 100% (mass conservation).

During MALINA, the Mackenzie Shelf was for the most part entirely ice-free, and the ice-pack was located beyond the shelf break (Fig. 2). The transition zone was characterized by different expanses of drifting sea-ice. Significant contributions of Meteoric Water (> 25%) to the surface mixed layer (SML) were only observed close to the Mackenzie River mouth and on the inner shelf (Fig. 43). A relatively small

fraction of sea-ice meltwater was detected beyond the shelf break, mostly along the transect 600. Below the SML, the wPML was the predominant water mass down to 100 m depth. The UHW extends from the interior ocean onto the outer shelf from 120 to 180 m of depth. Relatively high fractions of UHW were also found at 50 m depth along the Mackenzie and Kugmallit Canyons, which are recognized sites of enhanced shelf-break upwelling caused by wind- and ice-driven ocean surface stresses. Below 200 m depth, the LHW with an Atlantic origin was always the prevailing water mass.

4.2 Temperature and salinity from the CTD (Fig. 54)

Temperature and salinity for the first 100 m of transects 600 and 300, the two transects originating from the Mackenzie delta, are presented in Fig. 54. They confirm what was found by the water mass analysis (section 4.1): most of the freshwater is coming from the western part of the Mackenzie delta. This is also in accordance with many studies that documented that during the summer, a combination of ice melting and river runoff was generating a highly stratified surface layer (Carmack2002, Forest2013). The signature of an eddy may be observed at 75 m in the salinity data at 70° N, approximately 70 km from shore (Fig. 54B).

4.3 Underwater bio-optical data (Figs. 65-76)

4.3.1 Inherent Optical Properties (IOPs) profiling from the ship, the barge and the zodiac (Fig. 65)

The total, non-water, spectral absorption (a), attenuation (c) and backscattering coefficients (b_b) were measured using a AC9 attenuation and absorption meter and a BB9 scattering meter (WetLabs), a HydroScat-6P and a-Beta sensors (HOBI Labs)

either attached to the CTD-Rosette frame onboard the CCGS Amundsen or deployed separately from the barge or the Zodiac tender. These devices were using either 10 cm or 25 cm optical path lengths, depending on the turbidity of the water sampled. Detailed information about the deployment and the data processing of the IOP data can be found in Doxaran2012.

Fig. 65 shows cross-sections of the total absorption and backscattering coefficients at 440 nm ($a(440)$ and $b_b(440)$) derived as $b_b = b_{bp} + b_{bw}$, where b_{bw} is the backscattering coefficient of pure seawater (Morel1974). Both $a(440)$ and $b_b(440)$ showed the same patterns along the transects 600 and 300. Close to the estuary, higher absorption (Fig. 65A) and total scattering (Fig. 65B) can be observed at the surface, likely reflecting the important quantities of dissolved and particulate organic matter delivered by the Mackenzie River. Higher values are also observed in transect 600 compared to transect 300, which is further away from the mouth of the Mackenzie River. Both $a(440)$ and $b_b(440)$ decreased rapidly toward higher latitudes where the water of the Mackenzie River mixes with seawater from the Beaufort Sea.

4.3.2 Particulate and CDOM absorption (Fig. 76)

Chromophoric dissolved organic matter absorption (a_{CDOM}) was measured from water samples filtered with 0.2 μm GHP filters (Acrodisc Inc.), using an UltraPath (World Precision Instruments Inc.) between 200 and 735 nm. In most cases, a 2 meters optical path length was used for the measurement, except for coastal waters near the Mackenzie River mouth (Fig. 1) where a 0.1 meters optical path length was used. Particulate absorption (a_p) was measured using a filter-pad technique modified from Rottgers2012. Briefly, sea-water was filtered through a 25 mm Whatman GF/F (glass-fiber filters) less than 3h after sampling. Filters were

placed in the center of a 150 mm integrating sphere equipped with a handmade Spectralon filter holder. The spectral optical density ($OD(\lambda)$) of the particles retained on the filter was then measured using a PerkinElmer Lambda-19 spectrophotometer, ~~from 300 to 800 nm~~ from 300–800 nm at 1 nm resolution. More details about particulate and dissolved absorption measurements can be found in Rottgers2012, Belanger2013b and Matsuoka2012.

Examples of a_{CDOM} spectra measured at the surface for the northernmost and the southernmost stations of transects 600 and 300 are presented in Fig. [76A](#). The marked influence of the organic matter of terrestrial origin can be observed for the stations located at the mouth of the Mackenzie River (697 and 398). Because the organic matter delivered by the river is highly humic and ~~colored~~ coloured, the absorption at 254 nm was approximately 15 times higher at the southern shelf stations for both transects— compared to the northern stations (620 and 320). Likewise, the specific UV absorbance of dissolved organic carbon at 254 nm ($SUVA_{254}$), a metric commonly used as a proxy for assessing both chemical (weishaar2003, westerhoff2004) and biological reactivity (berggren2009, asmala2013) of the DOM pool in natural aquatic ecosystems, decreased rapidly along the south-north gradient in both transects 600 and 300 (Fig. [76C](#)). This observation is in accordance with a previous study that showed that $SUVA_{254}$ was higher in inland ecosystems due to elevated lateral connectivity with surrounding terrestrial landscape and organic matter inputs from the tributaries (Massicotte2017). The decrease in $SUVA_{254}$ toward north stations (Fig. [76C](#)) suggests that terrestrially-derived DOM transiting toward the ocean is gradually degraded into smaller and more refractory molecules.

Particulate absorption spectra (a_p) for the northernmost and the southernmost stations of transects 600 and 300 are presented in Fig. 76B. Particulate absorption at the stations located in the estuary (697 and 398) was much higher than that measured at the open water stations (620 and 320). For instance $a_p(443)$ measured at stations 620 (0.03 m^{-1}) and 697 (8.62 m^{-1}), the northernmost and the southernmost stations of transects at the mouth of the Mackenzie River, shows that a_p decreases rapidly along the latitudinal axes. This can be possibly explained because the drained organic and inorganic material from the surrounding landscape of the Mackenzie's watershed is degraded or sediment rapidly as it is transferred to the ocean.

4.3.3 Other optical measurements and radiometric quantities

Other optical instruments were attached to the rosette sampler. These include a transmissometer (Wetlabs C-Star, path 25 cm) for beam attenuation measurement, a chlorophyll fluorometer (SeaPoint) and a CDOM fluorometer (Optic & Mikroelektronik, Germany, see Amon2003). Additionally, a LISST-100X (Laser In Situ Scattering and Transmissometry, Sequoia Scientific) was attached to the rosette and provided beam attenuation (532 nm) and forward light scattering measurements at 32 angles from which particle size distribution was estimated. Various optical measurements were also made in the laboratory to determine other IOPs. These include the absorption of ~~colored~~ dissolved (a_{CDOM}) and particulate (a_p) organic matter, the absorption coefficients of non-algal particles (a_{NAP}) and phytoplankton (a_{PHI}). Apparent optical properties (AOPs) measurements included light transmittance (T), photosynthetically available radiation (PAR), downward irradiance (E_d), upwelled radiance (L_u) and global solar irradiance (E_s). The latter three radiometric quantities were measured simultaneously using a

Compact-Optical Profiling System (C-OPS) manufactured by Biospherical Instruments Inc. (San Diego, California) that was deployed during MALINA Leg2b. The principal data products obtained from the C-OPS data were the diffuse attenuation coefficient (K_d) plus the water-leaving radiance (L_w) including all normalized forms. Detailed methodology and results derived from C-OPS measurements can be found in Doxaran2012, Antoine2013, Belanger2013b, and Hooker2013.

4.4 Nutrients (Fig. 87)

Samples for nitrate, nitrite, soluble reactive phosphorus and silicate determination were collected into 20 mL polyethylene flasks, immediately poisoned with mercuric chloride (Kirkwood1992), and stored for subsequent laboratory analysis according to Raimbault1990 and Aminot2007. Ammonium concentrations (40 mL collected into 60 mL polycarbonate tubes) were measured onboard using the sensitive method of Holmes1999 having a detection limit of 5 nmoles L⁻¹. Samples for organic matter determination were collected into 50-mL Glass Schott bottles, immediately acidified with 100 µl of 0.5N H₂SO₄ and stored in the dark at 5 °C. Dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined at the laboratory using the wet-oxidation procedure according to Raimbault1999a.

Nitrate levels were always very low at the surface, with concentration generally lower than 0.01 µmoles L⁻¹, except in the Mackenzie plume (Fig. 87). It is interesting to note that nitrate was never entirely depleted, and some traces (0.005 to 0.01 µmoles L⁻¹) were always detectable in surface waters (Fig. 87A). Ammonium distribution showed the same pattern. Even if concentrations were very low (generally < 0.03 µmoles L⁻¹), this nutrient, like nitrate, was always detected,

suggesting that in situ sources of nitrate and ammonium exist offshore, certainly due to biological processes. Phosphate concentrations showed the opposite distribution (Fig. 87B). Despite nitrogen depletion, surface waters were always phosphate replete. ~~The highest~~^{Highest} concentrations, around $0.5 \mu\text{moles L}^{-1}$, were observed far from Mackenzie's mouth, revealing a clear west-east gradient. The silicate distribution was similar to that of nitrate. But Surface waters were always silicate-repleted with concentrations largely above the detection limit ($> 4 \mu\text{moles L}^{-1}$). The impact of the Mackenzie River was clear, close to the coast for inorganic nutrients and farther offshore for dissolved organic nutrients. A quarter of the estimated annual nutrient supply by the Mackenzie River occurred during July-August. The supply of DON was eight times larger than that of nitrate-N. By contrast, the amount of DOP supplied was only 2.5 times higher than the amount of phosphate (Tremblay2014). The Mackenzie River enriched the western Canadian Beaufort Shelf with inorganic and organic N, potentially supporting most of the primary production, but not with phosphate or ammonium. Large deliveries of N relative to P by rivers relax coastal communities from N limitation, allowing them to tap into the excess P originating from the Pacific Ocean. Then, river inputs locally rectified the strong regional deficit of inorganic N, i.e. negative N^* (Tremblay2014).

4.5 Dissolved Organic Carbon (DOC), Total Dissolved Nitrogen (TDN), Total Hydrolyzable Amino Acids (THAA), and Total Dissolved Lignin Phenols (TDLP₉) (Fig. 98)

Water samples were collected at selected stations and water masses for analyses of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), total hydrolyzable amino acids (THAA), and total dissolved lignin phenols (TDLP₉) concentrations. Samples for DOC, TDN, and THAA were gravity-filtered from Niskin bottles using

pre-combusted ~~glass-fibre~~ (GF/F) filters (0.7 μm pore size) and stored frozen (-20 °C) immediately after collection in pre-combusted borosilicate glass vials (Shen2012). Samples for TDLP₉ analysis (between 1 and 10 L) were gravity-filtered from Niskin bottles using Whatman Polycap AS cartridges (0.2- μm pore size), acidified to pH between 2.5 and 3 with sulfuric acid and extracted within a few hours using C-18 cartridges (Louchouart2000, Fichot2013). The C-18 cartridges were stored at 4 °C until elution with 30 mL of methanol (HPLC-grade), and the eluent was stored in sealed, pre-combusted glass vials at -20 °C until analysis. DOC and TDN concentrations were measured by high-temperature combustion using a Shimadzu total organic carbon analyzer (TOC-V) equipped with an inline chemiluminescence nitrogen detector and an autosampler (Benner1993). Blanks were negligible and the coefficient of variation between injections of a given sample was typically less than 1%. Analysis of a deep seawater reference standard (University of Miami) every sixth sample was used to check the accuracy and consistency of measured DOC and TDN concentration. Total hydrolyzable amino acids (THAA) were determined as the sum of 18 dissolved amino acids using an Agilent High-Performance Liquid Chromatography system equipped with a fluorescence detector (excitation: 330 nm; emission: 450 nm). Samples (100 μL) of filtered seawater were hydrolyzed with 6 mol L⁻¹ hydrochloric acid using a microwave-assisted vapour phase method (Kaiser2005). Free amino acids liberated during the hydrolysis were separated as o-phthalaldehyde derivatives using a Licrosphere RP18 or Zorbax SB-C18 column (Shen2012). Detailed methodological information can be found in Fichot2013 and Shen2012.

Surface DOC concentrations along the transects 300 and 600 behaved approximately conservatively with salinity, decreasing from 458 $\mu\text{mol L}^{-1}$ in the Mackenzie River end-member (salinity = 0.2 PSU) to 123 $\mu\text{mol L}^{-1}$ at a salinity of

26.69 PSU (Fig. 98A). DOC concentrations in surface waters further decreased to minimum values of $\sim 66 \mu\text{mol L}^{-1}$ offshore (Fichot2011). Concentrations generally increased by a few $\mu\text{mol L}^{-1}$ in the upper halocline relative to surface values, but then generally decreased with depth, reaching 53-57 $\mu\text{mol L}^{-1}$ in the lower halocline, and $\sim 43\text{-}50 \mu\text{mol L}^{-1}$ in deep water-masses (depth > 1000 m). Similar to DOC, surface TDLP₉ concentrations along transects 600 and 300 behaved approximately conservatively with salinity, decreasing from $\sim 93\text{-}96 \text{ nmol L}^{-1}$ in the Mackenzie River end-member (salinity = 0.2 PSU) to $\sim 12 \text{ nmol L}^{-1}$ at a salinity of 26.69 PSU (Fig. 98B). Surface concentrations reached minimum values of $\sim 2.5 \text{ nmol L}^{-1}$ offshore (Fichot2016). TDLP₉ concentrations generally decreased with depth, reaching minimum values of $< 1.5 \text{ nmol L}^{-1}$ below the halocline. Surface concentrations of THAA along the transects 600 and 300 decreased from 576 nmol L^{-1} in the Mackenzie River end-member (salinity = 0.2 PSU) to 317 nmol L^{-1} at a salinity of 26.69 PSU (Fig. 98C). Unlike DOC and TDLP₉, concentrations of THAA did not follow a conservative mixing line along the salinity gradient. Elevated concentrations of THAA were observed in mid-salinity waters in both transects, suggesting plankton production in these regions. In comparison, THAA concentrations in the slope and basin waters were lower and decreased with depth, reaching minimal values of $\sim 70 \text{ nmol L}^{-1}$ below the halocline (Shen2012).

4.6 Pigments (Fig. 109)

Water samples (volumes between 0.25 L and 2.27 L) were filtered through glass fibre GF/F filters (25 mm diameter, particle retention size 0.7 μm). They were immediately frozen at $-80 \text{ }^{\circ}\text{C}$, transported in liquid nitrogen, then stored at $-80 \text{ }^{\circ}\text{C}$ until analysis on land. Samples were extracted in 3 mL HPLC-grade methanol for two hours minimum. After sonication, the clarified extracts were injected (within 24

hours) onto a reversed-phase C8 Zorbax Eclipse column (dimension: 3 x 150 mm, 3.5 μm pore size). The instrumentation comprised an Agilent Technologies 1100 series HPLC system with diode array detection at 450, 667 and 770 nm of phytoplankton pigments (carotenoids, chlorophylls *a*, *b*, *c* and bacteriochlorophyll *a*). A total of 22 pigments were analyzed and quantified. Details of the HPLC analytical procedure can be found in Ras2008.

As illustrated in Fig. 910, the phytoplankton biomass, indicated by total chlorophyll-*a* concentrations, was the highest at the coast (up to 3.5 mg m^{-3}), decreasing offshore (to about 0.010 mg m^{-3}) with the formation of a Subsurface Chlorophyll Maximum (SCM) around 60 m. In terms of biomass integrated over the sampled depth, values range from 6.2 and 8.9 mg m^{-2} at the coast to 14.3 and 13.2 mg m^{-2} offshore for transects 300 and 600, respectively. In general, the most predominant accessory pigment was fucoxanthin, indicating that diatoms constitute a large proportion of the phytoplankton assemblage. However, in offshore waters and around the SCM, 19'-hexanoyloxyfucoxanthin concentrations were equivalent or sometimes higher than fucoxanthin, suggesting that, in these waters, haptophytes can predominate over diatoms. Other pigments such as chlorophyll-*b* and prasinoxanthin, suggest the presence of green algae, and probably micromonas-type cells, especially in coastal waters and at the surface. For more detailed information, see Coupel2015 who used this dataset applied to the CHEMTAX (CHEMical TAXonomy) chemotaxonomic tool to assess the distribution of phytoplankton communities.

4.7 Phytoplankton abundance and diversity (Figs. 110-124)

The abundance of the eukaryotic pico- and nano-phytoplankton was measured by flow cytometry onboard the Amundsen with a FACS Aria Instrument (Becton Dickinson, San Jose, CA, USA) following the protocol of Marie1999.

In transect 300 and 600 (Fig. 119), the abundance of pico- and nano-phytoplankton reached maximal values around 5000 and 3000 cells mL⁻¹ respectively. On transect 600, pico-eukaryotes higher abundances were restricted to the surface layer with a 5 to 10-fold drop at 30 m. In contrast, nano-eukaryotes formed clear deep maxima, especially at stations 610 and 680. On transect 300, pico-eukaryotes were also abundant in the surface at the more off-shore stations. Still, they decreased sharply near-shore, while nano-eukaryotes' highest concentrations were near the river mouth, linked to high diatom concentrations (Balzano2012a). The composition of eukaryotic phytoplankton was determined with two different approaches. We isolated 164 cultures using a range of techniques (single-cell isolation, serial dilution, flow cytometry sorting) that have been characterized morphologically and genetically (Balzano2012b, Balzano2017) and deposited to the Roscoff Culture Collection (www.roscoff-culture-collection.org). Among these cultures, several new species have been discovered such as the new species of green algae *Mantoniella beaufortii* (Yau2020) or the diatom *Pseudo-nitzschia arctica* (Percopo2016), but more await description in particular among Pelagophyceae. One of the strains isolated (RCC2488, *Chlamydomonas malina* nomen nudum) has been recently found to be suitable for biotechnology applications (Morales-Sanchez2020). We also used molecular approaches by sorting pico- and nano-eukaryotic communities and characterizing their taxonomic composition by TRFLP (terminal-restriction fragment length polymorphism) analysis and cloning/sequencing of the 18S ribosomal RNA gene (Balzano2012a). While the pico-phytoplankton was dominated by the species *Micromonas polaris*, the nano-phytoplankton was more diverse and dominated by

diatoms mostly represented by *Chaetoceros neogracilis* and *C. gelidus*, with the former mostly present at surface waters and the latter prevailing in the SDCM (Balzano2012a). Furthermore, *C. neogracilis* sampled from the Beaufort Sea consists of at least four reproductively isolated genotypes (Balzano2017). The comparison between the taxonomy of natural communities and isolated cultures (Fig. 124) reveals that although we succeeded at isolating some dominant species in the field such as *M. polaris*, *C. neogracilis* and *C. gelidus* some other important taxa such as the diatom *Fragiliaropsis* or the haptophyte *Chrysochromulina* were not recovered.

4.8 Carbon fluxes (Figs. 132-154)

In the context of climate change, the main objective of the MALINA oceanographic expedition was to determine how (1) primary production, (2) bacterial activity and (3) photo-degradation influence carbon fluxes and cycling of organic matter in the Arctic. In the following sections, we present an overview of these processes [in the water column](#) that are detailed in Ortega-Retuerta2012a, Xie2012, Tremblay2014, and [refer to Link2013aa, Tolosa2013 and Rontani2012a for the related processes at the sediment-water interface](#).

4.8.1 Phytoplankton primary production (Fig. 132)

At each station, when productivity was quantified, rates of carbon fixation (primary production) were determined using a ^{13}C isotopic technique (Raimbault2008). For this purpose, three 580 mL samples were collected at minimum sun elevation or before sunrise at 6-7 depths between the surface and the depth where irradiance was 0.3% of the surface value and poured into acid-cleaned polycarbonate flasks. Incubations were carried out immediately following the tracer addition in an on-deck incubator. This consisted of 6-7 opaque boxes, each with associated neutral and blue screens, allowing around 50%, 25%, 15%, 8%, 4%, 1% and 0.3% light

penetration. At five stations, incubations were also performed *in situ* on a drifting rig with incubation bottles positioned at the same depth where samples for on-deck incubations were collected. After 24h, samples were filtered through pre-combusted (450 °C) Whatman GF/F filters (25-mm diameter). After filtration, filters were placed into 2 mL glass tubes, dried for 24h in a 60 °C oven and stored dry until laboratory analysis. These filters were used to determine the final ^{13}C enrichment ratio in the particulate organic matter on an Integra-CN mass spectrometer. Filtrates were poisoned with HgCl_2 and stored to estimate ammonium regeneration and nitrification rates. The isotopic enrichment of particulate organic matter and dissolved NH_4^+ and NO_3^- at the end of incubations were used to calculate net C and N uptake and the recycling of NH_4^+ and NO_3^- (Raimbault1999).

Daily rates of primary production at the surface were generally very low across the survey area, ranging from $0.1 \text{ mg C m}^{-3} \text{ d}^{-1}$ offshore to a maximum of $545 \text{ mg C m}^{-3} \text{ d}^{-1}$ in Kugmallit Bay (Fig. 132) associated with the Mackenzie River discharge (Tremblay2014). Ammonification and nitrification followed the same coastal-offshore pattern with rates driving most, if not all, of the NH_4^+ and NO_3^- consumption in the surface layer. Primary production was generally maximum at the surface, but high rates were often observed at depth in the nitracline layer associated with a chlorophyll maximum. The range of uptake rates of ammonium at the surface generally overlapped with the range of nitrate uptake rates. Nitrate uptake below the surface amounted to 40–60% of total nitrogen uptake, a proportion that is approximately twice greater than at the surface (Ardyna2017).

Nitrification and ammonium regeneration were detectable over the whole water column ranging from 2 to $20 \text{ nmoles L}^{-1} \text{ d}^{-1}$. The highest rates were generally located at the base of the euphotic zone, leading to the formation of subsurface

ammonium and nitrite maximum layers. Surface communities and especially the accumulation of large cells thrived mostly on regenerative NH_4^+ and their reliance on NO_3^- increased with depth to reach a maximum in the subsurface chlorophyll maximum, where substantial levels of primary production occurred (Ardyna2017). This is consistent with Ortega-Retuerta2012a who reported elevated bacterial abundance and bacterial production rates in association with photoammonification of riverine organic matter (LeFouest2013). Nitrification accounted for a variable and sometimes a large share of the NO_3^- demand, consistent with the persistence of trace amounts of NO_3^- at the surface. Collectively, the data indicate that the coastal Beaufort Sea is an active regenerative system during summer, probably fuelled by large pools of organic matter brought by rivers. Consequently, new production was very low and often close to zero in the 0-40 m layer. But high nitrate uptake rates can be observed at depth (Station 135), often associated with high primary production located in the chlorophyll maximum layer being the place of significant new production. The impact of the Mackenzie River on shelf productivity during summer is moderate and associated mostly with localized nutrient recycling in the nearshore estuarine transition zone (Tremblay2014).

4.8.2 Photo-degradation (Fig. 143)

4.8.2.1 CO and CO₂ production from dissolved organic matter (Fig. 143A)

Surface water samples were gravity-filtered upon collection through a pre-cleaned Pall AcroPak 1000 filtration capsule sequentially containing 0.8 and 0.2 μm polyethersulfone membranes. Filtered water was stored in clear-glass bottles at 4 °C in darkness. CO photoproduction rates (P_{CO} , $\text{nmol L}^{-1} \text{h}^{-1}$) were determined aboard the *CCGS Amundsen* immediately after sample collection, whereas CO₂ photoproduction rates (P_{CO_2} , $\text{nmol L}^{-1} \text{h}^{-1}$) were measured in a land-based laboratory

in Rimouski, Québec within three months of sample collection. The sample-pretreatment and irradiation procedures followed those reported previously (Belanger2006, Song2013). Briefly, after minimizing the background CO and CO₂ concentrations, samples were transferred into combusted, quartz-windowed cylindrical cells (CO: i.d.: 3.4 cm, length: 11.4 cm; CO₂: i.d.: 2.0 cm, length: 14 cm) and irradiated at 4 °C using a SUNTEST XLS+ solar simulator equipped with a 1.5-kW xenon lamp. The radiation emitted from the solar simulator was screened with a Schott long-pass glass filter to remove UV radiation < 295 nm. The irradiations lasted for 10 min to 2 h for CO and 24 to 48 h for CO₂. The photon flux reaching the quartz windows of the cells was measured to be 835 μmol m⁻² s⁻¹ for CO and 855 μmol m⁻² s⁻¹ for CO₂ over the wavelength range from 280 to 500 nm.

Both P_{CO₂} and P_{CO} increased landward, with the difference between the most and least saline samples reaching a factor of ~5 along transect 300 and ~8 along transect 600 for P_{CO₂} and of ~7 along transect 600 for P_{CO} (Fig. 143A). This landward increase in P_{CO₂} and P_{CO} was due principally to the parallel augmentation in CDOM absorption, as demonstrated by the linear relationships between these two rates with CDOM absorption: P_{CO₂} = 279.1*a_{CDOM}(412) - 17.0 (R² = 0.964, n = 9) and P_{CO} = 17.5*a_{CDOM}(412) - 4.8 (R² = 0.966, n = 7), where a_{CDOM}(412) (m⁻¹) is the CDOM absorption coefficient at 412 nm published previously (Song2013, Taalba2013). The irradiance-normalized P_{CO₂}/P_{CO} ratio gradually decreased landward along transect 600, from 23.5 at station 691 to 16.2 at station 697, suggesting that the near-shore samples were more efficient at CO photoproduction relative to CO₂ photoproduction than the shelf samples. The P_{CO₂}/P_{CO} ratios at the two stations on transect 300 were, however, similar (18.9 for station 394 and 20.1 for station 396). Combining the P_{CO₂}/P_{CO} ratios from both transects arrives at an average ratio of 19.8 (± 2.5 SD), with a rather small relative standard deviation of 12.5%.

It should be pointed out that extrapolating the lab-determined CO₂ and CO photoproduction rates to the sampling area is practically infeasible due to the very different laboratory and real-environmental conditions. For instance, the water column in the Mackenzie estuary and shelf areas contains large amounts of particles (Doxaran2012), which are also optically active, whereas the irradiated samples were particles-free. Furthermore, the photoproduction rates in the water column would decrease rapidly with depth because of the strong light attenuation by CDOM and particles, while the laboratory radiation at best simulated the radiation of the top 1-2 cm layer of the water column even without considering the constant vs. varying irradiance from the solar simulator and natural sunlight, respectively. To estimate the areal photoproduction rates in the water column from lab-derived data often require coupled optical-photochemical modelling that incorporates spectral apparent quantum yields of the photoproduct of interest (Belanger2006, Xie2009, Fichot2010). Using this approach and CO data from the Malina cruise, Song2013 estimated a yearly-averaged areal CO photoproduction rate of 9.6 μmol m⁻² d⁻¹ in the Mackenzie estuary and shelf areas, which implies a yearly-averaged areal CO₂ photoproduction rate of 191.1 μmol m⁻² d⁻¹ based on the average P_{CO₂}/P_{CO} ratio of 19.8 obtained above. Aggregating the CO₂ and CO rates gives a total photomineralization rate of 199.7 μmol C m⁻² d⁻¹.

4.8.2.2 Autoxidation of suspended particulate material (Fig. 143B)

Water samples were filtered immediately after collection through a pre-combusted glass fibre filter (Whatman GF/F, 0.7 μm) under a low vacuum. The filters were frozen immediately at -20 °C until analysis and transported to the laboratory. Treatment of the filters involved NaBH₄ reduction and classical alkaline hydrolysis (Rontani2012). Reduction of labile hydroperoxides to alcohols is essential for

estimating the importance of autoxidative degradation in natural samples by gas chromatography-electron impact mass spectrometry (GC-EIMS) (Marchand2001). Autoxidative degradation of terrigenous particulate organic matter (POM) discharged by the Mackenzie River was monitored thanks to specific oxidation products of sitosterol (main sterol of higher plants) and dehydroabietic acid (a component of conifers).

The autoxidation state of these tracers increases strongly at the offshore stations (Fig. 143B) (reaching 89 and 86% at station 6980 and station 380, respectively, in the case of sitosterol, see Rontani2014). These results allowed us to demonstrate that in surface waters of the Beaufort Sea, autoxidation strongly affects vascular plant lipids and probably also the other components of terrestrial OM delivered by the Mackenzie River. Initiation of these abiotic oxidation processes was attributed to the involvement of some enzymes producing radicals (lipoxygenases) present in higher plant debris and whose activity is enhanced at high salinities (Galeron2018).

4.8.2.3 Bacterial production and respiration (Fig. 154A-154B)

Bacterial production (BP, assessed by ^3H -leucine incubations, $n = 171$), and respiration (BR, assessed by changes in O_2 by Winkler titration, $n = 13$), were measured from surface waters to 200_m waters at 44 sampling locations. Bacterial production ranged from 8.8 to 7078 $\mu\text{g C m}^{-3} \text{d}^{-1}$ and showed a marked decreasing pattern from the mouth of the Mackenzie to the open Beaufort Sea and from the surface to deep waters (Fig. 154). Temperature and labile dissolved organic matter (indicated as dissolved amino acids) controlled BP variability (Ortega-Retuerta2012a), and the nitrogen limitation of surface BP during the summer period was demonstrated experimentally (Ortega-Retuerta2012b). BR ranged from 5500 to 45500 $\mu\text{g C m}^{-3} \text{d}^{-1}$, leading to a bacterial growth efficiency of 8% on

average. BP and BR were low with respect to lower latitudes but within the range of those in polar ecosystems, suggesting the role of low temperatures driving carbon fluxes through bacteria (Kirchman2009). Bacterial carbon demand (BP + BR), which averaged $21500 \pm 14900 \mu\text{g C m}^{-3}$, was higher than primary production in the whole study area, indicating that the Mackenzie River platform and the Beaufort Sea are net heterotrophic during summer. This may suggest a temporal decoupling between carbon fixation and remineralization in the area.

4.8.3 Bacterial diversity (Fig. 154C)

Spatial variations in bacterial community structure were explored in surface waters from the Mackenzie River to the open Beaufort Sea ($n = 20$). By using 16S rRNA-based analysis, we investigated both particle-attached (PA, $> 3 \mu\text{m}$ size fraction) and free-living bacteria (FL, size fraction between 3 and $0.2 \mu\text{m}$) along a river to open sea transect. Multivariate statistical analysis revealed significant differences in community structure between the river, coastal and open sea waters, mainly driven by salinity, particle loads, chlorophyll a, and amino acid concentration (Ortega-Retuerta2013). Bacterial communities differed between PA and FL fractions only in open sea stations, likely due to the higher organic carbon content in particles with respect to particles from the river and coast, which were enriched in minerals. Alphaproteobacteria dominated in FL open sea samples, while the PA fraction was mainly composed of Gammaproteobacteria, Opitutae (Verrucomicrobia) and Flavobacteria. The coastal and river samples were dominated by Betaproteobacteria, Alphaproteobacteria, and Actinobacteria in both the PA and FL fractions (Fig. 154C). These results highlight the importance of particle quality, a variable that is predicted to change along with global warming, in influencing

bacterial community structure, and thus likely altering the biogeochemical cycles that they mediate.

5. Conclusions

The comprehensive data set assembled during the MALINA oceanographic cruise has given unique insights on the stocks and the processes controlling carbon fluxes in the Mackenzie River and the Beaufort Sea. In this paper, only a handful of variables ~~have~~ been presented. The reader can find the complete list of measured variables in Table 1, all of which are also fully available in the data repository. The uniqueness and comprehensiveness of this data set offer more opportunities to reuse it for other applications.

6. Code and data availability

Metadata and detailed information about measurements can be found in associated MALINA papers presented in Table 1. Data is provided as a collection of comma separated values (CSV) files that are regrouping measurements associated with a particular type of measure. To aid the user to merge these files, there is a lookup table file called stations.csv that can serve as a table to join all the data together based on date, time, station, cast, depth, longitude and latitude. Additionally, original ~~The raw~~ data provided by all the researchers, as well as additional ~~–~~metadata, are available on the LEFE-CYBER repository (http://www.obs-vlfr.fr/proof/php/malina/x_datalist_1.php?xxop=malina&xxcamp=malinaPROOF / LEFE CYBER CRUISE). The processed and tidied version of the data is hosted at SEANOE (SEA scieNtific Open data Edition)

under the CC-BY license (<https://www.seanoe.org/data/00641/75345/>, Massicotte2020b). The raw UVP5 large particulate data and images are all available from the EcoPart/Ecotaxa website (<https://ecotaxa.obs-vlfr.fr/part/>). ~~Detailed metadata are associated with each file, including the principal investigator's contact information.~~ Note that Table 1 also indicates if the measured variables are directly available in the data files or by contacting responsible principal investigators. For specific questions, please contact the principal investigator associated with the data (see Table 1). The code used to produce the figures and the analysis presented in this paper is available under the GNU GPLv3 ~~license~~ (<https://doi.org/10.5281/zenodo.4518943>).

Acknowledgments

This work is dedicated to the memory of Captain Marc Thibault (commanding officer of the *CCGS Amundsen*, Canadian Coast Guard), Daniel Dubé (CCGS Amundsen helicopter pilot, Transport Canada) and Dr. Klaus Hochheim (research scientist at the Centre for Earth Observation Science, University of Manitoba) who died in the *CCGS Amundsen* helicopter crash on the evening of 2013-09-09 in the icy waters of McClure Strait in the Canadian Arctic. We are very grateful to the captain (Marc Thibault) and crews of the Canadian research icebreaker *CCGS Amundsen* during the Malina cruise in the Beaufort Sea. This study was conducted as part of the Malina scientific program funded by ANR (Agence Nationale de la Recherche), INSU-CNRS (Institut National des Sciences de l'Univers - Centre National de la Recherche Scientifique), CNES (Centre National d'Études Spatiales) and ESA (European Space Agency). The International Atomic Energy Agency is grateful to the Government of the Principality of Monaco for the support provided to its Environment Laboratories.