Reconstructing Seasonal Changes in Surface Particulate Organic matter using Carbon Isotopes of Amino Acids

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INTRODUCTION:

Background:

- How climate change will affect biological carbon pump is not well understood (Henson et al. 2022)
- There is a lack of understanding on historical carbon trends and marine primary productivity
  - Paleo-proxy data can be used to fill in historic data gap

Carbon Isotopes:

- ^{12}C & ^{13}C are stable isotopes
- ^{12}C 98.9% Abundant
- ^{13}C 1.1% Abundant

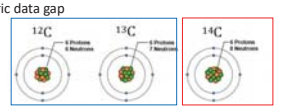


Figure 1. Diagram of Carbon Isotopes ^{12}C, ^{13}C, ^{14}C adapted from Schmittner 2021

Amino Acids:

- Amino Acids (AAs) make up the largest characterizable molecular fraction of organic material at all depths
- Essential Amino Acids (EAA's) are not modified up the food chain

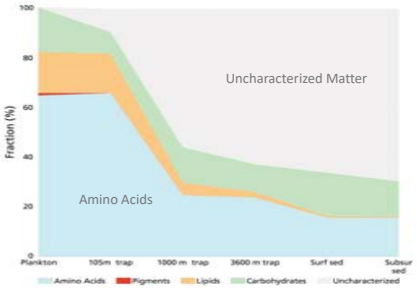


Figure 2. Biochemical composition of organic matter by depth adapted from Middleburg 2019.

Compound-specific Stable Isotope Analysis of Amino Acids (CSIA-AA)

- Delta 13 carbon ($\delta^{13}C$) can be used to create carbon fingerprints due to carbon fractionation
  - Different taxa have unique , ^{12}C to ^{13}C ratio: $\delta^{13}C$ values

$\delta^{13}C$

$$\delta^{13}C = \frac{{}^{13}C/{}^{12}C_{sample} - {}^{13}C/{}^{12}C_{standard}}{{}^{13}C/{}^{12}C_{standard}} \times 1000‰$$

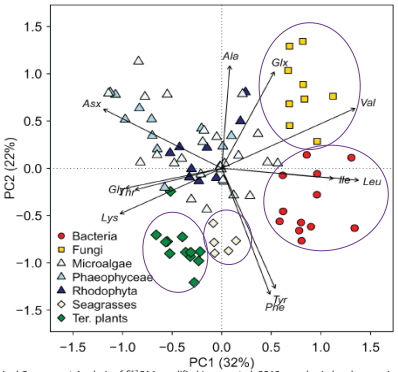


Figure 3. Principal Component Analysis of δ^{13}CAA modified Larsen et al. 2013, purple circles show major phylogenetic groupings.

Hypothesis:

- **That the seasonal transition in carbon source from large-cell, diatom-based production in spring to small-cell, flagellate-based production in summer is reflected in δ^{13}C-AA signatures of seawater residue.**

Objectives:

- Sample local coastal water for $\delta^{13}C$ bi-weekly following a spring to fall seasonally cycle
- Compare the found $\delta^{13}C$ values to those in the literature to validate carbon source composition
- Compare the values of δ13C-AA to the bulk δ13C values

METHODS:

Sample Site: Northwest Arm, Nova Scotia

- Oakland Park Road Dock (Halifax NS)
- Bi-weekly at High tide
- Surface seawater collected

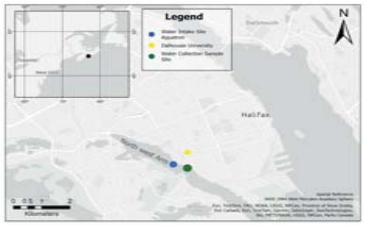
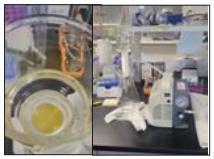


Figure 4 . Map of Study site, green dot shows Oakland Park Dock made by Rori Mulholland July 2024.

Field collection for water samples



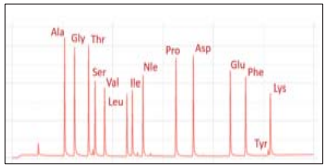
Water Filtered

Samples frozen and stored

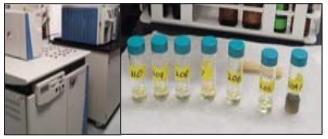
Samples freeze dried

$$\delta^{13}C_{DER} = X\delta^{13}C_{AA} + (1 - X)\delta^{13}C_{ISO,TFAA}$$

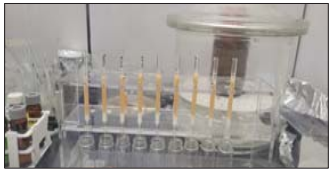
Formula to remove Additive Carbon



Raw chromatogram results



Samples run through GC-IRMS



Samples Purified and Processed via Wet Chemistry and Derivatization

Workflow: N-trifluoroacetyl i-propyl ester method

Hydrolysis

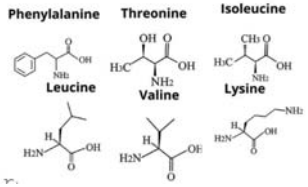
Column & Syringe Filtration

Cation Exchange Cleanup

Esterification

Acylation and Derivatization

Essential Amino Acid's:



RESULTS:

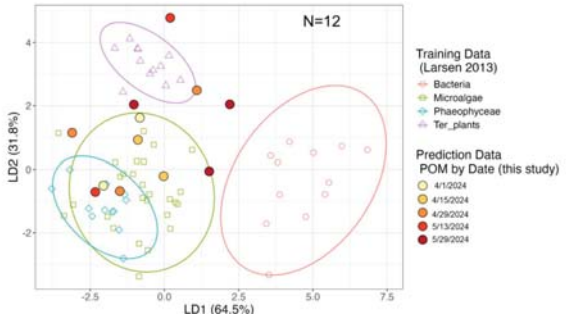


Figure 5. Linear Discrimination Analysis (LDA) of 5 spring sample dates using Larsen et al. 2013 training data.

- April samples fall into Microalgae and Phaeophyceae range
- May samples have increase pull to Bacteria and Terrestrial plants
  - Suggest higher terrestrial carbon input in later spring

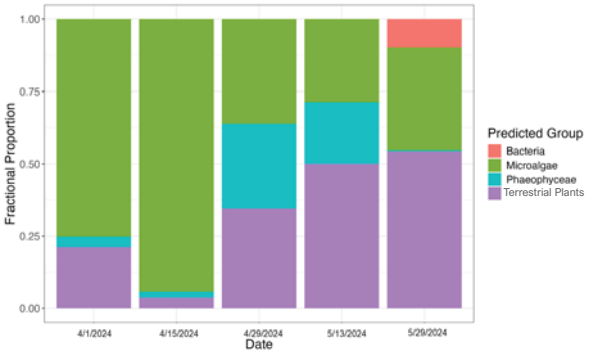


Figure 6. Time Series of Spring bloom sample dates showing fractional proportional of $\delta^{13}C$ signatures.

- Time series of fractional proportions support same findings as LDA
- Increase in Bacterial proportion in later May

CONCLUSIONS & NEXT STEPS:

- $\delta^{13}C$ values appear to identify carbon sources of seawater by major phylogenetic groups for 5 sample dates
- Analyze remaining 2024 sample dates
- Analyze bulk carbon and nitrogen data
- Expand training dataset

Figure 7. Image of large particulate matter at sample site, Photo by R. Mulholland

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