Optical properties of oceanic particles

What physical properties determine the optical properties of particles?

Size, composition (refractive index), shape, internal structure. These properties interact...

We will not address fluorescence and polarization.

Based, in part, on a lecture prepared by C. Roesler
What particles absorb and scatter in the ocean?

What particles absorb and scatter in the ocean?

Non-algal particles: Organic and inorganic.

Sand 
Silt 
clay 

Aggregates: 
Variable in scattering and absorption properties 

IOP Theory

No attenuation (recap: radiance is constant along a ray)
IOP Theory

$L_o$  $L_t$

Incident Radiance  Transmitted Radiance

Attenuation
Loss due to absorption

$L_o$ Incident Radiance

$La$ Absorbed Radiance

$Lt$ Transmitted Radiance
Loss due to scattering

$L_b$ Scattered Radiance

$L_o$ Incident Radiance

$L_t$ Transmitted Radiance
Loss due to absorption and scattering (attenuation)

\[ L_b \text{ Scattered Radiance} \]

\[ L_a \text{ Absorbed Radiance} \]

\[ L_t \text{ Transmitted Radiance} \]
Loss due to absorption and scattering (attenuation)

\[ L_0 = L_t + L_a + L_b \]
Beam Attenuation Measurement Theory

Attenuance
\[ C = \text{fraction of incident radiance attenuated} \]

\[ C = \frac{(L_b + L_a)}{L_o} \]

\[ C = \frac{(L_o - L_t)}{L_o} \]
Beam Attenuation
Measurement Theory

$c = \text{fractional attenuance per unit distance}$

\[
c = \frac{\Delta C}{\Delta x}
\]

\[c \Delta x = - \frac{\Delta L}{L}
\]

\[
\int_0^x c \, dx = -\int_0^x \frac{dL}{L}
\]

\[
L_t \cdot c(x-0) = -[ \ln(L_x) - \ln(L_0) ]
\]

\[
c \cdot x = -[ \ln(L_t) - \ln(L_0) ]
\]

\[
c \cdot x = -\ln(L_t/L_0)
\]

\[
c (\text{m}^{-1}) = \frac{-1}{x} \ln(L_t/L_0)
\]

\[\leftrightarrow L_t = L_o \exp(-c \cdot x)\]
$L_t = L_0 \exp(-c \cdot x)$

$\tau = c \cdot x \equiv \text{optical depth}$

Beer (1852), Lambert (1729), Bouguer (before 1729)

**Important characteristics:**

Absorption and scattering feature similarly.

c is Linear with concentration or added substances.

Assumes no internal sources.

Class demo with food color/maalox
Sinks for photons - absorbers.

What absorbs radiation in the oceans/lakes?

How do we measure absorption?
What is absorption:

Photons ‘disappear’ due to interaction with matter.

Following absorption energy could be reemitted (or not) at the same or different wavelength (e.g. scattering, fluorescence, thermal emission).

Absorption due to molecular:
Translational, rotational, vibrational and electronic modes (+combinations).

Observation include also spontaneous emission.

Explained by quantum mechanics.
Absorbers in ocean/lakes

- Water
- Phytoplankton
- Non-algal organic particles (CPOM)
- Inorganic mineral particles (CPIM)
- Dissolved organic matter (CDOM) - not addressed today

Note: most available information is in the visible (400-700nm). Why?
Absorption by (liquid) water:

Features:
- Extremely complex
- Variety of vibrational modes
- Combination possible

Assumes no internal sources.

http://www.lsbu.ac.uk/water/vibrat.html
Phytoplankton

Species-specific pigment composition

(Morel and Bricaud 1981)
Phytoplankton vs Chlorophyll

Sosik & Mitchell 1991


Packaging: $a/[\text{chl}]$ is function of size and [chl]

Duysens (1956)
Theoretical results:

\[ \frac{a}{V} = \frac{Q_{\text{abs}} G}{1.33 \pi r^3} \]

\[ n' = a_{\text{pure}} \frac{\lambda}{4\pi} \]

Particle absorption/volume \( \propto \frac{1}{D} \)

'Molecular absorption \( \propto \) volume.'
Non-algal particles

Heterotrophic Ciliates and Flagellates, and bacteria

Roesler et al., 1989

\[ a_{\text{CPOM}}(1) = a_{\text{CPOM}}(400) \times \exp(-S_{\text{CPOM}}(1-400)) \]

\[ S_{\text{CPOM}} = 0.007 \text{ to } 0.011 \]

Ahn and Morel, 1983

Iturriaga and Siegel, 1989

Detritus

Figure 2. (a) Efficiency factor for absorption as function of wavelength for ciliates and flagellates. (b) Spectral absorption values, normalized by their maximum near 415 nm, when measurements are carried out with cells collected onto a GF/F. (c) Absorption spectra (normalized as above) of acetone and methanol extracts for flagellates only.
**CDOM**: chromophoric dissolved organic matter

\[ a_{\text{CDOM}}(1) = a_{\text{CDOM}}(400) \times \exp(-S_{\text{CDOM}}(1-400)) \]

\[ S_{\text{CDOM}} = 0.011 \text{ to } 0.022 \]

Kirk 1983

Carder et al. 1989
Absorption Measurements

\[ a = \left(-\frac{1}{x}\right) \ln\left[\frac{(L_t + L_b)}{L_o}\right] \]

Detected flux measurement must include scattered flux.

Undetected scattered flux must be corrected for.
Ex. Absorption meter: WETLabs ac-9 & ac-S

• Dual path, a and c
• b inferred by difference.
• Correct for photon that are not collected
Ex. Absorption meter: WETLabs ac9/acS

- Detector FOV ~ 40°
- ~90% of scattered flux
Absorption Measurement

Integrating sphere:
Detected flux measurement includes all scattered flux.
Reflectance of sphere needs to be known very accurately (problems with fouling).
Absorption Measurement

QFT: quantitative filter-pad technique

Separate sample to dissolved and particulate. Concentrate particulate material on a filter.

Measure beam-c for dissolved.

Measure transmission through filter pad (correct for ‘filter effects’, path-length, etc').
Absorption Measurements

In all measurements of transmission (for a or c) there is a need for a ‘reference’.

Need for a stable (temperature, salinity) predictable standard.

Currently we use the cleanest waters we can get...
Scatterers in ocean/lakes

- Water + salts - not today
- Phytoplankton
- Non-algal organic particles (CPOM)
- Inorganic mineral particles (CPIM)
- Dissolved organic matter (CDOM) - mostly negligible
OPs are good predictors of PM.

Optics is a standard method to measure turbidity, a primary determinant of water quality (e.g. ISO-7027).

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<th>Model-PM/PM</th>
<th>c(660)</th>
<th>b_b(700)</th>
<th>b_s(880)</th>
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Angular dependence of scattering on size:

- Near forward scattering: Strong dependence on size, less on $n$.
- $b_b/b$: Strong dependence on $n$, less on size.
\( c/V = Q_{\text{ext}} \cdot G / \{1.33 \pi r^3\} \)

Resonant curve. Change of max with \( n \) (and \( \lambda \)).

\( c \propto a \) and Volume

\[ \sigma_{\text{ext}} = 2 \cdot \text{area} \rightarrow \frac{c}{V} \propto 1/D \]
Mie theory tells us that the relationship between optical properties and mass is size dependent:

- $b_{bp}/\text{Volume}$
- $b_p/\text{Volume}$

- All curves are 'resonant' curves
- Highest sensitivity for micron sized particles
- Size of max response varies
Scattering and absorption

Observations:

Mie theory:

A photon absorbed is not scattered (at any direction).
Beam attenuation:
\[ c = a + b \]

Spectral attenuation and PSD:

Mie Theory (homogenous spheres, Volz, 1954):

For non-absorbing particles of the same \( n \) and an hyperbolic distribution from \( D_{\text{min}} = 0 \) to \( D_{\text{max}} = \infty \),

If:

\[ N(D) = N_0 (D/D_o)^{\xi} \]

then:

\[ c_p(\lambda) = c_p(\lambda_0) \left( \frac{\lambda}{\lambda_0} \right)^{-\gamma}, \quad \xi = \gamma + 3 \]

→ expect a relation between attenuation spectrum and PSD.
The $b_b$ enigma?

Morel and Ahn, 1991: ‘Algal cells in open ocean, and to lesser extent small heterotrophs, dominate the scattering coefficients; ...On the contrary, these organisms are definitely insignificant contributors to the backscattering coefficient.’

Stramski et al., 2001: simulating open-ocean (oligotrophic, 0.18mg Chl/m$^3$), 2-3% of the backscattering coefficient is due to plankton. 50% from particles <0.2$\mu$m.
Phase functions:

Stramski et al., 2001
The $b_b$ enigma (or paradox):

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

Yet $b_{bp}$ correlates well with $[\text{chl}]$ and POC (>0.7 $\mu$m):

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 covary, hence the tight relationship.

2. Mie theory is not applicable. Organic particle actually backscatter more than we ascribe to them.
How do we obtain the backscattering in the ocean:

\[ b_b = 2\pi \chi \beta(\theta), \quad 0.7 < \chi < 1.3 \]

Uncertainty \( \sim 10\% \)

Boss and Pegau, 2001
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.

scattering measurements.
Shape consideration

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

Mie-Theory

T-matrix

Moderate Axis ratios (0.5<AR<2)

T-matrix

Axis ratios up to convergence limit

Particle radius (μm)

Axis ratio

0.1
0.5
1
2
10

Oblate

Size limit

Prolate

Slide From Volten
Clavano et al., 2007
Internal structure:

Backscattering dominated by membrane. 

Meyer, 1979
Measurements across the equatorial Pacific (Dall’olmo et al., 2009):

\[
\frac{b_{bp}(D<0.2\text{mm})}{b_{bp}(D>0.2\text{mm})} < 0.1
\]

No filter effect visible

Uncertainty dominated by uncertainty in \(b_b(H_2O)\)
Aggregate modeling:

For marine aggregates, size and solid fraction correlate.

- Points having size $F$ as in Maggi, 2007, or Khelifa and Hill, 2006.
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.
Laboratory experiment: aggregation

Start with $<D> \sim 7 \mu m$ clay

Add salt

As aggregate size changes from $7 \rightarrow 70 \mu m$, $c_p$/mass and $b_{bp}$/mass stay constant ($<\text{size}>$ confirmed by microscopy).
Remember:

The two fundamental IOPs: $a$ & $\beta$:

\[ b = \int \beta d\Omega \]

\[ c = a + b = a + \int \beta d\Omega \]

Advanced materials: inelastic scattering (Raman, CDM, and phytoplankton pigments), polarization.