Insights into Water Mass Circulation and Origins in the Central Arctic Ocean from in-situ Dissolved Organic Matter Fluorescence.

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November 30, 2022

Abstract

The Arctic Ocean receives a large loading of dissolved organic matter (DOM) from its catchment and shelf sediments, which can be traced across much of the basin. This signature can be used as a tracer of water mass circulation. On the shelf seas, the combination of freshwater loading from rivers and ice formation modify water mass densities and mixing considerably. These waters are the source of the halocline layer that covers much of the Arctic ocean. Our knowledge of the origins, formation and maintenance of the halocline has mostly arisen from CTD profiles and chemical tracers such as oxygen stable isotopes and inorganic nutrients, but the halocline also contains elevated levels of DOM (DOM). Here we demonstrate how this can be used as a tracer and help improve our understanding of ocean circulation. DOM fluoresce can be measured using in-situ fluorometers and mounted on autonomous platforms these can provide high spatial resolution measurements. Here we present data derived from several Ice Tethered Profilers. The data offer a unique spatial coverage of the distribution of DOM in the surface 800m below Arctic ice. Water mass analysis using temperature, salinity and DOM fluorescence, clearly distinguishs the halocline contribution of Siberian terrestrial DOM and marine DOM from the Chuckchi shelf. The findings offer a new approach to trace the distribution of Pacific waters and its export from the Arctic Ocean. Our results indicate the potential to extend the approach to fraction freshwater contributions from, sea ice melt, riverine discharge and Pacific water.

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2 **Organic Matter Fluorescence.**
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23 **Key Points:**

24 • Arctic surface waters with comparable temperature and salinity have contrasting in situ
25 dissolved organic matter fluorescence.

26 • Organic matter fluorescence can track low salinity waters feeding into the Transpolar
27 Drift and halocline layers.

28 • Siberian and Chukchi shelf waters can be separated based on their fluorescence to salinity
29 relationship.

30
31

Abstract

The Arctic Ocean receives a large supply of dissolved organic matter (DOM) from its catchment and shelf sediments, which can be traced across much of the basin's upper waters. This signature can potentially be used as a tracer. On the shelf, the combination of river discharge and sea-ice formation, modifies water densities and mixing considerably. These waters are a source of the halocline layer that covers much of the Arctic Ocean, but also contain elevated levels of DOM. Here we demonstrate how this can be used as a supplementary tracer and contribute to evaluating ocean circulation in the Arctic. A fraction of the organic compounds that DOM consists of fluoresce and can be measured using in-situ fluorometers. When deployed on autonomous platforms these provide high temporal and spatial resolution measurements over long periods. The results of an analysis of data derived from several Ice Tethered Profilers (ITPs) offer a unique spatial coverage of the distribution of DOM in the surface 800m below Arctic sea-ice. Water mass analysis using temperature, salinity and DOM fluorescence, can clearly distinguish between the contribution of Siberian terrestrial DOM and marine DOM from the Chukchi shelf to the waters of the halocline. The findings offer a new approach to trace the distribution of Pacific waters and its export from the Arctic Ocean. Our results indicate the potential to extend the approach to separate freshwater contributions from, sea-ice melt, riverine discharge and the Pacific Ocean.

1 Introduction

The central Arctic Ocean is surrounded by expansive shelf seas which influence ocean circulation and seawater properties (Figure 1). Shallow depths restrict deep water exchange to only occur in the Fram Strait. Much of the surface water inflow occurs over the expansive shelf sea areas, where river runoff and extensive seasonal sea-ice formation and melt modify the physical and chemical properties. Inflowing waters from the Pacific and Atlantic also loose heat to the atmosphere and are cooled during their passage over the shelves (Dmitrenko et al., 2009; Rudels et al., 1996; Rudels et al., 2000; Shimada, 2005). These waters are gradually modified and diluted by the freshwater discharge from major rivers with catchments in North America and Eurasia (Haine et al., 2015; Overeem & Syvitski, 2010; Peterson et al., 2002; Serreze et al., 2006). Sea-ice formation and subsequent export of ice off the shelf partially counteracts this dilution (Bauch et al., 2009, 2011). Brine rejection results in the formation of shelf waters very close to freezing temperature and with slightly increased salinity, as well as other dissolved constituents (Anderson et al., 1988).

The chemical composition of inflowing oceanic water is also altered during its passage over the shelves. Rivers supply high concentrations of terrestrial dissolved organic matter (DOM) (Amon et al., 2012). While inorganic nutrient concentrations in Arctic rivers are comparable to oceanic concentrations (Holmes et al., 2012), dissolved organic carbon (DOC) concentrations are an order of magnitude higher than in inflowing ocean water (Anderson & Amon, 2015). Further, interactions with shelf sea sediments also influence the chemical composition of these waters, as degradation and dissolution of particulate organic matter results in high porewater concentrations of DOC which subsequently diffuse to overlying waters (Chen et al., 2016). Concentrations of nutrients in shelf bottom waters are also higher as a result of elevated rates of organic matter mineralization (Bauch et al., 2011; Dmitrenko et al., 2011; Jones & Anderson, 1986). Denitrification in organic rich sediments is a sink for nitrate and results in

76 shelf waters having a nitrogen deficit relative to phosphate, in comparison to sub-Arctic ocean
77 waters (Anderson et al., 2013; Codispoti et al., 2005; Hardison et al., 2017; Jones & Anderson,
78 1986). Passage over the shelf therefore imparts a detectable chemical signature which is then
79 entrained into the larger scale circulation of the Arctic basin.

80   Surface waters of the Arctic Ocean are often referred to as the Polar Mixed Layer (PML;
81 e.g. Korhonen et al., 2013), which is shaped by repeated convective mixing due to brine release
82 from seasonal ice formation. It is often re-stratified during the melting season, bounded at the
83 bottom by a temperature minimum that is a remnant of the deeper mixed layer from the previous
84 winter's convection (Korhonen et al., 2013; Peralta-Ferriz & Woodgate, 2015; Rudels et al.,
85 2004). Below this, a striking characteristic of the water column in the Arctic Ocean is the
86 widespread presence of a halocline layer (HL) (Coachman & Aagaard, 1974), which consists of
87 cold waters with temperatures close to the freezing point for their given salinity, and salinities
88 ranging between 28-34.8 (Korhonen et al., 2013). The HL is fed by brine rejection (associated
89 with sea-ice formation) and convection occurring in open waters (Steele & Boyd, 1998) or in
90 adjacent shelf seas and subsequently advected off-shore (Aagaard et al., 1981). Halocline waters
91 can extend from near the surface (in areas of formation) to as deep as ~300 m in the southern
92 Amerasian Basin. The HL separates surface waters from warmer waters of Atlantic origin below
93 (hereafter referred to as Atlantic Water, AW). The stratification maintained by the halocline
94 facilitates the formation and persistence of sea-ice in the Arctic as the PML is largely insulated
95 from contact with warmer Atlantic waters below (Aagaard et al., 1981; Toole et al., 2010). Ice
96 free waters of the greater Arctic region are as such due to the absence of a persistent cold
97 halocline layer (Polyakov et al., 2020) or increased retention of summer heat in PML
98 (Timmermans et al., 2018).

99   The HL in the Arctic Ocean differs in composition and structure depending on location.
100 The lower halocline (LHC) has its origins in waters from the Atlantic and extends from a salinity
101 of 34 to the depth of the 0 °C isotherm (Korhonen et al., 2013). It is formed near the inflow
102 regions of AW north of the Fram Strait, the southern Nansen Basin and the Barents Sea (Rudels
103 et al., 1996). This forms the main transition between the PML, which has properties that vary
104 seasonally, and the deeper AW with potential temperatures above 0 ºC. In the Amerasian Basin
105 the HL extends deeper and is composed by two distinct layers: the upper halocline (UHC), right
106 underneath the PML (temperature minimum) and the LHC originating from the Eurasian Basin
107 (Rudels et al., 2004). The UHC is composed of low salinity water from the Pacific inflow
108 (S~32.5) (Coachman & Barnes, 1961) and a variable contribution from the East Siberian Sea
109 (Anderson et al., 2017). This is subject to seasonal variability and lateral intrusion of Pacific or
110 dense water formed during ice formation on the shelves (Bauch et al., 2014; Jones & Anderson,
111 1986). Contributions to the UHC are Pacific Summer Water (PSW) recognizable as a distinct
112 temperature maximum (warmer than -1 °C) with salinities between 31 and 33 (Steele et al.,
113 2004) and below this is a temperature minimum representing Pacific Winter Water (PWW) with
114 salinities of about 33.1 (Coachman & Barnes, 1961). Above the Amerasian UHC a near surface
115 temperature maximum (NSTM) can develop due to summertime warming from solar radiation
116 which is subsequently covered by a shallow surface layer of fresh water from ice melt (Jackson
117 et al., 2010).

118   Another distinct oceanographic feature in the central Arctic is the Transpolar Drift
119 (TPD). This is an ice and surface ocean current that connects the East Siberian and Laptev seas
120 to the Fram Strait (Morison et al., 2012; Steele et al., 2004) and segregates the surface water of

121   the Arctic Ocean. The positioning of the TPD can vary between generally along the Lomonosov
122   Ridge in periods with low Arctic Oscillation (AO) index to extending more towards the Chukchi
123   shelf in periods with a high AO (Figure 1)(Morison et al., 2012). As such the relative
124   contributions of waters from the Siberian shelf (Atlantic origin) and Chukchi shelf (Pacific) can
125   vary (Anderson et al., 2004). The TPD carries a clear terrigenous/riverine signal from the
126   Siberian shelves across the Arctic and onwards to the North Atlantic (Anderson et al., 2004;
127   Charette et al., 2020; Williford et al., 2021), but can also entrain a Pacific Water and East
128   Siberian shelf signal, most noticeable as a lack of nitrate and excess silicate (Anderson et al.,
129   2013; Bauch et al., 2011; Jones & Anderson, 1986; McLaughlin et al., 2004), or by having
130   distinctly different DOM properties (Amon et al , 2003; Gonçalves-Araujo et al., 2016; Stedmon
131   et al., 2011a; Williford et al., 2021). These geochemical signals can therefore be used as a tracers
132   of water origin and circulation in the Arctic Ocean.

133   Much of the empirical knowledge and insight on the origins and characteristics of the
134   Arctic halocline has been based on temperature and salinity profiles (Aagaard et al., 1981; B.
135   Rudels et al., 1996; Steele & Boyd, 1998). This was supplemented with water chemistry
136   measurements, primarily inorganic nutrients, alkalinity, barium and stable oxygen isotopes
137   (Bauch et al., 1995; Guay & Falkner, 1997; Jones & Anderson, 1986). The increasingly
138   widespread deployment of additional biogeochemical sensors (oxygen and a selection of optical
139   probes) on profiling instruments offers higher resolution measurements and an opportunity to
140   further explore processes involved with HL formation, and source fractionation of freshwater
141   distribution (Athanase et al., 2019; Bertosio et al., 2020; Boles et al., 2020; Dmitrenko et al.,
142   2019; Laney et al., 2014). A fraction of the organic compounds present in DOM fluoresce and
143   this can be used as a proxy for dissolved organic carbon in the Arctic (Amon et al., 2003;
144   Gonçalves-Araujo et al., 2016; Guay et al., 1999). This is particularly true for river water
145   entering the Arctic Ocean which has high concentrations of colored and fluorescent DOM
146   (Fichot et al., 2013; Stedmon et al., 2011a; Walker et al., 2013). Fluorescence provides a rapid
147   and sensitive method for characterizing and tracing DOM in the ocean (Stedmon & Nelson,
148   2015) with the major advantage that it can be measured in situ with readily available single- or
149   multichannel fluorometers (Belzile et al., 2006; Makarewicz et al., 2018). This potentially offers
150   high spatial resolution measurements although the full potential has not been realized due to the
151   lack of a robust and agreed upon cross-sensor calibration procedure. Initial studies from specific
152   instruments have demonstrated their utility for the study of DOM biogeochemistry and water
153   mass tracing in the Arctic Ocean (Amon et al., 2003; Cooper et al., 2005; Dmitrenko et al., 2019;
154   Guay et al., 1999; Williford et al., 2021).

155   One of the earliest studies measured underway in situ fluorescence at ~50 m depth along
156   the shelf break from the Beaufort Sea towards the Laptev Sea and captured an elevated DOM
157   signal in the Makarov and Amundsen basins from Eurasian river discharge, and a comparatively
158   lower DOM content in the Amerasian Basin (Guay et al., 1999). These findings were
159   subsequently confirmed by Guéguen et al., (2005, 2007) in the Amerasian Basin and Amon et al.
160   (2003) in the Fram Strait. Studies using spectral DOM absorption and fluorescence measured on
161   discrete water samples have been able to further distinguish between DOM in different rivers
162   (Mann et al., 2016; Walker et al., 2013) and differentiate between supply from rivers and shelf
163   sediments (Chen et al., 2016; Gonçalves-Araujo et al., 2016; Guéguen et al., 2007; Stedmon et
164   al., 2011a). What is currently lacking is a comparable calibrated dataset which offers a
165   comprehensive overview, linking the distribution of DOM across the Arctic Ocean to water

166 masses and their origins. This would provide a baseline from which to detect potential future
167 change and offer an additional tracer for use in model validation.

168   Here we present a comprehensive intercalibration and analysis of legacy data derived
169 from Ice Tethered Profilers (ITPs) deployed in the central Arctic Ocean which have been
170 equipped with single-channel organic matter fluorometers (often referred to as CDOM or FDOM
171 sensors). Building on the earlier data obtained from the Amerasian Basin (Laney et al., 2014) and
172 expanding the analysis to deeper waters, the data offers unique temporal and spatial coverage of
173 the distribution of DOM in the 800 m below Arctic sea-ice. We demonstrate the utility of high
174 resolution in situ DOM fluorescence as a tracer of Arctic water masses using temperature,
175 salinity and DOM fluorescence. This confirms the close connectivity between the halocline layer
176 composition and linkage to sea-ice formation in shelf waters influenced by river run off. This
177 further infers that winter sea-ice formation on the shelf plays an important role in maintaining
178 stratification in the surface 500 m of much of the Arctic Ocean, which is in turn a major factor
179 controlling sea-ice extent in the central Arctic. Our results also suggest that DOM in the central
180 Arctic Ocean mixes largely conservatively once it has entered the deep and ice-covered central
181 basin and can therefore be used as a tracer of waters of shelf origin and to detect surface
182 freshening due to sea-ice melt from in situ observations.

2 Materials and Methods

184 The data used for the analysis are summarized in Table 1. It consists of measurements made as
185 part of the Woods Hole Oceanographic Institution ITP program (Krishfield et al., 2008; Toole et
186 al., 2011) (http://www.whoi.edu/itp) and complemented with an ITP from the FRontiers in Arctic
187 marine Monitoring (FRAM) observatory (https://www.awi.de/en/expedition/observatories/ocean-
188 fram.html). These observations are supplemented with data from ship-based profiles from two
189 research cruises: Arctic GEOTRACES GN04 program cruise (PS94, TRANSARC II) with R/V
190 Polarstern and a cruise on the East Greenland Shelf with R/V Dana in 2012 as part of the Danish
191 NAACOS project.

192   The ITP data are level 3 data products pressure-bin-averaged at 1-db vertical resolution.
193 The ship-based observations are 1 m bin averages. For the ship-based observations, only data for
194 the surface 800 m are included in this analysis as this represented the depths covered by the ITPs.
195 The ITPs were programmed to perform two shallow casts to 200 m then a deep cast to ~750 m.
196 Each profile resulted in an up and a down cast with 6 hour interval in between for the period
197 March to October and 18 hour interval for the remaining months (Laney et al., 2014). The
198 shallowest depth in the processed data on the whole varied between ~5 and 12 m.   Figure 1
199 shows the spatial coverage of the different sensor platforms. In conjunction with the two
200 oceanographic cruises, water samples were collected and used to calibrate the DOM sensors
201 mounted on the ships CTD. ITP93 was deployed during the PS94 cruise and there is an overlap
202 between the first ITP profiles and a ship-based station located at the deployment site. Data from
203 the NAACOS cruise is used to independently verify the applied intercalibration procedure. The
204 profiles from both cruises are included in the data analysis. The instrument package design for
205 ITPs 48-65 and a presentation of the results for the surface 100 m has been published earlier
206 (Laney et al., 2014).

207   Water samples collected for DOM absorption and fluorescence analysis from the two
208 cruises were filtered through a 0.2 μm Millipore filter cartridge (part # KVGLA04HH3) attached

209   directly to the rosette sampler bottles once on deck. Then absorption and fluorescence properties
210   of DOM were measured shortly afterwards onboard. DOM fluorescence was measured with a
211   Horiba Aqualog spectrofluorometer and DOM absorption was measured on either a Perkin Elmer
212   Lambda 35 (PS94) or a Shimadzu UVPC2501 (NAACOS) using a 10 cm quartz cuvette and
213   fresh derived pure water (MilliQ with UV lamp) as a blank. Fluorescence data were processed
214   according to community guidelines (Murphy et al., 2010) resulting in inner filter corrected
215   spectra and fluorescence intensities in Raman Units, nm^{-1} (Lawaetz & Stedmon, 2009). The
216   fluorescence intensities at excitation 350 and emission 450 nm were used to calibrate the voltage
217   signal from the CTD mounted fluorometers. It should be noted that the DrHaardt instrument has
218   a slightly different wavelength range (excitation 350-460 nm, emission 550 nm) but that the
219   signal was linearly correlated to the excitation 350 nm and emission 450 nm signal (Figure S1).
220   Fluorescence at these wavelengths (ultraviolet excitation and visible emission) is often referred
221   to as "humic" due to its spectral similarity to soil extracted organic matter. However, it
222   represents a persistent ubiquitous fluorescent signal found in natural waters which originates
223   either from terrestrial organic matter supplied by rivers or from the degradation of marine
224   organic matter (Stedmon & Cory, 2014).

225   *ITP DOM Sensor Intercalibration*

226   The organic matter fluorescence signal from each ITP was first smoothed using a moving
227   average algorithm with a window of 20 m, in order to better recover DOM fluorescence
228   information at the low concentrations characteristic of the central Arctic Ocean. Thereafter the
229   data were checked for fluorescence sensor drift or baseline shifts by plotting the average and
230   standard deviations for each profile for measurements from depths greater than 700 m for
231   temperature (θ), practical salinity (S_p) and DOM fluorescence. At these depths the fluorescence
232   signal was very stable and sensor drift and baseline shifts could be easily identified as either a
233   systematic gradually changing fluorescence signal (typically over first month of a deployment,
234   despite little geographic movement) or a sudden shift (from one day to the next) in the deep-
235   water averages, whilst θ and S_p properties otherwise remained constant. It is likely that these
236   were caused by either gradual biofouling or episodic attachment of matter onto the fluorometer
237   sensor lens. These were corrected for by either subtracting a polynomial fit of the sensor drift or
238   by subtracting a constant value from the remaining data after a given date.

239   Initial comparison of the baseline corrected ITP data indicated that the fluorometers from
240   each platform required intercalibration (Figure S2). Although the data from the majority of the
241   sensors appear to be either factory or laboratory calibrated pre-deployment to a fluorescence
242   standard (quinine sulfate) there were still notable differences manifesting mostly as different
243   offsets (varying in raw FL units from -10 to +3). The post deployment intercalibration was
244   carried out in two stages. The first step was to calibrate the CTD mounted fluorometer from
245   PS94 to the water samples collected and measured onboard. A linear calibration curve was
246   obtained converting the voltage output signal to fluorescence in Raman Units, [nm^{-1}] (Figure
247   S1).

248   Secondly θ-S_p plots of individual profiles were examined for a common region in θ-S_p
249   space, representing the same waters were sampled by all platforms and ignoring surface
250   measurements. The region of mixing of lower halocline waters and AW, with salinities ranging
251   from 34.2 to 34.8, was identified to have the best overlap, but the data had to be segregated with

252   respect to the Eurasian and Amerasian Basins as there were notable differences in θ-S_p between
253   the two. For the Eurasian profiles the lower salinity data were colder and the (high salinity)
254   temperature maximum was warmer (Figure S3) as explained in Rudels et al., (2004). ITP48
255   sampled both water types during its deployment and could therefore be used to intercalibrate the
256   data between basins.

257   Data from selected profiles for each ITP were used for the intercalibration to the PS94
258   CTD mounted calibrated fluorescence (Figure S3). A linear regression between salinity (34.2 to
259   34.8) and DOM fluorescence was performed for each ITP and used to convert the measured
260   fluorescence to calibrated fluorescence in Raman Units. In order to assess the success of this
261   procedure, two comparisons were made. First, ITP93 was deployed during the PS94 cruise and
262   there was an overlap station from the shipboard CTD on 21 Sep 2015 and the first profile of the
263   ITP on 24 Sep 2015 (Figure S4). Second, the intercalibration approach could be assessed using
264   data from a separate cruise (NAACOS, 2012), calibrated with its own measurements onboard.
265   This was done in DOM-S_p space. Although modifications to polar waters and return AW do
266   occur as it is transported along the Greenland shelf, the clear overlap in the property-property
267   plots offered confidence to the success of the intercalibration of the sensors (Figure S5).

3 Results

269   The compiled dataset offers coverage of contrasting regions of the Arctic Ocean, namely the
270   Eurasian Basin (Nansen Basin, Gakkel Ridge and Amundsen Basin), the Transpolar Drift
271   (Lomonosov Ridge) and Amerasian Basin (Makarov Basin, Alpha Ridge and Beaufort Gyre)
272   (Figure 1). Histograms of the θ-S_p and DOM-S_p properties of the dataset indicate that the
273   majority of the volume of the upper 800 m in the central Arctic basins has salinities between 32
274   and 34.8 and potential temperatures ranging from close to their freezing point and increasing to
275   just under 2 °C (Figure 2). The data at lower salinities (<32) stem from the surface 50 m but
276   diverge at a salinity of about 30.5, with Eurasian Basin waters for the most part having
277   temperatures very close to freezing and Beaufort Gyre surface waters being responsible for the
278   warmer temperatures (Figure 2).
279   At S_p < 34 there is considerable spread in DOM fluorescence, revealing two major
280   branches of data (Figure 2), with the remaining data falling between, while the temperature
281   remains comparatively constant and low. The upper branch (higher fluorescence) is an
282   approximately linear extension of the inverse relationship between DOM fluorescence and
283   salinity seen at salinities greater than 34. The lower branch has a local DOM maximum at
284   salinities between 32 and 33, then decreases with decreasing salinity (Figure 2b). The upper
285   branch originates from surface waters in the Eurasian Basin which are influenced by the TPD
286   while the lower branch represents subsurface waters in the Beaufort Gyre originating from the
287   Chukchi Sea and East Siberian Sea (see later analysis).
288   These patterns are evident in three representative sections shown in Figure 3. The surface
289   waters (upper 50 m) of the Beaufort Gyre (ITP64) are characterized by low salinity and low
290   DOM fluorescence waters with variable temperature (local temperature maxima and minima
291   which are discussed later). Directly below the ice, temperatures are low but increase to a
292   subsurface maximum between 50 and 100 m. Below this is the HL with elevated DOM
293   fluorescence, extending down to approximately 250 m depth. Below the HL, waters mix with
294   warmer and more saline AW with low DOM fluorescence. The other sections shown are from
295   deployments in the Makarov Basin (ITP48) and over the Lomonosov Ridge (ITP93), and capture

296   the TPD with low salinity and very high DOM fluorescence in the surface 50 m, and also capture
297   an underlying HL with DOM fluorescence intensity comparable to that seen in the Beaufort Gyre
298   HL (Figure 3).
299
300   *3.1 Archetypical profiles*
301   Figures 4a-c show selected archetypical profiles for θ, S_p and DOM fluorescence in
302   different basins. A profile in the western Nansen Basin (green) has characteristics typical of low
303   DOM fluorescence AW entering the Arctic with surface waters being cooled and diluted by sea-
304   ice melt (Rudels et al., 2004). The winter mixed layer depth is apparent at around 100 m below
305   which there are coincident thermo-, halo- and DOM-clines. In this profile the winter mixed layer
306   is capped by a surface lens with temperatures above freezing for its given salinity (Figure 4d,
307   note deviation from freezing at salinity ~34), and reduced salinity ($S_p < 34.35$) and DOM
308   fluorescence that has decreased from 0.010 to 0.004 nm^{-1} (Figure 4e) consistent with previous
309   studies (Granskog, et al., 2015; Williford et al., 2021). This likely reflects the addition of
310   summer sea-ice melt water (Bauch et al., 2011; Paffrath et al., 2021) into the surface layer. Sea-
311   ice meltwater contributes comparatively little DOM fluorescence at the wavelengths measured
312   by these sensors and can be assumed to be lower than that found in Atlantic waters (fluorescence
313   <0.01 nm^{-1}) (Granskog, et al., 2015; Stedmon et al., 2011b). In this profile, the warm AW below
314   has the highest temperature, salinity and DOM fluorescence, although the DOM fluorescence is
315   low (<0.01 nm^{-1}) in the upper water column and represents the "pure" AW before it accumulates
316   any DOM signal on its path along the Arctic continental margin (Figure 1). For these waters
317   highest DOM fluorescence was measured at depth (deeper than 800 m, measured using
318   shipboard CTD, not shown), although still considerably lower than the surface DOM maxima
319   from the other regions sampled.
320   In the profiles in the eastern Amundsen basin (magenta) and in the Makarov basin (black)
321   (Figure 4a-c) the coincident thermo-, halo- and DOM-clines spanning from ~100 to 200 m
322   change character to cover a greater range in salinity and DOM fluorescence, and the direction of
323   the DOM fluorescence gradient changes (now increasing with decreasing salinity) compared to
324   in the Nansen basin. The temperature minimum is at approximately 50 m depth with
325   temperatures very close to freezing (Figure 4d). Below the temperature minimum there is a
326   distinct additional halocline extending to 100 m within which DOM fluorescence decreases
327   essentially linearly with increasing salinity. This reveals that the correlation between DOM and
328   salinity in these waters holds from the base of the PML (temperature minimum) to the AW
329   (Figure 4d and e).
330   In the surface waters of the Amundsen and Makarov basins there is mixing of underlying
331   halocline waters with sea-ice meltwater in summer. This is most evident for the Amundsen Basin
332   profile (magenta) and at the very surface for the Makarov profile (black). The dilution acts to
333   draw the data off the linear DOM-S_p mixing line (compare magenta and black profiles in Figure
334   4e) and towards a lower salinity and DOM fluorescence water type.
335   In Figure 4 two profiles from the Beaufort Gyre are shown (cyan and red). Although the
336   depth distributions differ (Figure 4a-c), the water mass characteristics (S_p and DOM fluorescence
337   in particular) of these two profiles overlap very closely (Figure 4d & e). The main deviation is in
338   the surface 50 m with salinities below 32 where temperatures are considerably warmer in the
339   profile that originates from closer to the Alaskan shelf (cyan, from June 2013) than in the central
340   basin (red, from September 2012). In these profiles an additional thick upper layer of the UHC is
341   evident underneath the PML, with salinities ranging from approximately 32 to 33. This layer has

342   an intermediate DOM fluorescence which is less than half that found at comparable salinities in
343   the Makarov Basin profile (black) but still much higher than that found in AW (green). The
344   DOM-S_p diagram reveals that this layer sits above the LHC waters (Figure 4e).
345   In the region of the Alpha Ridge (Figure 4, blue), surface waters are diluted tending
346   towards similar values for salinity and DOM fluorescence as that seen in the Beaufort Gyre
347   (Figure 4, red and cyan). Below this, the water column has similar properties to the Makarov and
348   Amundsen basin (black and magenta), with high DOM fluorescence and near freezing
349   temperatures. At 90-150 m depth there is an intrusion of intermediate fluorescence DOM signal
350   associated with UHC from the Beaufort Gyre (Figure 4e).
351   For comparison, a profile from the East Greenland shelf (brown) is also shown in Figure
352   4. At salinities between 32 and 33 and at ~34.8 there is clear overlap in θ-S_p and DOM-S_p space
353   with data from the central Arctic Ocean. Waters with these properties correspond to Beaufort
354   Gyre upper halocline and Atlantic waters, respectively. However, it should be noted that this
355   profile does not represent a widespread or typical signal for much of the East Greenland shelf. At
356   other stations, not highlighted here, there is no overlap with the UHC waters, but rather a more
357   predominant signal from the Siberian shelf contribution is apparent (Amon et al., 2003;
358   Gonçalves-Araujo et al., 2016).
359
360   *3.2 Characteristics of the DOM maximum, temperature maximum and temperature minimum*
361   The following section presents the results of an analysis of the properties and location of
362   three distinct features in the profiles: the DOM fluorescence maximum, the temperature
363   maximum and the temperature minimum. For each of the more than 5000 profiles the specific
364   depth of the above features was found and histograms of the water properties at these depths
365   were generated (Figure 5-7). These indicated the presence of distinct sub-groups of data. In order
366   to highlight these groups and aid in determination of the origins of the measurements
367   contributing to them, arbitrary distinctions are made depending on either salinity, DOM
368   fluorescence intensity or deviation from freezing temperature (see figure legends for boundaries
369   of these arbitrary groups). The emphasis should be on the shape of the histograms (with distinct
370   or overlapping distributions). The grouping allocated, indicated in the figures by different colors,
371   serve only to facilitate interpretation.
372   Figure 5 shows histograms of water properties at the DOM fluorescence maxima for each
373   profile for halocline waters (S_p 31-34). The histograms reduce the data considerably as there is
374   now only one data point per profile. This facilitates isolating the characteristics of different high
375   intensity DOM sources, in particular in the range of halocline salinities across the Arctic. It is
376   clear that DOM fluorescence maxima in the Arctic Ocean can be grouped into two based on their
377   temperature (or rather deviation from freezing temperature, DFT): either essentially at seawater
378   freezing temperatures (red group in Figure 5e) or centered around 0.4 °C above freezing (Figure
379   5e). The waters with the coldest (and closest to freezing) temperatures (red in Figure 5c) have the
380   highest DOM fluorescence (>0.030 nm^{-1} with a tail extending up to 0.0888 nm^{-1}). Similarly,
381   there is clear segregation with respect to depth. The DOM fluorescence maxima tend to be either
382   at the surface (red group, with corresponding highest DOM fluorescence) or much deeper
383   (between 100 and 250 m; Figure 5d) which is typically observed for the Beaufort Gyre stations
384   (west of 100 °W). The latter has lower DOM fluorescence centered around 0.03 nm^{-1} (blue and
385   yellow data in Figure 5c).
386   The surface maxima (red, Figure 5) can also be segregated to maxima at depths <25 m,
387   corresponding to profiles in the TPD, and maxima positioned slightly deeper immediately below

388   the PML at approximately 60 m (corresponding to the HL in the Eurasian Basin). These data
389   span a range in salinities from 31 to 33.2 and originate from profiles taken in the Amundsen
390   Basin, Lomonosov Ridge and near the North Pole. There is also a significant negative linear
391   correlation between DOM fluorescence intensity and salinity for these samples (r=-0.72,
392   p<0.01).
393   The lower DOM fluorescence intensity group (<0.030 nm^{-1}) could be separated further
394   into two, based on salinity, with an apparent threshold between them of 33.2 (blue and yellow in
395   Figure 5). Although there was a high degree of overlap in temperature (Figure 5b), typically
396   ranging from 0.3 to 0.75 °C DFT, a two sample t-test indicated that there was a significant
397   difference (p<0.01) with the higher salinity group (yellow) being significantly warmer. These
398   groups also differed slightly in position in the water column, with the lower salinity group (blue)
399   slightly shallower (mean depth 155 m) than the higher salinity group (mean depth 182 m, Figure
400   5d).
401   Another prominent feature of the water column in the Arctic Ocean is the intermediate
402   and deep temperature maxima which trace the warm Pacific and Atlantic waters, respectively,
403   that enter the Arctic (Jackson et al., 2010; Korhonen et al., 2013). In Figure 6 histograms of the
404   properties at the temperature maximum are shown but grouped based on their salinity and depth.
405   For this analysis, only profiles with a distinct deep θ maximum were included (i.e., shallow ITP
406   profiles to ~200 m where temperature was still increasing with depth were excluded). Here, one
407   can identify three groups with contrasting θ, S_p and DOM fluorescence (Figure 6). The
408   temperature maximum of the AW inflow waters (shown in blue) are widespread across the basin,
409   and are typically found at depths between 200 and 350 m, at S_p of ~34.9 and with θ ranging
410   between 0.5 and 2 °C. These waters are characterized by low DOM fluorescence (~0.01 nm^{-1}). In
411   the Amerasian Basin, salinity at the deep (AW) temperature maximum (0.7-0.9 °C), is slightly
412   lower (34.8), but has comparably low DOM fluorescence of ~0.01 nm^{-1} (shown in yellow, Figure
413   6) and is found deeper in the water column (350-400 m). The third group, shown in red in Figure
414   6, corresponds to warm near surface waters in the Amerasian Basin that have entered through the
415   Bering Strait, and been modified by warming and sea-ice melt. These waters have comparatively
416   higher DOM fluorescence, centered around 0.017 nm^{-1}, compared to the deep temperature
417   maxima (~0.01 nm^{-1}).
418   An analysis of the properties at the temperature minimum also revealed distinct groups
419   based on temperature and salinity (Figure 7). The deep temperature minimum (typically >100 m)
420   in the Amerasian Basin differed from the others by having temperatures that deviated more than
421   0.2 °C from seawater freezing (blue) and a DOM fluorescence of 0.028 nm^{-1}. In surface waters
422   the temperature minima were largely within 0.2 °C from seawater freezing but could be
423   segregated based on salinity. The lowest salinity temperature minimum (S<29) was restricted to
424   upper surface waters and the majority of the data had low DOM fluorescence (<0.012 nm^{-1}). At
425   salinities between 29.5 and 32 two distinct groups could be identified, a lower salinity group
426   with low DOM fluorescence (~0.02 nm^{-1}, S_p 30-31) and a higher salinity group with a higher
427   DOM fluorescence (~0.03 nm^{-1}, S_p 32-33). Both of these were found at depths between 40-70 m.
428
429   **4 Discussion**
430
431   Figure 8 shows the average properties of each of the identified end members from the DOM and
432   temperature maxima and temperature minima, superimposed on all the data (complete profiles)
433   in θ-S_p (Figure 8a) and DOM-S_p (Figure 8b) space. These are calculated across all profiles. It is

434   evident that the DOM fluorescence signal offers an additional parameter from which to separate

435   the properties of the surface waters of the Arctic Ocean (S_p<34 and θ<0), where temperatures are

436   often low and overlap considerably despite different water mass origins. In particular, the data

437   can resolve patterns in the UHC, while the changes in the DOM fluorescence of AW are minor

438   as it propagates through the Arctic Ocean.

439

440   *4.1 Oceanic DOM signal associated with AW branches.*

441   The DOM fluorescence signal found in the temperature maximum waters originating from AW

442   has comparable intensity to that found in earlier studies for ocean waters without a notable

443   influence from terrestrial input (Jørgensen et al., 2011; Zabłocka et al., 2020). This represents a

444   background recalcitrant oceanic signal produced from the long term microbial and

445   photochemical processing of marine organic matter in the world ocean (Jørgensen et al., 2011,

446   2014; Yamashita & Tanoue, 2008). AW enters the Arctic through the Fram Strait or via the

447   Barents Sea (Rudels et al., 2004). The Fram Strait and Barents Sea contributions to these surface

448   waters are cooled and diluted by sea-ice melt. This further decreases the DOM fluorescence

449   signal brought with it as seen in the Nansen Basin profile in Figure 4. At certain locations

450   microbial activity in sea-ice can result in the production and accumulation of fluorescent DOM

451   in sea-ice brines (Stedmon et al., 2011b). However, this fluorescence is dominated by DOM with

452   an ultraviolet fluorescence (emission < 400 nm) (Granskog, et al., 2015) which represents a

453   transient labile organic matter signature. When this material is introduced into surface waters as

454   a result of sea-ice melt, it is susceptible to mineralization by microbes. Visible wavelength

455   fluorescence (emission), such as that measured by the sensors deployed in this study, can also be

456   released during sea-ice melt but the signal intensities are lower, typically 0.005 nm^{-1} (Stedmon et

457   al., 2011b), but more resistant to degradation, and can therefore result in a slight reduction in the

458   surface AW signal.

459   Atlantic waters flow eastwards along the Siberian continental slope forming the Arctic

460   Circumpolar Boundary Current (ACBC) (Aksenov et al., 2011). The saline temperature

461   maximum group identified in Figure 6 trace the path of AW starting shallow (200-350 m) and

462   with variable warm temperatures in the Eurasian Basin (0.5-2 °C) (blue in Figure 6) and ending

463   as a deeper (400-500 m) and colder temperature maxima (0.7-0.9 °C) in the Amerasian Basin

464   (yellow in Figure 6) which is much more homogenous with respect to temperature and only

465   slightly less saline (S_p~34.8). The DOM fluorescence in these waters does not change reflecting

466   its refractory nature, similar AW origins, and indicating no entrainment of riverine or shelf

467   sediment organic matter signal during its passage. This has also been confirmed earlier using

468   terrestrial plant biomarker lignin measurements (Kaiser et al., 2017).

469   The waters of the LHC are defined as having salinities greater than 34 and temperatures

470   below 0 °C (Korhonen et al., 2013; Rudels et al., 1996). These originate from the freshening and

471   cooling of AW after entering the Arctic Ocean north of Svalbard or via the Barents Sea. As a

472   result, one would expect them to have a very low DOM fluorescence (as discussed above). The

473   majority of the water sampled with a salinity greater than 34 had higher DOM fluorescence than

474   expected for AW, 0.03 nm^{-1} rather than 0.01 nm^{-1}, (Figure 8) and was positioned on the Siberian

475   shelf–AW mixing line. Two regions are thought to contribute to the formation of the LHC, and

476   these results imply that the open ocean convective contribution to the LHC from winter waters in

477   the Nansen Basin (Rudels et al., 1996) may be of minor importance in the waters sampled here.

478   The distinct elevated DOM fluorescence emphasizes the importance of the Barents Sea branch

479   entering via the Kara Sea where there is a terrestrial DOM contribution from Ob and Yenisei

480 rivers. Almost all of the Atlantic-derived water beyond the Lomonosov Ridge is thought to have
481 come through the Barents Sea (Rudels et al., 1996) but the data here indicate a dominance of this
482 water also in the Amundsen Basin with little evidence for the Nansen Basin contribution along
483 the tracks covered by the ITPs and shipboard measurements.
484
485 *4.2 Shelf DOM signals*
486 A branch of the Barents Sea supply of AW contains a contribution from the Norwegian Coastal
487 Current and flows along the Siberian shelf and slope (Osadchiev et al., 2020; Rudels et al.,
488 2004). During this passage it collects freshwater (Bauch et al., 2014) and DOM from Siberian
489 rivers (Kaiser et al., 2017). Export of these waters northwards off the shelf and mixing with
490 underlying AW results in the negative correlation observed between DOM fluorescence and
491 salinity (black line in Figure 4e). The analysis of the properties of the DOM fluorescence
492 maxima identified three distinct groups with shelf origins. This demonstrates that different shelf
493 components are detectable in the HL as has been demonstrated based on neodymium (Nd)
494 isotopes for the Lapev and Kara seas components within the TPD (Paffrath et al., 2021). The
495 group with the highest DOM fluorescence values (red in Figure 5) overlap in salinity,
496 temperature and depth with previously defined Lower Salinity Halocline Waters (LSHW)
497 (Bauch et al., 2014; Bauch et al., 2011). These surface waters originate from the Laptev and East
498 Siberian seas (Bauch et al., 2014) and are exported northwards off shelf forming the surface
499 waters of the TPD (Rudels et al., 1999) and carry with them a high terrigenous DOM
500 fluorescence (Charette et al., 2020; Williford et al., 2021) and intermediate silicate
501 concentrations (Anderson et al., 2017) from Siberian river run off. DOM fluorescence at
502 salinities of 30 for shelf waters near the Lena River have been reported to be around 0.1 nm^{-1}
503 (Gonçalves-Araujo et al., 2015) and this aligns well if one extrapolates the mixing curve for the
504 Makarov Basin (black) shown in Figure 4. Measurement of the terrestrial plant biomarker lignin
505 has also shown that the DOM in these waters originates from the Ob, Yenisei and Lena rivers
506 (Kaiser et al., 2017; Williford et al., 2021). The strong linear correlation with salinity indicates
507 conservative mixing between LSHW of the TPD with the underlying AW at the temperature
508 maximum. The results also show that in places (Amerasian Basin side of TDP) this can be
509 subducted below lower salinity surface water from the Beaufort Gyre (Figure 4, blue; Figure 5,
510 red).
511   LSHW temperatures are very close to freezing (for the most part within 0.3 °C of
512 freezing for their given salinity), which confirms the role that brine release during sea-ice
513 formation has on shaping the properties of these waters (Aagaard et al., 1981). Mixing with sea-
514 ice melt water is apparent at the very surface of the profiles where both DOM fluorescence and
515 salinity is reduced (black profile in Figure 4) and is consistent with a recent study with extensive
516 coverage of the Siberian shelf water (Hölemann et al., 2021).
517   The highest salinity DOM fluorescence maximum group (S_p 33.7, Figure 8) lies on the
518 LSHW–AW mixing line, but is found at depths greater than 150 m (yellow in Figure 5), and
519 slightly warmer (~0.5 °C above seawater freezing). The fact that these data lie directly on this
520 mixing line hints to the fact that it is also formed on the Siberian shelf but contains a greater
521 contribution of Atlantic water. Although salinities range between 33.4-34.2, its depth and
522 location indicate that it represents part of the LHC in the Amerasian Basin.
523   A third group with similar DOM fluorescence but lower salinities (mean S_p 32.9) was
524 also identified (blue in Figure 5). These waters have temperatures approximately 0.4 °C above
525 seawater freezing, and represent Pacific inflow waters passing across the Chukchi Sea (Guéguen

526 et al., 2012; Jones & Anderson, 1986; Stedmon et al., 2011a) or East Siberian shelf water
527 (Anderson et al., 2017), which have accumulated DOM largely from shelf sediments. This is
528 confirmed by the fact that near identical water column characteristics can be found in the
529 Beaufort Gyre profiles (compare red and cyan data in Figure 4). As these waters pass over the
530 shelf, seasonal sea-ice formation (Shimada, 2005) acts to drive temperatures close to freezing
531 and there is a DOM contribution from marine organic matter degradation in shelf sediments.
532 Here the DOM released clearly differs in character from riverine material and likely originated
533 from the degradation of marine organic matter (Stedmon et al., 2011a). This aligns with the
534 nutrient signal reported for these waters (Anderson et al., 2017; Jones & Anderson, 1986). In the
535 Amerasian Basin, these waters lie above the LHC from the Eurasian Basin (red and cyan data in
536 Figure 3) however at the Alpha Ridge (blue profile in Figure 3) one can find contribution from
537 all three DOM groups with shelf UHC water inserted between LSHW and LHC. This fits with
538 earlier observations in the central Arctic (McLaughlin et al., 2004; Shimada, 2005; Woodgate et
539 al., 2007) and from the Wandel Sea off Northeast Greenland (Dmitrenko et al., 2019). Waters
540 with similar properties, overlapping in θ-S_p and DOM-S_p space, were also identified by the
541 analysis of the temperature minimum (Figure 8, blue and black points at S of ~33). The
542 temperature and salinity confirm its origin as PWW.
543   The shallow temperature maximum <100m in the Amerasian Basin represents the Pacific
544 inflow as PSW (Rudels et al., 2004). This was distinguished as a group of data with salinities
545 between 30 and 32 and intermediate DOM fluorescence (red in Figure 8). The location of these
546 data in DOM-S space indicate that they represent a dilution of the PWW (in both S and DOM),
547 with a contribution of freshwater from ice melt.
548   The characteristics of the waters contributing to the variability in DOM fluorescence in
549 the Arctic Ocean can be summarized as follows. At the surface low salinity (S<32.5) and high
550 DOM fluorescence waters (LSHW) that originate on the Siberian shelf and are exported
551 northwards with the TPD. Below this are the waters of the Atlantic derived LHC which have
552 intermediate DOM fluorescence indicating that they have also entrained terrestrial DOM from
553 the Siberian shelf during their formation before exported northwards and subducted. In addition
554 to being exported northwards together with the TPD a contribution is also diverted into the
555 Beaufort Gyre where it supplies terrestrial DOM into the LHC beneath the UHC. The UHC,
556 despite having a comparable DOM fluorescence to the LHC, has a lower salinity and collects its
557 (marine/shelf) DOM signal from the Chukchi shelf and East Siberian Sea. All three components
558 of HL can be captured in profiles near Alpha Ridge (e.g. Figure 4) and in the Fram Strait (not
559 shown). While the signal at the surface from the TPD, is diluted with sea-ice melt on its journey
560 out of the Arctic, the signals from the Pacific and Atlantic HL at depth are retained and
561 identifiable all the way to the East Greenland shelf. This is supported by comparing the data
562 collected from the Beaufort Gyre (cyan and red, Figure 4e) with measurements from the East
563 Greenland Shelf in DOM-S space (brown, Figure 4e), and supports earlier evidence based on
564 water samples (Gonçalves-Araujo et al., 2016).
565

5 Conclusions and outlook

567 The results shown indicate that two major freshwater sources to the Arctic, river discharge and
568 Pacific water, have clear and distinguishable DOM fluorescence signals associated with them.
569 This confirms earlier findings based on more in-depth water sample analysis in selected Arctic
570 regions (Amon et al., 2003; Gonçalves-Araujo et al., 2016; Stedmon et al., 2011a; Williford et

571 al., 2021) but here the high temporal and spatial resolution of in situ measurements throughout
572 the Arctic Ocean complements the regional studies with better analytical resolution of laboratory
573 measurements.
574   DOM fluorescence at the wavelengths measured by these sensors (ultraviolet excitation
575 and visible wavelength fluorescence), behaves largely conservatively relative to salinity during
576 sea-ice formation and subsequent brine rejection (Stedmon et al., 2011b). The released brine
577 (with slightly elevated salinities and DOM fluorescence, and near seawater freezing
578 temperatures) contributes to the formation of shelf waters that feed the halocline. While Siberian
579 shelf water contributes terrestrial DOM into the LHC, the water from the Chukchi shelf
580 contributes with marine DOM likely released from sediment below the highly productive
581 Chukchi shelf. Although high salinity waters of the LHC can contain a contribution from winter
582 mixing in the Nansen Basin, the evidence shown here indicates widespread dominance of shelf
583 water sources elsewhere.
584   In the upper 300 m of the Beaufort Gyre salinity profiles reflect the considerable storage
585 of freshwater in the region. Here DOM profiles from automated platforms may provide
586 additional insight to the source of the freshwater. River water and Pacific water will be
587 associated with high DOM fluorescence while accumulation of sea-ice melt will dilute DOM
588 fluorescence (resulting in positive correlation with salinity). The DOM fluorescence-S_p diagrams
589 clearly indicate an accumulation of sea-ice melt in the surface 50 m (S_p below 30). Combined
590 with additional biogeochemical sensors such as nitrate and oxygen (Athanase et al., 2019), DOM
591 fluorescence measurements provide an opportunity to fractionate freshwater contributions based
592 on in situ measurements alone. In addition, multi-channel in situ fluorometers would be able to
593 better differentiate between Arctic DOM sources as they differ in their spectral properties
594 (Gonçalves-Araujo et al., 2016; Makarewicz et al., 2018), while spectral absorption sensors such
595 as those used for nitrate can potentially provide high resolution estimates of DOC (Gonçalves-
596 Araujo et al., 2020). Surface DOM measurements can easily distinguish the frontal regions on
597 either side of the TPD, and in the vertical provides a powerful tool to guide water sampling of
598 other tracers in the water column (Charette et al., 2020; Williford et al., 2021). This offers a
599 valuable and currently underutilized additional tracer for deciphering Arctic circulation and
600 freshwater distribution. Some of these questions are addressed by a parallel paper in this special
601 issue by Williford et al.
602

Acknowledgments, Samples, and Data

624

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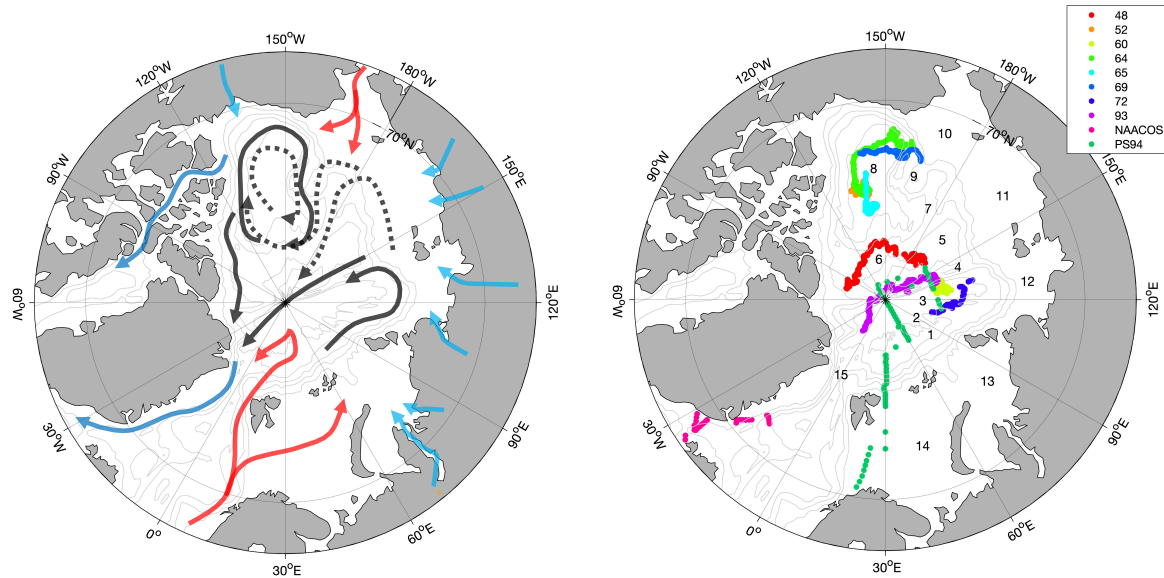
865

866   **Figure 1**. Left: schematic of general circulation pathways. Red arrows indicate inflowing ocean
867   water; blue arrows polar water exiting the Arctic, light blue are major Arctic rivers. Black arrows
868   indicate the two major circulation patterns of the central Arctic, Transpolar Drift extending from
869   the Siberian shelf over the North Pole towards the Fram Strait, and the Beaufort Gyre. Solid and
870   dotted lines indicate the position of these features during a positive and negative Arctic
871   Oscillation (Morison et al 2012). Right: ITP drift pathways, and cruise stations. The legend
872   indicates the ITP and cruise identity. The numbers on the map indicate geographic areas as
873   follows: 1) Nansen Basin; 2) Gakkel Ridge; 3) Amundsen Basin; 4) Lomonosov Ridge; 5)
874   Makarov Basin; 6) Alpha Ridge; 7) Mendeleev Ridge; 8) Beaufort Gyre; 9) Chukchi Plateau; 10)

875 Chukchi Sea; 11) East Siberian Sea; 12) Laptev Sea; 13) Kara Sea; 14) Barents Sea; 15) Fram
876 Strait.

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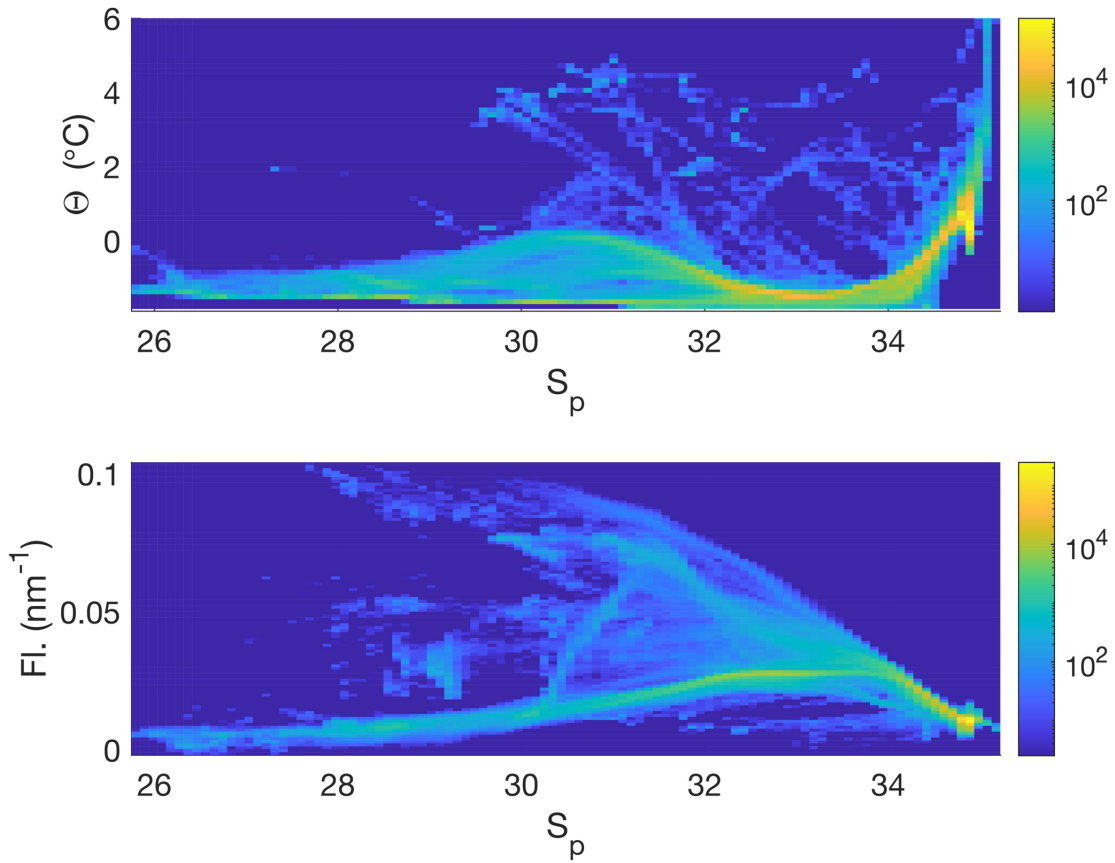
Figure 2. 2D histograms of potential temperature (top panel) and DOM fluorescence (bottom
panel) against practical salinity for all observations included in the study (0-800 m). Note that
data with temperatures warmer than 6 ºC are not shown.

881
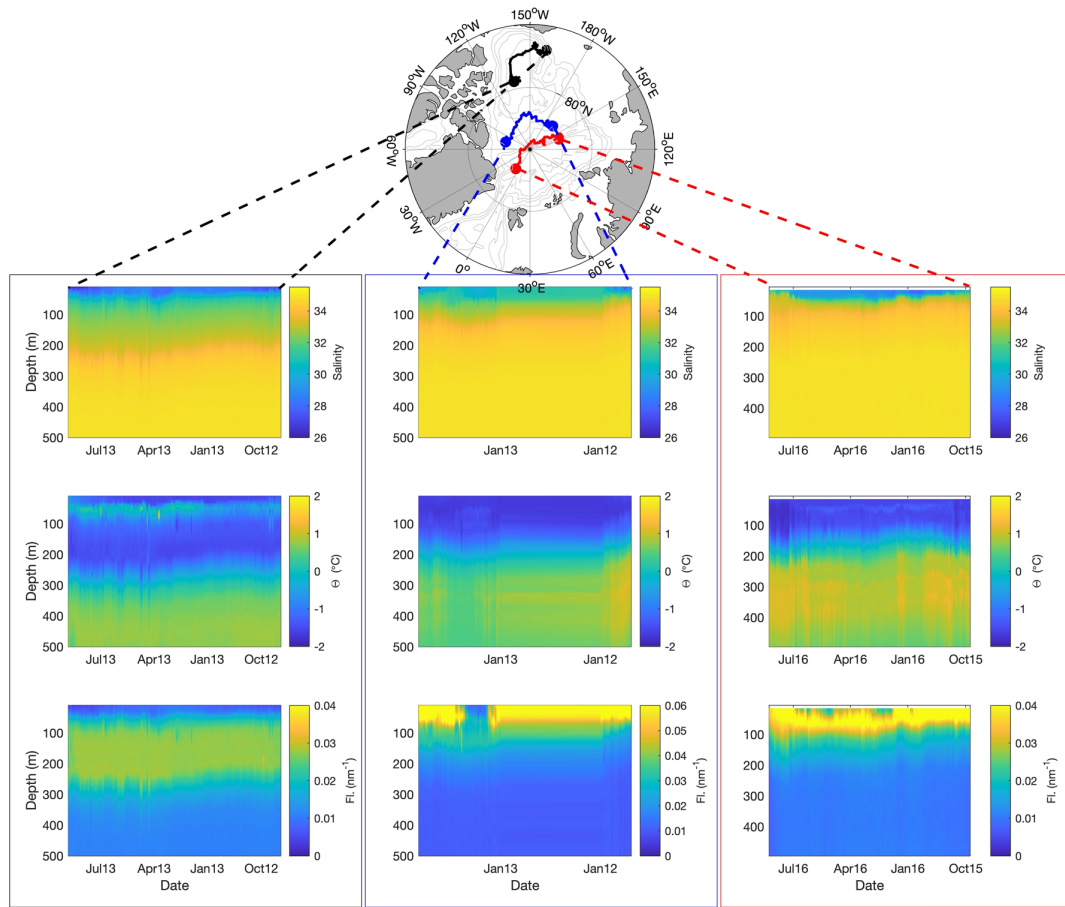
Figure 3. Section plots along the trajectories of ITP 64 (left column), 48 (middle column) and 93
(right column) for salinity (top row), potential temperature (middle row) and DOM fluorescence
(bottom row). The links to the map indicate where trajectories start and end. Note that the DOM

885   fluorescence scale is varies and that there are data from ITP 48 and 93 that are off scale (above
886   the maximum shown).
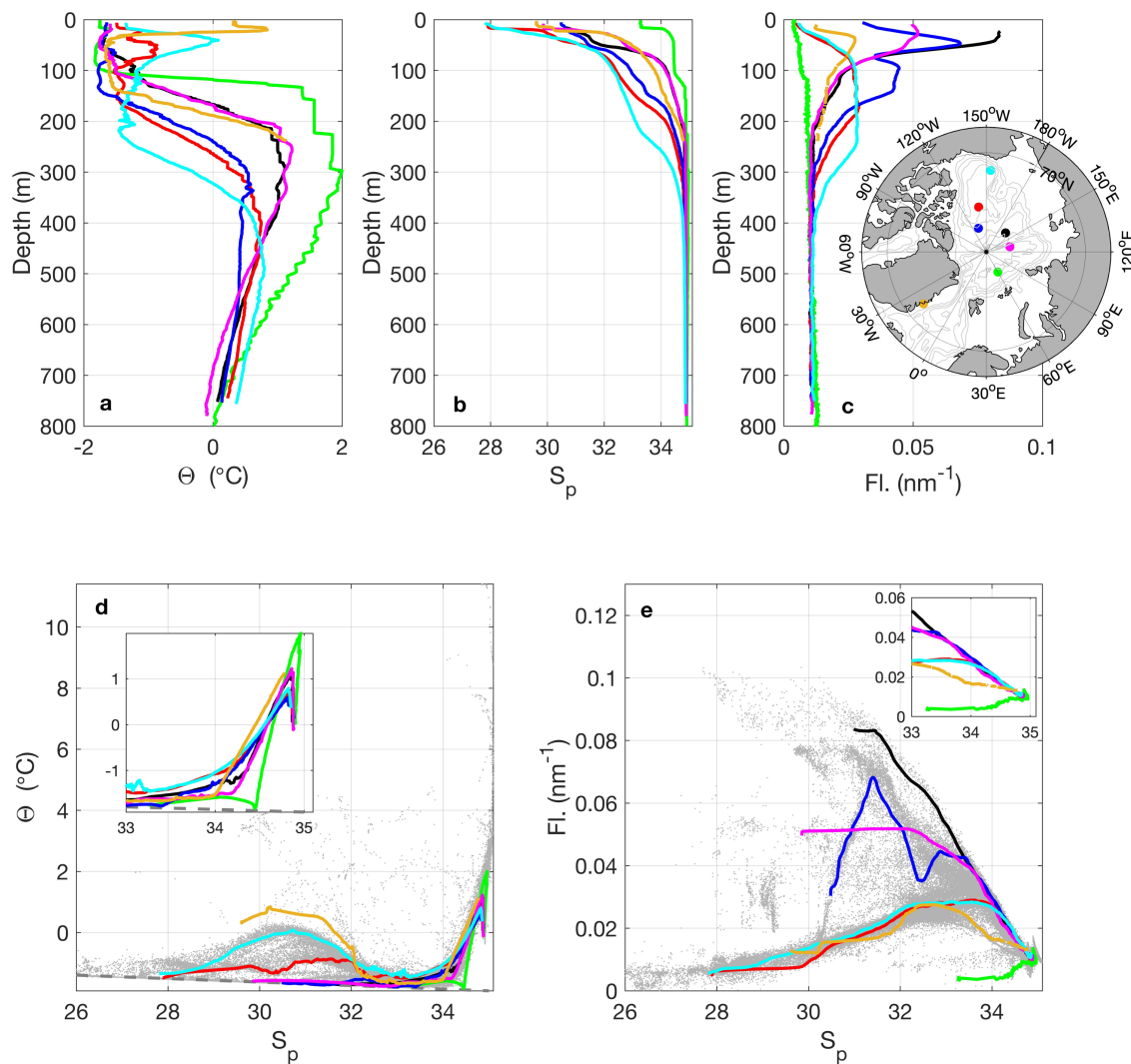
887

888   **Figure 4.** Archetypical water column profiles of a) potential temperature, b) practical salinity
889   and c) DOM fluorescence. The lower panels show property-property plots of d) potential
890   temperature against practical salinity (freezing temperature as grey dashed line) and e) DOM

891   fluorescence against salinity. Green-PS94; Magenta-ITP60; Black-ITP48; Blue-ITP48; Red-
892   ITP65; Cyan-ITP64; Brown-NAACOS.

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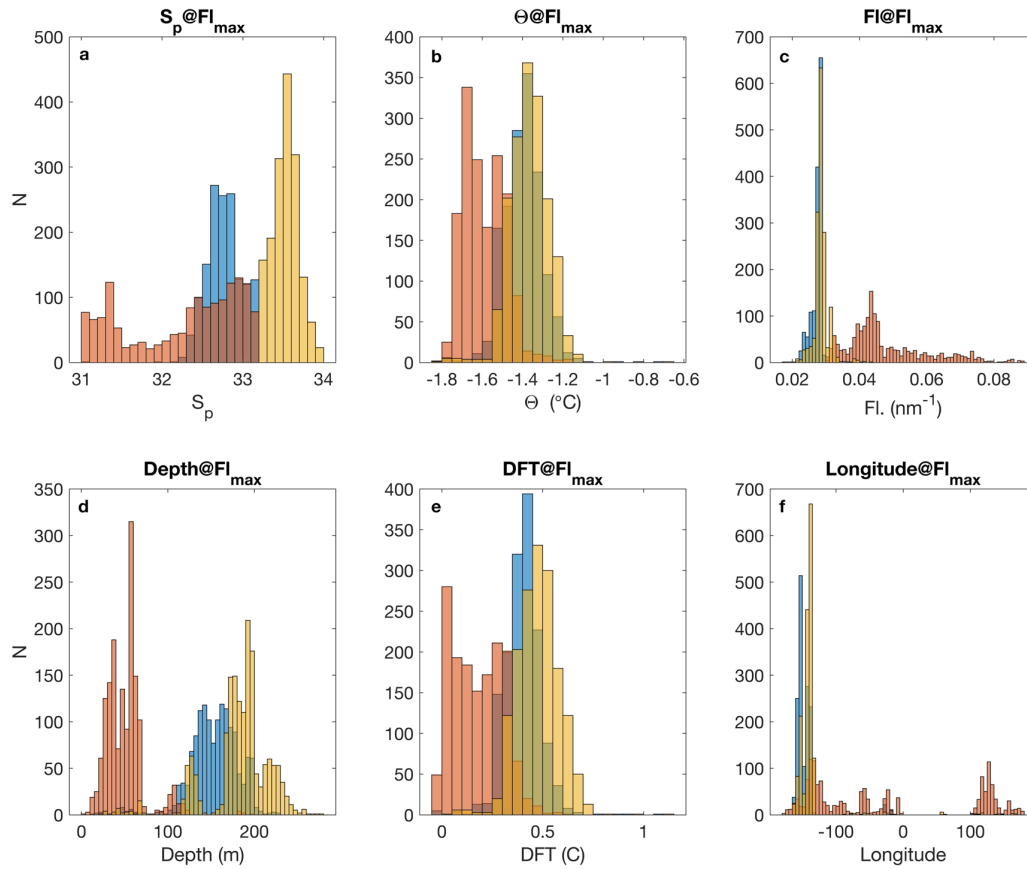
Figure 5. Histograms of properties of the DOM fluorescence maximum in the halocline (S 31-
34). The data are colored with respect to three groups, to illustrate different features: blue-
salinity 31-33.2 and DOM fluorescence <0.0305 nm^{-1}; red-salinity 31-33.2 and DOM
fluorescence >0.0305 nm^{-1}; yellow-salinity>33.2; a) practical salinity; b) potential temperature;
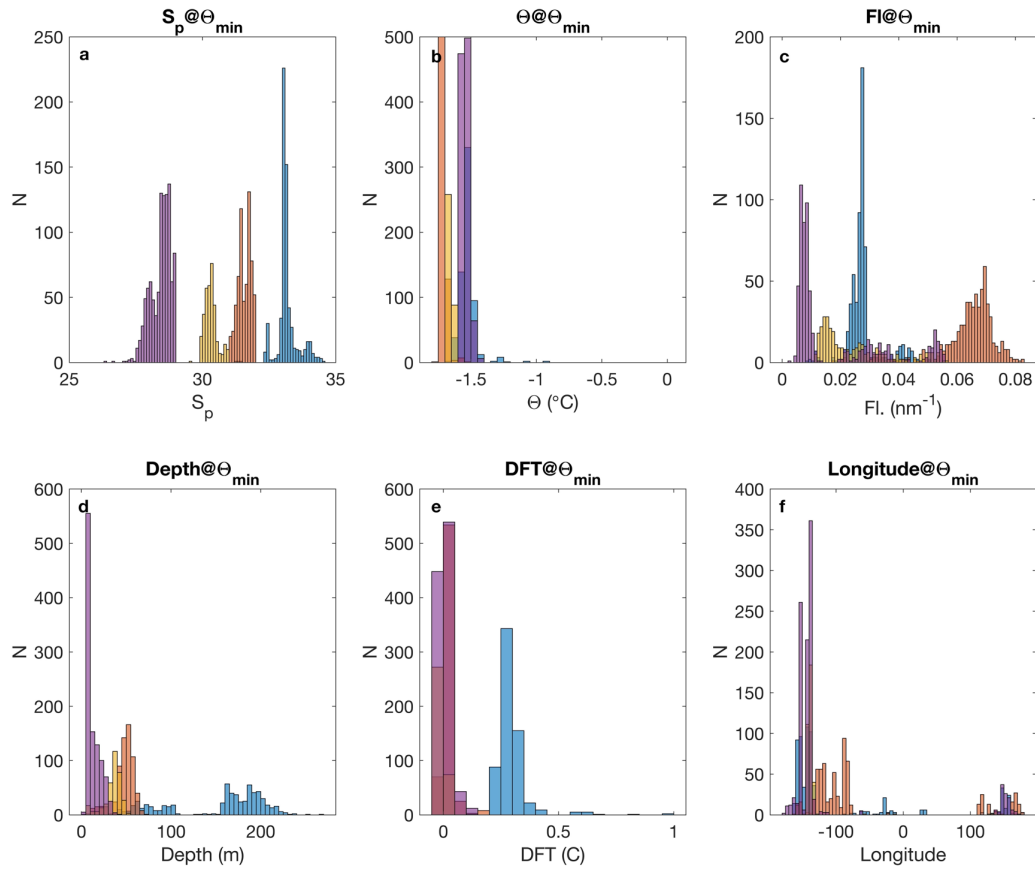c) DOM fluorescence; d) depth of DOM fluorescence maximum; e) deviation from freezing

899   temperature; and f) distribution of longitudinal position (positive is east of meridian) between
900   groups.
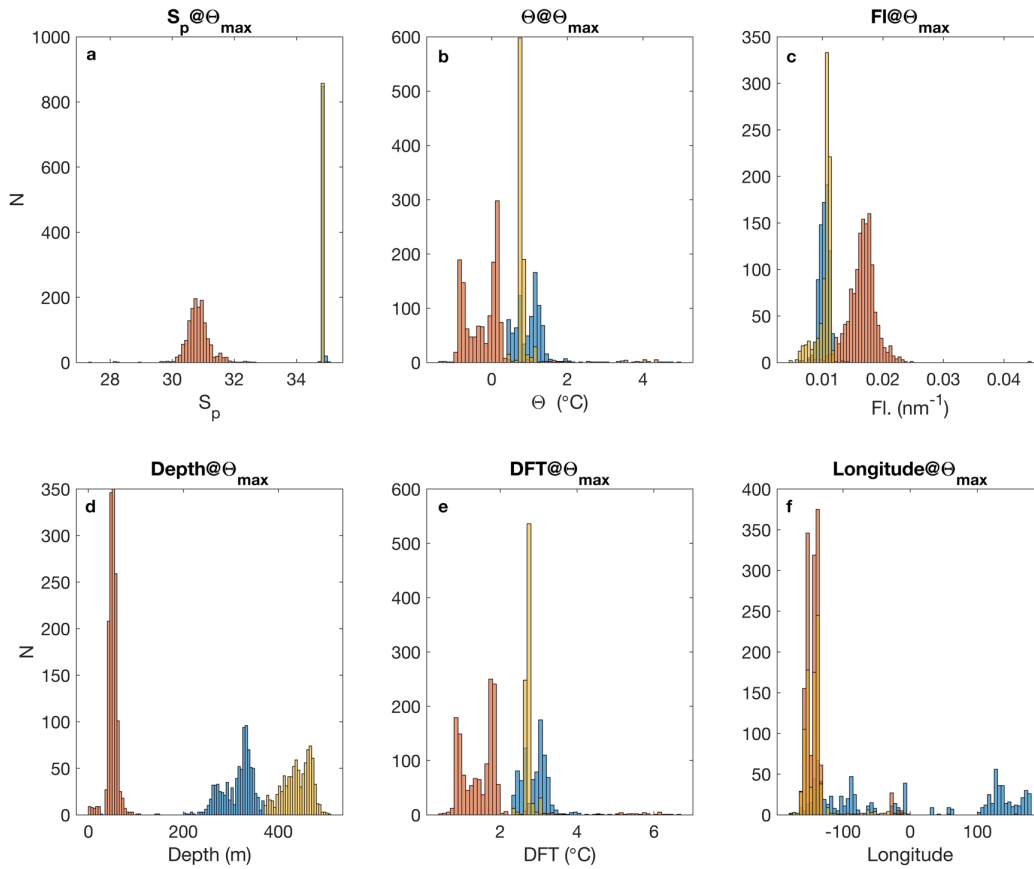
901

902   **Figure 6.** Histograms of properties of the potential temperature maximum. The data are colored
903   to illustrate different features: blue-salinity >33 and depth between 200 and 370 m; red-
904   salinity<33; yellow-salinity>33; a) practical salinity; b) potential temperature; c) DOM

905   fluorescence; d) depth of temperature maximum; e) deviation from freezing temperature; and f)
906   distribution of longitudinal position (positive is east of meridian) between groups.

907

908   **Figure 7.** Histograms of properties of the potential temperature minimum. The data are colored
909   to illustrate different features: blue - deviation from freezing temperature > 0.2 ºC; red -
910   deviation from freezing temperature < 0.2 ºC and 31<S<32; yellow - deviation from freezing
911   temperature < 0.2 ºC and 29.5<S<31; purple - deviation from freezing temperature < 0.2 ºC and
912   salinity <29; a) practical salinity; b) potential temperature; c) DOM fluorescence; d) depth of

913 temperature minimum; e) deviation from freezing temperature; and f) distribution of longitudinal
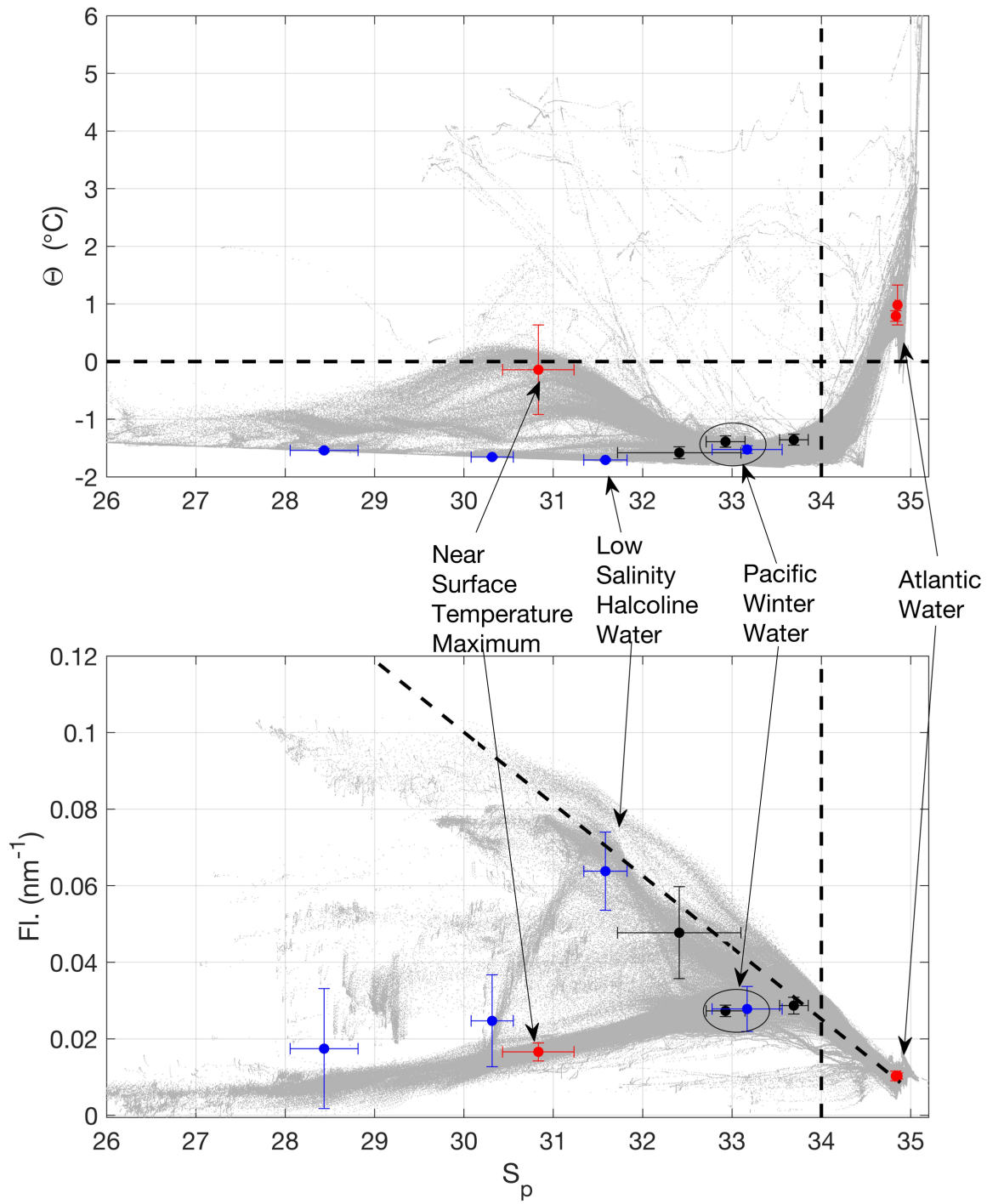914 position (positive is east of meridian) between groups.

915

916 **Figure 8.** Mean endmembers characteristics from the analysis of temperature maximum (red),
917 temperature minimum (blue) and DOM fluorescence (black) maximum properties plotted
918 together will all data (grey). The error bars indicate standard deviation. The top graph is potential
919 temperature against practical salinity and the bottom graph is DOM fluorescence against
920 practical salinity. The horizontal dashed line represents the 0 ºC isotherm and the vertical line the
921 34 isohaline. The diagonal represents a theoretical mixing line between Siberian shelf water
922 (Gonçalves-Araujo et al., 2016) and Atlantic water.

923

924 **Table 1.** Summary of the available data after quality control of the profile data. Only profiles
925 with complete records of temperature, salinity and CDOM fluorescence were selected.

Platform	Fluorescence Sensor***	Start (ITP deployment region)	End	# Profiles	Source
ITP48	*ECO* FLbb-CD	10/Sep/2011 (Lomonosov Ridge)	29/Oct/2012	1302	(Laney et al., 2014; Toole et al., 2016)
ITP52	*ECO* FLbb-CD	6/Aug/2011 (Beaufort Gyre)	14/Nov/2011	363	(Laney et al., 2014; Toole et al., 2016)
ITP60	*ECO* FLbb-CD	15/Sep/2012 (Amundsen Basin)	23/Dec/2012	259	(Laney et al., 2014; Toole et al., 2016)
ITP64	*ECO* FLbb-CD	29/Aug2012 (Beaufort Gyre)	25/Aug/2013	1079	(Laney et al., 2014; Toole et al., 2016)
ITP65	*ECO* FLbb-CD	28/Aug/2012 (Beaufort Gyre)	18/Feb/2013	397	(Toole et al., 2016)
ITP69	*ECO* FLbb-CD	29/Aug/2013 (Chukchi Plateau)	15/Feb/2014	343	(Toole et al., 2016)
ITP72	*ECO* FLbb-CD	31/Aug/2013 (Amundsen Basin)	16/Dec/2013	216	(Toole et al., 2016)
ITP93	*ECO* FLbb-CD	24/Sep/2015 (Lomonosov Ridge)	8/Aug/2016	944*	(Rabe et al., 2016a, 2016b)
PS94	DrHaardt	18/Aug/2015	9/Oct/2015	81**	(Rabe et al., 2016a, 2016b)
NAACOS	WETStar	3/Sep/2012	12/Sep/2012	60	unpublished

926 *Profiles after profile 955 are not included due to failure of the conductivity sensor.
927 ** Data from depths greater than 800m (max depth covered by ITPs) are not included in the
928 analysis.

929 ***ECO FLbb-CD and WETStar (both WET Labs Inc.): Excitation 370 and emission 460 nm;
930 DrHaardt: Excitation 350 – 460 nm, emission 550 nm.

1

3   Supporting Information for

4   Insights into Water Mass Origins in the Central Arctic Ocean from in-situ Dissolved
5   Organic Matter Fluorescence.

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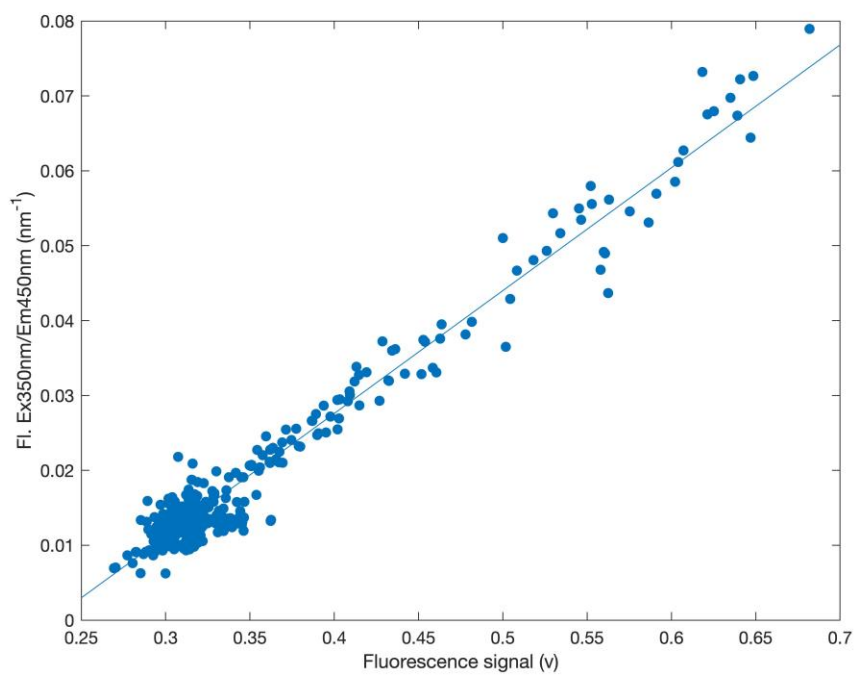20   [8] Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

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36 **Figure S1.** Calibration of the CTD mounted fluorometer on PS94 to water samples taken and
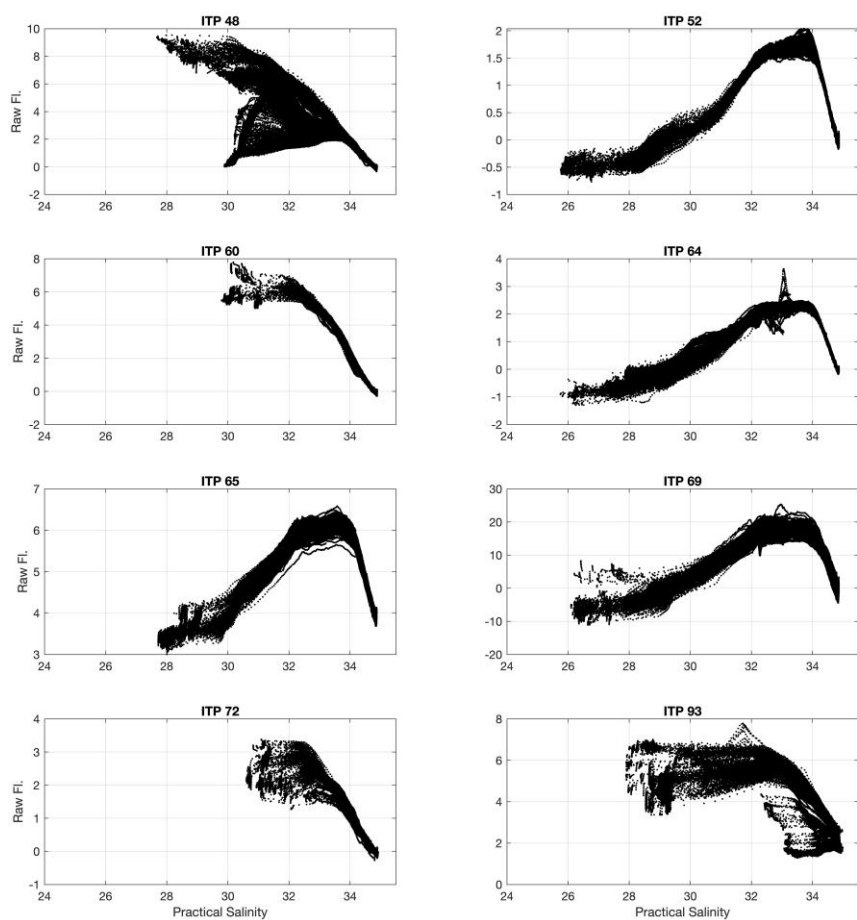37 measured onboard. Fl. = V * 0.1641 − 0.0380; R^2 = 0.96.
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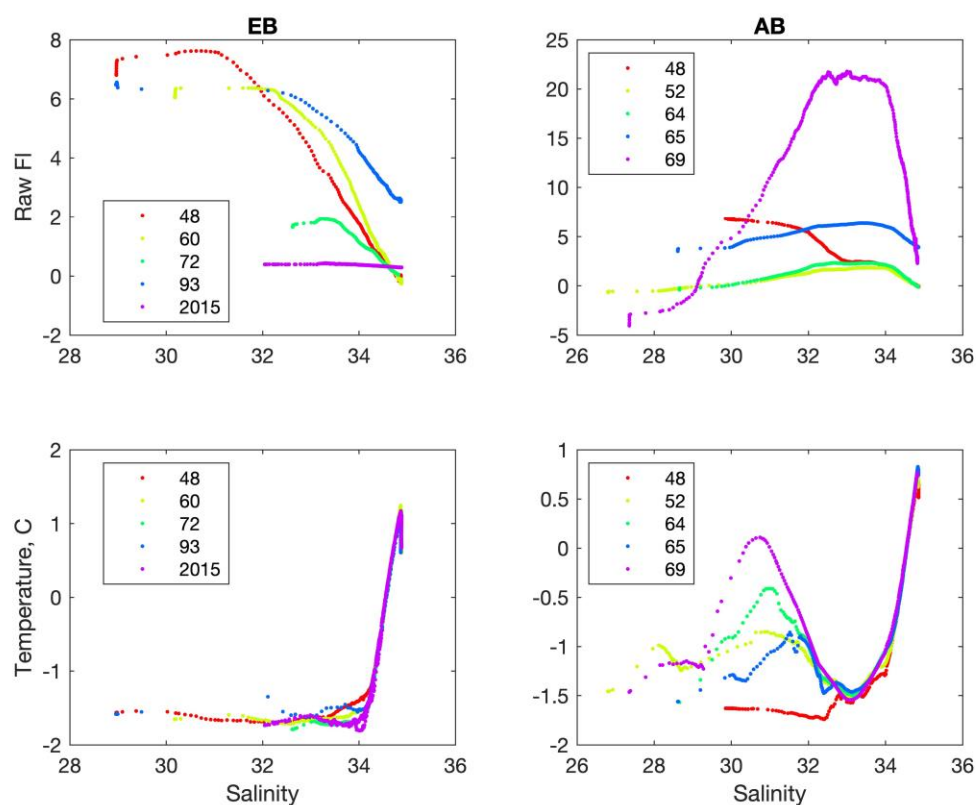40 **Figure S2.** Raw fluorescence signal from the ITPs.
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Figure S3. Data from selected profiles for Eurasian (EB) and Amerasian Basins (AB), where waters with common q-S were sampled and could be used to intercalibrate DOM fluorescence signal.
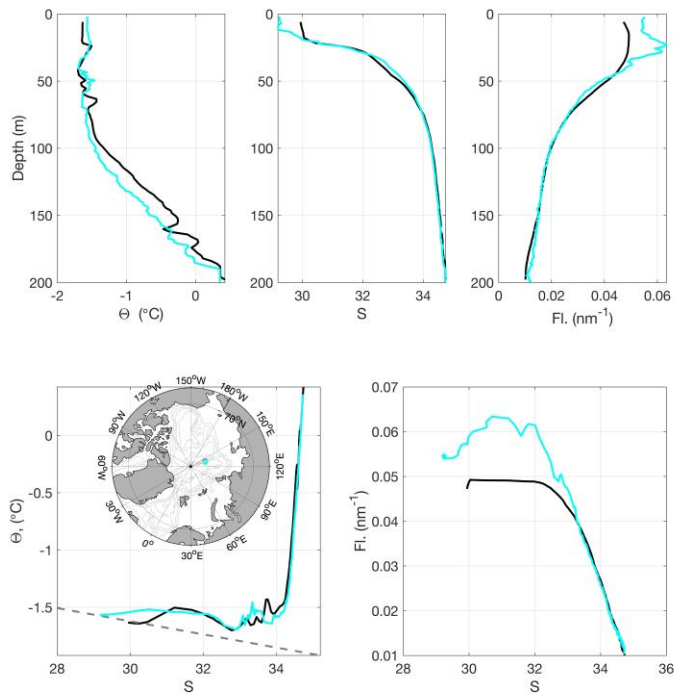
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49   **Figure S4**. Comparison of PS94 (blue) with ITP93 calibrated using the q-S space approach for a
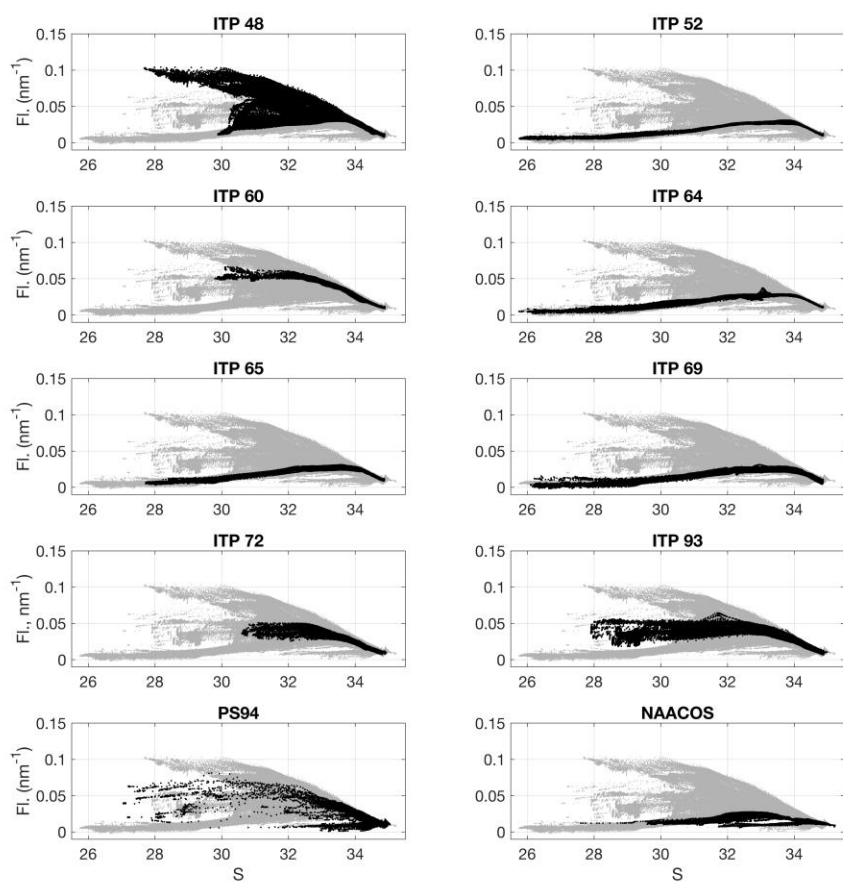50   station where ITP93 was deployed and a ship CTD cast was also performed.
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Figure S5. Calibrated organic matter fluorescence against practical salinity. Black data are for each specific ITP or cruise. Grey data points in the background are all data combined.