

Microbial Seasonality Shapes Dissolved Organic Matter Composition in the Northwestern Mediterranean Sea

Nawal Bouchachi, Anabel Von Jackowski, Barbara Marie, Olivier Crispi, Ingrid Obernosterer, Eva Ortega-Retuerta

Karine Escoubeyrou, Charles-Hubert Paulin

Hélène Lavanant, Isabelle Schmitt-Afonso, Carlos Afonso



DISSOLVED ORGANIC MATTER IN THE OCEAN

700 Gt C

Oceanic DOM

750 Gt C

Atmospheric CO₂

Understanding how DOM is cycled in the ocean is important to predict (among others):

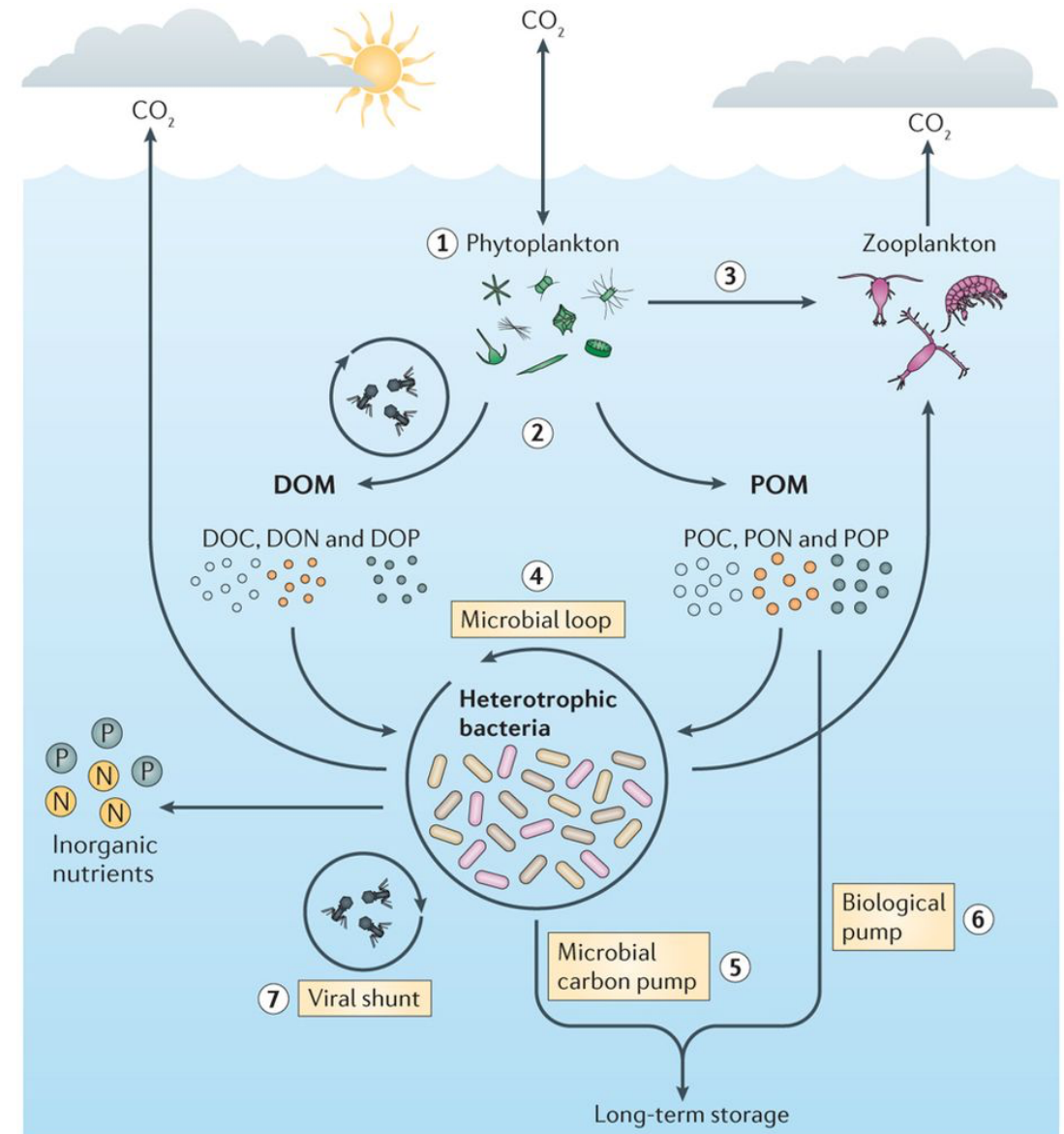
- Greenhouse gas exchanges (CO₂, CH₄, etc)
- Elemental cycling (N, Fe)
- Foodweb dynamics and changes in biodiversity

DISSOLVED ORGANIC MATTER IN THE OCEAN

700 Gt C

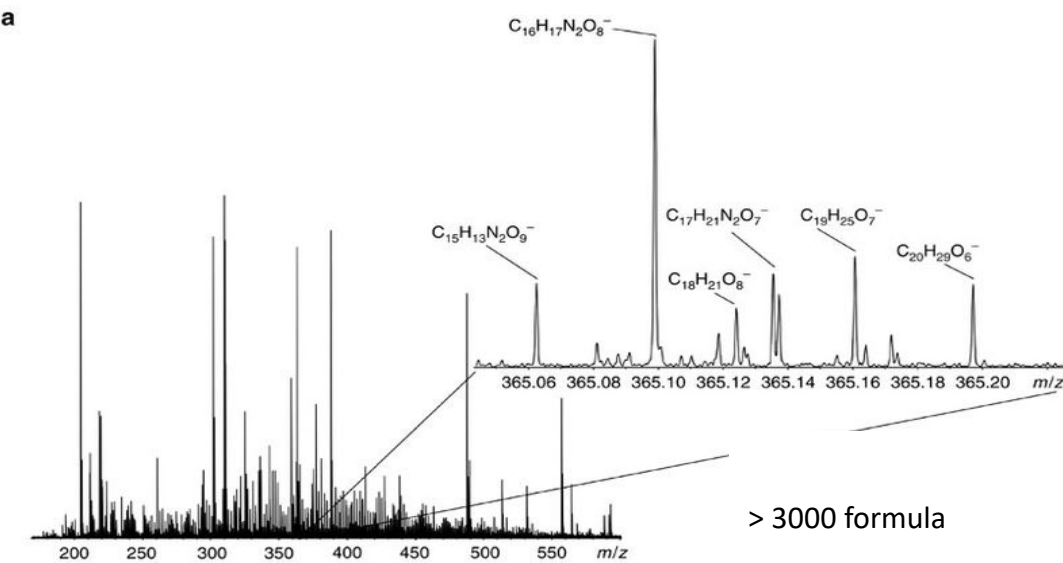
Oceanic DOM

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DISSOLVED ORGANIC MATTER IN THE OCEAN

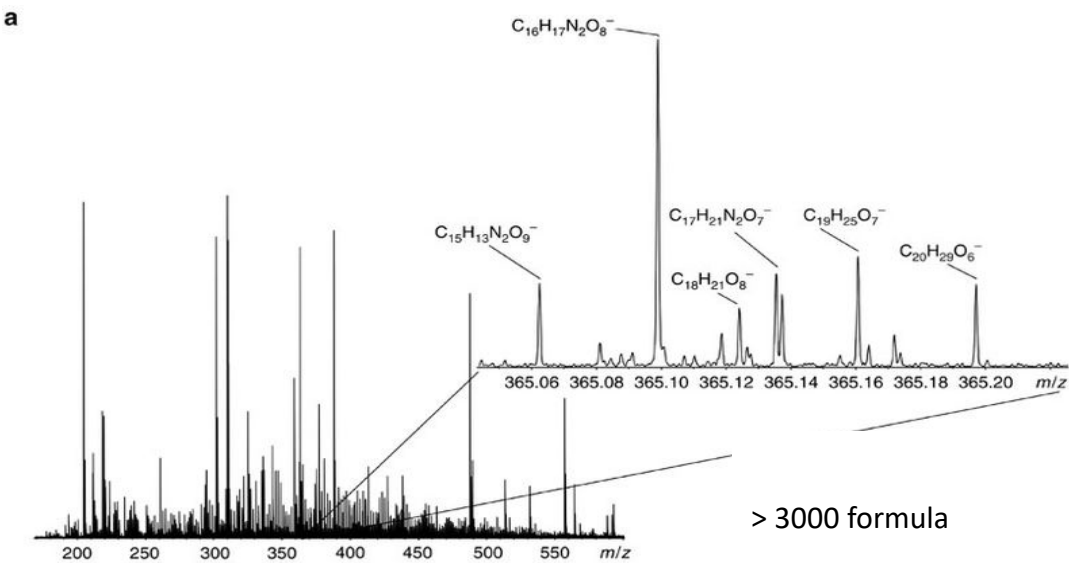
- Chemically diverse (thousands of compounds)



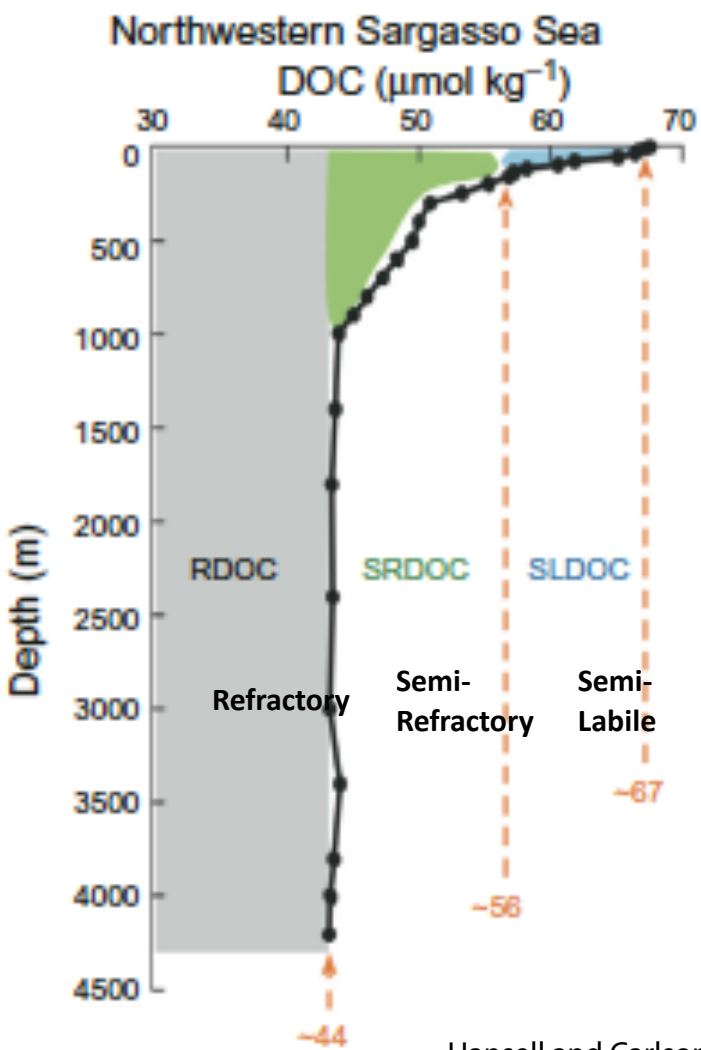
Kujawinski 2012

DISSOLVED ORGANIC MATTER IN THE OCEAN

- Chemically diverse (thousands of compounds)
- Variable reactivity (labile to refractory)

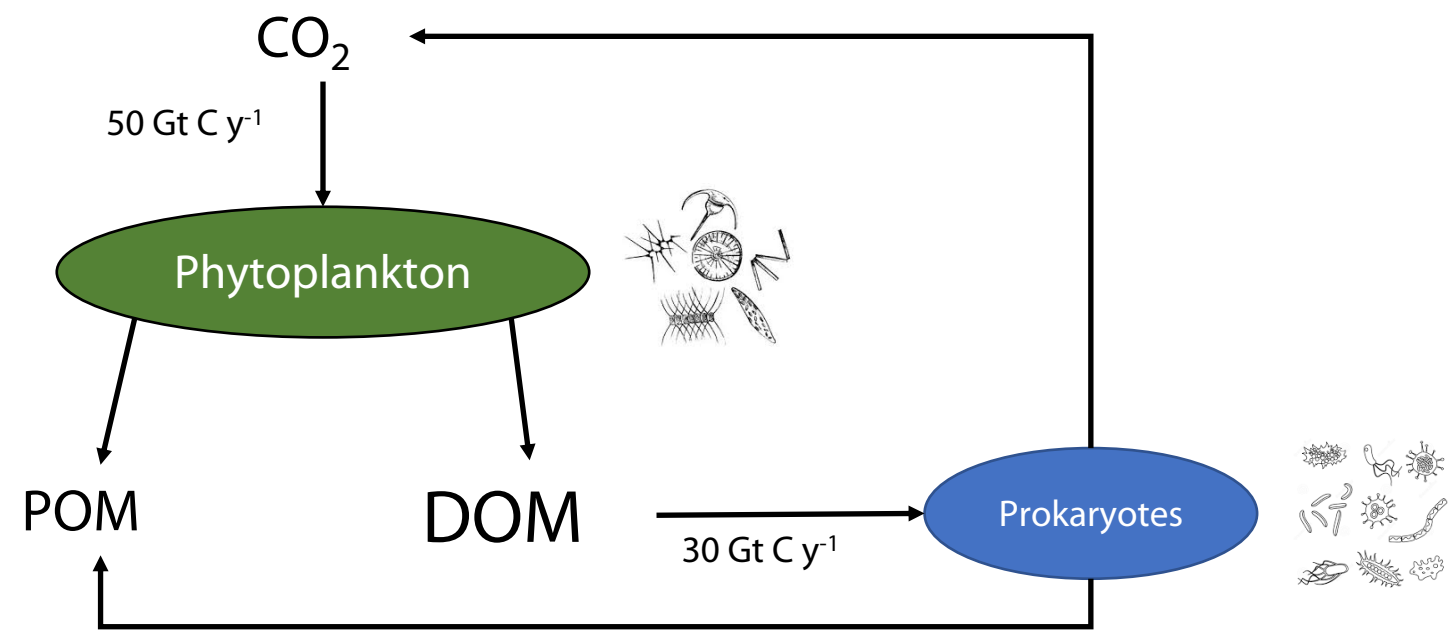


Kujawinski 2012

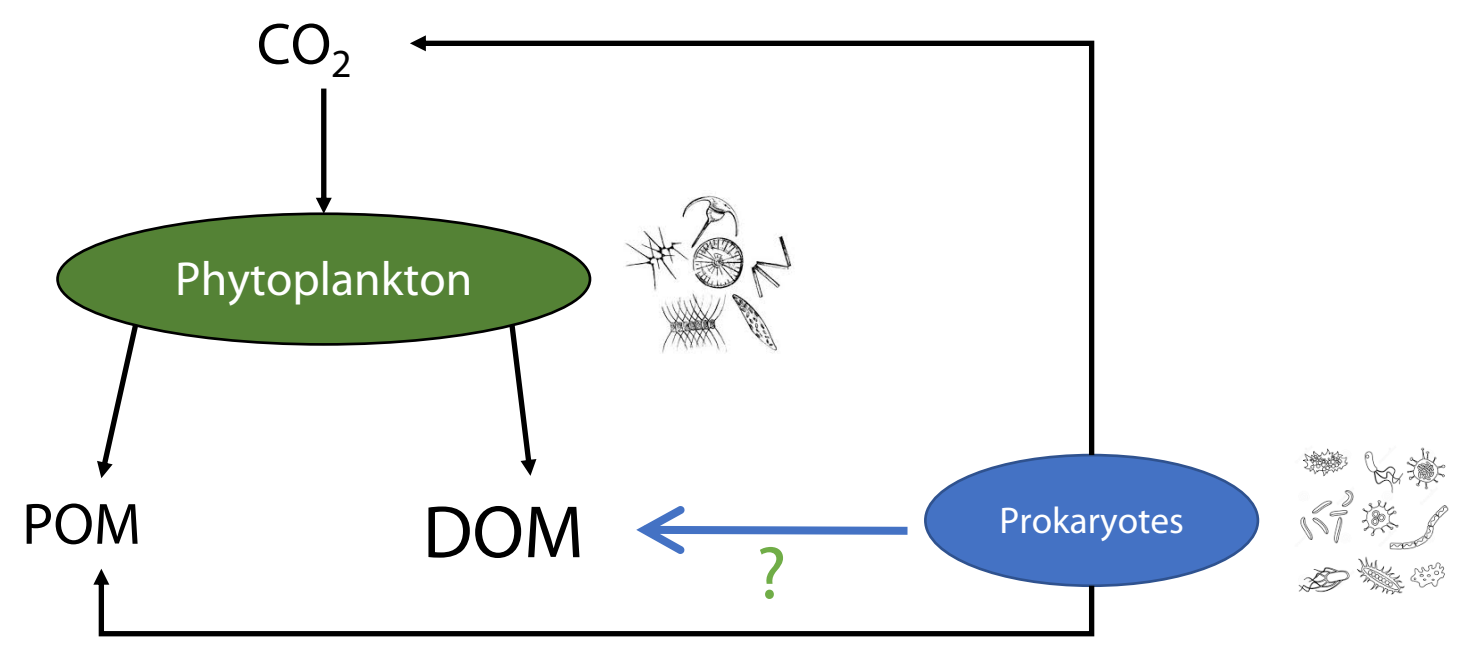


Hansell and Carlson 2014

Linkage between DOM and prokaryotes

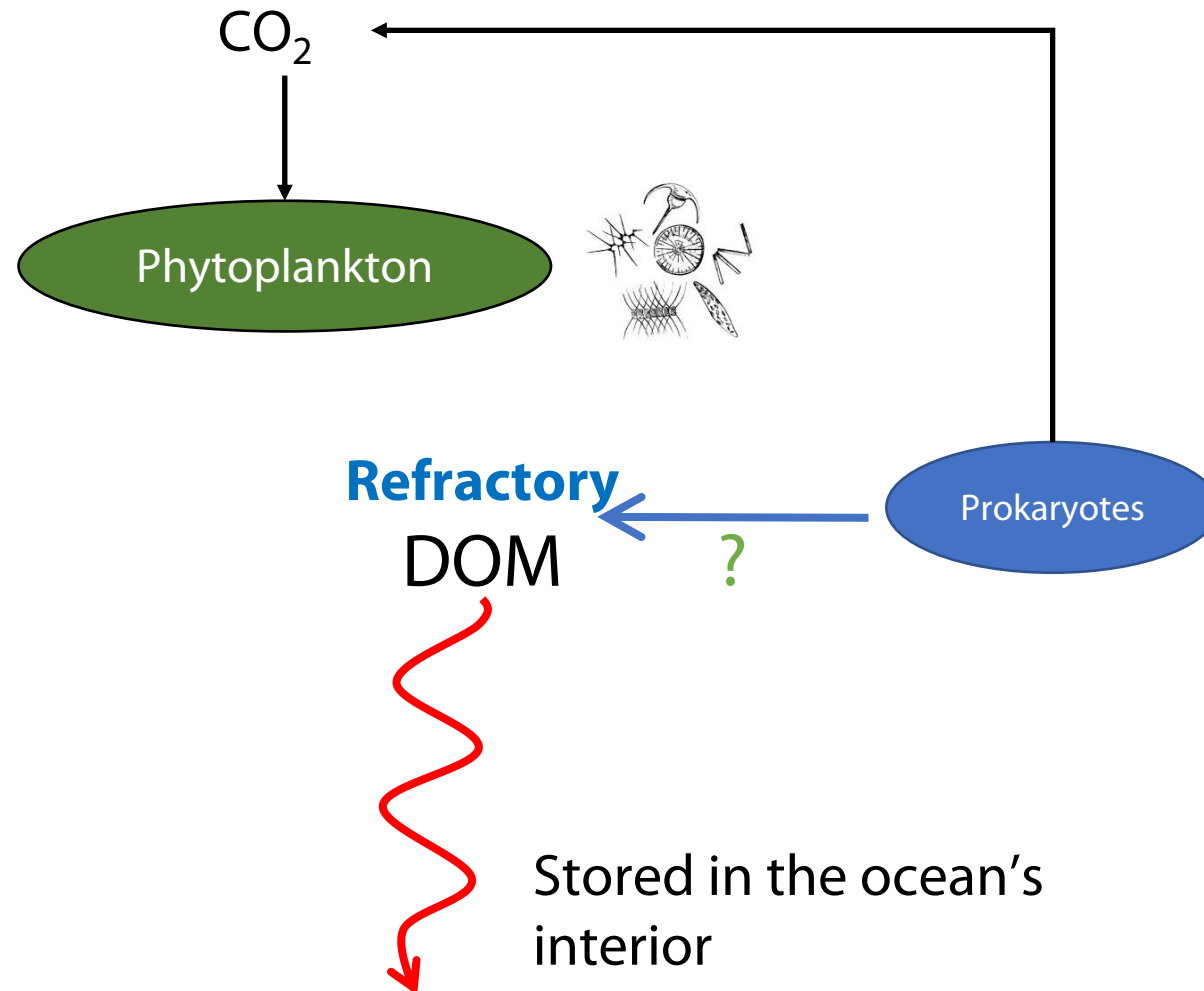


Prokaryotes uptake DOM...



... but also release organic compounds

The Microbial carbon pump



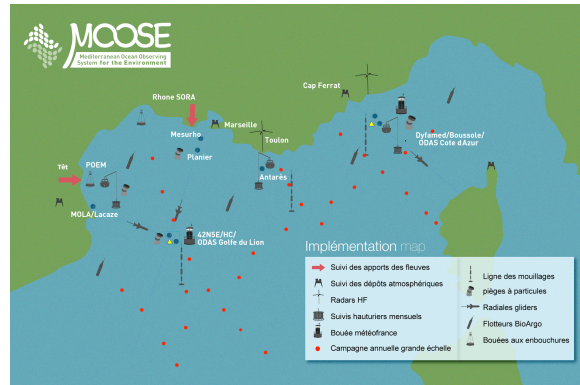
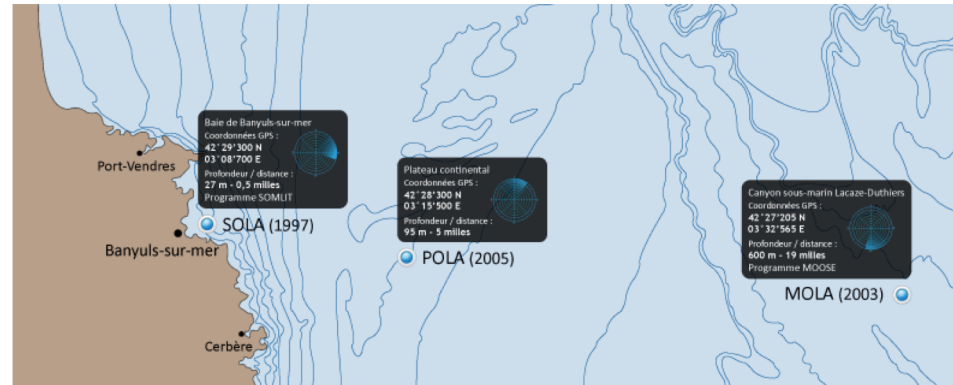
What is the role of microbes shaping DOM composition in the NW Mediterranean?

Case study:

DOM seasonal dynamics in the NW Mediterranean Sea



The MOLA site. Sampled monthly since 2003. 9 depths for >15 environmental parameters



Characterizing dissolved organic matter in marine ecosystems

How much? DOC concentration

Element ratios? C:N:P

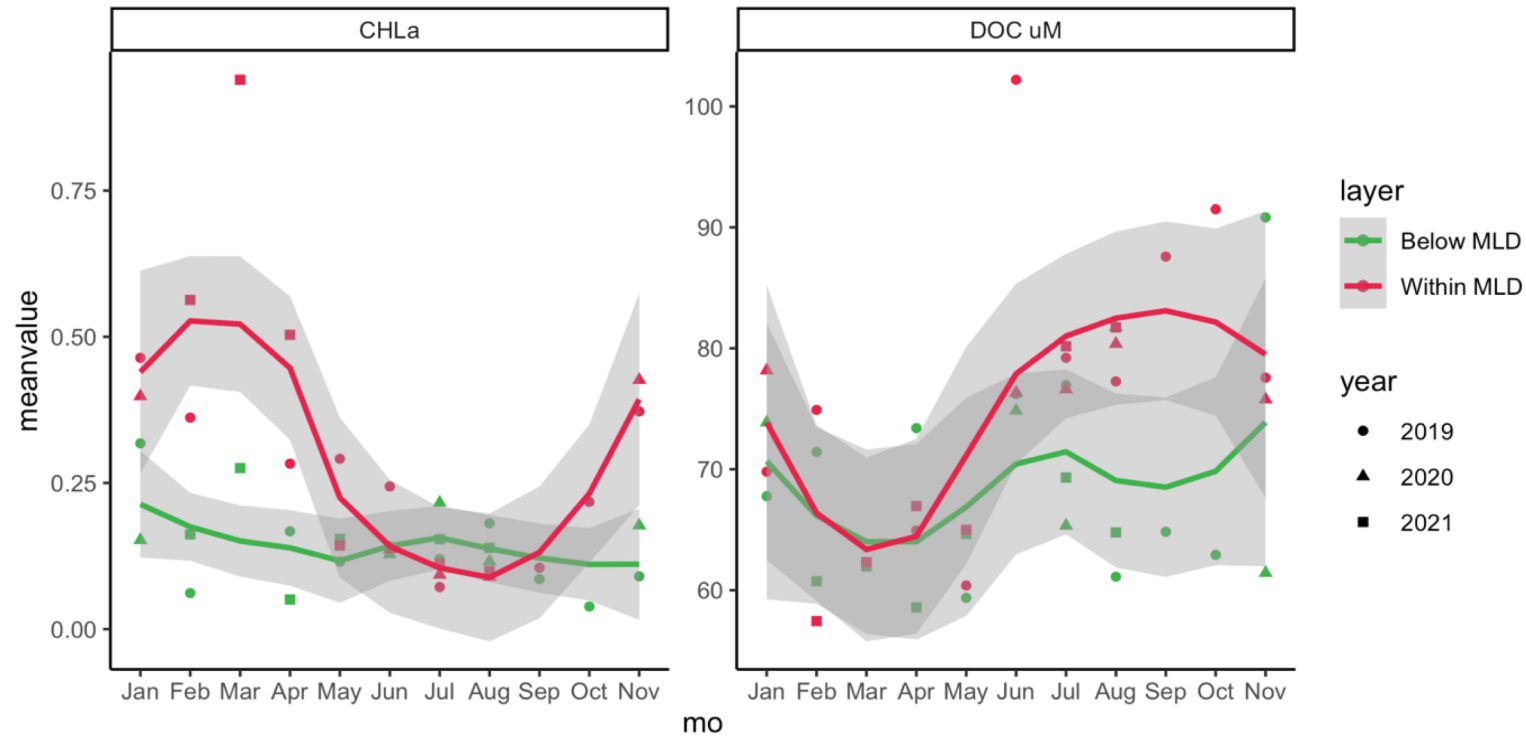
Optical properties? Absorbance and fluorescence of natural DOM

Major compounds? Carbohydrate, amino acid, lipid content

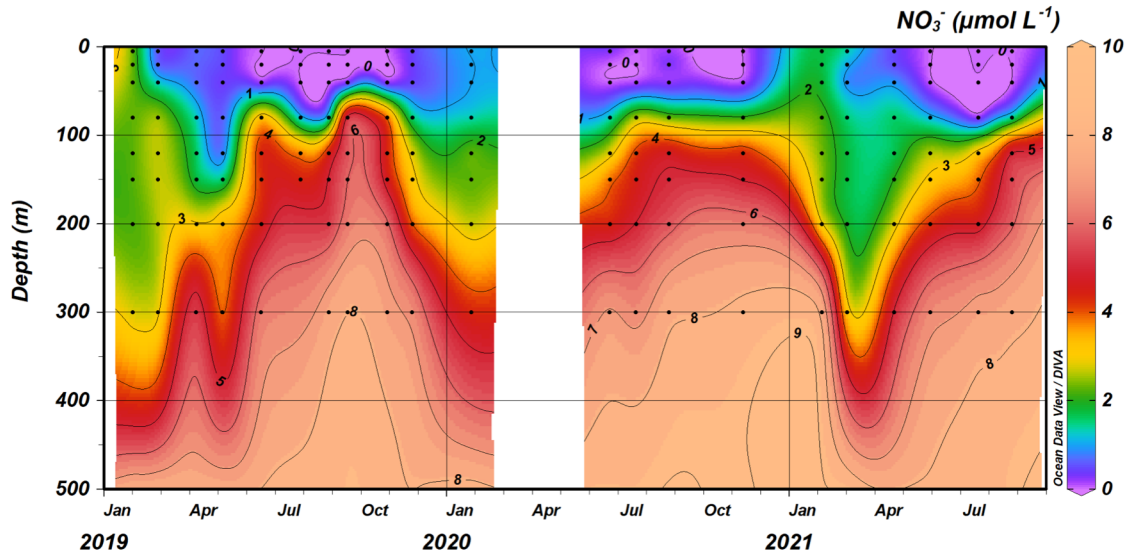
Molecular composition? High resolution mass spectrometry, NMR

Other properties: Sources, lability, size

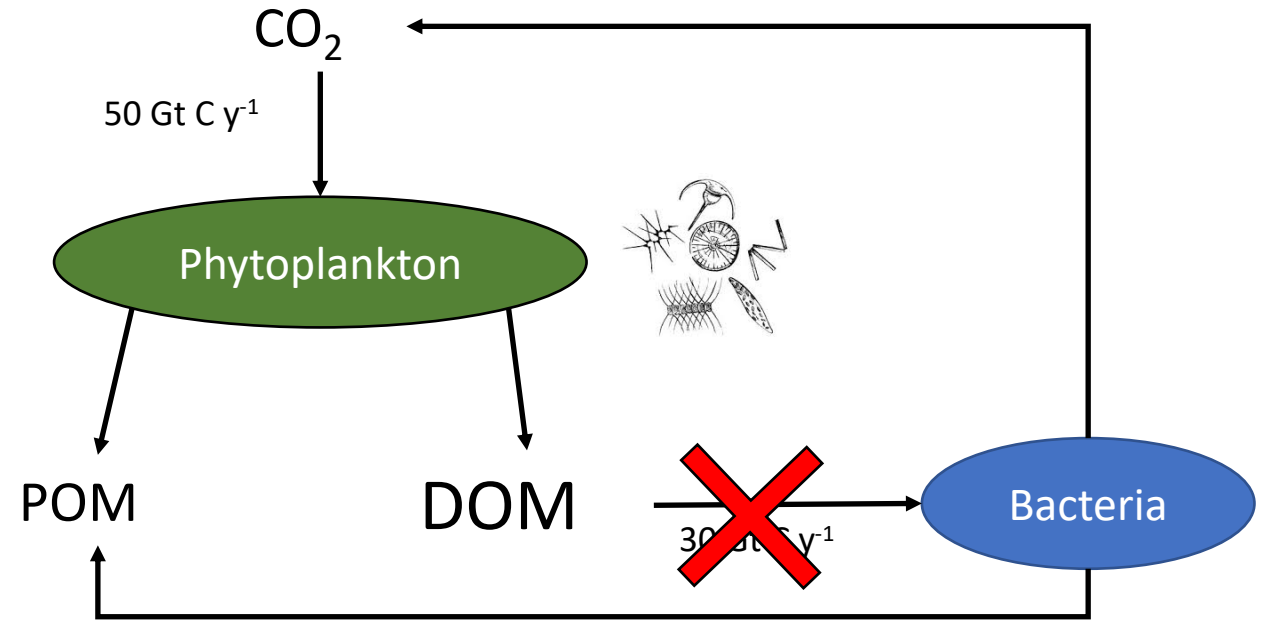
Dissolved organic carbon accumulates in the upper mixed layer in summer



Why are DOC and phytoplankton decoupled? Malfunctioning of the microbial loop

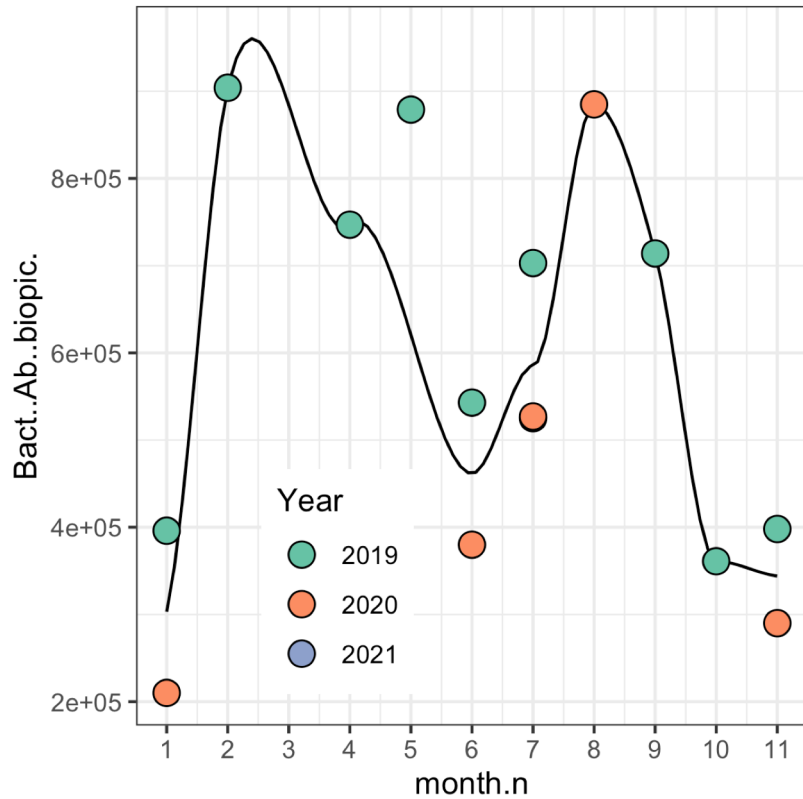
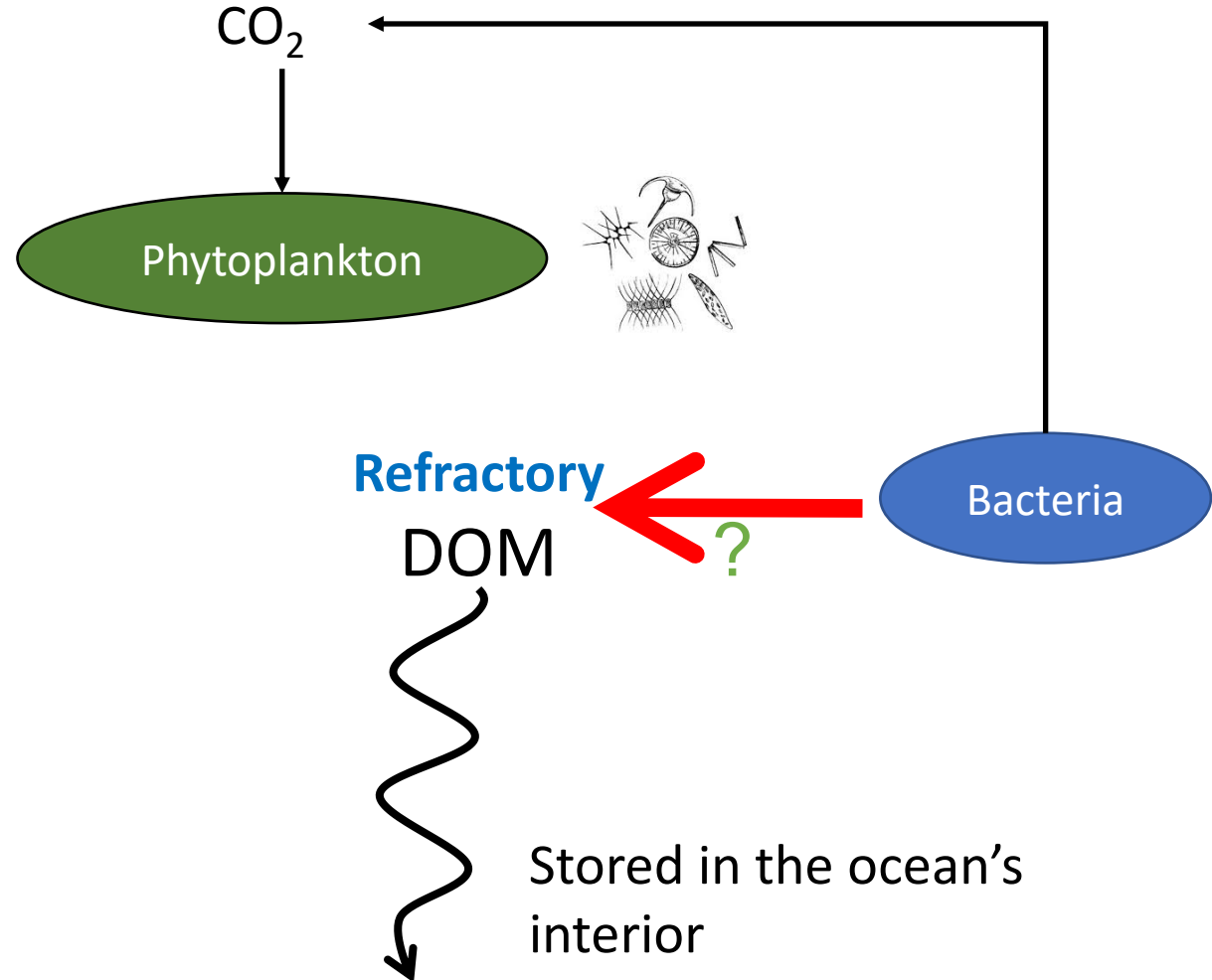


 NH_4 , NO_3 , PO_4



Why are DOC and phytoplankton decoupled?

Microbial carbon pump



Question:

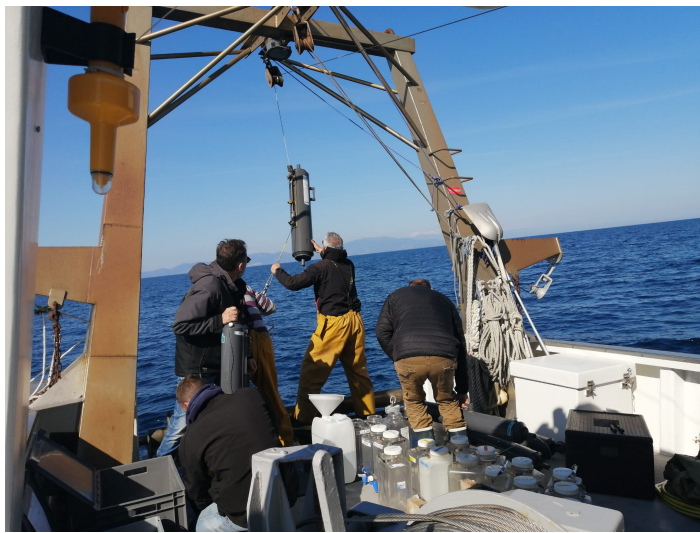
- How does DOM composition change along the year in the NW Mediterranean?

Working hypothesis:

- During the stratified period, DOM changes its composition:
 - From phytoplankton derived DOM to bacterial-derived DOM
 - From labile DOM to refractory DOM

Working plan:

- Characterize DOM composition changes with time (seasons) and depth (5 vs 500m)



Sampling scheme

- 2 years
- Monthly samples
- Surface (5m)
- One sample per season at 500m

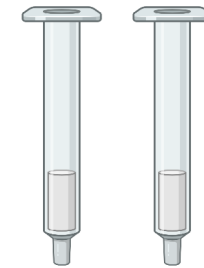


2 L water samples



Filtration through 0.2 µm

Acidification with HCl to pH < 2



SPE extraction
(PPL cartridges)

Elution in methanol

Sampling scheme



SPE extraction
(PPL cartridges)

Elution in methanol



2 L water samples

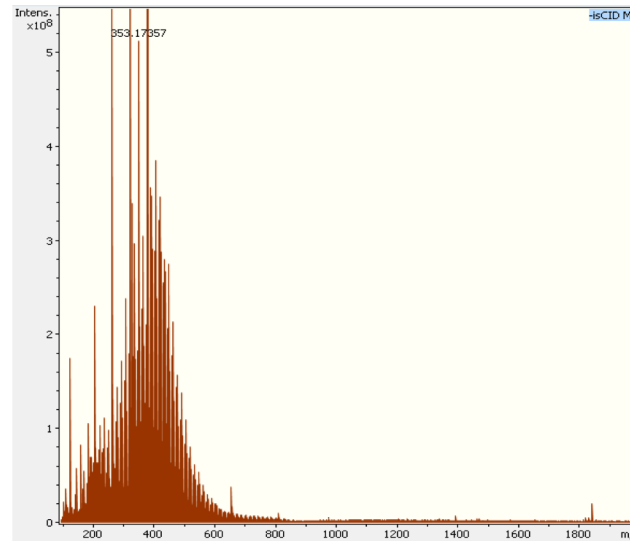
DOM composition and properties based on FT-ICR MS

DOM diversity indexes

- Simpson
- Distance
- Functional diversity

Molecular Formulae
Atom content:

CHONS



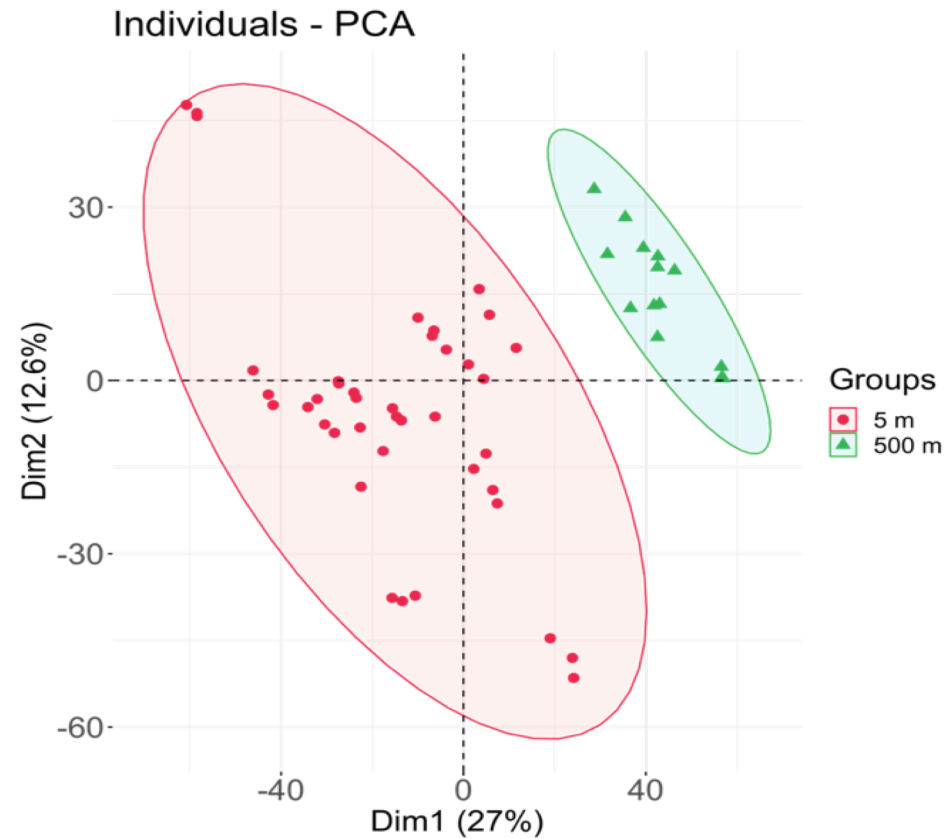
Compound class

- Peptides
- Polyphenols
- Highly unsaturated
- CRAMS
- Carbohydrates

Reactivity Indexes

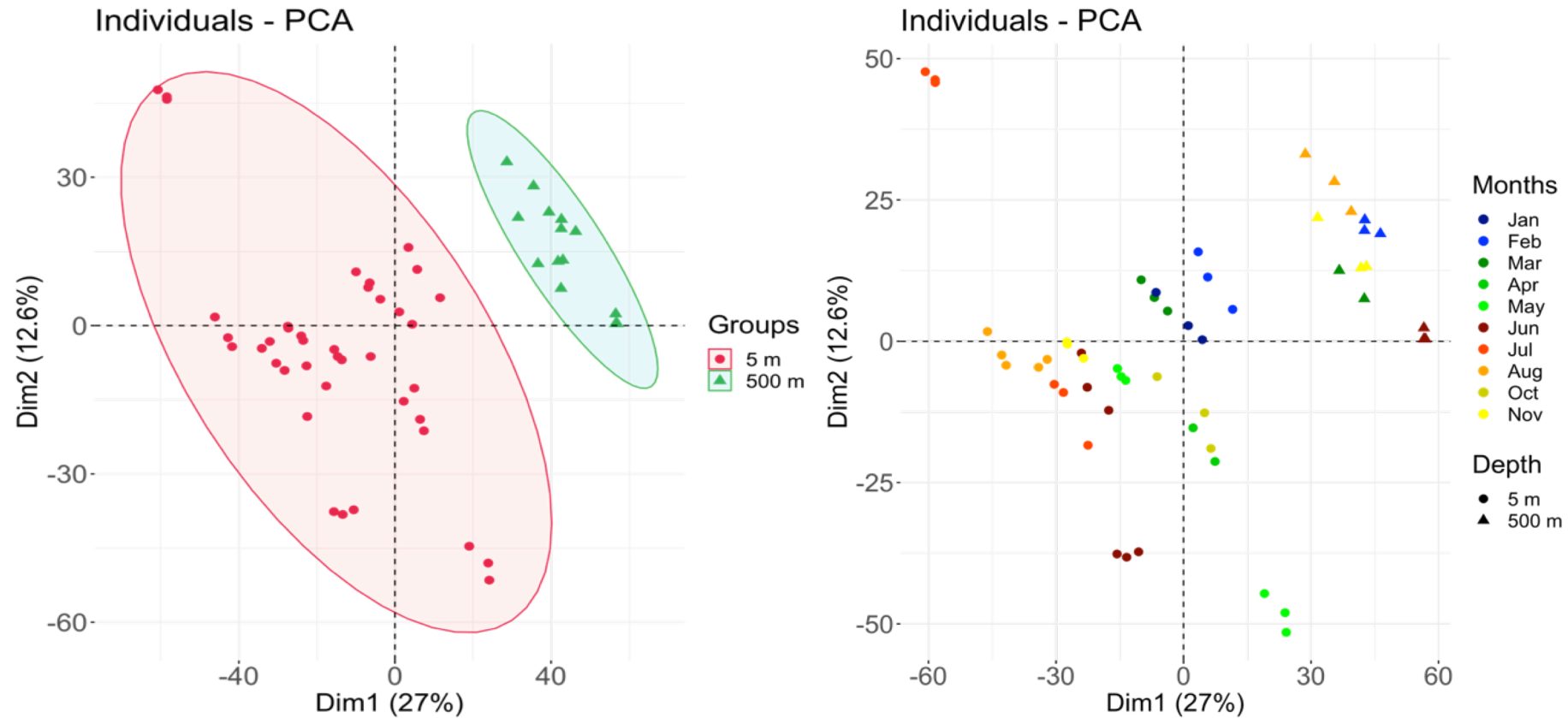
- Double Bond equivalent
- Mass to charge
- Aromaticity Index
- Oxidative state
- H/C

Principal Component Analysis



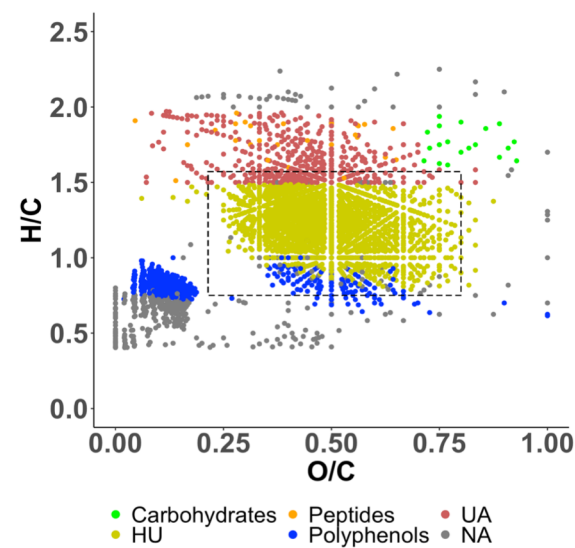
PC1 and PC2 explain component explain 27 and 12.6 % of the variance among the samples, respectively, accounting for 39.6 % of the variance

Principal Component Analysis

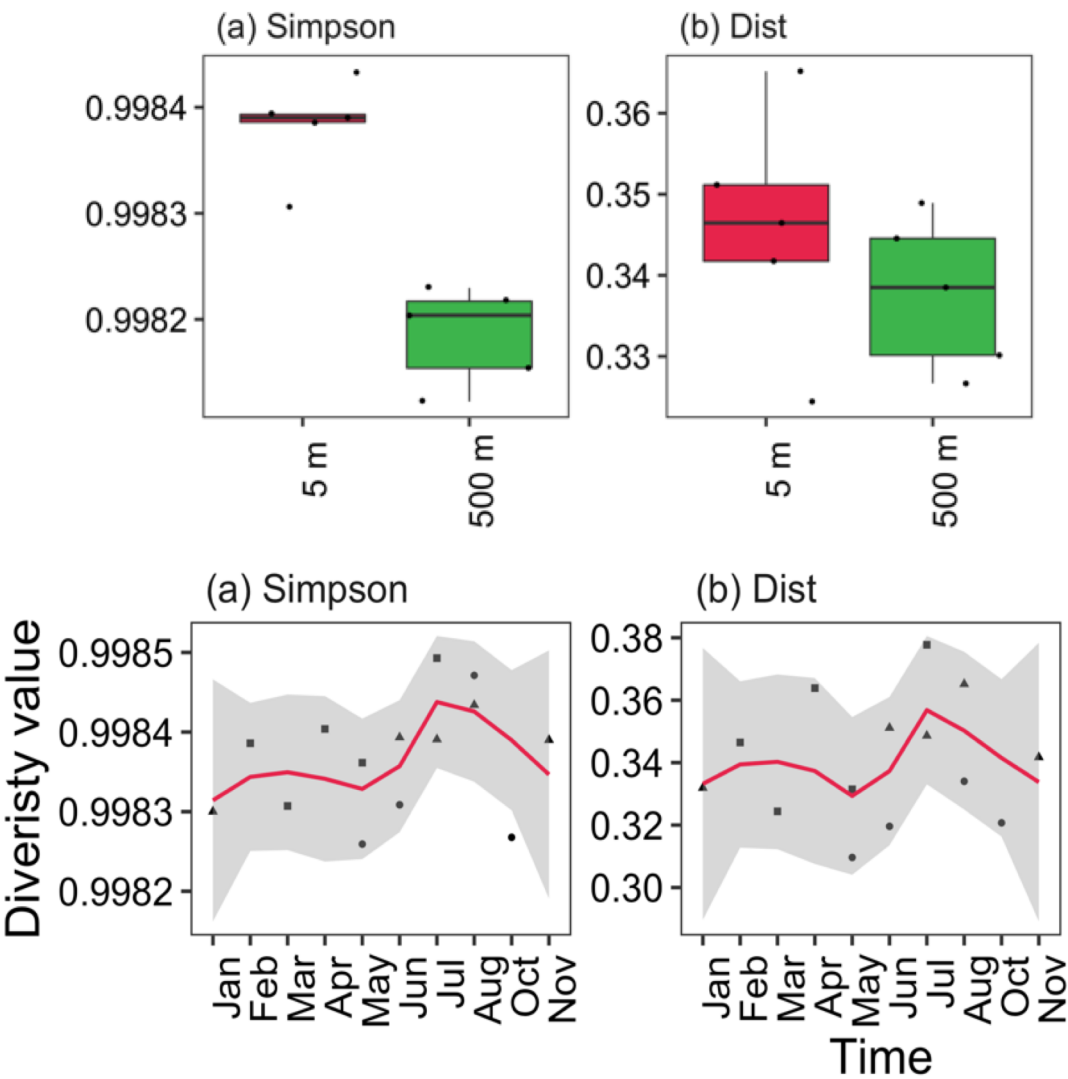


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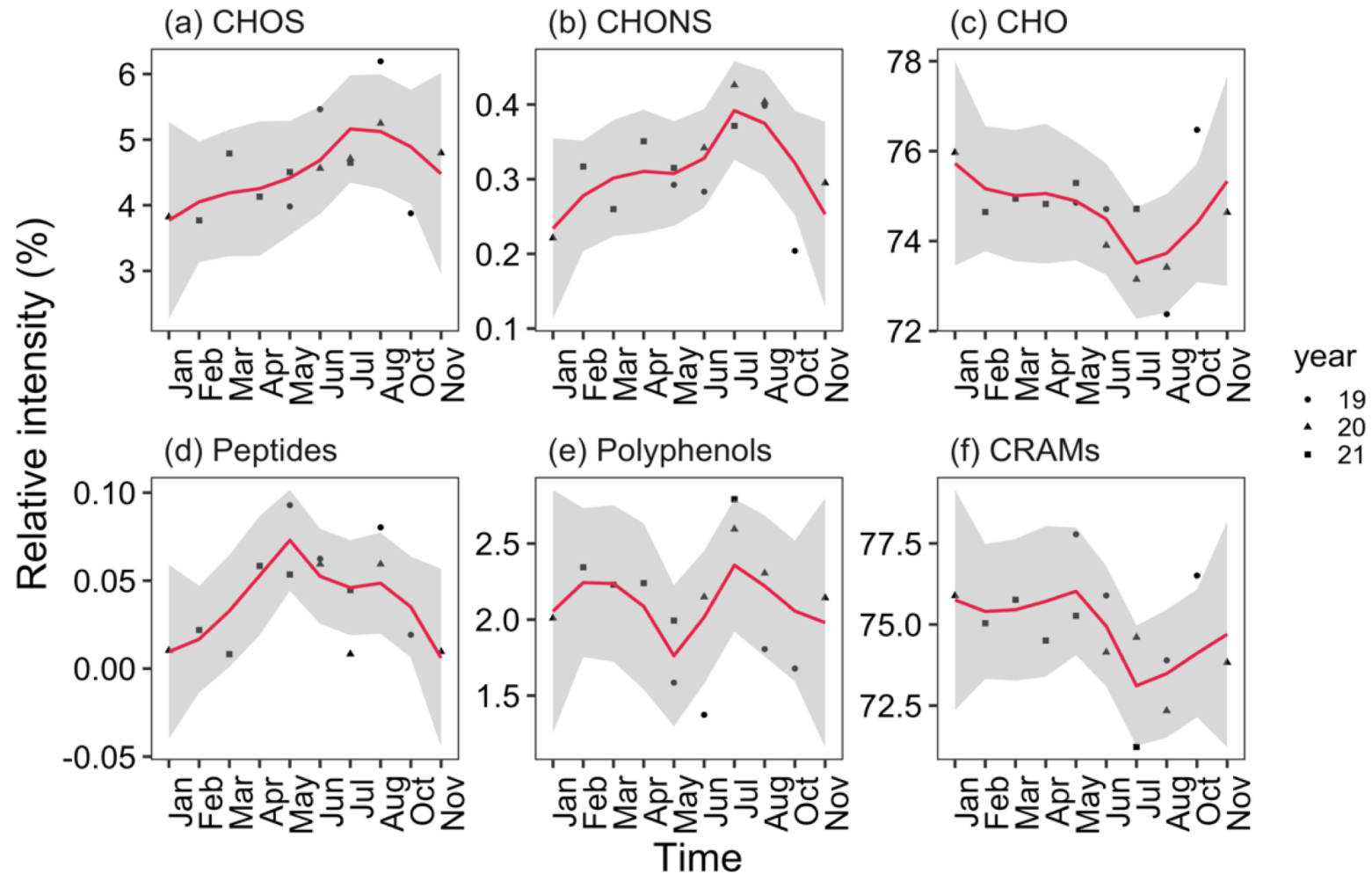
DOM diversity changes



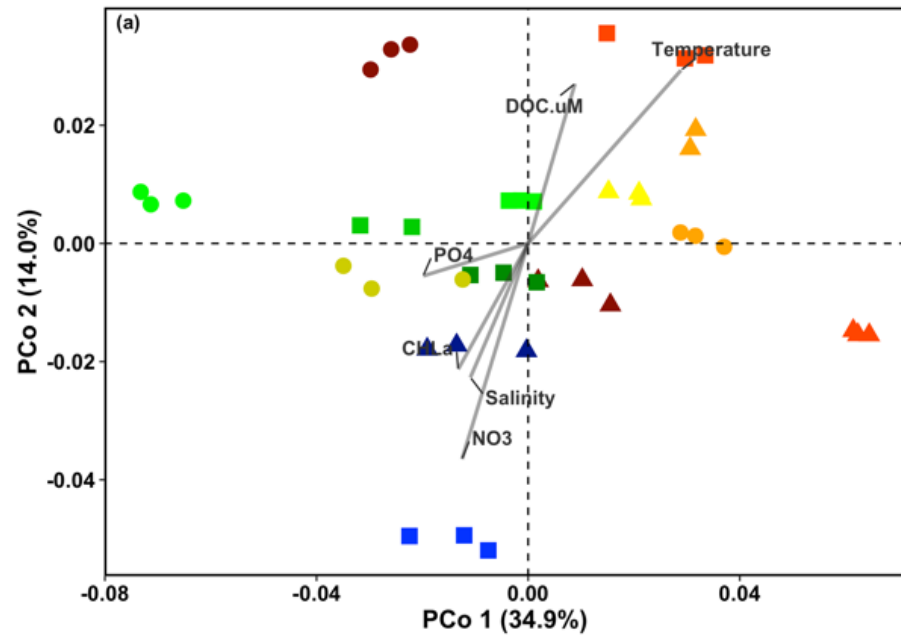
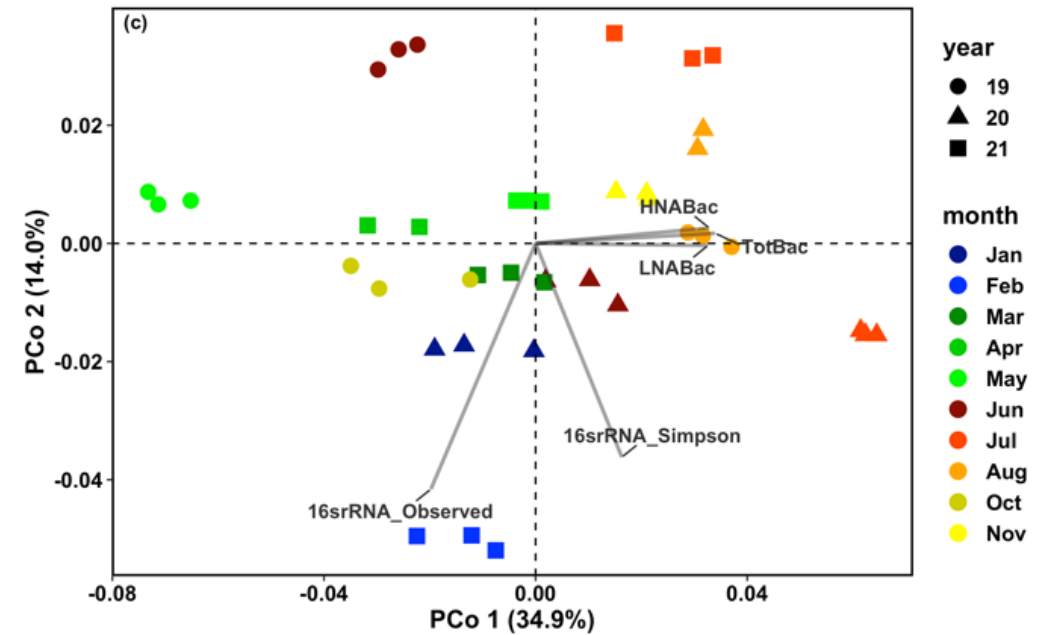
DOM is more diverse in surface waters and in summer, coinciding with DOM accumulation



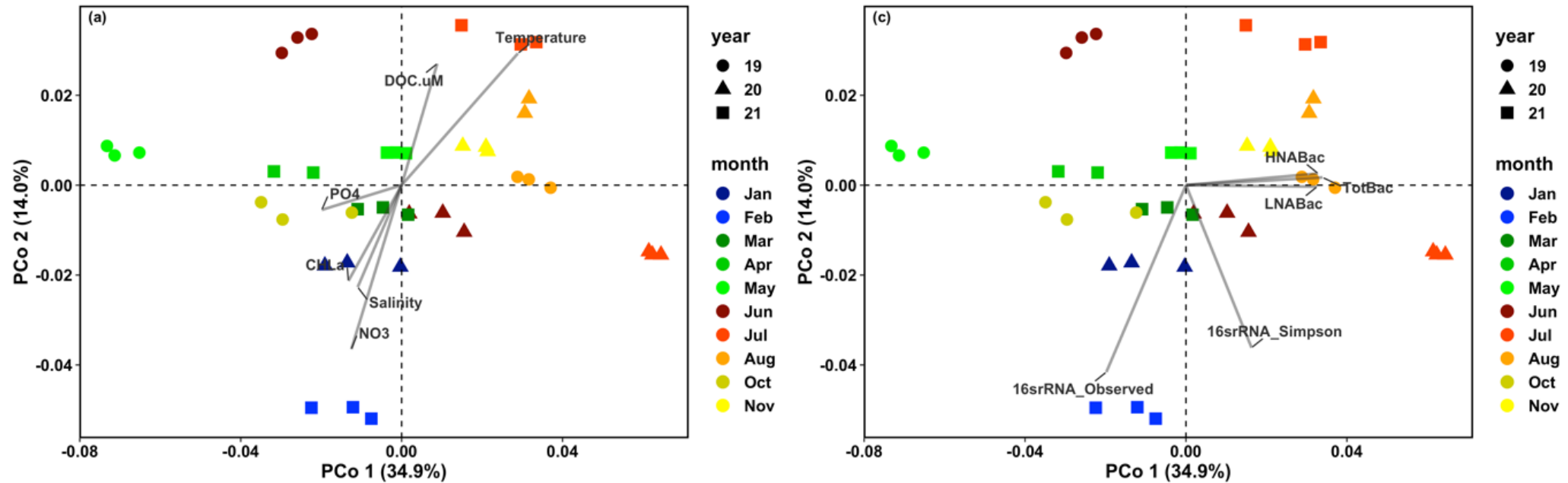
Molecular formulae and compound class distribution and changes



Summer DOM samples coincide with higher prokaryotic abundances and enzyme activities

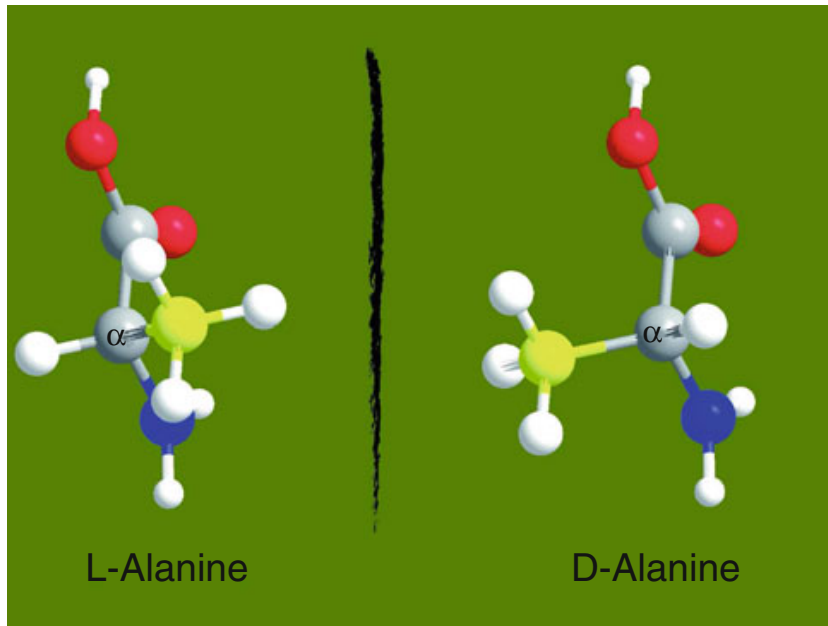


Summer DOM samples coincide with higher prokaryotic abundances and enzyme activities



Are prokaryotes the main source of DOM in summer?

D-amino acids: biomarkers of bacterial DOM



From Cava et al 2011

Major bacterial contribution to the ocean reservoir of detrital organic carbon and nitrogen

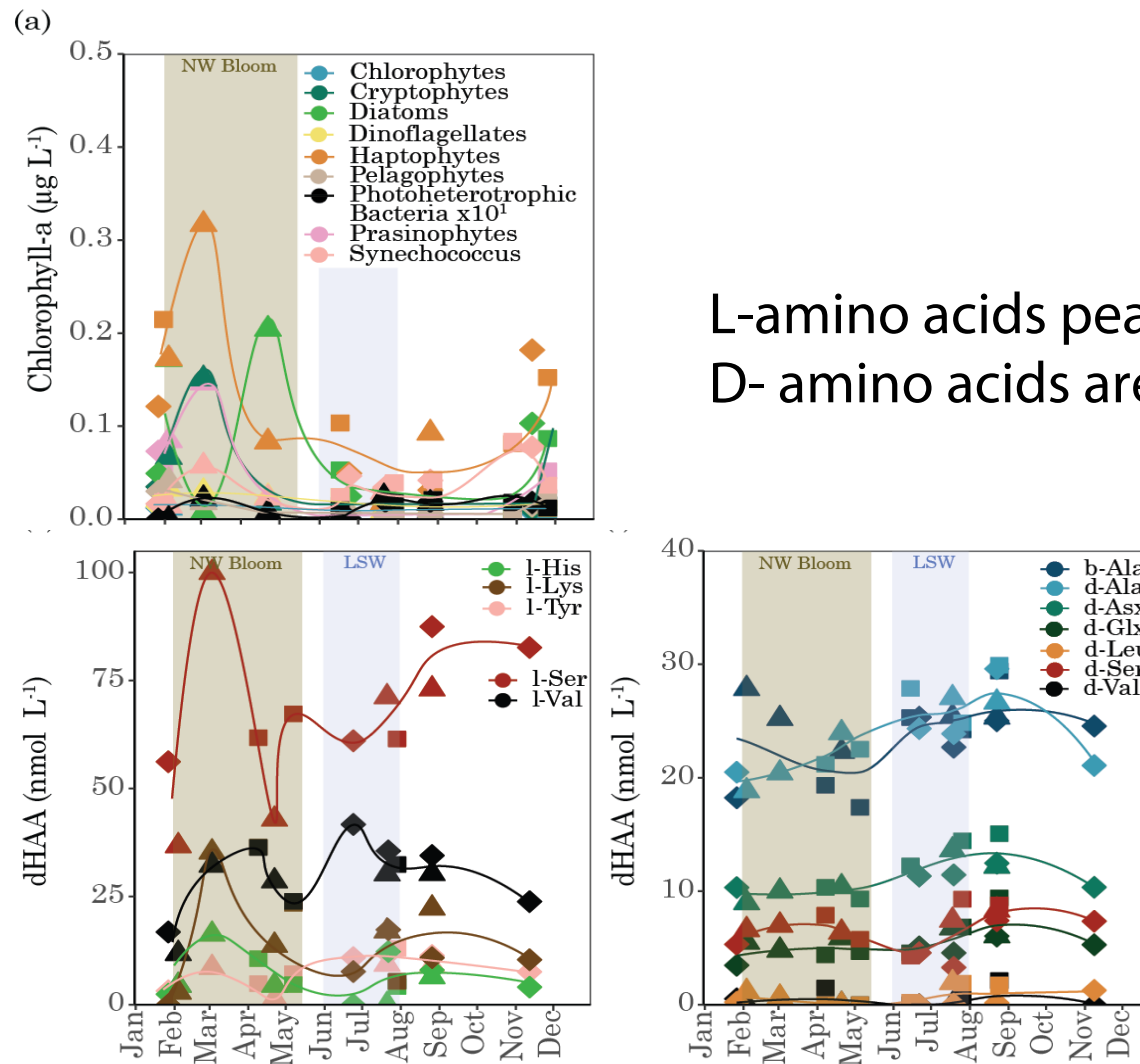
Karl Kaiser¹ and Ronald Benner

Marine Science Program, University of South Carolina, Columbia, South Carolina 29208

Amino acid enantiomers in old and young dissolved organic matter: Implications for a microbial nitrogen pump

Taylor A.B. Broek^{a,b,*,1}, Amy L. Bour^{a,1}, Hope L. Ianiri^a,
Thomas P. Guilderson^{a,b}, Matthew D. McCarthy^a

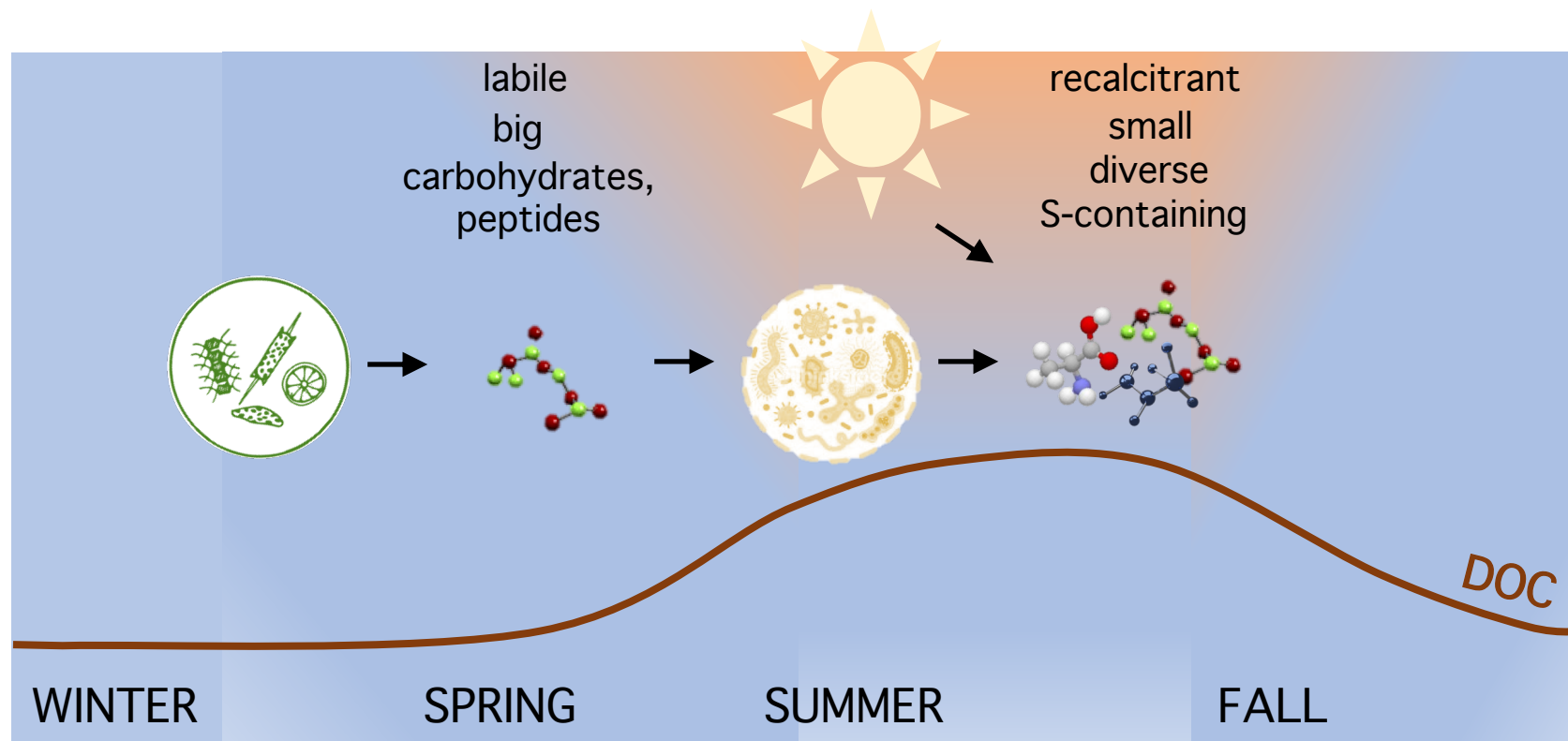
Seasonal changes in amino acids (Von Jackowski et. al. 2024 Organic Geochem)



L-amino acids peak in Winter-spring
D- amino acids are higher in summer

Summer DOC accumulation leads to:

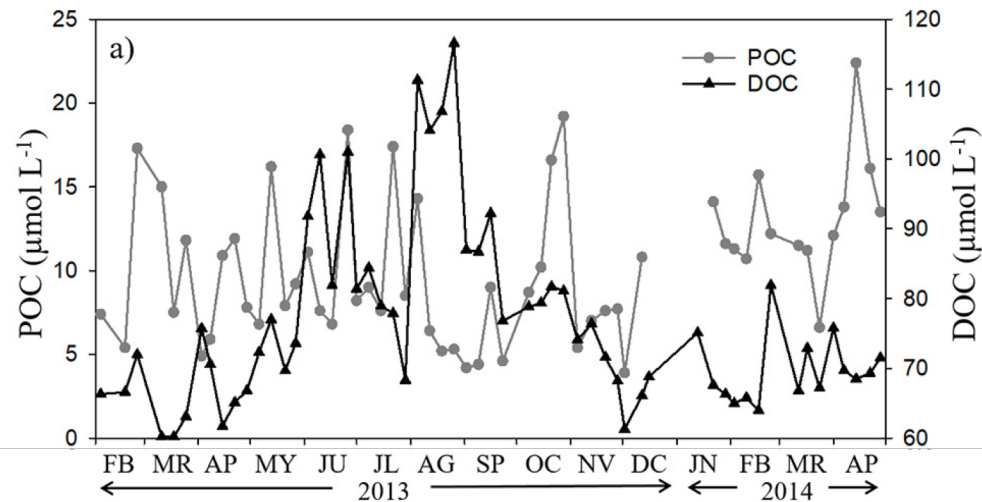
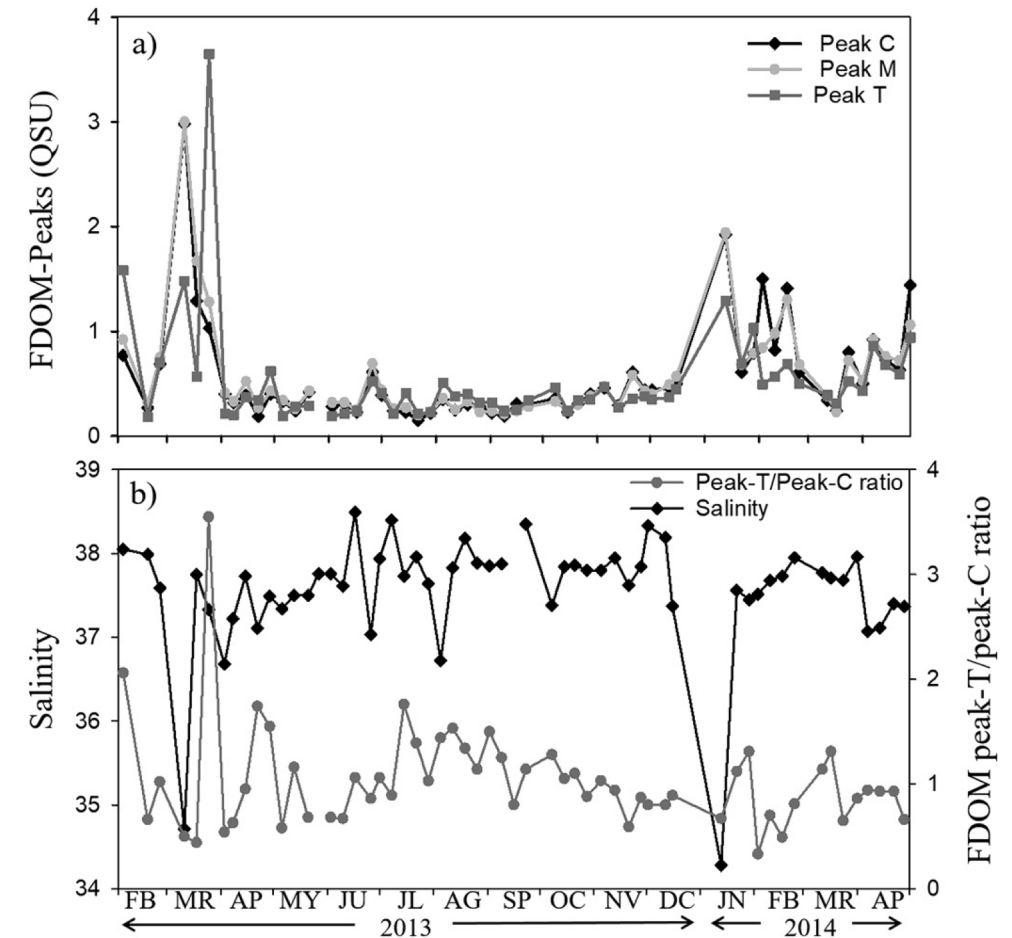
- A diversification of the DOM pool
- An accumulation of S containing compounds
- An increase in oxygenation state and double bonds
- An increase in bacterial-derived compounds



In SOLA (coastal Mediterranean Sea)

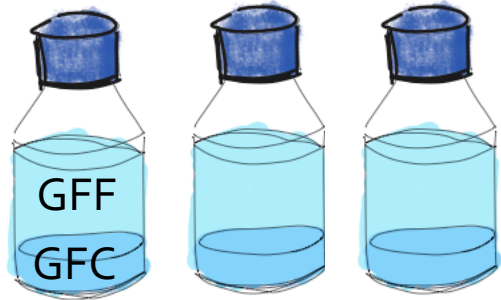
...but episodic events do matter

DOC also accumulates...



How does changes in P limitation affect DOM composition and lability over the year?

How does changes in P limitation affect DOM composition and lability over the year?



- Control (no additions)
- Pi (+ 0.4 $\mu\text{mol PO}_4$)
- OP (+ 0.4 $\mu\text{mol P}$ as ATP+Methyl phosphonate)

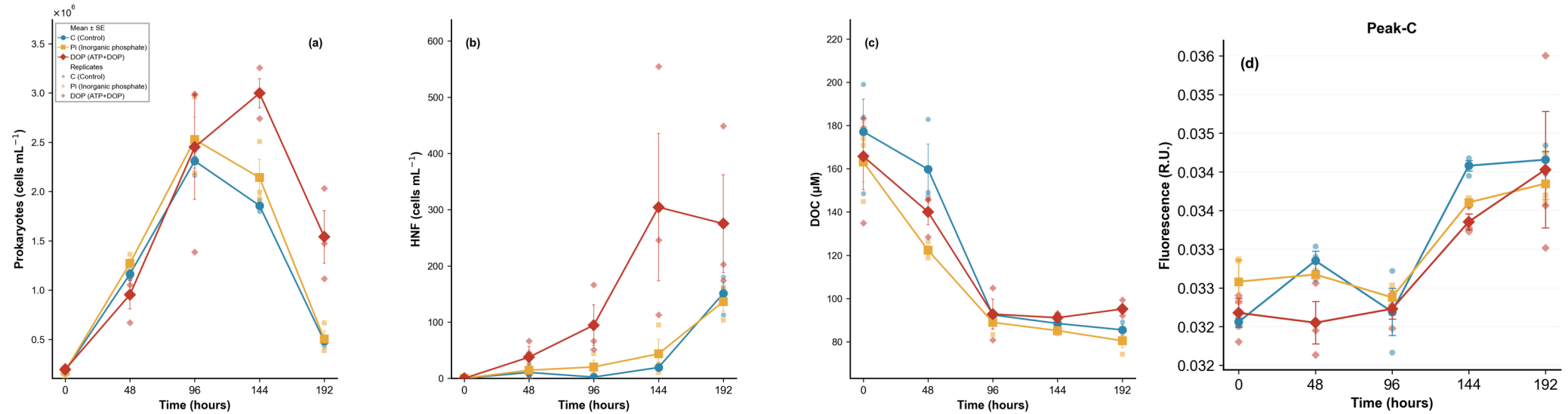
10 day incubations

2 phases:

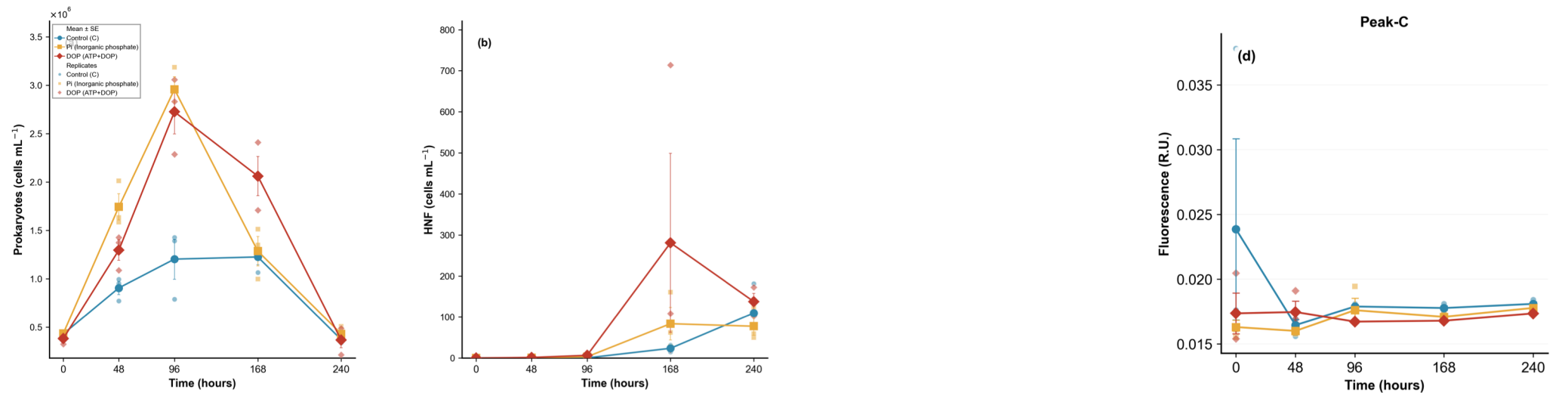
Bacterial growth (first 3-4 days), bacterial mortality due to grazers (days 5-10)

DOM degradation experiments along the year

January

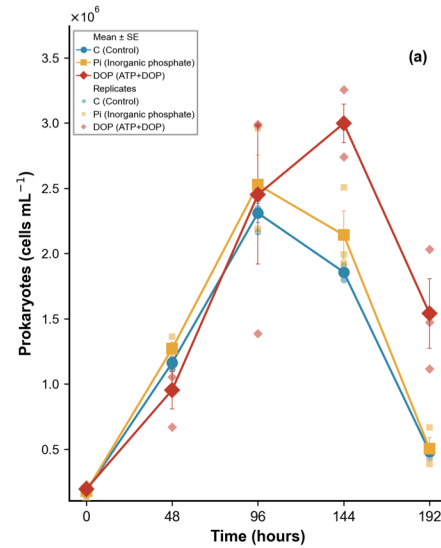
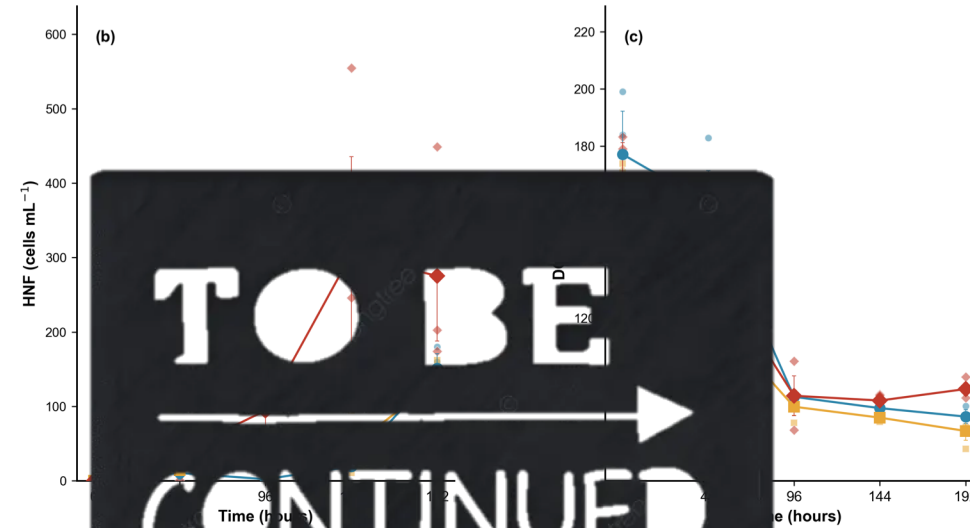
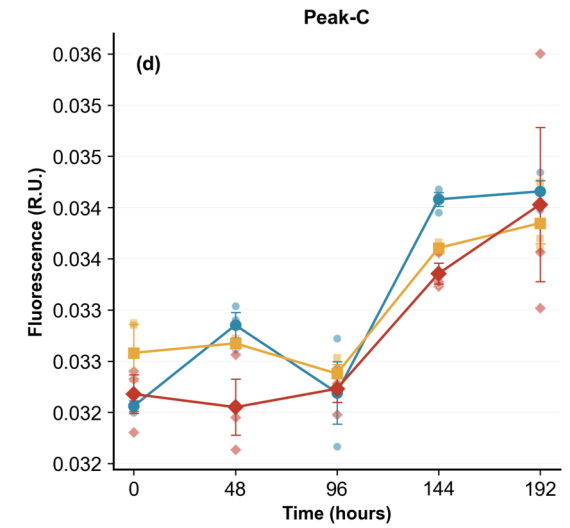


April

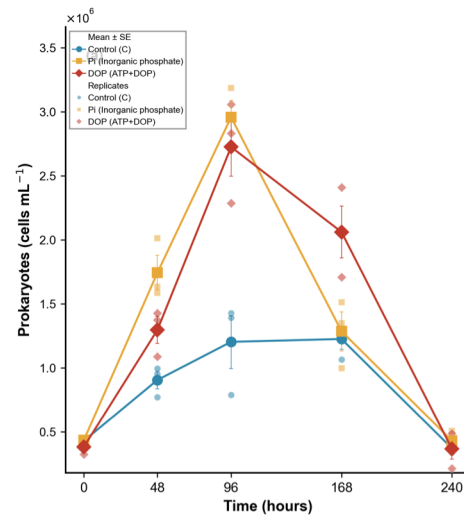
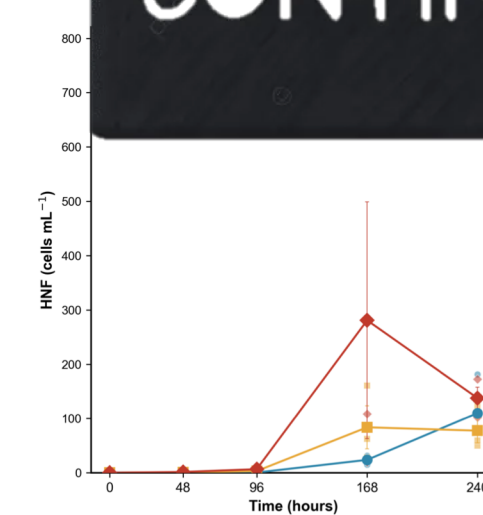
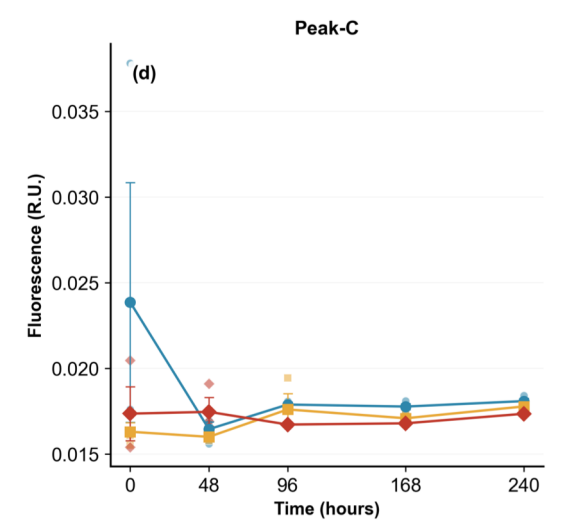


DOM degradation experiments along the year

January



April



Thank you

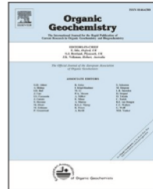




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Seasonality of amino acid enantiomers and microbial communities at MOLA time series in the NW Mediterranean Sea

Anabel von Jackowski^a, Nawal Bouchachi^a, Quentin-Boris Barral^b, Paul Labatut^c, Barbara Marie^a, Olivier Crispi^a, Karine Escoubeyrou^c, Charles-Hubert Paulin^c, Celine Dimier^d, Josephine Ras^e, Alexander Hayward^f, Eva Ortega-Retuerta^{a,*}

^a CNRS/Sorbonne Université, UMR7621 Microbial Oceanography Laboratory, Banyuls sur Mer, France
^b CNRS/Université de Toulouse, UMR5566 Laboratory of Space Geophysical and Oceanographic Studies, Toulouse, France
^c Oceanographic Observatory of Banyuls sur Mer (OOB), Banyuls sur Mer, France
^d CNRS/Sorbonne Université, Institut de la Mer de Villefranche (IMEV), Villefranche-sur-Mer, France
^e CNRS/Sorbonne Université, UMR 7093 Laboratoire d'Océanographie de Villefranche (LOV), Villefranche, France
^f Danish Meteorological Institute, København, Denmark

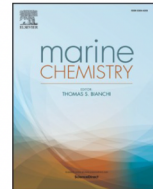
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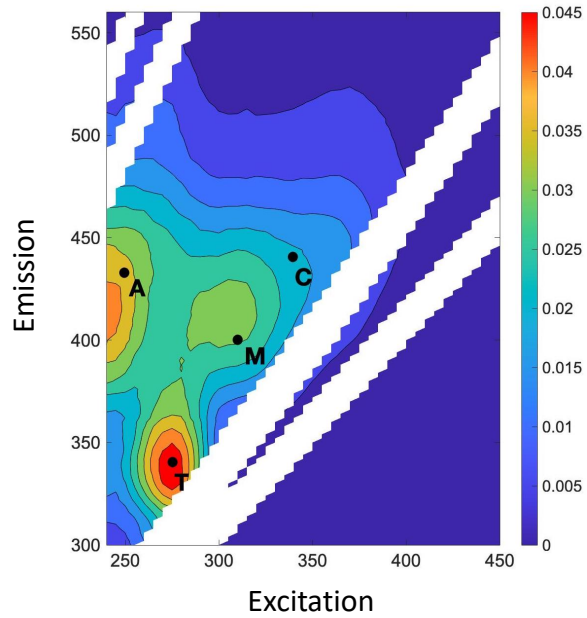
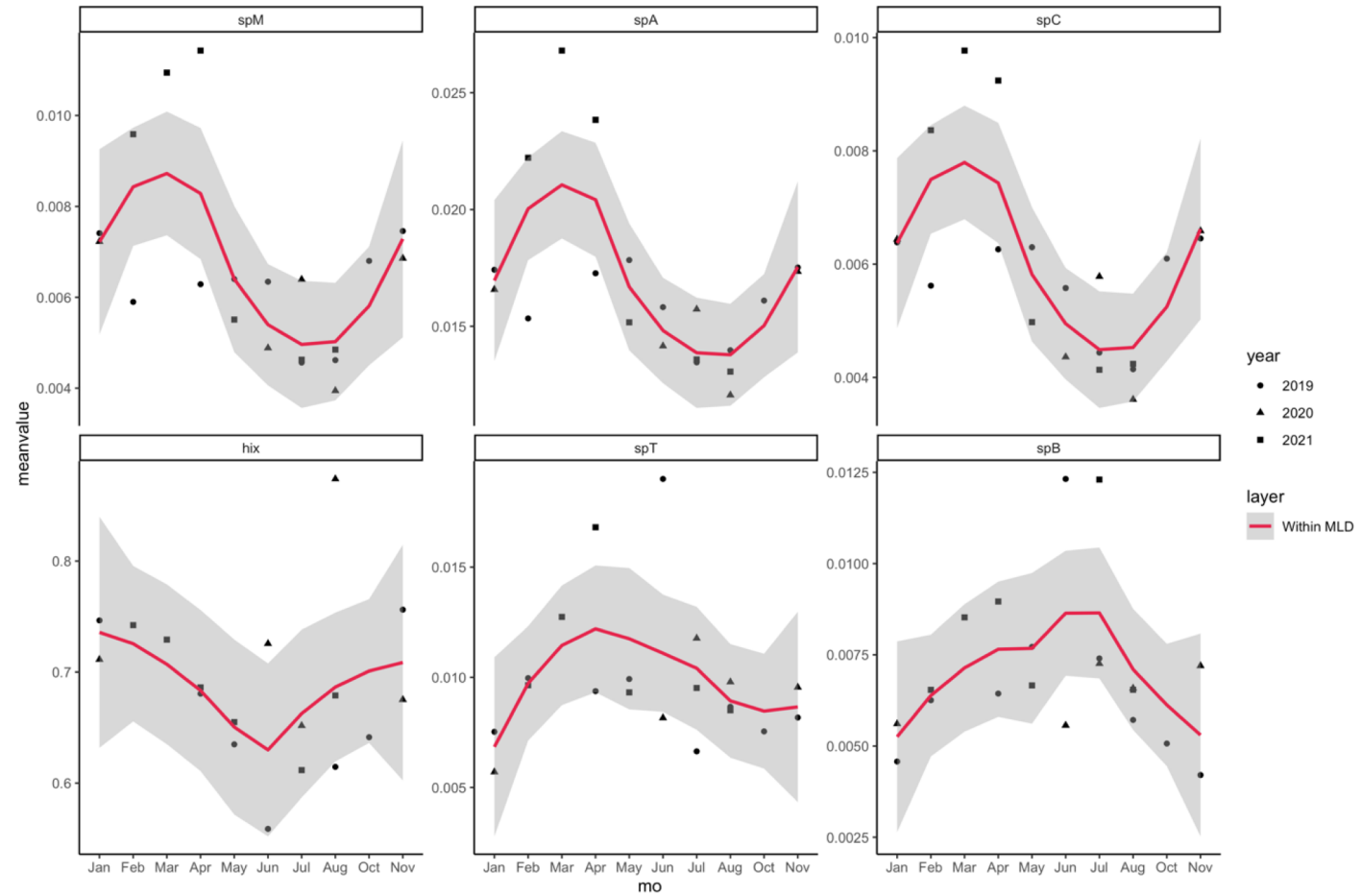


Seasonal dynamics of DOM diversity and molecular composition in the NW Mediterranean Sea

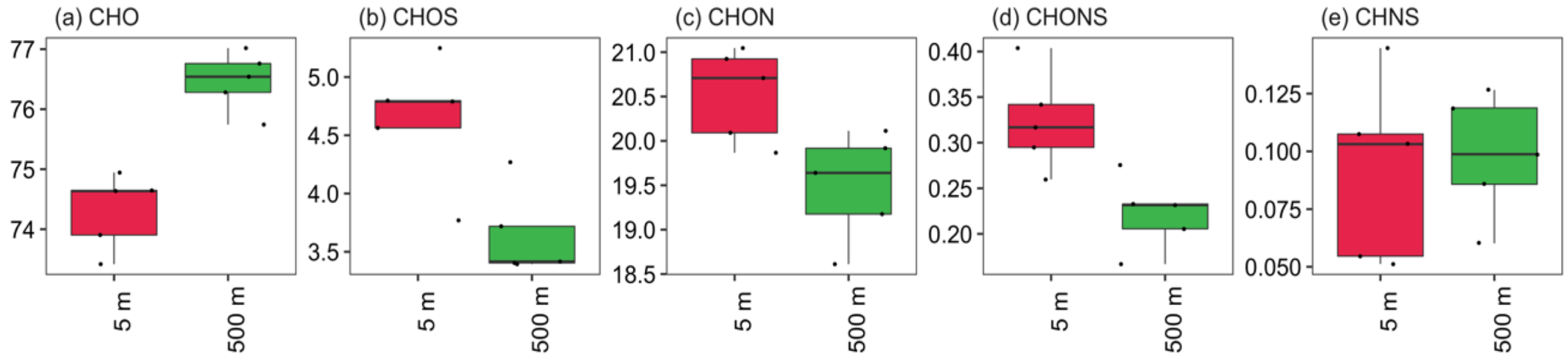
Nawal Bouchachi^a, Hélène Lavanant^b, Carlos Afonso^b, Isabelle Schmitz^{c,d}, Barbara Marie^a, Ingrid Obernosterer^a, Eva Ortega-Retuerta^{a,*}

^a Laboratoire d'Océanographie Microbienne, LOMIC UMR7621, CNRS, Sorbonne Université, Banyuls-sur-Mer, France
^b Univ Rouen Normandie, INSA Rouen Normandie, Univ Caen Normandie, ENSICAEN, CNRS, Institut CARMen UMR 6064, 76000 Rouen, France
^c Univ Rouen Normandie, INSA Rouen Normandie, CNRS, PBS UMR 6270, Rouen, France
^d Univ Rouen Normandie, HeRacLeS PISSARO, CNRS UAR 2026, HeRacLeS PISSARO, Rouen, France

Changes in fluorescent DOM peaks / DOC



Molecular formulae changes



Changes in reactivity indexes

