Lecture 3
Absorption physics and absorbing materials

Collin Roesler

10 July 2017
Lecture Overview

• Overview of the electromagnetic spectrum
• What is absorption?
• What are the major absorbers in the ocean?
• How do we measure absorption in the ocean?
Electromagnetic Radiation

- Charged particles (dipoles) create electric fields $\mathbf{E}$ (oscillation between +,-)
Electromagnetic Radiation

- Charged particles, dipoles, create electric fields $\mathbf{E}$ (oscillation between $+$, $-$)
- When a charged particle moves, it creates a magnetic field, $\mathbf{B}$ (or $\mathbf{H}$ depending on book)
- The electromagnetic field oscillates as the energy propagates $\mathbf{E} \times \mathbf{B}$ (right hand rule)
Electromagnetic Radiation

- Charged particles, dipoles, create electric fields $E$ (oscillation between +,-)
- When a charged particle moves, it creates a magnetic field, $B$ (or $H$ depending on book)
- The electromagnetic field oscillates as the energy propagates $E \times B$ (right hand rule)
- the range of oscillation frequencies is described by the EM spectrum

http://www.antonine-education.co.uk/physics_gcse
What is absorption?

• Since electromagnetic radiation is energy propagation, when materials absorb radiation, they absorb energy.

• The energy associated with each part of the spectrum is given by $E = \frac{hc}{\lambda}$.

• What happens to the molecule depends upon the amount of energy, hence the wavelength.
Interactions between energy and matter

- Nuclear configuration
- Photo-ionization
- Electron transition
- Molecular vibration
- Molecular rotation

 waved interaction:

- Gamma rays
- X-rays
- Extreme ultraviolet
- Ultra-violet
- Infrared
- Microwave

Increasing wavelength
Quantized electronic states

- Amount of energy required to move an electron to another orbital shell (electronic state transition) is quantized.
- A molecule can only absorb radiation of this specific quantized energy or wavelength.
- This determines the absorption peak.

\[ \lambda = \frac{hc}{E_2 - E_1} \]
Quantized vibrational states

- Each orbital shell is associated with a series of higher excited states, associated with vibrational energy, which are also quantized.
- These determine the wavelengths of the absorption side peaks which are higher (lower) energy but have a lower probability for absorption.
Quantized rotational states

- Each vibrational state is associated with a series of higher rotational states, which are also quantized.
- These determine the wavelengths of the absorption that smooth the absorption peaks.
Chlorophyll $a$ has two electronic states associated with the energy equivalent of blue (443 nm) and red (676 nm) photons.
Chlorophyll $\alpha$

http://scifun.chem.wisc.edu/chemweek/chlrphyl/chlrphyl.gif

http://www.photochembgsu.com/assets/images/graph2.gif
Chlorophyll

Phytol

Enzymatic

Heat/Acid

Blanching

Mg^{2+}

"Pheophytinization"

Pheophorbide

Chlorophyllide

Pheophytin

Rückmann et al 1999

Milenković et al. 2012
What are the major absorbers in the ocean?
Example of absorption spectra for three environments

- What do they have in common?
  - All have strong red absorption

- How do they differ?
  - Variable blue absorption
Absorption is a conservative property

• Total absorption = sum of individual absorbing constituents

\[ a_{\text{Total}} = a_{\text{water}} + \sum a_{\text{dissolved compounds}} + \sum a_{\text{particles}} \]

• Absorption is proportional to the concentration (Beer’s Law)

\[ a_{\text{chl}}(m^{-1}) = [\text{chl}](mg/m^3) \ast a^*_{\text{chl}} (m^2/mg) \]
It is impractical to measure absorption spectrum for each absorber.

\[ a_T = a_w + a_{CDOM} + a_{\phi} + a_{NAP} \]

Group components by their common absorption properties (an our inability to separate them operationally).
Absorbing Components: Water

R. M. Pope and E. S. Fry 1997
Integrating cavity absorption meter

Nice (but dated) compendium at
http://omlc.org/spectra/water/abs/index.html
Absorbing Components: Water

Fig. 1. Absorption coefficient of pure water as measured or compiled by several investigators.\textsuperscript{1,2,11,18,19,21,26–33} The discrepancy in the estimated absorption coefficients is largest at short wavelengths where absorption by organic contaminants is significant. At wavelengths longer than 550 nm the standard deviation of the estimates is between 5 and 10\% of the mean value.
Absorbing Components: Water

Temperature

Fig. 3. Absorption coefficient from 550 to 800 nm adjusted at 685 nm to the value of Tam and Patel (1979). The curves represent absorption at temperatures of 5, 10, 15, 21, 25, and 30°C as read from bottom to top at 750 nm. Pegau and Zaneveld 1993 Limnol Oceanogr.

natural variations  Sullivan et al. 2006 Appl Opt
Absorbing Components: Water

Salinity

Fig. 6. Attenuation coefficient at 715 nm as a function of salinity. This figure illustrates the linear dependence of the attenuation coefficient on salinity.

Sullivan et al. 2006 Appl Opt

Pegau et al. 1997 Appl Opt

natural variations
Absorbing Components: Dissolved inorganic matter

- Basic for UV detection of nitrate, ISUS


http://www.mbari.org/chemsensor/ISUShome.htm
Absorbing Components:
Colored dissolved organic matter (CDOM)

Fig. 3.5. Absorption spectra of soluble yellow material (gilvin) in various Australian natural waters (from Kirk, 1976). The lowest curve (Batemans Bay, NSW) is for coastal sea water near the mouth of a river; the next curve (Clyde River, NSW) is for an estuary; the remainder are for inland water bodies in the southern tablelands of New South Wales/Australian Capital Territory. The ordinate scale corresponds to the true in situ absorption coefficient due to gilvin.

Kirk 1983

Dierssen et al. 2006

http://clarklittlephotography.com
Absorbing Components: Colored dissolved organic matter (CDOM)

\[ a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_o) \exp(-S_{\text{CDOM}}(\lambda-\lambda_o)) \]

Fig. 3.5. Absorption spectra of soluble yellow material (gilvin) in various Australian natural waters (from Kirk, 1976b). The lowest curve (Batemans Bay, NSW) is for coastal sea water near the mouth of a river; the next curve (Clyde River, NSW) is for an estuary; the remainder are for inland water bodies in the southern tablelands of New South Wales/Australian Capital Territory. The ordinate scale corresponds to the true in situ absorption coefficient due to gilvin.

Kirk 1983

Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.
Carder et al. 1989 L&O
Absorbing Components: Colored dissolved organic matter (CDOM)

\[ a_{CDOM}(\lambda) = a_{CDOM}(\lambda_o) \exp(-S_{CDOM}(\lambda-\lambda_o)) \]

Carder et al. 1989 L&O

Simeon et al. 2003 JGR
Absorbing Components: Colored dissolved organic matter (CDOM)

Table 1. Ranges for the exponential coefficient, $C_2$, for gelbstoff and detritus for Eq. 6. Where coefficients were not listed, values were approximated from published spectra using an exponential model.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Site</th>
<th>Avg $C_2$ (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelbstoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kalle 1966</td>
<td>Baltic, North Sea</td>
<td>0.018</td>
</tr>
<tr>
<td>Jerlov 1968</td>
<td>Lakes, coast</td>
<td>0.015</td>
</tr>
<tr>
<td>Kirk 1976</td>
<td>Baltic</td>
<td>0.014</td>
</tr>
<tr>
<td>Lundgren 1976</td>
<td>Indo-Pacific</td>
<td>0.017</td>
</tr>
<tr>
<td>Kopelieiev and Burenkov 1977</td>
<td>Baltic</td>
<td>0.018</td>
</tr>
<tr>
<td>Bricaud et al. 1981</td>
<td>Mauritania</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>Gulf of Guinea</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Mediterranean</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>East Pacific</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>Lake Kizaki</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>Nabeta Bay</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>East Pacific</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Gulf of Mexico</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>Lakes</td>
<td>0.019</td>
</tr>
<tr>
<td>Carder and Steward 1985</td>
<td>Kiel Harbor</td>
<td>0.016</td>
</tr>
<tr>
<td>Davies-Colley and Vant 1987</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Published mean ± SD</td>
<td>San Juan Islands</td>
<td>0.016±0.002</td>
</tr>
<tr>
<td>This study mean ± SD</td>
<td>Marine humic acid</td>
<td>0.011</td>
</tr>
<tr>
<td>Carver et al. 1989</td>
<td>Marine fulvic acid</td>
<td>0.018</td>
</tr>
<tr>
<td>Detritus</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kishino et al. 1986</td>
<td>NW Pacific Ocean</td>
<td>0.006</td>
</tr>
<tr>
<td>Maske and Haardt 1987</td>
<td>Kiel Harbor</td>
<td>0.014</td>
</tr>
<tr>
<td>Iturraiga and Siegel 1988</td>
<td>Sargasso Sea</td>
<td>0.011</td>
</tr>
<tr>
<td>Cleveland and Perry in prep.</td>
<td>Sargasso Sea</td>
<td>0.013</td>
</tr>
<tr>
<td>Morrow et al. 1989</td>
<td>Sargasso Sea</td>
<td>0.009</td>
</tr>
<tr>
<td>Published mean ± SD</td>
<td>San Juan Islands</td>
<td>0.011±0.002</td>
</tr>
<tr>
<td>This study mean ± SD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Babin et al. 2003
(European coastal waters)

Roesler et al. 1989
(global synthesis)
Absorbing Components: Particles

Methanol extraction $\rightarrow$ Scan ($a_{nap}$)

Scan ($a_p$) $\rightarrow$ difference ($a_{phyt}$)

Water Sample Analyses

Kishino et al. 1985
Absorbing Components: Phytoplankton

Individual cells, microphotometry
Absorbing Components: Phytoplankton Species

Roesler et al. 1989 L&O
Absorbing Components: Phytoplankton

Pigment Packaging impact on absorption

(1) vary size, maintain constant intracellular pigment concentration

(2) maintain size, vary intracellular pigment concentration

Morel and Bricaud 1981 DSR
Absorbing Components: Phytoplankton

Babin et al. 2003

Global Relationships

Brécaud et al. 1995

\[ a_{\text{phyt}}^* (m^2/mg \text{ chl}) \]

\[ \frac{a_{\text{phyt}}(\lambda)}{a_{\text{phyt}}(440)} \]

Babin et al. 2003
Absorbing Components: other protists

ciliates and flagellates

cytochrome 412

heterotrophic bacteria

Morel and Ahn 1990 JMR
Absorbing Components: Non-algal particles

Roesler et al. 1989 (global synthesis)

Babin et al. 2003 (European coastal waters)
Absorbing Components: Non-algal particles → what are they?

Iturriaga and Siegel 1989 L&O

Photobleaching natural light levels

Nelson & Robertson: Detrital spectral absorption 1993 JMR
Absorbing Components: inorganic particles

Fig. 5. Absorbance spectra of natural assemblages of mineral particles from three different environments.

Babin and Stramski 2003

Fig. 8. Imaginary index of refraction for Saharan aerosols from each of the collection locations. The solid line represents the Tenerife sample; the dashed line, the Meteor sample; the dotted line, the Barbados sample; and the dashed-dotted line, the Sal Island sample.

Patterson et al. 1977 JGR
Absorbing Components: inorganic particles

2\textsuperscript{nd} Derivative used to quantify concentration of iron oxide minerals

Estapa et al. 2012
To model the impacts of absorbing constituents, add them up.

Which component dominates?
- blue waters
- green waters
  - phytoplankton (V-type)
  - inorganic particles (U-type)

Morel and Prieur 1977
More on absorption

• Phytoplankton absorption
  • Lecture tomorrow

• Measuring absorption
  • Lecture tomorrow

• CDOM absorption methods
  • Lab tomorrow

• Particulate absorption methods
  • Lab Wednesday