

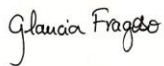
20<sup>th</sup> January, 2017 Editor, **Biogeosciences**

Dear Editor:

I, with my co-authors, would like to resubmit our article entitled “*Spring phytoplankton communities of the Labrador Sea (2005-2014): pigment signatures, photophysiology and elemental ratios*” for publication in **Biogeosciences**. We are pleased that the reviewers (Simon Wright and Reviewer #1) are now satisfied with most of our revisions. The paper has been further revised in accordance with both reviewers’ suggestions and the pending issues raised have now been addressed. A sheet detailing the changes made is included in this letter as well as in the revised manuscript (with and without track changes).

Thank you for your consideration, and we hope the paper is now acceptable.

Sincerely,



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Ms. Ref. No.: bg-2016-295

Title: Spring phytoplankton communities of the Labrador Sea (2005-2014): pigment signatures, photophysiology and elemental ratios. Resubmitted to Biogeosciences.

**We thank the two reviewers for their comments and suggestions, which we feel have greatly improved the manuscript. Below we respond to each comment in detail. RC refers to “Reviewer’s Comments” and AC to “Author’s comments”. We have enumerated the reviewer’s comments to organise our responses.**

Reviewer #1:

RC1.1: In general, the authors have improved the manuscript by incorporating the comments suggested by the reviewers. The new introduction and methodological sections and the use of the standardized abbreviations for pigments make the manuscript easier to read in its present form. The initial matrices used for the CHEMTAX analyses and the RMS are now presented. However I still have a few comments on the manuscript in its present form:

Abstract

Line 26, do the authors mean 70% of total chl a (TChla)?

**AC1.1 – Yes. We have now added “a” after total chlorophyll in the sentence (line 24).**

RC1.2 - Methods

Line 140, first time referring to chlorophyll a, add the abbreviation after chlorophyll a (chl a) and use the abbreviation through the rest of the manuscript. Please check through the manuscript for usage of Tchla or chl a (e.g. line 254, the abbreviation should be Tchla).

**AC1.2 – We have now defined the types of chlorophyll a measurements included in the manuscript and the abbreviation for each of them: chlorophyll a pigment (Chl a) (Table 2), fluorometric chlorophyll a (Chla) (line 147) and HPLC-based total chlorophyll a, including chlorophyllide (TChla) (line 195) and changed the abbreviations in the text accordingly.**

RC1.3 - Similarly, when the authors refer to the photosynthetically active radiation (PAR, line 481), please first define the abbreviation then use it through the manuscript, not the other way around.

**AC1.3 – Changed. Abbreviation of PAR is defined in line 193, where it is mentioned for the first time.**

RC1.4 - Line 143, add extracted “in the dark” for 24 h-

**AC1.4 – Changed. Line 150.**

RC1.5 - Line 152, remove samples and change to chl a fluorescence of water samples was determined on board after...

**AC1.5 – We rewrote the sentence as “Chlorophyll *a* concentrations were determined fluorometrically after 24 h of extraction...”. Line 159.**

RC1.6 Line 186, do the authors refer to the daily incident irradiance (integrated irradiance) averaged per month? Unclear.

**AC1.6 – We refer to the daily incident irradiance averaged over each month. We have now added this information in the text (line 193).**

RC1.7 - Table 2

Chl c3: diatoms type 2 contain this pigment (see Higgins et al. 2011, Coupel et al. 2015).

**AC1.7 – We used Vidussi et al. (2004) as a reference for diatoms in this study. Also, Coupel et al. (2015) did not allocate Chl c3 to diatoms, although Higgins et al. (2011) specifically referred to a second diatom group. A further explanation of why we have not considered the pigment ratio for diatoms according to Higgins et al. (2011) is included in comment AC1.12 (see below).**

RC.1.8 - TChl a row change the Chlide “alpha” to Chlide a.

**AC1.8 – Changed.**

RC.1.9 - Last row of the table, please change CHLA to Chl a.

**AC1.9 – Changed.**

RC1.10 - Table 3

Why are chlorophytes (CHLORO-1) and haptophytes (HAPTO-6) in capital letters?

**AC1.10 – We decided to keep the same terminology used in other references (where the pigment ratios were taken from) because we believe it is easier for the reader to go back to the original reference if needed. Higgins et al. (2011)**

refer to chlorophytes, such as *Dunaliella tertiolecta*, as CHLORO-1 (page 269 of Roy et al., 2011) and HAPTO-6, as *Emiliana huxleyi* (page 281 of Roy et al., 2011).

RC1.11 - According to Higgins et al. 2011, dinoflagellates containing peridinin should be named type 1, please change Dinoflagellates to dino-1 in your matrices. The use of dinoflagellates and then dino-2 is confusing otherwise.

**RC1.11 – Although it is true that dinoflagellates that contain peridinin are termed type 1 by Higgins et al. (2011), the initial pigment ratio for this group was taken from another reference - Coupel et al. (2015), who term them “dinoflagellates”, as well as Vidussi et al. (2004) where the pigment ratio in Coupel et al. (2015) originally came from. We are concerned that if we call it dino-1 it would infer that the pigment ratio was from Higgins et al. (2011), which is not true. For this reason, we have decided to keep the terminology consistent with the source of our pigment ratios. The methods section explains clearly the difference between dinoflagellates and dino-2.**

RC1.12 - Why did you assume that the diatoms present in your study did not contain chl c3? I think you should re-consider this. At least for the communities that are located in the shelves where the authors found high concentration of fucoxanthin together with high chl c3 and diatoms dominated the community.

Seeing the variety of diatom species found in the previous study (lines 565-570), it seems reasonable to think that some of the chl c3 to the total chl a should be attributed to the presence of diatoms type 1 (containing chl c3) and not only to diatoms type-2.

**AC1.12 – We agree with the reviewer that some of the chl c3 could come from diatoms because of the high diversity and abundance of this group found on the shelves. However, the initial pigment ratio selected for diatoms in this study (Vidussi et al. 2004) was carefully selected to avoid the underestimation of *Phaeocystis pouchetii*, given that Chl c3 has been shown to be the main marker of *Phaeocystis* in boreal waters (see explanation in lines 240 and 650) and this species was very abundant in the microscopic counts shown by Frago et al. (2016). Thus, making the changes suggested by the reviewer could result in a significant underestimation of *Phaeocystis* in our study. Moreover, the correlation between algal biomass (carbon estimated from microscopic counts versus CHEMTAX-derived algal chlorophyll *a*) for *Phaeocystis* ( $r^2 = 0.79$ ) and diatoms ( $r^2 = 0.74$ ) (line 639) confirms that the pigment ratios used were appropriate in this study.**

RC1.13 - Line 621, change Front with Font. If you cite this work you need to add the reference in the list.

**AC1.13 – Changed (lines 607, 631, 701).**

Reviewer #2, Simon Wright:

RC2.1 - GENERAL COMMENTS

This paper has been greatly improved from the previous version. Issues that other reviewers picked up issues with pigment analysis and CHEMTAX appear to have been sorted and I am happy with responses to my comments for the most part. I reiterate my earlier comment that this is a useful study that should be published, but unfortunately my major concern, the structure of the manuscript, is not quite there yet - in particular, the Aims are wrong\* - they are too vague and do not fully cover the material presented. They should be re-written as clear EXPLICIT goals for the paper, and other sections should be checked to ensure that the findings are clearly reported. A simple strategy is suggested below that would greatly improve the paper.

**AC2.1 – We appreciate and have accepted the reviewer’s suggestions (see comments below).**

RC2.2 - \*I make that provocative assertion deliberately to focus the following discussion and hopefully (if I may be so bold) to offer some practical guidance to a young scientist. Given that the previous version lacked an aim, and the problems with the aim of the current version (discussed below), I think a fuller explanation of the problem is warranted in the hope of improving subsequent papers as well as this one. Of course I know that in this case, the Aim was written after the rest of the paper, which is exactly what not we are supposed to do. Ideally the Aim (or far preferably, the Hypothesis) should be rigorously defined before designing the experiment, and the content of the resultant paper(s) should be planned as part of the research proposal. It makes the papers much easier to write. Of course that doesn't always happen, and it certainly didn't in many of my experimental papers. Often for surveys or monitoring programs, such as in the current study, the story is discovered as part of the analysis. Nevertheless the paper must be structured as clearly as if the Aim or Hypothesis was clear from the outset. The Aim or Hypothesis is the single most important statement in a paper - not only does it dictate the content of the entire paper, but it also tells the reader what to expect, and primes him or her to recognise the importance of results as they are presented and the relevance of discussion. Thus it is critical that it is VERY carefully considered, explicit, and crystal clear.

In my review of the previous version of this manuscript, I commented: *"This paper desperately needs a clear Aim to provide a basis for a narrative, to dictate what is included in (or excluded from) the paper, to provide a focus for the Results, Discussion and Conclusions, and by which to judge the success of the project."*

The authors responded: **AC2.3 - Clear aims have now been added in the last paragraph of the introduction and the Results, Discussion and Conclusions all link to these aims.**

These aims are set out in the Introduction (lines 88-93):

**The aim of this study is to provide a baseline description of the current distributions and biogeochemical traits of phytoplankton communities from distinct biogeographical regions of the Labrador Sea ..... In addition, we also examine the overall photophysiological and biogeochemical traits associated with these different phytoplankton communities.**

So what is wrong with this Aim? First, it is not clear. It is jargon - general hand-waving. Secondly, it is not explicit. What exactly is meant by terms like baseline description? What photophysiological and biogeochemical traits are examined? (Note the repetition of biogeochemical as well). These general terms should be replaced by explicit reference to P-E curves, fluorometry, POC/PON analysis etc. (many photophysiological and biogeochemical traits were NOT examined!). Thirdly, it is incomplete. There is no mention of the analysis of hydrographic variables that explain the distribution of phytoplankton communities, and thus technically these sections are irrelevant to the paper. In this regard, the Aims have failed the authors because if such an aim was explicitly identified, then they would have mentioned the fact that environmental variables explained 99.8 % of the variability in phytoplankton communities in the Conclusions and the Abstract, which they did not. Thus, what I consider to be an important result of the paper will not be apparent if I read the Title, Abstract, keywords, Aim and Conclusions.

My suggestion for this type of paper, involving post-hoc analysis of a data set, is to set out the Aims as a series of detailed questions that will be addressed in the paper. A useful strategy is to set out, in plain language, what questions the authors asked themselves when they were setting up the statistical analyses presented. Did they say, "Can we provide a baseline description of the current distributions and biogeochemical traits of phytoplankton communities from distinct biogeographical regions of the Labrador Sea"? I doubt it. How about, "Are there distinct communities of phytoplankton within the study region and if so, what are their main constituents? Where do these communities occur and are they stable year-to-year? Can the variability in phytoplankton communities be explained by environmental factors? *Et cetera*"?

**AC2.2 – We have now fully followed the reviewer’s suggestions. We have been through our result section again and listed all the potential specific questions relevant to our main findings. We have, however, avoided a long list, shortened these questions and added them to the end of the introduction to keep it short and direct (line 90).**

RC 2.3 - I hope it is obvious that clear explicit aims like these make it easier for the reader to understand the paper (and thus more likely to cite it), but also make it easier for the authors to write a clear, focused paper in the first place. (By the way, for my students, I normally suggest writing the questions for each test clearly while doing the analyses, as well as their results. Doing it at the time while immersed in the data simplifies the write-up. I also recommend that the statement of Aims in the Introduction should be followed by a brief paragraph describing the approach taken and another outlining the major findings.)

**AC2.3 – We have added a few lines after the questions describing our approach and highlighting our main findings (Line 96).**

RC2.4 - This can be fixed fairly easily without much rewriting. I suggest going through the paper, listing the major results, framing them as questions in the Aims, ensuring that the answers are clear in the Results, and highlighted in the Conclusions and Abstract, then getting on with the next paper and thesis!

**AC2.4 – As stated above, we have now framed the questions based in our results and highlighted our main findings in the conclusions (line 671).**

RC2.5 - I would discard the first sentence of the Aims (Line 88). Start the para, "Here, we investigate the multi-year (2005-2014) distributions" etc using the second and third sentences. Even though I complained about the third sentence, it can be used because it will be explained and expanded in the following sentence: "We address the following questions:" or similar, using the questions as above. The further hand-waving in the final sentence should be replaced by a brief synopsis of the major findings: e.g. " We show that several distinct communities exist ... etc. " More generally, beware of jargon and nominalization - they reduce readability and clarity.

**AC2.5 – We have discarded the first sentence of the aims (line 87) and included the research questions (line 90) and a brief synopsis of the main findings (line 96).**

#### OTHER COMMENTS

RC2.6 - 1. In my previous review, I asked: *RC2.19 -Section 3.2: Did the authors try further subdivision of group C3b? This group is by far the biggest, it is widest spread across the S-T diagram (Fig 5a), and its composition is "mixed", yet Fig 4a shows major divisions within the group. Would these subdivisions distinguish communities that were more coherent in composition and habitat?* The authors responded: **AC2.19 - Cluster C3b had the highest level of internal Bray-Curtis similarity in terms of sample composition (i.e. samples in this group were more similar (73%) to one another than to other groups). Hence, we decided not to further divide it as we could in theory continue to subdivide until each subgroup contains very few samples.** This is the authors' decision of course. My question was raised out of curiosity. However, I will make the more general point that with this sort of analysis, I suggest exploring the patterns and fully understand what they are showing about the data, rather than sticking to arbitrary cutoffs. Then, having understood the data, decide what groupings are appropriate to address the aims of the paper.

**AC2.6 – We appreciate the reviewer’s suggestions and we will take it into consideration in future publications.**

2. Line 74: Change "has" to "have"

**AC2.3 - Changed. Line 73.**

3. Line 154" "pelletised" misspelt

**AC2.4 - Changed. Line 161.**

4. Line 215 and elsewhere: There is a problem with the statement "Zea + Lut is not only found in prasinophytes-type 2, but is also the major accessory pigment of cyanobacteria". It is important to note that Zeaxanthin and Lutein are two separate pigments, despite the fact that they cannot be resolved in the author's HPLC system and elute as a single peak. It is wrong to say THE major accessory pigment of cyanobacteria, first because Zea + Lut is not a single pigment, but also because Cyanobacteria have Zeaxanthin but no Lutein. Likewise, it would be better to say Zea is also a minor pigment in chlorophytes, while Lutein is often the dominant carotenoid (Line 216). Note also that Zeax may be derived from non-photosynthetic bacteria (e.g. Flavobacteria)

**AC2.5 – We have now added a sentence that clarifies that Zea and Lut are different pigments that were co-eluted by the methods used in this study (line 197). We have rewritten the following sentences for clarification: “Zea is not only found in “prasinophytes type 2”, but is also the major accessory pigment of cyanobacteria (such as *Synechococcus* spp.) who have been observed in the Labrador Sea (particularly in Atlantic waters; Li et al., 2006). Zea is also a minor pigment in chlorophytes, while Lut is often the dominant carotenoid in this group (MacIntyre et al., 2010; Vidussi et al., 2004)”, (line 223).**

5. Line 323: "in the Labrador Sea during spring and early summer (2005-2014)" could be replaced by "defined above" (this redundant detail just makes it harder to read)

**AC2.6 - Changed. Line 333.**

6. Line 331: Shouldn't the sigma theta be greater than 27 kg m<sup>-3</sup> rather than less than?

**AC2.7 - Changed. Line 340.**

7. Line 352: Comma after variance



**AC2.8 – Changed. Line 362.**

8. Line 604: Presumably "relies" should not be italicised

**AC2.9 – Changed. Line 614.**

9. Line 621: Alou-Front et al (2016) is not in References, and presumably should be Alou-Font

**AC2.10 – Changed. Lines 607, 631, 701.**

10. Line 750: Gieskes and Kraay (1983) missing

**AC2.11 – Reference added. Line 768.**

CoupeL, P., Matsuoka, A., Ruiz-Pino, D., Gosselin, M., Marie, D., Tremblay, J. E. and Babin, M.: Pigment signatures of phytoplankton communities in the Beaufort Sea, *Biogeosciences*, 12(4), 991–1006, doi:10.5194/bg-12-991-2015, 2015.

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Higgins, H. W., Wright, S. W. and Schlüter, L.: Quantitative interpretation of chemotaxonomic pigment data, in *Phytoplankton Pigments: Characterization, Chemotaxonomy and Applications in Oceanography*, edited by S. Roy, C. Llewellyn, E. S. Egeland, and G. Johnsen, pp. 257–313, Cambridge University Press, Cambridge., 2011.

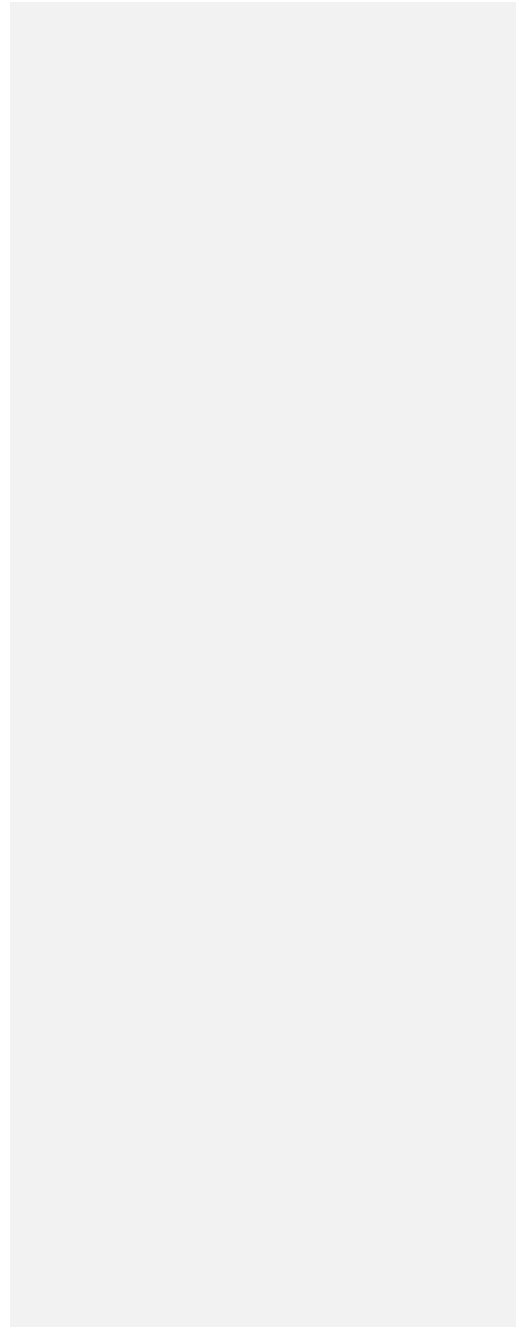
Li, W. K. W., Harrison, W. G. and Head, E. J. H.: Coherent assembly of phytoplankton communities in diverse temperate ocean ecosystems., *Proc. Biol. Sci.*, 273(August), 1953–1960, doi:10.1098/rspb.2006.3529, 2006.

MacIntyre, H. L., Lawrenz, E. and Richardson, T. L.: Taxonomic discrimination of phytoplankton by spectral fluorescence, in *Chlorophyll a fluorescence in aquatic sciences: methods and applications*, pp. 129–169, Springer Netherlands., 2010.

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Vidussi, F., Roy, S., Lovejoy, C., Gammelgaard, M., Thomsen, H. A., Booth, B., Tremblay, J.-E. and Mostajir, B.: Spatial and temporal variability of the phytoplankton community structure in the North Water Polynya, investigated using pigment biomarkers, *Can. J. Fish. Aquat. Sci.*, 61(11), 2038–2052, doi:10.1139/f04-152, 2004.

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## **Spring phytoplankton communities of the Labrador Sea (2005-2014): pigment signatures, photophysiology and elemental ratios**

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**Abstract.** The Labrador Sea is an ideal region to study the biogeographical, physiological and biogeochemical implications of phytoplankton community composition due to sharp transitions between distinct water masses across its shelves and central basin. ~~The aim of this study is to provide a baseline description of the distributions and biogeochemical traits of phytoplankton communities from distinct biogeographical regions of the Labrador Sea.~~ We have investigated the multi-year (2005-2014) distributions of late spring and early summer (May to June) phytoplankton communities in the various hydrographic settings of the Labrador Sea. Our analysis is based on pigment markers (using CHEMTAX analysis), and photophysiological and biogeochemical characteristics associated with each phytoplankton community. Diatoms were the most abundant group, blooming first in shallow mixed layers of haline-stratified Arctic shelf waters. Along with diatoms, chlorophytes co-dominated at the western end of the section (particularly in the polar waters of the Labrador Current (LC)), whilst *Phaeocystis* co-dominated in the east (modified polar waters of the West Greenland Current (WGC)). Pre-bloom conditions occurred in deeper mixed layers of the central Labrador Sea in May, where a mixed assemblage of flagellates (dinoflagellates, prasinophytes, prymnesiophytes, particularly coccolithophores, and chrysophytes/pelagophytes) occurred in low chlorophyll areas, succeeding to blooms of diatoms and dinoflagellates in thermally-stratified Atlantic waters in June. Light-saturated photosynthetic rates and saturation irradiance levels were highest at stations where diatoms were the dominant phytoplankton group (> 70 % of total chlorophyll *a*), as opposed to stations where flagellates were more abundant (from 40 % up to 70 % of total chlorophyll *a*). Phytoplankton communities from the WGC (*Phaeocystis* and diatoms) had lower light-limited photosynthetic rates, with little evidence of photo-inhibition, indicating greater tolerance to a high light environment. By contrast, communities from the central Labrador Sea (dinoflagellates and diatoms), which bloomed later in the season (June), appeared to be more sensitive to high light levels. Ratios of accessory pigments (AP) to total chlorophyll *a* (TChl*a*) varied according to phytoplankton community composition, with polar phytoplankton (cold-water related) having lower AP:TChl*a*. Polar waters (LC and WGC) also had higher and more variable particulate organic carbon (POC) to particulate organic nitrogen (PON) ratios, suggesting the influence of detritus from freshwater input, derived from riverine, glacial and/or sea-ice meltwater. Long-term observational shifts in phytoplankton communities were not assessed in this study due to the short temporal frame (May to June) of the data. Nevertheless, these results ~~provide~~ add to a our baseline of present day current understanding of phytoplankton group distribution, as well as an evaluation of the biogeochemical role (in terms of C:N ratios) of spring phytoplankton communities in the Labrador Sea, which will ~~improve~~ assist our understanding of potential long-term responses of phytoplankton communities in high-latitude oceans to a changing climate.

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#### 40 **Keywords**

Phytoplankton communities, CHEMTAX, hydrography, photophysiology, biogeochemistry, Labrador Sea

## 1. Introduction

Marine phytoplankton form a taxonomically and functionally diverse group, where communities are structured by a variety of factors, including nutrient and light availability, predation and competition for resources (Litchman and Klausmeier, 2008). Such environmental heterogeneity creates biogeographical patterns of abundance, composition, traits and diversity of phytoplankton communities in the global ocean (Barton et al., 2013; Follows et al., 2007; Hays et al., 2005). Phytoplankton communities within a biogeographical region are subject to similar environmental conditions, such as temperature (Bouman et al., 2003), nutrient concentration (Browning et al., 2014) and irradiance (Arrigo et al., 2010). These environmental factors, along with phytoplankton community composition itself (Bouman et al., 2005), affect the overall photo-physiological response and bulk rates of primary production.

The biogeography of phytoplankton communities and their photo-physiological characteristics, consequently, directly impact the structure of marine ecosystems due to their functional role in biogeochemical cycling and the transfer of energy to higher trophic levels. For example, distinct phytoplankton assemblages influence particulate (Martiny et al., 2013a, 2013b; Smith and Asper, 2001) and dissolved elemental stoichiometry (C:N:P) (Weber and Deutsch, 2010), the drawdown of gases (Arrigo, 1999; Tortell et al., 2002) and the efficiency of carbon export (Guidi et al., 2009; Le Moigne et al., 2015) in different ways. Patterns of phytoplankton stoichiometry may be consistent phylogenetically within higher taxonomic levels (Ho et al., 2003; Quigg et al., 2003), however, stoichiometry also varies according to nutrient supply ratios (Bertilsson et al., 2003; Rhee, 1978) and phenotypically within species of the same population (Finkel et al., 2006).

The sub-Arctic North Atlantic is a complex system with contrasting hydrography that structures plankton communities within distinct biogeographical provinces (Fragoso et al., 2016; Head et al., 2003; Li and Harrison, 2001; Platt et al., 2005; Sathyendranath et al., 1995, 2009). Biogeographical regions of the Labrador Sea shape phytoplankton community composition (Fragoso et al., 2016), bio-optical properties (Cota, 2003; Lutz et al., 2003; Platt et al., 2005; Sathyendranath et al., 2004; Stuart et al., 2000) and the seasonality of phytoplankton blooms (Frajka-Williams and Rhines, 2010; Lacour et al., 2015; Wu et al., 2007, 2008). Phytoplankton blooms, for example, occur first (April to early May) on the shelves due to haline-driven stratification driven by the input of Arctic-related waters, in addition to rapid sea ice melt on the Labrador Shelf near Canada (Frajka-Williams and Rhines, 2010; Wu et al., 2007). The central Labrador bloom occurs later in the season (late May to June) as result of thermal stratification (Frajka-Williams and Rhines, 2010). Fragoso et al. (2016) showed that the biogeography of phytoplankton communities in the Labrador Sea during spring and early summer is shaped by distinct species found in Atlantic or Arctic waters, which may have distinct influences on biogeochemical cycles and the transfer of energy to upper trophic levels. However, these authors focused on taxonomy and only investigated relatively large phytoplankton (> 4µm). The photo-physiological and biogeochemical signatures, such as particulate matter stoichiometry (C:N ratio) of these different spring phytoplankton communities occurring in distinct sectors of the Labrador Sea haves not been investigated.

Quantification of marine phytoplankton community composition, for a large numbers of samples, is challenging due to small cells (< 5µm) being difficult to identify and accurately count using light microscopy, in addition to being a very time-consuming method. To overcome these problems, quantification and analyses of phytoplankton pigments by high performance liquid chromatography (HPLC) has been widely used to monitor phytoplankton community distributions over large temporal and spatial scales (e.g., Aiken et al., 2009; Peloquin et al., 2013; Platt et al., 2005). The interpretation of the pigment data is not always straightforward, since some pigments are shared by several algal groups and can vary according to local nutrient and light conditions (e.g., DiTullio et al., 2007; van Leeuwe and Stefels, 1998, 2007). The chemotaxonomic tool, CHEMTAX (CHEMical TAXonomy), provides a valuable approach to estimate phytoplankton group abundances when used in conjunction with microscopic information (Irigoien et al., 2004; Mackey et al., 1996; Wright et al., 1996). CHEMTAX has the advantage of providing more information about phytoplankton groups than individual diagnostic pigments or ratios and has been used widely to investigate phytoplankton biogeography on regional scales (e.g., Muylaert et al., 2006; Wright and Van den Eenden, 2000) and globally (e.g., Swan et al., 2015).

The aim of this study is to provide a baseline description of the current distributions and biogeochemical traits of phytoplankton communities from distinct biogeographical regions of the Labrador Sea. For this purpose, here, we investigate the multi-year (2005-2014) distributions of late spring and early summer (May to June) phytoplankton communities in the various hydrographic settings across the shelves, slopes and deep basin of the Labrador Sea based on phytoplankton pigments. In addition, we also examine the overall photophysiological and biogeochemical traits associated with these different phytoplankton communities. The purpose of this study is to answer the following questions: are there distinct phytoplankton communities in the Labrador Sea and if so, what are their main constituents? How spatial and temporal variability in environmental factors may explain the phytoplankton community distribution and composition? What are the linkages between community composition and variability in both particulate matter stoichiometry (i.e. C:N ratios) and photo-physiological traits (parameters of the photosynthesis versus irradiance relationships) across the Labrador Sea?

~~In this study, we have~~ Our results provided a geographical description of the phytoplankton community structure in spring and early summer surface waters of the Labrador Sea based on pigment data and CHEMTAX analysis from over a decade of sampling (2005-2014). We show that several distinct phytoplankton communities exist, which, that they vary among between the distinct-different hydrographic zones of the Labrador Sea, and that they presented variable patterns in terms of C:N ratios as well as photo-physiological responses to the environmental conditions.

The results presented here will provide important information about the current condition of phytoplankton communities in the Labrador Sea during spring, and help to improve the understanding of potential long-term changes in high-latitude oceans.

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## 2. Methods

### 110 2.1 Study area

The Labrador Sea is a high latitude marginal sea located in the northwestern part of the Atlantic Ocean, and is an important transition zone between Arctic and sub-Arctic ecosystems. It is bounded by Davis Strait to the north, a line from Cape St. Francis in Newfoundland (47°45' N, 52°27' W) to Cape Farewell (southern tip of Greenland) to the southeast, and the coast of Labrador and Newfoundland to the west (Fig. 1) (International Hydrography Organization, 1953). The bathymetry of the  
115 Labrador Sea can be subdivided into the wide continental shelf and relatively gentle continental slope on its western side (the Labrador Shelf, > 500 km wide and < 250 m deep) and the narrow shelf and steep continental slope on the eastern side (the Greenland Shelf and Slope, < 100 km wide and < 2500 m deep).

The upper Labrador Sea (< 200 m) is comprised of waters originating from the North Atlantic and the Arctic (Yashayaev, 2009). Atlantic-influenced waters occur mostly in the central Labrador Sea, where waters are relatively warm, salty and mainly identified as the Irminger Current (IC). Cold, low salinity waters originate from the Arctic *via* the surrounding shelves and are mainly identified as the Labrador Current (LC) and the West Greenland Current (WGC) (Fig 1). Circulation in the central basin of the Labrador Sea is complex, often showing a gyre-like flow system that alternates in direction (Palter et al. 2016, Wang et al, 2016).  
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The inshore branch of the LC overlies the Labrador Shelf and includes Arctic waters originating from Baffin Bay and the Canadian Arctic Archipelago *via* Davis Strait and from Hudson Bay *via* Hudson Strait, together with inputs of melting sea ice that originates locally or from further north. The main branch of the LC flows along the Labrador slope from north to south and is centered around the 1000 m depth contour. It is composed of a mixture of Arctic water from Baffin Bay *via* Davis Strait and the branch of the WGC that flows west across the mouth of Davis Strait. The WGC, which flows from south to north over  
130 the Greenland shelf and along the adjacent slope, is a mixture of cold, low salinity Arctic water exiting the Nordic Seas with the East Greenland Current (EGC) (Yashayaev, 2007), together with sea ice and glacial melt water (Fig 1). The WGC often spreads westwards, forming a “tongue” of buoyant freshwater, which accumulation of low salinity waters is driven by high eddy kinetic activity in the central eastern Labrador Sea during spring (Frajka-Williams and Rhines, 2010). The WGC often  
135 floats over the IC in the central-eastern part of the Labrador Sea, however, the IC is usually observed in surface waters of the central-western Labrador Sea during spring. More detailed descriptions of the hydrography of the Labrador Sea can be found elsewhere (e.g. Fragoso et al., Head et al. 2013, Yashayaev and Seidov, Yashayaev 2007).

## 2.2 Sampling

140 Data used for this study were obtained along the AR7W Labrador Sea hydrography line (World Ocean Circulation Experiment Atlantic Repeat 7-West section, for details see Fragoso et al., 2016), which runs between Misery Point on the Labrador coast (through Hamilton Bank on the Labrador Shelf) and Cape Desolation on the Greenland coast. Stations were sampled during late spring and/or early summer, varying within a 6-week window (see sampling dates in Table 1) over a period of 10 years (2005-2014) by scientists from the Bedford Institute of Oceanography (BIO), Canadian Department of Fisheries and Oceans.

145 Fixed stations (total of 28), as well as some additional non-standard stations, were sampled across the shelves and central basin on the AR7W section, or slightly north or south of this transect (Fig. 1).

Vertical profiles of temperature and salinity were measured with a Seabird CTD system (SBE 911). Seawater samples were collected using 10-L Niskin bottles mounted on a rosette frame. Mixed layer depths were calculated from the vertical density ( $\sigma_\theta$ ) distribution and defined as the depth where  $\sigma_\theta$  changes by  $0.03 \text{ kg m}^{-3}$  from a stable surface value ( $\sim 10 \text{ m}$ ) (Weller and Plueddemann, 1996). A stratification index (SI) was also calculated as the seawater density difference (between 10 m to 60 m) normalised to the equivalent difference in depth.

Water samples from the surface layer ( $< 10 \text{ m}$ ) were collected (0.5 L–1.5 L) for the determination of *fluorometric chlorophyll  $a$*  (Chl $a$ ), accessory pigments, nutrients, particulate organic carbon (POC) and nitrogen (PON) analysis, and for primary production measurements. Filters for *chlorophyll-Chl $a$*  measurements were immediately put in scintillation vials containing 10 ml of 90% acetone, which were placed into a  $-20^\circ\text{C}$  freezer and extracted *in the dark* for 24 h. Samples for detailed pigment analysis were filtered onto 25 mm glass fibre filters (GF/F Whatman Inc., Clifton, New Jersey) and immediately flash frozen in liquid nitrogen, kept frozen in a freezer (at  $-80^\circ\text{C}$ ) until analysis in the BIO (2005-2013) or National Oceanography Center (UK) (2014) laboratories within 2-3 months of collection. Volumes of water sampled for *HPLC-pigment* analysis were adjusted, such that samples were filtered as quickly as possible ( $< 10 \text{ mins}$ ). Nutrient samples were kept refrigerated at  $5^\circ\text{C}$  and analysed at sea (within 12 h of collection) on a SEAL AutoAnalyser III. Samples for POC and PON were filtered (0.25 L–1 L) onto 25 mm pre-combusted ( $400^\circ\text{C}$ , 12 h) GF/F filters, frozen ( $-20^\circ\text{C}$ ) and returned to the BIO laboratory for later analysis.

## 2.3 Biogeochemical analysis

*Chlorophyll  $a$  concentrations were determined fluorometrically* ~~For chlorophyll  $a$  fluorescence of water samples, fluorescence was determined on board~~ after 24 h of extraction *in 90% acetone* using a Turner Designs fluorometer (Holm-Hansen et al., 1965). Back in the laboratory, POC/PON samples were oven-dried ( $60^\circ\text{C}$ ) for 8-12 hours, stored in a dessicator,

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170 pelletised in pre-combusted tin foil cups and analysed using a Perkin Elmer 2400 Series CHNS/O analyser, as described in  
Pepin and Head (2009).

#### 2.4 Pigment analysis

Pigments (chlorophyll *a* and accessory pigments) were quantified using reverse-phase, High-Performance Liquid  
175 Chromatography (HPLC). Methods for 2005-2013 (Hudson cruises), including information about the standards, calibration  
and quantification procedures are described in detail in Stuart and Head (2005), known as the “BIO method”. Methods for  
samples collected in 2014 (JR302 cruise) are described in Poulton et al. (2006). Quality control of both methods was applied  
according to Aiken et al. (2009). Precision of the instruments was tested by running samples and standards and the coefficient  
of variation for pigments were < 10% of the mean. Limits of detection were ~0.01 and 0.002 mg m<sup>-3</sup> for carotenoids and  
180 chlorins, respectively (Head, pers. comm, Poulton et al., 2006). Pigment concentrations below detection limits were not  
reported. A list of pigments identified and quantified for this study is included in Table 2.

#### 2.5 CHEMTAX analysis

The CHEMTAX software (Mackey et al., 1996) was used to estimate the relative abundance of distinct micro-algal groups to  
185 total chlorophyll *a* from *in situ* pigment measurements. The software utilises a factorization program that uses “best guess”  
ratios of accessory pigments to chlorophyll *a* that are derived for different groups from the literature available and marker  
pigment concentrations of algal groups that are known to be present in the study area, as reported in Fragoso et al. (2016). The  
program uses the steepest descent algorithm to obtain the best fit to the data based on assumed pigment to chlorophyll *a* ratios  
(for more detail, see Mackey et al 1996). Because CHEMTAX is sensitive to the seed values of the initial ratio matrix (Latasa,  
190 2007), we used a later version (v1.95) to obtain the more stable output matrices. In this CHEMTAX version, the initial matrices  
are optimized by generating 60 further pigment ratio tables using a random function (RAND in Microsoft Excel) as described  
in Wright et al. (2009). The results of the six best output matrices (with the smallest residuals, equivalent to 10 % of all  
matrices) were used to calculate the averages of the abundance estimates and final pigment ratios.

195 One of the main assumptions of the CHEMTAX method is that information about the phytoplankton taxonomy is used to  
assure that the pigment ratios are applied and interpreted correctly (Irigoien et al., 2004). To satisfy this requirement, initial  
pigment ratios were carefully selected and applied to each cluster to adjust the pigments to the appropriate groups according  
to previous microscopic observations (Fragoso et al., 2016) and literature information (see Table 3). Pigment ratio tables were  
based on the literature in waters having comparable characteristics to the Labrador Sea, such as Baffin Bay (Vidussi et al.,  
200 2004), the Beaufort Sea (Coupel et al., 2015) and the North Sea (Antajan et al., 2004; Muylaert et al., 2006) or from surface  
(high light) field data (Higgins et al., 2011) (Table 3). High light field ratios were chosen because samples were collected from

205 surface waters during May and June, when photosynthetic active radiation (PAR) is high (daily incident irradiance averaged monthly irradiance per month >30 mol PAR m<sup>-2</sup> d<sup>-1</sup>, Harrison et al 2013). The following pigments chosen for CHEMTAX analysis were: 19-butanoyloxyfucoxanthin (But-fuco), 19-hexanoyloxyfucoxanthin (Hex-fuco), alloxanthin (Allo), total chlorophyll *a* derived from HPLC analysis (TChl<sub>a</sub>, see Table 2), chlorophyll *b* (Chl *b*), chlorophyll *c*3 (Chl *c*<sub>3</sub>), fucoxanthin (Fuco), peridinin (Peri), prasinoxanthin (Pras) and zeaxanthin + lutein (Zea + Lut). Zeaxanthin (Zea) and lutein (Lut) are two different pigments that co-eluted as a single peak by the methods of pigment analyses applied in this study.

210 The other main requirement of the CHEMTAX method is that pigment ratios remain constant across the subset of samples that are being analysed (Mackey et al., 1996). To satisfy this assumption, *a priori* analysis was performed, where pigment data were sub-divided into groups using cluster analysis (Bray-Curtis similarity; PRIMER-e V7, see Section 2.7) and each group was processed separately by the CHEMTAX program (Table 3; for the final ratio matrix, see supplemental material). This approach was used as distinct phytoplankton communities have been previously observed in the Labrador Sea (Fragoso et al., 2016), so the ratio of accessory pigment to chlorophyll *a* likely varies within different water masses across the Labrador Sea (LC, IC and WGC). Absolute concentrations of selected pigments (But-fuco, Hex-fuco, Allo, Chl *b*, Chl *c*<sub>3</sub>, Fuco, Peri, Pras and Zea + Lut) were fourth-root transformed and standardized (converted to %) before being analysed. Due to the high abundance of diatoms in the data, we decided to apply a fourth-root transformation to increase the importance of less abundant groups, which would allow us to better discern the spatial-temporal patterns of the phytoplankton communities in the Labrador Sea.

220 An initial cluster analysis on the select pigment data identified five major groups having 60 % similarity between samples. Clusters included stations partially located: 1) on the shelves, where Fuco dominated at a few stations (I); 2) in the eastern part of the Labrador Sea, where most stations had high relative concentrations of Fuco and Chl *c*<sub>3</sub> (II); 3) in the central Labrador Sea, where a few stations had high proportions of Fuco, Hex-fuco and Peri (III); 4) on the western part of the section, where Chl *b* and Fuco were the main pigments at most stations (IV); and 5) in the central Labrador Sea, where most stations had a mixture of pigments (Fuco, Chl *c*<sub>3</sub>, Hex-fuco, Chl *b*, Peri and others) (V) (Fig. S1, supplemental material).

230 Prasinophytes were separated into “prasinophyte type 1”, which contains Pras, and “prasinophyte type 2”, such as *Pyramimonas* and *Micromonas*, with the latter previously found lacking Pras and containing Zea + Lut in the North Water Polynya (Canadian Arctic) (see Vidussi et al., 2004). Both genera were observed in light microscope counts in Labrador Sea samples (Fragoso, pers. obs.), *M. pusilla* has been observed in the Beaufort Sea (Coupel et al., 2015), and was found to be one of the main pico-eukaryotes in the North Water Polynya from April to July of 1998 (Lovejoy et al., 2002). ~~Zea+Lut~~ is not only found in “prasinophytes type 2”, but is also the major accessory pigment of cyanobacteria (such as *Synechococcus* spp.) who have been observed in the Labrador Sea (particularly in Atlantic waters; Li et al., 2006). ~~Zea+Lut~~ is also a minor pigment in chlorophytes, while Lut is often the dominant carotenoid in this group (MacIntyre et al., 2010; Vidussi et al., 2004). Due to

their association with the warmer Atlantic waters, cyanobacteria were assumed to be absent from very cold waters, such as the Labrador Current (see Fragoso et al., 2016). Prasinophytes contain Chl *b*, as well as chlorophytes (Vidussi et al., 2004) which were observed in large numbers with the microscope (Fragoso, pers. obs). Dinoflagellates were separated into species that contain Peri (*Heterocapsa* sp. and *Amphidium*; Coupel et al., 2015; Higgins et al., 2011), and those that do not (*Gymnodinium* spp.; herein defined as “dinoflagellates type-2” (Dino-2) according to Higgins et al. (2011)) and may contain Chl *c*<sub>3</sub>, But-fuco, Hex-fuco and Fuco. Dinoflagellates were observed in lower concentrations in the eastern Labrador Sea (Fragoso et al., 2016), so that “Dino-2” was assumed absent from this area (clusters I & II in Table 3). Cryptophytes (Table 3) are the only group to contain Allo.

245 Prymnesiophytes were divided into three groups: 1) *Phaeocystis pouchetii*, which was observed in high concentrations in the eastern Labrador Sea (Fragoso et al., 2016) (clusters I & II, Table 3); 2) “Prymnesiophyte 1” (as in Vidussi et al., 2004), associated with *Chrysocromulina* spp. and observed in the western Labrador Sea (Labrador Current, this study) (cluster IV, Table 3); and 3) “HAPTO-6” (as in Higgins et al. (2011)), which included the coccolithophores, particularly *Emiliania huxleyi* associated with Atlantic waters (central-eastern region of the Labrador Sea) (clusters I, II, III and V, Table 3). *Phaeocystis pouchetii* occurred in waters having low Hex-fuco and But-fuco concentrations and high Chl *c*<sub>3</sub> and Fuco concentrations (cluster II, Fig. S1, supplemental material). Similar pigment compositions were found in *Phaeocystis globosa* blooms in Belgian Waters (Antajan et al., 2004; Muylaert et al., 2006) and high ratios of Chl *c*<sub>3</sub> to Chl *a* have been used to identify *Phaeocystis pouchetii* in the Labrador Sea (see Stuart et al., 2000). Thus, Chl *c*<sub>3</sub> and Fuco were the only pigments that could be used to represent *Phaeocystis*. In addition to Chl *c*<sub>3</sub> and Fuco, “Prymnesiophyte 1” included Hex-fuco, while “HAPTO-6” included 255 Hex-fuco and But-fuco as in Higgins et al. (2011). Chrysophytes and pelagophytes (such as *Dictyocha speculum*) have high ratios of But-fuco to Chl *a* (Coupel et al., 2015; Fragoso and Smith, 2012), and finally diatoms were identified as containing high Fuco: Chl *a* ratios (Vidussi et al., 2004) (Table 3).

## 2.6 Photosynthesis versus irradiance incubations

260 Water samples were spiked with <sup>14</sup>C-bicarbonate and incubated in a light box under 30 different irradiance levels (from 1 - 600 W m<sup>-2</sup>) at *in situ* temperature for 2 to 3 hours to measure parameters derived from photosynthesis versus irradiance (P-E) curves as described by Stuart et al. (2000). Measurements were fitted to the equation of Platt and Gallegos (1980) to determine photosynthetic efficiency ( $\alpha^B$ ), the maximum photosynthetic rate normalized to chlorophyll biomass ( $P_m^B$ ), the light intensity approximating the onset of saturation ( $E_k$ ), the saturation irradiance ( $E_s$ ) and the photo-inhibition parameter ( $\beta$ ).

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## 2.7 Statistical analysis

Fragoso et al. (2016) found a significant linear relationship between phytoplankton carbon, calculated from phytoplankton cell counts, and POC data using results from 2011-2014 surveys in the Labrador Sea (i.e.  $POC = 1.01POC_{phyto} + 240.92$ ;  $r^2 = 0.47$ ;  $n = 44$ ;  $p < 0.0001$ ). To estimate phytoplankton-derived carbon ( $POC_{phyto}$ ) concentrations (as opposed to total POC, which includes detritus and heterotrophic organisms), regression analysis was performed using the carbon calculated from cell counts (derived from Fragoso et al., 2016) and measurements of fluorometric chlorophyll *a* (Chl*a*). This regression ( $POC_{phyto} = 38.9$  Chl*a*;  $r^2 = 0.9$ ;  $n = 41$ ;  $p < 0.0001$ ) was then applied to estimate  $POC_{phyto}$  for stations where phytoplankton cell counts were not available (2005-2010).

Phytoplankton community structure derived from pigment concentrations was investigated using PRIMER-E (v7) software (Clarke and Warwick, 2001). Chlorophyll *a* concentrations derived for each algal group resulting from CHEMTAX analysis were standardized (converted to percentage values) to obtain their relative proportions, which were fourth-root transformed to allow the least abundant groups to contribute to the analysis. Similarity matrices were generated from Bray-Curtis similarity for cluster analysis. A SIMPER (SIMilarity PERcentages) routine with a cut off of 90 % cumulative contribution to the similarity was used to reveal the contributions of each group to the overall similarity within clusters. One-way ANOSIM was also applied to determine whether taxonomic compositions of the clusters were significantly different.

A redundancy analysis (RDA) using the CANOCO 4.5 software (CANOCO, Microcomputer Power, Ithaca, NY) was performed to analyse the effects of different environmental factors on the Labrador Sea phytoplankton community structure (see also Fragoso et al. (2016)). Data were log-transformed and forward-selection (*a posteriori* analysis) identified the subset of environmental variables that significantly explained the taxonomic distribution and community structure when analysed individually ( $\lambda_1$ , marginal effects) or when included in a model where other forward-selected variables were analysed together ( $\lambda_a$ , conditional effects). A Monte Carlo permutation test ( $n = 999$ , reduced model) was applied to test the statistical significance ( $p < 0.05$ ) of each of the forward-selected variables.

### 3. Results

#### 3.1 Environmental variables

Sampling dates varied from May to June during this 10-year study, where samples from 2007, 2011 and 2013 were collected in early May, as opposed to samples from 2012 and 2104, which were collected later in the season (mid to late June) (Fig. 2b). Environmental parameters, as well as fluorometric chlorophyll *a* (Chl*a*) concentrations varied noticeably along the southwest-northeast section of the Labrador Sea (Fig. 2c-l). The shelf and slope regions (LSh, LSI, GSI, GSh) had colder and fresher waters ( $< 3$  °C and  $< 33.5$ , respectively) compared to the central basin (CB), where surface waters were saltier ( $> 33.5$ ) and warmer ( $> 3$  °C), particularly in 2005, 2006, 2012 and 2014 ( $> 5$  °C) (Fig. 2c, d). Shelf waters that were the coldest and freshest were also the most highly stratified ((stratification index (SI)  $> 5 \times 10^{-3}$  kg m<sup>-4</sup>), particularly on the Labrador Shelf (SI  $> 15 \times$

300  $10^{-3} \text{ kg m}^{-4}$ ), whereas waters from the CB were less stratified ( $SI < 5 \times 10^{-3} \text{ kg m}^{-4}$ ), apart from at stations collected later in the season (Fig. 2b), where waters were slightly warmer than usual ( $> 5^\circ\text{C}$ ) in 2005, 2012 and 2014 (Fig. 2e). Chl $a$  concentrations were highest ( $> 4 \text{ mg Chl}a \text{ m}^{-3}$ ) at stations where waters were highly stratified, particularly on the shelves (Fig. 2f). Nitrate, phosphate and silicate concentrations were inversely related to Chl $a$  concentration, being lowest ( $< 5$ , 0.5, and  $3 \mu\text{mol L}^{-1}$ , respectively) on the shelves, and during some years in the CB (e.g. 2012), where blooms formed (Fig. 2f-i). POC:PON ratios were  $> 8$  at most stations in shelf and slope waters and at a few stations in the CB during 2009 and 2011 (Fig. 2j). Shelf waters mostly had higher silicate:nitrate ( $\text{Si}(\text{OH})_4:\text{NO}_3^-$ ) ratios ( $> 1$ ) than the CB, particularly in the LSh (Fig. 2k). Labrador Sea surface waters usually had nitrate:phosphate ( $\text{NO}_3^-:\text{PO}_4^{3-}$ ) less than 16, although  $\text{NO}_3^-:\text{PO}_4^{3-}$  were relatively higher in the CB than in the shelf regions ( $> 10$ ) (Fig. 2l).

### 3.2 CHEMTAX interpretation and group distributions

310 Diatoms were the most abundant phytoplankton group found in the Labrador Sea, particularly at some stations on the shelves where they dominated almost 100% of the total phytoplankton community (Fig. 3a). Chlorophytes and prasinophytes were common in the central-western part (Fig. 3b,c), whereas *Phaeocystis* was highest at the eastern part of the Labrador Sea (Fig. 3d). Dinoflagellates were abundant in the central region of the Labrador Sea (Fig. 3e). Other prymnesiophytes, including coccolithophores and *Chrysochromulina*, were also common in the central part of the Labrador Sea (Fig. 3f). Overall, chrysophytes and pelagophytes were found in low abundances in the Labrador Sea, except at the central region of the Labrador Sea during 2011 (Fig. 3g). Cyanobacteria was most abundant at the Labrador Slope and Greenland Shelf, and during some years (2005 and 2012) in the central Labrador Sea (Fig. 3h). Cryptophytes comprised less than 10% of total phytoplankton chlorophyll concentrations (data not shown).

320 A cluster analysis of algal groups derived from CHEMTAX results revealed clusters of stations at various similarity levels (Fig. 4). Pairwise one-way analysis of similarity (*ANOSIM*) between clusters suggested that they were significantly different in terms of algal pigment composition ( $p = 0.001$ ). However, pairwise analysis of clusters C3a and C3b showed that these groups were more similar in composition (R statistic = 0.33) than other clusters (R statistic values approached 1) (see Clarke and Warwick, 2001). The first division occurred at 61 %, separating three main clusters (A, B and C) (Fig. 4a). Cluster C was subdivided at 65 % resulting in clusters C1, C2 and C3 (Fig. 4a). A third division (similarity of 73 %) occurred at cluster C3 resulting in two other clusters C3a and C3b (Fig. 4a). Overall, six functional clusters (A, B, C1, C2, C3a and C3b) represented the distinct phytoplankton communities occurring in the Labrador Sea (Fig. 4a). These communities generally occupied different regions of the Labrador Sea, namely the Labrador Shelf/Slope (west, Cluster C1 and, mainly, Cluster C3a), the Central Basin (middle, mainly Clusters C2 or C3b) and the Greenland Shelf/Slope (east, mainly Clusters C3a, A, B) (Fig. 4b,c).

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Chl $a$  concentrations were high at stations where diatoms were dominant (Fig. 4b,c). Diatoms were the most abundant phytoplankton group in Labrador Sea waters, particularly at stations on the shelves, where communities were sometimes

composed of almost 100 % diatoms (clusters A and C1) (Fig. 4b,c). Diatoms were also abundant at (or near to) the Greenland Shelf, where *Phaeocystis* was co-dominant (cluster B) and at (or near to) the Labrador Shelf in the west section, where chlorophytes were the second most abundant group (cluster C3a). Likewise, diatoms were dominant in the central Labrador Sea in some years (2008, 2012 and 2014, cluster C2), where dinoflagellates were also dominant (Fig. 4b,c). Most stations in the central basin had low Chl $a$  concentrations and high diversity of algal groups (cluster C3b), with mixed assemblages of diatoms, dinoflagellates and other flagellates (Fig. 4b,c). The positions of oceanographic fronts, usually characterised by sharp transitions in phytoplankton communities, varied from year to year but were generally located near the continental slopes (Fig. 4c).

### 3.3 Phytoplankton distributions and environmental controls

Distributions of surface phytoplankton communities ~~in the Labrador Sea during spring and early summer (2005-2014)~~ defined above varied according to the water mass distributions across the shelves and central basin of the Labrador Sea. Potential temperatures and salinities also varied among these water masses (Fig. 5a). In general, a community dominated by chlorophytes and diatoms (cluster C3a) was associated with the inshore branch of the Labrador Current (LC) on the Labrador Shelf. Surface waters from the LC were the coldest (temperature < 2°C) and least saline, with the lowest density ( $\sigma_{\theta}$  of most stations approximately < 26.5 kg m $^{-3}$ ) of all the surface water masses of the Labrador Sea (Fig. 5a). Mixed assemblages (cluster C3b), as well as blooms (chlorophyll average = 4 mg Chl $a$  m $^{-3}$ ) of dinoflagellates and diatoms (cluster C2) were associated with the Atlantic water mass, the Irminger Current (IC) (Fig. 5a). These were the warmest (temperature > 3°C), saltiest (salinity > 34) and densest ( $\sigma_{\theta}$  of most stations  $\geq$  27 kg m $^{-3}$ ) surface waters of the Labrador Sea (Fig. 5a). A community dominated by diatoms and *Phaeocystis* (cluster B) occurred in waters of the West Greenland Current (WGC), which had intermediate temperatures (mostly 0-4°C) and salinities (33-34.5) when compared to those of the LC and IC (Fig. 5a).

Redundancy analysis (RDA) was used to investigate the hydrographic variables that explained the variance (explanatory variables) in the phytoplankton communities identified from pigment analyses. The ordination diagram revealed that stations from each distinct cluster are concentrated in different quadrants (Fig. 5b), with the arrows in the ordination diagram representing the environmental variables. Positive or negative correlations indicate that the arrows are orientated parallel to the distribution of cluster stations (same direction = positive; opposite direction = negative correlations), with the strength of the correlation proportional to the arrow length. Table 4a indicates that the first axis (x-axis) of the redundancy analysis explained most of the variance (83.5 % of species-environment relationship; taxa-environmental correlation = 0.68). Summed, the canonical axes explained 99.8 % of the variance (axis 1,  $p = 0.002$ ; all axes,  $p = 0.002$ ) (Table 4a), which indicates that the environmental variables included in this analysis explained almost 100 % of the variability. Forward selection showed that five of the six environmental factors (silicate, temperature, salinity, nitrate and phosphate) included in the analysis best explained the variance in phytoplankton community composition when analysed together ( $p < 0.05$ , Table 4b). When all variables were analysed together (conditional effects, referred to as  $\lambda_a$  in Table 4b), silicate concentration was the most

significant explanatory variable ( $\lambda_a = 0.2$ ,  $p = 0.001$ ), followed by temperature ( $\lambda_a = 0.05$ ,  $p = 0.001$ ), salinity ( $\lambda_a = 0.02$ ,  $p = 0.002$ ), nitrate concentration ( $\lambda_a = 0.01$ ,  $p = 0.016$ ) and phosphate concentration ( $\lambda_a = 0.02$ ,  $p = 0.002$ ) (Table 4). Stratification Index (SI) was the only explanatory variable that had no statistical significance in explaining the distribution of phytoplankton communities (Table 4b).

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The first axis (x-axis) of the analysis, which explained most of the variance, clearly shows that the phytoplankton communities are associated with environmental parameters (Fig. 5b). Thus, stations in Arctic waters were to the left of the y-axis (low nutrients, temperatures and salinity values), while stations located in Atlantic waters were to the right (opposite trend, Fig. 5b). A community dominated by diatoms and chlorophytes (cluster C3a, upper left quadrant of Fig. 5b) was associated with lower salinities and temperatures, and highly stratified waters. Another community dominated by *Phaeocystis* and diatoms (cluster B, lower left quadrant of Fig. 5b) was associated with waters where nutrient concentrations (mainly nitrate, but also phosphate and silicate) were relatively low (average nitrate concentration for cluster B < 3  $\mu\text{M}$ , Table 5). In Atlantic waters (upper and lower right quadrants (Fig. 5b)), the phytoplankton community was composed of mixed taxa during May (orange circles), but became dominated by diatoms and dinoflagellates during the bloom in June (red circles), showing a clear temporal succession in these waters. Thus, mixed assemblages (cluster C3b) were associated with higher nutrient concentrations (pre-bloom conditions in Atlantic waters, upper right quadrant), whereas dinoflagellates and diatoms (cluster C2) were associated with warmer and saltier waters, resembling bloom conditions in Atlantic waters induced by thermal stratification (lower right quadrant of Figure 5b).

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#### 385 3.4 Phytoplankton distribution and elemental stoichiometry

Particulate organic carbon (POC) collected on filters can include organic carbon from a variety of sources, such as phytoplankton, bacteria, zooplankton, viruses and detritus (Sathyendranath et al., 2009). Assuming that phytoplankton associated organic carbon, as estimated from phytoplankton cell volumes ( $\text{POC}_{\text{phyto}}$ ) is strongly correlated with  $\text{Chl}_a$  values, the proportion of  $\text{POC}_{\text{phyto}}$  should increase in eutrophic waters, which usually occurs with high  $\text{Chl}_a$  and POC concentrations, and that it should be lower in oligotrophic waters. Indeed, our results showed higher proportions of  $\text{POC}_{\text{phyto}}$  (> 60 %) in waters with higher POC concentrations (Fig. 6a). However, there were several stations where POC levels were high and where the contribution of  $\text{POC}_{\text{phyto}}$  was low, suggesting that there may have been other sources of POC (e.g. detritus).

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To investigate the influence of phytoplankton community structure on the stoichiometry of particulate organic material of surface Labrador Sea waters, the relationships between  $\text{POC}_{\text{phyto}}$  (the estimated proportion of POC from phytoplankton) and the ratio of POC to PON were examined. In general, different phytoplankton communities had distinct relationships between  $\text{POC}_{\text{phyto}}$  and POC:PON. Stations in shelf regions, which have higher inputs of Arctic and glacial melt waters (lower salinity values), where diatoms co-dominated with chlorophytes in the west and east (cluster C3a) or with *Phaeocystis* in the east

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(cluster B), had higher and more variable values for POC:PON ratios than did stations influenced by Atlantic water (Fig. 6b).  
400 Some shelf stations had relatively high proportions of POC<sub>phyto</sub> to total POC, suggesting that phytoplankton community growth dominated by diatoms and chlorophytes (cluster C3a) contributed to a high proportion of the total POC (most stations from cluster C3a had POC<sub>phyto</sub> > 50 %) (Fig. 6b). On the other hand, some shelf stations, particularly the one dominated by a community composed of diatoms and *Phaeocystis* (cluster B) had high POC:PON ratios (> 10), with low POC<sub>phyto</sub> contributions, suggesting an increased contribution of detritus to the total POC (Fig. 6c). Stations influenced by Atlantic waters  
405 had generally lower contributions of POC<sub>phyto</sub> compared to Arctic-related waters, with most stations having POC:PON ratios < 6.6 (Fig. 6c).

### 3.5 Physiological patterns

Linear relationship of accessory pigment (AP) versus total chlorophyll *a* (TChl*a*) was investigated, given that it is often used  
410 as an index of quality-control in pigment analysis (Aiken et al., 2009). This relationship could also represent a response of phytoplankton communities to light conditions, given that AP allows a broader range of wavelengths to be absorbed (chromatic adaptation), whereas TChl*a* concentrations would vary according to light intensities (light-shade adaptation) (Boyton et al., 1983). The log-log linear relationship of accessory pigment (AP) versus total chlorophyll *a* (TChl*a*) from surface waters of the Labrador Sea varied within temperature (Fig. 7a) and among the distinct phytoplankton communities (Fig. 7b). Phytoplankton  
415 communities in cold waters (of Arctic origin), such as those co-dominated by diatoms and *Phaeocystis* in the east and diatoms and chlorophytes in the west, had a lower ratio of accessory pigments to TChl*a* (logAP:logTChl*a*) (slope = 0.86 and 0.89, respectively) than communities from warmer waters (Irminger Current from Atlantic origin), particularly those co-dominated by diatoms and dinoflagellates (logAP:logTChl*a*, slope = 1.03) (Fig. 7b). Slopes of the logAP to logTChl*a* relationships were  
not statistically different among the different communities (ANCOVA,  $p > 0.05$ ), except for those communities co-dominated  
420 by diatoms and *Phaeocystis* (cluster B), which had a slope that was statistically different from the others (ANCOVA,  $p = 0.016$ ).

Photosynthetic parameters differed among the different phytoplankton communities. Photosynthetic efficiencies ( $\alpha^B$ ) were the lowest in communities dominated by *Phaeocystis* and diatom communities in the east of the transect (near Greenland, cluster  
425 B) (average  $\alpha^B = 6.8 \times 10^{-2}$  mg C [mg Chl*a*] h<sup>-1</sup> [W m<sup>-2</sup>]<sup>-1</sup>) and the highest in communities dominated by diatoms and chlorophytes (cluster C3a) typically found in the west (Labrador Current) ( $\alpha^B = 9.2 \times 10^{-2}$  mg C [mg Chl*a*] h<sup>-1</sup> [W m<sup>-2</sup>]<sup>-1</sup>) (Table 5). The light intensity approximating the onset of saturation ( $E_k$ ) had the opposite pattern: it was highest in communities dominated by *Phaeocystis* and diatoms (average  $E_k = 60 \pm 33$  W m<sup>-2</sup>) and lowest at stations dominated by diatoms and chlorophytes ( $E_k = 29$  W m<sup>-2</sup>) (Table 5). *Phaeocystis* and diatom communities also showed little photo-inhibition ( $\beta = 4 \times 10^{-4}$  mg C [mg Chl*a*] h<sup>-1</sup> [W m<sup>-2</sup>]<sup>-1</sup>). Phytoplankton communities in Atlantic waters (clusters C3b and C2) had the highest levels  
430 of photoprotective pigments, such as those used in the xanthophyll cycle (diadinoxanthin (DD) + diatoxanthin (DT)):TChl*a* >



0.07), particularly those communities co-dominated by diatoms and dinoflagellates (cluster C2) from stratified Atlantic waters (Table 5). These communities were the most susceptible to photo-inhibition ( $\beta = 29 \times 10^{-4} \text{ mg C [mg Chla] h}^{-1} [\text{W m}^{-2}]^{-1}$ ), had the highest ratios of photoprotective pigments to  $\text{IChla}$  ( $(\text{DD}+\text{DT}):\text{IChla} = 0.12 \pm 0.01$ ), and the highest maximum photosynthetic rates ( $P_m^B = 3.3 \pm 0.7 \text{ mg C [mg Chla] h}^{-1}$ ) (Table 5).

## 4. Discussion

### 4.1 Biogeography of phytoplankton communities in the Labrador Sea

In this study, our assessment of phytoplankton pigments from surface waters of the Labrador Sea during spring/early summer are based on a decade of observations and show that the distribution of phytoplankton communities varied primarily within distinct waters masses in surface waters (Labrador, Irminger and Greenland Currents). However, a temporal succession of phytoplankton communities from the central region of the Labrador Sea was also observed as waters became thermally stratified from May to June. Major blooms ( $\text{Chla}$  concentrations  $> 3 \text{ mg Chla m}^{-3}$ ) occurred on or near the shelves in shallower mixed layers ( $< 33 \text{ m}$ , Table 5). Diatoms were abundant in these blooms, however, they often co-dominated with 1) chlorophytes in the west (mostly in the Labrador Current) and 2) *Phaeocystis* in the east in the West Greenland Current. A more diverse community with low chlorophyll *a* values (average  $\text{Chla}$  concentrations  $\sim 2 \text{ mg Chla m}^{-3}$ , Table 5) was found earlier in the season (May) in deeper mixed layers ( $> 59 \text{ m}$ , Table 5) in the central basin. Once these waters of the central basin became thermally-stratified (June), a third bloom co-dominated by diatoms and dinoflagellates occurred, revealing an ecological succession from mixed flagellate communities. These patterns are similar to those seen in other shelf and basin regions of Arctic/subarctic waters (e.g. Coupel et al., 2015; Fujiwara et al., 2014; Hill et al., 2005).

It is well known that diatoms tend to dominate in high-nutrient regions of the ocean due to their high growth rates, while their low surface area to volume ratios mean that they do not do as well as smaller nano- or picoplankton in low nutrient conditions (Gregg et al., 2003; Sarthou et al., 2005). The Labrador Sea is a high-nutrient region during early spring due to deep winter mixing (200 – 2300 m) that provides nutrients to the surface layers. Thus, high nutrient concentrations may have supported the blooms dominated by diatoms once light became available, as observed in previous studies (Fragoso et al., 2016; Harrison et al., 2013; Yashayaev and Loder, 2009).

Chlorophytes were the second most abundant phytoplankton group in this study, particularly in the central-western part of the Labrador Sea, but occasionally occurring in the east as well. Chlorophytes are thought to contribute 1-13 % of total chlorophyll *a* in the global ocean (Swan et al., 2015) and to inhabit transitional regions, where nutrient concentrations become limiting for diatoms but are not persistently low enough to prevent growth due to nutrient limitation, as occurs in the oligotrophic gyres (Gregg et al., 2003; Gregg and Casey, 2007; Ondrusek et al., 1991). The Labrador Shelf is a dynamic region during springtime,

465 where melting sea ice in May provides a local freshwater input (Head et al., 2003). Melting sea ice provides intense stratification and shallow mixed layers for the phytoplankton, with increased access to light and which promotes rapid growth of cold Arctic/ice-related phytoplankton near the sea ice shelf (Fragoso et al., 2016). It is possible that the rapid nutrient exhaustion in highly stratified ice-melt waters might have stimulated the growth of chlorophytes as a succession from large diatoms to smaller phytoplankton forms. Chlorophytes, as well as prasinophytes such as *Pyramimonas*, a genus found in high abundances in surface Labrador Shelf waters, has been previously associated to land-fast (Palmer et al., 2011) and melting sea ice, given that they have been found blooming (chlorophyll *a* concentration ~ 30 mg Chl*a* m<sup>-3</sup>) in low salinity melt waters (salinity = 9.1) under the Arctic pack-ice (Gradinger, 1996).

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475 Dinoflagellates, in this study, were associated with the Irminger Current, where they were occasionally found blooming with diatoms in the warmer, stratified Atlantic waters of the central basin. These blooms dominated by dinoflagellates and Atlantic diatom species, such as *Ephemera planamembranacea* and *Fragilariopsis atlantica*, start later in the season (end of May or June) as thermal stratification develops in the central Labrador Sea (Frajka-Williams and Rhines, 2010, Fragoso et al., 2016). Transition from diatoms to dinoflagellates has been well-documented in the North Atlantic between spring and summer, and occurs mainly as dinoflagellates can use mixotrophic strategies to alleviate nutrient limitation as waters become warmer, highly stratified and nutrient-depleted (Barton et al., 2013; Head et al., 2000; Head and Pepin, 2010; Henson et al., 2012; Leterme et al., 2005). The North Atlantic Oscillation index (NAO) and sea surface temperatures (Zhai et al., 2013) appear to influence the relative proportions of diatoms and dinoflagellates as well as the variability in the start date of the North Atlantic bloom. A negative winter phase of NAO is associated with weaker northwest winds over the Labrador Sea and reductions in the depth of winter mixing and supply of nutrients to the upper layers (Drinkwater and Belgrano, 2003). Vertical stability, thermal stratification and the initiation of the spring bloom tend to occur earlier under negative NAO conditions and the proportion of dinoflagellates in the warmer, more nutrient-limited waters may be higher (Zhai et al., 2013). Unfortunately, it was not possible to investigate the influence of NAO on the relative contribution of dinoflagellates and diatoms in the Labrador Sea section of the North Atlantic in this study, given that the sampling period varied from early/mid-May to mid/late-June. However, abundances of dinoflagellates appeared to be higher in warmer waters (> 5°C), suggesting that the communities were shifting from diatoms to dinoflagellates as the water became stratified and nutrient concentrations decreased.

490 In this study, a community dominated by *Phaeocystis* and diatoms was observed blooming together in waters of the WGC, in the eastern central part of the Labrador Sea. The occurrence of *Phaeocystis* in these waters has been observed before by several authors (Fragoso et al., 2016; Frajka-Williams and Rhines, 2010; Harrison et al., 2013; Head et al., 2000; Stuart et al., 2000; Wolfe et al., 2000). The eastern part of the Labrador Sea is a region with high eddy kinetic energy during spring (Chanut et al., 2008; Frajka-Williams et al., 2009; Lacour et al., 2015), which causes the accumulation of low-salinity surface waters from the West Greenland Current. This buoyant freshwater layer contains elevated levels of algal biomass of both *Phaeocystis* and diatoms (this study, Fragoso et al., 2016). Mesoscale eddies may stimulate growth of *Phaeocystis* and diatoms by inducing

partial stratification at irradiance levels that are optimal for their growth, but too low for their competitors (blooms in these eddies usually start in April). Lacour et al. (2015) showed that irradiance levels estimated from satellite-derived photosynthetically active irradiance (PAR) and mixed layer depth climatologies are similar for thermally and haline-stratified spring blooms in the Labrador Sea. Nonetheless, these authors recognise the need for *in situ* measurements to confirm whether Labrador Sea spring blooms, presumably composed of distinctive phytoplankton communities, respond in the same manner to light-mixing regimes. The ability of *Phaeocystis* to grow under dynamic light irradiances explains why they are often found in deeper mixed layers, such as those found in Antarctic polynyas (Arrigo, 1999; Goffart et al., 2000), although this genus can also occur in shallow mixed layers, such as those found close to ice edges (Fragoso and Smith, 2012; Le Moigne et al., 2015).

Mesoscale eddies are also often associated with elevated zooplankton abundances (Frajka-Williams et al., 2009; Yebra et al., 2009). In the Labrador Sea, lower grazing rates have been observed in blooms dominated/co-dominated by colonial *Phaeocystis*, which are often located in these eddies and which may, in turn, explain why this species is dominant (Head and Harris, 1996; Wolfe et al., 2000). Although the exact mechanism that facilitates *Phaeocystis* growth in the north-eastern region of the Labrador Sea is not clear, it is evident that blooms of this species are tightly linked to mesoscale eddies, and that this relationship needs further investigation to better explain their regular reoccurrence in these waters.

#### 4.2 Phytoplankton composition and related biogeochemistry

Particulate organic carbon (POC) and nitrogen (PON) concentrations, as well as the molar ratio of POC:PON varied within distinct hydrographic zones, indicating the presence of different biogeochemical provinces in the Labrador Sea. A canonical Redfield ratio of 6.6 for POC:PON appears to represent the global average (Redfield, 1958), although regional variations on the order of 15 to 20 % have also been reported (Martiny et al., 2013b). The POC:PON appears to be closer to the Redfield ratio of 6.6 in productive sub-Arctic/Arctic waters, such as the northern Baffin Bay (Mei et al., 2005), the north-eastern Greenland shelf (Daly et al., 1999), and in Fram Strait and the Barents Sea (Tamelander et al., 2012). Crawford et al. (2015), however, recently reported very low POC:PON ratios in oligotrophic Arctic waters of the Beaufort Sea and Canada Basin, where depth-integrated values of the POC:PON ratio were ~ 2.65, much lower than those in more productive domains, such as the sub-Arctic central Labrador Sea (POC:PON ~ 4).

In this study, highly productive surface waters of Arctic origin (near or over the shelves) had higher phytoplankton-derived particulate organic carbon ( $\text{POC}_{\text{phyto}} > 43\%$  of total POC, Fig. 6c), as well as higher and more variable POC:PON ratios (average  $> 6.9$ , Fig. 6b) compared with stations influenced by Atlantic water (average POC:PON  $< 6.3$ ,  $\text{POC}_{\text{phyto}} > 35\%$ , Fig. 6b). Diatoms have been suggested to contribute to higher phytoplankton-derived POC in Arctic/sub-Arctic waters (Crawford et al., 2015). The Labrador Shelf region, where blooms are generally dominated by large Arctic/ice-related diatoms (Fragoso et al., 2016), had relatively high contributions of  $\text{POC}_{\text{phyto}}$  ( $> 50\%$ ) to the total POC, even though smaller phytoplankton forms, such as chlorophytes, were also abundant. Low POC:PON ratios, as well as low  $\text{POC}_{\text{phyto}}$  concentrations, were associated with

Atlantic waters which had higher contributions of flagellates (particularly before bloom initiation). Similar findings were reported by Crawford et al. (2015), where low  $\text{POC}_{\text{phyto}}$  was associated with larger contributions of flagellates ( $< 8 \mu\text{m}$ ) in oligotrophic Arctic waters, such as the Beaufort Sea and Canada Basin. Crawford et al. (2015) also considered that POC:PON ratios might have been reduced by the presence of heterotrophic microbes (bacteria, flagellates and ciliates) since these microorganisms have POC:PON ratios much lower than the canonical Redfield ratio of 6.6 (Lee and Fuhrman, 1987; Vrede et al., 2002). Bacteria and other heterotrophic organisms were not quantified in our study, although Li and Harrison (2001) have shown that bacterial biomass from surface waters was 62 % greater (average from 1989 to 1998 =  $13.8 \text{ mg C m}^{-3}$ ) in the central region than in shelf areas of the Labrador Sea.

Changes in POC:PON may also be related to the physiological status of phytoplankton and/or community structure. In the North Water Polynya (Baffin Bay), POC:PON ratios during phytoplankton blooms increased between spring (5.8) and summer (8.9) as phytoplankton responded to nitrate starvation by producing N-poor photo-protective pigments (Mei et al., 2005). Daly et al. (1999) also found high POC:PON ratios (~8.9) in Arctic surface waters dominated by diatoms on the north-eastern Greenland shelf, which were attributed to nutrient limitation. Atlantic waters appear to have an excess of nitrate compared with Arctic waters (Harrison et al., 2013), which could explain why phytoplankton from Atlantic Waters had lower POC:PON ratios in our study (Figure 6c). Conversely, Arctic-influenced waters on or near the shelves had higher  $\text{Si(OH)}_4\text{:NO}_3^-$  and lower  $\text{NO}_3^-:\text{PO}_4^{3-}$  than those in the central basin in this study (Figures 2k and 2l), which could also have contributed to the observed high POC:PON ratios.

A few stations in shelf waters of the Labrador Sea also had remarkably high POC:PON ratios ( $> 10$ ), and low  $\text{POC}_{\text{phyto}}$  contributions, suggesting high contributions of detritus. These waters probably receive higher inputs of Arctic and glacial ice melt, which could introduce POC from external sources. Hood et al. (2015) showed that POC export from glaciers is large, particularly from the Greenland Ice Sheet and it occurs in suspended sediments derived from glacier meltwater. High POC:PON ratios ( $> 10$ ), particularly in waters where *Phaeocystis* were abundant, may also be linked to the mucilaginous matrix of the *Phaeocystis* colonies (Palmisano et al., 1986). The mucopolysaccharide appears to contain excess carbon, particularly when nutrients start to become depleted and colonies become senescent (Alderkamp et al., 2007; Wassmann et al., 1990).

#### 4.3 Physiological parameters of distinct phytoplankton communities

Accessory pigments (AP) are assumed to have a ubiquitous, global, log-log linear relationship with chlorophyll *a* in aquatic environments (Trees et al., 2000). This linear relationship is often used as an index of quality-control in pigment analysis, which are required due to uncertainties of the quantitative comparability of data among different surveys, and may be related to differences in analytical procedures and sample storage methods used in different laboratories. In the current study, the slope of AP to total chlorophyll *a* (TChl*a*) on a logarithm scale (Fig. 7) passed the quality control criteria of slopes ranging from 0.7

to 1.4 and  $r^2 > 0.90$  as applied in previous studies (e.g., Aiken et al., 2009; Peloquin et al., 2013; Thompson et al., 2011) and  
565 were within the range observed throughout worldwide aquatic systems (slope from 0.8 to 1.3 compared to 0.86 to 1.03 observed  
in our study) (Trees et al., 2000). An interesting trend was also found where phytoplankton pigment ratios varied clearly within  
distinct communities in the Labrador Sea. According to our data, phytoplankton communities found in colder waters (of Arctic  
origin) had lower accessory pigments ratios to total chlorophyll *a* ratio (logAP:logTChla) (slope = 0.86) when compared to  
communities from warmer waters (Irminger Current from Atlantic origin) (slope = 1.03). Changes in the ratios of  
570 logAP:logTChla as a function of phytoplankton community composition has also been previously observed by Stramska et al.  
(2006). These authors showed a higher slope of logAP:logTChla when dinoflagellates were dominant during summer in  
northern polar Atlantic waters as opposed to lower ratios associated with flagellates in spring. Trees et al. (2000) and Aiken  
et al. (2009) also reported lower logAP:logTChla (slope < 1.00) in oligotrophic waters dominated by picoplankton as opposed  
to higher ratios in upwelling waters where microplankton, particularly diatoms, were dominant.

575 Environmental parameters, such as nutrients and light conditions, have also been suggested to influence logAP:logTChla,  
regardless of community composition (Trees et al., 2000). However, in our study, these parameters, analysed as nitrate and  
silicate concentrations and Stratification Index, did not vary with logAP:logTChla (data not shown) as opposed to temperature.  
Phytoplankton community distributions varied clearly according to temperature with *Phaeocystis* occurring in colder Arctic  
580 waters and dinoflagellates in warmer Atlantic waters. Although both communities were co-dominated by diatoms (relative  
abundance > 70 % of total chlorophyll *a*), the ratio logAP:logTChla varied considerably, suggesting that diatom species from  
both Arctic and Atlantic waters varied intrinsically in pigment composition, as observed by the distinct Fuco to TChla ratios  
of shelf (Arctic) versus central (Atlantic) waters (Table S1, supplemental material). Fragoso et al. (2016) have previously  
585 observed that the diatom species from Arctic and Atlantic waters of the Labrador Sea during spring varied in terms of species  
composition. According to the study by Fragoso et al. (2016), the diatoms *Ephemera planamembranacea* and *Fragilariopsis*  
*atlantica* were typically found in Atlantic waters, whereas polar diatoms, including *Thalassiosira* species (*T. hyalina*, *T.*  
*nordenskiöldii*, for example), in addition to *Bacterosira bathyomphala*, *Fossula arctica*, *Nitzschia frigida* and *Fragilariopsis*  
*cylindrus* were all found in Arctic-influenced waters. It is possible that the distinct composition of diatoms from these  
590 biogeographical regions might have influenced the pigment composition in these waters. Likewise, it is possible that  
temperature had a strong physiological effect on the logAP:logTChla ratio. Many environmental factors, such as turbulence  
and coloured dissolved organic matter (CDOM) concentrations, could have contributed to the variance of chlorophylls (light-  
shade adaptation) and accessory pigments (chromatic adaptation) observed due to changes they cause in spectral light  
absorption by phytoplankton. Turbulence and CDOM, however, were not measured in this study and a direct physiological  
temperature-induced effect or taxonomic effect on logAP:logTChla is currently unknown.

595 The variation in photosynthetic parameters in the distinct phytoplankton biogeographical provinces demonstrated how each  
phytoplankton community responds to environmental conditions. Harrison and Platt (1986) found that the photophysiology of

phytoplankton from the Labrador Sea is influenced by temperature and irradiance. Nonetheless, phytoplankton composition may also influence the values of the photosynthetic parameters. Light-saturated photosynthetic rates and saturation irradiances, for instance, were higher at stations where diatoms were dominant (> 70 %), as opposed to stations where flagellates were more abundant (from 40 % up to 70 %). Similar findings were reported by Huot et al., (2013), who observed that light-saturated photosynthetic rates in the Beaufort Sea (Arctic Ocean) were higher for communities composed of large cells, presumably diatoms, compared to smaller flagellates.

Polar phytoplankton communities from shelf waters (east versus west) observed in this study had distinctive photo-physiological characteristics. Comparing these blooms, diatom/chlorophyte communities (west) had higher photosynthetic efficiency ( $\alpha^B = 9.2 \times 10^{-2} \text{ mg C [mg Chla] h}^{-1} [\text{W m}^{-2}]^{-1}$ ), lower onset light-saturation irradiance ( $E_k = 29 \text{ W m}^{-2}$ ) and higher photo-inhibition ( $\beta = 16 \times 10^{-4} \text{ mg C [mg Chla] h}^{-1} [\text{W m}^{-2}]^{-1}$ ) than communities from the east. This suggests that the community located in the Labrador Shelf waters (west) was more light-stressed compared to the community observed in the east (diatom/*Phaeocystis*). Haline-stratification due to the influence of Arctic waters occurs in both regions during spring, contributing to the shallow mixed layer depths (<33 m) observed (Table 5). However, waters from the Labrador Shelf (west, Cluster C3a) were more stratified than the Greenland Shelf (cluster B, see stratification index (SI) values, Table 5) because of the local sea ice melt observed in this area, which contributes to increased stratification in this region. The diatom species observed on the Labrador Shelf were mostly sea-ice related (*Fragilariopsis cylindrus*, *Fossula arctica*, *Nitzschia frigida*) compared to pelagic species observed in the Greenland Shelf waters (*Thalassiosira gravida*, for example) (Fragoso et al., 2016). Sensitivity of sea-ice related diatoms to irradiances > 15  $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$  has been reported (Alou-Font et al., 2016) (Alou-Font et al., 2016), which can help explain why phytoplankton communities from the west were photo-inhibited.

The communities dominated by *Phaeocystis*/diatoms located near Greenland (east) had the inverse pattern: low photosynthetic efficiency (average  $\alpha^B = 6.8 \times 10^{-2} \text{ mg C [mg Chla] h}^{-1} [\text{W m}^{-2}]^{-1}$ ) and high onset light-saturation irradiances ( $E_k = 60 \text{ W m}^{-2}$ ). This pattern in diatom/*Phaeocystis*-dominated communities mean that photosynthetic rates were relatively low at high light intensities, although photo-inhibition was low ( $\beta = 4 \times 10^{-4} \text{ mg C [mg Chla] h}^{-1} [\text{W m}^{-2}]^{-1}$ ). *Phaeocystis antarctica*, widespread in Antarctic waters, relies heavily on photo-damage recovery, such as D1 protein repair (Kropuenske et al., 2009), which could explain how these communities overcome photo-inhibition. Stuart et al. (2000), however, found a high photosynthetic efficiency ( $\alpha^B$ ) for a population dominated by *Phaeocystis* near Greenland and attributed this to the small cell size of *Phaeocystis*. In addition to the exposure of ice-related diatoms to high light levels due to increased stratification, the high concentration of chlorophytes and prasinophytes, which are also small in cell size, might also explain the higher  $\alpha^B$  observed in the Labrador Shelf waters (west, cluster C3a), when compared to values from a community dominated by diatom/*Phaeocystis* blooms (east, cluster B).

Phytoplankton communities from Atlantic waters (co-dominated by diatoms and dinoflagellates) were highly susceptible to photo-inhibition ( $\beta = 29 \times 10^{-4} \text{ mg C [mg Chl}a\text{] h}^{-1} [\text{W m}^{-2}\text{]}^{-1}$ ) compared with the other communities in the Labrador Sea. Days are longer and solar incidence is higher in June compared to May at these latitudes (Harrison et al., 2013). Dinoflagellates were found to bloom in the central Labrador Sea in June as a consequence of increased thermal stratification. To cope with high light levels and potential photo-damage, this phytoplankton community appeared to increase the levels of photoprotective pigments, such as those used in the xanthophyll cycle (diadinoxanthin (DD) + diatoxanthin (DT)). These communities also had high diatoxanthin levels compared with the other phytoplankton communities in this study, suggesting that the community was experiencing higher light intensities (Moisan et al., 1998). Increases in photoprotective pigments, including (DD+DT)/IChl<sub>a</sub>, have also been reported to occur in Arctic phytoplankton communities from spring to summer, presumably as a response to higher irradiance (Alou-Font et al., 2016)(Alou-Font et al 2016). Thus, photoprotective capacity can be a key determinant for phytoplankton survival and may also be related to the taxonomic segregation observed in Arctic and Atlantic phytoplankton communities.

#### 4.4 Phytoplankton communities assessed by HPLC and CHEMTAX methods

A number of studies have used CHEMTAX methods to determine phytoplankton community structure in Arctic/subarctic waters (e.g. Coupel et al., 2012, 2015; Lovejoy et al., 2007; Piquet et al., 2014; Vidussi et al., 2004; Zhang et al., 2015). Spring phytoplankton communities from the Labrador Sea have already been investigated in detail (Fragoso et al., 2016), although the analysis did not include nano- and pico-flagellates (except cryptophytes and *Phaeocystis pouchetii*) and was done over only four years (2011-2014) at selected stations along the L3 (=AR7W) transect. Here, we have combined phytoplankton information from Fragoso et al. (2016) with additional pigment analyses. Although cross comparison among these two techniques (carbon biomass estimated from microscopic counts versus algal group chlorophyll *a* estimated from CHEMTAX) should not be expected to give exactly equivalent results, given that most flagellates observed in the pigment analysis were not counted under the microscope, some comparability should be possible, at least for the larger cells (e.g. diatoms).

*Phaeocystis* ( $r^2 = 0.79$ ) and diatom ( $r^2 = 0.74$ ) biomasses were well correlated when carbon biomasses estimated from microscopic counts when compared with CHEMTAX-derived algal chlorophyll *a* biomass (data not shown). Diatoms are the group that usually show the best agreement between the two methods of biomass estimations (Vidussi et al. 2004, Coupel et al 2015, Mendes et al 2012). For *Phaeocystis*, a positive relationship between the two methods of biomass estimation (CHEMTAX and microscopy) confirms that using chlorophyll *c3* was appropriate for detecting and quantifying *Phaeocystis* biomass in the Labrador Sea. Similar associations have been observed for *Phaeocystis* from boreal waters (e.g. *P. pouchetii* and *P. globosa*), which lacks or has low 19- hexanoyloxyfucoxanthin (Antajan et al., 2004; Muylaert et al., 2006; Stuart et al., 2000; Wassmann et al., 1990). Conversely, 19- hexanoyloxyfucoxanthin is a characteristic pigment marker of *Phaeocystis*

665 from austral waters (*P. antarctica*) (Arrigo et al., 2010, 2014; Fragoso, 2009; Fragoso and Smith, 2012). Dinoflagellates gave  
a poor correlation between biomass estimates made using the two methods ( $r^2 = 0.12$ , data not shown). A lack of or weak  
relationship between both biomass estimations for dinoflagellates has been previously reported in Arctic waters (Vidussi et al  
2004 Coupel et al 2005). The argument for this inconsistency is that some heterotrophic dinoflagellates, which usually lack  
photosynthetic pigments, unless they ingest a prey that contains them, might have been included in the microscopic counts,  
and it is possible that the same occurred in Fragoso et al. (2016). Cryptophyte biomass estimates from both methods were not  
670 related (data not shown), likely as the biomass of this group was underestimated in microscopic counts. Inconsistencies between  
CHEMTAX and microscopy methods of estimating biomasses have also been observed in nanoflagellates and this is assumed  
to be because of the low accuracy of visual microscopic counts (Coupel et al., 2015; Gieskes and Kraay, 1983).

## 5. Conclusions

In this study, we have provided a geographical description of phytoplankton community structure in spring and early summer  
675 surface waters of the Labrador Sea based on pigment data from over a decade of sampling (2005-2014). Phytoplankton  
communities and their photophysiological and biogeochemical signatures were assessed using CHEMTAX, so that a  
geographical baseline of the major phytoplankton groups has been provided for the central Labrador Sea and its adjacent  
continental shelves. In spite of interannual variability (due to differences in survey dates and natural variability), spring  
phytoplankton communities showed distinct spatial variations from east to west and there were clear temporal differences  
680 between May and June. The ~~main~~ conclusions of our study are that: 1) phytoplankton communities varied among the distinct  
regions of the Labrador Sea; 2) Temperature, salinity and nutrient concentrations (of nitrate, silicate and phosphate)  
statistically linked to the explained the distribution of different phytoplankton communities; 3) in spite of some temporal  
variability, the distinct communities tended to reoccur in the same biogeographical regions, particularly at the shelves; 4) a  
strong temporal progression was observed in the central region of the Labrador Sea, where pre-bloom conditions in May  
685 dominated were characterised by a diverse, mixed assemblage dominated by flagellates were observed in May, whereas whilst  
blooms of diatoms and dinoflagellates occurred in June; 5) diatoms contributed the most to the chlorophyll *a* in waters where  
phytoplankton blooms were observed bloom conditions (> 3 mg Chl *a* m<sup>-3</sup>), while whilst other groups (chlorophytes,  
dinoflagellates and *Phaeocystis*) co-dominated and were geographically segregated within distinct hydrographical zones; 2) a  
diverse, mixed assemblage dominated by flagellates from several taxonomic groups occurred in low chlorophyll *a*, pre-bloom  
690 conditions in the central Labrador Sea; 6) 3) different distinct phytoplankton communities had different photophysiological  
parameters characteristics (level of photo-inhibition, photosynthetic efficiency, photosynthetic and rate, saturation irradiance)  
and -ratios of accessory pigments to total chlorophyll *a*, revealing distinct photo-adaptation strategies as a response to  
environmental conditions; and 7) 4) POC<sub>phyto</sub> and POC:PON ratios were directly influenced by phytoplankton community  
composition, although the latter was also influenced by as well as freshwater input of allochthonous carbon in shelf waters  
695 which have derived from nearby sources (e.g. i.e. melting glacial and sea-ice and local river outflows).

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**Table 1. Research cruises, sampling dates and number of samples per cruise (n) where pigment data were collected in the Labrador Sea during early spring and late summer (2005-2014). \*HUD-Year-ID and JR302 refers to expeditions carried out on board of the *CCGS Hudson* (Canada) and *RRS James Clark Ross* (UK), respectively.**

Cruise	Dates	Year	N
HUD-2005-16	29 May - 3 June	2005	25
HUD-2006-019	23 May - 31 May	2006	12
HUD-2007-011	11 May - 21 May	2007	32
HUD-2008-009	22 May - 29 May	2008	25
HUD-2009-015	18 May - 23 May	2009	26
HUD-2010-014	14 May - 24 May	2010	27
HUD-2011-009	11 May - 17 May	2011	33
HUD-2012-001	3 June - 11 June	2012	30
HUD-2013-008	9 May - 21 May	2013	27
JR302	10 June - 24 June	2014	16

Table 2. List of phytoplankton pigments and their distributions in algae groups, abbreviations and formulas.

Abbreviation	Name	Characteristic of the pigment	Present in/ Index of/Formula
PSC	Photosynthetic carotenoid	Light harvesting	All algae
PPC	Photoprotective carotenoid	Photoprotection	All algae
PPP	Photosynthetic pigment	Light harvesting	All algae
But-fuco	19'-butanoyloxyfucoxanthin	PSC	Prymnesiophytes, caryophytes and dinoflagellates Type 2* (lacking Peridin)
Hex-fuco	19'-hexanoyloxyfucoxanthin	PSC	Major in prymnesiophytes and dinoflagellates Type 2* (lacking Peridin)
Allo	Alloxanthin	PPC	Cryptophytes
$\alpha$ -Car	$\alpha$ -carotene	PPC	Dominant in prochlorophytes, rhodophyte and cryptophyte
$\beta$ -Car	$\beta$ -carotene	PPC	Dominant in cyanobacteria, prochlorophytes, chlorophytes, prasinophytes, euglenophytes and diatoms
Chl <i>b</i>	Chlorophyll <i>b</i>	PPP	Chlorophytes, prasinophytes, euglenophytes
Chl <i>c</i> <sub>1</sub> + <i>c</i> <sub>2</sub>	Chlorophyll <i>c</i> <sub>1</sub> + <i>c</i> <sub>2</sub>	PPP	Diatoms, prymnesiophytes, dinoflagellates, cryptophytes, chrysophytes and raphidophytes
Chl <i>c</i> <sub>3</sub>	Chlorophyll <i>c</i> <sub>3</sub>	PPP	Prymnesiophytes, chrysophytes and dinoflagellates Type 2* (lacking Peridin)
Chlide <u>g</u>	Chlorophyllide <i>a</i>	Degradation product of Chl <i>a</i>	Senescent phytoplankton
DD	Diadinoxanthin	PPC	Diatoms, prymnesiophytes, dinoflagellates, chrysophytes and raphidophytes
DT	Diatoxanthin	PPC	Diatoms, prymnesiophytes, dinoflagellates, chrysophytes and raphidophytes
Fuco	Fucoxanthin	PSC	Diatoms, prymnesiophytes, chrysophytes, pelagophytes and dinoflagellates Type 2* (lacking Peridin)
Chl <i>a</i>	Chlorophyll <i>a</i>	PPP	All phytoplankton except <i>Prochlorococcus</i>
Peri	Peridinin	PSC	Dinoflagellates Type 1*
Pras	Prasinolanthin	PPC	Prasinophytes Type 1**
Viola	Violaxanthin	PPC	Chlorophytes, prasinophytes and eustigmatophytes
Zea + Lut	Zeaxanthin + Lutein	PPC	Cyanobacteria, <i>Prochlorococcus</i> , chlorophytes and prasinophytes Type 2**
TChl <i>a</i>	Total chlorophyll <i>a</i> <u>derived from HPLC analysis</u>		Chl <i>a</i> + Chlide <i>a</i>
TC	Total carotenoids	Include all carotenoids	But-fuco + Hex-fuco + Allo + $\alpha$ -Car + $\beta$ -Car + DD + DT + Fuco + Peri + Pras + Viola + Zea + Lut
AP	Accessory pigments	Include all pigments except <u>TChl<i>a</i></u>	TC + Chl <i>b</i> + Chl <i>c</i> <sub>1</sub> + <i>c</i> <sub>2</sub> + Chl <i>c</i> <sub>3</sub>

985 According to Jeffrey et al (1997) or \*Higgins et al (2011) or \*\*Vidussi et al (2004).

Table 3 - Initial ratio matrix of accessory pigment to chlorophyll *a* for distinct algal groups for each cluster group. \*Rf refers to the literature where the pigment ratios were extracted. See explanation of each group in the methods section.

Region		I & II (Eastern Labrador Sea)									
Group / Pigment	Chl <i>b</i>	Chl <i>c</i> <sub>2</sub>	Fuco	Peri	Zea + Lut	Allo	But-fuco	Hex-fuco	Pras	TChl <i>a</i>	*Rf
Prasinophyte 1	0.512	0	0	0	0	0	0	0	0.075	1	2
Prasinophyte 2	0.738	0	0	0	0.008	0	0	0	0	1	2
CHLORO-1	0.339	0	0	0	0.047	0	0	0	0	1	4
Dinoflagellates	0	0	0	0.600	0	0	0	0	0	1	5
Cryptophytes	0	0	0	0	0	0.673	0	0	0	1	2
<i>Phaeocystis</i>	0	0.208	0.350	0	0	0	0	0	0	1	1
HAPTO-6	0	0.155	0.195	0	0	0	0.019	1.054	0	1	4
Chryso/Pelagophyte	0	0.114	0.398	0	0	0	0.595	0	0	1	2
Cyanobacteria	0	0	0	0	0.232	0	0	0	0	1	3
Diatoms	0	0	1.229	0	0	0	0	0	0	1	2
Region		III & V (Central Labrador Sea)									
Group / Pigment	Chl <i>b</i>	Chl <i>c</i> <sub>2</sub>	Fuco	Peri	Zea + Lut	Allo	But-fuco	Hex-fuco	Pras	TChl <i>a</i>	*Rf
Prasinophyte 1	0.512	0	0	0	0	0	0	0	0.075	1	2
Prasinophyte 2	0.738	0	0	0	0.008	0	0	0	0	1	2
CHLORO-1	0.339	0	0	0	0.047	0	0	0	0	1	4
Dinoflagellates	0	0	0	0.600	0	0	0	0	0	1	5
Dino-2	0	0.179	0.300	0	0	0	0.081	0.194	0	1	4
Cryptophytes	0	0	0	0	0	0.673	0	0	0	1	2
HAPTO-6	0	0.155	0.195	0	0	0	0.019	1.054	0	1	4
Chryso/Pelagophyte	0	0.114	0.398	0	0	0	0.595	0	0	1	2
Cyanobacteria	0	0	0	0	0.232	0	0	0	0	1	3
Diatoms	0	0	1.229	0	0	0	0	0	0	1	2
Region		IV (Western Labrador Sea)									
Group / Pigment	Chl <i>b</i>	Chl <i>c</i> <sub>2</sub>	Fuco	Peri	Zea + Lut	Allo	But-fuco	Hex-fuco	Pras	TChl <i>a</i>	*Rf
Prasinophyte 1	0.512	0	0	0	0	0	0	0	0.075	1	2
Prasinophyte 2	0.738	0	0	0	0.008	0	0	0	0	1	2
CHLORO-1	0.339	0	0	0	0.047	0	0	0	0	1	4
Dino-2	0	0.179	0.300	0	0	0	0.081	0.194	0	1	4
Dinoflagellates	0	0	0	0.600	0	0	0	0	0	1	5
Cryptophytes	0	0	0	0	0	0.673	0	0	0	1	2
Prymnesiophyte 1	0	0.038	0.416	0	0	0	0	1.108	0	1	2
Chryso/Pelagophyte	0	0.114	0.398	0	0	0	0.595	0	0	1	2
Diatoms	0	0	1.229	0	0	0	0	0	0	1	2

<sup>1</sup>(Antajan et al., 2004), <sup>2</sup>(Vidussi et al., 2004), <sup>3</sup>(Muyllaert et al., 2006), <sup>4</sup>(Higgins et al., 2011), <sup>5</sup>(Coupel et al., 2015)

Table 4 – Results of the Redundancy Analyses (RDA) with the eigen-values, taxa-environment correlations and percentages of variance explained used in the analysis (a). Automatic forward selection (*a posteriori* analysis) was used to determine the environmental variable(s) that best explain the variance of the data (b). The subset of environmental variable(s) that significantly explained phytoplankton distribution are referred to marginal effects ( $\lambda_1$ ) when analysed individually, or conditional effects ( $\lambda_c$ ) when analysed additively in the model (b). Explanatory variables are temperature ( $^{\circ}\text{C}$ ), salinity, nitrate ( $\text{NO}_3^-$ ;  $\mu\text{mol L}^{-1}$ ), phosphate ( $\text{PO}_4^{3-}$ ;  $\mu\text{mol L}^{-1}$ ), silicate ( $\text{Si(OH)}_4$ ;  $\mu\text{mol L}^{-1}$ ) and Stratification Index (SI) ( $\text{kg m}^{-4}$ ). Significant p-values ( $p < 0.05$ ) represents the variables that explain the variation in the analyses.

a) Axes	1	2	3	4	Total variance
Eigen-values	0.26	0.04	0.005	0	1
Taxa-environment correlations	0.68	0.4	0.321	0.25	
Cumulative percentage variance					
of species data	25.7	29.9	30.3	30.7	
of species-environment relation	83.5	97.2	98.8	99.8	
Sum of all eigenvalues					1
Sum of all canonical eigenvalues					0.31

b) Marginal Effects		Conditional Effects			
Variable	$\lambda_1$	Variable	$\lambda_c$	<i>P</i>	<i>F</i>
$\text{Si(OH)}_4$	0.2	$\text{Si(OH)}_4$	0.2	0.001	61.7
$\text{NO}_3^-$	0.19	Temperature	0.05	0.001	17.3
$\text{PO}_4^{3-}$	0.17	Salinity	0.02	0.002	6.94
Salinity	0.09	$\text{NO}_3^-$	0.01	0.016	4.31
Temperature	0.07	$\text{PO}_4^{3-}$	0.02	0.002	7.22
SI	0.06	SI	0.01	0.153	1.72

Table 5 – Average, standard errors and number of observations (in parenthesis) of environmental and biological variables of each cluster group. MLD = mixed layer depth, SI= Stratification index, NO<sub>3</sub><sup>-</sup> = nitrate, PO<sub>4</sub><sup>3-</sup> = phosphate, Si(OH)<sub>4</sub> = silicate, DT= diatoxanthin, DD= diadinoxanthin, POC= particulate organic carbon, PON= particulate organic nitrogen, POC<sub>phyto</sub> = phytoplankton-derived particulate organic carbon,  $\alpha^B$  = initial slope of the photosynthesis-irradiance curve,  $P_m^B$  = maximum normalised photosynthesis,  $E_k$  = onset saturation irradiance,  $E_s$  = saturation irradiance.

	Cluster A		Cluster B		Cluster C3a		Cluster C3b		Cluster C2		Cluster C1	
	DIAT (> 99%)		DIAT + PHAEO		DIAT + CHLORO		MIXED		DIATO + DINO		DIAT (> 93%)	
Temperature (°C)	2.8 ± 2.4	(17)	2.0 ± 1.8	(46)	1.6 ± 1.9	(62)	3.4 ± 1.9	(92)	4.8 ± 1.5	(32)	1.4 ± 1.7	(4)
Salinity	33.4 ± 1.5	(17)	33.7 ± 0.8	(46)	33.1 ± 1.2	(62)	34.1 ± 1.0	(92)	34.4 ± 0.5	(32)	33.0 ± 1.6	(4)
MLD (m)	32.2±43.8	(17)	32.6 ± 23.4	(46)	31.2 ± 28.5	(62)	59 ± 71.1	(92)	29.8 ± 17.0	(32)	16.0 ± 4.2	(4)
SI × 10 <sup>-3</sup> (kg m <sup>-4</sup> )	9.1 ± 6.3	(17)	6.3 ± 5.7	(46)	10.7 ± 8.5	(62)	5.0 ± 6.8	(92)	6.1 ± 4.5	(31)	6.6 ± 8.5	(4)
NO <sub>3</sub> <sup>-</sup> (µmol L <sup>-1</sup> )	2.9 ± 4.7	(17)	2.7 ± 3.5	(46)	3.4 ± 4.3	(58)	8.4 ± 4.1	(83)	3.7 ± 3.9	(32)	3.8 ± 6.8	(4)
Si(OH) <sub>4</sub> (µmol L <sup>-1</sup> )	2.2 ± 2.7	(17)	2.8 ± 2.1	(46)	3.5 ± 2.4	(58)	5.4 ± 2.2	(83)	3.0 ± 2.2	(32)	2.3 ± 3.4	(4)
PO <sub>4</sub> <sup>3-</sup> (µmol L <sup>-1</sup> )	0.3 ± 0.3	(17)	0.3 ± 0.2	(45)	0.4 ± 0.2	(55)	0.7 ± 0.2	(79)	0.3 ± 0.2	(32)	0.4 ± 0.3	(4)
Si(OH) <sub>4</sub> :NO <sub>3</sub> <sup>-</sup>	6.0 ± 11.8	(14)	3.6 ± 7.9	(37)	8.5 ± 18.2	(54)	1.1 ± 1.5	(82)	1.6 ± 1.8	(32)	3.9 ± 4.4	(4)
NO <sub>3</sub> <sup>-</sup> :PO <sub>4</sub> <sup>3-</sup>	8.2 ± 6.7	(11)	5.2 ± 5.0	(45)	5.9 ± 5.8	(55)	11.4 ± 4.1	(79)	8.7 ± 4.6	(32)	5.5 ± 7.1	(4)
Chlorophyll <i>a</i> (mg Chl <i>a</i> m <sup>-3</sup> )	3.8 ± 4.7	(17)	5.5 ± 4.8	(45)	7.7 ± 5.6	(59)	2.0 ± 1.7	(91)	4.0 ± 1.8	(31)	8.8 ± 9.6	(4)
DT:(DT+DD)	0.01±0.03	(16)	0.02±0.05	(44)	0.04±0.05	(62)	0.10±0.01	(92)	0.08±0.07	(32)	0.02±0.04	(4)
(DD+DT): $\int$ Chl <i>a</i>	0.08±0.07	(17)	0.03±0.03	(46)	0.04±0.02	(62)	0.07±0.03	(92)	0.12±0.03	(32)	0.07±0.04	(4)
POC (mg C m <sup>-3</sup> )	245 ± 90	(4)	498 ± 198	(27)	533 ± 198	(45)	234 ± 145	(63)	512 ± 179	(15)	393 ± 418	(2)
PON (mg N m <sup>-3</sup> )	39 ± 16	(4)	65 ± 23	(27)	74 ± 30	(45)	38 ± 26	(64)	83 ± 33	(15)	42 ± 41	(2)
POC <sub>phyto</sub> (%)	23.0 ± 5.2	(4)	49.2 ± 29.5	(26)	60.9 ± 25.6	(44)	33.3 ± 10.1	(64)	36.0 ± 11.4	(15)	37.8 ± 1.3	(2)
POC:PON	6.5 ± 1.2	(4)	7.8 ± 2.1	(27)	7.5 ± 2.1	(45)	6.6 ± 1.3	(64)	6.2 ± 0.9	(15)	8.6 ± 1.6	(2)
$\alpha^B \times 10^{-2}$ (mgC[mgChl <i>a</i> ]h <sup>-1</sup> [Wm <sup>-2</sup> ] <sup>-1</sup> )	-		6.8 ± 6	(9)	9.2 ± 10	(10)	7.1 ± 4	(18)	7.1 ± 1.5	(4)	-	
$P_m^B$ (mgC[mgChl <i>a</i> ]h <sup>-1</sup> )	-		3.0 ± 1.2	(9)	2.3 ± 0.8	(10)	2.3 ± 0.6	(18)	3.3 ± 0.7	(4)	-	
$E_k$ (W m <sup>-2</sup> )	-		60 ± 33	(9)	29 ± 13	(10)	39 ± 14	(18)	46 ± 5	(4)	-	
$E_s$ (W m <sup>-2</sup> )	-		62 ± 32	(9)	35 ± 18	(10)	43 ± 18	(18)	56 ± 8	(4)	-	
$\beta \times 10^{-4}$ (mgC[mgChl <i>a</i> ]h <sup>-1</sup> [Wm <sup>-2</sup> ] <sup>-1</sup> )	-		4 ± 7	(9)	16 ± 23	(10)	10 ± 16	(18)	29 ± 24	(4)	-	

## FIGURE LEGENDS

1025 Figure 1- Map showing stations along the AR7W transect and additional stations sampled during late spring and early  
summer (2005–2014). The station positions are superimposed on a composite image of sea surface temperature for the  
last three weeks of May 2006 collected by the NOAA satellite (AVHRR). White patches represent ice (Labrador and  
Greenland coasts). Circulation elements - colder currents (Labrador Current, Arctic Outflows and West Greenland  
1030 Current, blue solid arrows), warmer currents (Irminger Current (IC) and Extension, dark red and light solid arrows,  
respectively). The extended branch of the IC is a modified (cooled and freshened) water mass caused by lateral and  
vertical mixing along the Labrador slope.

1035 Figure 2 – Map with sampling stations and distances from a fixed reference position (Northeast Gulf of St Lawrence)  
in the x-axis shown by the star (a). Values are given at individual stations sampled between 2005 and 2014 (y-axis) for  
the following variables: date of sample collection (b), temperature (c), salinity (d), stratification index (SI) (e),  
chlorophyll *a* (f), nitrate ( $\text{NO}_3^-$ ) (g), phosphate ( $\text{PO}_4^{3-}$ ) (h), silicate ( $\text{Si}(\text{OH})_4$ ) concentrations (i), ratios of particulate  
organic carbon (POC) to particulate organic nitrogen (PON) (j), silicate to nitrate ( $\text{Si}(\text{OH})_4:\text{NO}_3^-$ ) ratios (k), and nitrate  
to phosphate ( $\text{NO}_3^-:\text{PO}_4^{3-}$ ) ratios (l). LSh = Labrador Shelf, LSI = Labrador Slope, CB = Central Basin, GSI = Greenland  
Slope, GSh = Greenland Shelf.

1040 Figure 3. Relative contribution (%) of chlorophyll *a* from distinct phytoplankton groups at each station from 2005 to  
2014 along the section distance from Labrador coast represented in Figure 2a (star symbol). LSh = Labrador Shelf,  
LSI = Labrador Slope, CB = Center Basin, GSI = Greenland Slope, GSh = Greenland Shelf. Note the distinct scales for  
each group.

1045 Figure 4. Dendrogram showing clustering of samples (a) and the proportion of chlorophyll *a* contributed by each  
phytoplankton group for each cluster (b). Spatial distribution of distinct phytoplankton communities (cluster groups)  
along the section, showing the distance from the star in Figure 2a (c). Bubble size in (c) represents total chlorophyll *a*  
biomass (minimum =  $0.3 \text{ mg Chl } a \text{ m}^{-3}$  and maximum =  $25 \text{ mg Chl } a \text{ m}^{-3}$ ).

1050 Figure 5- Positions of individual stations in relation to temperature ( $^{\circ}\text{C}$ ) and salinity (a) and redundancy analysis (RDA)  
ordination plot (b). The stations are colour-coded according to the cluster groups (see details in Figure 4). The TS plot  
(a) shows the approximate ranges of potential temperature ( $^{\circ}\text{C}$ ) and salinity of the Labrador Current (LC), the West  
Greenland Current (WGC) and the Irminger Current (IC). Arrows in (b) show the explanatory (environmental)  
variables used in the analysis.

1055 Figure 6- Relationship between particulate organic carbon (POC) and particulate organic nitrogen (PON) in a  
logarithmic scale, with the points (stations) as a function of phytoplankton-derived organic carbon content  
( $\text{POC}_{\text{phyto}}/\text{POC}$ , %) (a),  $\text{POC}:\text{PON}$  versus salinity (b), phytoplankton-derived organic carbon content ( $\text{POC}_{\text{phyto}}/\text{POC}$ ,  
%) versus the  $\text{POC}:\text{PON}$  ratio (c). The points (stations) in (b) and (c) are colour-coded according to the cluster groups  
(see details in Figure 4). Solid lines in (b) and (c) show the C:N Redfield ratio of 6.6 and the dashed line in (c) shows  
where  $\text{POC}_{\text{phyto}}$  contributes 50 % of the total POC.

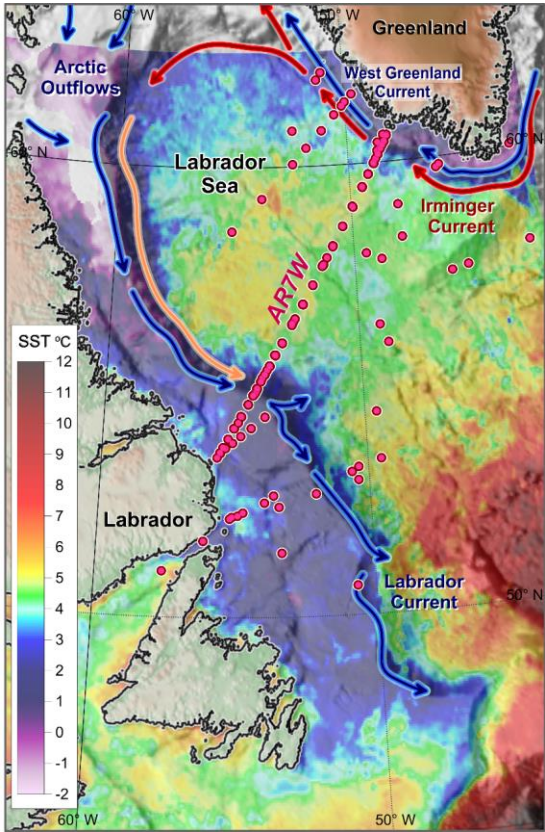
1060 Figure 7. Relationship between total accessory pigments ( $\text{mg AP m}^{-3}$ ) and total chlorophyll ( $\text{mg TChl } a \text{ m}^{-3}$ ) on a  
logarithmic scale, with the points (stations) according to temperature (a) and colour-coded according to phytoplankton  
community cluster group (see details in Figure 4) (b).





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Figure 1



1070

Figure 2

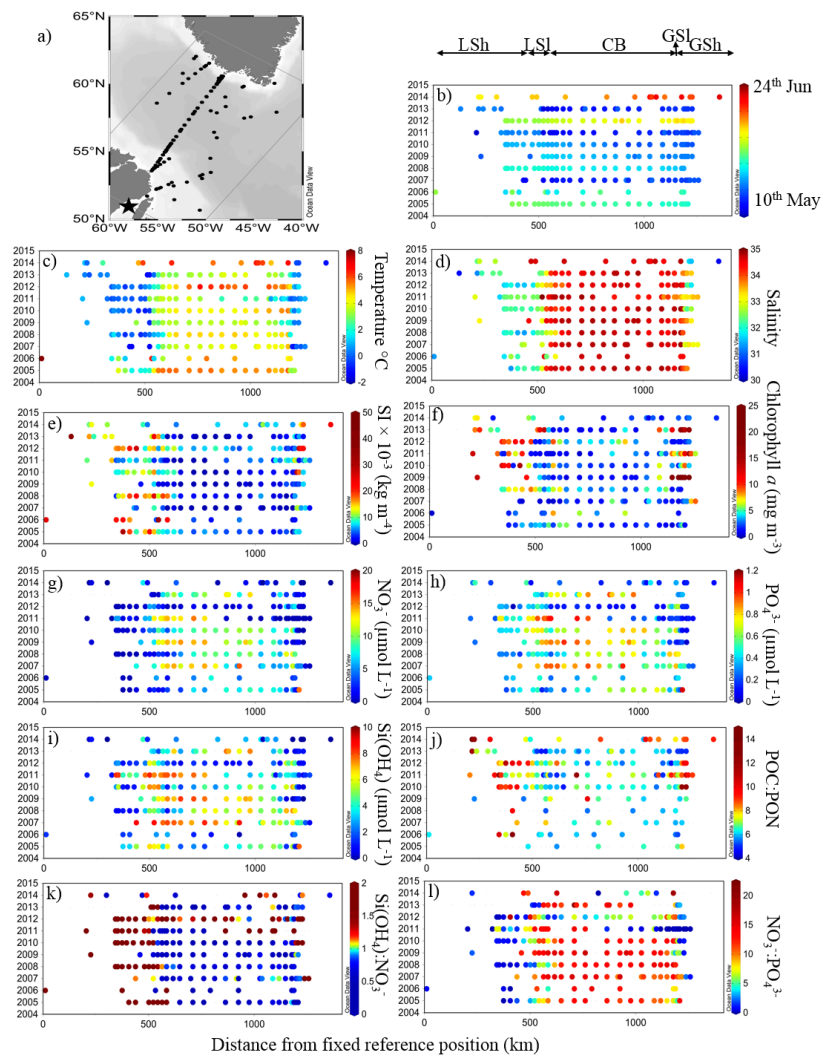
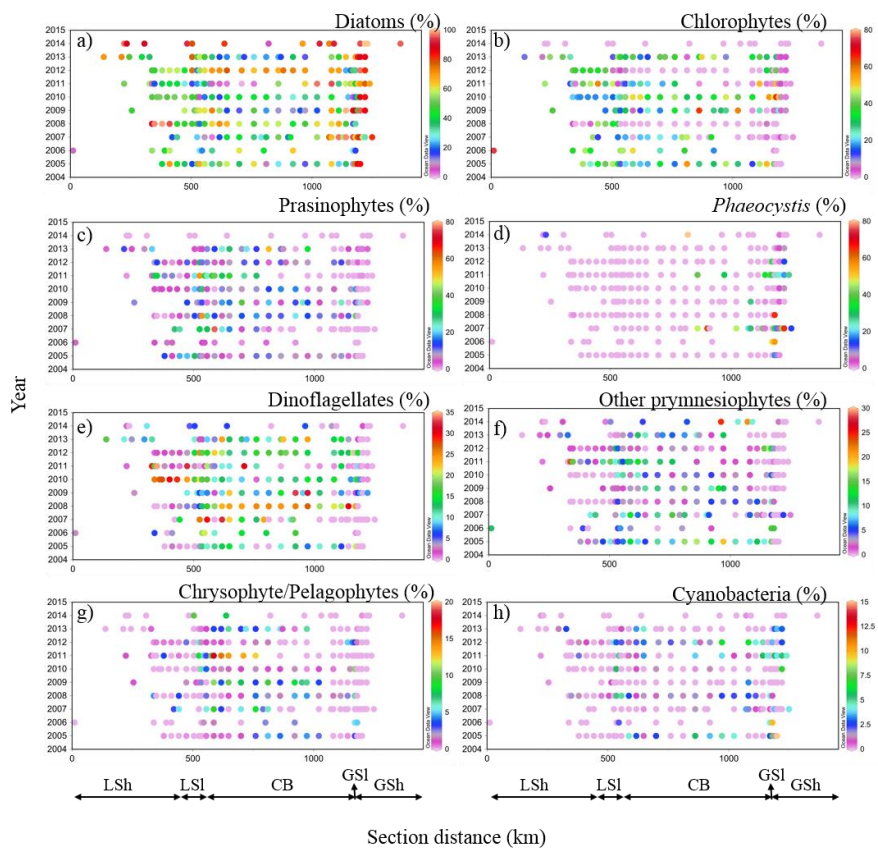


Figure 3



1085 **Figure 4**

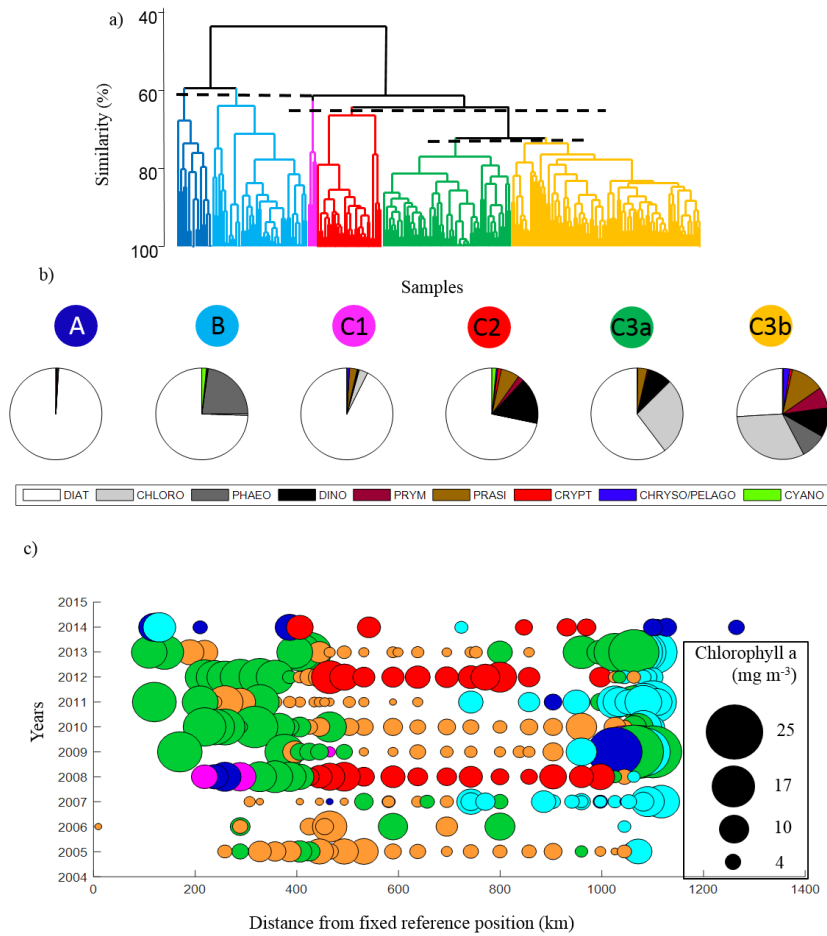


Figure 5

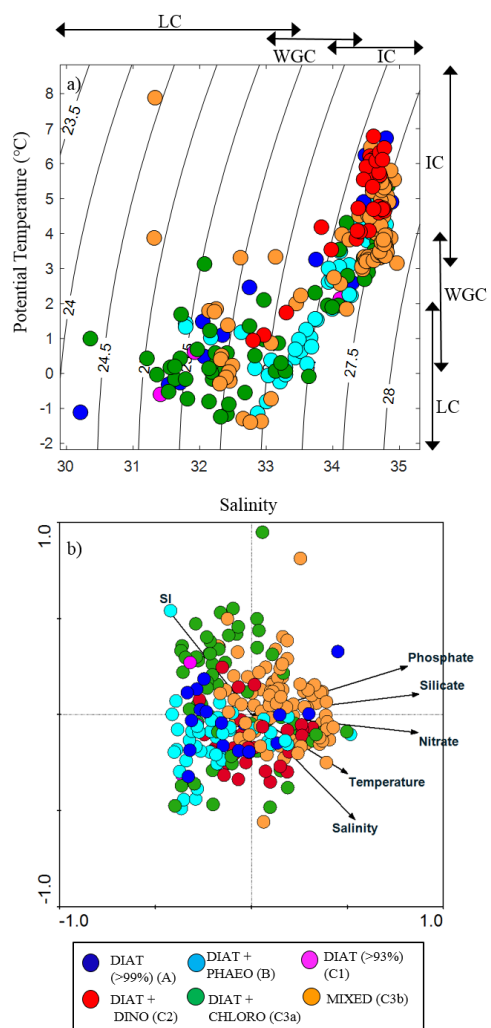


Figure 6

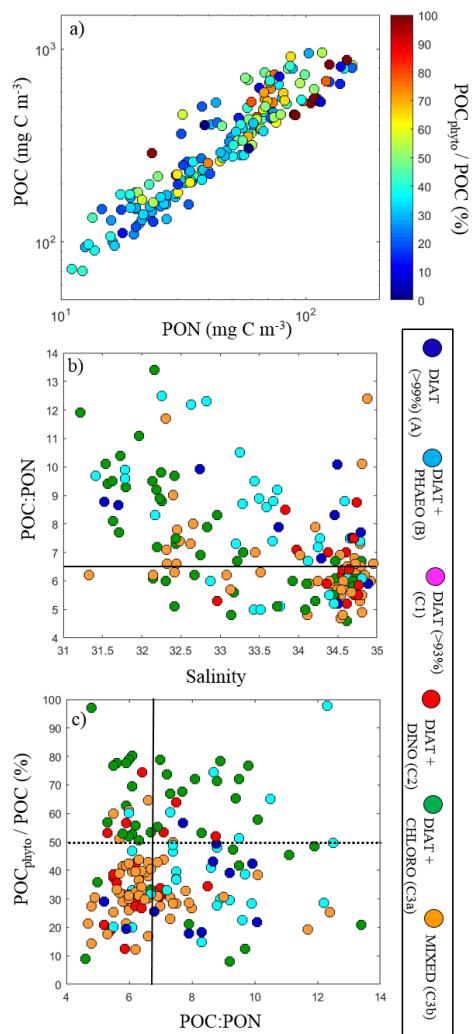
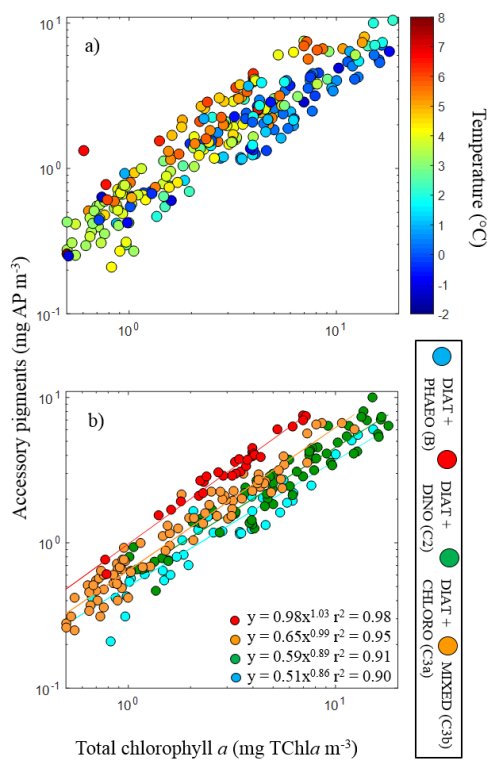


Figure 7



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