Retrieval of **phytoplankton pigments** from **underway spectrophotometry** in the Fram Strait

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Phytoplankton pigments

- Help **Snacking on SUNLIGHT** — photosynthesis
- Protect against **SUN BURNT** — photoprotection

Source: Bricaud et al., 2004

Light absorption spectra of various pigments

Source: Ocean Optics Web Book
Phytoplankton pigments in remote sensing applications

- Phytoplankton biomass
- Functional types:

![Chl-a](image)

Source: ESA Ocean Color CCI

Diatom, coccolithophore, cyanobacteria

Source: Losa et al., 2017

Develop, validate or refine bio-optical algorithms
Quantify phytoplankton pigments

1. **Measure** them using High Performance Liquid Chromatography (HPLC)

   Discrete water sampling ---» Filtration ---» HPLC

2. **Retrieve** them from optical measurements (e.g. absorption, reflectance)

   ✓ **Spectral decomposition:**
   
   \[ \text{phytoplankton absorption} = \text{absorption of (pigment 1 + pigment 2 + ...)} \]

   ✓ **Spectral reconstruction:**
   
   \[ \text{absorption of (pigment 1 + pigment 2 + ...)} = \text{phytoplankton absorption} \]

   ✓ ...

Esp. from *in situ* Optical sensors!

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**Fram Strait**

- Mass (75%), heat (90%) exchanges
- Sea ice mass export (10%)
  - Climate change
  - Light & nutrient conditions change
  - *phytoplankton community change*

**Satellite data**: poor spatial-temporal resolution; lack of assessment of the applicability of global bio-optical algorithms

**In situ data**: insufficient HPLC data, even less optical measurements

- diatom
- coccolithophore
- phaeocystis
**Data set**

**Expedition:** icebreaker *R/V Polarstern*
- PS93.2 (Jul - Aug 2015)
- PS99.2 (Jun - Jul 2016)
- PS107 (Jul - Aug 2017)

- HPLC pigments (18 types) from 299 discrete samples
- Collocated particle absorption $a_p$ from underway spectrophotometry

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Objectives

01 Adapt the 2 pigment retrieval algorithms to the Fram Strait: **Gaussian decomposition** (Chase et al., 2013) and matrix inversion technique (Moisan et al., 2011).

02 Retrieve pigments from **continuous in situ particulate absorption data** measured by underway spectrophotometry.

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Underway spectrophotometry

AC-S spectrophotometer

- Seawater overflow with bubbles
  - Debubbler
  - Seawater supply
  - Debubbled seawater
  - Valve controller
  - 0.2 μm filter

Diagram of the underway AC-S flow-through system

- Hyperspectral: 400-735 nm, > 80 wavelengths outputs
- Spectral resolution: 10 nm
- Sampling frequency: 4 Hz

Final output: particle absorption $a_p$

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Spikes removal
air bubbles

T & S correction
Temperature and salinity dependency of pure water abs.

Scattering &
Residual T correction

AC-S data quality control

01

03

05

02

04

06

1-min interval bin
4 measurements per sec.

\( a_p \) calculation
Linear interpolation

Validated with filter-pad data

Example a spectrum before/after T5 corrections

Uncorrected
T5 corrected T=4°C
T5 corrected T=0°C

\( a_{AI}(\mu \text{m}) \, \text{AC-S vs filter-pad} \)

Validated with filter-pad data

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Collocated $a_p(\lambda)$-pigment data set
Gaussian decomposition (Spectral decomposition)

First proposed by: Hoepffner and Sathyendranath (1993)
Adapted by: Chase et al. (2013)

- 12 Gaussian functions representing pigments’ absorption
- 1 non-algal particle (NAP) absorption

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Guassian decomposition (Spectral decomposition)

Our improvement to this method: pigment package effect normalization

- **R² = 0.87, MPE = 21%**
- **R² = 0.96, MPE = 12%**
- **R² = 0.50, MPE = 32%**
- **R² = 0.77, MPE = 22%**
- **R² = 0.82, MPE = 25%**
- **R² = 0.62, MPE = 27%**
- **R² = 0.57, MPE = 30%**
- **R² = 0.81, MPE = 27%**
- **R² = 0.91, MPE = 27%**
- **R² = 1, MPE = 4%**

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Matrix Inversion Technique (Spectral reconstruction)

- Reconstruction model: \( a_1^*(\lambda)\ c_1 + a_2^*(\lambda)\ c_2 + \ldots + a_3^*(\lambda)\ c_3 = a_{ph}(\lambda) \)
- \( a^*(\lambda) \) – pigment-specific absorption spectra (shape)
- \( c \) – pigment concentration (magnitude)

Normalization --- Increase the differences between \( a^*(\lambda) \) --- Reduce model sensitivity
Select 9 pigments

Our improvement to this method: reduce model sensitivity by
✓ Develop a scheme for selecting pigments involved
✓ Data perturbations based cross validation
Compare 2 methods: estimation errors

<table>
<thead>
<tr>
<th>pigments</th>
<th>Gaussian decomposition</th>
<th>Matrix inversion technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not normalized</td>
<td>Normalized</td>
</tr>
<tr>
<td>TChl-a</td>
<td>21%</td>
<td>4%</td>
</tr>
<tr>
<td>TChl-b</td>
<td>30%</td>
<td>27%</td>
</tr>
<tr>
<td>Chl-c1/2</td>
<td>34%</td>
<td>27%</td>
</tr>
<tr>
<td>Fuco</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Hex</td>
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<tr>
<td>Diadino</td>
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<tr>
<td>But</td>
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<td>-</td>
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<tr>
<td>Peri</td>
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<td>-</td>
</tr>
<tr>
<td>PSC</td>
<td>34%</td>
<td>20%</td>
</tr>
<tr>
<td>PPC</td>
<td>32%</td>
<td>22%</td>
</tr>
</tbody>
</table>

Leave-one-out cross validation

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Phytoplankton pigments time series

- Estimated using matrix inversion.
- Fuco (fucoxanthin): diatoms.
- Hex (19’-hexanoyloxyfucoxanthin): prymnesiophytes.

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Adapt the 2 pigment retrieval algorithms to the Fram Strait: Gaussian decomposition (Chase et al., 2013) and matrix inversion technique (Moisan et al., 2011).

**Gaussian decomposition**: TChl-a, TChl-b, Chl-c1/2, PSC and PPC. (20-34%)

- Normalization: estimation errors reduced. (12-27%)

**Matrix inversion technique**: TChl-a, TChl-b, Chl-c1/2, Fuco, Hex, Diadino. (37-65%)

- Normalization: +But, Peri (67-76%)
- Sensitivity reduction routine
Conclusions

Retrieve pigments from continuous *in situ* particulate absorption data measured by underway spectrophotometry.

- High resolution phytoplankton marker pigment data in the Fram Strait were obtained.
Outlook

Retrieve key phytoplankton groups in the Fram Strait.

coupling of phytoplankton composition and distribution to physical and biogeochemical properties.