# Lecture 3 Absorption physics and absorbing materials

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#### 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 E (oscillation between +,-)



### **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 **ExB** (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 **ExB** (right hand rule)
- the range of oscillation frequencies is described by the EM spectrum



## 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  $E = hc/\lambda$
- What happens to the molecule depends upon the amount of energy, hence the wavelength

#### Interactions between energy and matter



#### 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



#### 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





http://plantphys.info/plant\_physiology/light.shtml



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



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

$$a_{Total} = a_{water} + \Sigma a_{dissolved compounds} + \Sigma a_{particles}$$

 Absorption is proportional to the concentration (Beer's Law)



Group components by their common absorption properties (an our inability to separate them operationally)



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

Nice compendium at http://omlc.org/spectra/water/abs/index.html



Fig. 1. Absorption coefficient of pure water as measured or compiled by several investigators.<sup>1,2,11,18,19,21,26–33</sup> 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.

W. Scott Pegau, Deric Gray, and J. Ronald V. Zaneveld Absorption and attenuation of visible and near-infrared light in water: dependence on

temperature and salinity

#### 20 August 1997 / Vol. 36, No. 24 / APPLIED OPTICS

#### variations are methodological



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

temperature (°C)

10

-0.3

 $y = 0.0137x - 0.342 r^2 = 0.99$ 

15

20

100



Fig. 6. Attenuation coefficient at 715 nm as a function of salinity. This figure illustrates the linear dependence of the attenuation coefficient on salinity. Pegau etal. 1997 Appl.Opt.







Sullivan et al. 2006 Appl Opt



#### Absorbing Components: Dissolved inorganic matter

- Basic for UV detection of nitrate and HS, ISUS
- Johnson, K. S. and L. J. Coletti. 2002



http://www.mbari.org/chemsensor/ISUShome.htm



Kirk 1983

L. Ginninderra Burrinjuck Dam

L. George L. Burley Griffin

Cotter Dam Clyde River Batemans Bay

550

600

650

700

500



Dierssen et al. 2006



http://clarklittlephotography.com



 $a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0) \exp(-S_{CDOM}(\lambda - \lambda_0))$ 



Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.

Carder et al. 1989 L&O

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



Fig. 3. Spectral variation of the absorption coefficient due to marine humus or Gelbstoff as a function of the fulvic acid fraction of Gelbstoff for  $a^{\bullet}_{f} = 0.00732 \text{ m}^2 \text{ g}^{-1}$ ,  $a^{\bullet}_{h} = 0.131 \text{ m}^2 \text{ g}^{-1}$ ,  $B_f = 0.0186 \text{ nm}^{-1}$ , and B 0.0110 nm<sup>-1</sup>. The fulvic acid fraction is shown beside each curve.

Carder et al. 1989 L&O

**Equatorial Pacific** 



Table 1. Ranges for the exponential coefficient,  $C2_{xx}$  for gelbstoff and detritus for Eq. 6. Where coefficients were not listed, values were approximated from published spectra using an exponential model.

Reference	Site	Avg C2, (nm <sup>-1</sup> )	
Gelbstoff			
Kalle 1966	Baltic, North Sea	0.018	
Jerlov 1968	,	0.015	
Kirk 1976	Lakes, coast	0.015	
Lundgren 1976	Baltic 0.014		
Kopelevich and Burenkov 1977	Indo-Pacific	0.017	
Bricaud et al. 1981	Baltic	0.018	
	Mauritania	0.015	
	Gulf of Guinea	0.014	
	Mediterranean	0.014	
Okami et al. 1982	East Pacific	0.017	
Kishino et al. 1984	Lake Kizaki	0.016	
	Nabeta Bay	0.015	
	East Pacific	0.014	
Carder and Steward 1985	Gulf of Mexico 0.014		
Davies-Colley and Vant 1987	Lakes	0.019	
Maske and Flaardt 1987	NICI Harpor	0.016	
Published mean $\pm$ SD	-	$0.016 \pm 0.002$	
This study mean ± SD	San Juan Islands	$0.017 \pm 0.003$	
Cardor et al. 1707	Marine numic acid	0.011	
Detritus	Marine fulvic acid	0.018	
Kishino et al. 1986	NW Pacific Ocean	0.006	
Maske and Haardt 1987	Kiel Harbor	0.014	
Iturriaga and Siegel 1988	Sargasso Sea	0.011	
Cleveland and Perry in prep.	Sargasso Sea	0.013	
Morrow et al. 1989	Sargasso Sea	0.009	
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Babin et al. 2003 (European coastal waters)

Roesler et al. 1989 (global synthesis)

#### Absorbing Components: Particles



#### 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



or

(2) maintain size, vary intracellular pigment concentration

Fig. 2. Change in spectral absorption values with variable cell size (diameter, d, in  $\mu$ m) whereas the cell material forming the cells remains unchanged. The spectral absorption values of this material, somewhat arbitrarily adopted, are shown as the dotted curve. All curves are normalized, at  $\lambda = 430$  nm, to evidence the progressive deformation. The variations with size of the specific absolute value at 430 nm (m<sup>2</sup> mg<sup>-1</sup> Chl a) are shown in inset, under the same assumption of a constant absorption of the cell material ( $a_{cm} = 2 \times 10^5$  m<sup>-1</sup> at 430 nm) and with the additional assumption of a constant intracellular pigment concentration ( $c_{c} = 2.86 \times 10^6$  mg Chl a m<sup>-3</sup>).

#### Morel and Bricaud 1981 DSR

#### Absorbing Components: Phytoplankton



#### Absorbing Components: other protists



Morel and Ahn 1990 JMR

#### Absorbing Components: Non-algal particles $\rightarrow$ organic detrital particles



Nelson & Robertson: Detrital spectral absorption 1993] JMR



Iturriaga and Siegel 1989 L&O

Photobleaching natural light levels

#### Absorbing Components: Non-algal particles

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Babin et al. 2003 (European coastal waters)

Roesler et al. 1989 (global synthesis)

#### Absorbing Components: Non-algal or mineral particles





Fig. 3. Mass-specific absorption spectra of all samples analyzed here (n = 25). Heavy black line shows the mean, thin solid lines show samples from freshwater sites on the Atchafalaya and Mississippi Rivers, and dashed lines show samples from marine sites at Freshwater Bayou and the Atchafalaya River delta. River samples are suspended particulates only; marine samples include both sediments and suspended particulates.

Fig. 10. Second derivatives of mass-specific absorption spectra. Black lines denote freshwater samples, and gray lines denote marine samples. Bracketed arrows labeled  $\Delta a_{2,d}(382)$ and  $\Delta a_{2,d}(435)$  show locations of second-derivative maxima and minima used to compute iron absorption peak heights plotted in Fig. 11. Light-gray vertical bars highlight approximate ranges for electronic transition bands of various iron oxide minerals (Sherman and Waite 1985).

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#### Estapa et al. 2012

#### 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

# To model the impacts of absorbing constituents...add them up





#### Which component dominates?

- blue waters
- green waters

phytoplankton (V-type) inorganic particles (U-type)

# More on absorption

- Phytoplankton absorption
  - Lecture Today
- CDOM absorption methods
  - Lab today
- Particulate absorption methods
  - Lab Wednesday

# How do we measure absorption in the ocean?

- In situ meters
  - ac meters
  - ICAM (integrating cavity absorption meters)
- Discrete samples in the lab
  - Quantitative filter technique

# Absorption: Quantitative Filter Technique



- Separates particles from *dissolved*
- Concentrates particles from dilute medium

# Measure in Spectrophotometer

- Reference
  - Match optical density of filter pad
  - No variability



Compute absorption

$$a (m^{-1}) = 2.303$$
OD  
L (m)

What is L?





 $V_{\text{filtered}} = A_{\text{eff}} h$ =  $\frac{V (m^3)}{A (m^2)}$ 



Wavelength [nm]

- Filter pad
  - Creates nearly isotropic light field
  - Increases optical path length
  - Increases absorption signal
  - How to correct for it?

## $\beta$ correction: path length amplification

- Approach
  - Cultures or samples
  - Measure absorption in cuvette (IS-mode)
  - Measure absorption on filter pad (T-mode)
  - Determine ratio,  $\beta = OD_{filt} = optical$ .  $OD_{cuv}$  geometric







What about the scattering by the filter? Path length amplification, *uncertainty calculation* 

a (m<sup>-1</sup>) = 2.303 OD  
$$\frac{V(m^3)}{A(m^2)}$$

- Run three blank pads relative to your baseline
- Compute the standard deviation of the blank scans,  $\sigma_{\text{ODbl}}(\lambda)$
- substitute  $\sigma_{\text{ODbl}}(\lambda)$  for OD in the above equation to compute  $\sigma_{a}(\lambda)$
- note that the uncertainty will be different for each sample:
  - V is different for every sample
  - OD is different sample is different, so the signal:noise will be different

$$\sigma_{a} (m^{-1}) = 2.303 \quad \frac{\sigma_{ODbl}}{Vsample(m^{3})} \quad . \label{eq:sigma_a}$$

# Uncertainty example 1: impact of sample optical density





- Same volume filtered for each sample (100ml)
- OD<sub>sample1</sub>~10\*OD<sub>sample2</sub> (approx 0.1 vs 0.01)
- OD<sub>filter blanks</sub> ~ OD<sub>sample2</sub> for low particulate waters

# Uncertainty example 2: impact of volume filtered





• Different V filtered for each sample (100ml vs 1000ml)

•  $\sigma_{\text{ODfilter blank}} \sim 10\% \text{OD}_{\text{sample}}$ 

Better to filter more volume and obtain higher OD<sub>sample</sub> relative to blanks

#### Partitioning of particulate absorption

- First scan is total particles, a<sub>p</sub>
- Extract with methanol and scan again, a<sub>nap</sub>
- $a_{phyt} = a_p a_{nap}$
- Other issues
  - Phytoplankton "parts"
  - Detrital pigments
  - Phycobilipigments
  - Inorganics



# Summary Filter pad technique

- Filter sample, want high loading to overcome the variability in the blank filter pad absorption itself, but not muddy (0.1 to 0.4 absorbance (OD))
- Reference?
- Extraction to separate particulates, nap
- Computation
  - Offset correction, Stramski and Babin 2002
  - Beta correction, try all models
  - Absorption calculation, a<sub>p</sub> and a<sub>nap</sub>
  - Phytoplankton calculation,  $a_{phyt} = a_p a_{nap}$

# WETLabs ac9/acs sensors



- Quantitative measurements of absorption and attenuation
- Calibrated with pure water
- Corrections
  - Temperature and salinity of samples relative to pure water calibration
  - Non-ideal configurations for absorption and attenuation
- Strategies for robust measurements

- Measurement Reality Sensors
  - Reflecting tube absorption meters



Some scattered light not collected by absorption tube, leads to overestimation of absorption  $\rightarrow$  correction

Some scattered light collected by attenuation tube, leads to underestimation of attenuation  $\rightarrow$  report detection angle

#### An aside on

#### Beam attenuation acceptance angle

TABLE 5.2 Configuration specifications for commercially available beam attenuation meters

Instrument	Beam source	Beam width (mm)	Acceptance angle (°)	Path length (cm)
AlphaTracka transmissometer	Light emitting diode (LED)	15	0.86	5
SeaTech transmissometer	Collimated incandescent bulb	7	1.5	25
Sequoia LISST	Solid state diode laser	6	0.069(B), 0.006(F)	5, 10
WET Labs ac9, acs	Collimated incandescent bulb	10	0.93	25, 10
WET Labs cstar	LED	10	1.2	25, 10



Roesler and Boss 2008

# Absorption from ac9/acs



\*water calibration for quantitation air calibration to track instrument drift

- Obtain from factory
- Calibrate\* in the lab
- Place in deployment configuration
  - Black tubing
  - Copper tubing
  - Air valve
  - Seat bottom
  - Bracket top
- Calibrate\* on the frame
- Deploy
  - Take to depth to purge
  - Remove upcast observations (pump inversion)
- Calibrate\* upon recovery

# Absorption from ac9 (acs same)





#### The absorption/attenuation by water varies with temperature and salinity

If you calibrate at 25C with fresh water but measure in the ocean at 10C, you have not used a proper calibration standard



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. Pegau et al. 1997 Applied Optics

Sullivan et al. 2006 Applied Optics

wavelength (nm)

## Absorption from ac9



#### 2. Temperature and salinity correction

This is due to the fact that the in situ T and S are different than that of the calibration water  $\rightarrow$  Requires measurement of T, S in situ

- Data Analysis and Interpretation acs example
  - Collect sample scans
  - 1. correct for T, S



- Data Analysis and Interpretation acs example
  - 2. Correct sample scans for pure water values (T, S corr)



- Data Analysis and Interpretation acs example
  - 3. Scattering correct the absorption spec find wavelength where absorption is neg

 $\rightarrow$  measured *a* is actually scattering

if T and S have been accurately



- Data Analysis and Interpretation acs example
  - 3. Scattering correct the absorption spectra
    - a. Subtract  $a_m(NIR)$ "b not a function of  $\lambda$ " spectrophotometric approach

Stramski and Babin 2002



- Data Analysis and Interpretation acs example
  - 3. Scattering correct the absorption spectra b. Subtract spectral scattering contribution, fraction of  $b(\lambda)$  $b(\lambda) = c(\lambda) - a(\lambda)$ if a(NIR) = 0 signal is due to scattering  $fb(\lambda) = a(NIR)/b(NIR)$



- Data Analysis and Interpretation acs example
  - 4. Compute Scattering spectra  $b(\lambda) = c(\lambda) - a(\lambda)$



Best practices for obtaining Absorption/Attenuation from acs



- Review Data processing
  - Temperature/Salinity correct a and c of sample and calibration data
  - Subtract T,S-corrected pure water calibration from sample scans
  - Apply spectral scattering correction to absorption
  - Compute scattering spectrum (b = c a)

- Data Analysis and Interpretation acs example
  - Calibration independent method for partitioning
  - (Slade et al. 2010)
    - Measure whole water and filtered water, a<sub>tot</sub>, a<sub>filt</sub>
    - Apply Temperature, Salinity correction
    - Apply Scattering correction
    - Subtract filtered water scan from whole water scan, a<sub>part</sub>=a<sub>tot</sub> a<sub>filt</sub>
    - Yields a<sub>CDOM</sub> and a<sub>part</sub> *independent of calibration drift*



# Automated shipboard flow-through method, calibration-independent



Slade et al., 2010

An example of calibration independent approach on an automated shipboard flow-through configuration

