Université de Montréal

Origine, composition et destinée de la matière organique dissoute et ses interactions avec les communautés de procaryotes dans la mer du Labrador

par

Richard LaBrie

Département des sciences biologiques
Faculté des arts et des sciences

Thèse présentée en vue de l'obtention du grade de
Philosophiæ Doctor (Ph.D.)
en Écologie aquatique

Décembre 23, 2019

Université de Montréal

Faculté des études supérieures et postdoctorales

Cette thèse intitulée

Origine, composition et destinée de la matière organique dissoute et ses interactions avec les communautés de procaryotes dans la mer du Labrador

présentée par

Richard LaBrie

a été évaluée par un jury composé des personnes suivantes :

Jesse Shapiro
(président-rapporteur)

Roxane Maranger
(directeur de recherche)

Jérôme Comte
(membre du jury)

Boris Koch
(examinateur externe)

Résumé

Dans les océans, les procaryotes sont des acteurs clés dans le cycle du carbone puisqu'ils consomment une fraction importante de la matière organique dissoute (MOD) relâchée par les producteurs primaires. Puisque cette matière organique est très complexe et de biodisponibilité variable, les communautés de procaryotes qui la consomme sont très diversifiées et spécialisées pour certains types de composés organiques. En utilisant cette matière organique, les procaryotes contribuent à réintroduire ce carbone dans le réseau trophique, une source d'énergie essentielle dans les gyres oligotrophes de l'océan. Toutefois, puisque cette consommation n'est pas parfaite, une quantité importante de carbone est relâchée sous forme de CO_2 lors de la respiration, mais aussi sous forme de MOD récalcitrante, contribuant à séquestrer du carbone dans les océans.

Le but de cette thèse est d'une part, de dresser un portrait global de la biodisponibilité de la MOD et d'autre part, de déterminer l'influence de la biodisponibilité de cette dernière sur la composition et le métabolisme des procaryotes dans la mer du Labrador, une mer dont le rôle est critique dans la régulation du climat. Plus spécifiquement, nous identifions pour la première fois comment la distribution spatiale des procaryotes influencent leur métabolisme et est influencée par leur préférence alimentaire dans les eaux de surface de la mer du Labrador. Finalement, nous regardons comment la matière organique produite en surface est transformée et séquestrée en profondeur suite à la convection hivernale dans la mer du Labrador.

Le budget de carbone dans les océans n'est toujours pas balancé. Afin de mieux connaître les sources et la biodisponibilité du carbone dans les différents milieux aquatiques, nous avons évalué la biodisponibilité de la MOD à travers le continuum aquatique, des lacs jusqu'à l'océan. En menant une méta-analyse sur le sujet, nos résultats montrent que la proportion de matière organique labile, c'est-à-dire facilement utilisable par les procaryotes, est d'environ 6% dans tous les environnements aquatiques. Toutefois, la proportion de matière organique semi-labile, celle qui nécessite plus de transformation par les procaryotes, est grandement liée à la proximité au milieu terrestre. Les seuls écosystèmes aquatiques déviant de ces deux constats sont ceux en période d'efflorescence algale: ils contiennent beaucoup plus de carbone

labile et semi-labile que ceux à l'équilibre. Nous avons estimé que le carbone semi-labile peut soutenir 62% de la biomasse de procaryotes dans les lacs et les milieux côtiers.

Dans un deuxième temps, nous évaluons l'influence de la MOD sur le métabolisme et les communautés de procaryotes. Nous avons fait trois missions océanographiques sur la mer du Labrador à bord du navire Hudson pour déterminer la composition de la MOD et la communauté des procaryotes ainsi que leur métabolisme. En utilisant une approche novatrice, la modélisation de la distribution spatiale de l'abondance des procaryotes, nous avons montré à quel point celle-ci est importante pour déterminer leur préférence alimentaire ainsi que leur métabolisme. Nous avons également proposé un nouveau cadre conceptuel qui vise à faciliter la recherche à l'interface de la biogéochimie, de l'écologie microbienne et du métabolisme microbien.

Dans un dernier temps, nous avons comparé la capacité des procaryotes venant de différentes profondeurs océaniques à séquestrer le carbone. Lors de la consommation de la MOD, les procaryotes en relâche une petite fraction sous forme plus récalcitrante. En répétant ce processus, le carbone résiduel devient très récalcitrant et peut résister à la consommation par les procaryotes durant des centaines d'années. Nous avons montré que les procaryotes de l'océan profond sont plus efficaces pour séquestrer le carbone de cette façon. Nos résultats montrent que ce sont les taxons rares des procaryotes qui sont les éléments clés dans cette suite de transformation qui mène à la séquestration du carbone appelée pompe microbienne.

Cette thèse contribue à la compréhension du cycle du carbone dans la mer du Labrador et dans les écosystèmes aquatiques en général. Nous avons proposé une approche novatrice permettant de lier la qualité de la MOD à la composition des communautés de procaryotes qui la dégrade, un défi qui perdure depuis des dizaines d'années. De plus, nous montrons pour la première fois la que la pompe microbienne de carbone est un processus itératif fortement relié à la succession de la communauté de procaryotes. Nous montrons également que la pompe microbienne est active dans chaque strate océanique, mais que les procaryotes rares issus de l'océan profond sont plus efficaces à séquestrer le carbone. Mieux comprendre comment la composition de la MOD influence les procaryotes est primordial puisqu'ils sont centraux au cycle du carbone océanique.

Mots-clés : Cycle du carbone, matière organique dissoute, biodisponibilité, communauté de procaryotes, océan, mer du Labrador, écosystèmes aquatiques, pompe microbienne de carbone, diversité microbienne, métabolisme

Abstract

Oceanic prokaryotes are key players in the carbon cycle by consuming dissolved organic matter (DOM) produced by primary producers. As this organic matter is highly complex with varying degree of bioavailability, prokaryotic communities are highly diverse and different taxa target certain types of organic compounds. By consuming this organic matter, prokaryotes reintroduce this carbon into the food web, a critical energy flow in oligotrophic gyres. However, this consumption is not perfect and they release a lot of carbon as CO_2 through respiration, but also as recalcitrant DOM. Thus, they contribute to carbon sequestration in aquatic ecosystems.

The objective of this thesis is to characterize DOM bioavailability and its influence on the composition and metabolism of prokaryotic communities in the Labrador Sea, described as one of the Earth's climate system tipping elements. More precisely, we quantify for the first time how the spatial abundance distribution of prokaryotes influences ecosystem metabolism and organic matter association in the surface waters of the Labrador Sea. Lastly, we look at how DOM produced at the surface is transformed and sequestered following the Labrador Sea winter convective mixing.

The oceanic carbon budget is still unbalanced. In order to better understand its carbon sources and bioavailability, we characterize DOM bioavailability across the aquatic continuum, from lakes to the open ocean. Using a meta-analysis, our results show that the proportion of labile organic matter, i.e. readily available for prokaryotes, is similar at around 6% in all aquatic ecosystems. However, the proportion of semi-labile organic matter, i.e requiring transformations to be consumed by prokaryotes, is highly related to terrestrial connectivity. The only ecosystems that did not follow these patterns were in a phytoplankton bloom period and had a high proportion of labile and semi-labile organic matter as their counterparts at equilibrium. Finally, we estimated that semi-labile organic matter could sustain 62% of prokaryotic biomass in lakes and coastal zones.

Second, we evaluated the influence of DOM on prokaryotic metabolism and community composition. In order to determine organic matter composition, prokaryotic community composition and metabolic rates, we did three oceanic cruises in the Labrador Sea onboard

the Hudson ship. By using spatial abundance distribution modelling of prokaryotes, we identified strong associations between groups of this novel approach and organic matter composition. We also proposed a framework to bridge the gap between prokaryotic diversity, microbial ecology, and biogeochemistry among methods and across scales.

Lastly, we compared how prokaryotic communities from different oceanic strata could sequester carbon. When they consume organic matter, prokaryotes release a small amount in recalcitrant forms. Through this iterative process, called the microbial carbon pump, prokaryotes contribute to carbon sequestration by creating highly recalcitrant compounds that resist further degradation for hundreds of years. We have shown that all prokaryotes enable the microbial carbon pump, but that prokaryotes from deeper strata are more efficient. Our results also conclusively show that the rare prokaryotic taxa are key players in the microbial carbon pump.

This thesis contributes to better understand the carbon cycle in the Labrador Sea and in all aquatic ecosystems. We proposed a novel framework to relate biogeochemistry, prokaryotic diversity and microbial ecology which has been a challenge for decades. Moreover, we conclusively showed for the first time that the iterative process of the microbial carbon pump is related to prokaryotic succession. We also show that it happens in all oceanic strata, but that rare prokaryotes from the deep ocean are more efficient to sequester carbon. Better understanding how DOM composition influences prokaryotes is of prime importance as they are the main drivers of the oceanic carbon cycle.

Key words: Carbon cycle, dissolved organic matter, bioavailability, prokaryotic communities, ocean, Labrador Sea, aquatic ecosystems, microbial carbon pump, microbial diversity, metabolism

Table des matières

Liste des tableaux

Liste des figures

Liste des sigles et des abréviations

AA	Acide aminé et *amino acids*
AB	Abondance bactérienne
ADN	acide désoxyribonucléique
AIC	*Akaike information criterion*
ANCOVA	*Analysis of covariance*
ANOVA	*Analysis of variance*
Ala	*Alanine*
Arg	*Arginine*
ARN	acide ribonucléique
AR7W	*Atlantic repeat hydrography line 7 west*
ASV	*Amplicon sequence variant*

Asx	*Aspartic acid and asparagine*
AP	Abondance procaryotique
BDOC	*Bioavailable dissolved organic carbon*
BOD	*Biological oxygen demand*
C	Carbone et *carbon*
CB	Bassin central de l'anglais *Central basin*
CCGS	*Canadian coast guard ship*
CDOM	*Chromophoric dissolved organic matter*
CO_2	Dioxyde de carbone et *carbon dioxide*
COD	Carbone organique dissous
CODL	Carbone organique dissous labile
CODSL	Carbone organique dissous semi-labile
CODR	Carbone organique dissous réfractaire

CTD	*Conductivity, temperature and depth*
DNA	*Deoxyribonucleic acid*
DOC	*Dissolved organic carbon*
DOM	*Dissolved organic matter*
DON	*Dissolved organic nitrogen*
DPC	Demande procaryotique en carbone
DSOW	*Denmark Strait Overflow Water*
ECP	Efficacité de croissance procaryotique
EEM	*Excitation-emission matrix*
ESI-FT-ICR MS	*Electron spray ionization Fourier transform ion cyclotron resonance mass spectrometry*
FDOM	*Fluorescent dissolved organic matter*
FMM	Faible masse moléculaire

Glx	*Glutamic acid and glutamine*
Gly	*Glycine*
GMM	Grande masse moléculaire
GS	Plateau du Groenland de l'anglais *Greenland shelf*
HCl	Acide chlorhydrique et *Hydrochloric acid*
His	*Histidine*
HPLC	*High-performance liquid chromatography*
HTCO	*High temperature catalytic oxidation*
Ile	*Isoleucine*
IOB	Institut océanique de Bedford
LDOC	*Labile dissolved organic carbon*
Leu	*Leucine*
LS	Plateau du Labrador de l'anglais *Labrador shelf*

LSW	*Labrador Sea Water*
Lys	*Lysine*
MCP	*Microbial carbon pump*
MÉÉ	Matrice d'excitation-émission
MOD	Matière organique dissoute
MODC	Matière organique dissoute chromophorique
MODF	Matière organique dissoute fluorescente
MODL	Matière organique dissoute labile
MODSL	Matière organique dissoute semi-labile
MODR	Matière organique dissoute réfractaire
MODSR	Matière organique dissoute semi-réfractaire
MODUR	Matière organique dissoute ultra-réfractaire
N	Azote et *nitrogen*

NEADW	*North East Atlantic Deep Water*
NGCC	Navire de la garde-côtière canadienne
NH_4^+	Ammonium
NOD	Azote organique dissous
NO_2^-	Nitrite
NO_3^-	Nitrate
OPA	*o-phthaldialdehyde*
OTU	*Operational taxonomic unit*
P	Phosphore
PA	*Prokaryotic abundance*
PARAFAC	*Parallel factor analysis*
PCA	*Principle component analysis*
PES	*Polyethersulfone*

Phe	*Phenylalanine*
PHP	*Prokaryotic heterotrophic production*
PMC	Pompe microbienne de carbone
POC	*Particulate organic carbon*
PON	*Particulate organic nitrogen*
PP	Production primaire
PPH	Propduction procaryotique hétérotrophe
PR	*Prokaryotic respiration*
RC	Respiration de la communauté
RDOC	*Refractory dissolved organic carbon*
RNA	*Ribonucleic acid*
Ser	*Serine*
SiO_2	Silicate

SLDOC	*Semi-labile dissolved organic carbon*
SPAD	*Spatial abundance distribution*
TCA	*Trichloroacetic acid*
Thr	*Threonine*
TDN	*Total dissolved nitrogen*
TOC	*Total organic carbon*
TN	*Total nitrogen*
Tyr	*Tyrosine*
Val	*Valine*
VITALS	*Ventilation, Interactions and Transports Across the Labrador Sea*
WOCE	*World ocean circulation experiment*

Remerciements

Cette thèse est le résulat de six années de travaux, réflexions et de collaboration. Sans le soutien de nombreuses personnes, collègues, amis et famille, cette thèse ne serait pas ce qu'elle est. Je profite donc de ces quelques lignes pour vous remercier.

Tout à commencer quand Roxane Maranger m'a proposé un projet de recherche doctoral. Jeune et naïf, j'ai sauté sur l'occasion me disant que je m'épargnerais la maîtrise. Sortant tout juste d'un bac en géographie, la route a été longue et sinueuse pour me rendre jusqu'ici. Merci de m'avoir donné ma chance, permis de réaliser le doctorat que je voulais, aussi osé soit-il, aussi long a-t-il été. Le Richard qui est entré dans le labo en 2013 et celui qui écrit ces lignes ne sont pas les mêmes. J'ai beaucoup appris avec toi durant toutes ces années.

Je tiens à remercier les équipages du Hudson et tous les scientifiques de BIO que j'ai cotoyés sur ce petit navire de 90 mètres. Merci à Isabelle et Gabrièle qui ont fait ces missions et se sont gelées les mains avec moi à la rosette. Merci à Marc, toi qui a été d'une grande aide sur le plan scientifique et moral, avec toutes tes histoires plus invraisemblables les unes que les autres. A special thank to Igor: the first time we met was not easy, but we learned to work together and I hope I'll see you again at sea, my friend.

À Jean-François, pour les échanges sur le carbone et sur la bière; Simon, pour les missions sur le Hudson et ton attitude en général, j'ai beaucoup aimé travaillé avec toi; François, pour le meilleur conseil pour réussir un doctorat: «lâche pas». À tous mes autres co-auteurs, aussi nombreux êtes-vous, pour m'avoir aidé dans mes études doctorales.

Merci à mes collègues de labo, ceux et celles qui furent, et les autres qui sont encore. Stéphanie, pour l'initiation à l'échantillonnage d'hiver et aux filtrations péristaltiques dans les pires conditions: j'aurai su me débrouiller seul sur le Hudson après tout ça; Marie-Pier, pour ta joie de vivre et ton rire unique; Cynthia, pour toutes ces années et Nitropilipus, qui est dans un bien pire état que dans lequel tu me l'as légué; Charles, qui a tant essayé de me faire croire aux zones de résurgence; Dan, toi qui a si bien répondu à mes questions «ô

combien pertinentes» tout au long de mon doctorat et à Jean-Olivier et Morgan, vous qui étiez mes seuls collègues pendant plusieurs années. Lisa, pour soutenir mes idées toujours excellentes, et ton très bon tiramisu, Stéphanie, pour tes questions sur R «ô combien pertinentes» elles aussi, Daphnée, pour ton positivisme et ta présence, et Andréanne pour ton émerveillement devant la science qu'on fait. Un merci spécial aux *Lab Sea Slackers*, Bérangère et Nico. Merci beaucoup pour toute l'aide que vous m'avez apportée. Sans vous, ma thèse ne serait pas ce qu'elle est en ce moment.

À tout le personnel de soutien. Sans vous, la paperasse universitaire beaucoup trop complexe pour rien serait un réel cauchemar. À Dominique, pour qui un problème de machine est une tâche plaisante à regarder, comme donner un légo à un enfant. À Benjamin Constantineau, bibliothécaire au Département de physique, pour ta précieuse aide sur LaTex.

À mon ami de toujours, Nico, pour toutes les soirées à réinventer le monde et la société. Laurent, Fred, FX, Ju, Yan, pour toutes ces soirées de D&D où on ne pense pas à nos jobs. Alex, pour l'initiation à l'escalade il y a de nombreuses années, ça a été essentiel tout au long de ma thèse. Xilef, pour ces milles parties d'échec qui m'ont permis de focusser sur autre chose un bref instant, me permettant de continuer à travailler pendant de nombreuses heures. À tous mes amis qui ne m'ont jamais demandé quand j'allais terminer.

Merci à ma famille, qui m'a toujours soutenu dans mes changements drastiques d'orientation académique. Vous qui n'êtes pas en science, vous vous êtes toujours montré intéressé par ce que je fais, même quand je n'arrivais pas à vous expliquer ce que je faisais.

Merci à ma belle Virginie, pour ta bonne humeur et ta passion inconditionnelle de l'escalade. Tu ne cesses de repousser tes craintes et c'est inspirant de te voir aller. Un grand merci pour les dernières semaines de thèse; sans toi, je n'y serais pas arrivé. Je te rendrai l'ascenseur dans quelques mois quand ça sera ton tour de terminer cette aventure.

Je saisi l'occasion pour remercier Ryukahr, Grand POOBear et CarlSagan42 pour ces heures incalculables de divertissement.

Chapitre 1 : Introduction

1.1. Matière organique – production, classification et caractérisation

La quantité de matière organique dissoute (MOD) dans l'océan constitue une réserve d'environ 662 Pg de carbone (C), soit presque l'équivalent du carbone inorganique (CO_2) contenu dans l'atmosphère (750 Pg C) (Hansell and Carlson, 2014), ce qui représente un très grand réservoir d'énergie pour les procaryotes. Étonnamment, cette MOD est âgée en moyenne de quelques milliers d'années (Bauer et al., 1992). Il y a deux hypothèses qui tentent d'expliquer pourquoi la MOD persiste aussi longtemps dans les océans. La première, appelée pompe microbienne de carbone (PMC) (Jiao et al., 2010), stipule la MOD serait transformée par les procaryotes jusqu'à ce qu'elle n'ait plus de valeurs nutritives. En effet, les procaryotes ont besoin d'azote et de phosphore en plus du C pour combler leurs besoins énergétiques, et la MOD en profondeur des océans est très enrichie en C par rapport à l'azote et au phosphore (3500 : 200 : 1) (Hopkinson and Vallino, 2005). La seconde hypothèse est que la MOD est chimiquement trop diversifiée et représenterait une dépense énergétique pour les procaryotes qui la consommeraient (énergie obtenue < énergie dépensée) (LaRowe et al., 2012).

À l'origine, la majorité de la MOD provient du phytoplancton qui fixe le CO_2 par la photosynthèse. En moyenne, seulement 13 % de cette production primaire (PP) est libérée lorsqu'ils sont vivants (Baines and Pace, 1991; Nagata, 2000; Carlson and Hansell, 2015), mais peut représenter jusqu'à 80 % de la PP (Wetz and Wheeler, 2007) en considérant les exopolymères transparents particulaires, de la matière produite pour aider le phytoplancton a acquérir les éléments nutritifs. Le reste de la MOD provient d'interactions dans les réseaux trophiques, dont la principale est le broutage du phytoplancton par le zooplancton (par exemple les copépodes), ce qui relâche de la MOD qui équivaut à 10 à 30 % de la PP particulaire (Nagata, 2000). La lyse cellulaire (virale et bactérienne) ainsi que la production d'exo-métabolites pour consommer la matière particulaire participent également au renouvellement de la MOD, mais leur importance est encore indéterminée (Carlson

and Hansell, 2015; Lechtenfeld et al., 2015). Finalement, les apports riverains amènent également de la MOD d'origine terrestre, mais en très faible quantité en haute mer. La majorité de ces processus mènent à la création de MOD labile (MODL), c'est-à-dire facilement assimilable par les prokaryotes hétérotrophes. Par contre, la très grande majorité de la MOD est récalcitrante et par conséquent résistante à la consommation par les procaryotes.

Bien que cette MOD soit la principale source de C pour les procaryotes hétérotrophes, de 70 à 95 % de sa composition chimique demeure non-caractérisée (Benner, 2002). La MOD est séparée en deux classes de taille : de faible masse moléculaire (< 1000 Da), qui peut être directement consommée par les procaryotes, et de grande masse moléculaire (> 1000 Da), qui doit préalablement être brisée pour être incorporée dans la cellule. Par contre, ce ne sont pas toutes les molécules de faible masse moléculaire qui sont consommées par les procaryotes et la majorité de la MOD qui persiste dans les océans est de faible masse moléculaire (Benner and Amon, 2015). Ainsi, cette séparation des molécules selon leur taille n'est plus synonyme de labilité (Nagata et al., 2003; Hama et al., 2004; Yamashita and Tanoue, 2004) et une autre nomenclature qui ignore ces regroupements par classe de taille est préférable. Celle que j'utiliserai pour ma thèse a été proposée par Hansell (2013) et regroupe la MOD selon sa réactivité biologique (tableau 0.1).

Réservoir	**Stock global (Pg C)**	**Taux de production (Pc C a^{-1})**	**Temps de renouvellement**
Labile	<0,2	15 - 25	<heures - jours
Semi-labile	6 ± 2	∼3,4	Mois - années
Semi-réfractaire	14 ± 2	∼0,34	Décennies - siècles
Réfractaire	630 ± 32	∼0,0043	Millénaires
Ultra-réfractaire	>12	∼1,5x10^{-5}	Millénaires

Tableau 1.1. Description des réservoirs de MOD. Données tirées de Hansell (2013)

La MOD labile (MODL), qui est par définition rapidement utilisée par les procaryotes hétérotrophes, est produite par le phytoplancton et représente plus de 50 % de la PP nette (production – respiration) (Williams, 2000). Cette fraction de la MOD soutien le réseau trophique bactérien en surface de l'océan en lui fournissant de l'énergie rapidement utilisable. La MODL est donc d'intérêt limité pour la séquestration de C à long terme bien que certains chercheurs estiment que le C océanique est constitué de molécules labiles en trop faible concentration pour être utilisées (Arrieta et al., 2015). À l'échelle globale, la MODL représente un stock très faible, mais hautement dynamique (tableau 0.1), démontrant ainsi son rôle important dans le cycle du C.

De son côté, la MOD semi-labile (MODSL) n'est pas naturellement disponible pour les organismes : elle doit être dégradée par des enzymes ou des rayons UV. Puisqu'elle résiste à une dégradation rapide, elle peut s'accumuler en surface et être exporté dans la zone mésopélagique supérieure (< 500 m). Même si elle résiste à la dégradation par les communautés de procaryotes en surface, la MODSL peut être consommée par les communautés mésopélagiques et supporte leur besoins en C (Carlson et al., 2004). À l'échelle globale, ce flux vertical représente $\sim$ 1,5 Pg C an^{-1}, mais est aussi d'un intérêt limité pour la séquestration à long terme : le CO_2 produit lors de sa dégradation sera ventilé vers l'atmosphère en quelques années (Carlson and Hansell, 2015). Toutefois, si cette MOD pouvait se rendre plus en profondeur, sa contribution à la séquestration du C à long terme serait plus importante puisque le CO_2 produit resterait dans les profondeurs de l'océan durant plus d'un millier d'années (Morita, 1993).

La MOD semi-réfractaire (MODSR) constitue un réservoir de C très peu caractérisée. Les mécanismes de production et de dégradation sont encore inconnus. La MODSR est toutefois importante pour la séquestration de C puisqu'elle peut être exportée vers le bathypélagique et résiste à la dégradation pendant des centaines d'années.

La MOD réfractaire (MODR) constitue le réservoir de C le plus important, environ 630 Pg C. Elle est composée essentiellement de MOD FMM, mais sa composition chimique demeure inconnue. C'est ce vaste réservoir de C qui est au centre de la PMC (Jiao et al., 2010) et de l'hypothèse de dillution (Arrieta et al., 2015). Qu'elle soit constituée de molécules réfractaires ou d'une multitude de molécules labiles en apparence réfractaire, la MODR est d'une importance capitale pour le climat (Boyd, 2015).

La MOD ultra-réfractaire (MODUR) est le dernier réservoir de C. Les connaissances sur cette fraction sont encore plus éparses. La MODUR est probablement constituée de C noir issue de processus de combustion et représenterait un transfert du monde biologique au monde géologique (Carlson and Hansell, 2015).

Bien que ces réservoirs aient chacun leur importance dans le cycle du C, l'échelle de temps de la MODR et MODUR est trop grande pour que ces fractions soient utilisées expérimentalement. En menant des expériences en culture discontinue, il est possible d'isoler les processus qui nous intéressent et de contrôler d'autres variables qui seraient confondantes. Par exemple, il est possible d'isoler les processus de consommation et de transformation de la MOD par les procaryotes en menant des expériences sans lumière, évitant ainsi l'ajout de matière labile par la photosynthèse. Il est ainsi possible d'estimer les quantités de C de ces

différents réservoirs en fonction de leur consommation à travers le temps (Servais et al., 1987).

Afin de comprendre comment les communautés de procaryotes utilisent la MOD, il est nécessaire de mieux la caractériser. Plusieurs méthodes existent pour caractériser les différentes composantes de la MOD (p. ex. sucres, acides aminés), mais nous nous sommes concentrés sur les propriétés optiques car il s'agit de méthodes rapides et simples qui donnent un portrait général de la composition de la MOD. Nous pouvons distinguer deux types de méthode optique: celles basées sur la fraction colorée (MODC) et celles basées sur la fraction fluorescente (MODF) (Fig. 1.1). Le ratio des pentes spectrales de la MODC est corrélé à la taille des molécules (Helms et al., 2008), ce qui permet de distinguer si la source de la MOD est terrigène ou aquatique(Massicotte and Frenette, 2011). Puisque le budget océanique de C n'est toujours pas équilibré (Burd et al., 2010), pouvoir déterminer les sources de la MOD est primordial. La MODF est une fraction encore plus restreinte de la MOD, mais est sensée représenter l'ensemble de la MOD (Stubbins et al., 2014). Celle-ci est caractérisée par spectrofluorométrie pour produire une matrice d'excitation-émission (MÉÉ). Cette matrice était orginalement analysée visuellement pour identifier les différents fluorochromes (Coble, 1996; Ishii and Boyer, 2012). Cette technique permettait de discriminer la MOD provenant des milieux terrestres de celle produite en océan, notamment par une translation de ∼20 nm de la fluorescence des substances humiques vers les petites longueurs d'ondes (**?**).

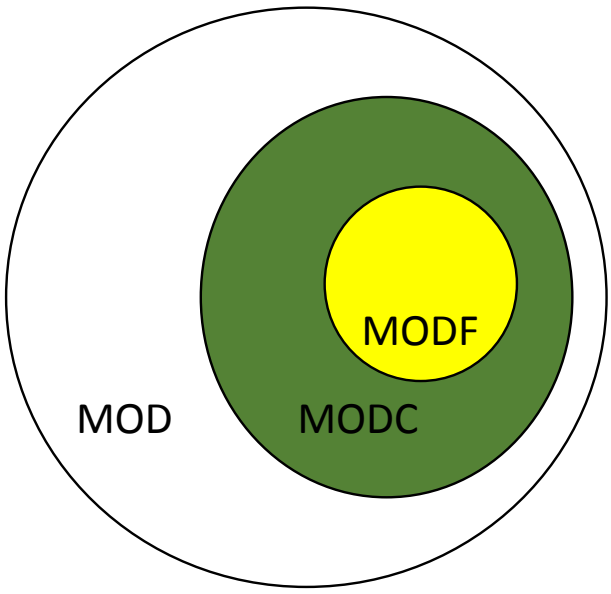


Fig. 1.1. MOD: matière organique dissoute MODC: fraction colorée de la MOD MODF: fraction fluorescente de la MOD. Traduit de Stubbins et al. (2014)

L'analyse de la MODF est maintenant couplée avec l'analyse en facteurs parallèles (PARAFAC). L'intégration de ce modèle statistique permet de traiter toutes les MÉÉs simultanément pour produire une solution unique pour l'ensemble des échantillons (Stubbins et al., 2014). Les spectres de fluorescences produits par le modèle PARAFAC sont alors analysés pour distinguer les grands groupes de fluorochromes, tel que des protéines ou des acides humiques, sans pouvoir identifier les molécules ni les quantifier (Stedmon and Markager, 2005; Kowalczuk et al., 2010). Les fluorochromes modélisés sont généralement mis en relation avec les différentes masses d'eau pour déterminer l'origine de la MOD (terrestre ou marine). En suivant le continuum aquatique, des lacs jusqu'à l'oécan, l'intensité du signal de la MODF diminue lorsque la salinité augmente (Kowalczuk et al., 2010; Cabaniss and Shuman, 1987; Osburn and Stedmon, 2011) puisque la concentration en MOD est beaucoup plus faible en milieu marin. Il est aussi possible de combiner la MODF avec la spectrométrie de masse pour mettre en relation des composés chimiques avec les fluorochromes afin de mieux comprendre ce qui compose la MODF (Stubbins et al., 2014). Toutefois, la caractérisation de la MOD peut également permettre de mieux comprendre comment la MOD est façonnée par les procaryotes, ce qui n'est que rarement fait (Alonso-Sáez et al., 2009).

1.2. Océan, microorganismes et processus

Les océans jouent un rôle fondamental dans la transformation du C en fixant autant de CO_2 que les environnements terrestres (Field et al., 1998). Ce C transite ensuite à travers les micro-organismes et réintègrera le réseau trophique ou sera transformé en CO_2. Deux processus métaboliques principaux contrôlent les flux de C dans l'océan : la PP et la respiration de la communauté (RC). Les producteurs primaires – le phytoplancton – fixent le CO_2 en biomasse organique et exsudent de la MOD, tandis que les communautés hétérotrophes la consomment. Une partie de cette MOD est emmagasinée sous forme de biomasse disponible pour les microbrouteurs, mais la majorité est reminéralisée en CO_2 via la respiration (R).

Actuellement, nous ne connaissons toujours pas le bilan métabolique des gyres océaniques oligotrophes, couvrant plus de 75 % de la surface marine (Dufour et al., 1999). Selon la méthode utilisée, le bilan est soit net autotrophe (PP > RC) ou hétérotrophe (PP < RC). Les méthodes in situ, comme le ratio oxygène (O_2)-argon, indiquent que ces écosystèmes sont autotrophes puisqu'elles ont un bilan de C positif et agissent comme une source de C organique (Williams et al., 2013). Les méthodes basées sur des incubations in vitro, comme les incubations au ^{14}C et ΔO_2, indiquent plutôt que ces écosystèmes sont hétérotrophes et agissent comme un puits de C organique (Duarte et al., 2013). Chacune de ces approches

possèdent leurs propres incertitudes et limitations.

Un nombre grandissant de données suggère que la respiration procaryotique (RP), un élément important de la RC, est sous-estimée (Jahnke and Craven, 1995; del Giorgio and Duarte, 2002). Rarement mesurée directement, elle est souvent estimée à l'aide de relations empiriques (del Giorgio and Cole, 1998; Rivkin and Legendre, 2001). Une partie du C consommé est stockée sous forme de biomasse, la production procaryotique hétérotrophique (PPH), tandis qu'une autre est reminéralisée via la RP. Ces deux processus constituent la demande procaryotique en C (DPC) : la quantité totale de C qui transite par les procaryotes. La DPC est souvent plus élevée que la PP lorsque celle-ci est inférieure à 35 g O_2 L^{-1} j^{-1} (Duarte and Agustí, 1998). Lorsque la DPC > PP, le système a besoin de C allochtone pour combler les besoins des micro-organismes.

Cette forte DPC place donc les micro-organismes au centre de la transformation de la MOD. En effet, très abondants, de 10^5 à 10^7 organismes ml^{-1}, ils représentent environ 40 % de la biomasse marine, dont près de 25 % uniquement pour les hétérotrophes (Pomeroy et al., 2007) (Fig. 1.2). Non seulement nombreux, les procaryotes représentent plus de 80 % de la surface biologique (Fig. 1.2) et sont en contact direct avec la MOD. De plus, leur métabolisme est proportionnel au ratio surface : volume (Pomeroy et al., 2007), approximé

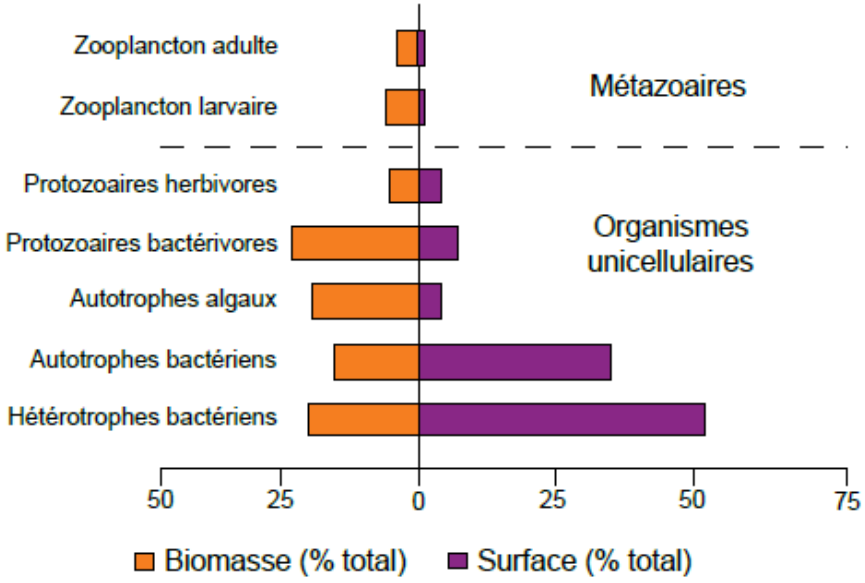


Fig. 1.2. Distribution de la biomasse et de la surface biologique des grands groupes planctoniques marins. Les données sont représentées en pourcentage du total. La ligne pointillée délimite les organismes unicellulaires (microbes) des organismes multi-cellulaires. Traduit de Pomeroy et al. (2007)

à 6/d, où d est le diamètre (< 1 μm). Leur abondance, leur surface biologique et leur très petite taille donnent une importance capitale aux procaryotes au niveau des principaux processus métaboliques liés au C.

Les procaryotes hétérotrophes consomment la MOD et l'emmagasine sous forme de biomasse. Ce C retourne dans le réseau trophique par les microbrouteurs : ces phénomènes sont regroupés sous l'appellation boucle microbienne (Fig. 1.3) (Azam et al., 1983; Ducklow, 1983). Cette notion de boucle microbienne a introduit la PPH : la quantité de biomasse produite par les organismes procaryotes.

Bien que facilement mesurable, la PPH ne considère pas les pertes du système lié à la RP. Ces deux processus sont regroupés sous la DPC qui produit une mesure appropriée pour quantifier le rôle des procaryotes dans les flux de C océanique. Cette mesure de la demande en C permet aussi de calculer l'efficacité de croissance procaryotique (ECP), défini comme le rendement en biomasse comparativement à la quantité totale de matière consommée (del Giorgio et al., 1997) (ECP = PPH / DPC). Ces quatre variables permettent de connaître la contribution précise des hétérotrophes au bilan de C d'un écosystème.

L'ECP est affectée par la température et la qualité de la MOD. La RP est davantage stimulée que la PPH par la température puisqu'elle est moins assujettie à la limitation en nutriments (López-Urrutia and Morán, 2007). Pour assimiler les nutriments de la MODSL ou de la MODSR, l'organisme doit éliminer beaucoup de C via la respiration pour conserver son ratio C : N : P stable. Ainsi, l'énergie dégagée par ces molécules est faible, diminue l'ECP et se traduit par un quotient de respiration élevé (Williams and del Giorgio, 2005; Berggren et al., 2012).

La contribution de la RP à la RC ne fait pas consensus dans la littérature : les valeurs varient entre 30 % et plus de 90 % (Rivkin and Legendre, 2001; Robinson and Williams, 2005), allant jusqu'à près de 300 % (Martinez-Garcia et al., 2013). La différence marquée entre ces résultats peut provenir de biais dans les méthodes (Robinson and Williams, 2005; Martinez-Garcia et al., 2013). Quoi qu'il en soit, la RP demeure un élément clé du cycle du C océanique (Duarte and Cebrian, 1996). Pourtant, il existe de 100 à 1000 fois moins de données sur la RP que sur la PP et la PPH (Williams and del Giorgio, 2005) et elles sont concentrées dans les basses latitudes. L'augmentation de la température de l'eau amplifie cette transition vers l'hétérotrophie et stimule d'avantage la RC que la PP (Yvon-Durocher et al., 2010). Ce faisant, les océans relâchent plus de CO_2 et créent une rétroaction positive sur le réchauffement climatique. Cette inversion du processus dominant (PP $<$ RC) affectera

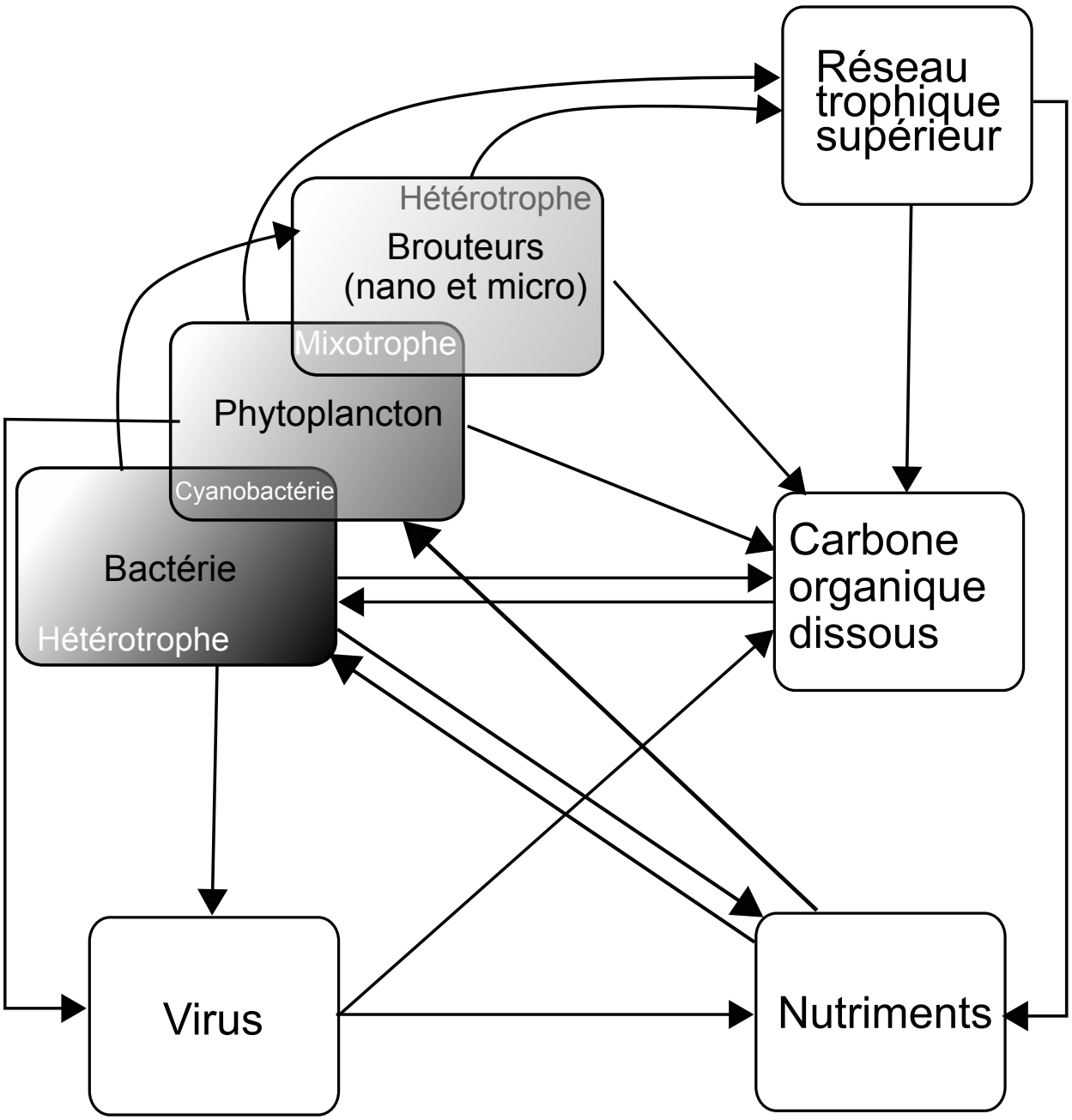


Fig. 1.3. Schéma simplifié de la boucle microbienne. Les boîtes représentent les différents éléments biotiques et abiotiques qui influencent les bactéries. Les flèches représentent quant à elles les interactions de ses différents éléments: consommation par broutage ou par lyse virale, utilisation ou régénérescence des ressources alimentaires (COD et nutriments). Traduit de Sarmento et al. (2010)

particulièrement les environnements froids et sensibles comme la mer du Labrador.

1.3. Diversité

Les communautés de procaryotes ont longtemps été considérées comme des boîtes noires, où seul le nombre de procaryotes était important pour déterminer leur importance dans le cycle du C. Or, comme tous les autres organismes vivants, les procaryotes ont des préférences alimentaires et ne consomment pas tous les mêmes molécules. Par exemple, les $\gamma-$protéobactéries préfèrent le glucose (Pinhassi and Berman, 2003; Alonso-Sáez et al., 2009); les $\alpha-$protébactéries consomment la MOD de FMM (Cottrell and Kirchman, 2000; Malmstrom et al., 2004; Elifantz et al., 2005; Alonso-Sáez and Gasol, 2007); Bactéroidetes a besoin d'un substrat abondant (Alonso-Sáez and Gasol, 2007) et est donc plus abondant lors des efflorescences et dans les zones de remontées (Riemann et al., 2000; Suzuki et al., 2001; Fuhrman and Hagström, 2008) et les Flavobacteriia, une classe de Bactéroidetes, préfèrent la MOD de GMM (Cottrell and Kirchman, 2000; Elifantz et al., 2005) et est souvent associé aux exopolymères transparents particulaires (Taylor et al., 2014). D'autres études ont toutefois rapporté des résultats différents concernant les $\gamma-$protéobactéries (Harvey et al., 2006; Alonso-Sáez et al., 2012).

Puisque les grands groupes de procaryotes ne consomment pas les mêmes types de molécule, la structure de leur communauté peut donc variée au courant de l'année (Nguyen et al., 2015) et même lors des efflorescences algales (Hagström et al., 2000; Arrieta and Herndl, 2002). Ces changements dans la composition de la communauté de procaryotes provient des changements dans le substrat disponible pour les procaryotes (Teeling et al., 2012; Guillemette et al., 2013). En effet, des études réalisées à l'aide d'expérience en culture discontinue ont montré que les différents groupes de phytoplancton ne relâchent pas les mêmes composés organiques (Romera-Castillo et al., 2011; Sarmento et al., 2013). Les résultats d'études comparatives menées dans des écosystèmes naturels (Judd et al., 2006; Niño-García et al., 2016) suggèrent eux aussi que la composition de la communauté procaryotique répond plus à la composition de la MOD qu'à la provenance de la communauté. Ainsi, les communautés de procaryotes peuvent varier à l'échelle régionale (Fig. 1.4) ainsi qu'à des échelles plus fines, comme lors d'une efflorescence algale (Teeling et al., 2012).

La composition de la communauté de procaryotes peut changer à l'échelle d'une efflorescence algale parce que les différents taxons peuvent employer deux stratégies différentes pour leur alimentation: généraliste ou spécialiste (Székely and Langenheder, 2014). Les taxons généralistes sont ceux qui peuvent proliférer dans une grande gamme d'environnement différent, par exemple à basse et haute température ou dans de grande variation de pH (Niño-García et al., 2016). Ces taxons représentent généralement une grande proportion de l'abondance de la communauté (Niño-García et al., 2016; Ruiz-González et al., 2019) et

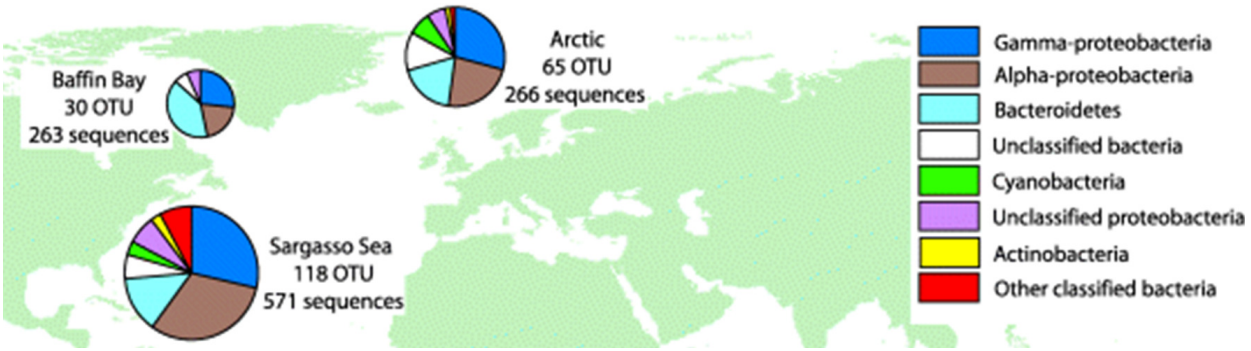


Fig. 1.4. Composition bactérienne basée sur le gène de l'ARN ribosomique 16S de régions adjacentes à la mer du Labrador. Les échantillons ont été récoltés à une profondeur de 5 mètres. Les $\gamma-$protéobactéries, $\alpha-$protéobactéries et Bactéroidétes représentent jusqu'à 80 % des bactéries séquencées. Simplifiée de Pommier et al. (2007)

une base taxonomique commune entre les différents écosystèmes. Par exemple, *Pelagibacter* se retrouve dans tous les océans, dans les gyres autant que les zones côtières et représente 25% de tous les planctons (Giovannoni, 2017). Les taxons spécialistes, quant à eux, vivent dans une gamme plus restreinte de condition environnementale et sont plus contraint dans l'espace (Niño-García et al., 2016).

Les spécialistes sont donc de bon candidats pour faire partie de la biosphère rare (Sogin et al., 2006), c'est-à-dire les procaryotes dont l'abondance représente moins de 0,1% de la communauté. Ces procaryotes rares sont un réservoir génétique pour la communauté (Lennon and Jones, 2011) : lorsque les conditions du milieu changent, les procaryotes abondants peuvent mourir et être remplacés par des procaryotes rares qui seraient mieux adaptés à ces nouvelles conditions. Les procaryotes rares ont aussi un rôle écologique démesuré par rapport à leur abondance (Jousset et al., 2017), par exemple dans la consommation d'hydrocarbure dans les sédiments (Dell'Anno et al., 2012) ou la réduction du souffre dans les tourbières (Pester et al., 2010). Cependant, le rôle de ces procaryotes rares dans les transformations de la MOD ainsi que dans la respiration de la communauté demeure inconnu.

1.4. Mer du Labrador

La mer du Labrador est un environnement dynamique unique caractérisé par l'importance de sa convection hivernale liant ses eaux profondes à l'atmosphère (Clarke and Coote, 1988; DeGrandpre et al., 2006; Lenton et al., 2008). La profondeur de mélange est généralement d'environ 1000 m (Lazier et al., 2002), mais a déjà atteint 2400 m en 1993 (Yashayaev et al., 2000). La convection varie en fonction du climat hivernal : la densité de

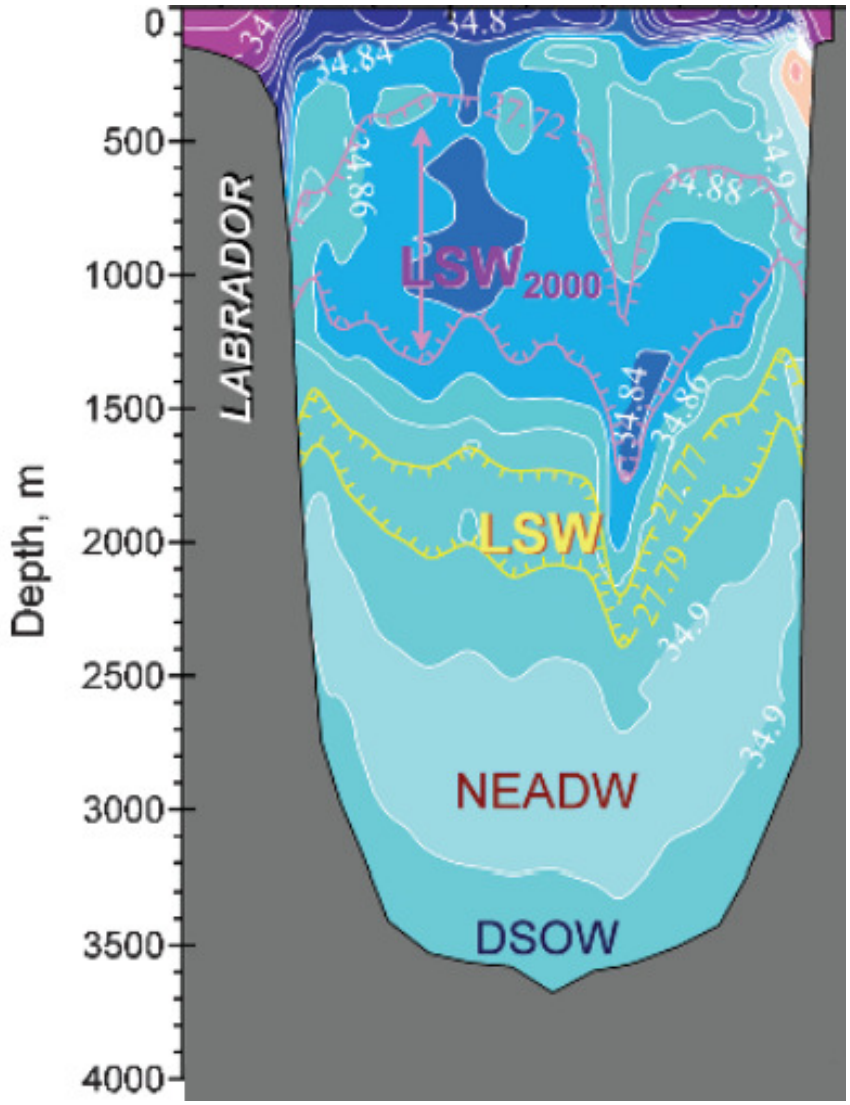


Fig. 1.5. Masses d'eau de la mer du Labrador. LSW2000: Labrador Sea Water à l'an 2000; LSW: Labrador Sea Water, profondeur historique; NEADW: North East Atlantic Deep Water; DSOW: Denmark Strait Overflow Water. Simplifiée de Yashayaev et al. (2008)

l'eau en surface s'accroît avec le transfert de chaleur vers l'atmosphère.

Malgré le brassage profond, la colonne d'eau est stratifiée. La plus grosse masse d'eau est la Labrador Sea Water (LSW) avec une profondeur allant jusqu'à 2400 m. La masse d'eau suivante North East Atlantic Deep Water (NEADW) qui se rend jusqu'à 3300 mètres et est caractérisée par sa forte salinité. La masse d'eau au fond du bassin, la Denmark Strait Overflow Water (DSOW) est caractérisée par sa densité (Fig. 1.5) (Lazier et al., 2002; Yashayaev et al., 2008). Le chenal au fond du bassin central mesure environ 70 km de diamètre et 70 m de profondeur et constitue une autre masse d'eau. Durant l'été, les 200 premiers mètres sont thermiquement stratifiés.

L'augmentation globale de la température affectera la stratification de la mer du Labrador de deux façons : en réchauffant les eaux en surface et en augmentant l'apport

en eau douce provenant de la fonte des glaciers. Selon la théorie métabolique de Brown et collaborateurs (2004), les taux métaboliques des communautés procaryotiques (RP et PPH) devraient augmenter de concert avec la température de l'eau. L'apport en eau douce riche en nutriments provenant principalement de l'Arctique et du Groenland pourrait également modifier les taux métaboliques, mais aussi favoriser différents phyla de procaryotes. Une caractérisation adéquate des interactions entre ces taux et les communautés hétérotrophes est essentielle pour comprendre comment ils évolueront avec le climat, et quelles seront leurs répercussions sur celui-ci.

En plus de sa stratification verticale, la mer du Labrador est composée de trois masses d'eau. La première est située près de la côte du Labrador (LS), la seconde est le bassin central (CB) et la dernière se situe près de la côte du Groenland (GS). Dans les 100 premiers mètres, tous les bassins sont limités en N, en différentes proportions. En effet, les valeurs de P* (éq. 0.1), la variation de la quantité de phosphore par rapport à l'azote en comparaison au ratio Redfield, sont respectivement de 0,33, 0,13 et 0,18 μM, indiquant une limitation en N. Les ratios POC : PON de 9,21, 7,63 et 8,42 mol C mol^{-1} N^{-1}, respectivement, indiquent également cette limitation. L'abondance bactérienne (AB) varie entre les bassins, 5,5 $\pm$ 0,9; 10,2 $\pm$ 1,3 et 6,0 $\pm$ 1,5 x 10^5 cellules ml^{-1}, respectivement, et répond négativement à la limitation en N. Seul le LSS n'est pas limité en SiO_2 pour les besoins des diatomées (éq. 0.2).

$$P* = P - N/16 \qquad \text{(eq. 1.1)}$$

$$SI* = Si - N \qquad \text{(eq. 1.2)}$$

Les communautés bactériennes ont très peu été étudiées dans la mer du Labrador. Les effets des variations environnementales et spatiales sur les bactéries, les archées et les virus ont été étudié dans trois mers, dont celle du Labrador (Winter et al., 2013). Toutefois, la structure de la communauté reste indéterminée, mais elle est connue dans les environnements voisins (Fig. 1.4)(Pommier et al., 2007). L'eau du nord de la mer du Labrador provient de l'Arctique et devrait donc avoir des communautés semblables. Ces données ne relatent que la diversité bactérienne et n'incluent pas les archées qui peuvent représenter une proportion importante de la biomasse, spécialement en profondeur (Kirchman et al., 2007). Nous évalurons donc la composition de la communauté de procaryotes dans la mer du Labrador afin de mieux comprendre comment elle façonne la composition de la MOD.

La mer du Labrador est un environnement propice pour réaliser cette étude. En effet, les multiples masses d'eau qui la compose proviennent d'environnements dont les conditions abiotiques et biotiques diffèrent considérablement. L'hétérogénéité spatiale de la mer du Labrador produit donc une vaste gamme de conditions propices à différentes communautés phytoplanctoniques et procaryotiques. À leur tour, ces communautés n'ont pas nécessairement le même métabolisme, ce qui peut fortement influencer la composition de la MOD.

L'objectif de cette thèse est de mieux comprendre les processus qui contrôlent la biodisponibilité de la matière organique et comment elle influence les procaryotes dans une zone clé de l'océan – la mer du Labrador. Pour ce faire, nous avons tout d'abord déterminer la quantité de MODL et MODSL tout au long du continuum aquatique en menant une méta-analyse. Ceci nous à aider à mieux comprendre la biodisponibilité de la MOD dans le mer du Labrador en temps d'efflorescence algale. Nous avons par la suite regardé comment la qualité la MOD influence la structure de la communauté, les processus métaboliques et l'abondance des procaryotes dans les eaux en surface de la mer du Labrador. Finalement, nous avons simulé la convection hivernale pour déterminer quel serait le destin de cette MOD une fois entraînée dans les zones profondes de l'océan, et quel est le rôle des procaryotes rares dans les transformations de cette MOD. Nous avons ainsi un portrait global du cycle du C dans la mer du Labrador : sa production pendant les efflorescences, son influence sur les communautés procaryotiques et sa séquestration en profondeur après la convection hivernale.

1.5. Objectifs spécifiques

1.5.1. Chapitre 2 : Estimer la quantité de COD biodisponible à travers le continuum aquatique

Pour mon deuxième chapitre de thèse, nous avons évalué la proportion de COD labile et semi-labile à travers le continuum aquatique, des lacs jusqu'à la haute mer. Pour ce faire, nous avons recensé la littérature scientifique sur les expériences en culture discontinue (batch culture experiment) qui monitoraient la dégradation du COD autant dans les milieux d'eaux douces (milieux humides, rivières et lacs) que dans les écosystèmes marins (lagunes, estuaires, mer intérieure, milieu côté et haute mer). L'objectif de ce chapitre était de déterminer comment ces différents réservoirs de carbone, qui soutiennent les procaryotes, changent le long du continuum aquatique. Nos résultats montrent que la proportion de matière labile est similaire dans tous les écosystèmes aquatiques à l'exception des périodes d'efflorescence et dans les zones de remontées océaniques. Par contre, la proportion de carbone semi-labile est fortement reliée aux apports terrigènes.

1.5.2. Chapitre 3 : Évaluation des interactions entre la matière organique dissoute, les communautés de procaryotes et leur métabolisme

Pour mon troisième chapitre de thèse, l'objectif principal était de mettre en relation les variables environnementales (COD, MODF, AA, chlorophylle *a*) avec la composition de la communauté (16S, marqueur taxonomique universel de l'ARN ribosomique pour les bactéries et les archées), sa structure (abondance et distribution spatiale) ainsi que son métabolisme (production et respiration) afin de mieux comprendre comment la qualité de la matière organique influençait les communautés de procaryotes. Pour ce faire, nous avons utilisé les données récoltées lors de mes trois missions océanographiques dans la mer du Labrador à bord du Hudson (Fig. 1.6) réalisées conjointement avec les chercheurs de l'Institut Océanographique de Bedford (IOB), un centre de recherche de Pêches et Océans Canada. Nos résultats corroborent les résultats d'études précédentes par rapport à l'abondance et le métabolisme des procaryotes, et nous avons mis de l'avant la grande influence de la distribution spatiale de leur abondance quant aux préférences alimentaires des procaryotes. Nous avons également développé un cadre conceptuel afin de mieux comprendre et étudier les liens existant entre la biogéochimie, l'écologie microbienne et les fonctions écosystémiques, ce qui est un défi depuis des dizaines d'années.

1.5.3. Chapitre 4 : Évaluer la capacité des communautés de procaryotes des zones épi-, méso- et bathypélagiques à produire du carbone réfractaire.

Pour mon quatrième chapitre, l'objectif principal était de déterminer si la PMC était aussi efficace entre les différentes profondeurs de l'océan. Nous avons donc élaboré une expérience en culture discontinue pour simuler la convection hivernale de la mer du Labrador. Nous avons utilisé de la matière organique de surface à laquelle nous avons inoculé une communauté une communauté provenant de l'épipélagique, du mésopélagique ou du bathypélagique. Nous avons montré que les communautés des eaux profondes étaient plus efficaces pour produire du COD réfractaire. Nous avons également montré que les acteurs principaux de cette réfractorisation de la MOD sont les procaryotes rares, et qu'une importante succession est nécessaire puisque la qualité de la MOD ne cesse de diminuer au cours de l'expérience. Finalement, nous avons émis l'hypothèse que la forte pression de la zone bathypélagique permet à certaines molécules de s'agglomérer, créant ainsi un autre processus de séquestration du carbone en eaux profondes.

Fig. 1.6. Le navire de la garde côtière canadienne Hudson (à droite) accosté à un des quais de l'Institut Océanographique de Bedford, Darthmouth

1.6. Cadre général de l'étude

Ma thèse doctorale s'insère dans le projet pan-Canadien, Ventilation, Interactions and Transports Across the Labrador Sea (VITALS), une collaboration d'une dizaine d'Universités partout au pays ainsi que de Pêches et Océans Canada et en particulier des chercheurs de l'IOB. Les objectifs de VITALS étaient de mieux comprendre les échanges de CO_2 et d'O_2 entre l'atmosphère et les eaux profondes de la mer du Labrador.

Le projet comportait plusieurs thèmes différents, dont les principaux portaient sur la physique, la chimie et la modélisation de ces échanges gazeux. Mon projet faisait partie de l'équipe biologie, et nous nous sommes arrimés du mieux possible à ce grand thème, en portant notre attention sur la MOD et le rôle des microorganismes, ces acteurs clés dans le cycle du carbone. Mon quatrième chapitre de thèse s'arrime bien avec les objectifs généraux de VITALS sur le rôle de la mer du Labrador dans la séquestration du C à long terme. En effet, en évaluant l'efficacité de la PMC dans la mer du Labrador, nous avons montré que les communautés de procaryotes bathypélagiques produisaient de la MODR en plus grande quantité que les autres communautés. Ce faisant, la convection hivernale de la mer du Labrador est non seulement un vecteur important pour enfouir du CO_2 dans les profondeurs de l'océan, mais également un endroit clé pour la PMC.

Premier article.

Contrasting patterns of labile and semi-labile dissolved organic carbon from continental waters to the open ocean

par

Richard LaBrie[1], Jean-François Lapierre[1] et Roxane Maranger[1]

([1]) Département des sciences biologiques et Groupe de recherche interuniversitaire en limnologie et environnement aquatique (GRIL), Université de Montréal, Pavillon Marie-Victorin C. P. 6128, succ. Centre-ville, Montréal, QC, Canada, H3C 3J7

Cet article est accepté pour publication dans Journal of Geophysical Research: Biogeosciences.

Contributions des auteurs

RL a compilé et analysé les données, écrit et édité le manuscrit, JFL a fourni des données, RM a élaboré l'étude et édité le manuscrit, tous ont révisé et accepté le manuscrit

Résumé. Les procaryotes marins et dulcicoles se nourrissent principalement de carbone organique dissous labile ($BDOC_L$), tandis que le DOC semi-labile ($BDOC_{SL}$) sert probablement de réserve d'énergie. Ces fractions sont opérationnellement définies ici comme étant le DOC consommé en un mois et d'un mois à un an et demi, respectivement. La matière organique de ces différents réservoirs provient de diverses sources autochtones et allochtones, mais leur proportion respective demeure inconnue dans les écosystèmes aquatiques. Afin de combler cette lacune, nous avons compilé des données tirées de la littérature scientifique des 20 dernières années qui comprenaient 655 expériences de biodégradation du DOC en culture discontinue dans huit types d'écosystèmes aquatiques. Nous montrons que la proportion de $BDOC_L$ dans tous les écosystèmes aquatiques était étonnamment constante (6,1 %) malgré une variation de deux ordres de grandeur dans les concentrations initiales de DOC, suggérant un équilibre entre la production et la consommation de DOC. Une proportion plus élevée de $BDOC_L$, 16,3 % en moyenne, a été observée dans les écosystèmes où la productivité était élevée. Quant au $BDOC_{SL}$, il diminue progressivement de 16,0 % dans les lacs, à 7,2 % dans les estuaires, et est indétectable en haute mer, ce qui suggère que la connectivité terrestre régule la proportion de $BDOC_{SL}$ à travers le continuum aquatique. Nos résultats confirment que la production primaire récente répond aux besoins à court terme en DOC des procaryotes, avec une dépendance croissante au $BDOC_{SL}$ à mesure que les écosystèmes s'approchent de l'interface terre-eau. Les expériences en culture discontinue que nous avons compilées montrent que le $BDOC_{SL}$ est métabolisable dans les environnements dulcicoles et côtiers, mais pas en haute mer. Nous estimons que le $BDOC_{SL}$ peut soutenir 62 % de la biomasse totale des procaryotes dans les lacs et les milieux côtiers, et représente 16,7 % de la biomasse des procaryotes à travers les biomes aquatiques.
Mots clés : Carbone organique dissous, Continuum aquatique, Connectivité terrestre

ABSTRACT. Marine and freshwater prokaryotes feed primarily on bioavailable labile dissolved organic carbon ($BDOC_L$), as well as the bioavailable fraction of the semi-labile DOC ($BDOC_{SL}$) pool. These fractions are operationally defined here as the DOC consumed within a month and greater than a month to a year and a half, respectively. Organic matter from these different pools comes from various autochthonous and allochthonous sources, but their relative bioavailability is unknown across aquatic ecosystems. To fill this gap, we compiled literature information that included 655 batch culture DOC biodegradation experiments across eight aquatic ecosystem types over the past 20 years. We show that the proportion of $BDOC_L$ across all aquatic ecosystems was surprisingly consistent (6.1%) despite a two orders of magnitude variation in initial DOC concentrations, suggesting an overall tight balance between carbon supply and consumption. A higher proportion of $BDOC_L$, 16.3% on average, was observed in high productivity ecosystems. $BDOC_{SL}$, on the other hand, gradually decreased from 16.0% in lakes to 7.2% in estuaries to undetectable in the open ocean, suggesting that terrestrial connectivity regulates $BDOC_{SL}$ across the continuum. Our results support that recent primary production fuels short-term prokaryotic DOC needs with an increasing reliance on the abundant $BDOC_{SL}$ pool as ecosystems approach the land–water interface. Batch culture experiments show that $BDOC_{SL}$ is metabolizable in freshwater and coastal environments, but not in the open ocean. We estimate that $BDOC_{SL}$ can sustain 62% of total prokaryotic biomass in inland waters and coasts, and an estimated total of 16.7% across aquatic biomes.

PLAIN LANGUAGE SUMMARY. Bacteria are the most abundant organisms in lakes, coasts, and oceans outweighing all the whales living in the ocean! But what do they consume? Bacteria eat organic carbon dissolved in water, but not all carbon compounds are equally easy to eat. Our aim was to understand the amount of carbon bacteria eat, and how well different organic carbon sources support bacteria across lakes, coasts, and oceans. We found that the relative amount of readily available carbon to support bacteria is the same no matter what aquatic ecosystems they live in. It is also less than what was previously thought. Second, the more an aquatic ecosystem is connected to land, the more carbon was available since some of it comes from soils, but it takes over a month for it to be consumed. Therefore, the more connected to land the aquatic ecosystem is, like a lake, the more the bacteria can rely on that additional terrestrial source of food. Surface bacteria of the open ocean appear to rely solely on readily available, locally produced organic matter (carbon), whereas bacteria from lakes and coasts have access to both readily available and partially decomposed organic matter from local production and terrestrial resources.
Keywords: Dissolved organic carbon, Water continuum, Terrestrial connectivity

1. Introduction

Heterotrophic prokaryotes incorporate large amounts of dissolved organic carbon (DOC) into their biomass that gets assimilated into higher trophic levels through the microbial loop (Azam et al., 1983; Pomeroy, 1974). This represents an essential component of energy transfer across all aquatic ecosystems, from inland freshwaters (del Giorgio and Cole, 1998) to oceanic gyres (del Giorgio and Duarte, 2002). Although the carbon conversion

efficiency of prokaryotes is often used to assess their role in this energy transfer (del Giorgio et al., 2011), another more direct way is to perform batch culture experiments where DOC consumption is monitored through time and substrate availability is considered a relative proportion of the whole (Servais et al., 1987). Indeed, quantifying how much of this bulk DOC is bioavailable to prokaryotes and how this varies across the aquatic continuum is of fundamental importance to characterize the energetic capacity of different aquatic ecosystems.

In the oceans, DOC is operationally defined as five different reactivity classes (Hansell, 2013). In order of decreasing reactivity, labile DOC (LDOC) represents the rapid turnover of surface DOC from a few days to a few weeks whereas semi-labile DOC (SLDOC) and semi-refractory (SRDOC) represent the differential DOC concentrations between the surface and the seasonal or permanent pycnoclines, respectively. Refractory DOC (RDOC) is the largest oceanic DOC pool that resists biodegradation for thousands of years but is nevertheless partially consumed within deep oceanic circulation timeframe whereas ultra-refractory DOC is essentially inert on circulation timeframe. Since these definitions are based on extended water residence times only applicable to the open ocean, the use of such a classification scheme is limited in freshwaters. DOC reactivity in freshwaters is generally based on the quantity of DOC consumed during batch culture experiments where bioavailable DOC (BDOC, or synonyms) is what is consumed, and recalcitrant DOC, is the fraction that remains e.g. (Lapierre et al., 2013; Stets et al., 2010; Obernosterer and Benner, 2004; Koehler et al., 2012). However, incubations are of variable time-frames (e.g. 14 to 1351 days) which makes these definitions rather arbitrary and study-specific. In terms of exploring different classes in freshwaters, one study suggested that the BDOC pool included a short-term labile pool (consumed within 2 days) and a long-term labile pool (comsummed within 28 days) (Guillemette and del Giorgio, 2011).

In the ocean as in freshwaters, the LDOC pool includes more rapidly assimilated amino acids and polysaccharides (Amon et al., 2001; Tranvik and Jorgensen, 1995), consumed within hours to a few days, as well as protein-like compounds that may take up to a month to be metabolized 12. The SLDOC pool, albeit ill-defined, is the carbon consumed over several weeks to within a year and a half that could be considered backup energy, i.e. a source of energy available to prokaryotes once LDOC is exhausted and no longer supplied to the ecosystem. In the ocean, distinctive carbohydrate compounds appear to be major constituents of the SLDOC pool (Aluwihare et al., 1997; Panagiotopoulos et al., 2007). In freshwaters, SLDOC is most often considered to be composed of large biopolymers and lignin degradation products of terrestrial origin (McKnight et al., 2001; Lehmann and Kleber, 2015), but can also be produced locally (Evans et al., 2017). Although SLDOC composition

differs between freshwaters and marine systems, it should be consumed within a similar time span. Therefore, in order to compare degradation dynamics across the aquatic continuum, we propose a hybrid nomenclature which includes $BDOC_L$, the fraction that is rapidly consumed in batch culture experiment, $BDOC_{SL}$, the fraction that requires longer incubation times, and RDOC, the fraction that persist at the end of the incubation. RDOC is defined here as what persists after a year and a half (or much longer) and is considered stable, i.e. unavailable to prokaryotes. Taken together, $BDOC_L$ and $BDOC_{SL}$ represents the total bioavailable pool (BDOC = $BDOC_L$ + $BDOC_{SL}$, Fig. 2.1). However, how these relative fractions change across the aquatic continuum is poorly understood and rarely compared.

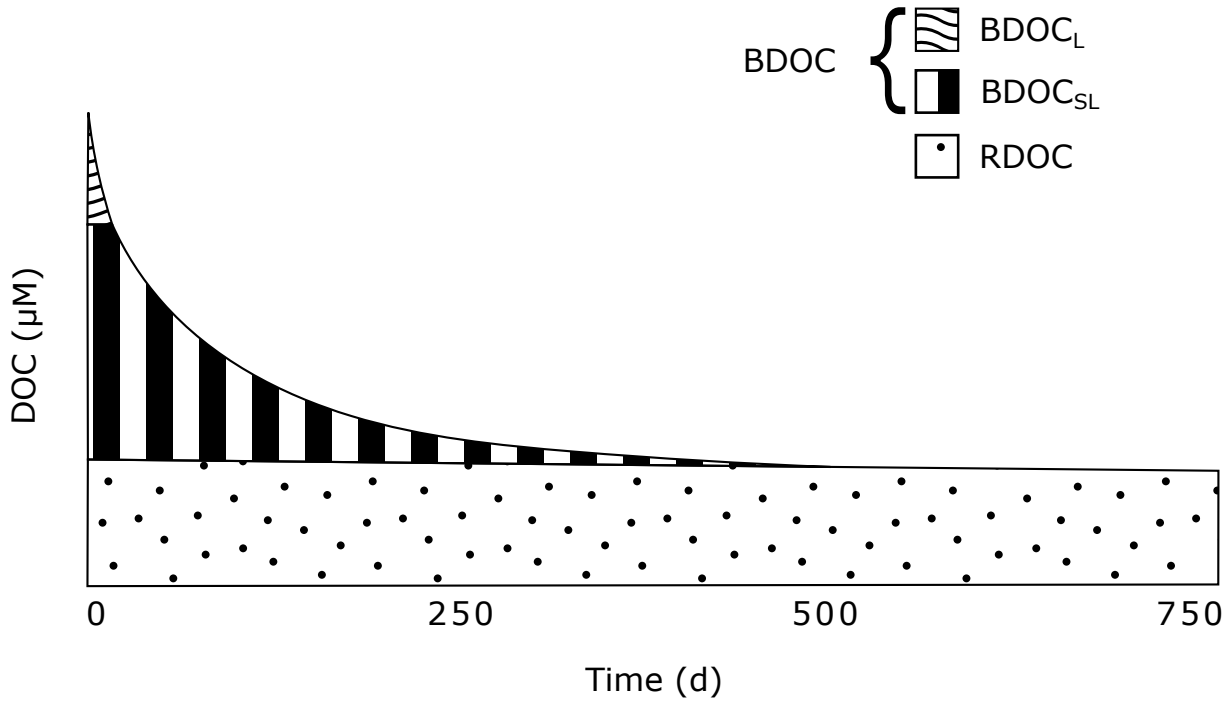


Fig. 2.1. Theoretical degradation of different DOC pools during a batch culture experiment over time. The bulk DOC is divided into three reactivity pools, rapidly degraded labile DOC (waves), semi-labile DOC (bars) used primarily as backup energy once the labile pool is consumed and refractory DOC which remains stable over long time periods (dots).

One way to look at the relative bioavailability of DOC across ecosystems is to look at bulk degradation dynamics over time among sites using batch cultures. Batch culture experiments consist of monitoring DOC concentrations over time in an isolated volume of water under controlled conditions, usually at near in situ temperature in the dark. These experiments enable us to quantify the bulk amount of $BDOC_L$ and $BDOC_{SL}$ and model

a decay curve if incubations are of sufficient length. This incubation approach of course has limits since there is no internal production via photosynthesis or external supply from adjacent environments, but nevertheless provides a snap-shot of how much bioavailable DOC is found in the ambient pool. The first study to look at DOC degradation across ecosystems focused primarily on productive environments, and essentially compared lakes versus coasts over relatively short incubation times of less than two weeks (Søndergaard and Middelboe, 1995). They found that the amount of $BDOC_L$ available to prokaryotes was high, and surprisingly similar between lakes and coasts, representing 19% of bulk DOC. A second study compared more ecosystem types, but incubation times remained short and consumption rates were temperature adjusted (del Giorgio and Davis, 2003). Since then, technical advances in measuring DOC have enabled the accurate detection of very small scale changes in DOC to assess consumption in the ultra-oligotrophic ocean (Carlson et al., 1999; Sharp, 1997), thus expanding our understanding of $BDOC_L$ dynamics in a broader range of aquatic environments. Furthermore, there has been an increasing interest in the relative role of $BDOC_{SL}$ as backup energy to prokaryotes in the ocean [Carlson et al. 2004], and in lakes (Koehler et al., 2012; Vähätalo et al., 2010), but how the relative amount of $BDOC_{SL}$ changes across ecosystem types remains unknown.

Therefore, since there has been a large number of batch culture experiments carried out across a number of different aquatic ecosystem types and over longer incubation times of more than several months (Koehler et al., 2012; Carlson et al., 1999; Farjalla et al., 2002), the goal of this study was to synthesize the available information on batch culture experiments to identify the relative amount of $BDOC_L$ and $BDOC_{SL}$ across the aquatic continuum. In particular, we aimed to quantify the relative amount and variability of the labile and semi-labile DOC pools across aquatic environments. This allowed us to better understand the potential gradients of $BDOC_L$ and $BDOC_{SL}$ that sustain energy transfer to prokaryotes from freshwaters to the open ocean. Finally, we provide a first order estimate of how much prokaryotic biomass could be supported by both $BDOC_L$ and $BDOC_{SL}$ standing stocks across biomes.

2. Materials and Methods

2.1. Data collection

A Web of Knowledge search was conducted in 2016 using multiple keywords, divided in three broad categories: 1) ecosystem type which included freshwater, lake, marine, coastal, and ocean, 2) substrate which included organic carbon, organic matter, DOC, and DOM, and 3) experiment which included batch culture, experiment, incubation, and regrowth.

Each search was conducted using one keyword per category until all combinations were tested. For papers that synthesized relevant information (Catalan et al., 2016; Lønborg and Álvarez-Salgado, 2012), we consulted the reference list and included those that were not found using the above combinations of keywords.

Of the 64 studies we identified in our initial search, 17 were not suitable because of limited access to relevant data, methodological constraints, or design differences that would limit comparability. Thus, in order to minimize bias, we only considered unamended natural DOC batch culture experiments in this study. Studies were excluded if samples were collected near sites with obvious anthropogenic influence (i.e. sites located near untreated or partially treated sewage), or were amended either via nutrient addition, model DOC compounds (e.g. glucose) or extracts (e.g. leaves or phytoplankton). This minimized the bias of nutrient amendments which augment the apparent bioavailability of phytoplankton produced polysaccharides (Myklestad, 1995). Any experiments performed using continuous cultures (e.g. chemostats), or monitored as changes in oxygen concentrations rather than DOC were also not retained. We also removed all non-HTCO (high-temperature catalytic oxidation) DOC measurements from marine sites since these are known to provide tenuous results (Sharp, 1997). No corrections for temperature were made to remain as close to natural conditions as possible. Incubations were largely carried out at near in situ temperatures where original microbial communities were used to follow degradation patterns. Overall, 47 studies published between 1995 and 2016 were retained, with a total of 653 batch culture experiments divided almost equally between freshwater and oceanic environments (Annexe 1, Table S2.1).

The following information was collected from each study: geographic coordinates of sites (from the reference or google maps), ecosystem type (as reported in the reference or via visual identification on maps), experimental details (temperature, volume of medium, inoculum and filter size when applicable) and incubation time. Since the DOC sampling time across studies was highly fragmented and in order to assemble the database, we chose a threshold of 9 days for $BDOC_L$ as it respects the time span suggested in Hansell (2013). However there is no formal consensus in the literature on what that cut-off may actually be. DOC concentrations were noted at the beginning (DOCini), at 9 days or less (DOC$\leq$9d), and at the end of the experiments (DOCend) which ranged from 10 days to around 1.5 years. Marine environments included five different ecosystem types: lagoons, inland seas, estuaries, coasts, and the open ocean. Information was available for both $BDOC_L$ and BDOC in all of these ecosystems. Freshwaters included three ecosystem types for $BDOC_L$: wetlands, rivers, and lakes, but BDOC was only available for lakes. Some studies reported that their sites were sampled in situations with unusually high productivity either in upwelling zones or under bloom conditions. We classified these experiments in a separate high productivity

or bloom condition category in order to explore whether unusually productive conditions may accumulate specific pools of DOC compared to other ecosystems where no obvious signs of this potential additional DOC production was reported. Most of our ecosystems were found in that latter category, and considered to be in steady state; cross ecosystem comparisons were focused primarily on those in steady state. Furthermore, we grouped different ecosystem types based on their "connectivity" with the terrestrial landscape for cross-system comparisons. While no formal measure or guideline exists to precisely quantify this connectivity, it is generally accepted that it decreases from wetlands, rivers, lakes for freshwaters, and from lagoons, inland seas, estuaries, coastal ecosystems to the open ocean using salinity as a general guideline. This typically represents a decreasing gradient of the relative importance of the land-water interface compared to the overall area of the aquatic ecosystem. Data were extracted from texts, tables and figures using WebPlotDigitizer3.8 desktop version.

2.2. Data location

In order to provide a better understanding of the spatial distribution of where most batch culture experiments were performed, site locations are presented on a world map (Fig. S2.1). Sampling was strongly biased towards the Northern hemisphere, with only a small number of studies carried out in the South (13 incubations in 4 different studies). However, most climate regions are covered in both marine and freshwaters (tropical, temperate and cold) (Walterscheid, 2011). Marine sites are mostly spread throughout the United States of America, Europe, and a few in eastern Asia while freshwaters are almost exclusively (approximately 90%) sampled in the boreal regions of Sweden and Quebec, Canada.

2.3. Data analysis

Once the database was assembled, $BDOC_L$ was estimated as DOCini - $DOC_{\leq 31d}$ (number of days for short-term DOC loss determined empirically post-hoc, see results), and BDOC as DOCini - DOCend only when incubations were long enough to include a $BDOC_{SL}$ fraction, where incubation times were >31 days. It has been suggested that there could be two phases of $BDOC_L$ to consider, one rapidly consumed within days and then another component of the $BDOC_L$ that takes a few weeks (Guillemette and del Giorgio, 2011). The structure of our dataset, which included incubations performed from a few days to over a year, allowed us to explore the potential length of incubation required to fully consume the $BDOC_L$ pool. We did so by plotting the %BDOC over time across incubations in both lakes and marine ecosystems and fit a linear vs piece-wise regression. A better fit using the piece-wise would indicate a shift in BDOC consumption rates at a given time, and this time would likely represent the time it takes for a prokaryotic community to deplete the immediately

available DOC (i.e. $BDOC_L$) and to shift to a pool with a longer renewal time (i.e. $BDOC_{SL}$).

We then explored cross-ecosystem patterns in DOC lability by calculating changes in DOC concentrations in relation to initial DOC concentrations (%$BDOC_L$ and %BDOC) for each individual experiment. Differences among ecosystem types were determined using an ANOVA and a post-hoc Tukey test with a Holm correction (Legendre and Legendre, 2012). The BDOC pool was used to derive the average $BDOC_{SL}$ pool for each ecosystem type since the literature on batch culture monitoring DOC is highly fragmented. The average $BDOC_{SL}$ was thus calculated by subtracting the $BDOC_L$ pool from the BDOC pool for each ecosystem type.

To test how consistently DOC was consumed within an ecosystem type and compare this consumption across ecosystems, we plotted %DOC remaining over time for all incubations in a single analysis and modeled the relationships with a multi-G model (Guillemette and del Giorgio, 2011; Jørgensen, 1978) using a non-linear least square regression with a Levenberg-Marquardt optimisation routine (Elzhov et al., 2016). This was done for lake and coastal ecosystems; other ecosystem types did not have sufficient data available for enough time points to fit a multi-G model. In order to represent all studies on a similar scale regardless of their initial DOC concentrations, we used %DOC remaining instead of the bulk change in DOC concentrations. To avoid pseudo-replication, we used the ecosystem's average %DOC remaining prior to 30 days since $BDOC_L$ is included in BDOC. The multi-G model is defined using the following equation:

$$DOC = BDOC * e^{-kt} + RDOC \qquad \text{(eq. 2.1)}$$

where BDOC is the metabolizable pool of DOC, k is the associated degradation constant, t is time, and RDOC is the stable carbon pool. The optimization routine iteratively fits a curve to these points by changing all parameters at once and the best model was chosen based on the lowest residuals of the sum-of-squares.

In order to put into perspective the proportion of $BDOC_L$ and $BDOC_{SL}$, we calculated the standing stock of $BDOC_L$ and $BDOC_{SL}$ per ecosystem type based on their average proportions. To do this, we first extrapolated the total volumetric DOC for the surface open ocean (top 100 m), surface coastal margins and large lakes at 30 m depth (de Boyer Montégut et al., 2004), and small lakes (Cael et al., 2017) worldwide (Table S2.1). We then multiplied these values with our proportional estimates for $BDOC_L$ and $BDOC_{SL}$ and reported average DOC concentrations of 63 μM for the open ocean (Aristegui et al., 2002), 126 μM for coasts (Barrón and Duarte, 2015), 148 μM for large lakes (Biddanda and Cotner, 2002; Bocaniov et al., 2013; Ramlal et al., 2003; Sobek et al., 2007; Verburg, 2007;

Yoshioka et al., 2002) and 631 μM for small lakes (Sobek et al., 2007). We then converted these DOC pools into potential prokaryotic biomass, assuming that standing stocks of labile and semi-labile DOC enter the food web using currently accepted prokaryotic growth efficiencies Table S2.2 (del Giorgio and Cole, 1998; Smith and Prairie, 2004; López-Urrutia and Morán, 2007). All statistics were computed with R version 3.4.1 using RStudio version 1.0.143 (R Core Team, 2017). The list of references used, all data, scripts, and associated details are available at http://www.github.com/laboMaranger/DOC-meta-analysis.

3. Results

3.1. Empirical determination of $BDOC_L$ and $BDOC_{SL}$ consumption over time

The average proportion of labile DOC (%$BDOC_L$), defined as the relative amount consumed in $\leq$9 days, corresponded to 5.3% $\pm$ 0.5% of the total DOC across all our studies. The average relative amount consumed was not statistically different among ecosystems (ANOVA, $F_{5,74} = 2.70$, $p = 0.37$, not shown) albeit ranging from 2.9% to 11.2%. We explored if this pre-determined threshold of $\leq$9 days was supported by the data by conducting a piecewise regression and comparing it to a linear least-square regression both in marine and freshwaters (Fig. 2.2a and b, Fig. S2.2). We found that the piecewise models provided a better fit (ΔAIC (Akaike information criterion) values of 3.1 and 13.2 for marine and freshwaters, respectively) and shows a flat line prior to 39 $\pm$ 11 days for marine ecosystems ($p = 0.34$) and 28 $\pm$ 11 days for lakes ($p = 0.89$), suggesting that it took about one month before communities relied primarily on $BDOC_{SL}$ as an energy source. Bayesian information criterion results (not shown) agreed with these results. As both thresholds were surprisingly close, we chose a cut-off of 1 month (31 days) for both biomes to distinguish $BDOC_L$ estimations from BDOC in our ensuing analysis. Overall the average %DOC consumed before 31 days was 6.1% $\pm$ 0.3%, and was not significantly different than the %DOC consumed before 9 days (Δ0.8% t-test, $p = 0.21$). This finding challenged our initial, pre-supposed $BDOC_L$ cut-off of 9 days, but we opted for 31 days since it was empirically determined and consistent with the literature (Guillemette and del Giorgio, 2011). Therefore, for subsequent analyses we consider $BDOC_L$ as the amount of DOC that was consumed within the first 31 days of incubation, and BDOC as the total amount consumed beyond 31 days of incubation.

3.2. Cross-ecosystem patterns in DOC lability

We compared the %$BDOC_L$ and %BDOC across 9 and 7 different ecosystem types, respectively, including unusually high productivity ecosystems (Figs 3a and b). When

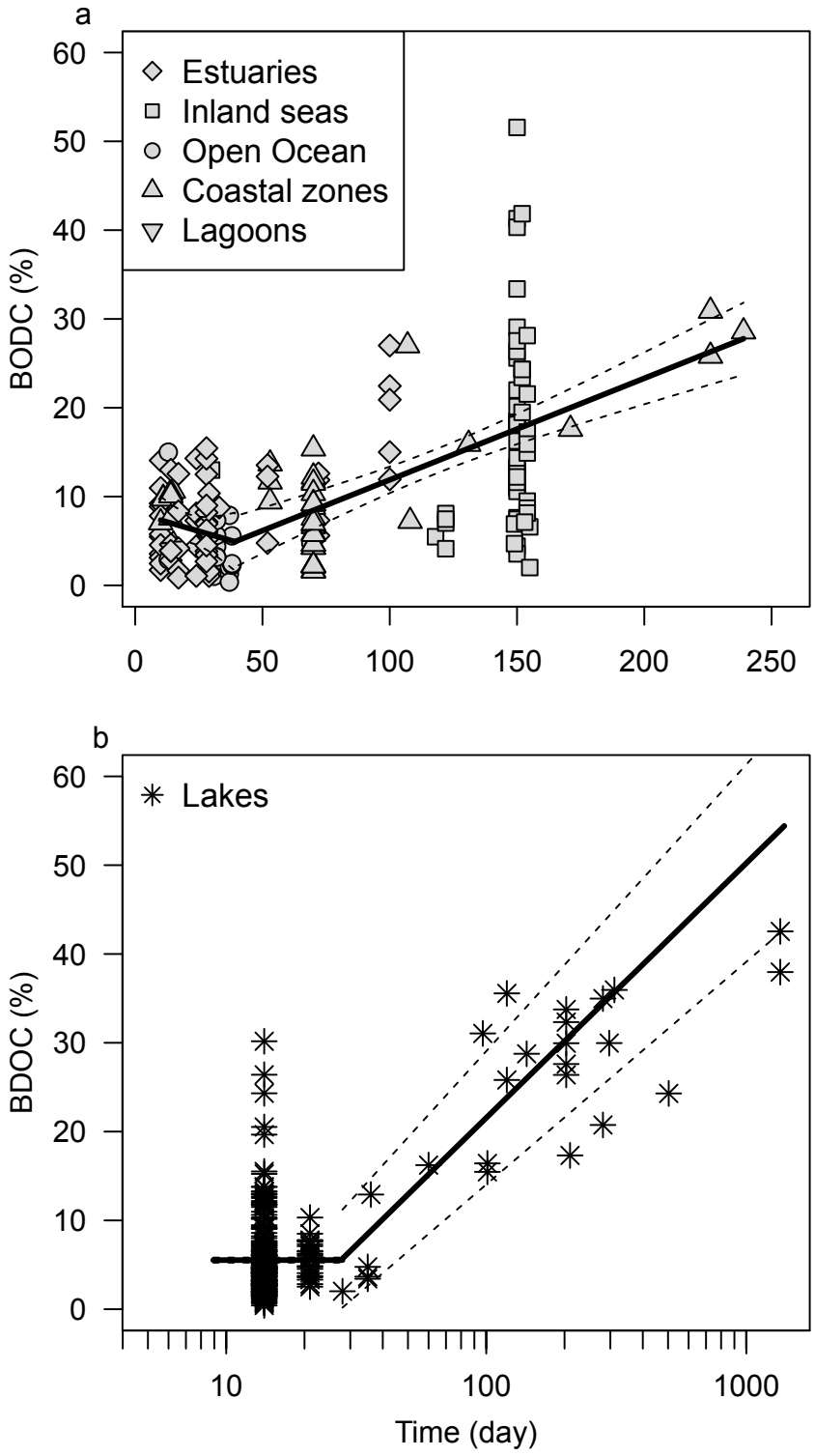


Fig. 2.2. Piecewise regressions of the proportion of bioavailable DOC (%BDOC) versus incubation time (days) for a) marine and b) freshwater ecosystems. The breakpoint in the relationship is 38 days for marine and 28 days freshwater. The difference between the AIC of the linear versus the piecewise regression was 3.1 and 13.2 in marine and freshwaters, respectively. The flat portion's standard error in panel b is within the bold line. The x axis is on a log scale for panel b.

highly productive ecosystems were excluded, the only significant but small difference observed in %BDOC$_L$ was between wetlands and lakes (Δ4.32%, ANOVA, $F_{7,472} = 4.5$, $p < 0.05$); the average proportion observed among all other ecosystems ranged from 4.0% to 6.7% and was not significantly different despite a near 90-fold range in initial DOC

concentration. However, a significantly higher proportion of $BDOC_L$ was observed in high productivity ecosystems with an average of 16.3% ± 1.8% (ANOVA, $F_{8,499} = 14.1$, $p < 0.05$, Fig. 2.3a). In contrast, there was a clear decrease in %BDOC along a gradient of decreasing terrestrial connectivity (ANOVA, $F_{5,141} = 9.9$, $p < 0.05$, Fig. 2.3b). Lakes and lagoons had the highest %BDOC whereas at the other end of this continuum in the open ocean, there was no remarkable difference between $\%BDOC_L$ and %BDOC. Again, %BDOC was higher in ecosystems under bloom conditions compared to all other environments. Ecosystem-specific $\%BDOC_{SL}$ was parsed out by subtracting the average $\%BDOC_L$ from the average %BDOC. This resulted in a conservative estimate of the $BDOC_{SL}$ pool of 17.3% for lakes, 13.7% in lagoons, 10.1% in inland seas, 7.2% for estuaries, 5.6% in coasts, and undetectable in the open ocean (Fig. 2.3c). The proportion of $BDOC_{SL}$ was 10.2% in high productivity ecosystems, lower than the $\%BDOC_L$, again suggesting their differential behavior as compared to steady state environments.

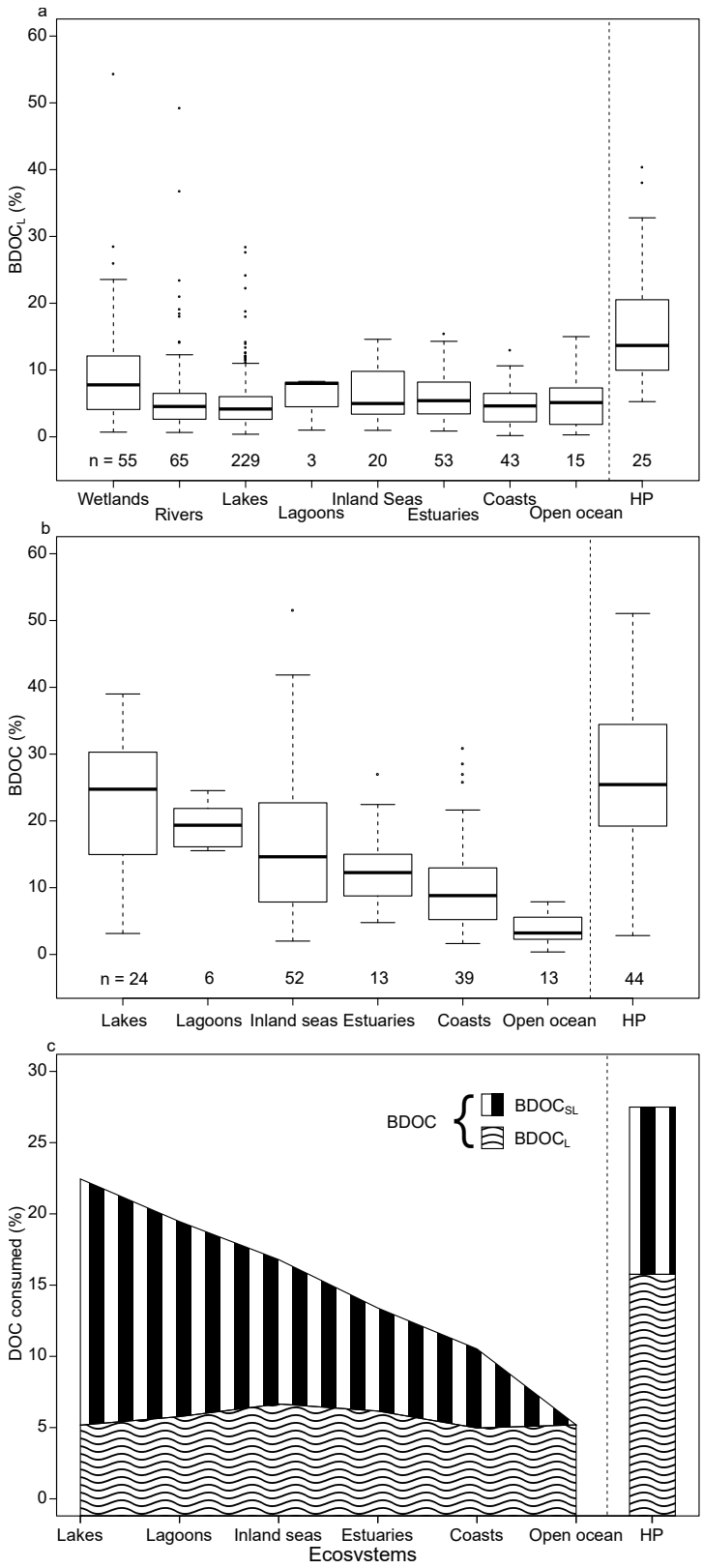


Fig. 2.3. Box-and-whisker plots showing the variation in the proportion of a) labile DOC (%BDOC$_L$), b) bioavailable DOC (%BDOC), and c) labile DOC (waves) versus semi-labile (%BDOC$_{SL}$, bars) for different ecosystem types. Ecosystem types are ordered along the aquatic continuum, from the most terrestrially connected aquatic ecosystem to the least. Separated with the dashed in both panel a) and b) are high productivity ecosystems (HP) values for %BDOC$_L$ and % BDOC respectively.

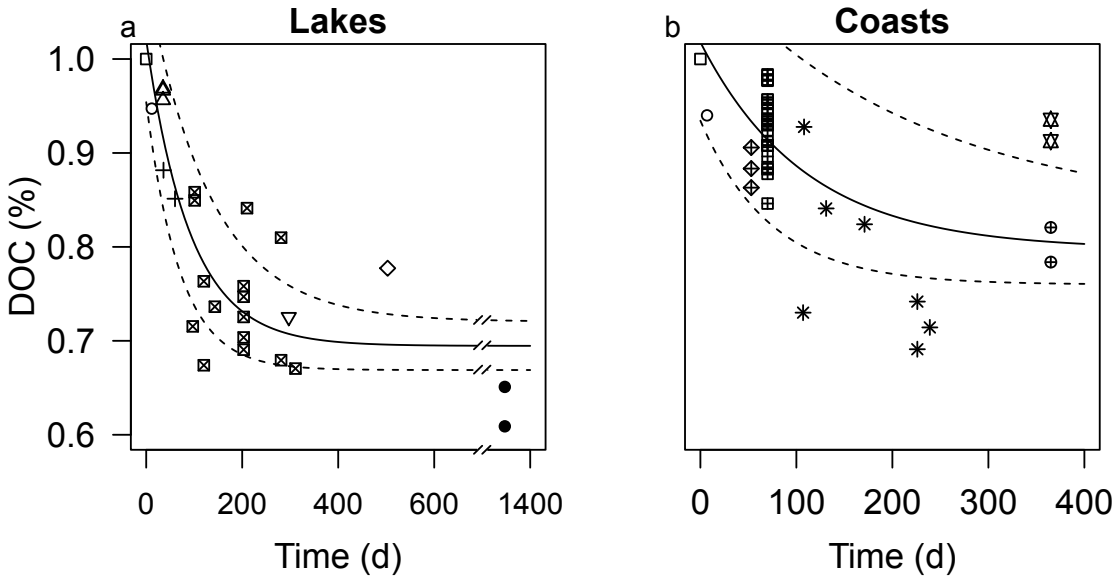


Fig. 2.4. DOC-decay curves applied on the proportion of remaining DOC across all available incubations, using a Multi-G model, for a) lakes and b) coasts. The dash-lines represent the confidence interval. Overall the %BDOC estimates are 32.6% and 22.1%, the kinetic constant, 0.011 ± 0.003d^{-1} and 0.0091 ± 0.005d^{-1}, and the R^2, 0.74 and 0.39 for lakes and coasts, respectively. The squares represent the initial DOC, the circles the average $BDOC_L$ loss and other symbols represent different studies.

3.3. Intra-ecosystem consistency in DOC lability over time

To test whether the relative amount of bioavailable DOC was generalizable across sites within a specific ecosystem type, we plotted the %DOC remaining for all incubations conducted in lakes and coasts with their corresponding incubation time to determine if they fit into a classic DOC decay curve using a multi-G model (eq. 2.1). Classic decay curves were observed for lakes ($t \geq 3.04$, df = 23, $p < 0.01$, DOC (%) = 33 * $e^{(-0.011*time)}$ + 69) and coastal ecosystems ($t \geq 2.06$, df = 38, $p \leq 0.05$, DOC(%) = 22 * $e^{(-0.0092*time)}$ + 80) (Fig. 2.4a and b). The decay constant was similar for lakes (0.011 ± 0.003 d^{-1}) and for coasts (0.0092 ± 0.004 d^{-1}), and implies a DOC turnover time of 455-637 days and 545-763 days respectively (i.e 5–7 times 1/k (d^{-1})). This timespan is similar to what suggested by Hansell (2013). The estimated %BDOC using this approach was 33% ± 4% for lakes and 22% ± 5% for coasts, consistent with their relative terrestrial connectivity and larger $BDOC_{SL}$ pool (Fig. 2.3c); the estimates for RDOC was 69% ± 3% and 80% ± 4% and were statistically different. Furthermore, the higher R2 observed in lakes at 0.74 as compared to coasts, 0.39, suggests a greater consistency related to DOC processing across lakes, regardless of initial DOC concentration or location in the world, than for coasts.

3.4. Prokaryotic biomass supported by $BDOC_L$ and $BDOC_{SL}$ across biomes

Using our proportional $BDOC_L$ and $BDOC_{SL}$ values for lakes, coasts, and the open ocean, we calculated the standing stock of each fraction in order estimate how much prokaryotic biomass could be supported per biome. The standing stock of $BDOC_L$ was 117.1 Tmol in all aquatic ecosystems, of which 1.3% was found in lakes, 4.1% in coasts, and 94.6% in the open ocean (average, minimum, and maximum values presented in Table 2.1). This translated into a total prokaryotic biomass transfer of 13 Tmol C across ecosystems. However, due to higher growth efficiencies, the contribution to biomass was relatively higher at 3.1% and 9.2% for lakes and coasts respectively, but the open ocean was still dominant at 87.7% given its immense volume. For $BDOC_{SL}$, assuming an equivalent of 100 Tmol in the first 100 m of the open ocean (Hansell, 2013), see SI, we calculated a standing stock of 110.4 Tmol with 4.5%, 4.9%, and 90.6% found in lakes, coasts, and open ocean, respectively. However, based on our results suggesting that $BDOC_{SL}$ was only available in lakes and coasts and not in the open ocean (Fig. 2.3c), we estimated that of the remaining 10.4 Tmol $BDOC_{SL}$, 2.6 Tmol C is transferred into prokaryotic biomass with 48.3% of this occurring in lakes and 51.7% in coasts (Table 2.1), while little to no $BDOC_{SL}$ would sustain prokaryotic biomass in the oceans. In the latter scenario, the dominant prokaryotic carbon biomass supported by both DOC pools was still found in the open ocean with 73.2% of total despite no access to the $BDOC_{SL}$ pool. $BDOC_L$ supported 38% of the prokaryotic biomass in lakes and coasts while $BDOC_{SL}$ supported 62%. The overall prokaryotic biomass supported by the $BDOC_{SL}$ pool alone represented 16.7% of the total across biomes.

Tableau 2.1. Global Standing Stocks and Biomass supported by $BDOC_L$ and $BDOC_{SL}$

	Lakes			**Coasts**	**Oceans**
	Small	**Large**	**All**		
Total $BDOC_L$ (Tmol)	1.3 [1.1, 1.5]	0.2 [0.2, 0.3]	1.5 [1.2, 1.8]	4.8 [2.4, 7.6]	110.8 [88.6, 133.6]
Total $BDOC_{SL}$ (Tmol)	4.3 [3.3, 5.3]	0.8 [0.5, 1.2]	5.0 [3.8, 6.5]	5.4 [2.3, 9.5]	0
Biomass[a] $BDOC_L$ (Tmol)	0.3 [0.3, 0.4]	0.06 [0.04, 0.08]	0.4 [0.3, 0.5]	1.2 [0.6, 1.9]	11.4 [9.1, 13.7]
Biomass[a] $BDOC_{SL}$ (Tmol)	1.1 [0.8, 1.3]	0.2 [0.2, 0.3]	1.3 [0.9, 0.3]	1.3 [0.6, 2.4]	0
Biomass[a] $BDOC_L$ (%)	2.4	0.4	2.9	9.2	87.9
Biomass[a] $BDOC_{SL}$ (%)	40.8	7.5	48.3	51.7	0

Note. Values in brackets represent ± standard deviation applied on each variable. Details for calculations are provided in Annexe 1.

[a] **Prokaryotic biomass supported**

4. Discussion

In this study, we showed that labile DOC ($BDOC_L$), the fraction of DOC consumed within 31 days, represents an unexpectedly stable proportion of the total DOC pool across a wide range of aquatic ecosystems at 6.1% on average. One possible explanation for this is that its origin is tightly coupled to primary production (Yamashita and Tanoue, 2003; Wünsch et al., 2019) when conditions are in steady-state (non-blooming), where production is on par with consumption and DOC does not accumulate. This is in part supported by the three-fold higher proportion of $BDOC_L$ in ecosystems where rates of primary production are very high (upwellings and bloom conditions), where the rapid production of $BDOC_L$ by excessive phytoplankton growth apparently overrides the metabolic capacity of prokaryotes to consume it, thus enabling DOC to accumulate. Semi-labile DOC ($BDOC_{SL}$), the fraction of DOC consumed beyond 31 days, appeared to be related primarily to terrestrial inputs rather than primary production in aquatic ecosystems considered at steady-state. The highest proportion of $BDOC_{SL}$ was observed in lakes, then gradually decreased along the aquatic continuum. This decrease in $BDOC_{SL}$ is also a function of increasing water residence time where the ongoing consumption of the terrestrial fraction as it transits from land to sea depletes $BDOC_{SL}$ to an undetectable amount in the open ocean. High productivity ecosystems, once again, behave differently where $BDOC_{SL}$ was relatively more abundant, and is likely also produced by the phytoplankton community in combination with bacterial reprocessing. Overall, these results suggest that prokaryotic communities across aquatic ecosystems rely primarily on readily available DOC for their basic energetic needs, but that increasing terrestrial connectivity provides access to a larger proportion of $BDOC_{SL}$, or background energy, a pool of organic matter slowly consumed in parallel to $BDOC_L$, originating predominantly from the continent.

The bioavailability of carbon is constrained by both the intrinsic properties of different DOC substrates (e.g. sugars are easier to consume than aromatics), as well as external factors, such as temperature (Rivkin and Legendre, 2001), nutrients availability (Zweifel et al., 1993) and prokaryotic community composition (Pedler et al., 2014), all contributing to the observed variability in $BDOC_L$ and BDOC across the aquatic continuum. Using an empirical approach, we found that a small fraction of DOC is rapidly metabolized by prokaryotes within 31 days across biomes, after which it appears the $BDOC_{SL}$ pool became the main energy source. This finding agrees with the literature where the most labile substrates are rapidly consumed within a few days (Hansell, 2013; Hopkinson et al., 2002), but that a slightly longer-term labile pool likely also exists 12. We propose that this threshold of 31 days probably represents a shift in the community structure from taxa that are adapted to degrading more labile substrates to those adapted to consuming more

semi-labile ones. Examples of such community shifts have been observed with changing ice conditions, within oceans (Nguyen et al., 2015; El-Swais et al., 2015) and in lakes (Kankaala et al., 2006) when light limits the production of the most labile substrates by phytoplankton photosynthesis. In the Arctic, communities shifted from being dominated by Flavobacteria to Alphaproteobacteria when light returned in spring (Nguyen et al., 2015), likely representing the consumption of more semi-labile versus more labile forms of DOC, respectively. In lakes, methane oxidizers became relatively more abundant during winter in ice-covered lakes as methane became an increasingly important source of carbon to the community (Kankaala et al., 2006; Sundh et al., 2005). There are only a few examples of such community shift as an acclimatation to DOC composition in batch cultures (Carlson et al., 2004; McCarren et al., 2010), and these were of limited length. Our results suggest that there may be a shift in communities' reliance on $BDOC_L$ to $BDOC_{SL}$ after about a month in batch culture experiments, coherent with changes in prokaryotic community structures observed in natural ecosystems when the supply of $BDOC_L$ was likely limited. $BDOC_{SL}$ may thus be viewed both as background energy (Fig 4a, $R^2 = 0.74$) as it is continuously consumed across the aquatic continuum and delivered in low amounts to the open ocean, and as backup energy (Fig. S2.2, $R^2 = 0.66$) in cases where the seasonal production of $BDOC_L$ is stopped for a prolonged period of time, inducing a shift in the prokaryotic community .

The average proportion of $BDOC_L$ we found was three fold lower than what was previously reported in the literature (Søndergaard and Middelboe, 1995). This difference may be explained by the different initial DOC concentrations observed between studies and the fact that we concentrated on ecosystems that were not necessarily in a state of elevated productivity. In Søndergaard and Middelboe (1995), the average initial DOC value for their coastal sites was around 260 μM whereas, in this synthesis, the average initial concentration was 75 μM for coastal sites considered in steady state. The average initial DOC concentrations ofthe high productivity coastal sites here were still much lower to those of Søndergaard and Middelboe (1995) at 109 μM, but the $\%BDOC_L$ was closer at 15.7%, suggesting that this synthesis focused on more productive study sites. The low proportion and remarkable stability in $BDOC_L$ across biomes observed in this synthesis implies a strong coupling between primary producers and heterotrophic prokaryotes (Carlson and Hansell, 2015) as well as a rapid turnover of autochthonous DOC, particularly in the ocean, preventing its accumulation in the water column regardless of ecosystem type. This low concentration of $BDOC_L$ in the surface open ocean ($\sim$4 μM) is in agreement with the hypothesis that substrate availability limits prokaryotic growth efficiency (López-Urrutia and Morán, 2007) rather than temperature (Rivkin and Legendre, 2001), since there is an increased rate of DOC consumption in higher productivity ecosystems. As such, in

the absence of an additional source of energy, the rapid renewal of $BDOC_L$ by primary production in the open ocean is critical to sustain prokaryotic communities.

Aquatic ecosystems that are more connected to the terrestrial landscape (lakes, rivers, coastal waters) have access to an additional pool of BDOC originating from land. Given the average 10-fold higher initial concentrations of DOC in lakes as compared to the ocean, part of the terrestrial inputs likely accounts for some component of the observed $BDOC_L$ in freshwaters (Kritzberg et al., 2004; Guillemette et al., 2013), but that local production becomes relatively more important moving to coasts (Siegel et al., 2002). However, the most notable feature is the higher proportion of $BDOC_{SL}$ in relation to this terrestrial connectivity across biomes, similar to the pattern observed with chromophoric DOC (Massicotte et al., 2017). $BDOC_{SL}$ enters freshwaters via the leaching of soil organic carbon, and is composed of various large biopolymers and aromatic chains (Lehmann and Kleber, 2015), and even carbohydrates and proteins that were somewhat protected in terrestrial environments, but become more bioavailable in aquatic ecosystems due to favorable environmental conditions (water, light, oxygen, temperature) (McCallister et al., 2004; Schmidt et al., 2011). Moreover, $BDOC_{SL}$ may also be produced within the aquatic continuum; inputs of terrestrial nutrients together with increased water residence time appear to stimulate the within aquatic ecosystem production of $BDOC_{SL}$ (Evans et al., 2017). Biological and photochemical processes oxidize this $BDOC_{SL}$ in a matter of weeks to months within continental waters where only a fraction eventually makes it to coastal ecosystems (Weyhenmeyer et al., 2012). This emphasizes the role of allochthonous sources in sustaining BDOC in inland waters, and that this role gradually decreases as water residence time increases (Catalan et al., 2016; Lapierre and del Giorgio, 2014). Our results suggest that much of this BDOC is semi-labile and that the water residence argument appears to hold even as we move into the marine realm, where $BDOC_{SL}$ decreases from estuaries to coasts to the open ocean.

The relative difference in $BDOC_{SL}$ availability may also help explain differential processing patterns across the aquatic continuum. Respiration, photochemical degradation, and sedimentary burial through flocculation are the main loss pathways of $BDOC_{SL}$, but the latter two are not accounted for in batch culture experiments. In freshwaters, higher microbial abundance (Simon et al., 1992) results in higher relative community respiration losses as compared to marine environments (del Giorgio et al., 1997), with significant losses in rivers (Hotchkiss et al., 2015) and lakes (Tranvik et al., 2009). The metabolism of $BDOC_{SL}$ is likely facilitated by the prokaryotic community composition in freshwaters, which is similar to those found in soil communities (Crump et al., 2012; Ruiz-González et al., 2015). This may explain their ability to transform the large $BDOC_{SL}$ component

of the BDOC pool into prokaryotic biomass and to contribute to high respiratory losses. The photodegradation of chromophoric DOC can also be a significant organic matter loss in freshwaters (Lapierre et al., 2013). Photodegradation produces CO_2 directly, but the process also creates $BDOC_L$ from SLDOC, which may then be more readily assimilated by prokaryotes (Miller and Zepp, 1995). This process appears to be strongly related to water color, with darker waters containing more aromatic compounds capable of absorbing more light energy (Traina et al., 1990). On average photodegradation accounts for around 10% of DOC losses in lakes and rivers, but this loss is predominantly from the SLDOC pool (Koehler et al., 2014). The process of flocculation is a major SLDOC removal pathway in estuaries when the high DOC riverine waters mix with seawater; this results in limited to no delivery of particles to nearby coastal regions (Lisitsyn, 1995). However, less is known about this process in other aquatic ecosystems, although flocculation can apparently contribute to as much loss through formation and sedimentation as either photodegradation or respiration (Koehler et al., 2014; von Wachenfeldt and Tranvik, 2008).

Communities tend to shift from freshwater to the marine realm where there is a decreasing and more variable dependence on $BDOC_{SL}$ of terrestrial origin. There is likely a high variability in the amount of terrestrially derived $BDOC_{SL}$ entering different estuaries and coasts across regions as a function of riverine chromophoric DOC load, and even in inland seas when salinity reaches oceanic values (Siegel et al., 2002). Indeed, the increased variability in the degradation kinetics among coastal ecosystems as compared to lakes observed in this study using the multi-G approach suggests a much more variable dependence of $BDOC_{SL}$ in coasts, ranging from 6.5 to 30.9% as compared to 15.9 to 33.0% in lakes for incubations between 200 and 400 days. This increased variability in coasts is also likely due to the creation of some of this $BDOC_{SL}$ during moments of higher productivity or as a function of eutrophication (Evans et al., 2017; Asmala et al., 2018). For example, labile and semi-labile substrates accumulated in high productivity ecosystems despite the increased abundance of prokaryotes (Romera-Castillo et al., 2011). These substrates likely persist after the bloom and contribute to the greater overall %BDOC in productive coasts. This is likely as a function of prokaryotic reprocessing of the excess $BDOC_L$ (Ogawa et al., 2001) and the additional release of carbon compounds when phytoplankton productivity is nutrient stressed towards the end of a bloom (Wear et al., 2015).This broad range in the proportion of coastal $BDOC_{SL}$ reported is therefore likely driven by variability in allochthonous inputs and local production across sites.

To put the relative proportion of metabolizable DOC in bottle incubations into perspective across ecosystem types, we provide a first order estimate of the ability of these different fractions to support prokaryotic biomass. One of the caveats of our approach is that we

do not consider the flux within those fractions, but simply a snapshot of the amounts of bioavailable DOC. Rates of primary production as well as terrestrial loading rates would need to be accounted for to get at the overall biomass that could be sustained. However, this approach is representative of what can be supported in the absence of external fluxes, and would adequately captures ambient DOC dynamics, for example, in ice covered regions. Nevertheless, it appears that most of the prokaryotic energy transfer in aquatic ecosystems is sustained by $BDOC_L$ (Table 2.1), most of which occurs in the open ocean. The overall biomass supported by $BDOC_{SL}$ was equivalent in both lakes and coasts, but at a much higher relative fraction, at near 76% of total in lakes as compared to 52% for coasts. Accordingly, a significant fraction of terrestrial DOC is lost as it travels through inland waters (Cole et al., 2007) and this fraction is known to support bacterial communities (Kritzberg et al., 2004). The first order estimates calculated here have large uncertainties, given the assumptions in prokaryotic growth efficiency for lakes and coasts and the high variability in the proportion of $BDOC_{SL}$ in coasts. Nevertheless, prokaryotic energetic needs likely depend more on $BDOC_{SL}$ in lakes than in coasts, as a function of higher relative proportion and overall concentrations of this pool in lakes. Another assumption we make is that no $BDOC_{SL}$ is available to surface oceanic prokaryotes since no consumption was observed across batch cultures. In fact, the composition of open ocean surface communities may not be adapted to consume this semi-labile fraction whereas deeper communities appear to have this capability (Carlson et al., 2004), therefore the relative availability of this large pool to surface microbes remains unknown.

5. Conclusions

In this study, we found that a shift in DOC bioavailability occurred within 30 days of incubation, and argue that future studies should consider whether this is a function of a shift within the prokaryotic community. We further demonstrated that the proportion of $BDOC_L$ is consistent across aquatic ecosystems when systems are under steady state, regardless of the 90-fold range initial overall DOC concentrations. In contrast, there is considerable variability in the relative proportion of $BDOC_{SL}$, which decreases with reduced terrestrial connectivity across the aquatic continuum. This $BDOC_{SL}$ may support a relatively high proportion of the prokaryotic biomass in lakes as well as coasts, whereas results from batch culture experiments carried out in the open ocean show no consumption of the $BDOC_{SL}$ pool. Overall, our results suggest that open ocean prokaryotes mostly rely on a $BDOC_L$ pool that may be much lower than previously estimated by the previous synthesis, whereas $BDOC_{SL}$ supports an increasingly important fraction of prokaryotic biomass approaching the land-water interface. Future work should consider how the kinetic degradation of the different DOC pools change across ecosystem types, and how rapidly different microbial

communities may respond.

6. Acknowledgments, Samples, and Data

We thank M. Botrel and N. Fortin St-Gelais for their helpful suggestions, and P. del Giorgio for sharing published data from the CarBASS project. We would like to thank several anonymous reviewers for helpful comments that improved the manuscript; one provided particularly insightful comments for which we are very grateful. No financial benefits were received from this publication, and all authors declare no conflict of interest. This work was funded by an FQRNT student scholarship to RL, a NSERC-CCAR and an NSERC Discovery to RM. This work is a contribution to the Groupe de recherché interuniversitaire en limnologie (GRIL) and Ventilation, Interactions and Transports Across the Labrador Sea (VITALS - RGPCC 433898). The list of references used, all data, scripts, and associated details are available at http://www.github.com/laboMaranger/DOC-meta-analysis (doi: 10.5281/zenodo.3608290).

Références bibliographiques

Aluwihare, L. I., Repeta, D. J., and Chen, R. F. (1997). A major biopolymeric component to dissolved organic carbon in surface sea water. *Nature*, 387(6629):166.

Amon, R. M. W., Fitznar, H. P., and Benner, R. (2001). Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. *Limnology and Oceanography*, 46(2):287–297.

Aristegui, J., Duarte, C. M., Agusti, S., Doval, M., Alvarez-Salgado, X. A., and Hansell, D. A. (2002). Dissolved organic carbon support of respiration in the dark ocean. *Science*, 298(5600):1967–1967.

Asmala, E., Haraguchi, L., Markager, S., Massicotte, P., Riemann, B., Staehr, P. A., and Carstensen, J. (2018). Eutrophication leads to accumulation of recalcitrant autochthonous organic matter in coastal environment. *Global Biogeochemical Cycles*.

Azam, F., Fenchel, T., Field, J., Gray, J., Meyer-Reil, L., and Thingstad, F. (1983). The ecological role of water-column microbes in the sea. *Marine ecology progress series. Oldendorf*, 10(3):257–263.

Barrón, C. and Duarte, C. M. (2015). Dissolved organic carbon pools and export from the coastal ocean. *Global Biogeochemical Cycles*, 29(10):1725–1738.

Biddanda, B. A. and Cotner, J. B. (2002). Love handles in aquatic ecosystems: The role of dissolved organic carbon drawdown, resuspended sediments, and terrigenous inputs in the carbon balance of lake michigan. *Ecosystems*, 5(5):431–445.

Bocaniov, S. A., Barton, D. R., Schiff, S. L., and Smith, R. E. H. (2013). Impact of tributary dom and nutrient inputs on the nearshore ecology of a large, oligotrophic lake (georgian bay, lake huron, canada). *Aquatic Sciences*, 75(2):321–332.

Cael, B. B., Heathcote, A. J., and Seekell, D. A. (2017). The volume and mean depth of earth's lakes. *Geophysical Research Letters*, 44(1):209–218.

Carlson, C. A., Bates, N. R., Ducklow, H. W., and Hansell, D. A. (1999). Estimation of bacterial respiration and growth efficiency in the ross sea, antarctica. *Aquatic Microbial Ecology*, 19(3):229–244.

Carlson, C. A., Giovannoni, S. J., Hansell, D. A., Goldberg, S. J., Parsons, R., and Vergin, K. (2004). Interactions among dissolved organic carbon, microbial processes, and community structure in the mesopelagic zone of the northwestern sargasso sea. *Limnology and Oceanography*, 49(4):1073–1083.

Carlson, C. A. and Hansell, D. A. (2015). *Chapter 3 - DOM Sources, Sinks, Reactivity, and Budgets*, pages 65–126. Academic Press, Boston.

Catalan, N., Marce, R., Kothawala, D. N., and Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geosci*, 9(7):501–504.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10(1):172–185.

Crump, B. C., Amaral-Zettler, L. A., and Kling, G. W. (2012). Microbial diversity in arctic freshwaters is structured by inoculation of microbes from soils. *The ISME journal*, 6(9):1629.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., and Iudicone, D. (2004). Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. *Journal of Geophysical Research: Oceans*, 109(C12).

del Giorgio, P. A. and Cole, J. J. (1998). Bacterial growth efficiency in natural aquatic systems. *Annual Review of Ecology and Systematics*, pages 503–541.

del Giorgio, P. A., Cole, J. J., and Cimbleris, A. (1997). Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. *Nature*, 385(6612):148–151.

del Giorgio, P. A., Condon, R., Bouvier, T., Longnecker, K., Bouvier, C., Sherr, E., and Gasol, J. M. (2011). Coherent patterns in bacterial growth, growth efficiency, and leucine metabolism along a northeastern pacific inshore-offshore transect. *Limnology and Oceanography*, 56(1):1–16.

del Giorgio, P. A. and Davis, J. (2003). *Patterns in dissolved organic matter lability and consumption across aquatic ecosystems*, pages 399–424. Elsevier.

del Giorgio, P. A. and Duarte, C. M. (2002). Respiration in the open ocean. *Nature*, 420(6914):379–384.

Elzhov, T. V., Mullen, K. M., Spiess, A.-N., and Bolker, B. (2016). *minpack.lm: R Interface to the Levenberg-Marquardt Nonlinear Least-Squares Algorithm Found in MINPACK, Plus Support for Bounds*. R package version 1.2-1.

El-Swais, H., Dunn, K. A., Bielawski, J. P., Li, W. K., and Walsh, D. A. (2015). Seasonal assemblages and short-lived blooms in coastal north-west a tlantic o cean bacterioplankton. *Environmental microbiology*, 17(10):3642–3661.

Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Frogbrook, Z., and Kothawala, D. N. (2017). Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nature Geoscience*, 10(11):832.

Farjalla, V. F., Faria, B. M., and Esteves, F. A. (2002). The relationship between doc and planktonic bacteria in tropical coastal lagoons. *Archiv für Hydrobiologie*, 156(1):97–119.

Guillemette, F. and del Giorgio, P. A. (2011). Reconstructing the various facets of dissolved organic carbon bioavailability in freshwater ecosystems. *Limnology and Oceanography*, 56(2):734–748.

Guillemette, F., McCallister, S. L., and del Giorgio, P. A. (2013). Differentiating the degradation dynamics of algal and terrestrial carbon within complex natural dissolved organic carbon in temperate lakes. *Journal of Geophysical Research: Biogeosciences*, 118(3):963–973.

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5.

Hopkinson, C. S., Vallino, J. J., and Nolin, A. (2002). Decomposition of dissolved organic matter from the continental margin. *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 49(20):4461–4478.

Hotchkiss, E., Hall Jr, R., Sponseller, R., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., and Karlsson, J. (2015). Sources of and processes controlling co 2 emissions change with the size of streams and rivers. *Nature Geoscience*, 8(9):696.

Jørgensen, B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments.

Kankaala, P., Huotari, J., Peltomaa, E., Saloranta, T., and Ojala, A. (2006). Methanotrophic activity in relation to methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake. *Limnology and Oceanography*, 51(2):1195–1204.

Koehler, B., Landelius, T., Weyhenmeyer, G. A., Machida, N., and Tranvik, L. J. (2014). Sunlight-induced carbon dioxide emissions from inland waters. *Global Biogeochemical Cycles*, 28(7):696–711.

Koehler, B., Wachenfeldt, E., Kothawala, D., and Tranvik, L. J. (2012). Reactivity continuum of dissolved organic carbon decomposition in lake water. *Journal of Geophysical Research: Biogeosciences*, 117(G1).

Kritzberg, E. S., Cole, J. J., Pace, M. L., Granéli, W., and Bade, D. L. (2004). Autochthonous versus allochthonous carbon sources of bacteria: Results from whole-lake 13c addition experiments. *Limnology and Oceanography*, 49(2):588–596.

Lapierre, J. F. and del Giorgio, P. A. (2014). Partial coupling and differential regulation of biologically and photochemically labile dissolved organic carbon across boreal aquatic networks. *Biogeosciences*, 11(20):5969–5985.

Lapierre, J.-F., Guillemette, F., Berggren, M., and del Giorgio, P. A. (2013). Increases in terrestrially derived carbon stimulate organic carbon processing and co2 emissions in boreal aquatic ecosystems. *Nature communications*, 4.

Legendre, P. and Legendre, L. F. (2012). *Numerical ecology*, volume 24. Elsevier.

Lehmann, J. and Kleber, M. (2015). The contentious nature of soil organic matter. *Nature*, 528(7580):60.

Lisitsyn, A. (1995). The marginal filter of the ocean. *Oceanology of the Russian Academy of Sciences*, 34(5):671–682.

López-Urrutia, A. and Morán, X. A. G. (2007). Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling. *Ecology*, 88(4):817–822.

Lønborg, C. and Álvarez-Salgado, X. A. (2012). Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump. *Global Biogeochemical Cycles*, 26(3).

Massicotte, P., Asmala, E., Stedmon, C., and Markager, S. (2017). Global distribution of dissolved organic matter along the aquatic continuum: Across rivers, lakes and oceans. *Science of the Total Environment*, 609:180–191.

McCallister, S. L., Bauer, J. E., Cherrier, J. E., and Ducklow, H. W. (2004). Assessing sources and ages of organic matter supporting river and estuarine bacterial production: A multiple-isotope (δ^{14}C, δ^{13}C, and δ^{15}N) approach. *Limnology and Oceanography*, 49(5):1687–1702.

McCarren, J., Becker, J. W., Repeta, D. J., Shi, Y., Young, C. R., Malmstrom, R. R., Chisholm, S. W., and DeLong, E. F. (2010). Microbial community transcriptomes reveal microbes and metabolic pathways associated with dissolved organic matter turnover in the sea. *Proceedings of the National Academy of Sciences*, 107(38):16420–16427.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46(1):38–48.

Miller, W. L. and Zepp, R. G. (1995). Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophysical Research Letters*, 22(4):417–420.

Myklestad, S. M. (1995). Release of extracellular products by phytoplankton with special emphasis on polysaccharides. *Science of the total Environment*, 165(1-3):155–164.

Nguyen, D., Maranger, R., Balagué, V., Coll-Llado, M., Lovejoy, C., and Pedros-Alio, C. (2015). Winter diversity and expression of proteorhodopsin genes in a polar ocean. *The ISME journal*, 9(8):1835.

Obernosterer, I. and Benner, R. (2004). Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. *Limnology and Oceanography*, 49(1):117–124.

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., and Benner, R. (2001). Production of refractory dissolved organic matter by bacteria. *Science*, 292(5518):917–920.

Panagiotopoulos, C., Repeta, D. J., and Johnson, C. G. J. O. g. (2007). Characterization of methyl sugars, 3-deoxysugars and methyl deoxysugars in marine high molecular weight dissolved organic matter. 38(6):884–896.

Pedler, B. E., Aluwihare, L. I., and Azam, F. (2014). Single bacterial strain capable of significant contribution to carbon cycling in the surface ocean. *Proceedings of the National Academy of Sciences of the United States of America*, 111(20):7202–7207.

Pomeroy, L. R. (1974). The ocean's food web, a changing paradigm. *Bioscience*, 24(9):499–504.

R Core Team (2017). *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.

Ramlal, P. S., Hecky, R. E., Bootsma, H. A., Schiff, S. L., and Kingdon, M. J. (2003). Sources and fluxes of organic carbon in lake malawi/nyasa. *Journal of Great Lakes Research*, 29:107–120.

Rivkin, R. B. and Legendre, L. (2001). Biogenic carbon cycling in the upper ocean: Effects of microbial respiration. *Science*, 291(5512):2398–2400.

Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrasé, C. (2011). Net production and consumption of fluorescent colored dissolved organic matter by natural bacterial assemblages growing on marine phytoplankton exudates. *Applied and Environmental Microbiology*, 77(21):7490–7498.

Ruiz-González, C., Niño-García, J. P., and del Giorgio, P. A. (2015). Terrestrial origin of bacterial communities in complex boreal freshwater networks. *Ecology letters*, 18(11):1198–1206.

Schmidt, M. W., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kögel-Knabner, I., Lehmann, J., and Manning, D. A. (2011). Persistence of soil organic matter as an ecosystem property. *Nature*, 478(7367):49.

Servais, P., Billen, G., and Hascoët, M.-C. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters. *Water research*, 21(4):445–450.

Sharp, J. H. (1997). Marine dissolved organic carbon: Are the older values correct? *Marine Chemistry*, 56(3-4):265–277.

Siegel, D., Maritorena, S., Nelson, N., Hansell, D., and Lorenzi-Kayser, M. (2002). Global distribution and dynamics of colored dissolved and detrital organic materials. *Journal of Geophysical Research: Oceans*, 107(C12):21–1–21–14.

Simon, M., Cho, B. C., and Azam, F. (1992). Significance of bacterial biomass in lakes and the ocean: comparison to phytoplankton biomass and biogeochemical implications. *Marine Ecology Progress Series*, 86(2):103–110.

Smith, E. M. and Prairie, Y. T. (2004). Bacterial metabolism and growth efficiency in lakes: the importance of phosphorus availability. *Limnology and Oceanography*, 49(1):137–147.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52(3):1208–1219.

Stets, E. G., Striegl, R. G., and Aiken, G. R. (2010). Dissolved organic carbon export and internal cycling in small, headwater lakes. *Global Biogeochemical Cycles*, 24(4).

Sundh, I., Bastviken, D., and Tranvik, L. J. (2005). Abundance, activity, and community structure of pelagic methane-oxidizing bacteria in temperate lakes. *Applied and environmental microbiology*, 71(11):6746–6752.

Søndergaard, M. and Middelboe, M. (1995). A cross-system analysis of labile dissolved organic carbon. *Marine ecology progress series. Oldendorf*, 118(1):283–294.

Traina, S. J., Novak, J., and Smeck, N. E. (1990). An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *Journal of environmental quality*, 19(1):151–153.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., and Knoll, L. B. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54(6part2):2298–2314.

Tranvik, L. J. and Jorgensen, N. O. G. (1995). Colloidal and dissolved organic-matter in lake water: Carbohydrate and amino acid composition, and ability to support bacterial growth. *Biogeochemistry*, 30(2):77–97.

Vähätalo, A. V., Aarnos, H., and Mäntyniemi, S. (2010). Biodegradability continuum and biodegradation kinetics of natural organic matter described by the beta distribution. *Biogeochemistry*, 100(1-3):227–240.

Verburg, P. (2007). The need to correct for the suess effect in the application of δ13c in sediment of autotrophic lake tanganyika, as a productivity proxy in the anthropocene. *Journal of Paleolimnology*, 37(4):591–602.

von Wachenfeldt, E. and Tranvik, L. J. (2008). Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems*, 11(5):803–814.

Walterscheid, S. K. (2011). Climate classification for the earth's oceanic areas using the köppen system. *Master thesis. Kansas State University.*

Wear, E. K., Carlson, C. A., James, A. K., Brzezinski, M. A., Windecker, L. A., and Nelson, C. E. (2015). Synchronous shifts in dissolved organic carbon bioavailability and bacterial community responses over the course of an upwelling-driven phytoplankton bloom. *Limnology and Oceanography*, 60(2):657–677.

Weyhenmeyer, G. A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., and Tranvik, L. J. (2012). Selective decay of terrestrial organic carbon during transport from land to sea. *Global Change Biology*, 18(1):349–355.

Wünsch, U. J., Bro, R., Stedmon, C. A., Wenig, P., and Murphy, K. R. (2019). Emerging patterns in the global distribution of dissolved organic matter fluorescence. *Analytical Methods*, 11(7):888–893.

Yamashita, Y. and Tanoue, E. (2003). Chemical characterization of protein-like fluorophores in dom in relation to aromatic amino acids. *Marine Chemistry*, 82(3-4):255–271.

Yoshioka, T., Ueda, S., Khodzher, T., Bashenkhaeva, N., Korovyakova, I., Sorokovikova, L., and Gorbunova, L. (2002). Distribution of dissolved organic carbon in lake baikal and its watershed. *Limnology*, 3(3):0159–0168.

Zweifel, U. L., Norrman, B., and Hagström, A. (1993). Consumption of dissolved organic carbon by marine bacteria and demand for inorganic nutrients. *Marine Ecology-Progress Series*, 101:23–23.

Deuxième article.

Spatial abundance distribution of bacteria is defined by their dissolved organic matter preferences

par

Richard LaBrie[1], Simon Bélanger[2], Ronald Benner[3] et Roxane Maranger[1]

([1]) Département des sciences biologiques et Groupe de recherche interuniversitaire en limnologie et environnement aquatique (GRIL), Université de Montréal, Pavillon Marie-Victorin C. P. 6128, succ. Centre-ville, Montréal, QC, Canada, H3C 3J7

([2]) Département de biologie, chimie et géographie, groupes BORÉAS et Québec-Océan, Université du Québec à Rimouski, Campus de Rimouski, 300 Allée des Ursulines, Rimouski, QC Canada G5L 3A1

([3]) Department of Biological Sciences and the School of the Earth, Ocean and Environment, 715 Sumter Street, University of South Carolina, Columbia, SC, USA 2920882

Cet article a été soumis dans Limnology and Oceanography.

Contributions des auteurs

RL a analysé les données et écrit le premier manuscrit; RM et RL ont révisé le premier manuscrit; RL et SB ont fait le travail de terrain; SB et RB ont contribué à l'expertise

technique et aux révisions; RM, SB et RB ont contribué financièrement; RM a élaboré l'étude. Tous ont accepté le manuscrit

Résumé. Dans les écosystèmes aquatiques, les transformations de la matière organique dissoute sont principalement le fruit de la structure de la communauté de bactéries et leur taux métaboliques. Bien que des avancées méthodologiques récentes aient révélées l'importante complexité chimique de la matière organique, la diversité des bactéries et le nombre de fonction cellulaire qu'ils possèdent, comprendre ce qui influence les relations entre ces propriétés des écosystèmes reste un défi majeur en écologie microbienne. Dans cette étude, nous avons utilisé des données empiriques recueillies dans la mer du Labrador au cours de trois efflorescences algales printanières consécutives pour caractériser les relations entre les conditions environnementales, la structure de la communauté de bactéries et leurs taux métaboliques. En utilisant la modélisation de la distribution spatiale de l'abondance des bactéries (SPAD), nous avons identifié de fortes associations entre les groupes de SPAD et différents substrats organiques. Les *amplicon sequence variants* (ASV) cosmopolites, c'est-à-dire avec une distribution plutôt normale, étaient liées aux apports de matière organique fraîche tandis que les ASV rares (logistiques) étaient associées à des formes plus complexes de matière organique. En outre, les Flavobactéries cosmopolites étaient influencés par la présence d'acides aminés libres et combinés facilement biodisponibles tandis que les $\delta-$protéobactéries rares étaient influencées par des substrats organiques plus complexes. Étant donné l'importance et la complexité de relier les conditions environnementales, la structure de la communauté de bactéries et les fonctions de l'écosystème, nous proposons un cadre conceptuel pour mieux étudier les liens entre entre ces domaines.

Mots clés : Matière organiqu dissoute, carbone organique dissous, biogéochimie, écologie microbiene, métabolisme bactérien, structure de la communauté, distribution spatiale de l'abondance

Abstract. Dissolved organic matter processing in aquatic ecosystems is mainly driven by bacterial community structure and metabolic rates. Although recent methodological advancements revealed the diversity and complexity of organic matter, bacterial diversity, and potential cellular activity, understanding what influences the relationships among these ecosystem properties remains a major challenge in microbial ecology. Here, we used empirical data collected in the Labrador Sea during three consecutive spring bloom events to characterize relationships among environmental conditions, bacterial community structure, and metabolic processing. By using spatial abundance distribution (SPAD) modelling of bacteria, we identified strong associations of different SPAD groups with specific organic substrates that influenced ecosystem processing. Amplicon sequence variants (ASVs) with more ubiquitous distributions (i.e. ubiquitous) were related to fresh organic matter inputs whereas rare ASVs (i.e. logistic) were associated with complex forms of organic matter. The SPAD of different ASV classes like cosmopolitan Flavobacteriia were influenced by the presence of readily bioavailable free and combined amino acids, whereas rare $\delta-$proteobacteria, were influenced by more complex substrates. Given the importance and complexity of linking environmental conditions, bacterial community structure, and ecosystem function, we propose a framework to bridge the gap between bacterial diversity, microbial ecology, and biogeochemistry among methods and across scales.
Keywords: Dissolved organic matter, dissolved organic carbon, biogeochemistry, microbial ecology, bacterial metabolism, community structure, spatial abundance distribution

1. Introduction

Dissolved organic matter (DOM) is the largest pool of bioavailable carbon and nitrogen that provides the basic metabolic needs of heterotrophic aquatic bacterial communities (Pomeroy, 1974; Azam et al., 1983). Large scale positive relationships between substrate availability and bacterial heterotrophic production (BHP, formerly referred to as bacterial production) (López-Urrutia and Morán, 2007; Nguyen et al., 2012) and biomass (Duarte et al., 2005; Simon et al., 1992), which in turn influences bacterial respiration (BR) rates (Nguyen et al., 2012; del Giorgio et al., 1997), are foundational knowledge in aquatic microbial ecology. Many studies have built upon these concepts to gain better insight of DOM cycling (Catalan et al., 2016; Hopkinson et al., 2002; LaBrie et al., viewb) by bacterial communities, from a mechanistic understanding (Koch et al., 2014; Pedler et al., 2014; Romera-Castillo et al., 2011) to the processing of organic matter at larger regional (Nguyen et al., 2012; Alonso-Saez et al., 2007; Wear et al., 2015) and global (Aristegui et al., 2009; Herndl and Reinthaler, 2013) scales. Technical advances in geochemistry (Moran et al., 2016) have unraveled a highly complex and heterogeneous DOM pool composed of tens to hundreds of thousands of different molecular formulas (Zark et al., 2017). Similarly, heterotrophic bacteria are not simply members of a homogeneous black box, but a rather diverse community (Sogin et al., 2006) targeting different groups of compounds (Kirchman, 2008), having different lifestyles (Jones and Lennon, 2010) and very different spatial

distribution (Fierer and Jackson, 2006; Niño-García et al., 2016; Ruiz-González et al., 2019). Yet linking this complex mixture of DOM compounds to bacterial structure and ultimately ecosystem function remains a grand challenge in microbial ecology.

Developing techniques to better characterize the DOM pool has been a prime focus in oceanic carbon biogeochemistry for the past decades (Moran et al., 2016; Hertkorn et al., 2006; Broek et al., 2017). Indeed, knowing the bioavailability of individual compounds (Davis and Benner, 2007) could potentially increase our ability to predict microbial carbon fluxes in the oceans. However, it is a bit overwhelming to genuinely connect complex bacterial communities to thousands of DOM compounds to address large-scale carbon fluxes. Perhaps an intermediary step is required, one which considers how substrates are grouped with how communities are clustered to then better understand their role in ecosystem function. As a first step to reduce the complexity of working with DOM, considerable attention has been given to free and combined amino acids (AA) (Kaiser and Benner, 2005; Benner, 2002), bioavailable compounds that are released from phytoplankton during growth and grazing (Simon and Rosenstock, 2007). AAs are thought to represent a disproportionate amount of bioavailable DOC and dissolved organic nitrogen (Amon et al., 2001) albeit consisting of only about 20 different molecules (Kaiser and Benner, 2005; Amon et al., 2001; Escoubeyrou and Tremblay, 2014). A different approach that targets a broader group of dissolved molecules is the use of fluorescence spectroscopy for the characterization of fluorescent DOM (FDOM) (Coble, 1996; Stedmon et al., 2000). Coupling FDOM emission-excitation matrices (EEMs) with parallel factor analysis (PARAFAC) provides a rapid and easy way to characterize DOM functional groups, such as complex aromatics and protein-like compounds. These components of FDOM influence carbon sequestration (Catalá et al., 2015) and rapid DOM turnover (Lønborg et al., 2015), respectively, and are thought to be broadly representative of DOM (Stubbins et al., 2014). Together with AA composition, FDOM characterization is useful for understanding how different environmental conditions influence bacterial community and function.

When trying to elucidate the role how different bacterial communities influence DOM cycling, a taxonomic approach is often used (Fuhrman and Hagström, 2008; Cottrell and Kirchman, 2000; Elifantz et al., 2005). Typically, α-proteobacteria are thought to target amino acids, whereas Bacteroidetes are often associated with particulate organic matter and high-molecular-weight DOM. However, contradicting results have been reported at finer taxonomic rank. For example, two different Amplicon Sequence Variants (ASVs) from the β-proteobacteria Herminiimonas genus were associated with the consumption of either low or high molecular weight DOM (Logue et al., 2015), suggesting different metabolic pathways between them. Yet details in the specific pathways of ASVs albeit informative, mask the

ability to identify more generalized patterns of community structure in association to DOM availability and functional processes. One promising way to structure and describe bacterial communities is by characterizing their spatial abundance distribution (SPAD), which may be viewed as a response trait (Violle et al., 2007). This approach was originally developed for understanding the species distribution of tropical trees across spatial scales (Conlisk et al., 2012), but has been successfully adapted for aquatic bacteria (Niño-García et al., 2016; Ruiz-González et al., 2019). The method clusters ASVs into normal-like, bimodal, lognormal or logistic distributions which represent taxa that are considered ubiquitous, bloomers and rare, respectively, each of them potentially having their own ecological role.

In this study, we evaluated the relationships among substrate availability, ecosystem processing and community structure at different scales of inquiry. Using field data collected across distinctive water masses in the Labrador Sea over three consecutive springs (2014-2016), we first tested classic relationships associating ecosystem metabolism with classic environmental and bacterial features. Second, we explored the relationships of microbial communities to broad classes of DOM composition (FDOM) using an intermediate step of characterizing the bacterial community structure using SpAD modelling. We then went further into our inquiry by combining taxonomic information (ASVs) with SpAD groups to look at their association with specific compounds (AAs). Through this exploration, we propose a conceptual framework linking environmental conditions with elements of bacterial community structure and ecosystem function at different level of characterization to advance our understanding of microbial-DOM interactions.

2. Materials and methods

2.1. Study site

Sampling occurred in the Labrador Sea between days of year 127 and 136 in 2014, 2015 and 2016 along the World Ocean Circulation Experiment (WOCE) Atlantic Repeat Hydrography Line 7 West (AR7W) onboard the CCGS Hudson. We sampled 5, 4 and 6 stations along the transect in 2014, 2015 and 2016, respectively, at surface (2m) and at 30m depth (Fig. S3.1). The Labrador Sea is characterized by the mixing of numerous Atlantic and Arctic water masses (Lazier; Yashayaev and Clarke, 2008). There is typically a spring bloom (Marchese et al., 2019) around that sampling period, and there is a known protistan biogeography (Fragoso et al., 2016; Péquin et al., shed) across the masses. Water was collected using a conductivity, temperature and depth (CTD) mounted on a rosette and transported to the lab in polyethylene carboys. All materials used were acid-washed and glassware was combusted at 450°C for 4 hours.

2.2. Environmental conditions

2.2.1. *Dissolved organic carbon and nitrogen and chlorophyll a*

Samples for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were filtered with 0.7 μm pre-combusted glass fiber filters (Whatman, UK). In 2015 and 2016, additional unfiltered samples were taken for total organic carbon (TOC) and total nitrogen (TN). Tests showed that there were no significant differences between filtered and unfiltered samples, and thus DOC and TDN data of the three years are considered in our study. Samples were acidified to pH 2 with ACS grade HCl, stored at 4°C until processes using the high temperature catalytic oxidation (HTCO) method for DOC and chemiluminescence for TDN on a TOC-Vcpn analyzer (Shimadzu, Japan). Samples for inorganic nitrogen species (NO_3^-, NO_2^- and NH_4^+) were filtered through 0.7 μm pre-combusted glass fiber filters, where nitrate and nitrite were stored frozen until measured in the lab using a colorimetric method on a Bran and Luebbe Autoanalyzer II (SEAL Analytical, WI, USA) whereas NH4+ was measured onboard using derivatization with o-phthaldialdehyde (OPA) and fluorometric detection on a TD-700 fluorimeter (Turner Designs, CA, USA) following Holmes (1999). Dissolved organic nitrogen (DON) was calculated as the difference between TDN and inorganic nitrogen species. Chlorophyll *a* was extracted in 90% acetone and analyzed fluorometrically following Holm-Hansen and collaborators (1965).

2.2.2. *Chromophoric and fluorescent DOM, and Amino Acids*

In 2014 and 2015, samples for chromophoric (CDOM) and fluorescent DOM (FDOM) were filtered through 0.2 μm using capsule filter composed of glass microfiber (GMF) prefilter over a nylon membrane (Polycap AS 36, Whatman, UK) and stored at 4°C in the dark for 2 months before analysis in Rimouski. In 2016, the samples were filtered using Opticap XL4 Durapore 0.22 μm capsule (Millipore, MA, USA) and the FDOM was measured onboard within a few hours after water collection. The CDOM was measured on a dual-beam Lambda-850 UV-Vis spectrophotometer (Perkin Elmer, MA, USA) with a 10cm optical path length and corrected in R (R Core Team, 2017) with the RspectroAbs package (Bélanger, 2019). FDOM was measured on a Cary Eclipse spectrofluorometer (Agilent, CA, USA), with both excitation and emission slit widths of 5 nm. EEMs were produced by repeatedly scanning over even emission wavelengths between 230 nm and 600 nm for each excitation wavelength between 220 nm and 450 nm with a 5 nm excitation increment. Detector power was set to high to magnify the low signal characteristic of the open ocean. Standard corrections were applied to each EEM using the paRafac.correction R library (LaBrie et al., 2017a). It should be noted that additional profiles were done for

CDOM and FDOM to capture ecosystem variability along the AR7W.

A data set of 62, 133 and 225 samples for the 2014, 2015 and 2016 cruises, respectively, consisting of surface (60 m) and deep (3500 m) profiles was compiled and analysed using parallel factor analysis (PARAFAC) on MATLAB (R2016a) with drEEM (v0.1.0) toolbox (Murphy et al., 2013). Only stations where community composition were sampled are presented here (28 samples over the three sampling years). The first 50 nm wavelength in emission and 30 nm wavelength in excitation were removed to avoid modelling instrument noise. Five independent fluorescent components (Fig. S3.2) were validated by split half and random initialization parameters. Components are presented as follows, $F_{\lambda em}X$, where F refers to FDOM, and $_{\lambda em}X$ is the emission wavelength at which the fluorescence intensity was maximum. This notation was chosen since each component must have distinct emission values that reflect their aromaticity (Romera-Castillo et al., 2011), and although Coble's terminology (Coble, 1996) is widely used, each peak now refers to a large fluorescent region (Wünsch et al., 2019) and is thus less informative than the emission wavelength. The correspondence to Coble's terminology is presented in the SI (Table S1).

Samples for AAs were filtered using 0.2 μm polycarbonate filters and stored frozen until processing in the lab. AAs were determined using a high-performance liquid chromatography (HPLC) 1100 series system (Agilent, CA, USA) equipped with a LiCrospher RP18 (Merck, Germany) (4 x 250 mm column with 5 μm particles) and a fluorescence detector. Samples were hydrolyzed in the vapor phase with 6 M HCl at 150°C for 32.5 min. After hydrolysis, samples were neutralized and separated as OPA derivatives (Lindroth and Mopper, 1979). Asparagine and glutamine were deaminated during the hydrolysis and were quantified as aspartic acid (Asx) and glutamic acid (Glx). Protein amino acids (i.e. L-amino acids, see Fig. 3.4) are considered here as readily bioavailable molecules (Nagata et al., 2003; Dauwe et al., 1999).

2.2.3. *Bacterial abundance, community composition and structure*

Samples were fixed with 0.1% final concentration glutaraldehyde grade I (Sigma-Aldrich G5882, MO, USA), flash-frozen onboard and kept at -80°C until analysis. Samples were thawed in water at room-temperature, stained with SYBR green 1 (Invitrogen, CA, USA) in tris-EDTA buffer (10 mM Tris, 1 mM EDTA) (Belzile et al., 2008) for 10 minutes and 1 μm microspheres (Fluoresbrite plain YG, Polysciences, IL, USA) were added to each as an internal standard. Enumeration was done on an Epics Altra flow cytometer (Beckman Coulter, CA, USA) equipped with a 488 nm laser (15 mW output) at a flow rate of $\sim$ 200 μl/s during 180s.

Water for DNA extraction was sequentially filtered on board with a peristaltic pump using silicone tubing, which was acid washed between each sample run. Samples were first filtered through a 3 μm polycarbonate filter, followed by a 0.2 μm polyethersulfone (PES) filters (Sterivex, Millipore, MA, USA). Filters were conserved in lysis buffer (EDTA 40 mM, Tris 50 mM and sucrose 750 mM), flash frozen, and stored at -80°C until further processing.

DNA was extracted using an extraction kit (Qiagen, DNeasy Power Water) and DNA quantification was done with a Qubit 2.0 fluorometer (Invitrogen, Life Technologies, CA, USA) high sensitivity kit, following manufacturers' instructions. From a total of 148 samples extracted for the three years, 28 samples filtered at 0.2μm were sequenced to cover all water masses. DNA amplification, library preparation and Illumina sequencing of 16S rRNA gene were done at the Integrated Microbiome Resources in Dalhousie University (Comeau et al., 2017). Briefly, a dual-indexing, one-step PCR was done using a Nextera XT v2 kit (Illumina) with the adapters and index provided by the kit. Region V6-V8, bacterial 16S rRNA gene was targeted with primers B969F (ACGCGHNRAACCTTACC) and BA1406R (ACGGGCRGTGWGTRCAA). PCR amplification was run for 30 cycles. The amplicons quality was visualized with a 96-well E-gel (Invitrogen), purified and normalized with the high-throughput SequalPrep 96-well plate kit (Invitrogen). Samples were pooled to make one library and quantify using Qubit double-stranded DNA high-sensitivity kit (Invitrogen).

Reads were analyzed with the DADA2 pipeline following the tutorial v.1.14 (Callahan et al., 2016) using the R software v.3.6.2. Briefly, the Dada2 pipeline filters sequences of less than 270 and less than 200 for forward and reverse sequencing, respectively; dereplicates all sequences, i.e. combines identical sequencing reads into unique sequences; combines forward and reverse sequences and removes chimeras. After the processing, 1701 amplicon sequence variants (ASV) were obtained (1 235 277 reads) and taxonomically classified based on the SILVA database v128.

All ASV abundances were corrected for the number of gene copy (NGC) using information provided on the rrnDB website (https://rrndb.umms.med.umich.edu/, February 2020), resulting in 708 500 "corrected" reads. When the 16S NGC was not found at the genus level, we took the average 16S copy of the next taxonomic rank until all ASV abundances were corrected. The average NGC was 3.7 $\pm$ 0.5 for Genus only, 2.0 $\pm$ 1.4 for all ASV and 66.5% of ASV were corrected by the Order taxonomic level. Then, all ASV with a number of sequences equal to or less than 10 in a single sample were treated as noise and removed (679 ASV, 703 226 reads). In order to focus on DOM-consumers interactions, we kept only heterotrophs (we removed cyanobacteria). Finally, we transformed the number of reads in relative values for each site and multiplied by the total abundance as measured by flow

cytometry (575 ASVs).

Spatial Abundance Distribution (SPAD) modelling was computed following Nino-Garcia and collaborators (2016). Briefly, each ASV was categorized as "bimodal" if they deviated from unimodality (p-value < 0.05). All other ASVs were fitted with "normal-like" distributions (normal, Weibull, gamma and Cauchy), lognormal and logistic distributions. To do so, all sites were pooled together to construct a distribution of the abundance of each ASV across all sites (log10 transformed), i.e. the number of sites as a function of abundance, independently of the location of sampling (Fig. S3.3 a to d). The best fit was chosen based on the lowest Akaike information criterion (AIC). All ASV distributions were verified visually to make sure they were well categorized in their SPAD group; 69 out of 575 ASVs (12%) were erroneously classified before this cross-check and were manually reassigned (e.g. Fig. S3.3 e to g).

2.2.4. *Bacterial heterotrophic production and respiration*

Samples were collected and maintained at 4°C in the dark for a maximum of 3 hours before processing. Bacterial heterotrophic production (BHP) was measured following Smith and Azam (1992) with minor modifications. Samples of 1.5 ml were incubated in the dark at 4°C with [3, 4, 5-^{3}H]-L-leucine (∼10 nM final concentration, Perkin Elmer) for 3 hours in triplicate with a TCA killed control (5% final concentration). Incubations were terminated by adding TCA (5% final concentration) and briefly vortexed before being frozen until further processing in the lab. Samples were thawed at room temperature, centrifuged at 17 000 G (13 000 RPM) using an accuSpin micro17 centrifuge (Thermo Fisher, MA, USA) and gently siphoned to the last drop. Samples were acidified with TCA, vortexed, centrifuged and siphoned again. Vials were filled with 1.5 ml of scintillation cocktail (ScintiVerse, Thermo Fisher) and stored for 1 hour before counting on a Tri-carb 2800TR (Perkin Elmer). Carbon incorporation rates were calculated back using 1550 g C mol leucine^{-1}.

Bacterial respiration (BR) measurements were performed using Winkler titration (Carignan et al., 1998) on a potentiometric G20 compact titrator (Metler-Toledo, OH, USA) in 2015 and 2016. Water was pre-screened by passage through a 53 μm nylon mesh (prewashed with nano-pure water) to remove large particles and zooplankton. Dissolved oxygen was measured in triplicate in 300 ml BOD bottles at time zero while another set of triplicates were incubated at near in situ temperature (-3.6°C to 4.4°C), in the dark, for 24 to 36 hours in refrigerated circulators (ARCTIC A10B, Thermo Fisher). Oxygen consumption rates were calculated by subtracting oxygen concentrations in post-incubation from concentrations in pre-incubation BOD bottles and divided by the incubation time. An oxygen-to-carbon ratio of 1 mol O_2: mol C was used to transform O_2 into CO_2.

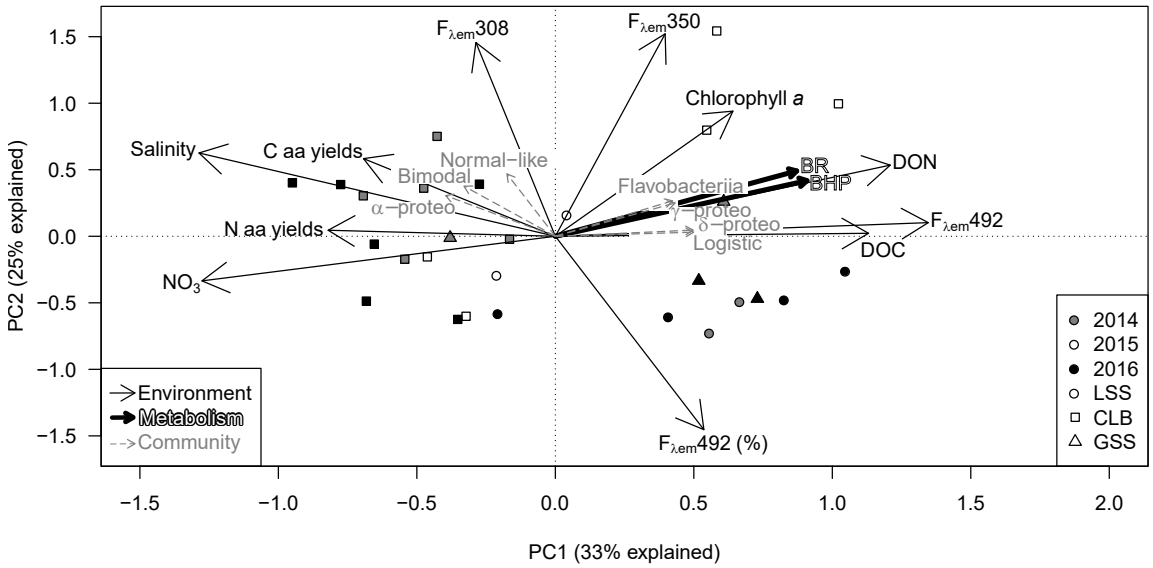
2.3. Statistical analysis

In order to best characterize our different sites, all environmental variables were plotted using a principal component analysis (PCA). Variables that represent components of community structure and metabolism (BHP and BR) were then projected using the env.fit() function of the vegan (Oksanen et al., 2018) package. In order to fill the gaps of missing data to perform the PCA (largely AAs in 2016, BR in 2014), we imputed values with a random forest using the MissForest() function from the MissForest R package (Stekhoven, 2013). These imputed values were only used for the PCA.
Linear regressions and spearman rank correlation were used to explore different relationships between bacterial community structure, metabolism and different DOM components.
When required, variables were log transformed to meet normality assumptions of some of the tests. All statistics and graphs were produced using the R software v.3.4.1.

3. Results

In order to explore how the community structure related to both environmental variables and metabolism, we considered both the main taxonomic classes ($\alpha-, \gamma-, \delta-$ proteobacteria, Flavobacteriia) as well as the different SPAD groups of the entire set of ASVs. In terms of the SPAD, only 21 ASVs were identified as ubiquitous distributed in the dataset (i.e. normal-like SPAD), which consisted of $\alpha-$proteobacteria (SAR11, Rickettsiales and Rhodobacterales), $\gamma-$proteobacteria (Oceanospirillales and Cellvibrionales) and Flavobacteriia (Flavobacteriales), but together represented on average 65% of the total abundance. The bloomer SPAD group was more diverse with 76 ASVs, but was dominated by the same orders as the ubiquitous group (e.g. 32x SAR11, 17x Flavobacteriales and 11x Oceanospirillales). Overall, bloomer ASVs represented 24% of the total abundance. Minor contributors to the bloomer group included Alteromonadales (4x), Rhodobacterales (7x), Rhodospirillales (5x). ASVs in the lognormal and logistic SPAD behaved similarly across all site (Fig. S3.4, r = 0.77). These were merged together for subsequent analyses and referred to as spatially constrained, or rare SPAD ASVs. This was the most diverse SPAD group with 381 different ASVs (see Fig. S3.5 for relationships between SPAD group abundance and diversity indices), again belonging to the same orders as cosmopolitans (e.g. 124x SAR11, 28x Rhodospirillales and 41x Flavobacteriales), but it also contained orders that were always rare (e.g. 3x Cytophagales and 4x Verrucomicrobiales). The complete taxonomy and its association to SPAD groups is available in the SI. We further explored the use of the SPAD groups, but within taxonomic classes (e.g. $\alpha-$proteobacteria ubiquitous SPAD group).

In order to summarize the spatial heterogeneity along the Labrador Sea transect, over the three sampling years, we represented general environmental conditions on a PCA


$F_{\lambda em}308$
$F_{\lambda em}350$
Chlorophyll *a*
Salinity
C aa yields
Normal−like
Bimodal
Flavobacterija
BR
BHP
DON
α−proteo
γ−proteo
δ−proteo
Logistic
$F_{\lambda em}492$
N aa yields
DOC
NO_3
$F_{\lambda em}492$ (%)
Environment
Metabolism
Community
2014
2015
2016
LSS
CLB
GSS
PC2 (25% explained)
PC1 (33% explained)
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−1.5
−1.0
−0.5
0.0
0.5
1.0
1.5
2.0

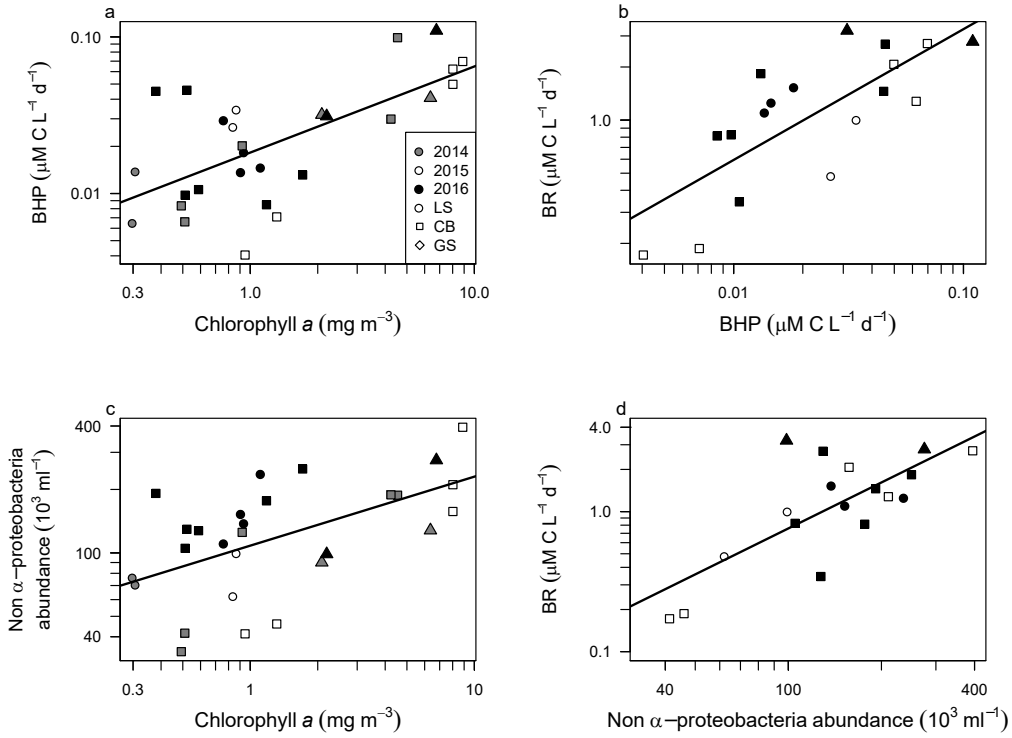


Fig. 3.2. Classical relationships between BHP and chlorophyll a (panel a) and BR (panel b), abundance and chlorophyll a (panel c) and BR (panel d). Figure legend (panel a) stands for all panels. All data are displayed on a log scale. LS: Labrador shelf; CB: Central basin; GS: Greenland shelf

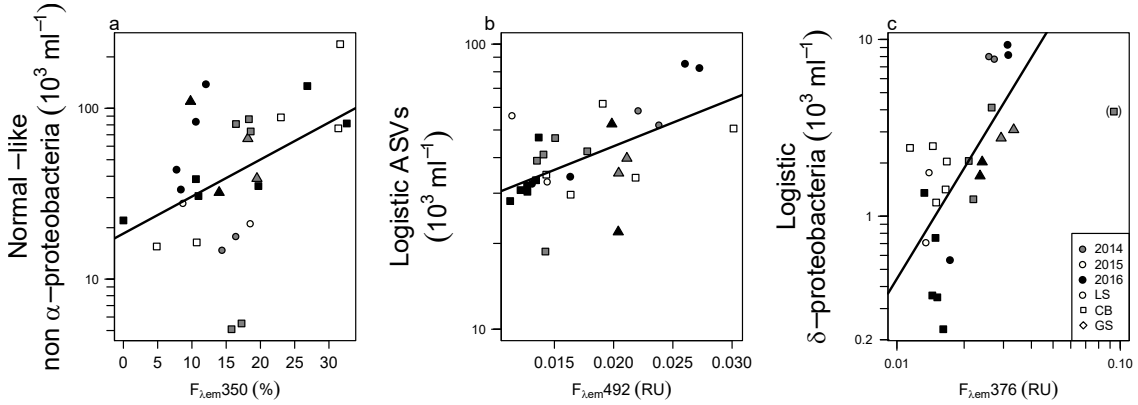


Fig. 3.3. Relationships between SPAD groups and FDOM. SPAD groups are displayed on a log axis. Parenthesis denote an outlier that was not considered in the linear regression (panel c). Figure legend (panel c) stands for all panels. LS: Labrador shelf; CB: Central basin; GS: Greenland shelf

and quality (Fig. 3.2). In terms of metabolism, there was a significant relationship with BHP ($R^2 = 0.55$, $p < 0.05$, Fig. 3.2a), but the relationship with respiration was not significant ($R^2 = 0.17$, $p = 0.09$, not shown). However, there was a significant relationship between BHP and BR ($R^2 = 0.58$, $p < 0.05$, Fig. 3.2b). Despite a broad range in chlorophyll *a* concentrations, we did not find a significant relationship with total bacterial abundance

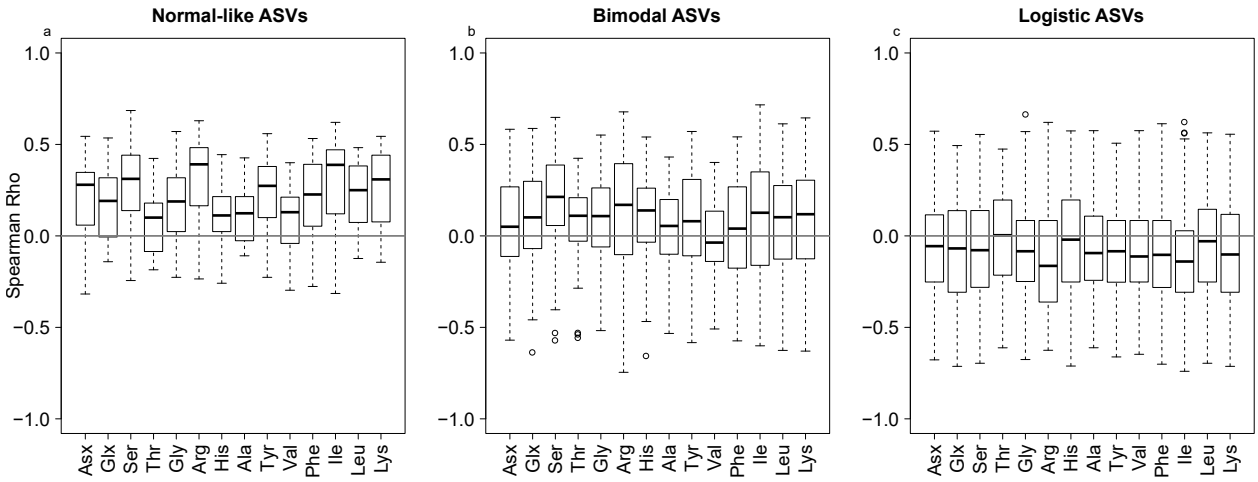


Fig. 3.4. Box-and-whiskers plots of Spearman correlations between each ASV grouped by ubiquitous (a, n = 21), bloomer (b, n = 76) and spatially constrained (c, n = 381) SPADs with individual amino acids. The grey line is at zero. Bold lines represent the median; boxes represent 25% − 75% interval and the whiskers represent 95% interval. Asx: aspartic acid and asparagine; Glx: glutamic acid and glutamine; Ser: Serine; Thr: threonine; Gly: glycine; Arg: arginine; His: histidine; Ala: alanine; Tyr: tyrosine; Val: valine; Phe: phenylalanine; Ile: isoleucine; Leu: leucine; Lys: lysine

($R^2 = 0.11$, $p = 0.08$, not shown). When we removed the dominant $\alpha-$proteobacteria and considered non $\alpha-$proteobacteria bacterial abundance only, we found a much better relationship with increased chlorophyll *a* ($R^2 = 0.31$, $p < 0.05$, Fig. 3.2c). We did find that both BR ($R^2 = 0.23$, $p < 0.05$, not shown) and BHP ($R^2 = 0.18$, $p < 0.05$, not shown) were positively associated with bacterial abundance, albeit rather weakly. However, when we only considered non $\alpha-$proteobacteria abundances the relationships with both BR ($R^2 = 0.55$, $p < 0.05$, Fig. 3.2d) and BHP ($R^2 = 0.41$, $p < 0.05$, not shown) were much stronger, suggesting that although $\alpha-$proteobacteria were the most abundant bacteria in our dataset, the subdominant classes influenced metabolism relatively more strongly. BR rates were even better explained when we considered non $\alpha-$proteobacteria abundance and BHP together ($R^2_{adj} = 0.68$, $p < 0.05$, not shown), suggesting that biomass production and community abundance have their own role in regards to DOM remineralization.

In order to better understand the links between bacterial community structure and organic matter bioavailability at an intermediate level of characterization, we looked at the relationship of different FDOM components that represent a gradient of lability with different facets of the community modelled using SPAD groups (Fig. 3.3). Ubiquitous bacterial taxa that were not $\alpha-$proteobacteria were associated with the proportion of fresh organic matter represented here with $F_{\lambda em}350$ ($R^2 = 0.18$, $p < 0.05$, Fig. 3.3a). The relationship was not significant when $\alpha-$proteobacteria were included ($R^2 = 0.09$, $p =$

0.12, not shown), again suggesting that they were not as responsive as the subdominant classes. On the other hand, spatially constrained bacteria were associated with more complex forms of DOM, $F_{\lambda em}492$ ($R^2 = 0.29$, $p < 0.05$, Fig. 3.3b) and spatially constrained $\delta-$proteobacteria in particular was more closely associated with $F_{\lambda em}492$ ($R^2 = 0.40$, $p < 0.05$, not shown) as well as with another form of complex DOM, $F_{\lambda em}376$ ($R^2 = 0.49$, $p < 0.05$, Fig. 3.3c). Overall, this class of prokaryote was strongly associated with overall DOC concentrations ($R^2 = 0.57$, $p < 0.05$, not shown) as well as with the complex aromatic groups combined ($F_{\lambda em}376 + F_{\lambda em}492$, $R^2 = 0.56$, $p < 0.05$, not shown). These results suggest that ubiquitous and spatially constrained bacterial taxa are associated with distinctive DOM classes and therefore have different ecological roles with regards to DOM cycling.

To explore this ecological role further, we summarized Spearman correlations between each ASV belonging to ubiquitous (panel a), bloomer (panel b) and spatially constrained (panel c) SPAD groups and each AA using box-and-whiskers plots (Fig. 3.4). Overall, the relationships between ubiquitous ASVs and AAs were positive. The median Spearman correlation coefficients were slightly above zero for bloomer ASVs (Fig. 3.4b) and slightly negative for spatially constrained ASVs (Fig. 3.4c), with an overall similar span. The results for spatially constrained ASVs are coherent with what was observed with FDOM in that they were associated with more complex forms of DOM rather than simpler forms like AAs.

By combining community structure (SPAD modelling) and composition at the class level, we were able to better partition the variation of these relationships with the different AAs (Fig. 3.5). Correlation coefficients between ubiquitous $\alpha-$-proteobacteria and AAs were generally around zero (Fig. 3.5a, n = 10). However, patterns with non-$\alpha-$ proteobacteria classes were much more apparent. Ubiquitous $\gamma-$protebacteria (Fig. 3.5b, n = 4) and Flavobacteriia (Fig. 3.5c, n = 7) were generally positively correlated with most AAs. Finally, spatially constrained $\delta-$proteobacteria were negatively correlated with most amino acids, with a median Spearman correlation of around -0.30 (Fig. 3.5d, n = 4).

To look at patterns between community structure and composition with ecosystem metabolism, we tested all relationships between respiration or production rates with these categories: total abundance, SPAD groups abundance, taxonomic abundance at the class level (single and 2 classes) and a combination of SPAD with taxonomy. We compared those linear log-log regressions using Akaike Information Criteria (AIC) and reported only one per category that better explained metabolic rates as compared to total abundance (table 1). For both metabolic rates, the variance explained by SPAD groups alone was similar to total abundance. For production rates, single and dual taxonomic classes abundance along with

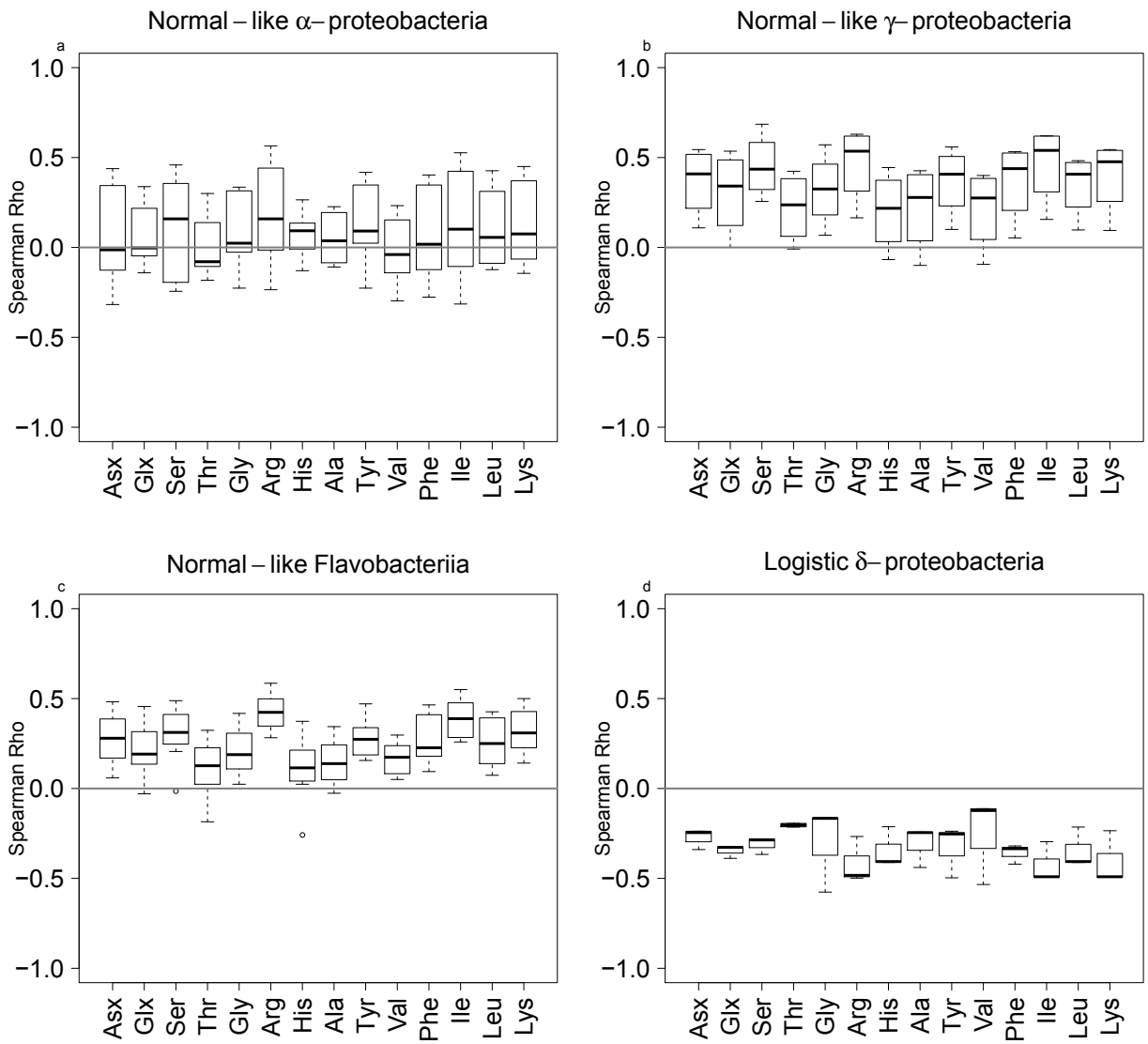


Fig. 3.5. Box-and-whiskers plots of Spearman correlations between each ASV grouped by their SPAD group and taxonomy (at the class level) with individual amino acids. The grey line is at zero. Bold lines represent the median; boxes represent 25% − 75% interval and the whiskers represent 95% interval. Asx: aspartic acid and asparagine; Glx: glutamic acid and glutamine; Ser: Serine; Thr: threonine; Gly: glycine; Arg: arginine; His: histidine; Ala: alanine; Tyr: tyrosine; Val: valine; Phe: phenylalanine; Ile: isoleucine; Leu: leucine; Lys: lysine

SPAD-taxonomy performed similarly, with a R^2 of around 0.40 ($p < 0.05$). However, the combination of SPAD modelling with taxonomy generated the best and most parsimonious fit for respiration rates with a R^2 of 0.62. These results suggest that SPAD modelling is a promising tool to relate bacterial community composition and structure to ecosystem metabolism.

Tableau 3.1. Summary table of metabolic rates as a function of community structure and composition.

Metabolic rate	Explanatory variable(s)	Regression line	R^2	p-value	AIC
Respiration	Total abundance	-12.98 + 0.99A	0.24	*	46.7
	Bloomer abundance	-11.96 + 1.02A	0.25	*	46.6
	$\gamma-$proteo	-9.83 + 0.91A	0.45	**	40.8
	$\gamma-$proteo + Flavobacteriia	-13.02 + 0.78A + 0.43B	0.56	***	36.5
	Ubi Flavobacteriia + bloomer $\gamma-$proteo	-10.28 + 0.47A + 0.53B	0.62	***	33.8
Production	Total abundance	-13.3 + 0.72A	0.18	*	72
	Bloomer abundance	-11.38 + 0.59A	0.17	*	72.3
	$\gamma-$proteo	-12.12 + 0.78A	0.38	***	63.9
	$\gamma-$proteo + Flavobacteriia	-14.23 + 0.64A + 0.33B	0.42	***	62.1
	Ubi Flavobacteriia + bloomer $\gamma-$proteo	-11.8 + 0.37A + 0.42B	0.42	***	62.1

Note. Parameters A and B under the regression line column represent the first and second explanatory variable, respectively. For multiple regressions, reported R^2 are the adjusted R^2. All variables were log-transformed. *: less than 0.05; **: less than 0.01; ***: less than 0.001 Ubi: ubiquitous; SPAD: spatial abundance distribution; AIC: Akaike Information Criterion

4. Discussion

One of the main goals in aquatic microbial ecology is to relate resource bioavailability with bacterial community composition and link interactions to large-scale ecosystem function. However, the challenge is trying to identify those patterns between community structure, resource availability, and metabolic processing across different scales of inquiry using multiple approaches. In this study, we found that the dominant bacterial class, $\alpha-$proteobacteria, was not as associated with chlorophyll *a*, metabolism (BR and PHO) and abundance (Fig. 3.2) as the subdominant classes were. Additionally, SPAD modelling increased our ability to relate bacterial community structure to resource limitation, both at the community SPAD level with FDOM, but also at the genus level with AAs. Finally, combining SPAD modelling taxonomic composition best described the association between community structure and resource availability (Fig. 3.5).

In this study, substrate bioavailability influenced patterns in both metabolic processing and community structure. Using chlorophyll *a* concentrations as a proxy for fresh organic matter inputs, we found good relationships with BHP but not with PR, as was observed in other studies (López-Urrutia and Morán, 2007; Nguyen et al., 2012; Regaudie-de Gioux and Duarte, 2010). However, the relationship between chlorophyll *a* and abundance only

emerged when the dominant bacterial class $\alpha-$proteobacteria was removed from the total. This lack of a relationship with $\alpha-$proteobacteria has been previously reported (Alonso-Sáez et al., 2012). One possible explanation is that $\alpha-$proteobacteria were never limited by substrate availability, and thus no pattern could emerge with environmental conditions or metabolic rates. Therefore, by using the range in abundance of non $\alpha-$proteobacteria, patterns with chlorophyll *a* emerged. The sub-dominant groups likely became more active as phytoplankton abundance increases, moving from dormancy (Jones and Lennon, 2010) or a low activity state to higher metabolic activity. Indeed, BR rates were best explained when both the sub-dominant bacterial abundance was considered together with BHP. This suggests that substrate availability limited their growth, which in turn regulated carbon remineralization.

Spatial abundance distribution modelling emerged as a rather simple and effective tool to characterize bacterial ecological niches. The abundance of the ubiquitous and spatially constrained SPAD groups responded to very different types of organic matter: freshly produced $F_{\lambda em}350$ and the more recalcitrant $F_{\lambda em}492$, respectively. To our knowledge, patterns of this type are yet to be reported. Although the relationship between ubiquitous and $F_{\lambda em}350$ was a bit weak, this FDOM peak is known to be cycled rapidly (Romera-Castillo et al., 2011,0), presumably consumed by ubiquitous bacteria, since its behavior resembles those of amino acids (Yamashita and Tanoue, 2003). On the other hand, spatially constrained ASVs seemed to feed on more complex forms of DOM, or potentially produce them (Ogawa et al., 2001; Jiao et al., 2010), which represented on average 60% of the total FDOM pool. This association between spatially constrained ASVs and recalcitrant DOM is a plausible explanation to the dominance of the spatially constrained SPAD group in regards to total bacterial diversity (Fig. S3.7). It also helps to explain why environments that hold vast amounts of recalcitrant DOM (Hansell, 2013), such as the deep oceans (Hansell and Carlson, 1998), highly terrestrially connected freshwaters 10 and soils bear such a large bacterial diversity (Sogin et al., 2006; Fierer and Jackson, 2006; Crump et al., 2012). As a concrete example of this association of rare classes with more recalcitrant DOM, ASVs of the $\delta-$proteobacteria class, which all belonged to the spatially constrained SPAD group in our study, were very strongly related with $F_{\lambda em}492$ as well as with another complex form of DOM, $F_{\lambda em}376$.

Using SPAD modelling allowed us to coarsely group ASVs based on their potential ecological niche to represent their correlation with specific compounds (amino acids). This approach again showed that ubiquitous ASVs responded generally positively to fresh organic matter while spatially constrained ASVs responded negatively, both coherent with FDOM patterns. However, it also revealed that bloomer ASVs seemed to respond as both

ubiquitous and spatially constrained ASVs. Although SPAD was developed to summarize spatial distribution (Conlisk et al., 2012), we found that the bimodal distribution also captures temporal variations in ASV abundance. Clear examples in our dataset are four ASVs belonging to the genus Pseudoalteromonas which were absent in most stations in 2014 and/or 2015, but highly abundant in 2016, or vice-versa. If the three sampling years had been analyzed separately, these ASVs would have been classified as spatially constrained or ubiquitous, respectively, suggesting a potential high diversity in this genus. Over the timescale of a bloom, many ASVs would be categorized as bloomer since many are known to have very dynamic abundances (Teeling et al., 2012) that act in a successional pattern. Thus, they could be categorized as ubiquitous if the period of sampling fell only during their maximal abundance and as spatially constrained while on decline. This may be why we observe this pattern among years with Pseudoalteromonas.

By further grouping ASVs using their SPAD group as well as their higher taxonomic rank enabled us to find distinctive patterns with AAs, but once again, these were not apparent for $\alpha-$proteobacteria. The responses of the sub-dominant classes $\gamma-$proteobacteria, Flavobacteriia, and $\delta-$proteobacteria were more constrained toward higher and lower Spearman values for both ubiquitous and spatially constrained ASVs, respectively. Surprisingly, Flavobacteriia were positively associated with AAs concentrations despite the fact that they typically do not consume them (Kirchman, 2002); these are known to feed primarily on high molecular weight DOM, such as transparent exopolymer particles (TEP) (Taylor et al., 2014; Kappelmann et al., 2019). We suspect that AAs concentrations and TEP covaried in the Labrador Sea since both are produced by Phaeocystis pouchetii (Eberlein et al., 1985; Passow, 2002), which was the dominant phytoplankton species during the spring bloom on the eastern side of the Labrador Sea (Fragoso et al., 2016; Péquin et al., shed). These good relationships between AAs and $\gamma-$proteobacteria and Flavobacteriia provide insight to better understand carbon processing. Indeed, production rates were well explained by these prokaryotic classes abundance, presumably as these ASVs were well associated with labile substrates. Respiration rates were also well explained by these two classes. However, the combination of SPAD groups with taxonomic composition best explained respiration rates. Overall, SPAD modelling is a great complementary tool to taxonomic composition and both act in synergy to identify microbial ecological niches.

Finding approaches to better understand this intimate relationship is a common pursuit in microbial ecology, but remains a challenge, particularly in natural settings. Trying to disentangle these different relationships between bacterial community structure, ecosystem functions, and environmental conditions in the dynamic region of the Labrador Sea was a challenge. Through this exploration, however, it became apparent that we are often looking

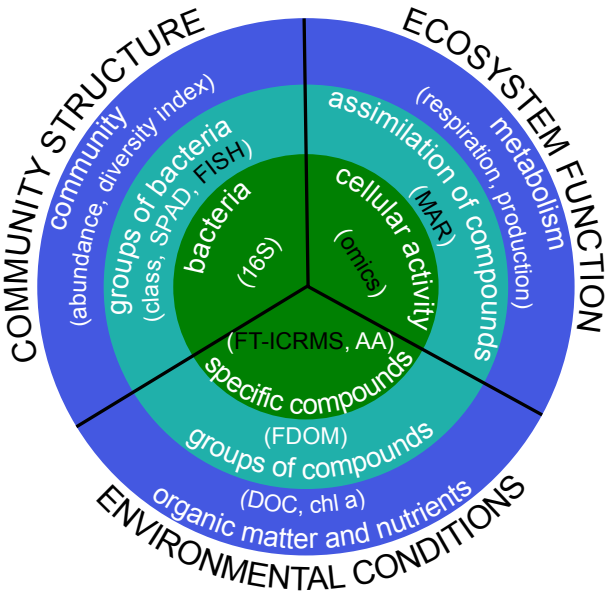


Fig. 3.6. Conceptual figure on how environmental conditions, microbial community structure and ecosystem functions interact across different scales. Rings represent the different levels of characterization of these three component parts using techniques often used in microbial ecology, environmental chemistry, geochemistry and biogeochemistry that can be most realistically compared. Techniques and approaches represented in the middle ring can be used to bridge elements from the more macroscale to more detailed elements of inquiry (represented in outer and inner rings, respectively). Words in white are examples of variables measured in this study and those in blacks are approaches that likely apply, but that were not performed here.

at different ecosystem properties across multiple scales of inquiry that are difficult to relate. As such, we propose a novel framework that enables a better understanding of how various levels of characterization of different variables could be interlinked among ecosystem properties (Fig. 3.6). Finding conclusive patterns between bacterial community structure, ecosystem functioning, and environmental conditions requires matching techniques that reflect the scale of inquiry of different variables.

We suggest that comparisons should be done primarily between methods and approaches at the same level of characterization (Fig. 3.6), which is similar to the observation made by Martiny and collaborators (2015) regarding the conservation of genes across multiple taxonomic ranks. Throughout this study, we used this model as a guideline for our analyses (e.g. chlorophyll *a* and BHP, Fig. 3.2a, SPAD and FDOM, Fig. 3.3, AAs and ASVs, Figs 3.4-3.5). Examples from the literature that have successfully done these associations at the middle ring level include the use of MAR-FISH to bridge compound assimilation to specific groups of bacteria (Nielsen and Nielsen, 2005) in both aquatic (Teira et al., 2006) and soil environments (Rogers et al., 2007). At a more detailed level of inquiry, the combined use of ultra-high-resolution mass spectrometry (FT-ICR MS) with meta-proteomic linked specific compounds to microbial protein expression (Maier et al., 2017) in the gut microbiome. These examples bridge two ecosystem properties within the same ring, or scale of inquiry (Fig. 3.6). We propose that the middle ring can act as a bridge between scales and across ecosystem properties. Indeed, we show that SPAD modelling offers a simple and efficient way to cluster ASVs based on their ecological niche as evidenced by the preference of SPAD ASV classes for different compounds and increases the predictive power of taxonomic

composition on key ecosystem processes.

In this study, we show that SPAD modelling served as a very useful approach to elucidate how different ASVs responded to rather specific environmental conditions and ecosystem functioning. Specifically, SPAD modelling allowed us to identify novel relationships that related prokaryotic classes to the availability of different groups of organic compounds. Finally, we believe that figure 3.6 can act as a useful framework to better design, guide us and challenge how we approach the relationships between biogeochemistry, prokaryotic diversity, and microbial ecology to better understand how carbon flows in aquatic ecosystems.

5. Data availability

Raw reads were deposited on NCBI Sequence Read Archive (accession number PRJNA578129). All other data and scripts are available at www.github.com/laboMaranger/LabradorSeaTransect and attributed a DOI using Zenodo (will be made available upon acceptance).

6. Acknowledgement

We'd like to thank all crew members and officers of the CCGS Hudson. Special thanks to Bérangère Péquin (UdeM) for preforming the DNA extractions and help with preliminary ASV interpretation, Yuan Shen (USC) for Amino Acid analyses and Alexandre Théberge (UQAR) for CDOM and FDOM analyses. No financial benefits were received from this publication, and all authors declare no conflict of interest. This work was funded by an FQRNT student scholarship to Richard LaBrie, a NSERC Discovery to Roxane Maranger and a NSERC-CCAR. This work is a contribution to the Groupe de recherche interuniversitaire en limnologie (GRIL) and Ventilation, Interactions and Transports Across the Labrador Sea (VITALS - RGPCC 433898 - led by P. Myers, U. Alberta).

Références bibliographiques

Alonso-Saez, L., Gasol, J. M., Aristegui, J., Vilas, J. C., Vaque, D., Duarte, C. M., and Agusti, S. (2007). Large-scale variability in surface bacterial carbon demand and growth efficiency in the subtropical northeast atlantic ocean. *Limnology and Oceanography*, 52(2):533–546.

Alonso-Sáez, L., Sánchez, O., and Gasol, J. M. (2012). Bacterial uptake of low molecular weight organics in the subtropical atlantic: Are major phylogenetic groups functionally different? *Limnology and Oceanography*, 57(3):798–808.

Amon, R. M. W., Fitznar, H. P., and Benner, R. (2001). Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. *Limnology and Oceanography*, 46(2):287–297.

Aristegui, J., Gasol, J. M., Duarte, C. M., and Herndl, G. J. (2009). Microbial oceanography of the dark ocean's pelagic realm. *Limnology and Oceanography*, 54(5):1501–1529.

Azam, F., Fenchel, T., Field, J., Gray, J., Meyer-Reil, L., and Thingstad, F. (1983). The ecological role of water-column microbes in the sea. *Marine ecology progress series. Oldendorf*, 10(3):257–263.

Bélanger, S. (2019). *RspectroAbs: Routines to convert spectrophotometric optical depth (Absorbance) to absorption coefficient for dissolved and particulate matter and apply spectral analyses*. R package version 1.4.

Belzile, C., Brugel, S., Nozais, C., Gratton, Y., and Demers, S. (2008). Variations of the abundance and nucleic acid content of heterotrophic bacteria in beaufort shelf waters during winter and spring. *Journal of Marine Systems*, 74(3-4):946–956.

Benner, R. (2002). Chemical composition and reactivity. *Biogeochemistry of marine dissolved organic matter*, 3:56–90.

Broek, T. A., Walker, B. D., Guilderson, T. P., and McCarthy, M. D. (2017). Coupled ultrafiltration and solid phase extraction approach for the targeted study of semi-labile high molecular weight and refractory low molecular weight dissolved organic matter. *Marine Chemistry*, 194:146–157.

Callahan, B. J., McMurdie, P. J., Rosen, M. J., Han, A. W., Johnson, A. J. A., and Holmes, S. P. (2016). Dada2: high-resolution sample inference from illumina amplicon data. *Nature methods*, 13(7):581.

Carignan, R., Blais, A. M., and Vis, C. (1998). Measurement of primary production and community respiration in oligotrophic lakes using the winkler method. *Canadian Journal of Fisheries and Aquatic Sciences*, 55(5):1078–1084.

Catalá, T. S., Reche, I., Fuentes-Lema, A., Romera-Castillo, C., Nieto-Cid, M., Ortega-Retuerta, E., Calvo, E., Álvarez, M., Marrasé, C., Stedmon, C. A., and Álvarez-Salgado, X. A. (2015). Turnover time of fluorescent dissolved organic matter in the dark global ocean. *Nat Commun*, 6.

Catalan, N., Marce, R., Kothawala, D. N., and Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geosci*, 9(7):501–504.

Coble, P. G. (1996). Characterization of marine and terrestrial dom in seawater using excitation-emission matrix spectroscopy. *Marine chemistry*, 51(4):325–346.

Comeau, A. M., Douglas, G. M., and Langille, M. G. I. (2017). Microbiome helper: a custom and streamlined workflow for microbiome research. *MSystems*, 2(1).

Conlisk, J., Conlisk, E., Kassim, A. R., Billick, I., and Harte, J. (2012). The shape of a species' spatial abundance distribution. *Global Ecology and Biogeography*, 21(12):1167–1178.

Cottrell, M. T. and Kirchman, D. L. (2000). Natural assemblages of marine proteobacteria and members of the cytophaga-flavobacter cluster consuming low-and high-molecular-weight dissolved organic matter. *Applied and Environmental Microbiology*, 66(4):1692–1697.

Crump, B. C., Amaral-Zettler, L. A., and Kling, G. W. (2012). Microbial diversity in arctic freshwaters is structured by inoculation of microbes from soils. *The ISME journal*, 6(9):1629.

Dauwe, B., Middelburg, J. J., Herman, P. M., and Heip, C. H. (1999). Linking diagenetic alteration of amino acids and bulk organic matter reactivity. *Limnology and Oceanography*, 44(7):1809–1814.

Davis, J. and Benner, R. (2007). Quantitative estimates of labile and semi-labile dissolved organic carbon in the western arctic ocean: A molecular approach. *Limnology and Oceanography*, 52(6):2434–2444.

del Giorgio, P. A., Cole, J. J., and Cimbleris, A. (1997). Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. *Nature*, 385(6612):148–151.

Duarte, C. M., Agusti, S., Vaque, D., Agawin, N. S. R., Felipe, J., Casamayor, E. O., and Gasol, J. M. (2005). Experimental test of bacteria-phytoplankton coupling in the southern ocean. *Limnology and Oceanography*, 50(6):1844–1854.

Eberlein, K., Leal, M., Hammer, K., and Hickel, W. (1985). Dissolved organic substances during a phaeocystis pouchetii bloom in the german bight (north sea). *Marine Biology*, 89(3):311–316.

Elifantz, H., Malmstrom, R. R., Cottrell, M. T., and Kirchman, D. L. (2005). Assimilation of polysaccharides and glucose by major bacterial groups in the delaware estuary. *Applied and Environmental Microbiology*, 71(12):7799–7805.

Escoubeyrou, K. and Tremblay, L. (2014). Quantification of free, dissolved combined, particulate, and total amino acid enantiomers using simple sample preparation and more robust chromatographic procedures. *Limnology and Oceanography-Methods*, 12:421–431.

Fierer, N. and Jackson, R. B. (2006). The diversity and biogeography of soil bacterial communities. *Proceedings of the National Academy of Sciences of the United States of America*, 103(3):626–631.

Fragoso, G. M., Poulton, A. J., Yashayaev, I. M., Head, E. J., Stinchcombe, M., and Purdie, D. A. (2016). Biogeographical patterns and environmental controls of phytoplankton communities from contrasting hydrographical zones of the labrador sea. *Progress in Oceanography*.

Fuhrman, J. A. and Hagström, A. (2008). Bacterial and archaeal community structure and its patterns. *Microbial Ecology of the Oceans, Second Edition*, pages 45–90.

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5.

Hansell, D. A. and Carlson, C. A. (1998). Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature*, 395(6699):263–266.

Herndl, G. J. and Reinthaler, T. (2013). Microbial control of the dark end of the biological pump. *Nature Geoscience*, 6(9):718–724.

Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A., and Hedges, J. I. (2006). Characterization of a major refractory component of marine dissolved organic matter. *Geochimica et Cosmochimica Acta*, 70(12):2990–3010.

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., and Strickland, J. D. H. (1965). Fluorometric determination of chlorophyll. *ICES Journal of Marine Science*, 30(1):3–15.

Holmes, R. M., Aminot, A., Kérouel, R., Hooker, B. A., and Peterson, B. J. (1999). A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences*, 56(10):1801–1808.

Hopkinson, C. S., Vallino, J. J., and Nolin, A. (2002). Decomposition of dissolved organic matter from the continental margin. *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 49(20):4461–4478.

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., Kirchman, D. L., Weinbauer, M. G., Luo, T., and Chen, F. (2010). Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nature Reviews Microbiology*, 8(8):593–599.

Jones, S. E. and Lennon, J. T. (2010). Dormancy contributes to the maintenance of microbial diversity. *Proceedings of the National Academy of Sciences*, 107(13):5881–5886.

Kaiser, K. and Benner, R. (2005). Hydrolysis-induced racemization of amino acids. *Limnology and Oceanography: Methods*, 3(8):318–325.

Kappelmann, L., Krüger, K., Hehemann, J.-H., Harder, J., Markert, S., Unfried, F., Becher, D., Shapiro, N., Schweder, T., Amann, R. I., and Teeling, H. (2019). Polysaccharide utilization loci of north sea flavobacteriia as basis for using susc/d-protein expression for predicting major phytoplankton glycans. *The ISME Journal*, 13(1):76–91.

Kirchman, D. L. (2002). The ecology of cytophaga–flavobacteria in aquatic environments. *FEMS microbiology ecology*, 39(2):91–100.

Kirchman, D. L. (2008). Microbial ecology of the oceans. 36.

Koch, B. P., Kattner, G., Witt, M., and Passow, U. (2014). Molecular insights into the microbial formation of marine dissolved organic matter: recalcitrant or labile? *Biogeosciences*, 11(15):4173–4190.

LaBrie, R., Fortin St-Gelais, N., and Bélanger, S. (2017). *paRafac.correction: an R Package to correct EEMs and derive CDOM and FDOM indices*.

LaBrie, R., Lapierre, J.-F., and Maranger, R. (Under review). Contrasting patterns of labile and semi-labile dissolved organic carbon from continental waters to the open ocean. *Journal of Geophysical Research: Biogeosciences*.

Lazier, J. R. The renewal of labrador sea water. In *Deep Sea Research and Oceanographic Abstracts*, volume 20, pages 341–353. Elsevier.

Lindroth, P. and Mopper, K. (1979). High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde. *Analytical Chemistry*, 51(11):1667–1674.

Logue, J. B., Stedmon, C. A., Kellerman, A. M., Nielsen, N. J., Andersson, A. F., Laudon, H., Lindström, E. S., and Kritzberg, E. S. (2015). Experimental insights into the importance of aquatic bacterial community composition to the degradation of dissolved organic matter. *The ISME Journal*.

López-Urrutia, A. and Morán, X. A. G. (2007). Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling. *Ecology*, 88(4):817–822.

Lønborg, C., Yokokawa, T., Herndl, G. J., and Álvarez-Salgado, X. A. (2015). Production and degradation of fluorescent dissolved organic matter in surface waters of the eastern north atlantic ocean. *Deep-Sea Research Part I-Oceanographic Research Papers*, 96:28–37.

Maier, T. V., Lucio, M., Lee, L. H., VerBerkmoes, N. C., Brislawn, C. J., Bernhardt, J. r., Lamendella, R., McDermott, J. E., Bergeron, N., and Heinzmann, S. S. (2017). Impact of dietary resistant starch on the human gut microbiome, metaproteome, and metabolome. *MBio*, 8(5):e01343–17.

Marchese, C., de la Guardia, L. C., Myers, P. G., and Bélanger, S. (2019). Regional differences and inter-annual variability in the timing of surface phytoplankton blooms in the labrador sea. *Ecological indicators*, 96:81–90.

Martiny, J. B., Jones, S. E., Lennon, J. T., and Martiny, A. C. J. S. (2015). Microbiomes in light of traits: a phylogenetic perspective. 350(6261):aac9323.

Moran, M. A., Kujawinski, E. B., Stubbins, A., Fatland, R., Aluwihare, L. I., Buchan, A., Crump, B. C., Dorrestein, P. C., Dyhrman, S. T., and Hess, N. J. (2016). Deciphering ocean carbon in a changing world. *Proceedings of the National Academy of Sciences*, pages 3143–3151.

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. parafac. *Analytical Methods*, 5(23):6557–6566.

Nagata, T., Meon, B., and L Kirchman, D. (2003). Microbial degradation of peptidoglycan in seawater. *Limnology and oceanography*, 48(2):745–754.

Nguyen, D., Maranger, R., Tremblay, J. E., and Gosselin, M. (2012). Respiration and bacterial carbon dynamics in the amundsen gulf, western2 canadian arctic. *Journal of Geophysical Research-Oceans*, 117:12.

Niño-García, J. P., Ruiz-González, C., and Del Giorgio, P. A. (2016). Landscape-scale spatial abundance distributions discriminate core from random components of boreal lake bacterioplankton. *Ecology letters*, 19(12):1506–1515.

Nielsen, J. L. and Nielsen, P. H. (2005). Advances in microscopy: microautoradiography of single cells. *Methods in enzymology*, 397:237–256.

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., and Benner, R. (2001). Production of refractory dissolved organic matter by bacteria. *Science*, 292(5518):917–920.

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P. R., O'Hara, R. B., Simpson, G. L., Solymos, P., Stevens, M. H. H., Szoecs, E., and Wagner, H. (2018). *vegan: Community Ecology Package*. R package version 2.4-6.

Passow, U. (2002). Production of transparent exopolymer particles (tep) by phyto-and bacterioplankton. *Marine ecology-progress series*, 236:1–12.

Pedler, B. E., Aluwihare, L. I., and Azam, F. (2014). Single bacterial strain capable of significant contribution to carbon cycling in the surface ocean. *Proceedings of the National Academy of Sciences of the United States of America*, 111(20):7202–7207.

Péquin, B., Fortin St-Gelais, N., LaBrie, R., and Maranger, R. (Unpublished). Bloom timing explains succession of protistan functional community structure.

Pomeroy, L. R. (1974). The ocean's food web, a changing paradigm. *Bioscience*, 24(9):499–504.

R Core Team (2017). *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.

Regaudie-de Gioux, A. and Duarte, C. M. (2010). Plankton metabolism in the greenland sea during the polar summer of 2007. *Polar Biology*, 33(12):1651–1660.

Rogers, S. W., Moorman, T. B., and Ong, S. K. (2007). Fluorescent in situ hybridization and micro-autoradiography applied to ecophysiology in soil. *Soil Science Society of America Journal*, 71(2):620–631.

Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrase, C. (2010). Production of chromophoric dissolved organic matter by marine phytoplankton. *Limnology and Oceanography*, 55(1):446–454.

Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrasé, C. (2011). Net production and consumption of fluorescent colored dissolved organic matter by natural bacterial assemblages growing on marine phytoplankton exudates. *Applied and Environmental Microbiology*, 77(21):7490–7498.

Ruiz-González, C., Logares, R., Sebastián, M., Mestre, M., Rodríguez-Martínez, R., Galí, M., Sala, M. M., Acinas, S. G., Duarte, C. M., and Gasol, J. M. (2019). Higher contribution of globally rare bacterial taxa reflects environmental transitions across the surface ocean. *Molecular ecology*, 28(8):1930–1945.

Simon, M., Cho, B. C., and Azam, F. (1992). Significance of bacterial biomass in lakes and the ocean: comparison to phytoplankton biomass and biogeochemical implications. *Marine Ecology Progress Series*, 86(2):103–110.

Simon, M. and Rosenstock, B. (2007). Different coupling of dissolved amino acid, protein, and carbohydrate turnover to heterotrophic picoplankton production in the southern ocean in austral summer and fall. *Limnology and Oceanography*, 52(1):85–95.

Smith, D. C. and Azam, F. (1992). A simple, economical method for measuring bacterial protein synthesis rates in seawater using 3h-leucine. *Mar. Microb. Food Webs*, 6(2):107–114.

Sogin, M. L., Morrison, H. G., Huber, J. A., Welch, D. M., Huse, S. M., Neal, P. R., Arrieta, J. M., and Herndl, G. J. (2006). Microbial diversity in the deep sea and the underexplored "rare biosphere". *Proceedings of the National Academy of Sciences*, 103(32):12115–12120.

Stedmon, C. A., Markager, S., and Kaas, H. (2000). Optical properties and signatures of chromophoric dissolved organic matter (cdom) in danish coastal waters. *Estuarine, Coastal and Shelf Science*, 51(2):267–278.

Stekhoven, D. J. (2013). *missForest: Nonparametric Missing Value Imputation using Random Forest*. R package version 1.4.

Stubbins, A., Lapierre, J.-F., Berggren, M., Prairie, Y., Dittmar, T., and Del Giorgio, P. (2014). What's in an eem? molecular signatures associated with dissolved organic fluorescence in boreal canada. *Environmental science & technology*, 48(18):10598–10606.

Taylor, J. D., Cottingham, S. D., Billinge, J., and Cunliffe, M. (2014). Seasonal microbial community dynamics correlate with phytoplankton-derived polysaccharides in surface coastal waters. *The ISME Journal*, 8(1):245.

Teeling, H., Fuchs, B. M., Becher, D., Klockow, C., Gardebrecht, A., Bennke, C. M., Kassabgy, M., Huang, S., Mann, A. J., and Waldmann, J. (2012). Substrate-controlled succession of marine bacterioplankton populations induced by a phytoplankton bloom. *Science*, 336(6081):608–611.

Teira, E., Van Aken, H., Veth, C., and Herndl, G. J. (2006). Archaeal uptake of enantiomeric amino acids in the meso-and bathypelagic waters of the north atlantic. *Limnology and Oceanography*, 51(1):60–69.

Violle, C., Navas, M., Vile, D., Kazakou, E., Fortunel, C., Hummel, I., and Garnier, E. (2007). Let the concept of trait be functional! *Oikos*, 116(5):882–892.

Wear, E. K., Carlson, C. A., James, A. K., Brzezinski, M. A., Windecker, L. A., and Nelson, C. E. (2015). Synchronous shifts in dissolved organic carbon bioavailability and bacterial community responses over the course of an upwelling-driven phytoplankton bloom. *Limnology and Oceanography*, 60(2):657–677.

Wünsch, U. J., Bro, R., Stedmon, C. A., Wenig, P., and Murphy, K. R. (2019). Emerging patterns in the global distribution of dissolved organic matter fluorescence. *Analytical*

Methods, 11(7):888–893.

Yamashita, Y. and Tanoue, E. (2003). Chemical characterization of protein-like fluorophores in dom in relation to aromatic amino acids. *Marine Chemistry*, 82(3-4):255–271.

Yashayaev, I. and Clarke, A. (2008). Evolution of north atlantic water masses inferred from labrador sea salinity series. *Oceanography*, 21(1):30–45.

Zark, M., Christoffers, J., and Dittmar, T. (2017). Molecular properties of deep-sea dissolved organic matter are predictable by the central limit theorem: Evidence from tandem ft-icr-ms. *Marine Chemistry*, 191:9–15.

Troisième article.

Deep ocean prokaryotes produce increasingly stable dissolved organic carbon

par

Richard LaBrie[1,2], Nicolas Fortin St-Gelais[1,2], Bérangère Péquin[1], Jennifer Cherrier[3], Yves Gélinas[4], François Guillemettre[2,5] David C. Podgorski[6], Robert Spencer[7], Luc Tremblay[8] et Roxane Maranger[2,1]

([1]) Département des sciences biologiques, Université de Montréal, Pavillon Marie-Victorin C. P. 6128, succ. Centre-ville, Montréal, QC, Canada, H3C 3J7

([2]) Groupe de recherche interuniversitaire en limnologie et environnement aquatique (GRIL), Université de Montréal, Pavillon Marie-Victorin C. P. 6128, succ. Centre-ville, Montréal, QC, Canada, H3C 3J7

([3]) Department of Earth and Environmental Sciences, The City University of New York, 365 Fifth Avenue, New York, NY 10016, USA

([4]) Department of Chemistry & Biochemistry, Concordia University, Richard J. Renaud Science Complex, 7141 Sherbrooke W. Montréal, QC, Canada, H4B 2A7

([5]) Département des sciences de l'environnement, Université du Québec à Trois-Rivières, 3351 Boulevard des Forges, Trois-Rivières, QC, Canada, G8Z 4M3

([6]) Department of Chemistry, The University of New Orleans, 2000 Lakeshore Dr, New Orleans, LA 70148, USA

([7]) Department of Earth, Ocean & Atmospheric Science, Florida State University, 303 Oceanography Building, Tallahassee, FL 32306, USA

([8]) Département de chimie et biochimie, Université de Moncton, 18, avenue Antonine-Maillet, Moncton, NB, Canada, E1A 3E9

Cet article sera soumis dans Nature.

Contributions des auteurs

RL a fait le travail de terrain, analysé les données et écrit le premier manuscrit; RL a fait le travail de laboratoire et BP a aidé au travail de laboratoire; NFSG et BP ont aidé dans l'analyse des données; JC, YG, FG, DCP et RS ont contribué des données; JC, FG, DCP, RS et LT ont fourni une expertise technique; RM et RL ont édité l'article; JC, FG et LT feront la première révision; RM a élaboré l'étude; tous réviseront et accepteront le manuscrit.

Résumé. Une énigme majeure en biogéochimie du carbone est la stabilité apparente du carbone organique dissous (DOC) dans l'océan profond alors que ce COD est un immense réservoir d'énergie potentielle pour les procaryotes. À l'inverse de l'hypothèse de dillution qui stipule que les molécules sont trop diluées pour êtres consommées (Arrieta et al., 2015), la pompe microbienne de carbone (MCP) (Jiao et al., 2010) suggère que les transformations successives de DOC labile par les procaryotes produit du DOC intrinsèquement stable et réfractaire (RDOC) (Ogawa et al., 2001). Dans cette étude, nous avons expérimentalement testé l'hypothèse de la MCP dans une région de convection profonde de l'océan en exposant de l'eau de surface à des communautés épipélagiques, mésopélagiques et bathypélagiques et en suivant les changements dans les concentrations de DOC, la composition moléculaire et la structure de la communauté de procaryote au fil du temps. Nous avons constaté que tous les traitements ont tous atteint des concentrations de DOC similaires à environ 52 μM, mais que les procaryotes bathypélagiques étaient plus efficaces pour consommer le DOC et produire du RDOC, comme le montre la création de formules moléculaires plus oxygénées. De plus, nous avons démontré de façon concluante que le processus itératif de création du RDOC nécessite une succession de taxons spécialisés, principalement issu de la biosphère rare. Après 92 jours d'incubation, des taxons de Verrucomicrobia sont apparus dans tous les traitements, mais étaient plus diversifiés dans le traitement bathypélagique, suggérant qu'il joue un rôle important dans la production de RDOC. Cette étude est la première à notre connaissance à confirmer l'hypothèse de la MCP.

Mots clés : Pompe microbienne de carbone, composition de la matière organique dissoute, composition de la communauté de procaryotes, biosphère rare, mer du Labrador

Abstract. A major conundrum in oceanic carbon biogeochemistry is the apparent stability of dissolved organic carbon (DOC) in the deep ocean despite being an immense reservoir of potential energy. In contrast to the dilution hypothesis suggesting that molecules are too diluted to be consumed (Arrieta et al., 2015), the microbial carbon pump (MCP) (Jiao et al., 2010) suggests that the successive transformation of labile DOC by prokaryotes produces intrinsically stable, refractory DOC (RDOC) (Ogawa et al., 2001), leading to its accumulation in the water column. Here, we experimentally tested the MCP hypothesis in a deep convection region of the ocean, by exposing surface water to epipelagic, mesopelagic, and bathypelagic communities and tracking changes in DOC concentration, molecular composition, and prokaryotic community structure over time. We found that all treatments eventually reached a similar DOC concentrations at around 52 μM, but that bathypelagic prokaryotes were more efficient at consuming DOC and producing RDOC as evidenced by the creation of more oxygenated molecular formulas at a faster rate. Moreover, we conclusively showed that the iterative process of creating refractory DOC require a succession of specialized prokaryotes, mainly by rare taxa. After 92 days, taxa from the Verrucomicrobia appeared in all treatments, but were more diverse in the bathypelagic treatment suggesting their role in RDOC production as more RDOC was produced in the bathypelagic treatment. This study is the first to our knowledge to provide strong experimental support for the MCP hypothesis.
Keywords: Microbial carbon pump, dissolved organic matter composition, prokaryotic community composition, rare biosphere, Labrador Sea

1. Introduction

The ocean holds as much dissolved organic carbon (DOC) as there is CO_2 in the atmosphere with most of it resisting biodegradation for thousands of years. This reservoir is thus critical for climate regulation. It has been suggested that this highly recalcitrant DOC comes either from being too diluted (Jannasch, 1967; Arrieta et al., 2015) or from the successive transformation of labile DOC by prokaryotes, a hypothesis referred as the Microbial Carbon Pump (MCP) (Jiao et al., 2010). The hypothesis supposes that labile and semi-labile DOC is processed and reprocessed by prokaryotes to produce stable semi-refractory and refractory DOC (hereafter referred to as RDOC) (Ogawa et al., 2001). Although initially largely produced by photosynthesis in the surface ocean, the fate of DOC, be it consumed, mineralized or transformed, is likely associated to the communities processing it. Community composition is known to differ among major ocean stratas (Mestre et al., 2018). Given that different prokaryotic taxa are known to prefer certain types of molecular compounds (Fuhrman and Hagström, 2008; Cottrell and Kirchman, 2000), communities from different strata may be more efficient than others to produce refractory compounds from labile ones.

Deep prokaryotic communities are known to be very diverse and as a consequence likely harbor a rich rare biosphere (Sogin et al., 2006): the number of individual taxa that represents less than 0.1% of total abundance. Taxa in the rare biosphere likely possess a myriad of metabolic pathways to transform DOC and may serve as a seed bank (Lennon and Jones, 2011). Thus, when conditions become favorable, rare taxa may become more abundant and potentially play a critical role in the process of creating RDOC through the MCP. However, it is still unknown whether the diversity and the composition of the rare biosphere is similar between surface and deep communities. Indeed, semi-labile compounds from the surface ocean have been shown to be labile for mesopelagic communities (Carlson et al., 2004).

The Labrador Sea (Rhein et al., 2017; Yashayaev and Loder, 2016) is a region of deep convective mixing, described as one of the tipping points of the Earth's system (Lenton et al., 2008) because of its role in CO_2 and O_2 export to the deep ocean. This convective mixing depth changes among years, some years only reaching the shallow zones of the mesopelagic (540 m) and on others reaching well within the bathypelagic (2000 m) (Yashayaev and Loder, 2016), thus influencing the efficiency of the solubility pump (DeGrandpre et al., 2006). However, on top of entraining biogenic gases, surface organic matter also reaches these deeper strata through this convective overturn (Hansell et al., 2012), where it can be degraded by deep prokaryotic communities (Carlson et al., 2004). The unique convective mixing feature of the Labrador Sea makes it the ideal location to test the efficiency of epi-, meso- and bathypelagic communities in stimulating the MCP and assess which prokaryotic taxa may be involved the production of RDOC.

2. Results & Discussion

In order to assess the efficiency of MCP, through changes in DOC degradation, changes in DOM composition using ultra-high resolution mass-spectrometry, ESI-FT-ICR-MS (Kujawinski, 2002)) and shifts in community composition (16S Illumina sequencing), we filtered surface water at 0.2 μm and inoculated it with prokaryotic communities (53 μm) from the epi-, meso- and bathypelagic. The DOC decay constant (k) was slightly higher in the bathypelagic treatment at $0.099 \pm 0.037 d^{-1}$, but this rate was not significantly different from the k for the epi-, and mesopelagic treatments at $0.059 \pm 0.016 d^{-1}$, $0.061 \pm 0.023 d^{-1}$, respectively. The bathypelagic reached its baseline of 52 μM at 50 days of incubation versus around 85 days for the other two treatments (Fig. S4.1), in part as a function of the higher specific biomass production observed in the bathypelagic treatment (Fig. S4.2). Although overall DOC concentrations were similar, molecules targeted and created by prokaryotes could differ among strata, leading to end products with differential level of recalcitrance.

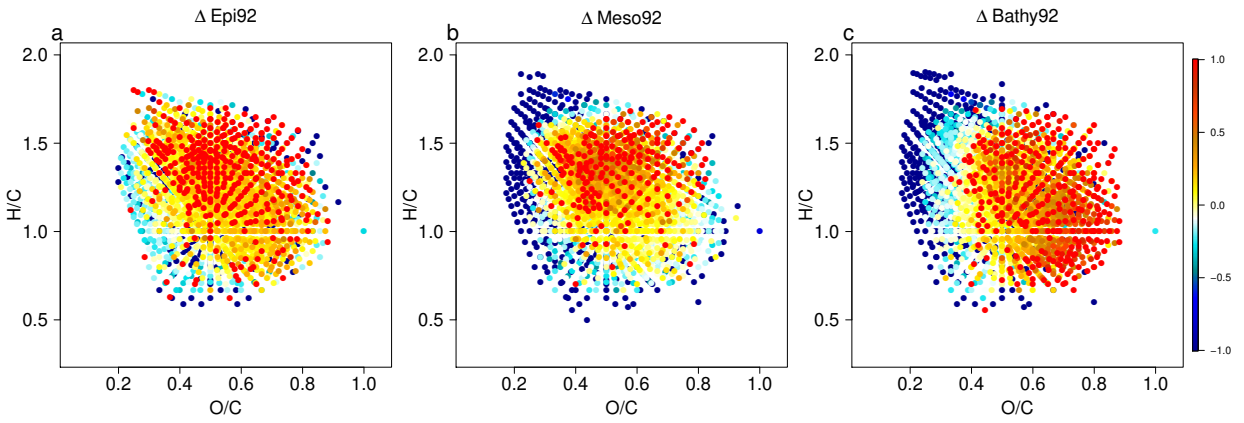


Fig. 4.1. Changes in DOM composition after 92 days of incubation. This figure shows the relative change in the abundance of molecular formulas (MF) using van Krevelen diagrams comparing 92 days of incubation with time 0 in the epi- (a), meso- (b) and bathypelagic (c) treatments. Each point represents a MF and is positioned based on its elemental stoichiometry (oxygen: carbon on the x axis, hydrogen: carbon on the y axis). Cold colors represent a loss of MFs and hot colors an increase.

After 92 days of incubation, shortly after the DOC plateau was reached, different patterns of molecular formula (MF) were observed among treatments (Fig. 4.1 a-c) suggesting differential processing of the DOC over this time frame. Less oxygenated MF that were consumed (dark blue dots) had a much higher range O/C in the bathypelagic (0.2-0.4 O/C) as compared to the mesopelagic treatment (0.2-0.3 O/C), whereas few MF in that lower O/C window were consumed completely by epipelagic communities (Fig. 4.1). An inverse pattern was observed for the produced MF (red dots), indicating that DOM processed by deep prokaryotic communities had higher nominal oxidation state of carbon (NOSC, O/C ratio) values on average. This pattern was observed after 20 days of incubation (Fig. S4.3) and got stronger over time (Fig. 4.1). This confirms the iterative process of creating refractory DOC as compounds with higher NOSC values that are known to be thermodynamically more stable (LaRowe and Van Cappellen, 2011).

Furthermore in all treatments, there was a decrease in carboxyl-rich alicyclic molecules (CRAM) abundance, a major constituent of the island of stability (Lechtenfeld et al., 2014) in van Kreleven plots. This suggests that although they are pervasive in the oceans, not all of these molecules are completely refractory and more oxygenated molecules that are presumably more stable can be created. While ESI-FT-ICR-MS data cannot unequivocally show an increase or decrease in compound abundance as it gives a relative intensity signal, other studies have shown a production of complex DOM from simple substrates through incubations (Ogawa et al., 2001; Koch et al., 2014). In this study, we found that total fluorescence of DOM increased over time (Fig. S4.4a), implying the production

of fluorescent molecules thus supporting the creation of more refractory compounds by prokaryotes. Therefore, this experiment is the first, to our knowledge, to confirm the MCP hypothesis.

Most of the prokaryotic taxa found at the end of the incubation were not detected at the beginning (Fig. 4.2), confirming the role of the rare biosphere as a "seed-bank" (Lennon and Jones, 2011) (Fig. S4.5 and S4.6). We suggest that the emergence of different taxa from the rare biosphere arriving in succession (Fig. S4.6) is contributing to the iterative transformation of DOC leading to the production of RDOC (Fig. 4.1). Moreover, the prokaryotic communities in deep treatments were more diverse than those at the surface (Fig. S4.7), suggesting a greater diversity in the rare biosphere. Deep treatments' diversity crashed in the first few weeks but increased later and remained higher than in the surface treatment. Thus succession of the community as DOC became more recalcitrant is coherent with succession theory (Fierer et al., 2010) and with the potential differential metabolic pathways of the rare biosphere. Indeed, many Amplicon Sequence Variants (ASV)s belonging to Verrucomicrobia, a phylum virtually absent in early stages of succession (Fig. S4.8a), were detected and abundant after 92 days of incubation suggesting their affinity with recalcitrant forms of DOC. During the first 20 days, between 30% and 75% of the deep prokaryotic communities belonged to the Thaumarchaeota (Fig. S4.8b). Several taxa of the Thaumarchaeota are known to be chemoautotrophs oxidizing ammonium to nitrite (Könneke et al., 2005), their high abundance not only suggests their role in DOC consumption in the deep ocean (Karner et al., 2001), but the production of DOC through chemosynthesis may prime other heterotroph to consume more semi-labile compounds (Sebastián et al., 2018). A similar prokaryotic succession was reported during long term incubations of Mediterranean bathypelagic water (Sebastián et al., 2018). This suggests that the communities responsible for the creation of RDOC as observed in our study are likely playing the same role in other deep-sea regions of the world.

Previous work has shown that surface waters inoculated with deeper prokaryotic communities (250 m) were better able to consume DOC from the semi-labile fraction whereas surface ones apparently could not (Carlson et al., 2004). Yet in our study, the same overall consumption was observed in all treatments and no significant differences in final DOC concentrations after 1.5 years of incubation (Fig. S4.1). One possible explanation for this beyond that the original incubation time of the Carlson study (Carlson et al., 2004) was shorter, is that the surface water used in that experiment was not sampled during a bloom period. Negligible amounts of labile DOC would have been available in the surface water during that period, and this may have impinged on any observed consumption by the prokaryotic surface community. One of the caveats in our study is that surface water

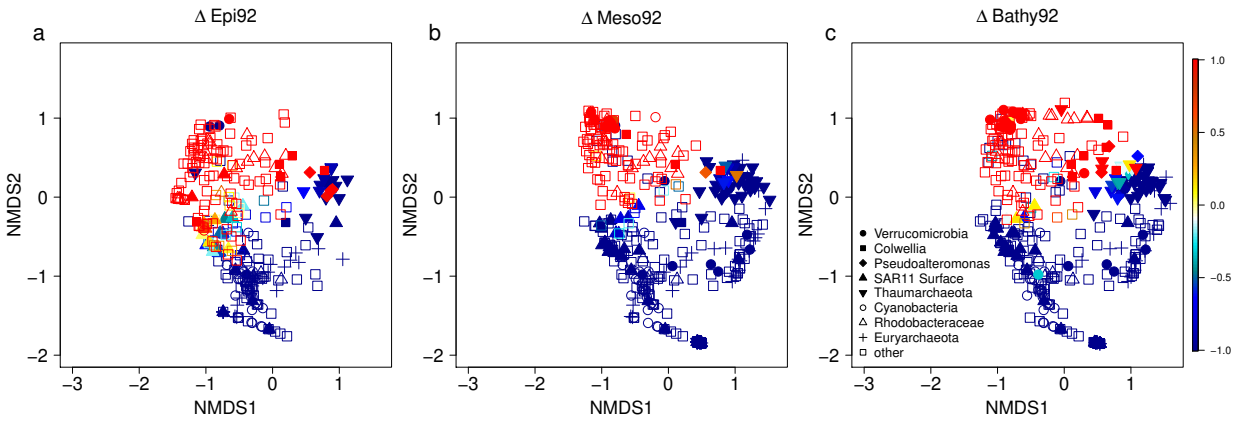


Fig. 4.2. Prokaryotic community shifts during the experiment among treatments. This figure shows the relative change of ASV abundance using a non-metric multidimensional scaling (NMDS) comparing 92 days of incubation with time 0 in the epi- (a), meso- (b) and bathypelagic (c) treatments. Each point represents a different ASV. Cold colors represent a decrease in abundance and hot colors an increase, where -1 indicates that the ASV disappeared and +1 indicates that the ASV appeared, or at least doubled in abundance between the two time points. Symbols represent different prokaryotic groups and are the same for each panel. We see that most of the prokaryotes present after 92 days were not detected at the beginning and that communities from all treatments converged. This suggests that a shift in communities is required in order to consume and transform an increasingly refractory DOM pool. These NMDS were performed using the average abundance of treatment's replicates. The 2D NMDS stress is 0.12.

was sampled during the spring, and therefore includes fresher, labile DOC that is likely not entrained at the time of deep winter convective mixing (Yashayaev and Loder, 2016). Another caveat is that the prokaryotic inoculum was 20% of the total initial volume of our incubations and therefore introduced some DOC from the different strata that may have resulted in differential initial DOC composition among treatments. Both caveats however provided additional rich information to our study.

In terms of the initial DOC MF composition, the epi- and mesopelagic treatments were more similar to one another than to that of the bathypelagic (Fig. S4.9 a-c). Surprisingly there were relatively less oxygenated compounds in the bathypelagic treatment at T0 compared to the two others. We would have anticipated the opposite given that this component is the most refractory in the van Krevelen plot. This differential starting point needs to be considered when we evaluate the composition at different times throughout the incubations, among treatments. All treatments ultimately reached the same final DOC concentration of 52 μM, the background oceanic concentration of semi-refractory and refractory DOC as described by Hansell (2013) (Hansell, 2013). However the MF composition after 92 days was more similar between the meso- and bathypelagic treatments, whereas the epipelagic

treatment was clearly distinctive (Fig. S4.9 d-f). This supports that relatively more RDOC was produced by the bathypelagic community as compare to the others (compare Fig. S4.9c with Fig. 4.1c). Indeed, this study provides the first experimental evidence showing that the MCP is active in the whole water column, where all prokaryotic communities are capable of iteratively producing differential MF, but that RDOC production is best enabled in the bathypelagic (Fig. 4.3). This is likely a function of the increased diversity in the rare biosphere (Fig. S4.5 and Fig. S4.7). Deeper convective mixing in the Labrador Sea would therefore not only sequester more C through the solubility pump, but through the MCP as well.

Given the relatively larger production of oxygenated MF in the bathypelagic treatment, the fact that there were fewer oxygenated MF at the beginning of the experiment is a bit of an enigma (Fig. S4.9 b-c). One possible explanation is that these MF are removed from the ecosystem potentially through DOM self-aggregation (Verdugo et al., 2008) under in situ pressure (15 MPa) either through the formation of higher molecular weight compounds or particles. This is concordant with the increased abundance of Verrucomicrobia, a phylum thought to prefer a particle-attached lifestyle (Freitas et al., 2012). While very little is known about the effect of hydrostatic pressure on DOM and particles, one study found that it reduces dissolution rates (Tamburini et al., 2009) of particles, thus helping their removal from the ecosystem under high in situ pressure. Neutrally buoyant, or non-sinking particles (Bochdansky et al., 2010) are abundant in the deep ocean and are hotspots of microbial transformation as they are highly colonized by prokaryotes (Nagata et al., 2010). We propose that bathypelagic communities would not only be more efficient in burying carbon through the MCP, but would also bridge the dissolved low molecular weight with either the high molecular weight and particulate pools, creating ecological niches for other prokaryotes and another pathway of carbon sequestration (Fig. 4.3). This hypothesis however needs to be tested.

In terms of semi-refractory and refractory DOC, Jiao and collaborators (Jiao et al., 2014) suggested the existence of two types: context dependent and concentration limited. As the deep ocean sequesters carbon for thousands of years, which enables it to play a critical role in regulating the Earth's climate (Boyd, 2015), ocean storage of RDOC can be compared to C stored in peatlands. Accumulated carbon in peat is stored for millennia when peatland sites remain under stable anoxic conditions; thus storage is context dependent. However, deep ocean RDOC persists for thousands of years under oxic conditions and through many oceanic circulation cycles: it is therefore likely not context dependent as a function of movement. The concentration limited recalcitrance echoes the dilution hypothesis (Arrieta et al., 2015), stating that a large proportion of oceanic DOC is potentially labile but is too diluted to be energetically profitable for prokaryotes to consume it (LaRowe et al., 2012). A

LDOC
SLDOC
Successive DOC processing
Succession of prokaryotes
LMW/HMW
SRDOC
?
Sinking POC
Distinct communities
SAR 11
Thaumarchaeota
Verrucomicrobia
Planctomycetes
Self-aggregation
POC?
HMW?
RDOC
LMW
Epipelagic
Mesopelagic
Bathypelagic
Increased rare biosphere diversity

recent study (Arrieta et al., 2015) examined the dilution hypothesis by concentrating deep ocean DOC and monitoring its concentration and prokaryotic activity over time. While prokaryotic growth was stimulated, at most 5% of DOC was consumed within 40 days (Jiao et al., 2015), a timeframe long enough to consume labile DOC (LaBrie et al., viewb) in many different aquatic ecosystems, thus limiting the role of dilution to only a small fraction of deep ocean DOC.

Our results strongly supports the MCP hypothesis over the dilution one. We found that the MCP can be stimulated by communities from all oceanic strata and that more refractory compounds are iteratively produced through prokaryotic succession (Fig. 4.3). However, we demonstrate that the MCP is most efficient when DOC encounters bathypelagic communities which were found to be more diverse. Said, we cannot discard the dilution hypothesis. Final concentrations in our incubations emulated those of the deep ocean, but different prokaryotic communities generated independent MF profiles. For example, the DOC processed by the surface community technically had more semi-labile compounds that could be consumed in a different context. Furthermore, we suggest that aggregate formation of the more refractory compounds produced in the bathypelagic could help explain particle formation in the deep ocean and accentuate permanent carbon sequestration. Our results indicate that in regions of deep convective mixing such as the Labrador Sea, more C is sequestered through the MCP in years when winter convection reaches the bathypelagic. Given that a warmer climate may reduces the depth of convection (Lenton et al., 2008), this may create a positive feedback by sequestering less carbon in the deep ocean.

3. Materials and methods

3.1. Study site

Sampling occurred in the Labrador Sea on May 14, 2016 at station 16.5 (lat-long) along the Atlantic Repeat Hydrography Line 7 West (AR7W) as part of the World Ocean Circulation Experiment (WOCE) onboard the CCGS Hudson. Epipelagic water was sampled at 20 m, mesopelagic at 540m and bathypelagic at 1500m using a conductivity, temperature and depth (CTD) mounted on a rosette, collected in acid-washed polyethylene carboys and transported to the lab immediately for processing.

3.2. Experimental setup

Within 3 hours of collection, epipelagic water was consecutively filtered through a 3 μm polycarbonate (PC) filter and a 0.2 μm polyethersulfone (PES) filter using a peristaltic system equipped with silicone tubing in the lab. The filtrate (medium) was stored in an acid-washed polyethylene carboy for homogenization. Time series incubations were carried

out in 11 L acid and base washed glass carboys with silicone stoppers (referred to here after as "mesocosm") in duplicates. There were three experimental treatments where each mesocosm received 8 L of epipelagic 0.2 μm filtered medium and 2 L of 53 μm filtered water as the inoculum source collected from either the epi- (20 m), meso- (540 m), or bathypelagic (1500 m) depths (referred to as epi-, meso- and bathypelagic treatments, Fig. S4.10). Mesocosms were done in duplicates and were kept in the dark at 4°C during the entire length of the experiment and were sampled several times (11 time points) over the course of 1.5 years. To avoid any possible contamination in the experimental mesocosms, during each sampling event 1 L of water was transferred into an acid-washed and pre-conditioned glass bottle which was further subsampled using nano-pure water rinsed and pre-conditioned silicone tubing with a 60 mL glass syringe. Water was collected for subsequent analysis of DOM (DOC, ESI-FT-ICR MS, and FDOM), prokaryotic metabolism (production and abundance) and community composition (16S rDNA gene), chosen to describe different components of DOM-microbe interactions (LaBrie et al., viewa).

Samples for organic carbon concentration were not filtered again, but will be referred to as DOC as particles should represent a negligible amount as 80% of the water in the microcosm was finely filtered at 0.2 μm prior to the experiment. Samples were acidified at pH $<$ 2 using high grade HCl and stored in pre-burned (450°C) amber glass vials. All samples were measured using high-temperature catalytic oxidation (HTCO) method on an Aurora 1030C mounted with a GD-100 CO_2 trap (Lalonde et al., 2014) or a Shimadzu TOC-L/TN-TMNL analyzer. Several samples were run on both machines to cross-validate the results. Internal standards and Consensus Reference Material (deep seawater reference) were used to validate results.

To characterize the DOM pool that was available and produced by prokaryotes during the experiment, we used Fourier transform ion cyclotron resonance mass spectrometer using negative electrospray ionization mode (ESI-FT-ICR MS). Water was sequentially filtered through a 3 μm PC filter, followed by a 0.2 μm PES filter with a peristaltic pump using silicone tubing, which was acid washed between each sample. Water samples were then acidified to pH $<$ 2 using HCl (12M, Fisher Scientific ACS Plus) and frozen until extraction. Extractions were performed using bond elut PPL cartridges (Agilent, 100 mg) with an estimated extraction recovery of 40% (Dittmar et al., 2008). The volume of each sample was adjusted based on DOC concentration in order to extract the same quantity of carbon. PPL cartridges were dried using pure N_2 gas and DOM was recovered using methanol (HPLC grade). Samples were injected into a 9.4 T ESI-FT-ICR MS at the National High Magnetic Field Laboratory (Tallahassee, FL) (Kellerman et al., 2018). Formula assignment was performed using an in-house protocol (EnviroOrg (Corilo, 2015))

within these limits: $C_{1-45}H_{1-92}N_{0-4}O_{1-25}S_{0-2}$. In order to standardize all samples to an equivalent noise threshold, we normalized the numbers of assigned peaks as follow: 1. f(x) = 0 if x < Threshold; 2. f(x) = x if x >= Threshold and 3. f(x) = x *10 000 / sum of sample signal, where x is the intensity signal and Threshold is the second worst noise signal.

In order to characterize the DOM pool that was available and produced by prokaryotes during the experiment, we used Fourier transform ion cyclotron resonance mass spectrometer using negative electron spray ionization mode (ESI-FT-ICR-MS). Water was then acidified to pH < 2 using high grade pure HCl and frozen until extraction. Extractions were performed using bond elut PPL cartridges with an estimated extraction recovery of 40%. The volume of each sample was corrected for DOC concentration in order to extract the same quantity of carbon. PPL cartridges were dried using pure N_2 gas and organic carbon was recovered using methanol. Samples were injected in a 9.4 T ESI-FT-ICR-MS at the National High Magnetic Field Laboratory (Tallahassee, FL) (Kellerman et al., 2018). Formula assignment was performed using an in-house protocol (EnviroOrg) within the bounds of $C_{1-45}H_{1-92}N_{0-4}O_{1-25}S_{0-2}$. In order to standardize all samples to an equivalent noise threshold, we normalized the numbers of assigned peaks as follow: 1. f(x) = 0 if x < Threshold; 2. f(x) = x if x >= Threshold and 3. f(x) = x *10 000 / sum of sample signal, where x is the intensity signal and Threshold is the second worst noise signal.

We summarized FT-ICR-MS data to easily look at changes in molecular formulas (MF) over time and among treatments by calculating relative change in MF as follow: (Sample 1 – Sample 2) / Sample 2. We represented the results in van Krevelen spaces by color coding MF based on the relative change. In cases where no MF were detected in sample 2 but were in Sample 1, we modified the relative change to 1.

In order to identify which prokaryotes consumed and transformed DOC, we monitored the community composition using 16S rRNA gene. Water for DNA extraction was sequentially filtered through a 3 μm polycarbonate filter, followed by a 0.2 μm PES with a peristaltic pump using silicone tubing, which was acid washed between each sample. Filters were conserved in lysis buffer (EDTA 40 mM, Tris 50 mM and sucrose 750 mM), flash frozen, and stored at $-80°C$ until further processing.

DNA was extracted using an extraction kit (Qiagen, DNeasy Power Water) and DNA quantification was done with a Qubit 2.0 fluorometer high sensitivity kit, following manufacturers' instructions. DNA amplification, library preparation and Illumina sequencing of 16S rRNA gene were done at the Integrated Microbiome Resources at Dalhousie University (Comeau et al., 2017). Briefly, a dual-indexing, one-step PCR was done using a Nextera

XT v2 kit (Illumina) with the adapters and index provided by the kit. Region V6-V8, 16S rRNA gene for bacteria was targeted with primers B969F (ACGCGHNRAACCTTACC) and BA1406R (ACGGGCRGTGWGTRCAA) and for Archaea with A956F (YAATYGGANTCAACRCC) and A1401R (CRGTGWGTRCAAGGRGCA). PCR amplification was run for 30 cycles. The amplicons quality was visualized with a 96-well E-gel (Invitrogen), purified and normalized with the high-throughput SequalPrep 96-well plate kit (Invitrogen). Samples were pooled to make one library and quantify using Qubit double-stranded DNA high-sensitivity kit (Invitrogen).

Reads were analyzed with the DADA2 pipeline following the tutorial v.1.4 (Callahan et al., 2016) using the R software v.3.4.1. After the processing, 2096 amplicon sequence variants (ASV, 2 048 513 reads) were obtained for bacterial sequencing and 319 ASV (695 993 reads) for archaea. These were then taxonomically classified based on the SILVA database v128. Archaea were removed from the bacterial dataset and bacteria were removed from the archaeal dataset to avoid duplication; datasets were then combined (45 000 reads $\pm$ 11000, mean $\pm$ sd).

We corrected the number of sequences with the average number of 16S copy for each ASV using information provided on the rrnDB website (https://rrndb.umms.med.umich.edu, November 2018). When the 16S copy number was not found at the genus level, we took the average 16S copy of the next taxonomic rank until all ASVs abundances were corrected. Then, all ASVs with a number of sequences equal to or less than 10 in a single sample were treated as noise and removed, for a final count of 946 ASVs. Shannon diversity index was calculated using the vegan(Oksanen et al., 2018) package on R.

To quantify the activity of the community over time, we measured prokaryotic heterotrophic production (PHP) following Smith and Azam (Smith and Azam, 1992) with minor modifications. Samples of 1.5 ml were incubated on ice in the dark at with [3, 4, 5-3H]-L-leucine ($\sim$10 nM final concentration) for 3 hours in triplicate with a TCA killed control (5% final concentration). Incubations were stopped by adding TCA (5% final concentration) and briefly vortexed before being frozen until further processing in the lab. Samples were thawed at room temperature, centrifuged at 17 000 G (13 000 RPM) using an accuSpin micro17 centrifuge and gently siphoned to the last drop. Samples were acidified with 5% TCA, vortexed, centrifuged and siphoned again. Vials were filled with 1.5 ml of scintillation cocktail and stored for 1 hour at room temperature before counting on a Tri-carb 2800TR. Carbon incorporation rates were calculated using 1550 g C mol leucine^{-1}.

In order to calculate specific production rates, we measured prokaryotic abundance using flow cytometry. Samples were fixed with 0.1% final concentration glutaraldehyde grade I, flash-frozen and kept at −80°C until analysis. Samples were thawed on ice at room-temperature, stained with SYBR green 1 (1% final concentration) in tris-EDTA buffer (10 mM Tris, 1 mM EDTA) (Belzile et al., 2008) for 10 minutes in the dark. We measured an average of 5400 events/s with an average of 312 events/μl and enumeration was done on a BD accuri C6 flow cytometer. Specific production was calculated as the ratio of production over abundance.

As ESI-FT-ICR-MS only gives a relative intensity signal, we needed another method to measure an absolute change in DOM composition and thus we measured fluorescent DOM (FDOM). FDOM was measured on a Cary Eclipse spectrofluorometer, with both excitation and emission slit widths of 5 nm. EEMs were produced by repeatedly scanning over even emission wavelengths between 230 nm and 600 nm for each excitation wavelength between 220 nm and 450 nm with a 5 nm excitation increment. Standard corrections were applied to each EEM using the paRafac.correction R library (LaBrie et al., 2017b) except for the inner-filter effect which was not corrected for as we did not measured absorption. This should have minimal influence on our fluorescence values.

The parallel factor analysis (PARAFAC) model was done with 56 samples on MATLAB using drEEM (v0.1.0) toolbox (Murphy et al., 2013). The first 50 nm wavelength in emission and 30 nm wavelength in excitation were removed to avoid modelling instrument noise. Four independent fluorescent components (Fig. S4.4b) were validated by split half and random initialization parameters.

3.3. Caveat

This study was performed using bottle experiments and has some caveats to keep in mind. The first caveat is inherent to all bottle experiments, the so-called "bottle effect", stating that an increased growth of bacteria may reduce the validity of the observed changes. However, bacterial growth is not necessarily observed in batch culture experiment, regardless of the bottles' volume (Hammes et al., 2010). A second plausible "bottle effect" would be a selective pressure on different bacterial taxa, thus limiting the applicability of this study to natural settings. Although prokaryotic communities were different in the inoculum as compared to the incubation's end point, the prokaryotic diversity was similar at the beginning and after 180 days of incubation. Tthe last caveat is related to the time-frame of the experiment. According to Hansell's terminology (2013), semi-refractory and refractory DOC have extremely long half-lives, from centuries to millennia. Our 92 days time-frame for FT-ICR-MS measurements is thus much too short to fully support the

creation of RDOC. However, such time-frame is impossible to recreate in batch culture experiments and we found strong evidences that support the production of more recalcitrant compounds, in agreement with the MCP hypothesis.

3.4. Statistical analysis

In order to estimate the time required to reach the DOC baseline, DOC decay curves were modeled with a two-pool multi-G approach (LaBrie et al., viewb; Jørgensen, 1978) using a Levenberg-Marquardt optimisation routine (Elzhov et al., 2016). The model output gives the decay constant (k) associated to the metabolizable pool along with the proportion of both metabolizable (BDOC) and constant (RDOC) pools. The optimization routine iteratively fits a curve to these points by changing all parameters (BDOC, k, RDOC) at once and the best model was chosen based on the lowest residuals of the sum-of-squares. The time required to reach the plateau can be estimated as such: 1/k * 5.

To represent how the communities shifted during the experiment, we conducted a 2D non-metric multidimensional scaling (NMDS) (Oksanen et al., 2018) based on Bray-Curtis transformed data. We represented ASVs (Fig. 4.2) using relative changes in abundance as described for ESI-FT-ICR-MS and sites (Fig. S4.6) to show both how each ASV and the overall community changed over time, respectively. Using a third axis reduced the overall stress from 0.12 to 0.06 but did not change the interpretation. All statistics were done using R v3.4.1 (R Core Team, 2017).

4. Data availability

Raw reads were deposited on NCBI (PRJNA598915), all other data and scripts are available at www.github.com/laboMaranger/MCP.

5. Acknowledgement

Références bibliographiques

Arrieta, J. M., Mayol, E., Hansman, R. L., Herndl, G. J., Dittmar, T., and Duarte, C. M. (2015). Dilution limits dissolved organic carbon utilization in the deep ocean. *Science*, 348(6232):331–333.

Belzile, C., Brugel, S., Nozais, C., Gratton, Y., and Demers, S. (2008). Variations of the abundance and nucleic acid content of heterotrophic bacteria in beaufort shelf waters during winter and spring. *Journal of Marine Systems*, 74(3-4):946–956.

Bochdansky, A. B., Van Aken, H. M., and Herndl, G. J. (2010). Role of macroscopic particles in deep-sea oxygen consumption. *Proceedings of the National Academy of Sciences*, 107(18):8287–8291.

Boyd, P. W. (2015). Toward quantifying the response of the oceans' biological pump to climate change. *Frontiers in Marine Science*, 2:77.

Callahan, B. J., McMurdie, P. J., Rosen, M. J., Han, A. W., Johnson, A. J. A., and Holmes, S. P. (2016). Dada2: high-resolution sample inference from illumina amplicon data. *Nature methods*, 13(7):581.

Carlson, C. A., Giovannoni, S. J., Hansell, D. A., Goldberg, S. J., Parsons, R., and Vergin, K. (2004). Interactions among dissolved organic carbon, microbial processes, and community structure in the mesopelagic zone of the northwestern sargasso sea. *Limnology and Oceanography*, 49(4):1073–1083.

Comeau, A. M., Douglas, G. M., and Langille, M. G. I. (2017). Microbiome helper: a custom and streamlined workflow for microbiome research. *MSystems*, 2(1).

Corilo, Y. (2015). Enviroorg. pages Tallahassee, FL: Florida State University.

Cottrell, M. T. and Kirchman, D. L. (2000). Natural assemblages of marine proteobacteria and members of the cytophaga-flavobacter cluster consuming low-and high-molecular-weight dissolved organic matter. *Applied and Environmental Microbiology*, 66(4):1692–1697.

DeGrandpre, M. D., Kortzinger, A., Send, U., Wallace, D. W. R., and Bellerby, R. G. J. (2006). Uptake and sequestration of atmospheric co_2 in the labrador sea deep convection region. *Geophysical Research Letters*, 33(21):5.

Dittmar, T., Koch, B., Hertkorn, N., and Kattner, G. (2008). A simple and efficient method for the solid-phase extraction of dissolved organic matter (spe-dom) from seawater. *Limnology and Oceanography: Methods*, 6(6):230–235.

Elzhov, T. V., Mullen, K. M., Spiess, A.-N., and Bolker, B. (2016). *minpack.lm: R Interface to the Levenberg-Marquardt Nonlinear Least-Squares Algorithm Found in MINPACK, Plus Support for Bounds*. R package version 1.2-1.

Fierer, N., Nemergut, D., Knight, R., and Craine, J. M. (2010). Changes through time: integrating microorganisms into the study of succession. *Research in microbiology*, 161(8):635–642.

Freitas, S., Hatosy, S., Fuhrman, J. A., Huse, S. M., Welch, D. B. M., Sogin, M. L., and Martiny, A. C. (2012). Global distribution and diversity of marine verrucomicrobia. *The ISME journal*, 6(8):1499.

Fuhrman, J. A. and Hagström, A. (2008). Bacterial and archaeal community structure and its patterns. *Microbial Ecology of the Oceans, Second Edition*, pages 45–90.

Hammes, F., Vital, M., and Egli, T. (2010). Critical evaluation of the volumetric "bottle effect" on microbial batch growth. *Appl. Environ. Microbiol.*, 76(4):1278–1281.

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5.

Hansell, D. A., Carlson, C. A., and Schlitzer, R. (2012). Net removal of major marine dissolved organic carbon fractions in the subsurface ocean. *Global Biogeochemical Cycles*, 26(1).

Jannasch, H. W. (1967). Growth of marine bacteria at limiting concentrations of organic carbon in seawater 1. *Limnology and Oceanography*, 12(2):264–271.

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., Kirchman, D. L., Weinbauer, M. G., Luo, T., and Chen, F. (2010). Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nature Reviews Microbiology*, 8(8):593–599.

Jiao, N., Legendre, L., Robinson, C., Thomas, H., Luo, Y.-W., Dang, H., Liu, J., Zhang, R., Tang, K., and Luo, T. (2015). Comment on "dilution limits dissolved organic carbon utilization in the deep ocean". *Science*, 350(6267):1483–1483.

Jiao, N., Robinson, C., Azam, F., Thomas, H., Baltar, F., Dang, H., Hardman-Mountford, N., Johnson, M., Kirchman, D., and Koch, B. (2014). Mechanisms of microbial carbon sequestration in the ocean–future research directions. *Biogeosciences*, 11(19):5285–5306.

Jørgensen, B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments.

Karner, M. B., DeLong, E. F., and Karl, D. M. (2001). Archaeal dominance in the mesopelagic zone of the pacific ocean. *Nature*, 409(6819):507–510.

Kellerman, A. M., Guillemette, F., Podgorski, D. C., Aiken, G. R., Butler, K. D., and Spencer, R. G. (2018). Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. *Environmental science & technology*, 52(5):2538–2548.

Koch, B. P., Kattner, G., Witt, M., and Passow, U. (2014). Molecular insights into the microbial formation of marine dissolved organic matter: recalcitrant or labile? *Biogeosciences*, 11(15):4173–4190.

Könneke, M., Bernhard, A. E., José, R., Walker, C. B., Waterbury, J. B., and Stahl, D. A. (2005). Isolation of an autotrophic ammonia-oxidizing marine archaeon. *Nature*, 437(7058):543.

Kujawinski, E. B. (2002). Electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (esi ft-icr ms): Characterization of complex environmental mixtures. *Environmental Forensics*, 3(3-4):207–216.

LaBrie, R., Bélanger, S., Benner, R., and Maranger, R. (Under reviewa). Spatial abundance distribution of prokaryotes is defined by their dissolved organic matter preferences.

LaBrie, R., Fortin St-Gelais, N., and Bélanger, S. (2017). *paRafac.correction: an R Package to correct EEMs and derive CDOM and FDOM indices*.

LaBrie, R., Lapierre, J.-F., and Maranger, R. (Under reviewb). Contrasting patterns of labile and semi-labile dissolved organic carbon from continental waters to the open ocean.

Journal of Geophysical Research: Biogeosciences.

Lalonde, K., Middlestead, P., and Gélinas, Y. (2014). Automation of 13c/12c ratio measurement for freshwater and seawater doc using high temperature combustion. *Limnol. Oceanogr.: Methods*, 12:816–829.

LaRowe, D. E., Dale, A. W., Amend, J. P., and Van Cappellen, P. (2012). Thermodynamic limitations on microbially catalyzed reaction rates. *Geochimica et Cosmochimica Acta*, 90:96–109.

LaRowe, D. E. and Van Cappellen, P. (2011). Degradation of natural organic matter: a thermodynamic analysis. *Geochimica et Cosmochimica Acta*, 75(8):2030–2042.

Lechtenfeld, O. J., Kattner, G., Flerus, R., McCallister, S. L., Schmitt-Kopplin, P., and Koch, B. P. (2014). Molecular transformation and degradation of refractory dissolved organic matter in the atlantic and southern ocean. *Geochimica et Cosmochimica Acta*, 126:321–337.

Lennon, J. T. and Jones, S. E. (2011). Microbial seed banks: the ecological and evolutionary implications of dormancy. *Nature reviews microbiology*, 9(2):119.

Lenton, T. M., Held, H., Kriegler, E., Hall, J. W., Lucht, W., Rahmstorf, S., and Schellnhuber, H. J. (2008). Tipping elements in the earth's climate system. *Proceedings of the National Academy of Sciences of the United States of America*, 105(6):1786–1793.

Mestre, M., Ruiz-González, C., Logares, R., Duarte, C. M., Gasol, J. M., and Sala, M. M. (2018). Sinking particles promote vertical connectivity in the ocean microbiome. *Proceedings of the National Academy of Sciences*, 115(29):E6799–E6807.

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. parafac. *Analytical Methods*, 5(23):6557–6566.

Nagata, T., Tamburini, C., Aristegui, J., Baltar, F., Bochdansky, A. B., Fonda-Umani, S., Fukuda, H., Gogou, A., Hansell, D. A., Hansman, R. L., Herndl, G. J., Panagiotopoulos, C., Reinthaler, T., Sohrin, R., Verdugo, P., Yamada, N., Yamashita, Y., Yokokawa, T., and Bartlett, D. H. (2010). Emerging concepts on microbial processes in the bathypelagic ocean - ecology, biogeochemistry, and genomics. *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 57(16):1519–1536.

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., and Benner, R. (2001). Production of refractory dissolved organic matter by bacteria. *Science*, 292(5518):917–920.

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P. R., O'Hara, R. B., Simpson, G. L., Solymos, P., Stevens, M. H. H., Szoecs, E., and Wagner, H. (2018). *vegan: Community Ecology Package*. R package version 2.4-6.

R Core Team (2017). *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.

Rhein, M., Steinfeldt, R., Kieke, D., Stendardo, I., and Yashayaev, I. (2017). Ventilation variability of labrador sea water and its impact on oxygen and anthropogenic carbon: a

review. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 375(2102):20160321.

Sebastián, M., Auguet, J., Restrepo-Ortiz, C. X., Sala, M. M., Marrasé, C., and Gasol, J. M. (2018). Deep ocean prokaryotic communities are remarkably malleable when facing long-term starvation. *Environmental microbiology*, 20(2):713–723.

Smith, D. C. and Azam, F. (1992). A simple, economical method for measuring bacterial protein synthesis rates in seawater using 3h-leucine. *Mar. Microb. Food Webs*, 6(2):107–114.

Sogin, M. L., Morrison, H. G., Huber, J. A., Welch, D. M., Huse, S. M., Neal, P. R., Arrieta, J. M., and Herndl, G. J. (2006). Microbial diversity in the deep sea and the underexplored "rare biosphere". *Proceedings of the National Academy of Sciences*, 103(32):12115–12120.

Tamburini, C., Goutx, M., Guigue, C., Garel, M., Lefèvre, D., Charrière, B., Sempéré, R., Pepa, S., Peterson, M. L., and Wakeham, S. (2009). Effects of hydrostatic pressure on microbial alteration of sinking fecal pellets. *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(18):1533–1546.

Verdugo, P., Orellana, M. V., Chin, W.-C., Petersen, T. W., van den Eng, G., Benner, R., and Hedges, J. I. (2008). Marine biopolymer self-assembly: implications for carbon cycling in the ocean. *Faraday discussions*, 139:393–398.

Yashayaev, I. and Loder, J. W. (2016). Recurrent replenishment of labrador sea water and associated decadal-scale variability. *Journal of Geophysical Research: Oceans*, 121(11):8095–8114.

Chapitre 5 : Conclusion

5.1. Biodisponibilité de la matière organique dissoute

La matière organique dissoute (MOD) et les procaryotes sont au centre du cycle du carbone et jouent donc un rôle important sur le climat. C'est pourquoi, tout au long de cette thèse, nous avons regardé comment la biodisponibilité de la MOD changeait entre les milieux aquatiques, comment elle influençait le métabolisme et la diversité des communautés de procaryotes, et comment elle pouvait être séquestrée dans les profondeurs de l'océan.

En réalisant notre méta-analyse, nous avons été surpris de voir à quel point la proportion de la MOD labile (MODL) était similaire entre les écosystèmes à l'équilibre. En effet, nous envisagions que les milieux d'eaux douces contiendraient une plus grande proportion de MODL que les milieux marins puisqu'ils sont plus productifs et reçoivent en plus des apports terrestres. Ces apports se sont en fait révélés être une composante essentielle de la MOD semi-labile (MODSL), qui peut servir de réserve énergétique pour les écosystèmes. Finalement, les périodes d'efflorescence algale semblent jouer un rôle critique pour soutenir autant les communautés de procaryotes locales, c'est-à-dire celles qui se retrouvent au sein de l'efflorescence, mais également celles des environnements voisins en recevant des apports de carbone qui n'auraient pas été consommé.

Nous avons également profités des données colligées pour estimer la quantité de biomasse que pouvait soutenir ces différents réservoirs de carbone. Alors que nos estimations comportent une marge d'erreur importante, elles sont néanmoins les premières à donner un ordre de grandeur de la biomasse que peut supporter les stocks de MODL et MODSL. Afin de raffiner ces estimations, il est nécessaire de mieux contraindre les estimations d'efficacité de croissance des procaryotes, spécialement dans les milieux côtiers. Il est aussi nécessaire de mieux comprendre ce qui cause la variabilité dans les proportions de MODL et MODSL. En effet, bien que la moyenne de la proportion de MODL soit similaire dans tous les milieux aquatiques, l'étendue autour de cette moyenneest grande. Une piste d'explication se trouve dans la différence de concentration en carbone organique dissout (COD) entre les

écosystèmes. Si la concentration en COD est proche de celle des eaux profondes de l'océan, très peu de carbone pourra être consommé. Par contre, dans des écosystèmes plus riches comme les lacs et les mers intérieures, la quantité de COD consommée est probablement davantage contrainte par le temps d'incubation que la quantité de COD.

Une autre façon de pousser cette étude plus loin serait de retourner dans les études compilées et de colliger toutes les données sur le COD qui sont fournies. De cette façon, il serait possible de non seulement estimer la quantité de MODL et MODSL à travers le continuum aquatique, mais il serait également possible d'estimer la constante de dégradation pour chacune de ces expériences. Ceci permettrait de mieux estimer les apports de carbone à l'océan en ayant une meilleure idée du temps requis par les communautés de procaryotes pour consommer ces différents réservoirs de carbone. En connaissant les constantes de dégradation dans chaque type d'écosystème, il serait alors possible de comparer ces taux de dégradation avec des taux de production primaire pour estimer la contribution de l'allochtonie dans la boucle microbienne.

Finalement, la majorité des études que nous avons trouvées se trouvent dans l'hémisphère nord, surtout dans les milieux tempérés. La température étant un élément important dans le métabolisme des procaryotes, est-ce que les écosystèmes aquatiques tropicaux répondent de la même façon que ceux que nous avons compilés? Dans le même ordre d'idée, qu'en est-il des mares de thermokarsts dont la température est beaucoup plus basse, mais qui reçoivent d'importante quantité de MOD libérée par la fonte du pergélisol? À quel point ces mares seront des sources de MODL et MODSL pour l'océan Arctique?

5.2. Communauté de procaryotes

Dans cette thèse, nous avons montré que les communautés de procaryotes réagissent fortement à la qualité de la MOD à laquelle elles sont exposées. Que ce soit en surface de l'océan, ou dans les eaux profondes, les communautés se sont adaptées pour transformer la MOD. En surface, nous avons montré pour la première fois que l'affinité des procaryotes pour certains types de matière organique définissait leur distribution spatiale. Les taxons cosmopolites étaient associés à la matière organique fraîche, que ce soit par consommation directe ou comme proxy pour un autre élément du cycle du C que nous n'avions pas mesuré. Les taxons avec une distribution logistique, c'est-à-dire les taxons rares, avaient quant à eux une affinité avec la MOD plus complexe. Cette affinité s'est montrée cruciale pour la pompe microbienne de carbone dans les océans profonds où la biosphère rare jouait un rôle central dans la production de COD réfractaire.

Ceci étant dit, il reste néanmoins des questions en suspens. Nous avons montré le rôle que la distribution spatiale des procaryotes avaient dans la mer du Labrador, mais à quel point est-ce généralisé dans les océans et les autres écosystèmes? Aussi, serait-il possible d'utiliser le même genre de technique avec la diversité des molécules organiques? Y aurait-il une adéquation entre les procaryotes cosmopolites et les molécules cosmopolites? Au niveau des communautés, les cosmopolites représentent les taxons qui prolifèrent avec la MOD fraîche. Hors, la MOD fraîche est libérée essentiellement par la photosynthèse et est donc localement produite. Les molécules cosmopolites représenteraient donc le background général et donc les molécules les plus réfractaires. Cette hypothèse reste à tester et fournirait du même coup une meilleure compréhension du mouvement de la MOD et des communautés de procaryotes dans les écosystèmes.

Un autre résultat fort de cette thèse est le rôle des procaryotes rares dans la dégradation et la séquestration de la MOD. Est-ce que le rôle de la biosphère rare est le même dans tous les écosystèmes aquatiques? D'autres études ont aussi montré leur rôle démesuré dans les processus biogéochimiques du carbone et du souffre. Contribuent-ils aussi à rendre l'azote et le phosphore réfractaire dans les écosystèmes aquatiques?

5.3. Préservation du carbone dans les océans

Dans cette thèse, nous avons démontré expérimentalement le rôle de la pompe microbienne de carbone (PMC) dans la séquestration à long terme du carbone dans les océans. Nous avons montré qu'elle est active dans chacune des strates océaniques, mais qu'elle est particulièrement efficace dans les eaux profondes. Serait-il possible de montrer, d'une façon similaire, qu'il y a une pompe microbienne d'azote et de phosphore dans les océans? Si oui, à quel point ces pompes sont efficaces considérant que les procaryotes des eaux profondes de l'océan ont un rôle important de remise en circulation des nutriments sous forme inorganique. Est-ce que ces deux rôles sont complémentaires, d'un côté en retirant des océans une partie des apports anthropique en nutriments, et de l'autre en fournissant des nutriments inorganiques au phytoplancton.

Notre étude ne permettait pas, toutefois, d'écarter l'hypothèse de dilution. Est-ce que ces deux processus, la création de carbone réfractaire et la dilution de matière labile, ciblent les mêmes composantes de la MOD? Une avenue intéressante pour le tester serait de refaire l'expérience menée par Arrieta et collaborateurs (2015), mais en monitorant la composition de la matière organique au lieu de l'activité microbienne. Ce faisant, nous pourrions déterminer quelles molécules étaient trop diluées pour être consommées.

5.4. Limite des méthodes utilisées

Les découvertes mises de l'avant dans cette thèse proviennent d'observations réalisées avec une multitude de méthode qui comportent certaines limites. Par exemple, les expériences en culture discontinue permettent d'isoler certains phénomènes naturels afin de mieux les comprendre, mais ne reflètent pas complètement ce qui se passe dans l'écosystème. Toutefois, il s'agit d'une des meilleures méthodes existantes pour déterminer la biodisponibilité de la MOD et déterminer les taux métaboliques des procaryotes.

Outre les expériences en culture discontinue, chaque méthode possède des limites plus ou moins grandes qui méritent d'être prises en compte. Afin de déterminer la composition de la communauté de procaryotes, nous avons besoin de faire une série de manipulations qui sont légèrement biaisées. Par exemple, l'amplification de l'ADN n'est pas équivalente entre les taxons car certains taxons sont plus facilement amplifiés, et seraient ainsi surreprésentés. Toutefois, il est peu probable que l'utilisation d'une autre méthode pour déterminer la composition de la communauté aurait mené à des conclusions différentes.

Au niveau de la composition de la matière organique, la spectrométrie de masse à très haute résolution comporte elle aussi des limites. Premièrement, comme nous l'avons mentionné dans l'introduction de cette thèse, nous pouvons classifier la matière organique selon sa masse moléculaire. Hors, la méthode de spectrométrie de masse à très haute résolution que nous avons utilisée est presque aveugle aux molécules de grande masse moléculaire, alors qu'il s'agit d'une importante fraction de la MOD produite par le phytoplancton. Aussi, ce n'est pas tous les composés qui s'ionisent de la même façon. Par exemple, les lipides s'ionisent très mal et sont donc sous représenté avec cette méthode. Finalement, l'isolation de la MOD de l'eau ne fonctionne qu'à environ 40%, et donc plus de la moitié de la MOD disponible pour les procaryotes n'était pas détectable avec cette méthode. Alors qu'il s'agit de limites importantes dans notre étude, la spectrométrie de masse à très haute résolution est tout de même une des techniques les plus efficaces pour déterminer la composition de la MOD.

5.5. Perspectives futures

Dans cette thèse, nous avons proposé un cadre conceptuel visant à faciliter la recherche à l'interface de la biogéochimie, la diversité de la communauté de procarytoes et l'écologie microbienne. Ce cadre conceptuel s'est révélé très important pour notre étude afin de guider nos analyses vers les relations les plus probables. Toutefois, nous n'avons pas eu l'opportunité de tester chacune des relations que nous avons incluses dans le cadre

conceptuel. À ce titre, vérifier qu'il est réellement possible de relier la métagénomique à la composition moléculaire de la MOD en milieu naturel donnerait encore plus de valeurs à ce cadre conceptuel. Il serait également très intéressant de trouver d'autres variables que la MOD fluorescente et la distribution spatiale de l'abondance des procaryotes pour faire le pont entre les différentes échelles d'analyses. La découverte de ses variables est essentielle afin de relier les processus métaboliques des procaryotes et la composition de la matière organique aux processus écosystémiques qui régissent la biogéochimie du carbone, et, par ce fait, le climat.

Fig. 5.1. Une parcelle d'océan et ses innombrables procaryotes qui contribuent à la stabilité du climat

Références bibliographiques

Alonso-Sáez, L. and Gasol, J. M. (2007). Seasonal variations in the contributions of different bacterial groups to the uptake of low-molecular-weight compounds in northwestern mediterranean coastal waters. *Applied and environmental microbiology*, 73(11):3528–3535.

Alonso-Saez, L., Gasol, J. M., Aristegui, J., Vilas, J. C., Vaque, D., Duarte, C. M., and Agusti, S. (2007). Large-scale variability in surface bacterial carbon demand and growth efficiency in the subtropical northeast atlantic ocean. *Limnology and Oceanography*, 52(2):533–546.

Alonso-Sáez, L., Sánchez, O., and Gasol, J. M. (2012). Bacterial uptake of low molecular weight organics in the subtropical atlantic: Are major phylogenetic groups functionally different? *Limnology and Oceanography*, 57(3):798–808.

Alonso-Sáez, L., Unanue, M., Latatu, A., Azua, I. n., Ayo, B. n., Artolozaga, I., and Iriberri, J. (2009). Changes in marine prokaryotic community induced by varying types of dissolved organic matter and subsequent grazing pressure. *Journal of plankton research*, page fbp081.

Aluwihare, L. I., Repeta, D. J., and Chen, R. F. (1997). A major biopolymeric component to dissolved organic carbon in surface sea water. *Nature*, 387(6629):166.

Amon, R. M. W., Fitznar, H. P., and Benner, R. (2001). Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. *Limnology and Oceanography*, 46(2):287–297.

Aristegui, J., Duarte, C. M., Agusti, S., Doval, M., Alvarez-Salgado, X. A., and Hansell, D. A. (2002). Dissolved organic carbon support of respiration in the dark ocean. *Science*, 298(5600):1967–1967.

Aristegui, J., Gasol, J. M., Duarte, C. M., and Herndl, G. J. (2009). Microbial oceanography of the dark ocean's pelagic realm. *Limnology and Oceanography*, 54(5):1501–1529.

Arrieta, J. M. and Herndl, G. J. (2002). Changes in bacterial $\beta-$glucosidase diversity during a coastal phytoplankton bloom. *Limnology and Oceanography*, 47(2):594–599.

Arrieta, J. M., Mayol, E., Hansman, R. L., Herndl, G. J., Dittmar, T., and Duarte, C. M. (2015). Dilution limits dissolved organic carbon utilization in the deep ocean. *Science*, 348(6232):331–333.

Asmala, E., Haraguchi, L., Markager, S., Massicotte, P., Riemann, B., Staehr, P. A., and Carstensen, J. (2018). Eutrophication leads to accumulation of recalcitrant autochthonous organic matter in coastal environment. *Global Biogeochemical Cycles*.

Azam, F., Fenchel, T., Field, J., Gray, J., Meyer-Reil, L., and Thingstad, F. (1983). The ecological role of water-column microbes in the sea. *Marine ecology progress series. Oldendorf*, 10(3):257–263.

Baines, S. B. and Pace, M. L. (1991). The production of dissolved organic matter by phytoplankton and its importance to bacteria: patterns across marine and freshwater systems. *Limnology and Oceanography*, 36(6):1078–1090.

Barrón, C. and Duarte, C. M. (2015). Dissolved organic carbon pools and export from the coastal ocean. *Global Biogeochemical Cycles*, 29(10):1725–1738.

Bauer, J. E., Williams, P. M., and Druffel, E. R. (1992). 14c activity of dissolved organic carbon fractions in the north-central pacific and sargasso sea. *Nature*, 357(6380):667.

Bélanger, S. (2019). *RspectroAbs: Routines to convert spectrophotometric optical depth (Absorbance) to absorption coefficient for dissolved and particulate matter and apply spectral analyses*. R package version 1.4.

Belzile, C., Brugel, S., Nozais, C., Gratton, Y., and Demers, S. (2008). Variations of the abundance and nucleic acid content of heterotrophic bacteria in beaufort shelf waters during winter and spring. *Journal of Marine Systems*, 74(3-4):946–956.

Benner, R. (2002). Chemical composition and reactivity. *Biogeochemistry of marine dissolved organic matter*, 3:56–90.

Benner, R. and Amon, R. M. (2015). The size-reactivity continuum of major bioelements in the ocean. *Annual review of marine science*, 7:185–205.

Berggren, M., Lapierre, J. F., and del Giorgio, P. A. (2012). Magnitude and regulation of bacterioplankton respiratory quotient across freshwater environmental gradients. *Isme Journal*, 6(5):984–993.

Biddanda, B. A. and Cotner, J. B. (2002). Love handles in aquatic ecosystems: The role of dissolved organic carbon drawdown, resuspended sediments, and terrigenous inputs in the carbon balance of lake michigan. *Ecosystems*, 5(5):431–445.

Bocaniov, S. A., Barton, D. R., Schiff, S. L., and Smith, R. E. H. (2013). Impact of tributary dom and nutrient inputs on the nearshore ecology of a large, oligotrophic lake (georgian bay, lake huron, canada). *Aquatic Sciences*, 75(2):321–332.

Bochdansky, A. B., Van Aken, H. M., and Herndl, G. J. (2010). Role of macroscopic particles in deep-sea oxygen consumption. *Proceedings of the National Academy of Sciences*, 107(18):8287–8291.

Boyd, P. W. (2015). Toward quantifying the response of the oceans' biological pump to climate change. *Frontiers in Marine Science*, 2:77.

Broek, T. A., Walker, B. D., Guilderson, T. P., and McCarthy, M. D. (2017). Coupled ultrafiltration and solid phase extraction approach for the targeted study of semi-labile high molecular weight and refractory low molecular weight dissolved organic matter. *Marine Chemistry*, 194:146–157.

Brown, J. H., Gillooly, J. F., Allen, A. P., Savage, V. M., and West, G. B. (2004). Toward a metabolic theory of ecology. *Ecology*, 85(7):1771–1789.

Burd, A. B., Hansell, D. A., Steinberg, D. K., Anderson, T. R., Aristegui, J., Baltar, F., Beaupre, S. R., Buesseler, K. O., DeHairs, F., Jackson, G. A., Kadko, D. C., Koppelmann, R., Lampitt, R. S., Nagata, T., Reinthaler, T., Robinson, C., Robison, B. H., Tamburini, C., and Tanaka, T. (2010). Assessing the apparent imbalance between geochemical and biochemical indicators of meso- and bathypelagic biological activity: What the @$#! is wrong with present calculations of carbon budgets? *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 57(16):1557–1571.

Cabaniss, S. E. and Shuman, M. S. (1987). Synchronous fluorescence spectra of natural waters: tracing sources of dissolved organic matter. *Marine Chemistry*, 21(1):37–50.

Cael, B. B., Heathcote, A. J., and Seekell, D. A. (2017). The volume and mean depth of earth's lakes. *Geophysical Research Letters*, 44(1):209–218.

Callahan, B. J., McMurdie, P. J., Rosen, M. J., Han, A. W., Johnson, A. J. A., and Holmes, S. P. (2016). Dada2: high-resolution sample inference from illumina amplicon data. *Nature methods*, 13(7):581.

Carignan, R., Blais, A. M., and Vis, C. (1998). Measurement of primary production and community respiration in oligotrophic lakes using the winkler method. *Canadian Journal of Fisheries and Aquatic Sciences*, 55(5):1078–1084.

Carlson, C. A., Bates, N. R., Ducklow, H. W., and Hansell, D. A. (1999). Estimation of bacterial respiration and growth efficiency in the ross sea, antarctica. *Aquatic Microbial Ecology*, 19(3):229–244.

Carlson, C. A., Giovannoni, S. J., Hansell, D. A., Goldberg, S. J., Parsons, R., and Vergin, K. (2004). Interactions among dissolved organic carbon, microbial processes, and community structure in the mesopelagic zone of the northwestern sargasso sea. *Limnology and Oceanography*, 49(4):1073–1083.

Carlson, C. A. and Hansell, D. A. (2015). *Chapter 3 - DOM Sources, Sinks, Reactivity, and Budgets*, pages 65–126. Academic Press, Boston.

Catalá, T. S., Reche, I., Fuentes-Lema, A., Romera-Castillo, C., Nieto-Cid, M., Ortega-Retuerta, E., Calvo, E., Álvarez, M., Marrasé, C., Stedmon, C. A., and Álvarez-Salgado, X. A. (2015). Turnover time of fluorescent dissolved organic matter in the dark global ocean. *Nat Commun*, 6.

Catalan, N., Marce, R., Kothawala, D. N., and Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geosci*,

9(7):501–504.

Clarke, R. A. and Coote, A. R. (1988). The formation of labrador sea water. part iii: The evolution of oxygen and nutrient concentration. *Journal of Physical Oceanography*, 18(3):469–480.

Coble, P. G. (1996). Characterization of marine and terrestrial dom in seawater using excitation-emission matrix spectroscopy. *Marine chemistry*, 51(4):325–346.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, 10(1):172–185.

Comeau, A. M., Douglas, G. M., and Langille, M. G. I. (2017). Microbiome helper: a custom and streamlined workflow for microbiome research. *MSystems*, 2(1).

Conlisk, J., Conlisk, E., Kassim, A. R., Billick, I., and Harte, J. (2012). The shape of a species' spatial abundance distribution. *Global Ecology and Biogeography*, 21(12):1167–1178.

Corilo, Y. (2015). Enviroorg. pages Tallahassee, FL: Florida State University.

Cottrell, M. T. and Kirchman, D. L. (2000). Natural assemblages of marine proteobacteria and members of the cytophaga-flavobacter cluster consuming low-and high-molecular-weight dissolved organic matter. *Applied and Environmental Microbiology*, 66(4):1692–1697.

Crump, B. C., Amaral-Zettler, L. A., and Kling, G. W. (2012). Microbial diversity in arctic freshwaters is structured by inoculation of microbes from soils. *The ISME journal*, 6(9):1629.

Dauwe, B., Middelburg, J. J., Herman, P. M., and Heip, C. H. (1999). Linking diagenetic alteration of amino acids and bulk organic matter reactivity. *Limnology and Oceanography*, 44(7):1809–1814.

Davis, J. and Benner, R. (2007). Quantitative estimates of labile and semi-labile dissolved organic carbon in the western arctic ocean: A molecular approach. *Limnology and Oceanography*, 52(6):2434–2444.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., and Iudicone, D. (2004). Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. *Journal of Geophysical Research: Oceans*, 109(C12).

DeGrandpre, M. D., Kortzinger, A., Send, U., Wallace, D. W. R., and Bellerby, R. G. J. (2006). Uptake and sequestration of atmospheric co_2 in the labrador sea deep convection region. *Geophysical Research Letters*, 33(21):5.

del Giorgio, P. A. and Cole, J. J. (1998). Bacterial growth efficiency in natural aquatic systems. *Annual Review of Ecology and Systematics*, pages 503–541.

del Giorgio, P. A., Cole, J. J., and Cimbleris, A. (1997). Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. *Nature*, 385(6612):148–151.

del Giorgio, P. A., Condon, R., Bouvier, T., Longnecker, K., Bouvier, C., Sherr, E., and Gasol, J. M. (2011). Coherent patterns in bacterial growth, growth efficiency, and leucine metabolism along a northeastern pacific inshore-offshore transect. *Limnology and Oceanography*, 56(1):1–16.

del Giorgio, P. A. and Davis, J. (2003). *Patterns in dissolved organic matter lability and consumption across aquatic ecosystems*, pages 399–424. Elsevier.

del Giorgio, P. A. and Duarte, C. M. (2002). Respiration in the open ocean. *Nature*, 420(6914):379–384.

Dell'Anno, A., Beolchini, F., Rocchetti, L., Luna, G. M., and Danovaro, R. (2012). High bacterial biodiversity increases degradation performance of hydrocarbons during bioremediation of contaminated harbor marine sediments. *Environmental pollution*, 167:85–92.

Dittmar, T., Koch, B., Hertkorn, N., and Kattner, G. (2008). A simple and efficient method for the solid-phase extraction of dissolved organic matter (spe-dom) from seawater. *Limnology and Oceanography: Methods*, 6(6):230–235.

Duarte, C. M. and Agustí, S. (1998). The co_2 balance of unproductive aquatic ecosystems. *Science*, 281(5374):234–236.

Duarte, C. M., Agusti, S., Vaque, D., Agawin, N. S. R., Felipe, J., Casamayor, E. O., and Gasol, J. M. (2005). Experimental test of bacteria-phytoplankton coupling in the southern ocean. *Limnology and Oceanography*, 50(6):1844–1854.

Duarte, C. M. and Cebrian, J. (1996). The fate of marine autotrophic production. *Limnology and Oceanography*, 41(8):1758–1766.

Duarte, C. M., Regaudie-de Gioux, A., Arrieta, J. M., Delgado-Huertas, A., and Agusti, S. (2013). The oligotrophic ocean is heterotrophic. *Annual Review of Marine Science, Vol 5*, 5:551–569.

Ducklow, H. W. (1983). Production and fate of bacteria in the oceans. *Bioscience*, 33(8):494–501.

Dufour, P., Charpy, L., Bonnet, S., and Garcia, N. (1999). Phytoplankton nutrient control in the oligotrophic south pacific subtropical gyre(tuamotu archipelago). *Marine Ecology Progress Series*, 179:285–290.

Eberlein, K., Leal, M., Hammer, K., and Hickel, W. (1985). Dissolved organic substances during a phaeocystis pouchetii bloom in the german bight (north sea). *Marine Biology*, 89(3):311–316.

Elifantz, H., Malmstrom, R. R., Cottrell, M. T., and Kirchman, D. L. (2005). Assimilation of polysaccharides and glucose by major bacterial groups in the delaware estuary. *Applied and Environmental Microbiology*, 71(12):7799–7805.

Elzhov, T. V., Mullen, K. M., Spiess, A.-N., and Bolker, B. (2016). *minpack.lm: R Interface to the Levenberg-Marquardt Nonlinear Least-Squares Algorithm Found in MINPACK, Plus Support for Bounds*. R package version 1.2-1.

El-Swais, H., Dunn, K. A., Bielawski, J. P., Li, W. K., and Walsh, D. A. (2015). Seasonal assemblages and short-lived blooms in coastal north-west a tlantic o cean bacterioplankton. *Environmental microbiology*, 17(10):3642–3661.

Escoubeyrou, K. and Tremblay, L. (2014). Quantification of free, dissolved combined, particulate, and total amino acid enantiomers using simple sample preparation and more robust chromatographic procedures. *Limnology and Oceanography-Methods*, 12:421–431.

Evans, C. D., Futter, M. N., Moldan, F., Valinia, S., Frogbrook, Z., and Kothawala, D. N. (2017). Variability in organic carbon reactivity across lake residence time and trophic gradients. *Nature Geoscience*, 10(11):832.

Farjalla, V. F., Faria, B. M., and Esteves, F. A. (2002). The relationship between doc and planktonic bacteria in tropical coastal lagoons. *Archiv für Hydrobiologie*, 156(1):97–119.

Field, C. B., Behrenfeld, M. J., Randerson, J. T., and Falkowski, P. (1998). Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science*, 281(5374):237–240.

Fierer, N. and Jackson, R. B. (2006). The diversity and biogeography of soil bacterial communities. *Proceedings of the National Academy of Sciences of the United States of America*, 103(3):626–631.

Fierer, N., Nemergut, D., Knight, R., and Craine, J. M. (2010). Changes through time: integrating microorganisms into the study of succession. *Research in microbiology*, 161(8):635–642.

Fragoso, G. M., Poulton, A. J., Yashayaev, I. M., Head, E. J., Stinchcombe, M., and Purdie, D. A. (2016). Biogeographical patterns and environmental controls of phytoplankton communities from contrasting hydrographical zones of the labrador sea. *Progress in Oceanography*.

Freitas, S., Hatosy, S., Fuhrman, J. A., Huse, S. M., Welch, D. B. M., Sogin, M. L., and Martiny, A. C. (2012). Global distribution and diversity of marine verrucomicrobia. *The ISME journal*, 6(8):1499.

Fuhrman, J. A. and Hagström, A. (2008). Bacterial and archaeal community structure and its patterns. *Microbial Ecology of the Oceans, Second Edition*, pages 45–90.

Giovannoni, S. J. (2017). Sar11 bacteria: the most abundant plankton in the oceans. *Annual review of marine science*, 9:231–255.

Guillemette, F. and del Giorgio, P. A. (2011). Reconstructing the various facets of dissolved organic carbon bioavailability in freshwater ecosystems. *Limnology and Oceanography*, 56(2):734–748.

Guillemette, F., McCallister, S. L., and del Giorgio, P. A. (2013). Differentiating the degradation dynamics of algal and terrestrial carbon within complex natural dissolved organic carbon in temperate lakes. *Journal of Geophysical Research: Biogeosciences*, 118(3):963–973.

Hagström, A., Pinhassi, J., and Zweifel, U. L. (2000). Biogeographical diversity among marine bacterioplankton. *Aquatic Microbial Ecology*, 21(3):231–244.

Hama, T., Yanagi, K., and Hama, J. (2004). Decrease in molecular weight of photosynthetic products of marine phytoplankton during early diagenesis. *Limnology and oceanography*, 49(2):471–481.

Hammes, F., Vital, M., and Egli, T. (2010). Critical evaluation of the volumetric "bottle effect" on microbial batch growth. *Appl. Environ. Microbiol.*, 76(4):1278–1281.

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5.

Hansell, D. A. and Carlson, C. A. (1998). Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature*, 395(6699):263–266.

Hansell, D. A. and Carlson, C. A. (2014). *Biogeochemistry of marine dissolved organic matter*. Academic Press.

Hansell, D. A., Carlson, C. A., and Schlitzer, R. (2012). Net removal of major marine dissolved organic carbon fractions in the subsurface ocean. *Global Biogeochemical Cycles*, 26(1).

Harvey, H. R., Dyda, R. Y., and Kirchman, D. L. (2006). Impact of dom composition on bacterial lipids and community structure in estuaries. *Aquatic microbial ecology*, 42(2):105–117.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, 53(3):955–969.

Herndl, G. J. and Reinthaler, T. (2013). Microbial control of the dark end of the biological pump. *Nature Geoscience*, 6(9):718–724.

Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A., and Hedges, J. I. (2006). Characterization of a major refractory component of marine dissolved organic matter. *Geochimica et Cosmochimica Acta*, 70(12):2990–3010.

Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., and Strickland, J. D. H. (1965). Fluorometric determination of chlorophyll. *ICES Journal of Marine Science*, 30(1):3–15.

Holmes, R. M., Aminot, A., Kérouel, R., Hooker, B. A., and Peterson, B. J. (1999). A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences*, 56(10):1801–1808.

Hopkinson, C. S. and Vallino, J. J. (2005). Efficient export of carbon to the deep ocean through dissolved organic matter. *Nature*, 433(7022):142–145.

Hopkinson, C. S., Vallino, J. J., and Nolin, A. (2002). Decomposition of dissolved organic matter from the continental margin. *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 49(20):4461–4478.

Hotchkiss, E., Hall Jr, R., Sponseller, R., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., and Karlsson, J. (2015). Sources of and processes controlling co 2 emissions change with the size of streams and rivers. *Nature Geoscience*, 8(9):696.

Ishii, S. K. L. and Boyer, T. H. (2012). Behavior of reoccurring parafac components in fluorescent dissolved organic matter in natural and engineered systems: A critical review. *Environmental Science & Technology*, 46(4):2006–2017.

Jahnke, R. A. and Craven, D. B. (1995). Quantifying the role of heterotrophic bacteria in the carbon cycle: A need for respiration rate measurements1. *Limnology and Oceanography*, 40(2):436–441.

Jannasch, H. W. (1967). Growth of marine bacteria at limiting concentrations of organic carbon in seawater 1. *Limnology and Oceanography*, 12(2):264–271.

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., Kirchman, D. L., Weinbauer, M. G., Luo, T., and Chen, F. (2010). Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nature Reviews Microbiology*, 8(8):593–599.

Jiao, N., Legendre, L., Robinson, C., Thomas, H., Luo, Y.-W., Dang, H., Liu, J., Zhang, R., Tang, K., and Luo, T. (2015). Comment on "dilution limits dissolved organic carbon utilization in the deep ocean". *Science*, 350(6267):1483–1483.

Jiao, N., Robinson, C., Azam, F., Thomas, H., Baltar, F., Dang, H., Hardman-Mountford, N., Johnson, M., Kirchman, D., and Koch, B. (2014). Mechanisms of microbial carbon sequestration in the ocean–future research directions. *Biogeosciences*, 11(19):5285–5306.

Jones, S. E. and Lennon, J. T. (2010). Dormancy contributes to the maintenance of microbial diversity. *Proceedings of the National Academy of Sciences*, 107(13):5881–5886.

Jousset, A., Bienhold, C., Chatzinotas, A., Gallien, L., Gobet, A., Kurm, V., Küsel, K., Rillig, M. C., Rivett, D. W., and Salles, J. F. (2017). Where less may be more: how the rare biosphere pulls ecosystems strings. *The ISME journal*, 11(4):853.

Judd, K. E., Crump, B. C., and Kling, G. W. (2006). Variation in dissolved organic matter controls bacterial production and community composition. *Ecology*, 87(8):2068–2079.

Jørgensen, B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments.

Kaiser, K. and Benner, R. (2005). Hydrolysis-induced racemization of amino acids. *Limnology and Oceanography: Methods*, 3(8):318–325.

Kaiser, K. and Benner, R. (2008). Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen. *Limnology and Oceanography*, 53(1):99–112.

Kankaala, P., Huotari, J., Peltomaa, E., Saloranta, T., and Ojala, A. (2006). Methanotrophic activity in relation to methane efflux and total heterotrophic bacterial production in a stratified, humic, boreal lake. *Limnology and Oceanography*, 51(2):1195–1204.

Kappelmann, L., Krüger, K., Hehemann, J.-H., Harder, J., Markert, S., Unfried, F., Becher, D., Shapiro, N., Schweder, T., Amann, R. I., and Teeling, H. (2019). Polysaccharide utilization loci of north sea flavobacteriia as basis for using susc/d-protein expression for predicting major phytoplankton glycans. *The ISME Journal*, 13(1):76–91.

Karner, M. B., DeLong, E. F., and Karl, D. M. (2001). Archaeal dominance in the mesopelagic zone of the pacific ocean. *Nature*, 409(6819):507–510.

Kellerman, A. M., Guillemette, F., Podgorski, D. C., Aiken, G. R., Butler, K. D., and Spencer, R. G. (2018). Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. *Environmental science & technology*, 52(5):2538–2548.

Kirchman, D. L. (2002). The ecology of cytophaga–flavobacteria in aquatic environments. *FEMS microbiology ecology*, 39(2):91–100.

Kirchman, D. L. (2008). Microbial ecology of the oceans. 36.

Kirchman, D. L., Elifantz, H., Dittel, A. I., Malmstrom, R. R., and Cottrell, M. T. (2007). Standing stocks and activity of archaea and bacteria in the western arctic ocean. *Limnology and Oceanography*, 52(2):495–507.

Koch, B. P., Kattner, G., Witt, M., and Passow, U. (2014). Molecular insights into the microbial formation of marine dissolved organic matter: recalcitrant or labile? *Biogeosciences*, 11(15):4173–4190.

Koehler, B., Landelius, T., Weyhenmeyer, G. A., Machida, N., and Tranvik, L. J. (2014). Sunlight-induced carbon dioxide emissions from inland waters. *Global Biogeochemical Cycles*, 28(7):696–711.

Koehler, B., Wachenfeldt, E., Kothawala, D., and Tranvik, L. J. (2012). Reactivity continuum of dissolved organic carbon decomposition in lake water. *Journal of Geophysical Research: Biogeosciences*, 117(G1).

Könneke, M., Bernhard, A. E., José, R., Walker, C. B., Waterbury, J. B., and Stahl, D. A. (2005). Isolation of an autotrophic ammonia-oxidizing marine archaeon. *Nature*, 437(7058):543.

Kowalczuk, P., Cooper, W. J., Durako, M. J., Kahn, A. E., Gonsior, M., and Young, H. (2010). Characterization of dissolved organic matter fluorescence in the south atlantic bight with use of parafac model: Relationships between fluorescence and its components, absorption coefficients and organic carbon concentrations. *Marine Chemistry*, 118(1):22–36.

Kritzberg, E. S., Cole, J. J., Pace, M. L., Granéli, W., and Bade, D. L. (2004). Autochthonous versus allochthonous carbon sources of bacteria: Results from whole-lake 13c addition experiments. *Limnology and Oceanography*, 49(2):588–596.

Kujawinski, E. B. (2002). Electrospray ionization fourier transform ion cyclotron resonance mass spectrometry (esi ft-icr ms): Characterization of complex environmental mixtures. *Environmental Forensics*, 3(3-4):207–216.

LaBrie, R., Bélanger, S., Benner, R., and Maranger, R. (Under reviewa). Spatial abundance distribution of prokaryotes is defined by their dissolved organic matter preferences.

LaBrie, R., Fortin St-Gelais, N., and Bélanger, S. (2017a). *paRafac.correction: an R Package to correct EEMs and derive CDOM and FDOM indices*.

LaBrie, R., Fortin St-Gelais, N., and Bélanger, S. (2017b). *paRafac.correction: an R Package to correct EEMs and derive CDOM and FDOM indices*.

LaBrie, R., Lapierre, J.-F., and Maranger, R. (Under reviewb). Contrasting patterns of labile and semi-labile dissolved organic carbon from continental waters to the open ocean. *Journal of Geophysical Research: Biogeosciences*.

Lalonde, K., Middlestead, P., and Gélinas, Y. (2014). Automation of 13c/12c ratio measurement for freshwater and seawater doc using high temperature combustion. *Limnol. Oceanogr.: Methods*, 12:816–829.

Lapierre, J. F. and del Giorgio, P. A. (2014). Partial coupling and differential regulation of biologically and photochemically labile dissolved organic carbon across boreal aquatic networks. *Biogeosciences*, 11(20):5969–5985.

Lapierre, J.-F., Guillemette, F., Berggren, M., and del Giorgio, P. A. (2013). Increases in terrestrially derived carbon stimulate organic carbon processing and co2 emissions in boreal aquatic ecosystems. *Nature communications*, 4.

LaRowe, D. E., Dale, A. W., Amend, J. P., and Van Cappellen, P. (2012). Thermodynamic limitations on microbially catalyzed reaction rates. *Geochimica et Cosmochimica Acta*, 90:96–109.

LaRowe, D. E. and Van Cappellen, P. (2011). Degradation of natural organic matter: a thermodynamic analysis. *Geochimica et Cosmochimica Acta*, 75(8):2030–2042.

Lazier, J., Hendry, R., Clarke, A., Yashayaev, I., and Rhines, P. (2002). Convection and restratification in the labrador sea, 1990-2000. *Deep-Sea Research Part I-Oceanographic Research Papers*, 49(10):1819–1835.

Lazier, J. R. The renewal of labrador sea water. In *Deep Sea Research and Oceanographic Abstracts*, volume 20, pages 341–353. Elsevier.

Lechtenfeld, O. J., Hertkorn, N., Shen, Y., Witt, M., and Benner, R. (2015). Marine sequestration of carbon in bacterial metabolites. *Nature communications*, 6.

Lechtenfeld, O. J., Kattner, G., Flerus, R., McCallister, S. L., Schmitt-Kopplin, P., and Koch, B. P. (2014). Molecular transformation and degradation of refractory dissolved organic matter in the atlantic and southern ocean. *Geochimica et Cosmochimica Acta*, 126:321–337.

Legendre, P. and Legendre, L. F. (2012). *Numerical ecology*, volume 24. Elsevier.

Lehmann, J. and Kleber, M. (2015). The contentious nature of soil organic matter. *Nature*, 528(7580):60.

Lennon, J. T. and Jones, S. E. (2011). Microbial seed banks: the ecological and evolutionary implications of dormancy. *Nature reviews microbiology*, 9(2):119.

Lenton, T. M., Held, H., Kriegler, E., Hall, J. W., Lucht, W., Rahmstorf, S., and Schellnhuber, H. J. (2008). Tipping elements in the earth's climate system. *Proceedings of the National Academy of Sciences of the United States of America*, 105(6):1786–1793.

Lindroth, P. and Mopper, K. (1979). High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde. *Analytical Chemistry*, 51(11):1667–1674.

Lisitsyn, A. (1995). The marginal filter of the ocean. *Oceanology of the Russian Academy of Sciences*, 34(5):671–682.

Logue, J. B., Stedmon, C. A., Kellerman, A. M., Nielsen, N. J., Andersson, A. F., Laudon, H., Lindström, E. S., and Kritzberg, E. S. (2015). Experimental insights into the importance of aquatic bacterial community composition to the degradation of dissolved organic matter. *The ISME Journal*.

López-Urrutia, A. and Morán, X. A. G. (2007). Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling. *Ecology*, 88(4):817–822.

Lønborg, C. and Álvarez-Salgado, X. A. (2012). Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump. *Global Biogeochemical Cycles*, 26(3).

Lønborg, C., Yokokawa, T., Herndl, G. J., and Álvarez-Salgado, X. A. (2015). Production and degradation of fluorescent dissolved organic matter in surface waters of the eastern north atlantic ocean. *Deep-Sea Research Part I-Oceanographic Research Papers*, 96:28–37.

Maier, T. V., Lucio, M., Lee, L. H., VerBerkmoes, N. C., Brislawn, C. J., Bernhardt, J. r., Lamendella, R., McDermott, J. E., Bergeron, N., and Heinzmann, S. S. (2017). Impact of dietary resistant starch on the human gut microbiome, metaproteome, and metabolome. *MBio*, 8(5):e01343–17.

Malmstrom, R. R., Kiene, R. P., Cottrell, M. T., and Kirchman, D. L. (2004). Contribution of sar11 bacteria to dissolved dimethylsulfoniopropionate and amino acid uptake in the north atlantic ocean. *Applied and environmental microbiology*, 70(7):4129–4135.

Marchese, C., de la Guardia, L. C., Myers, P. G., and Bélanger, S. (2019). Regional differences and inter-annual variability in the timing of surface phytoplankton blooms in the labrador sea. *Ecological indicators*, 96:81–90.

Martinez-Garcia, S., Fernandez, E., del Valle, D. A., Karl, D. M., and Teira, E. (2013). Experimental assessment of marine bacterial respiration. *Aquatic Microbial Ecology*, 70(3):189–205.

Martiny, J. B., Jones, S. E., Lennon, J. T., and Martiny, A. C. J. S. (2015). Microbiomes in light of traits: a phylogenetic perspective. 350(6261):aac9323.

Massicotte, P., Asmala, E., Stedmon, C., and Markager, S. (2017). Global distribution of dissolved organic matter along the aquatic continuum: Across rivers, lakes and oceans. *Science of the Total Environment*, 609:180–191.

Massicotte, P. and Frenette, J.-J. (2011). Spatial connectivity in a large river system: resolving the sources and fate of dissolved organic matter. *Ecological Applications*, 21(7):2600–2617.

McCallister, S. L., Bauer, J. E., Cherrier, J. E., and Ducklow, H. W. (2004). Assessing sources and ages of organic matter supporting river and estuarine bacterial production: A multiple-isotope (δ^{14}C, δ^{13}C, and δ^{15}N) approach. *Limnology and Oceanography*, 49(5):1687–1702.

McCarren, J., Becker, J. W., Repeta, D. J., Shi, Y., Young, C. R., Malmstrom, R. R., Chisholm, S. W., and DeLong, E. F. (2010). Microbial community transcriptomes reveal microbes and metabolic pathways associated with dissolved organic matter turnover in the sea. *Proceedings of the National Academy of Sciences*, 107(38):16420–16427.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46(1):38–48.

Mestre, M., Ruiz-González, C., Logares, R., Duarte, C. M., Gasol, J. M., and Sala, M. M. (2018). Sinking particles promote vertical connectivity in the ocean microbiome. *Proceedings of the National Academy of Sciences*, 115(29):E6799–E6807.

Miller, W. L. and Zepp, R. G. (1995). Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the oceanic organic carbon cycle. *Geophysical Research Letters*, 22(4):417–420.

Moran, M. A., Kujawinski, E. B., Stubbins, A., Fatland, R., Aluwihare, L. I., Buchan, A., Crump, B. C., Dorrestein, P. C., Dyhrman, S. T., and Hess, N. J. (2016). Deciphering ocean carbon in a changing world. *Proceedings of the National Academy of Sciences*, pages 3143–3151.

Morita, R. Y. (1993). *Bioavailability of energy and the starvation state*, pages 1–23. Springer.

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R. (2013). Fluorescence spectroscopy and multi-way techniques. parafac. *Analytical Methods*, 5(23):6557–6566.

Myklestad, S. M. (1995). Release of extracellular products by phytoplankton with special emphasis on polysaccharides. *Science of the total Environment*, 165(1-3):155–164.

Nagata, T. (2000). Production mechanisms of dissolved organic matter. *Microbial ecology of the oceans*, pages 121–152.

Nagata, T., Meon, B., and L Kirchman, D. (2003). Microbial degradation of peptidoglycan in seawater. *Limnology and oceanography*, 48(2):745–754.

Nagata, T., Tamburini, C., Aristegui, J., Baltar, F., Bochdansky, A. B., Fonda-Umani, S., Fukuda, H., Gogou, A., Hansell, D. A., Hansman, R. L., Herndl, G. J., Panagiotopoulos, C., Reinthaler, T., Sohrin, R., Verdugo, P., Yamada, N., Yamashita, Y., Yokokawa, T., and Bartlett, D. H. (2010). Emerging concepts on microbial processes in the bathypelagic ocean - ecology, biogeochemistry, and genomics. *Deep-Sea Research Part Ii-Topical Studies in Oceanography*, 57(16):1519–1536.

Nguyen, D., Maranger, R., Balagué, V., Coll-Llado, M., Lovejoy, C., and Pedros-Alio, C. (2015). Winter diversity and expression of proteorhodopsin genes in a polar ocean. *The ISME journal*, 9(8):1835.

Nguyen, D., Maranger, R., Tremblay, J. E., and Gosselin, M. (2012). Respiration and bacterial carbon dynamics in the amundsen gulf, western2 canadian arctic. *Journal of Geophysical Research-Oceans*, 117:12.

Niño-García, J. P., Ruiz-González, C., and Del Giorgio, P. A. (2016). Landscape-scale spatial abundance distributions discriminate core from random components of boreal lake bacterioplankton. *Ecology letters*, 19(12):1506–1515.

Nielsen, J. L. and Nielsen, P. H. (2005). Advances in microscopy: microautoradiography of single cells. *Methods in enzymology*, 397:237–256.

Obernosterer, I. and Benner, R. (2004). Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. *Limnology and Oceanography*, 49(1):117–124.

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., and Benner, R. (2001). Production of refractory dissolved organic matter by bacteria. *Science*, 292(5518):917–920.

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P. R., O'Hara, R. B., Simpson, G. L., Solymos, P., Stevens, M. H. H., Szoecs, E., and Wagner, H. (2018). *vegan: Community Ecology Package*. R package version 2.4-6.

Osburn, C. L. and Stedmon, C. A. (2011). Linking the chemical and optical properties of dissolved organic matter in the baltic–north sea transition zone to differentiate three allochthonous inputs. *Marine chemistry*, 126(1):281–294.

Panagiotopoulos, C., Repeta, D. J., and Johnson, C. G. J. O. g. (2007). Characterization of methyl sugars, 3-deoxysugars and methyl deoxysugars in marine high molecular weight dissolved organic matter. 38(6):884–896.

Passow, U. (2002). Production of transparent exopolymer particles (tep) by phyto-and bacterioplankton. *Marine ecology-progress series*, 236:1–12.

Pedler, B. E., Aluwihare, L. I., and Azam, F. (2014). Single bacterial strain capable of significant contribution to carbon cycling in the surface ocean. *Proceedings of the National Academy of Sciences of the United States of America*, 111(20):7202–7207.

Péquin, B., Fortin St-Gelais, N., LaBrie, R., and Maranger, R. (Unpublished). Bloom timing explains succession of protistan functional community structure.

Pester, M., Bittner, N., Deevong, P., Wagner, M., and Loy, A. (2010). A 'rare biosphere'microorganism contributes to sulfate reduction in a peatland. *The ISME journal*, 4(12):1591.

Pinhassi, J. and Berman, T. (2003). Differential growth response of colony-forming $\alpha-$and $\gamma-$proteobacteria in dilution culture and nutrient addition experiments from lake kinneret (israel), the eastern mediterranean sea, and the gulf of eilat. *Applied and Environmental Microbiology*, 69(1):199–211.

Pomeroy, L. R. (1974). The ocean's food web, a changing paradigm. *Bioscience*, 24(9):499–504.

Pomeroy, L. R., Williams, P. J. I., Azam, F., and Hobbie, J. E. (2007). The microbial loop. *Oceanography*, 20(2):28.

Pommier, T., Canbäck, B., Riemann, L., Boström, K., Simu, K., Lundberg, P., Tunlid, A., and Hagström, A. (2007). Global patterns of diversity and community structure in marine bacterioplankton. *Molecular ecology*, 16(4):867–880.

R Core Team (2017). *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.

Ramlal, P. S., Hecky, R. E., Bootsma, H. A., Schiff, S. L., and Kingdon, M. J. (2003). Sources and fluxes of organic carbon in lake malawi/nyasa. *Journal of Great Lakes Research*, 29:107–120.

Regaudie-de Gioux, A. and Duarte, C. M. (2010). Plankton metabolism in the greenland sea during the polar summer of 2007. *Polar Biology*, 33(12):1651–1660.

Rhein, M., Steinfeldt, R., Kieke, D., Stendardo, I., and Yashayaev, I. (2017). Ventilation variability of labrador sea water and its impact on oxygen and anthropogenic carbon: a review. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 375(2102):20160321.

Riemann, L., Steward, G. F., and Azam, F. (2000). Dynamics of bacterial community composition and activity during a mesocosm diatom bloom. *Applied and Environmental Microbiology*, 66(2):578–587.

Rivkin, R. B. and Legendre, L. (2001). Biogenic carbon cycling in the upper ocean: Effects of microbial respiration. *Science*, 291(5512):2398–2400.

Robinson, C. and Williams, P. l. B. (2005). Respiration and its measurement in surface marine waters. *Respiration in aquatic ecosystems*, pages 147–181.

Rogers, S. W., Moorman, T. B., and Ong, S. K. (2007). Fluorescent in situ hybridization and micro-autoradiography applied to ecophysiology in soil. *Soil Science Society of America Journal*, 71(2):620–631.

Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrase, C. (2010). Production of chromophoric dissolved organic matter by marine phytoplankton. *Limnology and Oceanography*, 55(1):446–454.

Romera-Castillo, C., Sarmento, H., Álvarez-Salgado, X. A., Gasol, J. M., and Marrasé, C. (2011). Net production and consumption of fluorescent colored dissolved organic matter by natural bacterial assemblages growing on marine phytoplankton exudates. *Applied and Environmental Microbiology*, 77(21):7490–7498.

Ruiz-González, C., Logares, R., Sebastián, M., Mestre, M., Rodríguez-Martínez, R., Galí, M., Sala, M. M., Acinas, S. G., Duarte, C. M., and Gasol, J. M. (2019). Higher contribution of globally rare bacterial taxa reflects environmental transitions across the surface ocean. *Molecular ecology*, 28(8):1930–1945.

Ruiz-González, C., Niño-García, J. P., and del Giorgio, P. A. (2015). Terrestrial origin of bacterial communities in complex boreal freshwater networks. *Ecology letters*, 18(11):1198–1206.

Sarmento, H., Montoya, J. M., Vazquez-Dominguez, E., Vaque, D., and Gasol, J. M. (2010). Warming effects on marine microbial food web processes: how far can we go when it comes to predictions? *Philosophical Transactions of the Royal Society B-Biological Sciences*, 365(1549):2137–2149.

Sarmento, H., Romera-Castillo, C., Lindh, M., Pinhassi, J., Sala, M. M., Gasol, J. M., Marrase, C., and Taylor, G. T. (2013). Phytoplankton species-specific release of dissolved free amino acids and their selective consumption by bacteria. *Limnology and Oceanography*, 58(3):1123–1135.

Schmidt, M. W., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., Kleber, M., Kögel-Knabner, I., Lehmann, J., and Manning, D. A. (2011). Persistence of soil organic matter as an ecosystem property. *Nature*, 478(7367):49.

Sebastián, M., Auguet, J., Restrepo-Ortiz, C. X., Sala, M. M., Marrasé, C., and Gasol, J. M. (2018). Deep ocean prokaryotic communities are remarkably malleable when facing long-term starvation. *Environmental microbiology*, 20(2):713–723.

Servais, P., Billen, G., and Hascoët, M.-C. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters. *Water research*, 21(4):445–450.

Sharp, J. H. (1997). Marine dissolved organic carbon: Are the older values correct? *Marine Chemistry*, 56(3-4):265–277.

Siegel, D., Maritorena, S., Nelson, N., Hansell, D., and Lorenzi-Kayser, M. (2002). Global distribution and dynamics of colored dissolved and detrital organic materials. *Journal of Geophysical Research: Oceans*, 107(C12):21–1–21–14.

Simon, M., Cho, B. C., and Azam, F. (1992). Significance of bacterial biomass in lakes and the ocean: comparison to phytoplankton biomass and biogeochemical implications. *Marine Ecology Progress Series*, 86(2):103–110.

Simon, M. and Rosenstock, B. (2007). Different coupling of dissolved amino acid, protein, and carbohydrate turnover to heterotrophic picoplankton production in the southern ocean in austral summer and fall. *Limnology and Oceanography*, 52(1):85–95.

Smith, D. C. and Azam, F. (1992). A simple, economical method for measuring bacterial protein synthesis rates in seawater using 3h-leucine. *Mar. Microb. Food Webs*, 6(2):107–114.

Smith, E. M. and Prairie, Y. T. (2004). Bacterial metabolism and growth efficiency in lakes: the importance of phosphorus availability. *Limnology and Oceanography*, 49(1):137–147.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52(3):1208–1219.

Sogin, M. L., Morrison, H. G., Huber, J. A., Welch, D. M., Huse, S. M., Neal, P. R., Arrieta, J. M., and Herndl, G. J. (2006). Microbial diversity in the deep sea and the underexplored "rare biosphere". *Proceedings of the National Academy of Sciences*, 103(32):12115–12120.

Stedmon, C. A. and Markager, S. (2005). Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using parafac analysis. *Limnology and Oceanography*, 50(2):686–697.

Stedmon, C. A., Markager, S., and Kaas, H. (2000). Optical properties and signatures of chromophoric dissolved organic matter (cdom) in danish coastal waters. *Estuarine, Coastal and Shelf Science*, 51(2):267–278.

Stekhoven, D. J. (2013). *missForest: Nonparametric Missing Value Imputation using Random Forest*. R package version 1.4.

Stets, E. G., Striegl, R. G., and Aiken, G. R. (2010). Dissolved organic carbon export and internal cycling in small, headwater lakes. *Global Biogeochemical Cycles*, 24(4).

Stubbins, A., Lapierre, J.-F., Berggren, M., Prairie, Y., Dittmar, T., and Del Giorgio, P. (2014). What's in an eem? molecular signatures associated with dissolved organic fluorescence in boreal canada. *Environmental science & technology*, 48(18):10598–10606.

Sundh, I., Bastviken, D., and Tranvik, L. J. (2005). Abundance, activity, and community structure of pelagic methane-oxidizing bacteria in temperate lakes. *Applied and environmental microbiology*, 71(11):6746–6752.

Suzuki, M. T., Preston, C. M., Chavez, F. P., and DeLong, E. F. (2001). Quantitative mapping of bacterioplankton populations in seawater: field tests across an upwelling plume in monterey bay. *Aquatic Microbial Ecology*, 24(2):117–127.

Székely, A. J. and Langenheder, S. (2014). The importance of species sorting differs between habitat generalists and specialists in bacterial communities. *FEMS microbiology ecology*, 87(1):102–112.

Søndergaard, M. and Middelboe, M. (1995). A cross-system analysis of labile dissolved organic carbon. *Marine ecology progress series. Oldendorf*, 118(1):283–294.

Tamburini, C., Goutx, M., Guigue, C., Garel, M., Lefèvre, D., Charrière, B., Sempéré, R., Pepa, S., Peterson, M. L., and Wakeham, S. (2009). Effects of hydrostatic pressure on microbial alteration of sinking fecal pellets. *Deep Sea Research Part II: Topical Studies in*

Oceanography, 56(18):1533–1546.

Taylor, J. D., Cottingham, S. D., Billinge, J., and Cunliffe, M. (2014). Seasonal microbial community dynamics correlate with phytoplankton-derived polysaccharides in surface coastal waters. *The ISME Journal*, 8(1):245.

Teeling, H., Fuchs, B. M., Becher, D., Klockow, C., Gardebrecht, A., Bennke, C. M., Kassabgy, M., Huang, S., Mann, A. J., and Waldmann, J. (2012). Substrate-controlled succession of marine bacterioplankton populations induced by a phytoplankton bloom. *Science*, 336(6081):608–611.

Teira, E., Van Aken, H., Veth, C., and Herndl, G. J. (2006). Archaeal uptake of enantiomeric amino acids in the meso-and bathypelagic waters of the north atlantic. *Limnology and Oceanography*, 51(1):60–69.

Traina, S. J., Novak, J., and Smeck, N. E. (1990). An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *Journal of environmental quality*, 19(1):151–153.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., and Knoll, L. B. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54(6part2):2298–2314.

Tranvik, L. J. and Jorgensen, N. O. G. (1995). Colloidal and dissolved organic-matter in lake water: Carbohydrate and amino acid composition, and ability to support bacterial growth. *Biogeochemistry*, 30(2):77–97.

Vähätalo, A. V., Aarnos, H., and Mäntyniemi, S. (2010). Biodegradability continuum and biodegradation kinetics of natural organic matter described by the beta distribution. *Biogeochemistry*, 100(1-3):227–240.

Verburg, P. (2007). The need to correct for the suess effect in the application of δ13c in sediment of autotrophic lake tanganyika, as a productivity proxy in the anthropocene. *Journal of Paleolimnology*, 37(4):591–602.

Verdugo, P., Orellana, M. V., Chin, W.-C., Petersen, T. W., van den Eng, G., Benner, R., and Hedges, J. I. (2008). Marine biopolymer self-assembly: implications for carbon cycling in the ocean. *Faraday discussions*, 139:393–398.

Violle, C., Navas, M., Vile, D., Kazakou, E., Fortunel, C., Hummel, I., and Garnier, E. (2007). Let the concept of trait be functional! *Oikos*, 116(5):882–892.

von Wachenfeldt, E. and Tranvik, L. J. (2008). Sedimentation in boreal lakes—the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems*, 11(5):803–814.

Walterscheid, S. K. (2011). Climate classification for the earth's oceanic areas using the köppen system. *Master thesis. Kansas State University.*

Wear, E. K., Carlson, C. A., James, A. K., Brzezinski, M. A., Windecker, L. A., and Nelson, C. E. (2015). Synchronous shifts in dissolved organic carbon bioavailability and bacterial community responses over the course of an upwelling-driven phytoplankton bloom. *Limnology and Oceanography*, 60(2):657–677.

Wetz, M. S. and Wheeler, P. A. (2007). Release of dissolved organic matter by coastal diatoms.

Weyhenmeyer, G. A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., and Tranvik, L. J. (2012). Selective decay of terrestrial organic carbon during transport from land to sea. *Global Change Biology*, 18(1):349–355.

Williams, P. J. l. B., Quay, P. D., Westberry, T. K., and Behrenfeld, M. J. (2013). The oligotrophic ocean is autotrophic*. *Annual review of marine science*, 5:535–549.

Williams, P. l. B. (2000). Heterotrophic bacteria and the dynamics of dissolved organic material. *Microbial ecology of the oceans. Wiley-Liss*, pages 153–200.

Williams, P. l. B. and del Giorgio, P. A. (2005). Respiration in aquatic ecosystems: history and background. *Respiration in aquatic ecosystems. Oxford University Press, Oxford*, pages 1–17.

Winter, C., Matthews, B., and Suttle, C. A. (2013). Effects of environmental variation and spatial distance on bacteria, archaea and viruses in sub-polar and arctic waters. *The ISME journal*, 7(8):1507–1518.

Wünsch, U. J., Bro, R., Stedmon, C. A., Wenig, P., and Murphy, K. R. (2019). Emerging patterns in the global distribution of dissolved organic matter fluorescence. *Analytical Methods*, 11(7):888–893.

Yamashita, Y. and Tanoue, E. (2003). Chemical characterization of protein-like fluorophores in dom in relation to aromatic amino acids. *Marine Chemistry*, 82(3-4):255–271.

Yamashita, Y. and Tanoue, E. (2004). Chemical characteristics of amino acid-containing dissolved organic matter in seawater. *Organic Geochemistry*, 35(6):679–692.

Yashayaev, I. and Clarke, A. (2008). Evolution of north atlantic water masses inferred from labrador sea salinity series. *Oceanography*, 21(1):30–45.

Yashayaev, I., Clarke, R., and Lazier, J. (2000). Recent decline of the labrador sea water. *International Council for the Exploration of the Sea CM*, 50:18.

Yashayaev, I., Holliday, N. P., Bersch, M., and van Aken, H. M. (2008). *The history of the Labrador Sea Water: Production, spreading, transformation and loss*, pages 569–612. Springer.

Yashayaev, I. and Loder, J. W. (2016). Recurrent replenishment of labrador sea water and associated decadal-scale variability. *Journal of Geophysical Research: Oceans*, 121(11):8095–8114.

Yoshioka, T., Ueda, S., Khodzher, T., Bashenkhaeva, N., Korovyakova, I., Sorokovikova, L., and Gorbunova, L. (2002). Distribution of dissolved organic carbon in lake baikal and its

watershed. *Limnology*, 3(3):0159–0168.

Yvon-Durocher, G., Jones, J. I., Trimmer, M., Woodward, G., and Montoya, J. M. (2010). Warming alters the metabolic balance of ecosystems. *Philosophical Transactions of the Royal Society B-Biological Sciences*, 365(1549):2117–2126.

Zark, M., Christoffers, J., and Dittmar, T. (2017). Molecular properties of deep-sea dissolved organic matter are predictable by the central limit theorem: Evidence from tandem ft-icr-ms. *Marine Chemistry*, 191:9–15.

Zweifel, U. L., Norrman, B., and Hagström, A. (1993). Consumption of dissolved organic carbon by marine bacteria and demand for inorganic nutrients. *Marine Ecology-Progress Series*, 101:23–23.

Annexe A

Supplementary information for chapter 2

B.1. Introduction

In the supplementary information (SI), we provide a summary on the number of batch culture experiments and studies carried out across the aquatic continuum. We also provide more details on how we calculated the total standing stock of DOC and how we estimated the total biomass derived from $BDOC_L$ and $BDOC_{SL}$ standing stocks.

B.2. Number of batch culture experiments and studies summary

We summarized the number of batch culture experiments and studies that were suitable for our analysis in Table S1.1 and represented them on a world map (Fig. S2.1). The sum of rows and sum of columns do not add up to the total or subtotal reported in the table because several studies had both values for $BDOC_L$ and BDOC. The number of batch culture experiments and studies reported in the productive environments category include studies conducted in lakes (n = 2), coasts (n = 7) and the open ocean (n = 1). The number of batch culture experiments lasting at least 31 days (our threshold for BDOC) represents only 29.6% of the total, emphasizing the need to conduct longer experiments to better constrain the role of the semi-labile pool.

B.3. Piecewise regression

In order to compare piecewise regressions between marine and freshwater systems on the same scale, we did a piecewise regression using non-log data for lakes (Fig S2.2). We found two breakpoints: the first one at 31 ± 12 days, very close to the result obtained on log-transformed data, and the second one at 120 ± 15 days. This second breakpoint likely

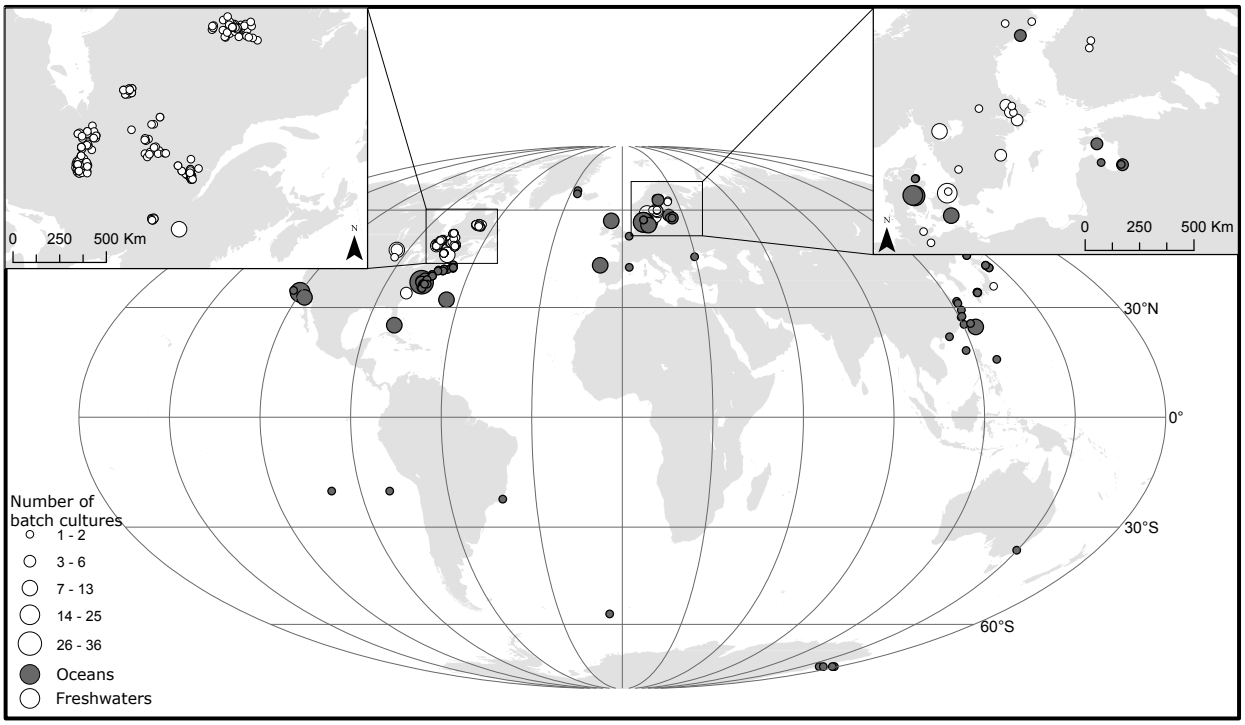


Fig. S2.1. Location of all batch cultures experiments, covering all continental and oceanic climate regions (Walterscheid, 2011). Regions with a high density of experimental sites are represented in insets. Dot size represents number of incubations for freshwaters (white) and marine ecosystems (grey).

represents the moment when the consumption of semi-labile DOC slows down, close to the plateau observed in DOC degradation curves. This piecewise regression was better than a linear fit as suggested by both Akaike and Bayesian information criteria (Δ151 and Δ137, respectively).

B.4. Estimating total standing stocks and supported prokaryotic biomass

In order to estimate how much prokaryotic biomass could be supported by $BDOC_L$ and $BDOC_{SL}$, we first needed to upscale the total amount of DOC available among biomes. For this comparison, we considered the entire volume of small inland lakes (Cael et al., 2017), but for larger ecosystems we limited the volume to the surface mixed layers of large lakes and coasts considered 30 m on average, and 100 m from the open ocean (de Boyer Montégut et al., 2004) which were then multiplied with estimated surface area (Cael et al., 2017; Barrón and Duarte, 2015). We of course recognize that the mixed layer varies considerably across space and through time in these ecosystems, but wanted to constrain

volumes to something relatively comparable with regards to the sampling sites tested in batch cultures. Assuming these relative volumes are comparable within this context, we calculated the bulk quantity of DOC by multiplying these estimated volumes with the average DOC concentrations reported for small and large lakes (Sobek et al., 2007), for coasts (Barrón and Duarte, 2015) and for the open ocean (Aristegui et al., 2002) (Table S2.2).

The relative proportion of the bulk DOC that could be attributed to the $BDOC_L$ and $BDOC_{SL}$ pool for different ecosystem types could then be determined using the proportional estimates derived in this study (Fig. 2.4; Table 2.1). The exception was the $BDOC_{SL}$ for the open ocean, where no meaningful proportion was consumed. Therefore, in order to estimate the bulk $BDOC_{SL}$ in the top 100 m of the open ocean, we assumed that the bulk amount of $BDOC_{SL}$ in the first 500 m of the open ocean of 500 Tmol $BDOC_{SL}$ (Hansell, 2013), was distributed homogeneously.

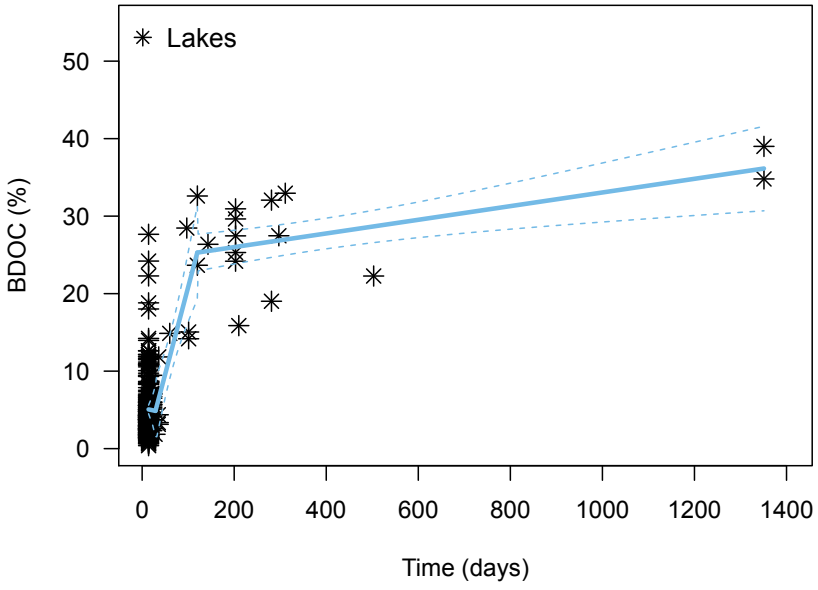


Fig. S2.2. Piecewise regressions of the proportion of bioavailable DOC (%BDOC) versus incubation time (days) for freshwater ecosystems. The breakpoints in the relationship are at 31 ± 12 days and 120 ± 15 days. The difference between the Akaike information criteria and Bayesian information criteria of the linear versus the piecewise regression was 151 and 137, respectively.

To estimate the biomass that could be sustained by $BDOC_L$ and $BDOC_{SL}$ among ecosystems, we multiplied these specific bulk pool by the bacterial growth efficiencies reported in the literature (del Giorgio and Cole, 1998; Smith and Prairie, 2004; López-Urrutia and Morán, 2007) for these different biomes (Table S2.2). We assumed that the same growth efficiencies applied for both the $BDOC_L$ and $BDOC_{SL}$ pools for lakes and coasts. However, for the open ocean, since none of the $BDOC_{SL}$ pool was considered available to prokaryotes in batch cultures experiment, we thus considered no transfer to prokaryotic biomass from this pool to surface open ocean microbes.

We finally assessed how much prokaryotic biomass was supported by $BDOC_L$ and $BDOC_{SL}$ per ecosystem type as a proportion of the total (eq. S2.1), and how much biomass was supported by $BDOC_{SL}$ alone (eq. S2.2). Using these calculations we were able to estimate to which extent inland waters, coasts, and the open ocean contribute to potential microbial biomass through assimilation of $BDOC_L$ and $BDOC_{SL}$, respectively.

$$\frac{Ecosystem_i BDOC_L(Tmol) + BDOC_{SL}(Tmol)}{\sum Ecosystem_i BDOC_L(Tmol) + BDOC_{SL}(Tmol)} * 100\% \qquad \text{(eq. S2.1)}$$

$$\frac{Ecosystem_i BDOC_{SL}(Tmol)}{\sum Ecosystem_i BDOC_L(Tmol) + BDOC_{SL}(Tmol)} * 100\% \qquad \text{(eq. S2.2)}$$

To calculate the overall uncertainty, we followed the same procedure as described above, but instead of using the average values, we used plus or minus one standard-deviation as upper and lower boundaries respectively.

References

Aristegui, J., Duarte, C. M., Agusti, S., Doval, M., Alvarez-Salgado, X. A., and Hansell, D. A. (2002). Dissolved organic carbon support of respiration in the dark ocean. *Science*, 298(5600):1967–1967.

Barrón, C. and Duarte, C. M. (2015). Dissolved organic carbon pools and export from the coastal ocean. *Global Biogeochemical Cycles*, 29(10):1725–1738.

Cael, B. B., Heathcote, A. J., and Seekell, D. A. (2017). The volume and mean depth of earth's lakes. *Geophysical Research Letters*, 44(1):209–218.

de Boyer Montégut, C., Madec, G., Fischer, A. S., Lazar, A., and Iudicone, D. (2004). Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. *Journal of Geophysical Research: Oceans*, 109(C12).

Table S2.1. Number of Experiments and Studies

		$BDOC_L$	BDOC	Total
Freshwater	Wetlands	55 (1)	0 (0)	55 (1)
	Rivers	65 (1)	0 (0)	65 (1)
	Lakes	229 (1)	24 (7)	252 (11)
	Subtotal	*351 (7)*	*24 (7)*	*372 (11)*
Marine ecosystems	Lagoons	3 (2)	6 (1)	9 (3)
	Estuaries	53 (6)	13 (2)	67 (7)
	Inland seas	20 (4)	52 (2)	72 (6)
	Coasts	42 (5)	39 (4)	58 (8)
	Open ocean	15 (7)	13 (3)	25 (7)
	Subtotal	*133 (25)*	*123 (12)*	*231 (33)*
Productive environments		28 (6)	44 (5)	52 (10)
Total		*520 (36)*	*194 (24)*	*655 (47)*

Note. Number of experiments (number of studies).

Table S2.2. Values Used to Estimate Global Stocks of DOC

	Lakes			Coasts	Oceans
	Small	**Large**	**All**		
Area (106 km^2)	4.11	1.02	5.13	25.3	336.7
Depth (km)[a]	-	0.03	-	0.03	0.1
Volume (106 km^3)	0.04 ± 0.003	0.03	0.07 ± 0.003	0.8 ± 0.008	33.7 ± 0.3
Concentration (μM)	631.7 ± 15.8	148.1 ± 47.5	-	126.4 ± 55.8	63.2 ± 0.00
BGE[b]	-	-	24.8 ± 12.1[c]	24.9 ± 15.8[d]	10.0 ± 8.1[e]
Total DOC (Tmol)	24.6 ± 2.5	5.1	29.7 ± 2.5	96.1 ± 43	2134.4 ± 28

Note. Details for calculations are provided in SI.
[a] Values approximated from (de Boyer Montégut et al., 2004)
[b] Bacterial growth efficiency (BGE)
[c] (Smith and Prairie, 2004)
[d] (del Giorgio and Cole, 1998) and references therein
[e] (López-Urrutia and Morán, 2007)

del Giorgio, P. A. and Cole, J. J. (1998). Bacterial growth efficiency in natural aquatic systems. *Annual Review of Ecology and Systematics*, pages 503–541.

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5.

López-Urrutia, A. and Morán, X. A. G. (2007). Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling. *Ecology*, 88(4):817–822.

Smith, E. M. and Prairie, Y. T. (2004). Bacterial metabolism and growth efficiency in lakes: the importance of phosphorus availability. *Limnology and Oceanography*, 49(1):137–147.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J. (2007). Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnology and Oceanography*, 52(3):1208–1219.

Walterscheid, S. K. (2011). Climate classification for the earth's oceanic areas using the köppen system. *Master thesis. Kansas State University.*

Annexe C

Supplementary information for chapter 3

Relationships between abundance, diversity indices and spatial abundance distribution (SPAD) are presented in Fig S2.5. Total abundance is mostly explained by the abundance of normal-like ASVs and then by bimodal ASVs whereas logistic ASVs better described prokaryotic diversity.

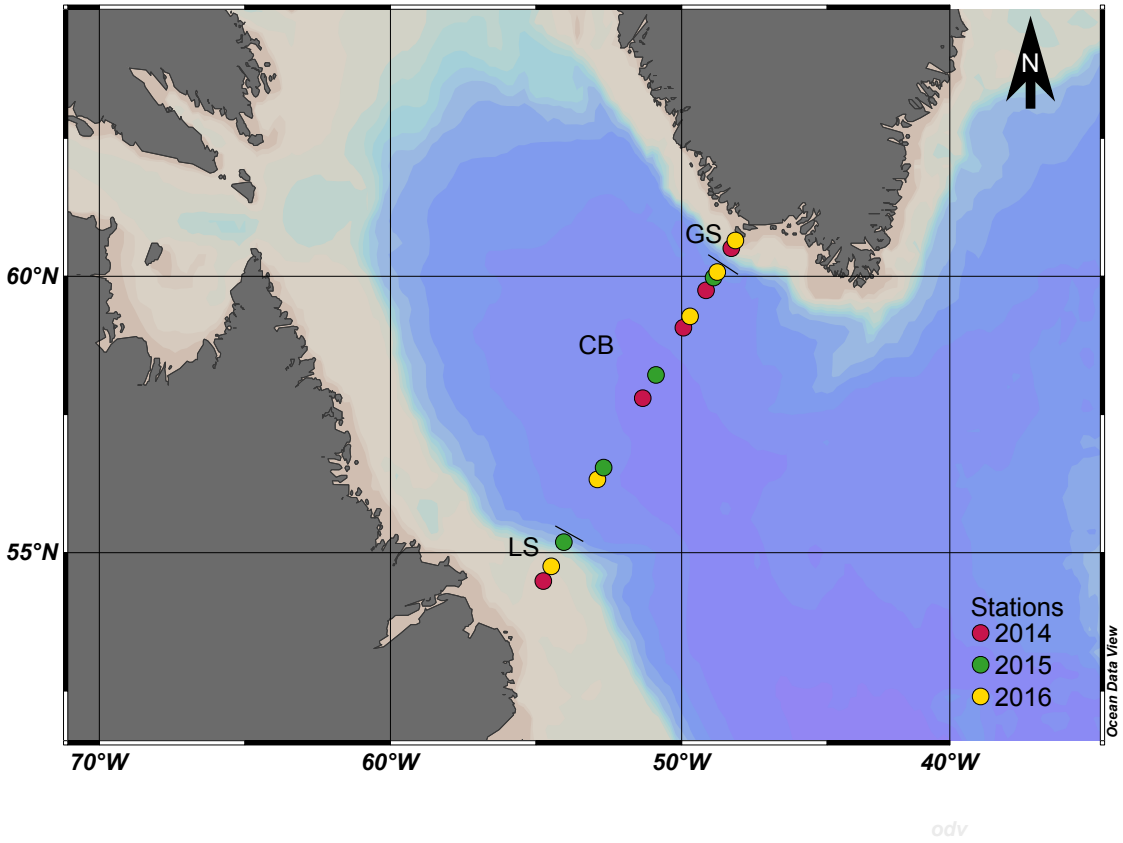


Fig. S3.1. Location of our sampling sites along the AR7W line in the Labrador Sea. The short black lines delimitate water masses. LS: Labrador Shelf; CB: Central Basin; GS: Greenland Shelf

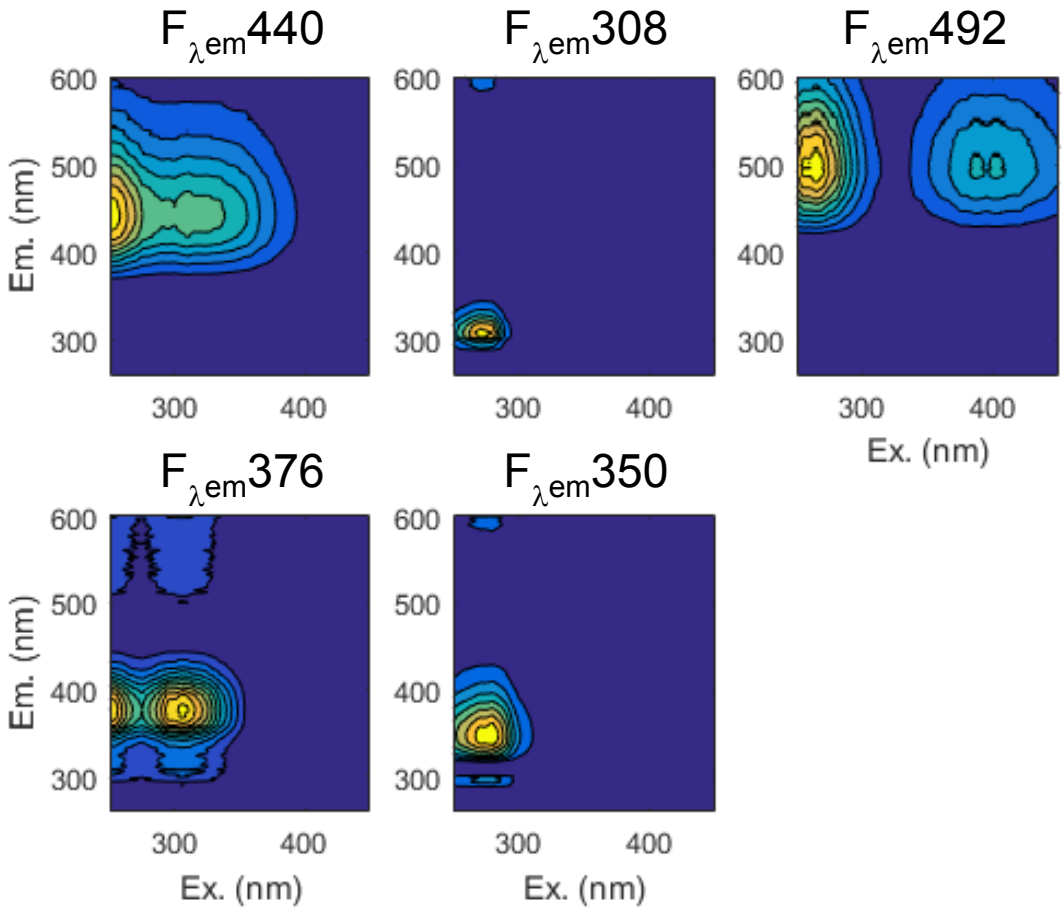


Fig. S3.2. Fluorescent components modelled using PARAFAC. Sea table S3.1 for their correspondence with Coble's nomenclature (1996)

Relationships between FDOM components and DOC concentrations are presented in figure S2.4. The three components with a higher complexity, $F_{\lambda em}492$, $F_{\lambda em}440$ and $F_{\lambda em}376$ are well correlated with DOC concentrations whereas fresher compounds, $F_{\lambda em}350$ and $F_{\lambda em}308$ are not. However, the fluorescence intensity of $F_{\lambda em}308$ is high, suggesting that the DOC pool is relatively fresh. Also, these measurements are snapshots and thus do not take into account the presumably faster turnover rates of $F_{\lambda em}350$ and $F_{\lambda em}308$.

Amino acids carbon yield has been used in other studies to assess the quality of the organic matter pool (Kaiser and Benner, 2008). Therefore, we investigated whether it could be related to various ecosystem conditions, functions and community composition. All relationships that were tested were not statistically significant. One hypothesis to explain this lack of significant relationships is that amino acids represent a labile component of the DOM pool whereas DOC concentration was more related to refractory components of the DOM pool. Therefore, combining these two variables resulted in an amino acid carbon yield

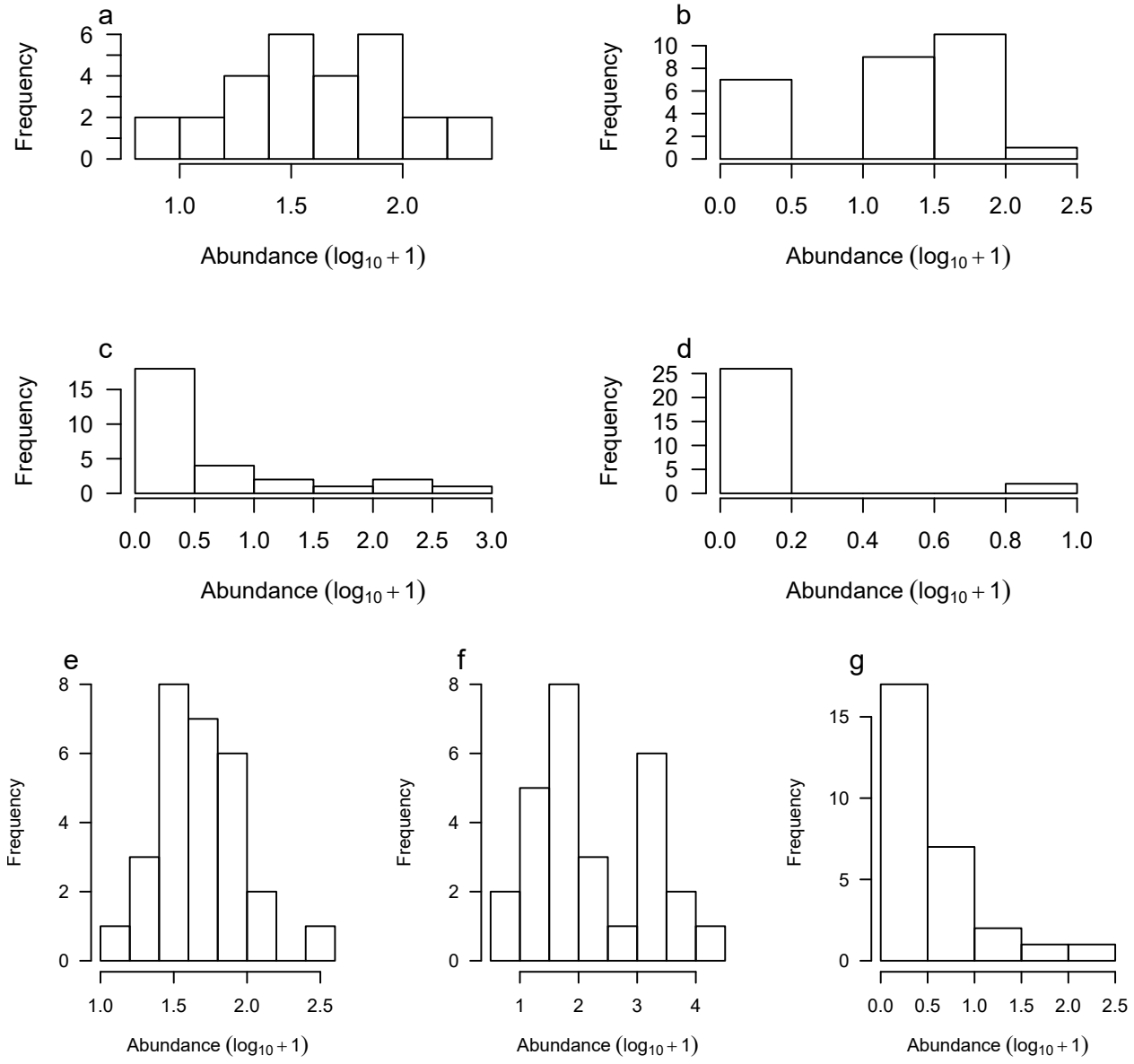


Fig. S3.3. Example of spatial abundance distribution (SPAD) for normal-like (a); bimodal (b); lognormal (c) and logistic (d). Other panels are examples of misclassified Amplicon Sequence Variants (ASV): e was classified as lognormal instead of normal-like; f as normal-like instead of bimodal and g was classified as normal-like instead of lognormal

that could not explain metabolic rates nor community composition.

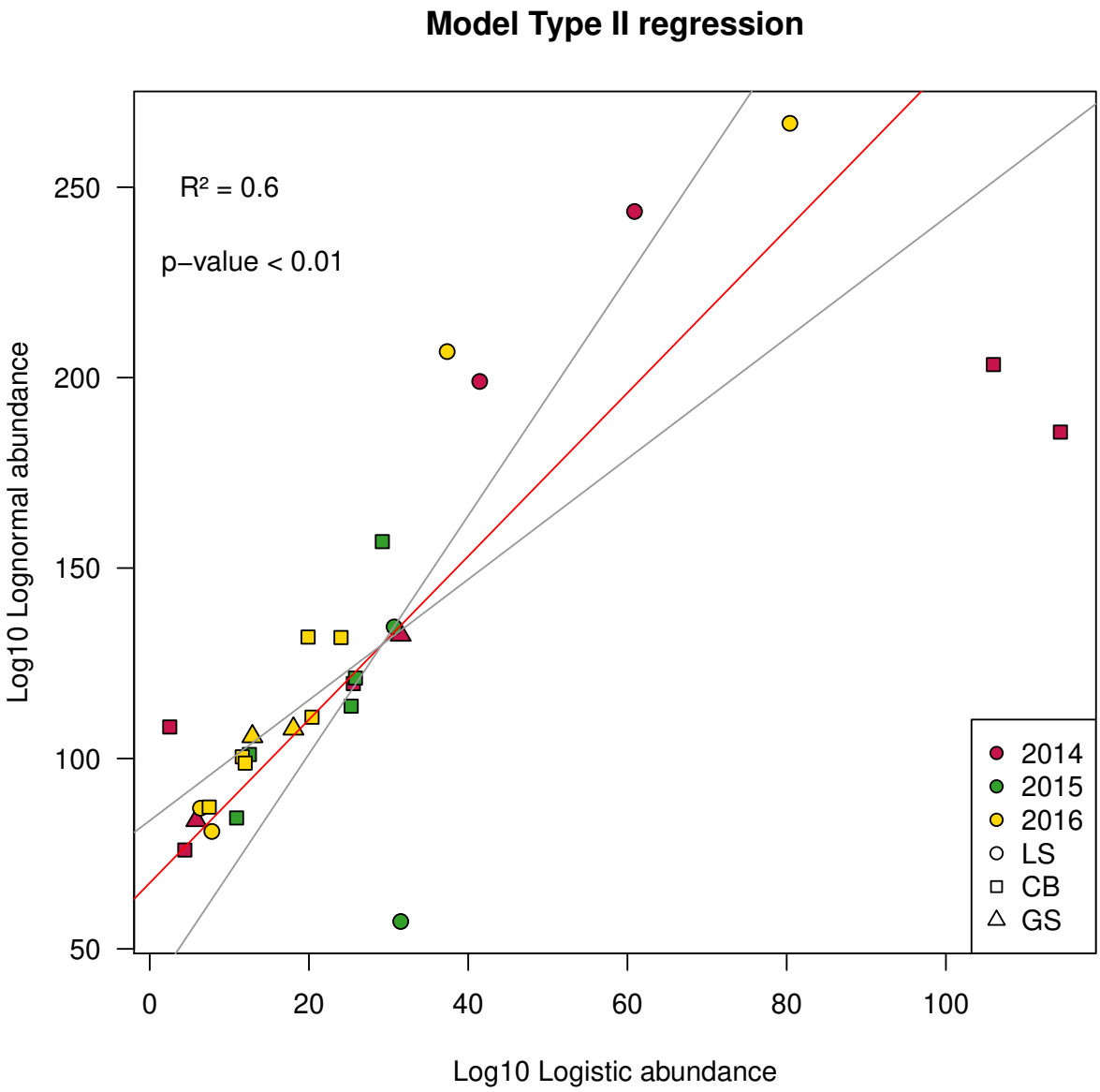


Fig. S3.4. Relationship between logistic and lognormal ASVs' abundance. The black line represents the model II regression line and the grey lines the 95% confidence interval. LS: Labrador shelf; CB: Central Basin; GS: Greenland shelf

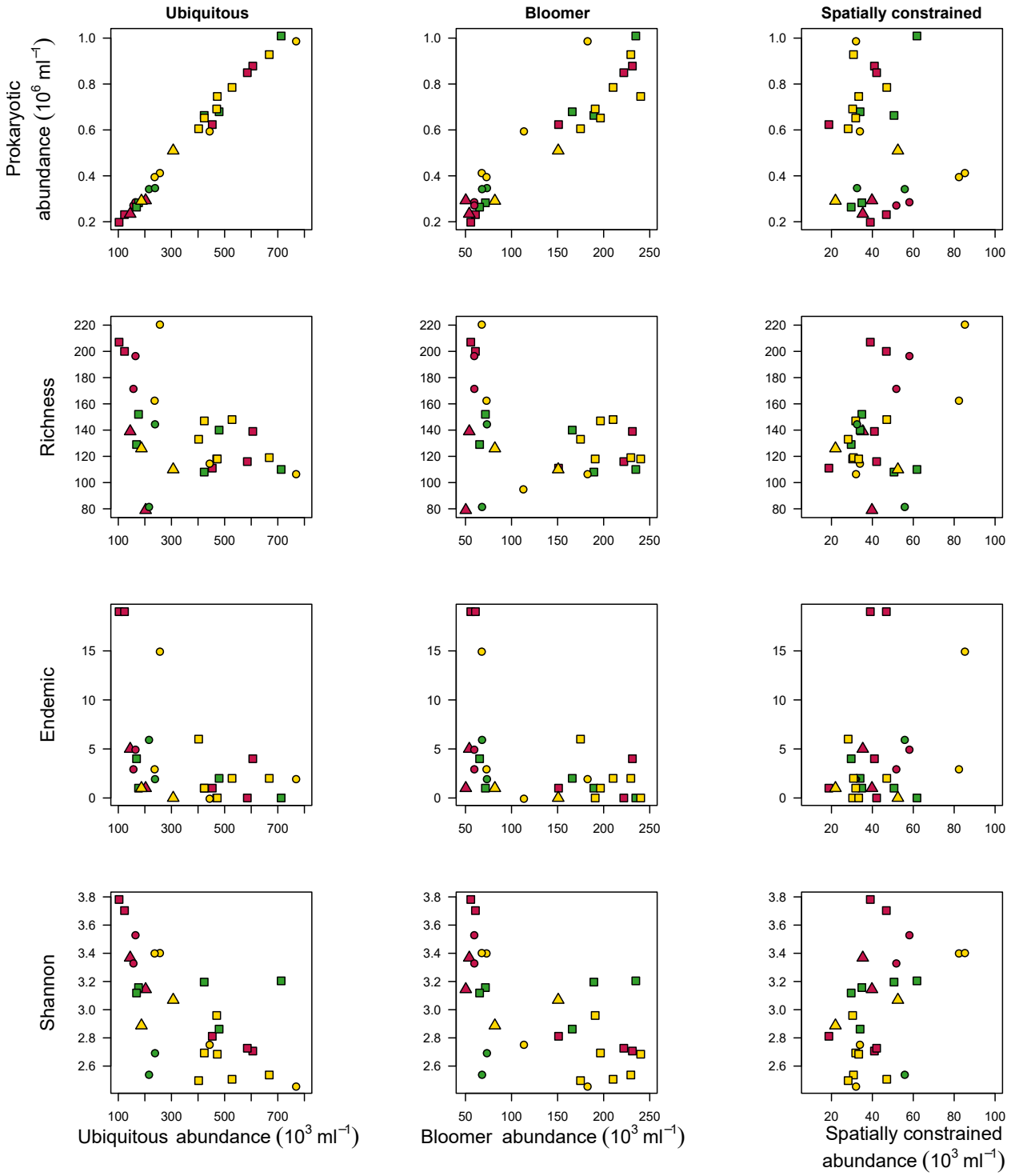


Fig. S3.5. Relationships between SPAD groups and different diversity indices. Each column represents a different SPAD group. Shannon diversity index was calculated using the vegan package in R. Richness was calculated as the number of different ASVs at each site and endemism was calculated as the number of ASVs that were unique to a site. Red: 2014; green: 2015; yellow: 2016; circles: Labrador shelf; squares: Central basin; triangles: Greenland shelf

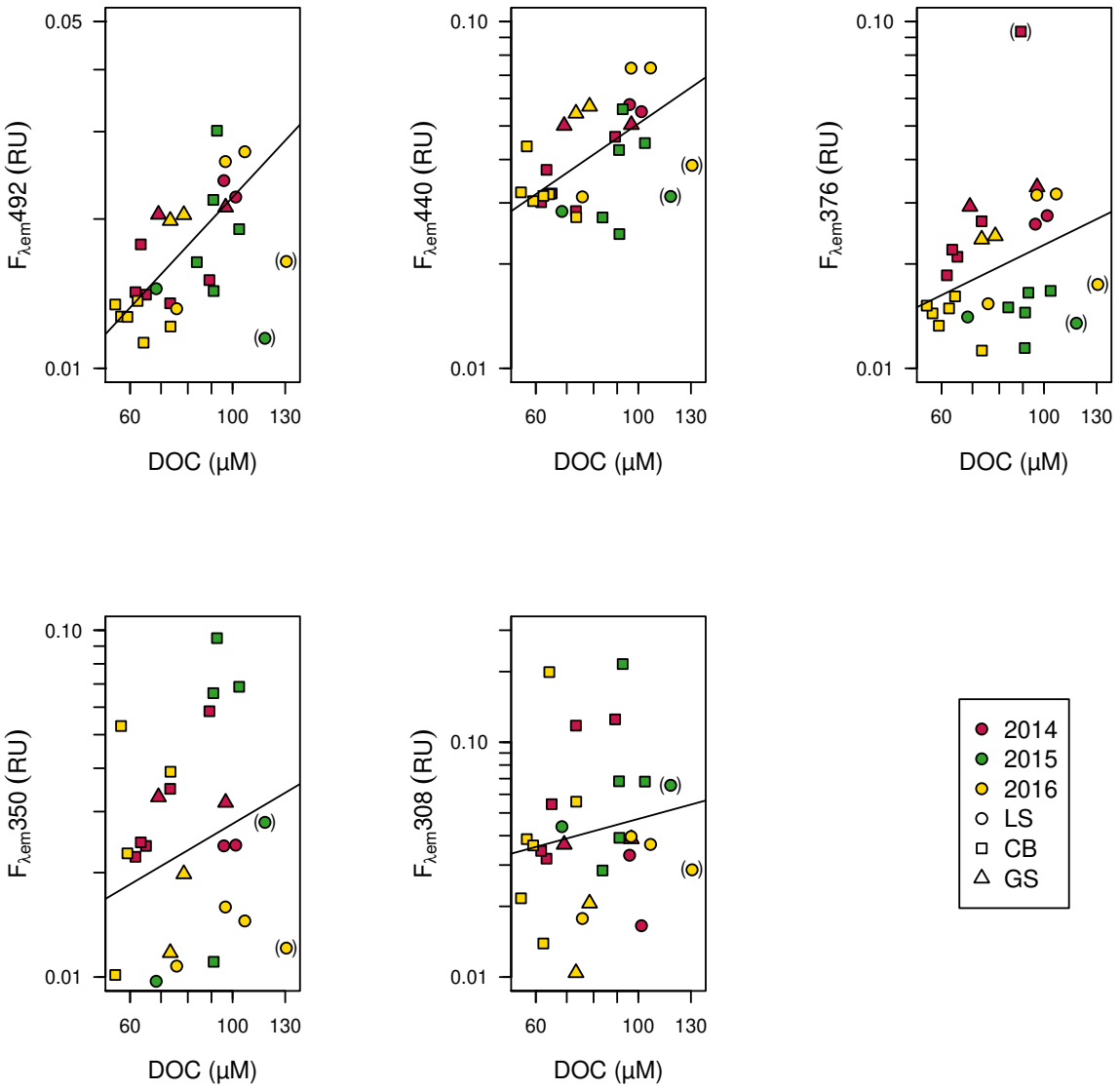


Fig. S3.6. Relationships between DOC and each FDOM components, going from highest complexity (top left) to lowest complexity (middle right). The legend (bottom right) applies for all graphs. Parenthesis denotes outliers (two for DOC, one for $F_{\lambda em}376$) based on the other depths of the same station (DOC) or two-fold increased as compared to the second highest value ($F_{\lambda em}376$). Outliers were not considered in the regressions. LS: Labrador shelf; CB: Central Basin; GS: Greenland shelf

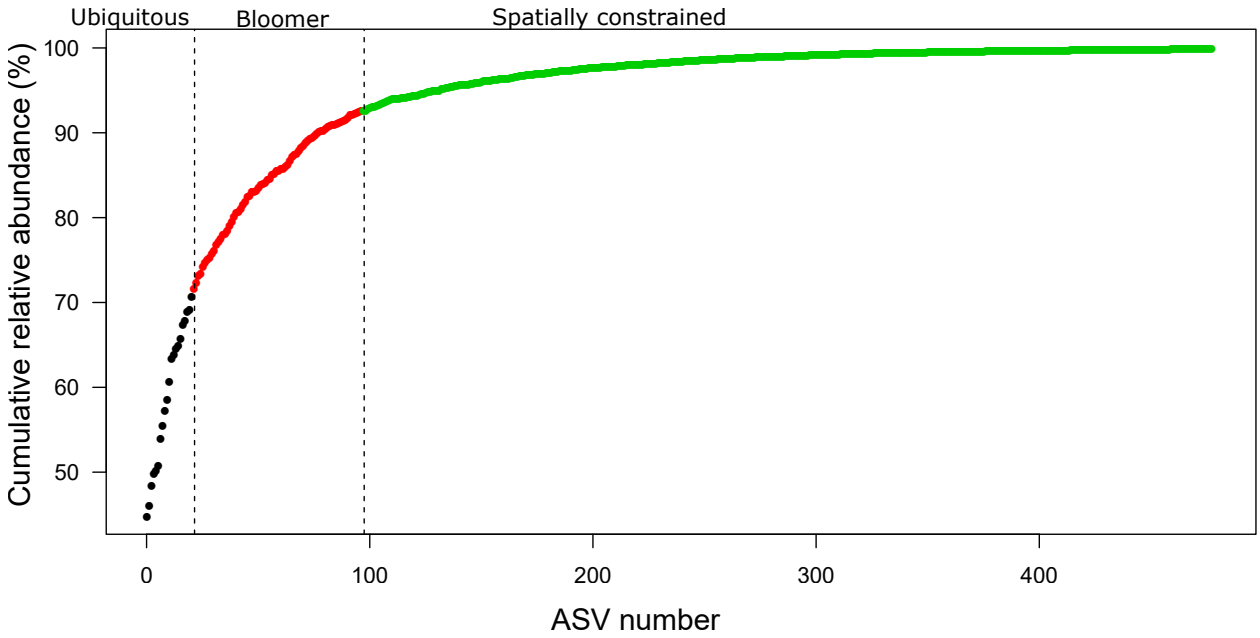


Fig. S3.7. This figure shows how SPAD groups represents the abundance and diversity of the community. The Y-axis represents the cumulative relative abundance across all samples. Note that the X-axis was ordered to have all normal-like ASVs in sequence followed by bimodal and then logistic ASVs. Black: normal-like ASVs; red: bimodal ASVs; Green: logistic ASVs.

This Study	Coble's terminology	Meaning	Excitation wavelength (nm)
$F_{\lambda em}308$	Peak B	Labile, protein-like	270
$F_{\lambda em}350$	Peak T	Labile, protein-like	280
$F_{\lambda em}376$	Peak M	Recalcitrant, complex aromatic	305
$F_{\lambda em}440$	Peak A	Recalcitrant, complex aromatic	250
$F_{\lambda em}492$	Peak D	Recalcitrant, complex aromatic	265

Table S3.1. Correspondence of fluorescent component names between this study and Coble's terminology and meaning, and the associated excitation wavelength. Note that components are presented here on ascending order of emission wavelengths, a proxy for their complexity

References

Coble, P. G. (1996). Characterization of marine and terrestrial dom in seawater using excitation-emission matrix spectroscopy. *Marine chemistry*, 51(4):325–346.

Kaiser, K. and Benner, R. (2008). Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen. *Limnology and Oceanography*, 53(1):99–112.

Annexe D

Supplementary information for chapter 4

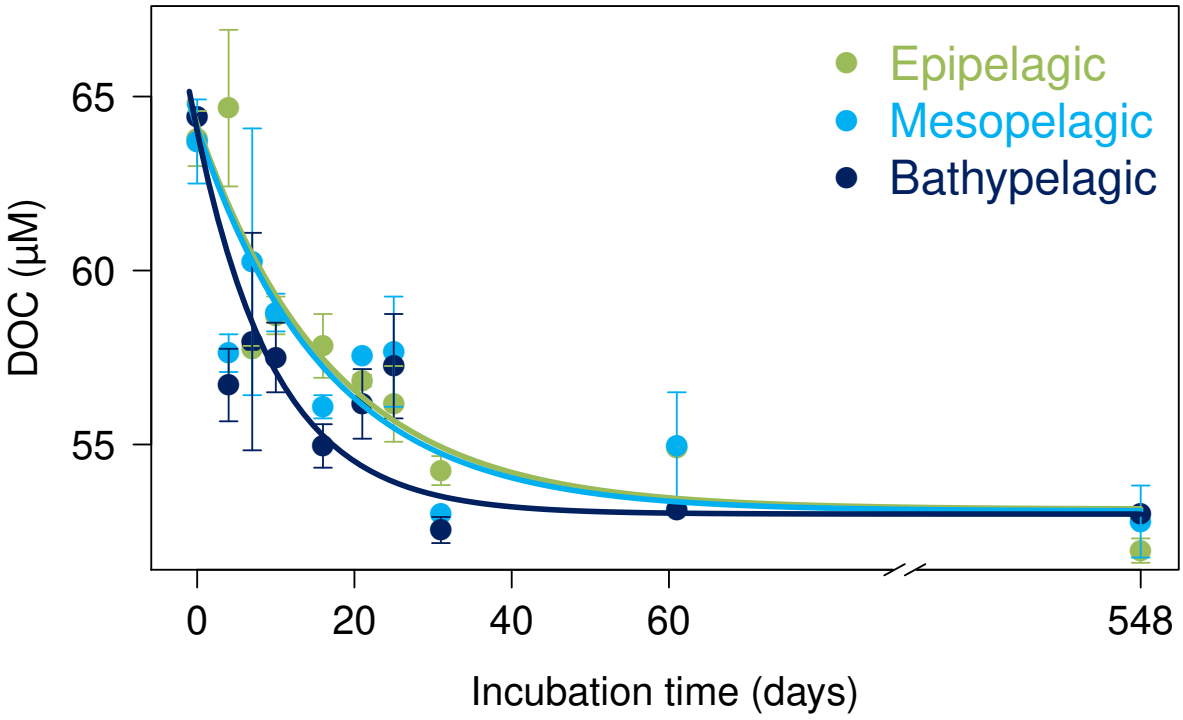


Fig. S4.1. DOC decay curve. DOC concentrations in μM as a function of incubation time (days). The DOC decay curves were performed using a two pools multi-G approach. Decay constants were rather similar at $0.059 \pm 0.016 d^{-1}$, $0.061 \pm 0.023 d^{-1}$ and $0.099 \pm 0.037 d^{-1}$ for the epi-, meso- and bathypelagic, respectively. A DOC plateau was reach at around 50 days for the bathypelagic and 85 days for the epi- and mesopelagic treatments (1/k * 5). The axis was truncated in order to better visualize all data points. Error bars represent the standard deviation between treatment replicates. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic.

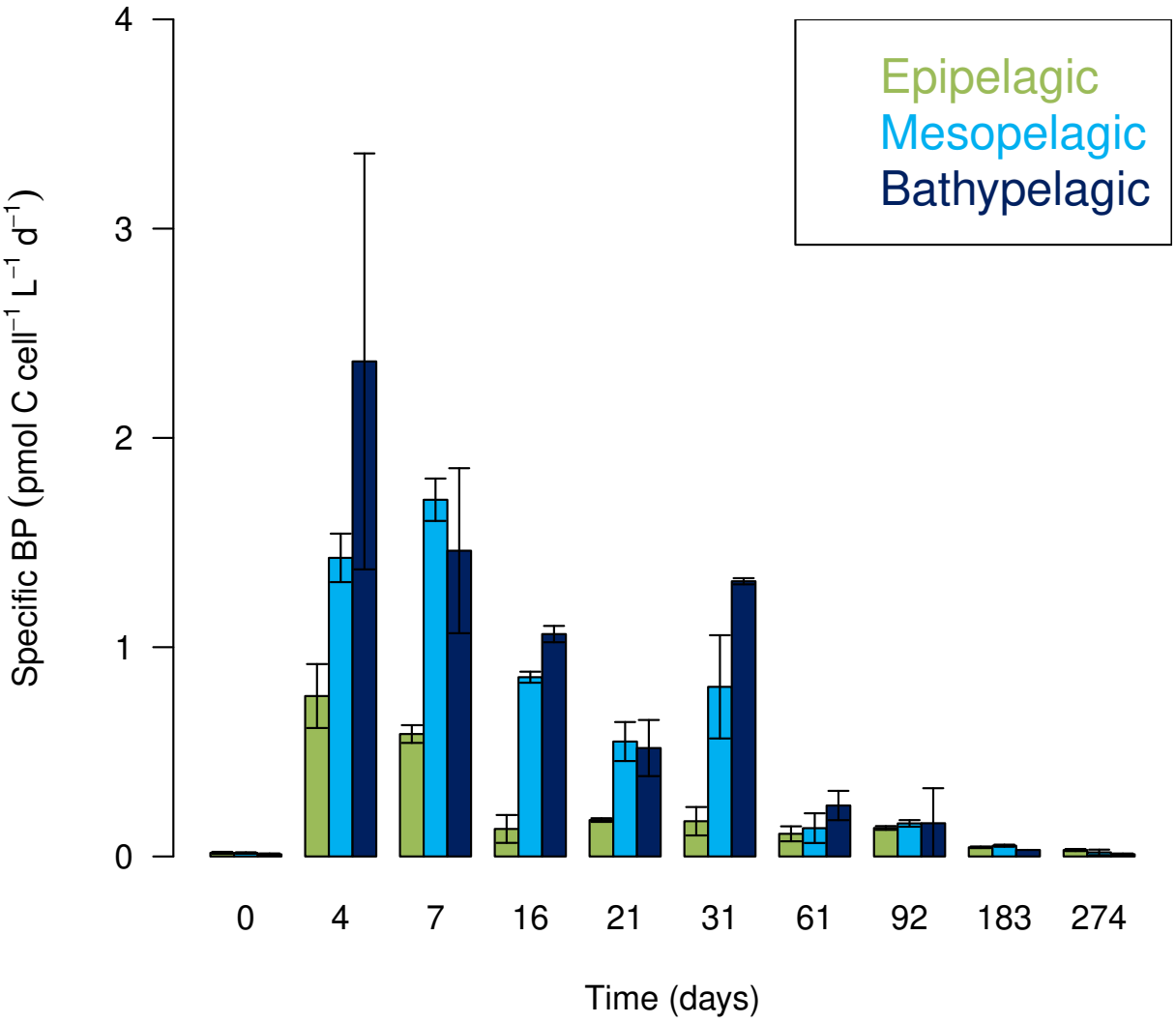


Fig. S4.2. Specific production rates as a function of incubation time. Specific production rates, i.e. biomass production normalized to abundance, was at least 2-fold higher in the bathypelagic treatment as compared to the epipelagic treatment during the first 2 months of the experiment, and was generally higher than the mesopelagic treatment. Error bars represent the standard deviation between treatment replicates. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic.

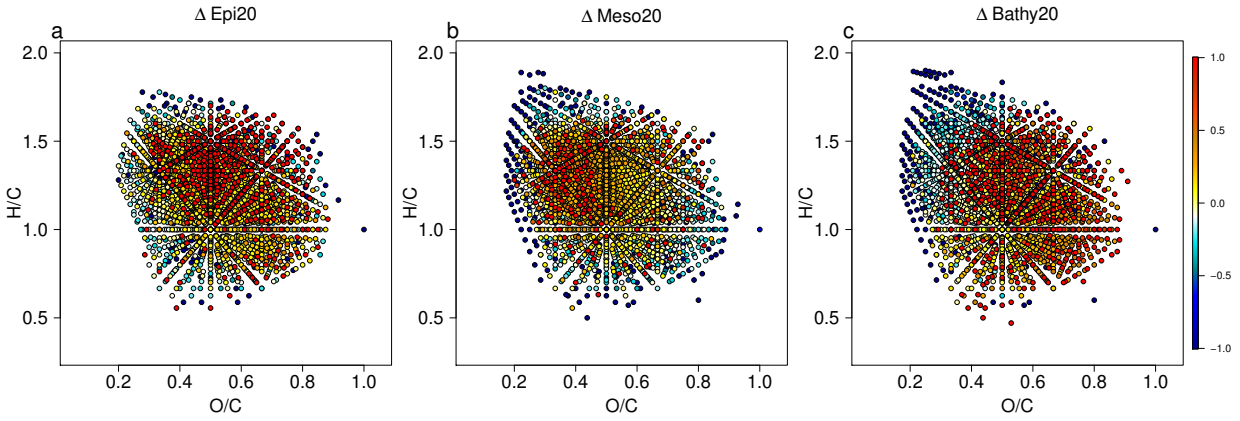


Fig. S4.3. Relative change in DOM composition after 20 days of incubation. This figure shows the relative change in the abundance of molecular formulas (MF) using van Krevelen diagrams comparing 20 days of incubation with time 0 in the epi- (a), meso- (b) and bathypelagic (c) treatments. Each point represents a MF and is positioned based on its elemental stoichiometry (oxygen: carbon on the x axis, hydrogen: carbon on the y axis). Cold colors represent a loss of MFs and hot colors an increase. We see that the consumed MF are on a wide range of O/C in the bathypelagic (0.2-0.35), a smaller range in the mesopelagic (0.2-0.3) and narrower still in the epipelagic with only few MF that were completely consumed. The MF that are produced are mostly in the 1 to 1.75 H: C range for all treatments. The bathypelagic treatment produced MF with higher O/C ratio as compared to the other two treatments.

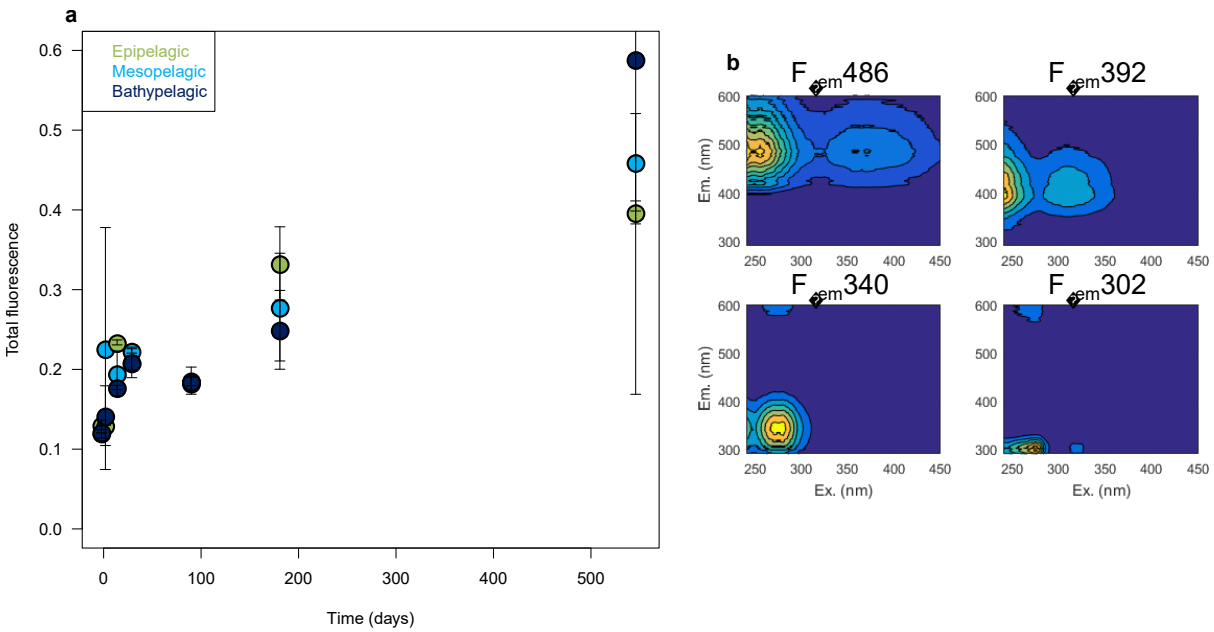


Fig. S4.4. Changes in total fluorescence during the experiment and fluorescence components. Panel a shows the increase in total fluorescence during the experiment as a function of time. In contrast to ESI-FT-ICR-MS, fluorescence analysis provides absolute values. Thus, an increase in total fluorescence provides strong evidence that molecules are produced by prokaryotes. Together with Fig. 1 and S3, these results support the iterative process of creating refractory DOC. Error bars represent the standard deviation between treatment replicates. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic. Panel b shows the fluorescence components modeled using parallel factor analysis (PARAFAC). Component names are based on the emission wavelength at which fluorescence was maximal.

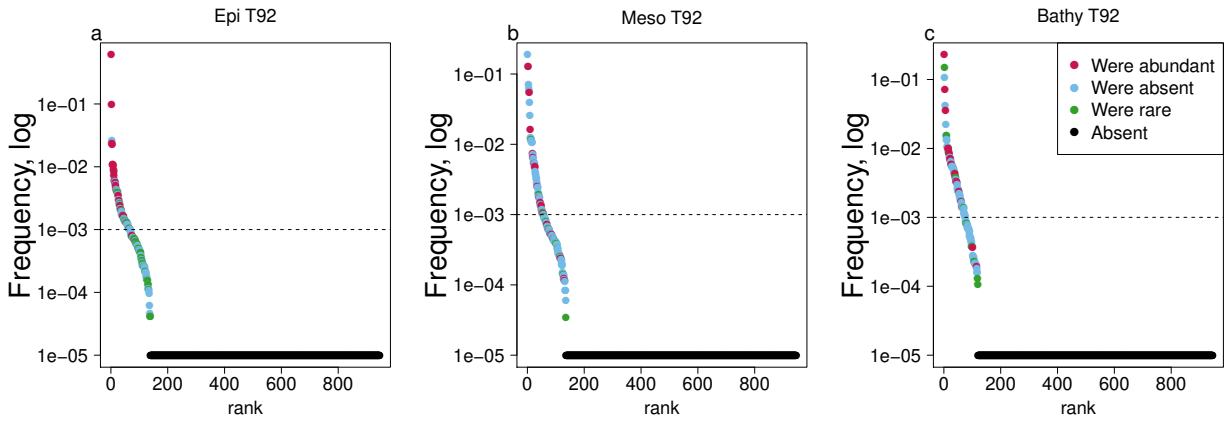


Fig. S4.5. Frequency curve represented on a log Y axis. This figure shows Amplicon Sequence Variants (ASVs) frequency curves after 92 days of incubation in the epi- (a), meso- (b) and bathypelagic (c) treatments. All points (ASVs) above the dashed line (0.1% of abundance) are considered abundant and all below are considered rare. The colors indicate the ASV's abundance at the beginning of the incubation and the black points are ASVs that are absent but were detected either in other treatments or at different incubation times. This demonstrate the dominant role of the rare biosphere in the deep ocean as most ASVs after 92 days of incubation were rare (green) or not detected (blue) at the beginning of the experiment. In contrast, most ASVs after 92 days of incubation in the surface experiment were already abundant (red) at the beginning. Red: abundant ($> 0.1\%$), blue: not detected; green: rare ($< 0.1\%$) and black: absent.

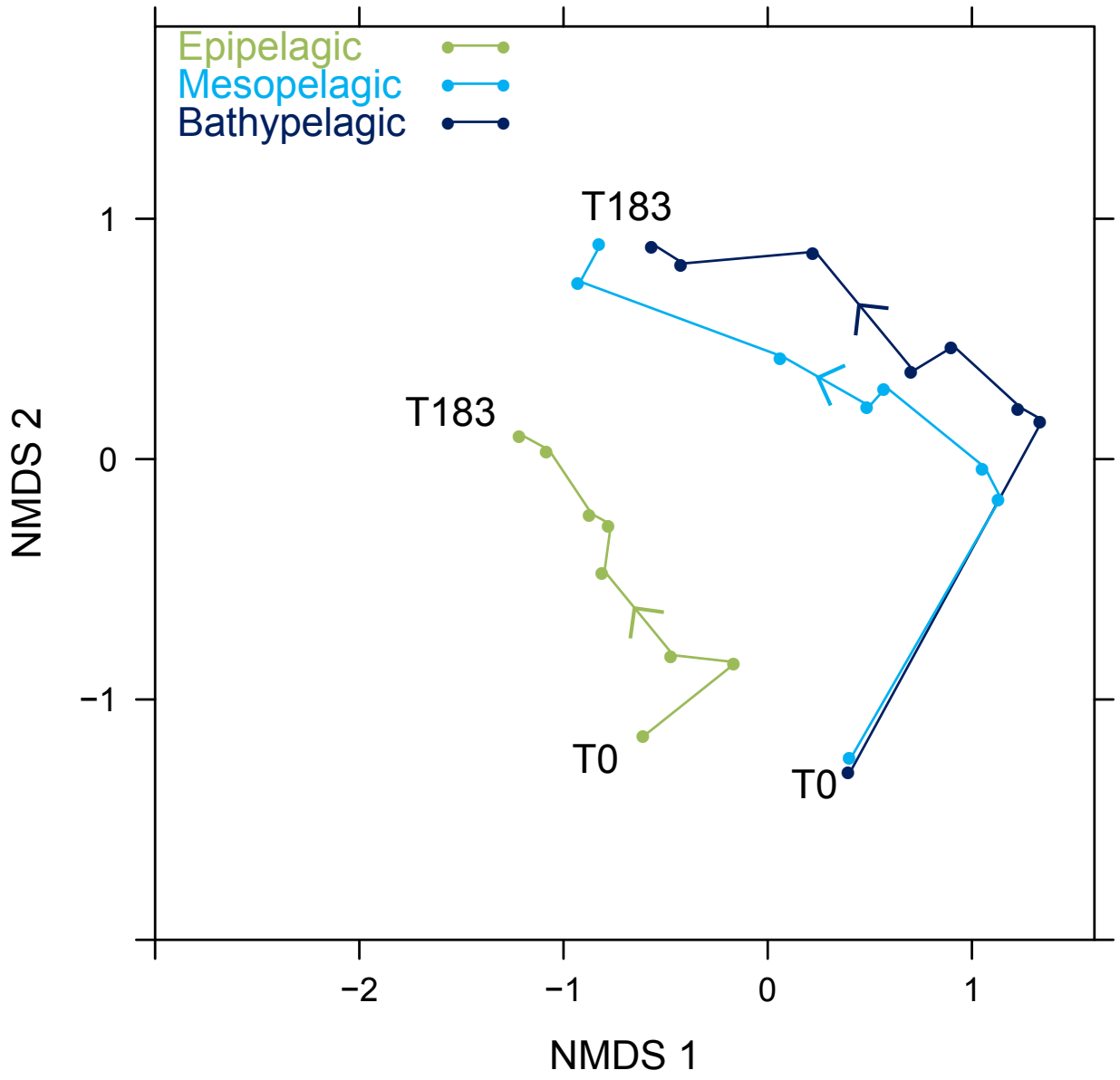


Fig. S4.6. Shifts in community composition during the experiment. This figure shows the change in the prokaryotic communities over time for the three different treatments using a 2D NMDS with Bray-Curtis transformed data. Each point represents a different incubation time. The arrows represent the direction of the communities shift over time and all time points are in the right chronological order. We see that the deep communities are rather similar during the whole experiment and rather different from the surface communities. The 2D NMDS stress is 0.12. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic.

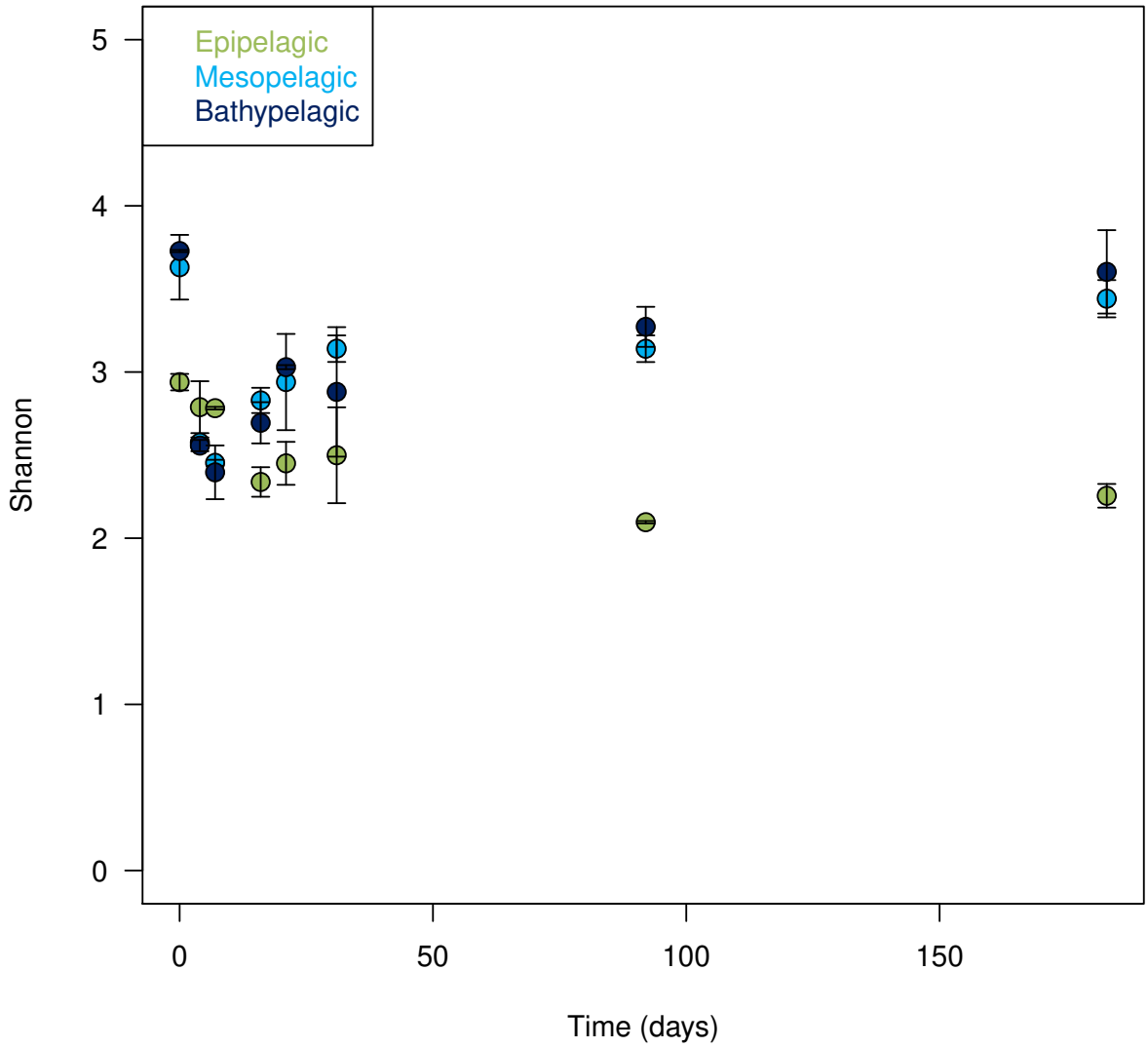


Fig. S4.7. Changes in Shannon diversity index during the experiment. This figure shows the evolution of the prokaryotic diversity during the experiment using the Shannon index. At the beginning of the experiment, there was an increase in diversity over depths providing concrete evidence that bathypelagic communities are more diverse than epipelagic ones. Shortly (4 days) after the introduction of fresh DOM, there is a decrease in deep communities' diversity, suggesting a rapid adaptation of the community to the inputs of labile DOC. The decrease in prokaryotic diversity is much lower in the epipelagic treatment, presumably because they are adapted to this fresh DOM. As the DOM gets increasingly more recalcitrant, the deep communities regain their diversity. After 183 days of incubation, the diversity is close to what it was at the beginning. In contrast, once epipelagic diversity decreased after 2 weeks of incubation, it did not raised again, suggesting that the rare biosphere isn't as diverse, as indicated by Fig. S5. Error bars represent the standard deviation between treatment replicates. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic.

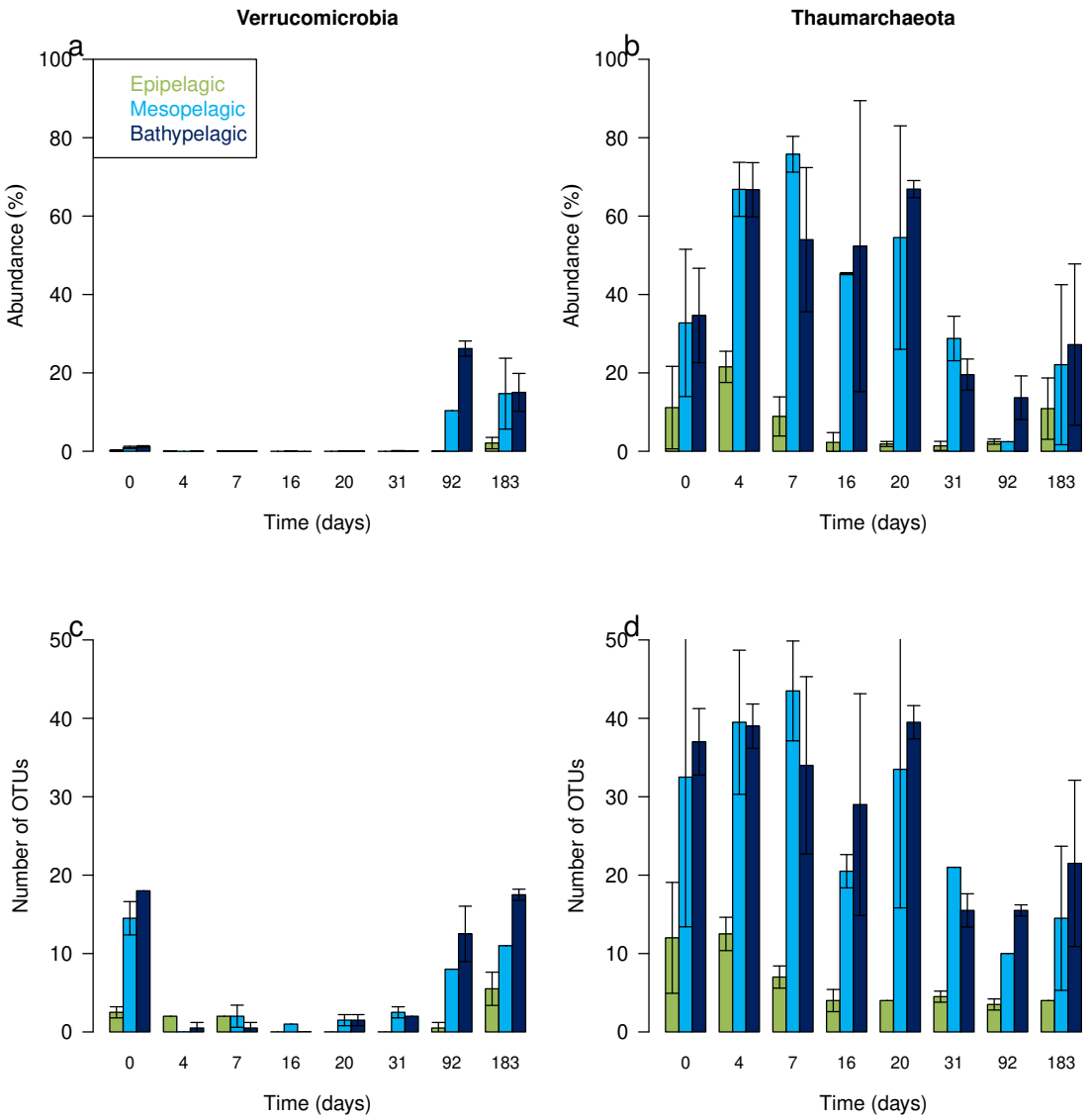


Fig. S4.8. Relative abundance of Verrucomicrobia and Thaumarchaeota during the experiment. This figure shows the change in the relative abundance of Verrucomicrobia (a) and Thaumarchaeota (b) and the number of ASVs belonging to these groups in c and d, respectively. We see that Verrucomicrobia started relatively diverse in the deep treatments but accounted for a negligible proportion of the community up until 92 days of incubation. In the epipelagic, they were less diverse and remained low during the whole experiment. This increase in abundance in the deep ocean suggests its affinity with refractory DOM. Thaumarchaeota dominated the deep communities and were very diverse during the first 20 days. Their abundance decreased after 31 days as did their diversity, but both remained relatively high up until the end of the incubation. Thaumarchaeota are known to be chemolitautrophs, their abundance high abundance not only suggests their role in DOC consumption, but the production of DOC through chemosynthesis may prime heterotrophic prokaryotes to consume more semi-labile compounds. Error bars represent the standard deviation between treatment replicates. Green: epipelagic; light blue: mesopelagic and dark blue: bathypelagic.

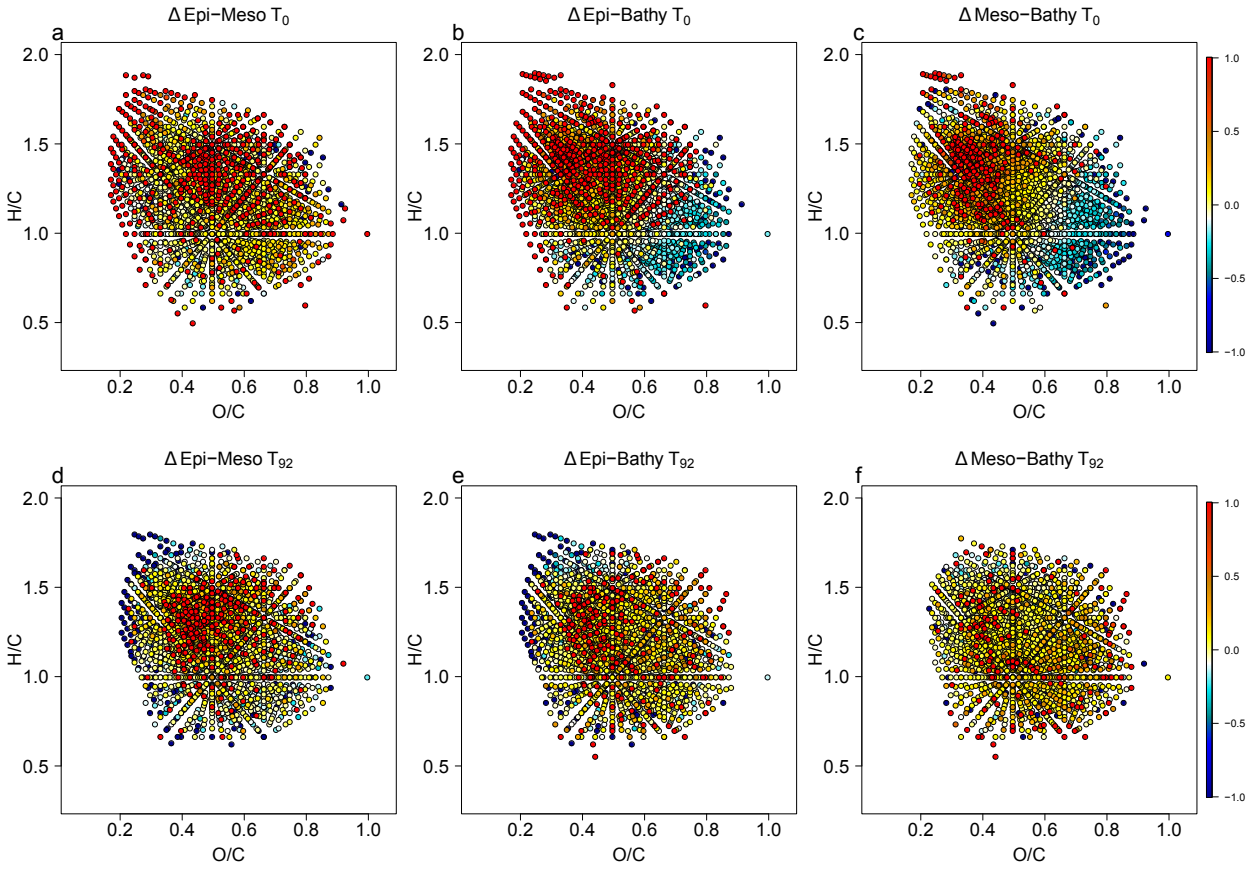


Fig. S4.9. Differential DOM composition between treatments. This figure shows the relative change in molecular formulas (MF) using van Krevelen diagrams comparing treatments at the beginning of the incubation (a, b, c) and after 92 days on incubation (d, e, f). Comparison of treatments are made column-wise, with the epi- and mesopelagic in a) and d); epi- and bathypelagic in b) and e) and meso- and bathypelagic c) and f). Each point represents a MF and is positioned based on its elemental stoichiometry (oxygen: carbon on the x axis, hydrogen: carbon on the y axis). Cold colors represent a higher number of MF in the second term (ex. Bathypelagic in c) and hot colors a higher number of molecular formulas in the first term (Ex. Mesopelagic in c). We see that DOM composition was more similar between epi- and mesopelagic (a) than with the bathypelagic (b, c) which had a lower abundance of more oxygenated molecules. After 92 days of incubation, however, the meso- and bathypelagic treatments were very similar (f) in contrast to the epipelagic treatment (d, e). Although the epipelagic contained less aliphatic compounds than the deep treatments (∼0.3 O/C ratio, 1.25-1.8 H/C ratio, panels a and b), these molecules were in higher abundance in the epipelagic after 92 days of incubation (d, e) suggesting that they belong to the semi-labile pool.

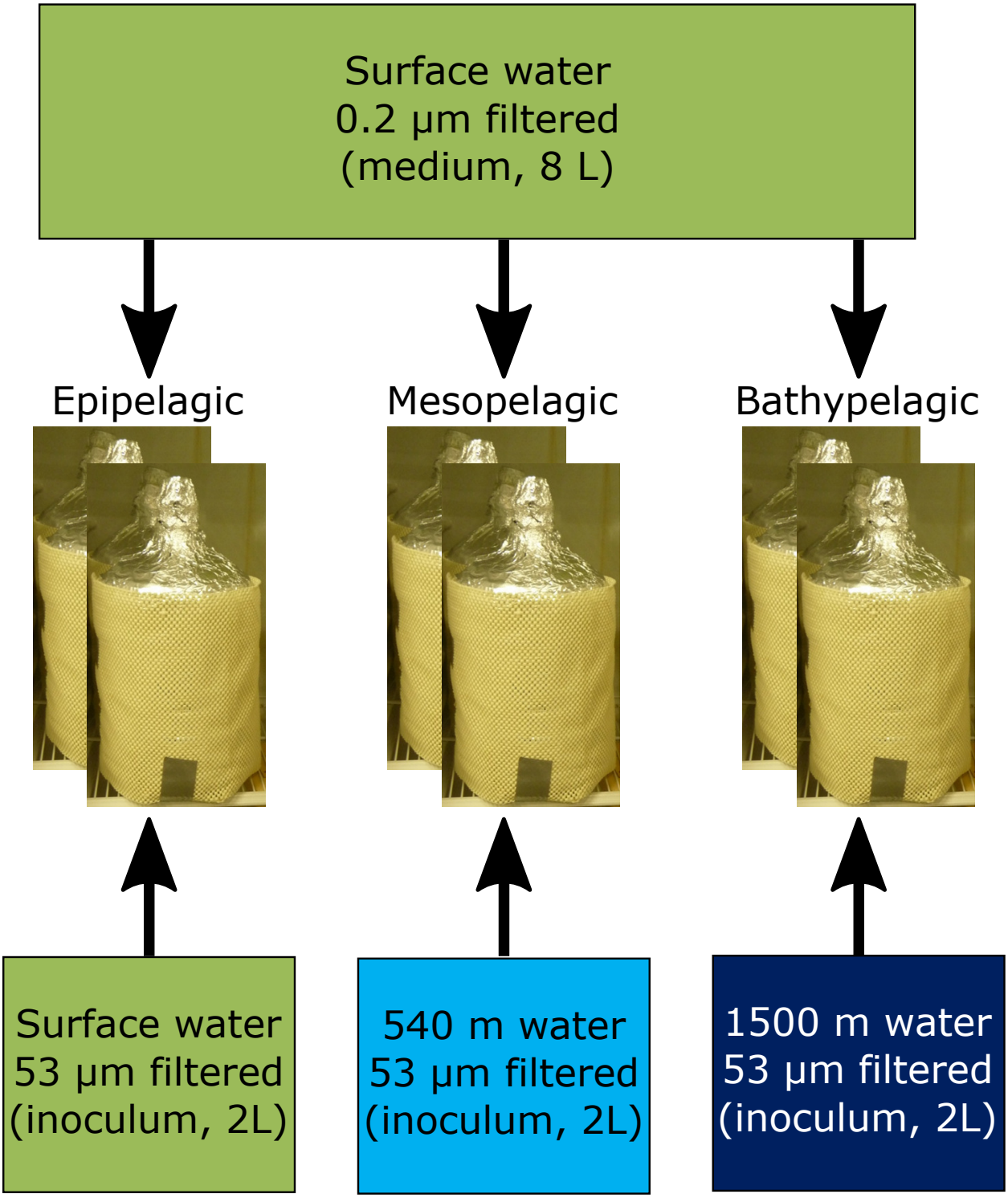


Fig. S4.10. Experimental setup. Each bottle received 8 L of filtered surface water (0.2 μm) and 2 L of inoculum (53 μm). Treatments were done in duplicates and kept in the dark at 4°C.