From Inherent Optical Properties to Biogeochemical Properties

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• Forward and inverse problems.
• The basis for the relationship (theoretical, empirical, hybrid).
• Concept of a 'proxy'.
• Bulk vs. single particle property (FCM).
• Supportive lab studies (controlled compared to ocean).
• Extensive vs. intensive properties.
• Some intensive proxies involve ratio of proxies.
• Uncertainties...

Remember: this is the major reason the field of Oceanography cares about optics!!!
$1^\text{st}$ order variability in optical properties is due to concentration (optical parameter are additive $\leftarrow$ Beer-Lambert-Bouger law).

What is the range of changes in concentration?
What else affects optical properties ($2^\text{nd}$ order variability)?
- Composition (index of refraction)
- Size (what is size?)
- Shape (e.g. axis ratio, micro)
- Internal structure (e.g. cell wall, organelle)
- Packing (fluid fraction in aggregate)
Proxies for particulate mass (extensive)

- Many comparisons, starting in the 70s.
- Used to study sediments (signal to noise).
- Moved to open ocean as calibration/stability improved.

Which regression type should one use for a proxy?

Optics is a standard method to measure turbidity, a primary determinant of water quality (e.g. ISO-7027).
$c_p(660)$ vs. mass:

**Theory:**

**Observations:**

$\pm 50\%$

Hill et al., 2011
$c_p(660)$ vs. POC (extensive)

Opposite trend to Hill's. Why?

Cetinic et al., 2012
Angular dependence of scattering on size

Near forward scattering: Strong dependence on size, less on $n$.

LISST detector:

Roesler and Boss, 2008
Spectral $c_p$

(1) Assuming a power-law particle size distribution (PSD)

$N(D) \sim D^{-\xi}$

$\Rightarrow c_p(\lambda)$ is described well as a power law function of wavelength ($\lambda$)

$c_p(\lambda) \sim \lambda^{-\gamma}$

$\gamma \approx \xi - 3$

$\Rightarrow$ Flatter beam attenuation spectra (small $\gamma$) implies flatter particle size distribution (small $\xi$)

(2) Assuming spherical non-absorbing particles

Volz, 1957, Diehl and Haardt 1980
Particle size spectra between 1 μm and 1 cm at Monterey Bay determined using multiple instruments

Jackson et al., 1997  
Focus is different
Closure: LISST vs. IOP spectra

Field data, MVCO

Slade and Boss, 2015

\[ \gamma = -0.014D_{\text{avg}} + 0.93 \]

\[ R^2 = 0.832 \text{ NRMSD} = 10\% \]

\[ \gamma = -0.049D_{\text{avg,50}} + 1.2 \]

\[ R^2 = 0.83 \text{ NRMSD} = 11\% \]
Method of fluctuation (Shifrin, 1988)

**Closure: LISST vs. fluctuations**

**Lab aggregation exp.**

$$\bar{A}_{cp} = \frac{\text{Var}[c_p(t)] V}{E[c_p(t)] Q_c \alpha(\tau)}$$

Sample volume

Measurement time

$$\bar{D} = 2\sqrt{\bar{A}\pi^{-1}}$$

Briggs et al., 2013
Composition – index of refraction (an intensive parameter)

Zaneveld et al., 2002, OOXVI.
Compiled from:
Aas (1983)
Carder et al. (1972)
Carder et al. (1974)

Babin et al., 2003

Fig. 7. The index of refraction relative to seawater for various minerals as a function of particle density. The $n$ and $\rho$ values (also listed in Table 6) are from Lide (2001). The $n$ values are the arithmetic average of the values given for the two or three structure coordinate axes. The plotted minerals are aragonite (A), calcite (Ca), chlorite (Ch), gibbsite (G), illite (I), kaolinite (K), montmorillonite (M), opal (Op), and quartz (Q). The theoretical relationship between $n$ and $\rho$ is also shown for organic matter (see text for details).
The making of a composition proxy:

*Mie theory*: the $b_{bp} = b_{bp}/b_p$ is very sensitive to $n$ and less so to the PSD:

Twardowski et al., 2001

![Graph showing the relationship between $b_{bp}$ and $\xi$ for different $n$ values. The graph has curves for different $n$ values, with labels for 'Inorganic' and 'Organic'. The x-axis is labeled 'differential Junge slope, $\xi$' and the y-axis is labeled '$b_{bp}$'. There are labels for 'Large <$D$>' and 'Small <$D$>' at the bottom of the graph.]}
Observations

Twardowski et al., 2001:

Gulf of California

\[ \tilde{b}_{pp} \]

\[ \tilde{\eta}_p = 1.20 \]

\[ \tilde{\eta}_p = 1.02 \]

differential Junge slope, \( \xi \)

 estimated index of refraction near Leo15(N=55,000)

Jersey shore

English channel

Loisel et al., 2004

Boss et al., 2004

Carter Lake

Boss et al., 2007
Proxy validation

Varies from: phytoplankton → inorganic particles.
Mie theory tells us that the relationship between optical properties and mass is **composition and size** dependent:

\[
\frac{b_{bp}}{\text{Volume}} \quad \frac{b_p}{\text{Volume}} \quad \frac{b_{sp}}{\text{Mass}}
\]

**Very different from:**

\[
\frac{1}{D} \quad D^3
\]

Baker and Lavelle, 1984

Boss et al., 2004

- All curves are 'resonant' curves
- Highest sensitivity for micron sized particles ($c_p$ and $b_s$).
- Size of max response varies
The $b_b$ enigma (or paradox):

Based on Mie theory, backscattering should be dominated by inorganic particles and sub-micron particles (the least known).

Yet $b_{bp}$ correlates well with [chl] and POC (>0.7mm):

Huot et al., 2008
Stramski et al., 2008
Possible explanation for the $b_b$ enigma:

1. Mie results are correct. However, all particles in the open ocean co-vary, hence the tight relationship inconsistent with spectrum of $b_{bp}/b_p$.

2. Mie theory is not applicable. Organic particle actually backscatter more than we ascribe to them.

- This last seems more consistent with size fractionated measurements (e.g. Dall’Olmo et al., 2009) and cultures (Whitmire et al., 2010, Poulin et al., 2018). Recent work supports modeling as coated sphere.
Backscattering by Nonspherical Particles: A Review of Methods and Suggested New Approaches

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When criticized for using Mie theory where its applicability is dubious, modelers sometimes respond that although they know that Mie theory is inadequate, it is the only game in town. Better to do wrong calculations than to do none at all. Modelers have to model.

We suggest an alternative to modeling. It is called not modeling—not modeling, that is, until adequate methods are at hand.
Internal structure:

Backscattering dominated by membrane.  

Meyer, 1979
Possible explanation for the $b_b$ enigma:

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Back to $c_p$-SPM. Why so good?

**Observations:**

- Hill et al., 2011

**If:**

$\rho = 2x(n - 1)$

**Why:**

$\pm50\%$

Hill et al., 2011
Hypothesis: aggregation reduces dependence of mass proxies on size.

Field manipulation:

Experiment

One LISST Pumped (red) and the other not (blue)

Control

both instruments deployed unpumped

Slade et al., 2011
On average, observed beam attenuation increases by 30% when aggregates are broken. Significantly smaller change than expected from Mie (x10 from 100→10µm).
Aggregation in the marine environment

Aggregation is a \([\text{concentration}]^2\) phenomena.

Mechanisms for encounter: Brownian motion, differential settling, and turbulent shear.

Aggregate sink faster than their component particles.

Aggregates break when shear is too high.

Camera pictures at 1mab at a 12m deep site within 1day:

Dominated by \(<100\mu\text{m particles}\)

Dominated by \(>1000\mu\text{m particles}\)
Aggregate modeling:

For marine aggregates size and solid fraction correlate.

-points having size-F as in Maggi, 2007, or Khelifa and Hill, 2006.
Theoretical calculations: monodispersion

Mass normalized beam attenuation for aggregates assuming a relationship between solid fraction and size as in Khelifa and Hill, 2006 (blue lines) and solid particles (red lines). Solid lines denote particles with $n=1.05+i0.0001$, dashed lines $n=1.05+0.005$ and dotted lines $n=1.15+0.0001$. Each data point represent a population of particle all of a single size.

Boss et al., 2009
Theoretical calculations: populations

Mass normalized beam attenuation for populations of aggregates assuming a relationship between solid fraction and size as in Khelifa and Hill, 2006 (blue lines) and populations of solid particles (red lines) both as function of power-law exponent of the disaggregated particle populations. Solid lines denote particles with $n=1.05+i0.0001$, dashed lines $n=1.05+0.005$ and dotted lines $n=1.15+0.0001$.

Note: model is sensitive to size of primary particle, $D_{\text{max}}$, $F(D_{\text{max}})$ and acceptance angle.
A proxy for aggregate packing

If $c_p$ is a good proxy of mass, and near-forward scattering is a good proxy of volume distribution, than we could obtain and aggregate density proxy by: $c_p/\Sigma$ volume.

Aggregation experiment:
Start with $\langle D \rangle \sim 7 \mu m$ clay

Add salt

Slade et al., 2011
A proxy for aggregate packing- consistency check

\[ \log_{10} \rho_a = -1.31(\pm 0.05) \log_{10} D_A + 1.30(\pm 0.07) \]
\[ n_o = 81, \ n_x = 1, \ r = -0.83(\pm 0.13) \]
\[ \text{RMSE}=0.11(\text{kg L}^{-1}), \ MPE=22\% \]

\[ \log_{10} \rho_a = -1.24(\pm 0.05) \log_{10} D_A + 1.15(\pm 0.08) \]
\[ n_o = 140, \ n_x = 1, \ r = -0.78(\pm 0.13) \]
\[ \text{RMSE}=0.13(\text{kg L}^{-1}), \ MPE=32\% \]

\[ \log_{10} \rho_a = -1.30(\pm 0.32) \log_{10} D_A + 0.87(\pm 0.45) \]
\[ n_o = 35, \ n_x = 1, \ r = -0.50(\pm 0.27) \]
\[ \text{RMSE}=0.13(\text{kg L}^{-1}), \ MPE=36\% \]

Neukermans et al., 2012
From Inherent Optical Properties to Biogeochemical Properties

Summary of first lecture

• In this lecture we looked at scattering and attenuation the proxies derived by them.

• Lab studies are critical to test proxies.

• Utility of a proxy is application dependent (tolerance for uncertainties varies).

• Always test the applicability of a proxy before/while you use it.
愚者不問，問者不愚。
The fool does not ask, he who asks is no fool
Shape consideration

Clavano et al., 2007
Shape approximations for light scattering calculations

- Mie-Theory
- T-matrix
- Axis ratios up to convergence limit
- T-matrix
- Moderate Axis ratios (0.5<AR<2)

Diagram showing particle radius (µm) and axis ratio with size limit.
Figure 13.6  Polar scattering diagrams for equal-volume spheroids. The incident light is unpolarized. From Latimer et al. (1978).
Karp-Boss et al., 2007

Ceratium longipes

Mean cell Diameter (µm)

Date

10/17/03
12/2/03
3/17/04

LISST mode (µm)

C. radiatus

L. polyedra

Volume Concentration (µL/L)

Volume Concentration (µL/L)

ESD (µm)

ESD (µm)

ESD (µm)
Quantifying differences due to shape:

Clavano et al., 2007
Internal structure:

Backscattering dominated by membrane.

Meyer, 1979