Lecture 5

Absorption Part 2 – measuring absorption

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How do we measure absorption in the ocean?

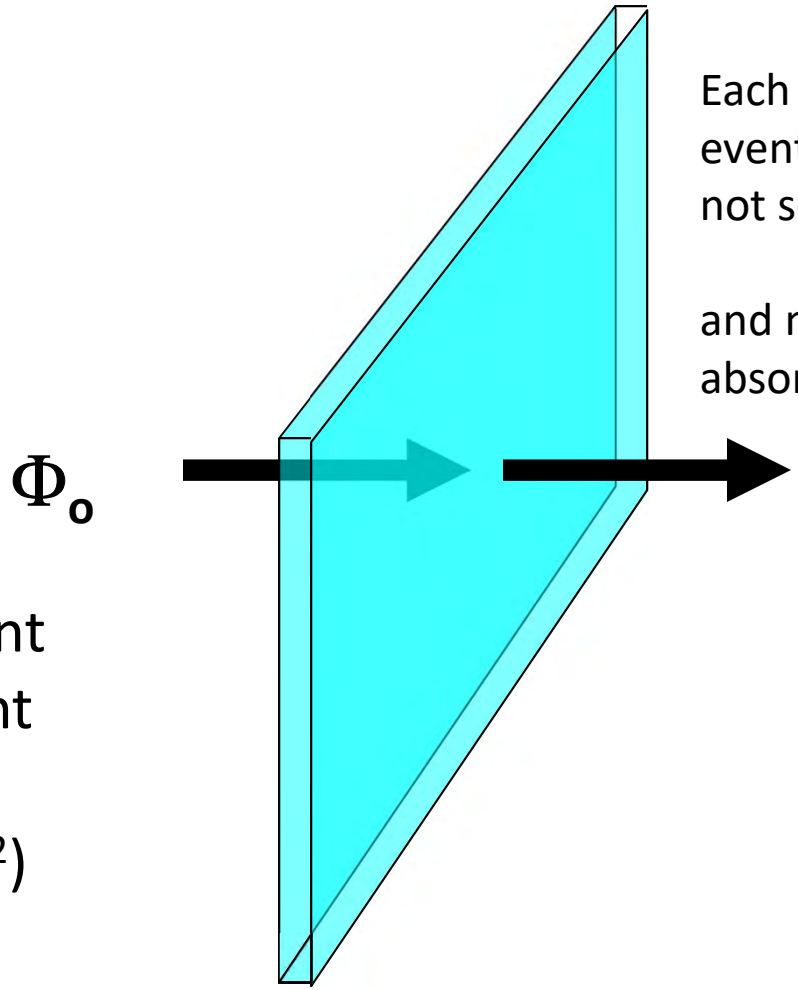
- In situ meters
  - ac meters
  - (ICAM)
- Discrete samples in the laboratory spectrophotometer
  - Cuvettes
  - Filter pad

Before *measuring* IOPs it is helpful to review measurement *theory*

Thin slab of material, what is *thin*?

Each photon has probability for one optical event (transmitted or scattered or absorbed, not scattered then absorbed)

and no event is shaded (e.g., one layer of absorbing molecules)



Φ_o

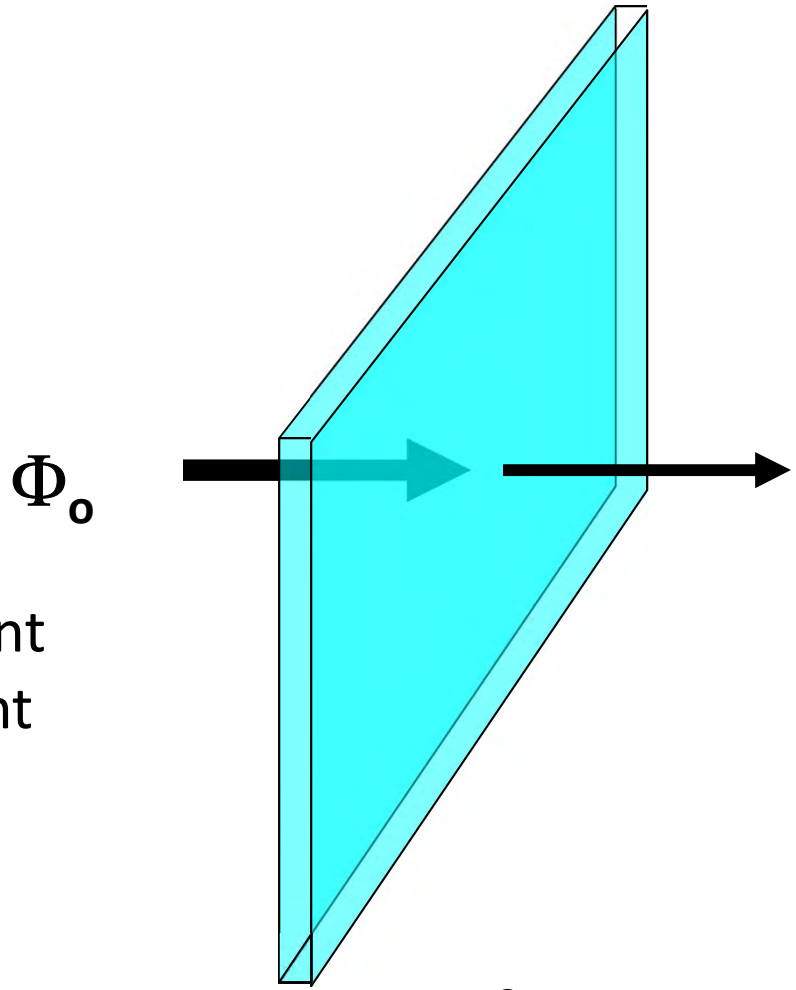
Incident Radiant Power (W/m^2)

Φ_t

Transmitted Radiant Power (W/m^2)

$\Phi_o = \Phi_t$ No attenuation

IOP *Theory*

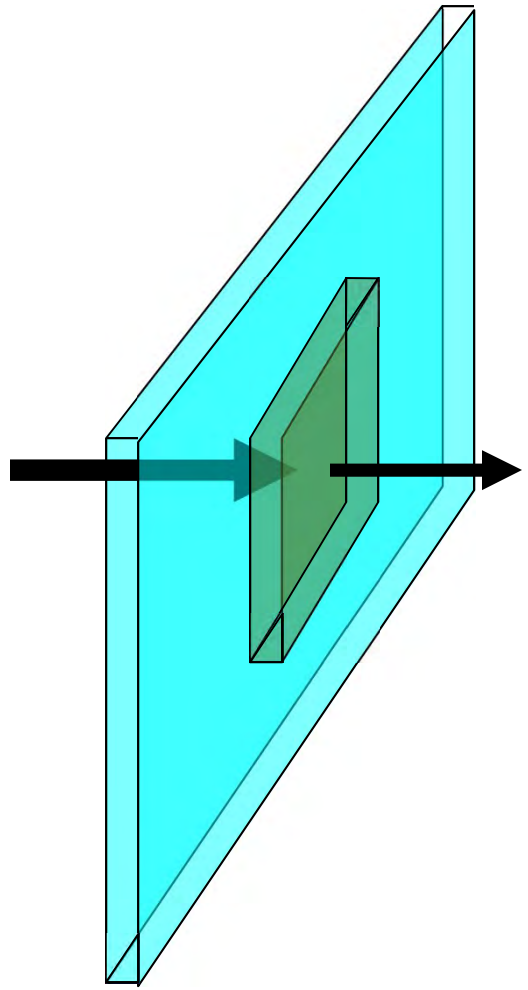


Incident Radiant Power

Transmitted Radiant Power

If $\Phi_t < \Phi_o$ there is attenuation

Loss due solely to absorption



Φ_a Absorbed Radiant Power

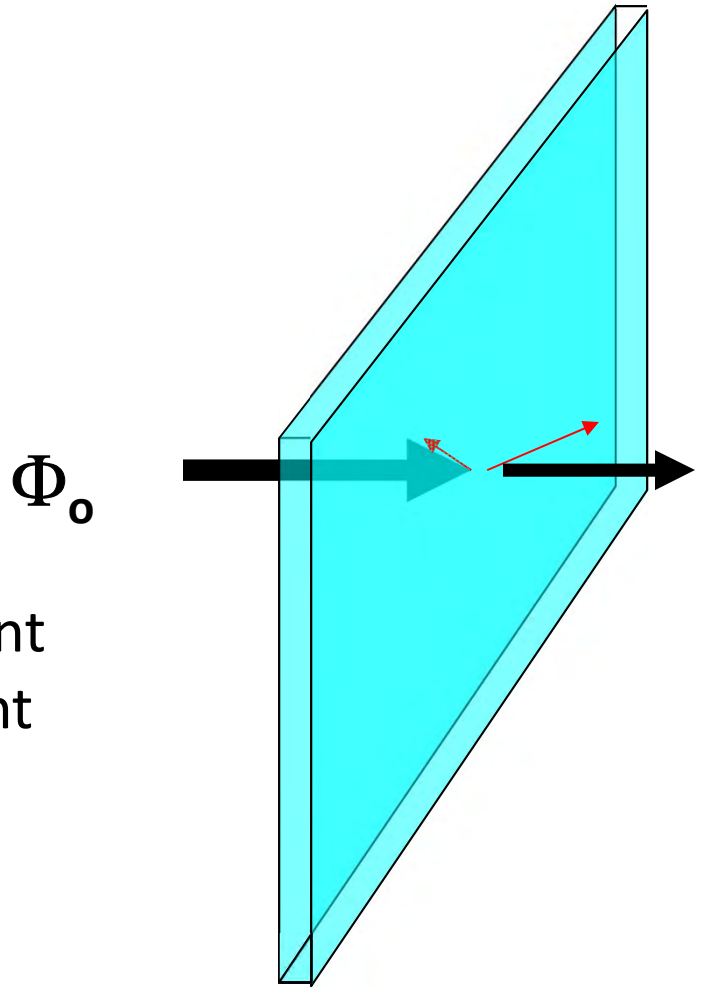
Φ_o

Incident
Radiant
Power

Φ_t

Transmitted
Radiant
Power

Loss due solely to scattering



Φ_b Scattered Radiant Power

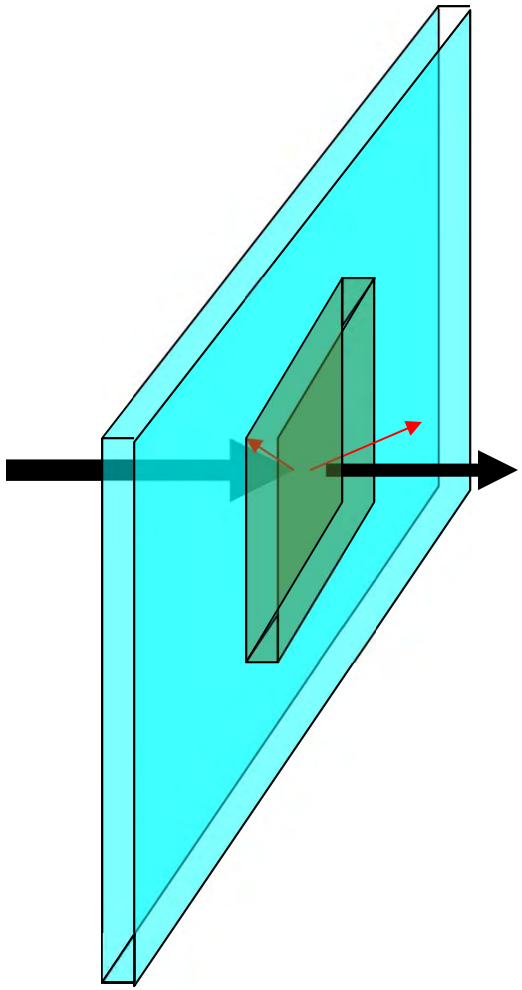
Φ_o

Incident
Radiant
Power

Φ_t

Transmitted
Radiant
Power

Loss due to beam attenuation (absorption + scattering)



Φ_b Scattered Radiant Power

Φ_a Absorbed Radiant Power

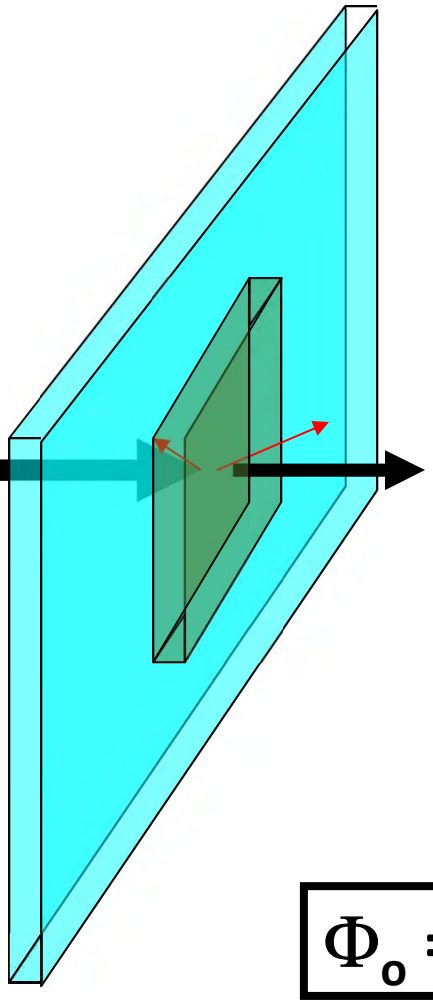
Φ_o

Incident Radiant Power

Φ_t

Transmitted Radiant Power

Conservation of radiant power



Φ_b Scattered Radiant Power

Φ_a Absorbed Radiant Power

Φ_o

Incident Radiant Power

Φ_t

Transmitted Radiant Power

$$\Phi_o = \Phi_t + \Phi_a + \Phi_b$$

Derivation of Absorption

Absorptance

$\boldsymbol{A}$ = fraction of incident radiant power absorbed

$$\boldsymbol{A} = \frac{\Phi_a}{\Phi_o}$$

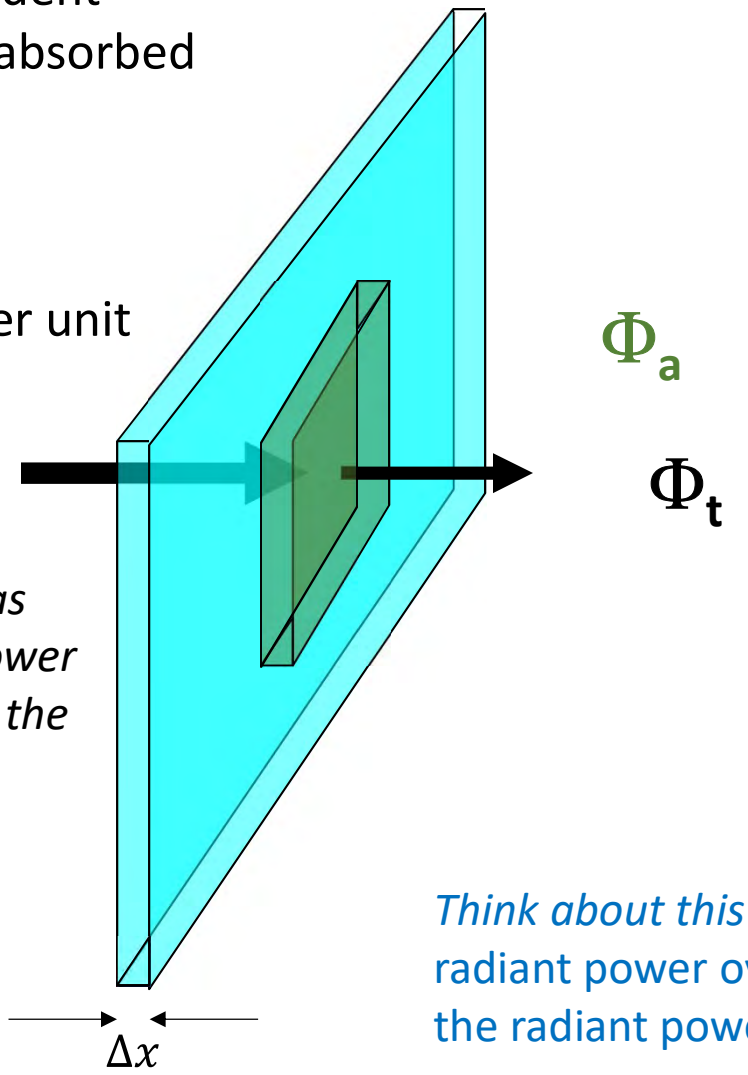
If no scattering

$$\boldsymbol{A} = \frac{\Phi_o - \Phi_t}{\Phi_o}$$

Absorption

a = absorptance per unit distance (m^{-1})

$$\mathrm{a} = \frac{\boldsymbol{A}}{\Delta x}$$



Rearrange, express as fractional radiant power loss to absorption in the layer

$$\mathrm{a}\Delta x = \frac{-\Delta\Phi}{\Phi}$$

$$\frac{-\Delta\Phi}{\Delta x} = \Phi\ \mathrm{a}$$

Think about this equation: the fractional loss or radiant power over the layer is linearly related to the radiant power → *"Lambert 1760"*

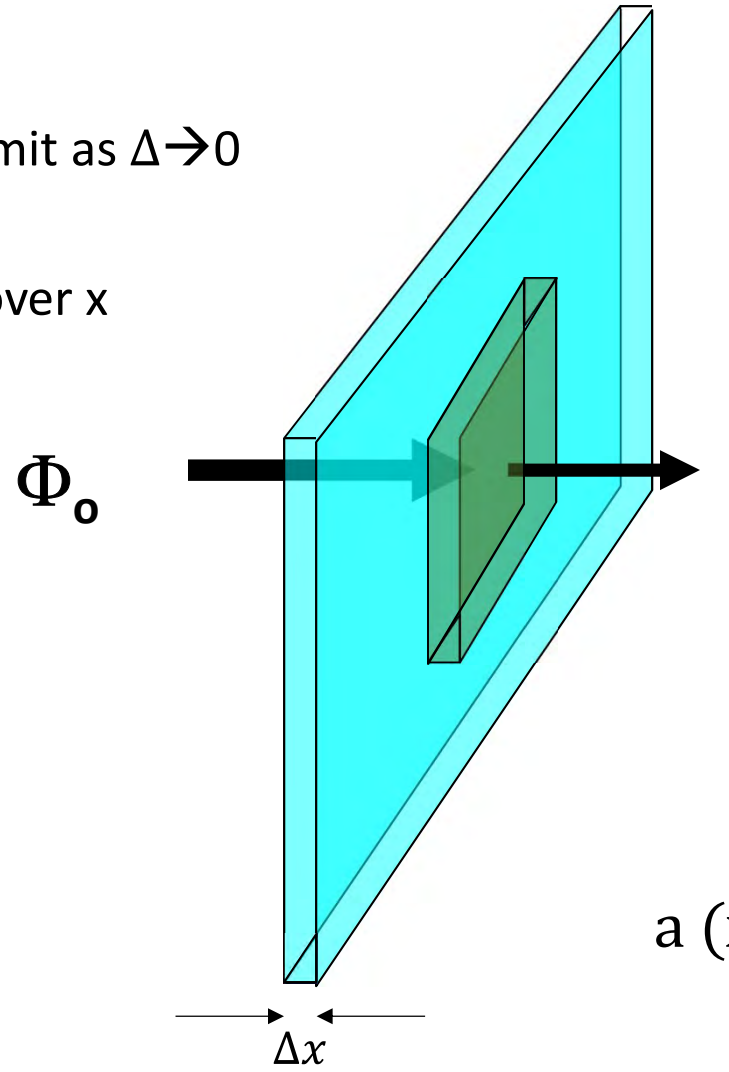
Derivation of Absorption

$$a\Delta x = \frac{-\Delta\Phi}{\Phi}$$

Take the limit as $\Delta \rightarrow 0$

$$a\Delta x = \lim_{\Delta x \to 0} \frac{-\Delta\Phi}{\Phi}$$

Integrate over x



$$\int_0^x a\, dx = -\int_0^x \frac{d\Phi}{\Phi}$$

Evaluate

$$a\, x\,|_0^x = -\ln \Phi\,|_0^x$$

$$a\,(x - 0) = -(\ln \Phi(x) - \ln \Phi(0))$$

Derivation of Absorption

Evaluate

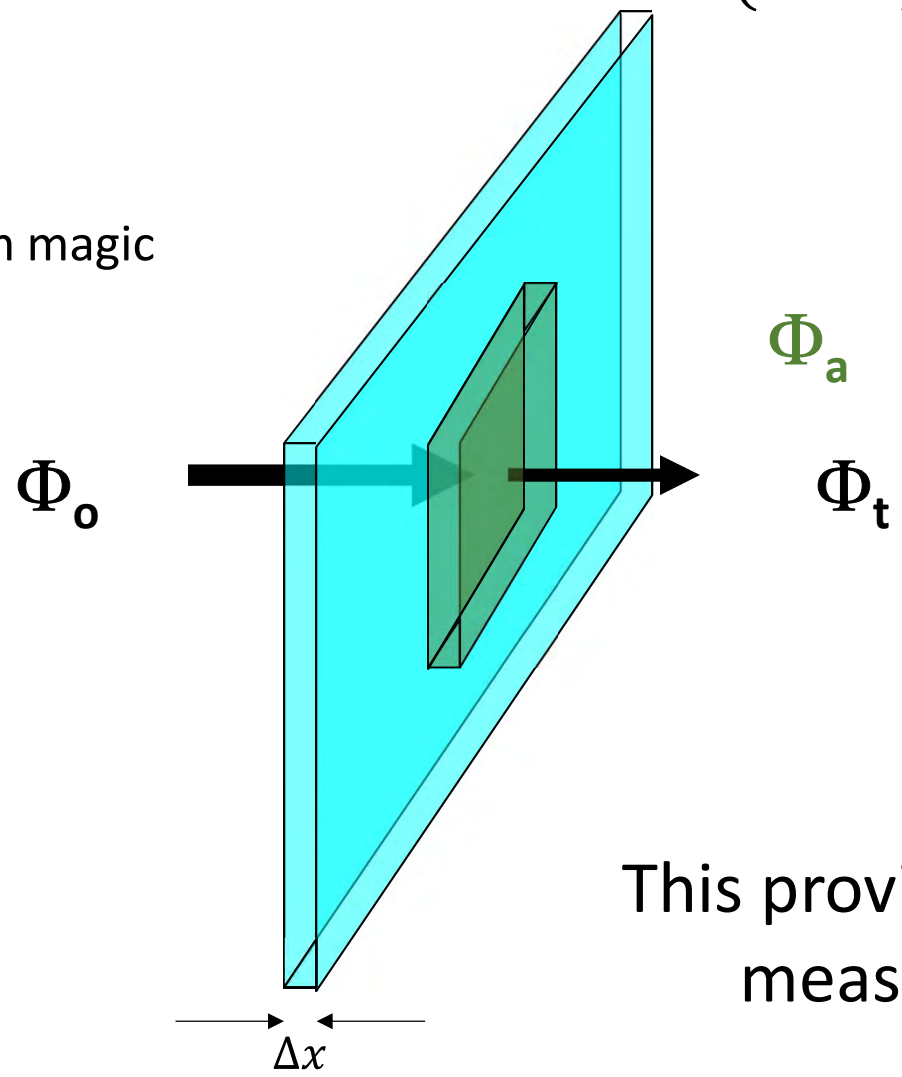
Logarithm magic

$$a\,(x-0) = -(\ln \Phi(x) - \ln \Phi(0))$$

$$a\,x = -(\ln \Phi_t - \ln \Phi_0)$$

$$a\,x = -(\ln \frac{\Phi_t}{\Phi_0})$$

$$a\,(m^{-1}) = \frac{-1}{x}(\ln \frac{\Phi_t}{\Phi_0})$$



Absorption coefficient (m^{-1})

a = loss of radiant power per unit distance

This provides a guide towards measurements (lab 2)

Absorption through particles

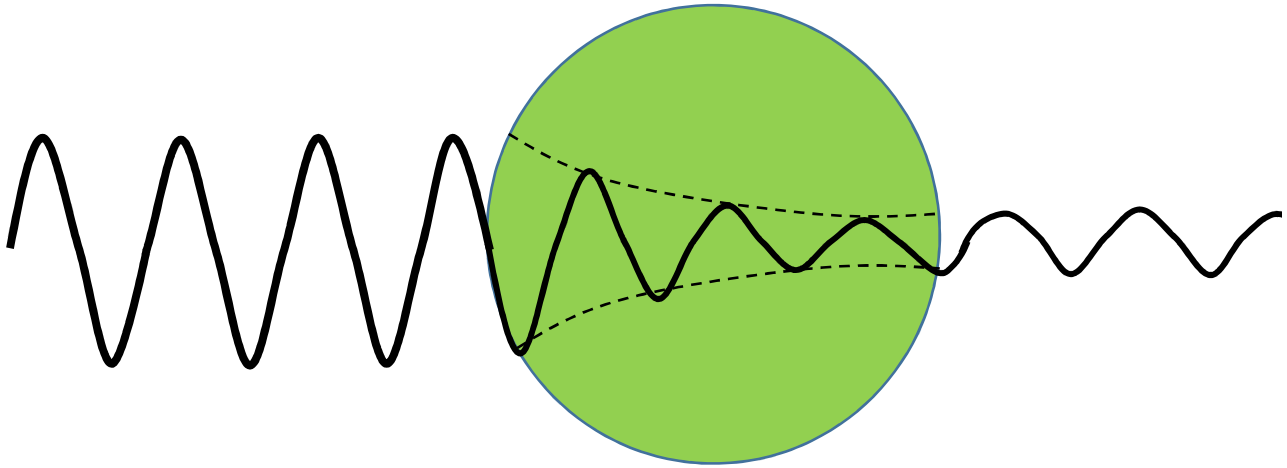
$$\mathrm{a}\ (m^{-1}) = \frac{-1}{x}\left(\ln\frac{\Phi_t}{\Phi_0}\right)$$

$$\ln\frac{\Phi_t}{\Phi_0} = -\,\mathrm{a}x$$

$$\frac{\Phi_t}{\Phi_0} = e^{-\mathrm{a}x}$$

$$\Phi(x) = \Phi_0\, e^{-\mathrm{a}x}$$

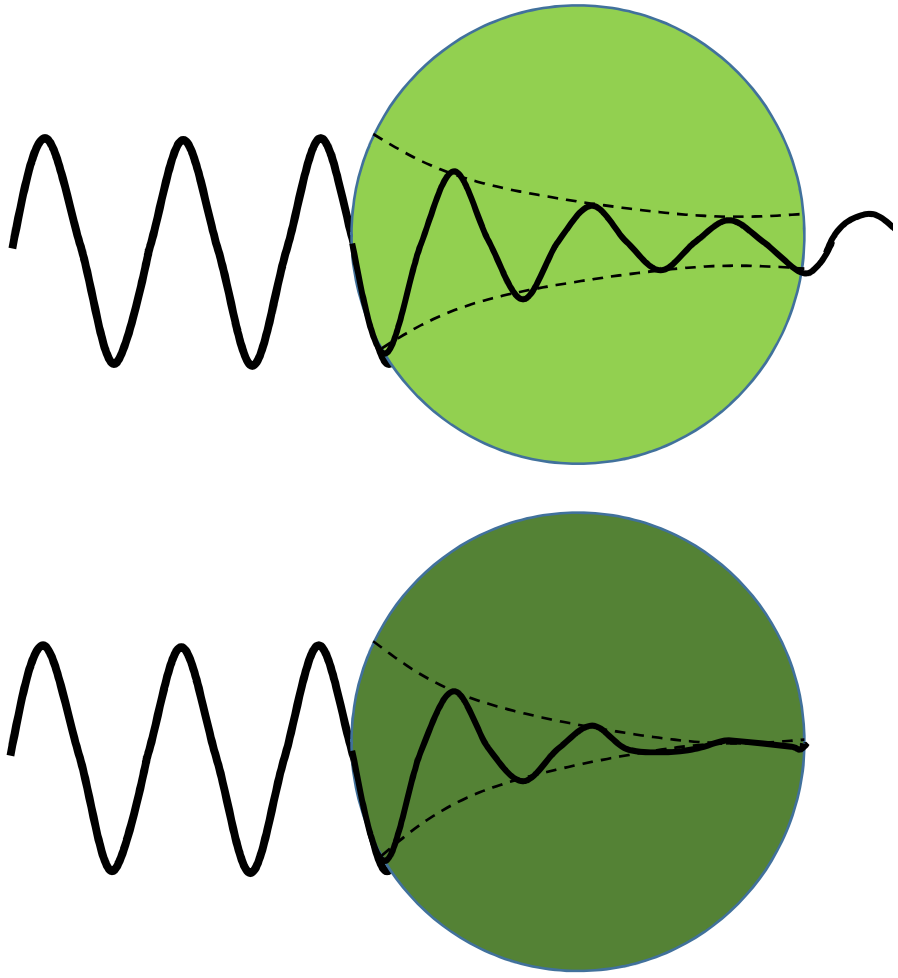
- As the EM wave passes through the absorbing matter
- Amplitude decreases exponentially



- Wavelength does not change

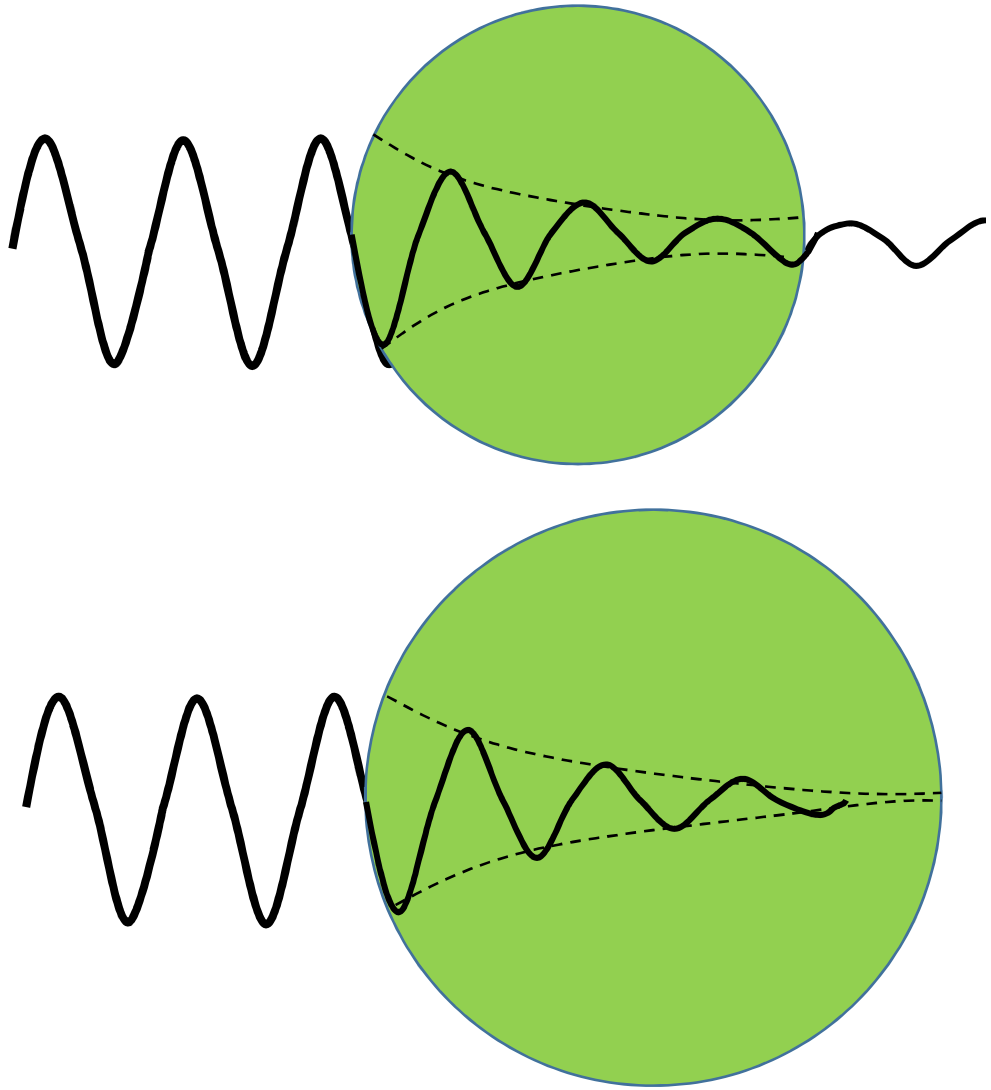
Absorption through particles

- As the **absorption coefficient** increases, less light passes through the particle



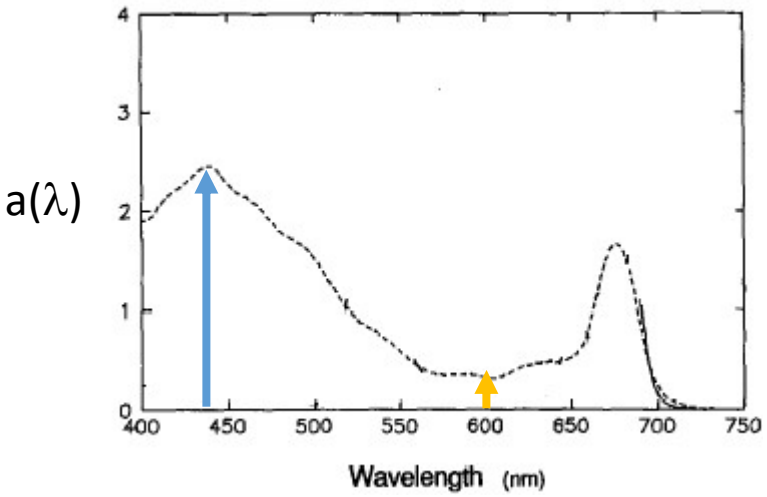
Absorption through particles

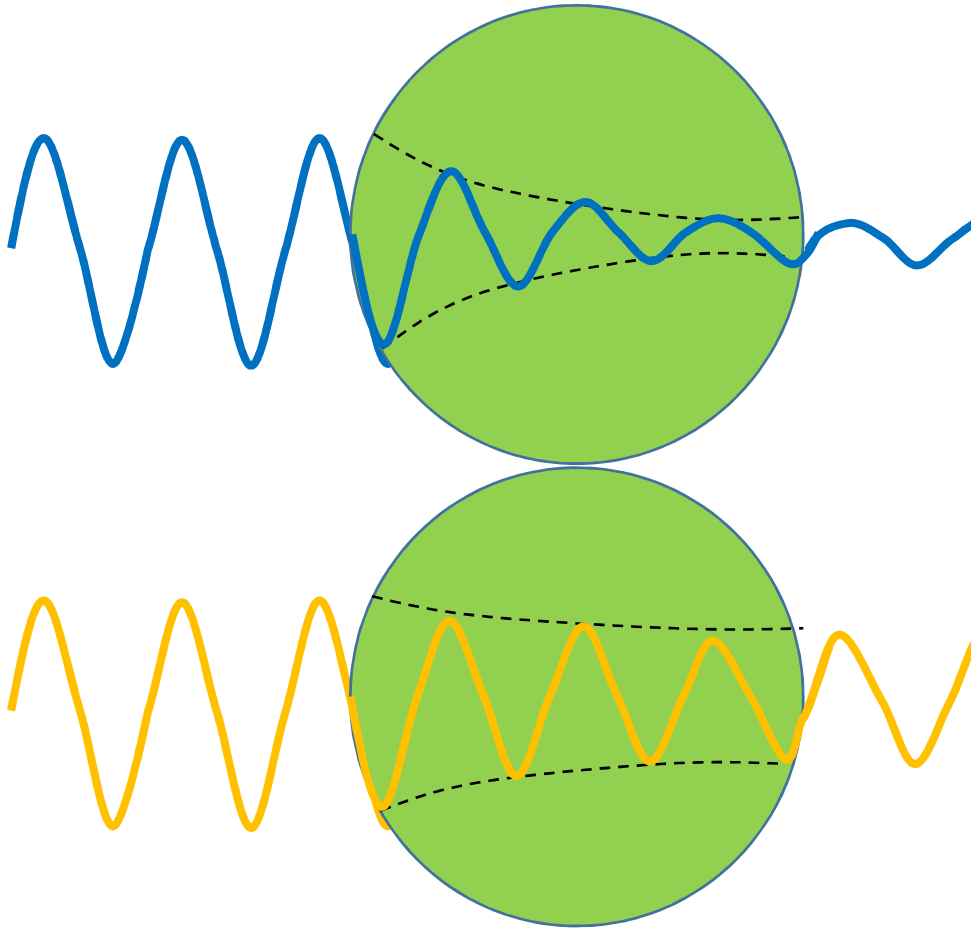
- As the **pathlength** through the particle increases, the less light passes through the particle



Absorption through particles

- Each wavelength of the absorption spectrum is attenuated differently through the particle (e.g., phytoplankton cell)





Pigment packaging

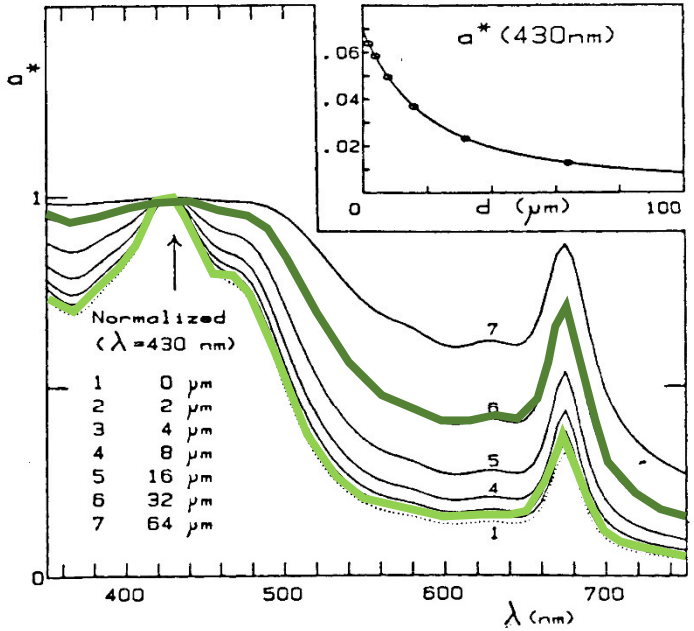
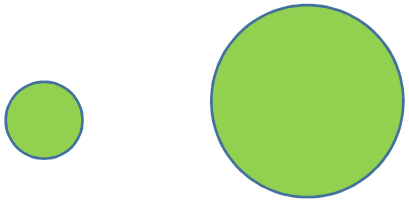


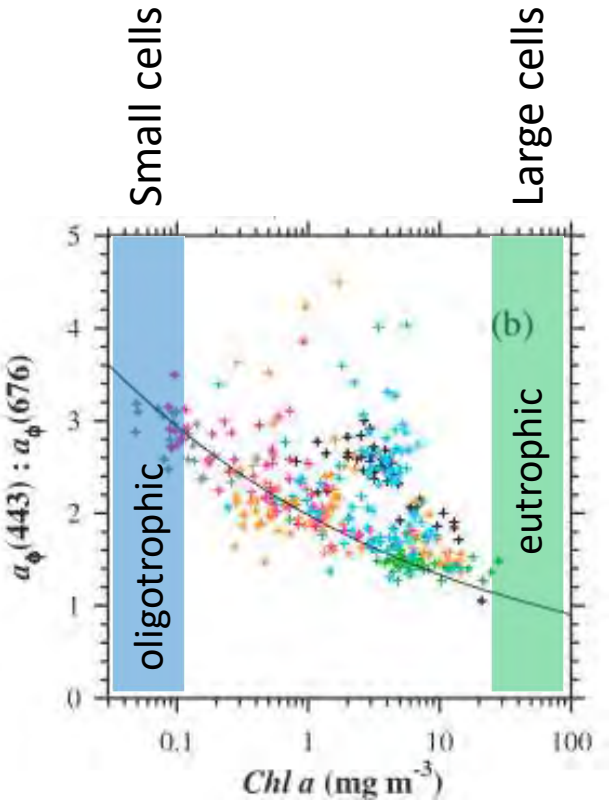
Fig. 2. Change in spectral absorption values with variable cell size (diameter, d, in μm) whereas the cell material forming the cells remains unchanged. The spectral absorption values of this material, somewhat arbitrarily adopted, are shown as the dotted curve. All curves are normalized, at $\lambda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

Morel and Bricaud 1981 DSR

(1) vary size, maintain constant intracellular pigment concentration

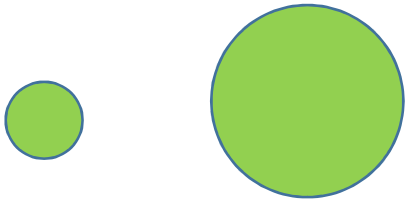


Phytoplankton ecology and pigment packaging

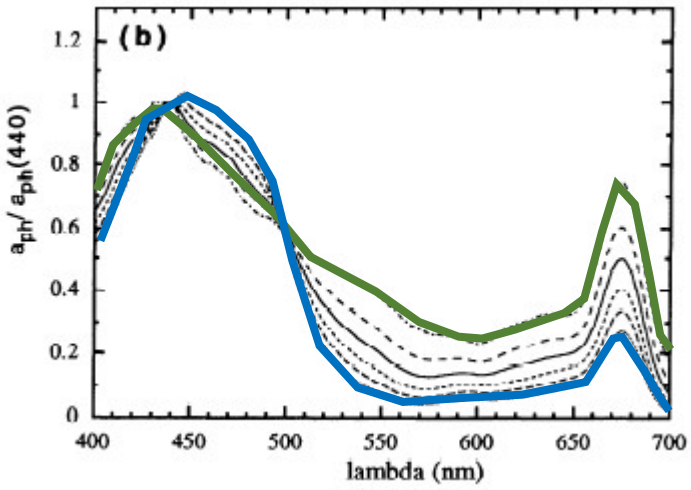


Babin et al. 2003

Bricaud et al. 1995

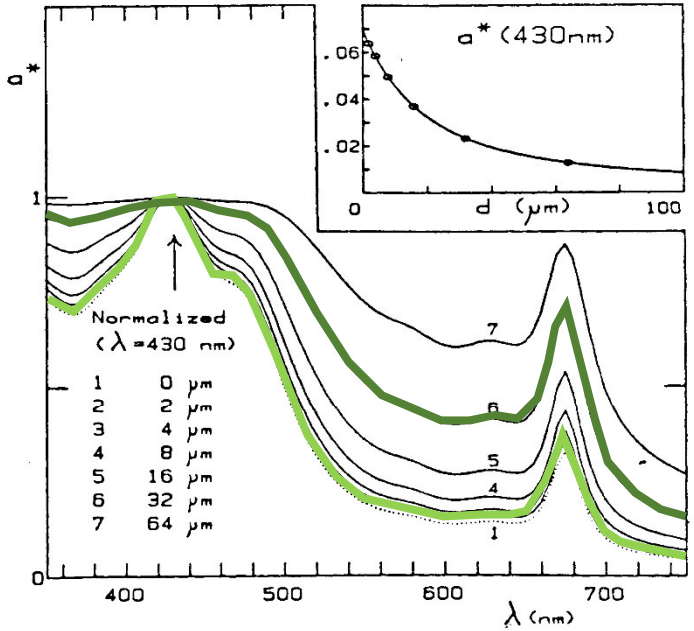


$a_{phyt}(\lambda)$
$a_{phyt}(440)$



Global Relationships

Pigment packaging



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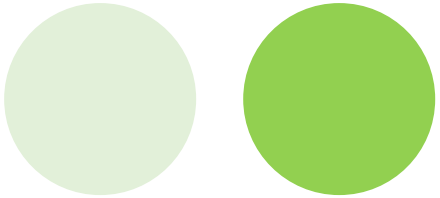
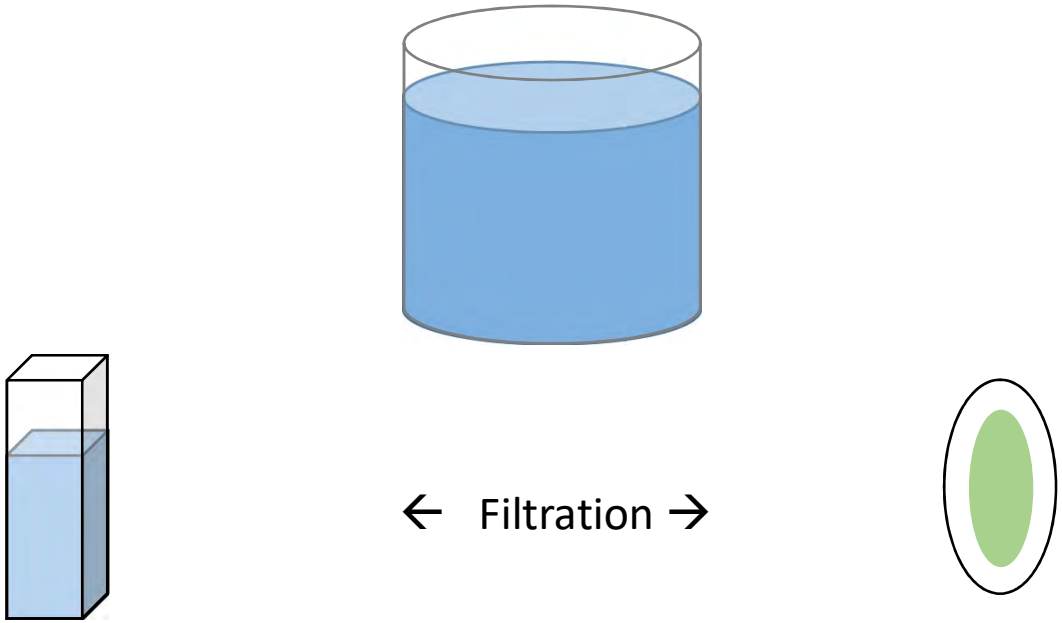
Morel and Bricaud 1981 DSR

(2) maintain size, vary intracellular pigment concentration



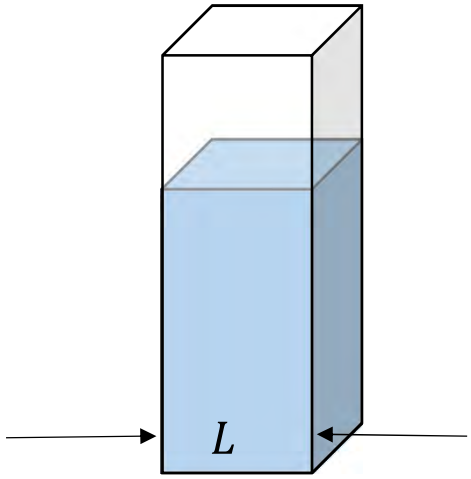
Measuring Absorption



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

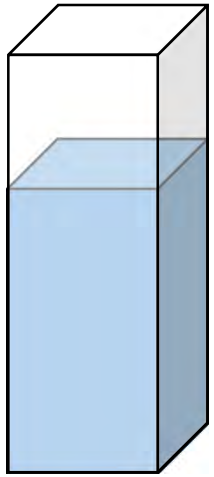
Measuring absorption - solutions

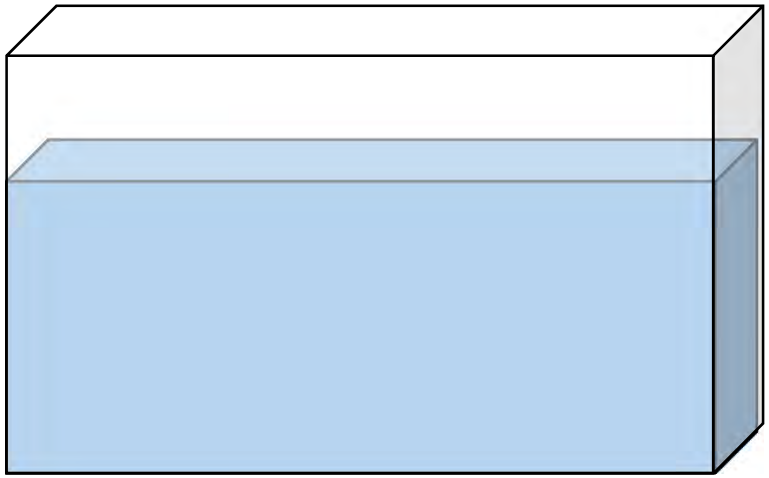
- Spectrophotometers output *absorbance, A,* rather than *absorptance, $\boldsymbol{A}$*
  - $\boldsymbol{A} = \frac{\Phi_a}{\Phi_o}$
  - $A = log_{10}\left(\frac{\Phi_0}{\Phi_t}\right) = -log_{10}\left(\frac{\Phi_t}{\Phi_o}\right) = -log_{10}(1-\boldsymbol{A})$
  - Absorbance sometimes called *optical density*
- Reference material (Baseline correction)
  - $A_{sample} - A_{ref}$
  - $= -\left(log_{10}\left(\frac{\Phi_t}{\Phi_o}\right)_{\boldsymbol{sample}} - log_{10}\left(\frac{\Phi_t}{\Phi_o}\right)_{\boldsymbol{ref}}\right)$
  - $= -log_{10}\left(\frac{\Phi_{t,sample}}{\Phi_{t,ref}}\right)$
- $a = \ln(10) \times \frac{A}{L} = 2.303 \times \frac{A}{L(m)}$



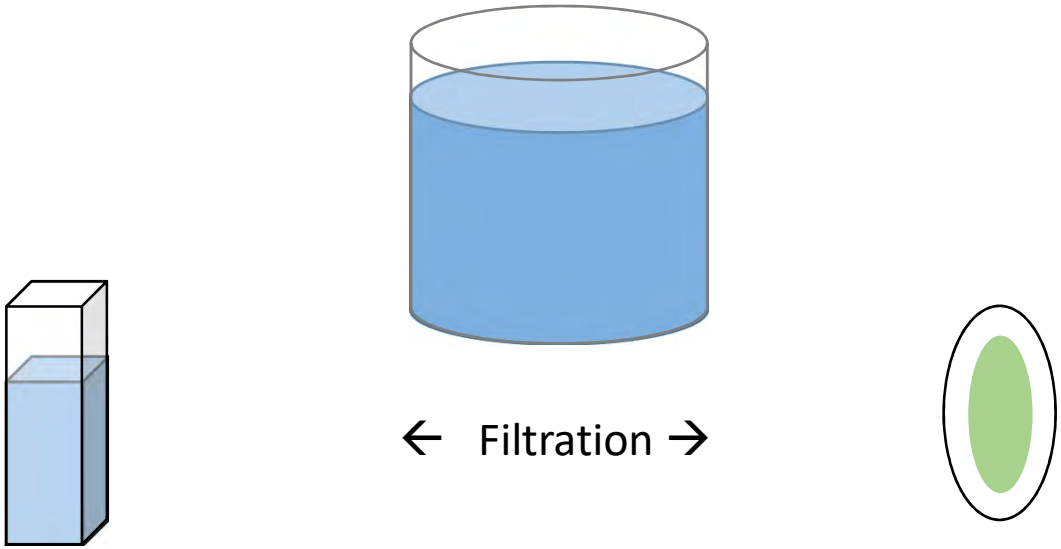
Measuring absorption

- Sample is not an infinitesimally thin layer
- absorbance, $A = -log_{10}\left(\frac{\Phi_t}{\Phi_o}\right)$
- Recommendation
  - $0.1 < A < 0.4$
  - $80\% < T < 40\%$
- Adjust the pathlength to maintain correct A range
- May require two different pathlengths along the spectrum

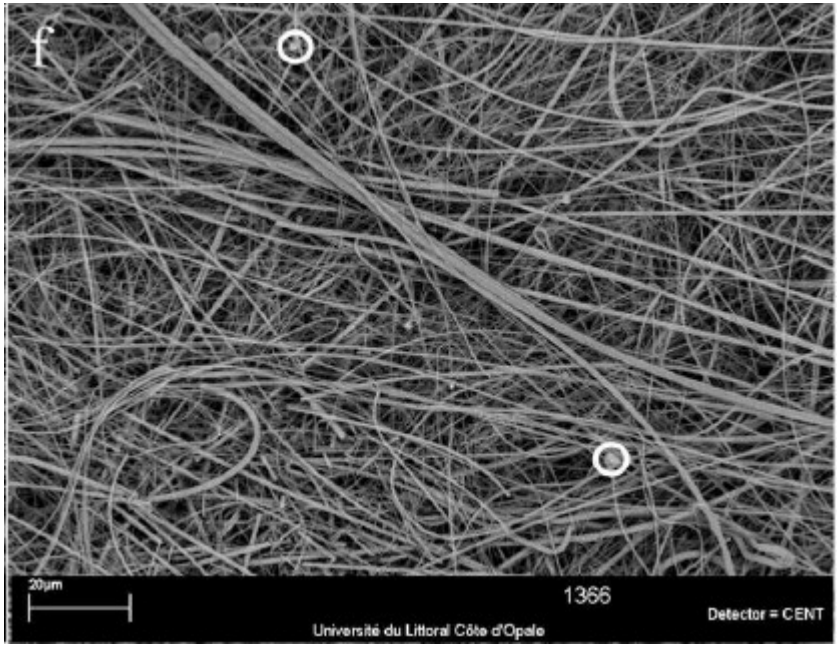




Measuring Absorption – Particles on Filters



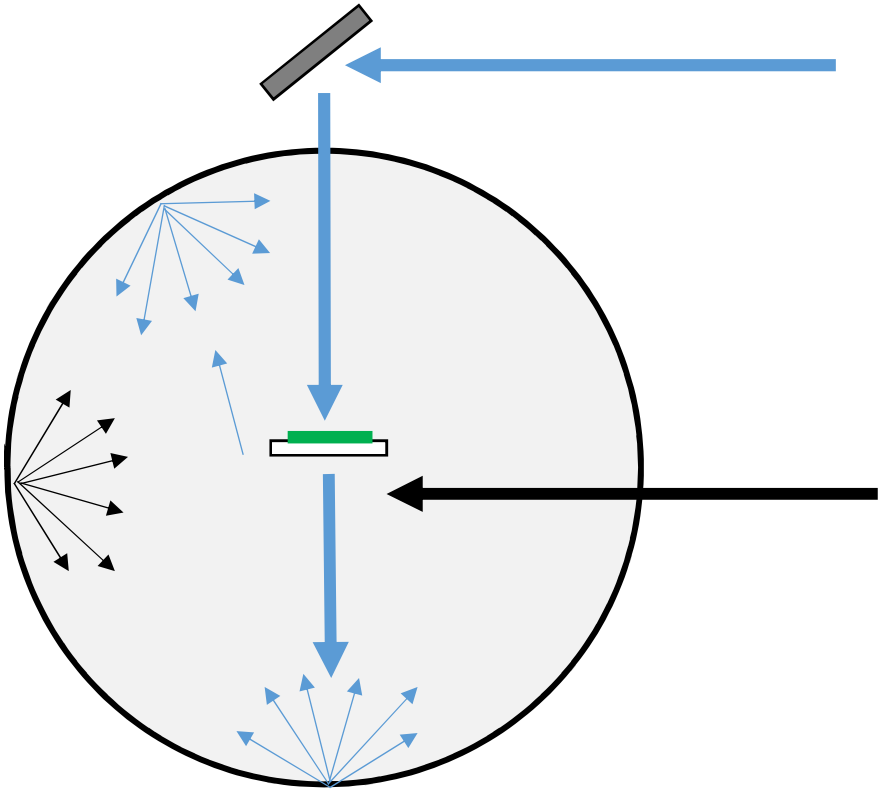
- Separates particles from *dissolved*
- Concentrates particles from dilute medium onto a glass fiber filters →



Neukermans et al 2012 Limnol Oceanogr

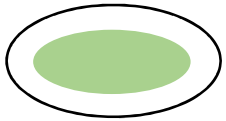
Measure in Spectrophotometer with Center-mounted Integrating Sphere

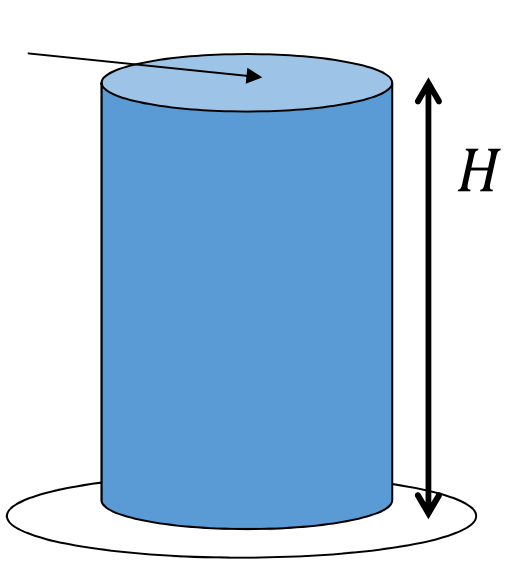
- Sample Beam
  - Passes through sample filter first → sample absorption
  - Multiply scatters off reflective sphere
  - Pass through sample multiple times → pathlength amplification
- Reference Beam
  - Multiply scatters off reflective sphere
  - Pass through sample multiple times → pathlength amplification
- Sample Beam – Reference Beam = single pass through filter



Compute absorption

- $a = 2.303 \times \frac{A}{L(m)}$
- What is the pathlength, L?
- Convert the volume filtered into a cylinder of water of area, S, and height, H
- The pathlength is $H = \frac{V_{filt}}{\pi\, r_{eff}{}^2}$

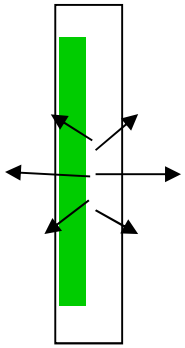


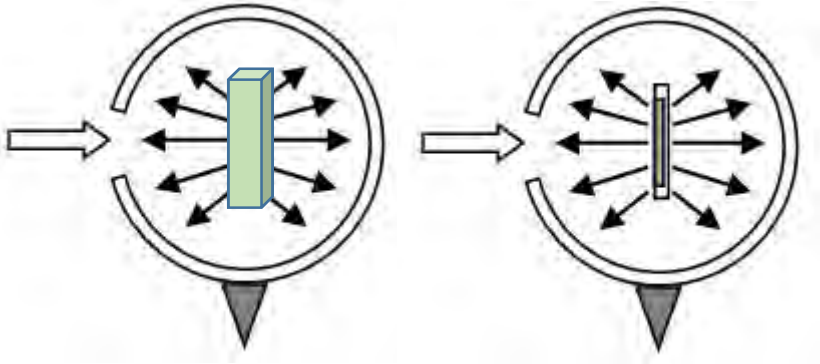


- $a = 2.303 \times 100 \left(\frac{cm}{m}\right) \times \frac{A}{\left(\frac{V_{filt(ml)}}{\pi\, r_{\mathrm{eff}}{}^2 (cm^2)}\right)}$

Filter pad

- Optical properties of the filter pad subtracted in baseline
- Creates highly scattering environment around the particles
  - multiple scattering increases probability of absorption,
  - Overestimates absorption
  - Pathlength Amplification Correction – derive from paired suspension and filter pad measurements





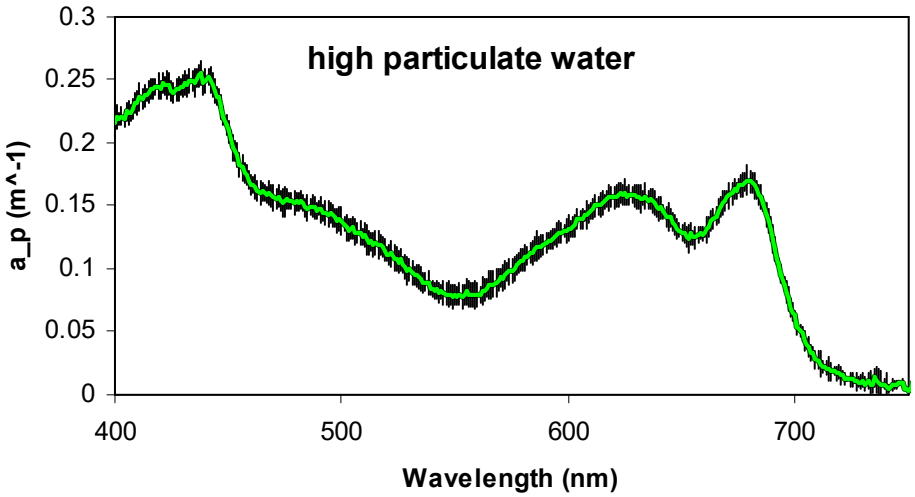
Compute absorption

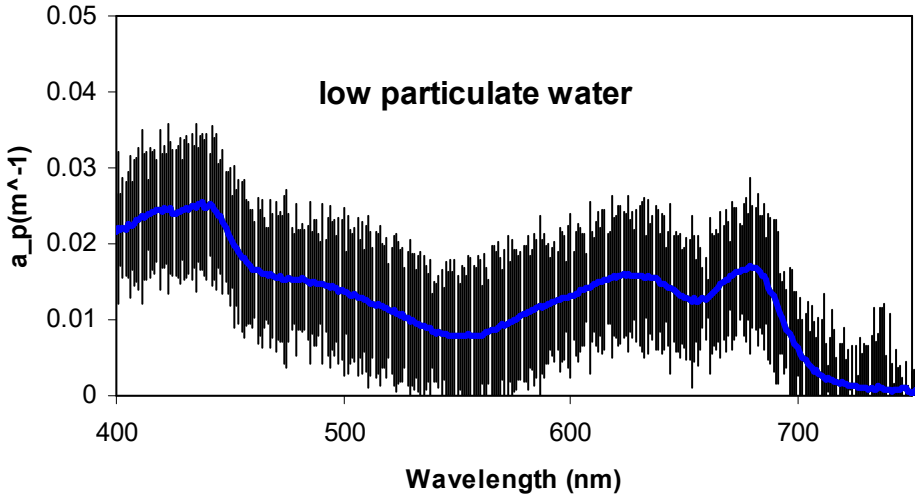
- *Measure* baseline corrected sample
- $A_{sample\_Bcorr}(\lambda) = A_{sample\_on\_pad}(\lambda)$ - $A_{Baseline\_blankpad}(\lambda)$
- *Apply pathlength amplification correction (Stramski et al. 2015)*
- $A_{sample_{BcorrAcor}}\ (\lambda) = 0.323\ \times\ A_{sample\_Bcorr}(\lambda)^{1.0867}$
- *Compute spectral absorption coefficient*
- $a_{part}(\lambda) = 2.303 \times 100 \left(\frac{cm}{m}\right) \times \frac{A_{sample_{BcorrAcorr}}(\lambda)}{\left(\frac{V_{filt}(ml)}{\pi\, r_{\mathrm{eff}}{}^{2}(cm^2)}\right)}$

Absorption - *uncertainty calculation*

- Run three blank pads relative to your baseline
- Compute the standard deviation of the blank scans, $\sigma_{A\_bl}(\lambda)$
- substitute $\sigma_{A\_bl}(\lambda)$ for A in the absorption equation to compute $\sigma_a(\lambda)$
- note that the uncertainty will be different for each sample:
- V is different for every sample
- *A* is different for each sample, so the signal:noise will be different
- $\sigma_a(\lambda) = 2.303 \times 100 \left(\frac{cm}{m}\right) \times \frac{A_{bl}(\lambda)}{\left(\frac{V_{filt}(ml)}{\pi\, r_{\mathrm{eff}}{}^2(cm^2)}\right)}$

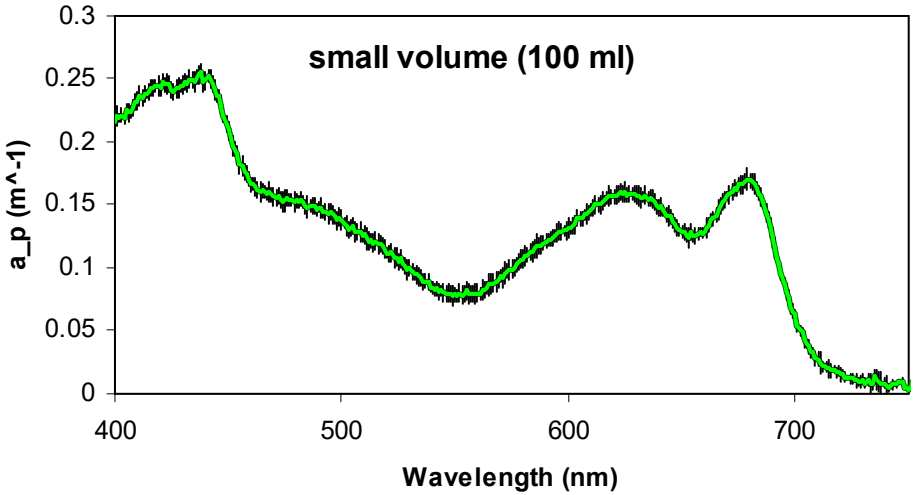
Uncertainty example 1: impact of sample optical density

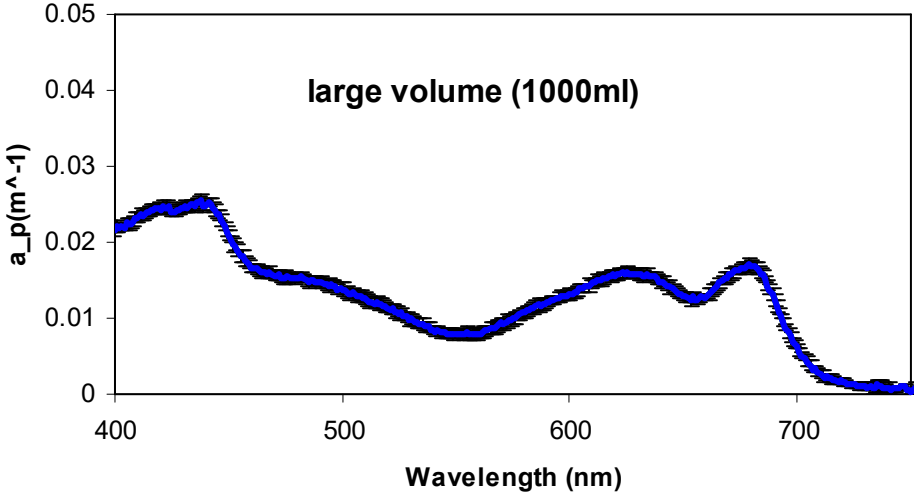




- Same volume filtered for each sample (100ml)
- $A_{\text{sample1}} \sim 10 * A_{\text{sample2}}$ (approx 0.1 vs 0.01)
- $A_{\text{filter blanks}} \sim A_{\text{sample2}}$ for low particulate waters

Uncertainty example 2: impact of volume filtered



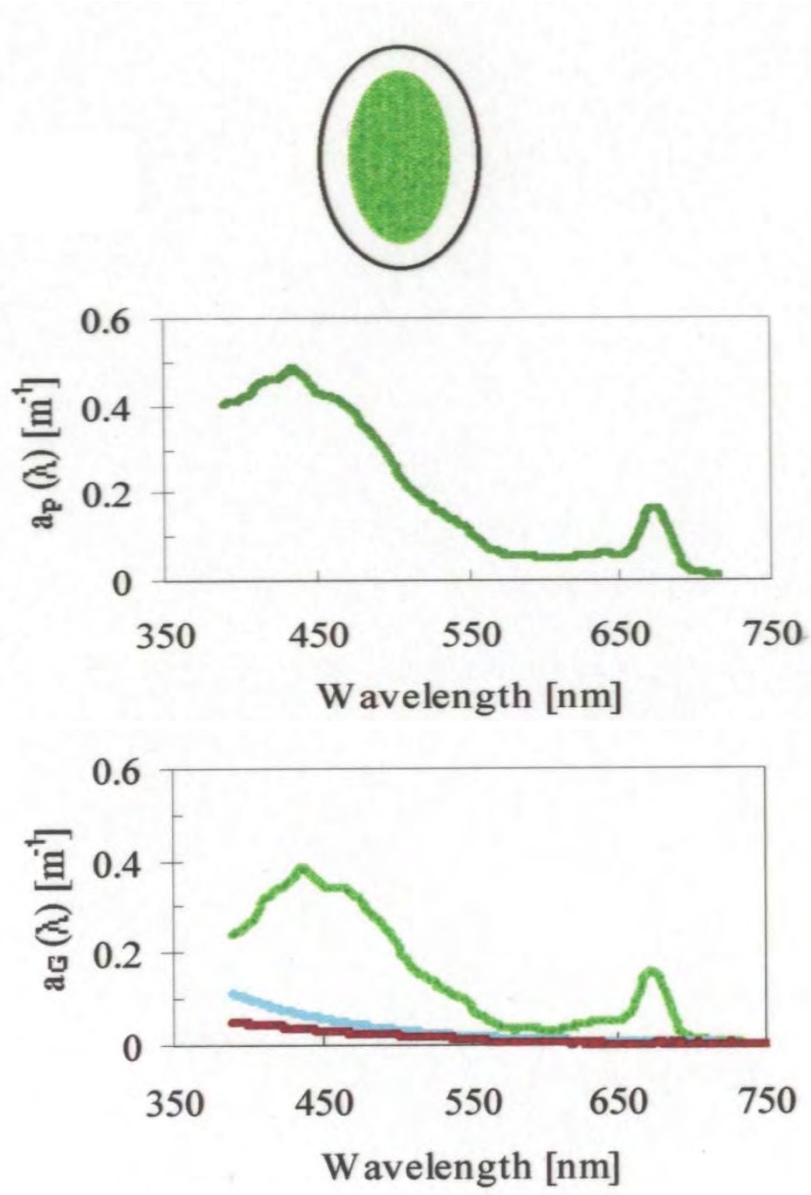


- Different V filtered for each sample (100ml vs 1000ml)
- $OD_{sample1}=OD_{sample2}$ (~0.1)
- $\sigma_{ODfilter\ blank}$~10%OD_{sample}

Better to **filter more volume** and obtain **higher OD_{sample}** relative to blanks

Partitioning of particulate absorption

- First scan is total particles, a_p
- Extract with methanol and scan again, a_{nap}
- $a_{phyt} = a_p - a_{nap}$
- 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
  - Geometric pathlength
  - Pathlength amplification (optical pathlength)
  - Absorption calculation, a_p and a_{nap}
  - 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

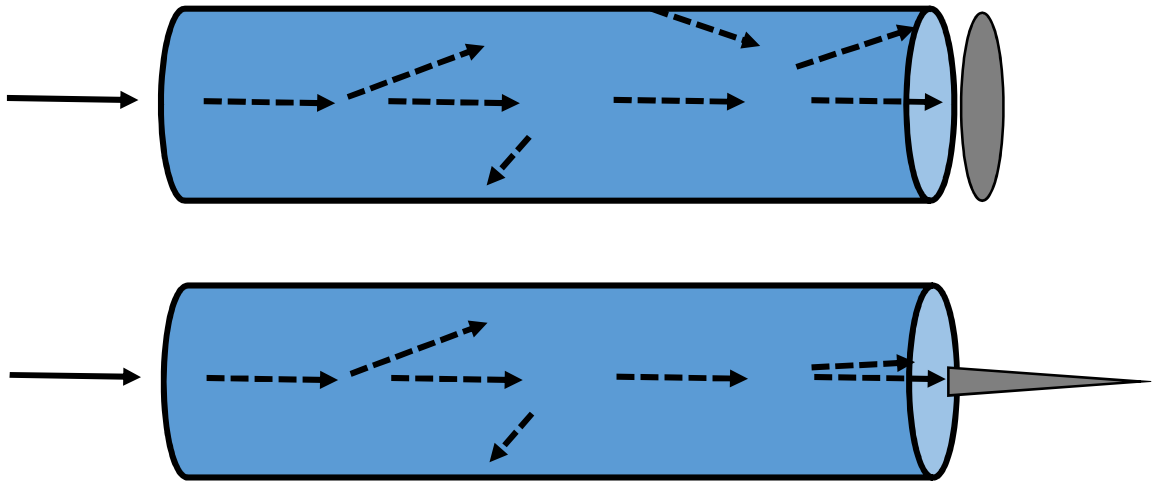
Bio-optical Sensors - Absorption

- Measurement Reality – Sensors
  - Reflecting tube absorption meters

a - Maximize scattered light collection
absorption

c – minimize scattered light collection
beam attenuation

b = c – a **scattering**



Some scattered light not collected by absorption tube, leads to overestimation of absorption →correction

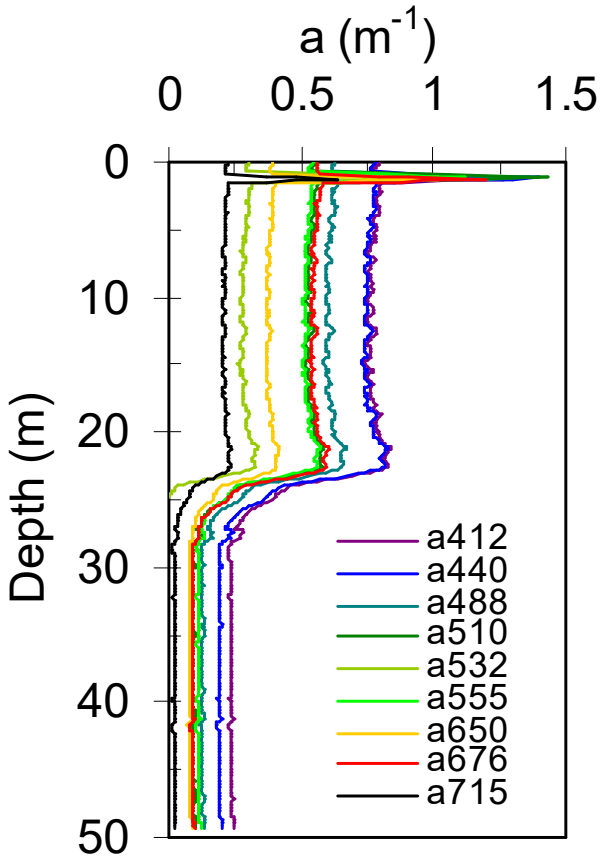
Some scattered light collected by attenuation tube, leads to underestimation of attenuation → report detection angle

Absorption from ac9/acs

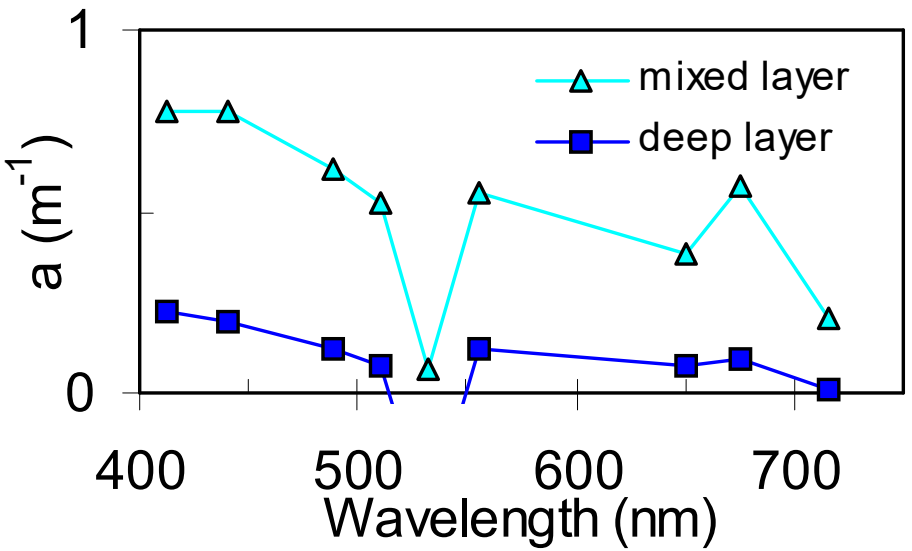
- Obtain from factory
- Calibrate* in the lab
- Place in deployment configuration
  - Black tubing
  - Copper tubing
  - Air valve
  - Seat bottom
  - Bracket top
- Calibrate* on the frame
- Deploy
  - Take to depth to purge
  - Remove upcast observations (pump inversion)
- Calibrate* upon recovery

*water calibration for quantitation
air calibration to track instrument drift

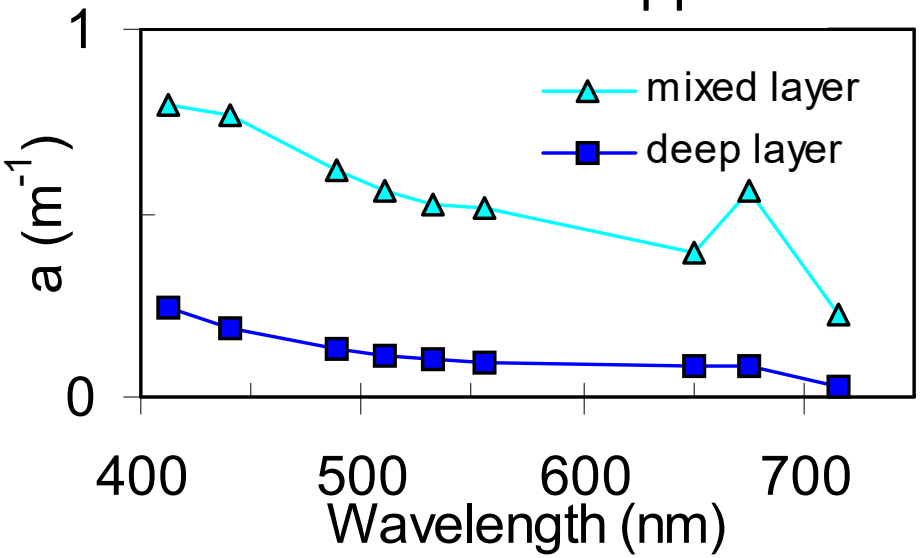
Absorption from ac9 (acs same)



But spectra are problematic



water calibration applied



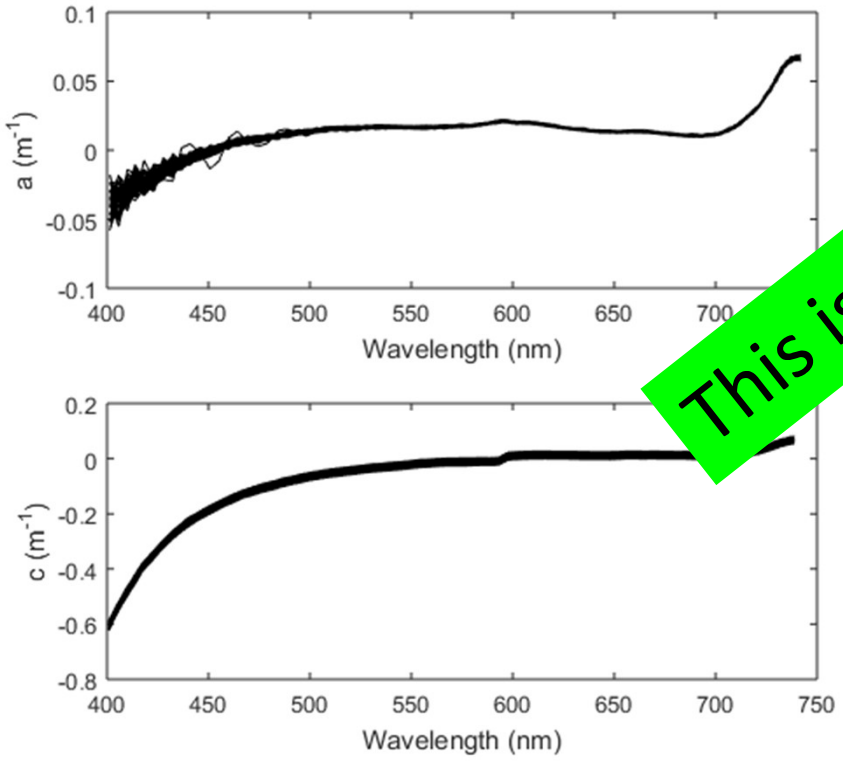
1. Pure water calibration

   $a = a_{meas} - a_{H20}$

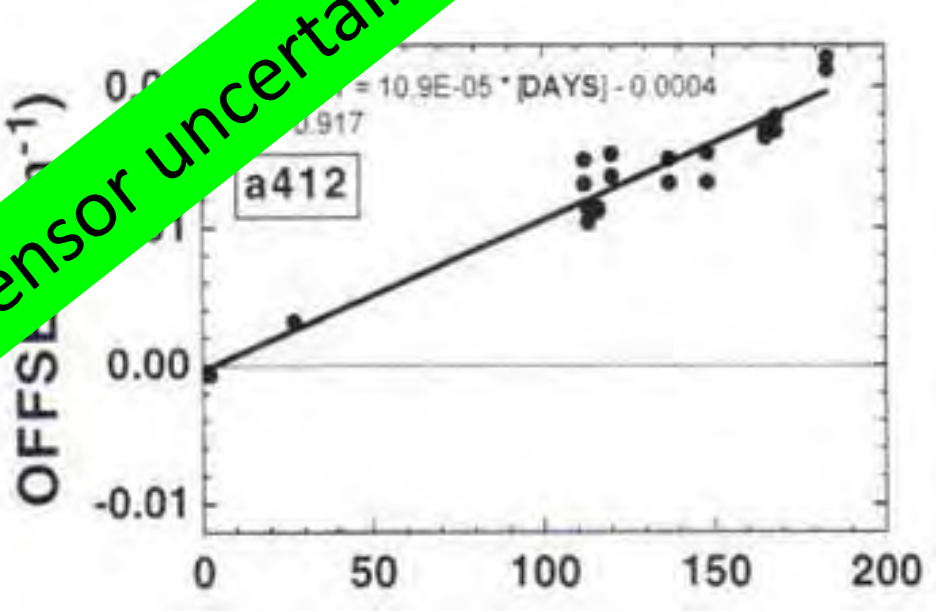
Roesler and Boss 2008

Bio-optical Sensors - Absorption

- Data Analysis and Interpretation – acs example
  1. Measure pure water scans



This is sensor uncertainty



Twardowski et al, 1997
(true for a and c)

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**

Temperature

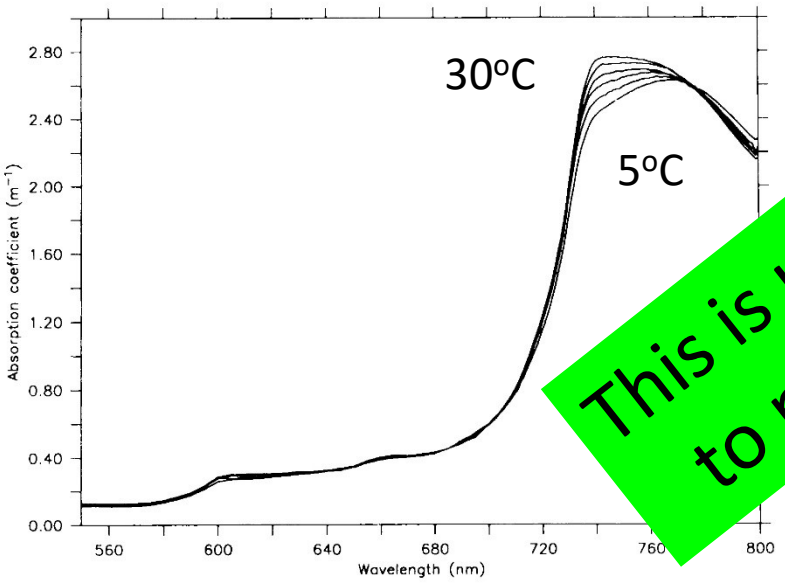
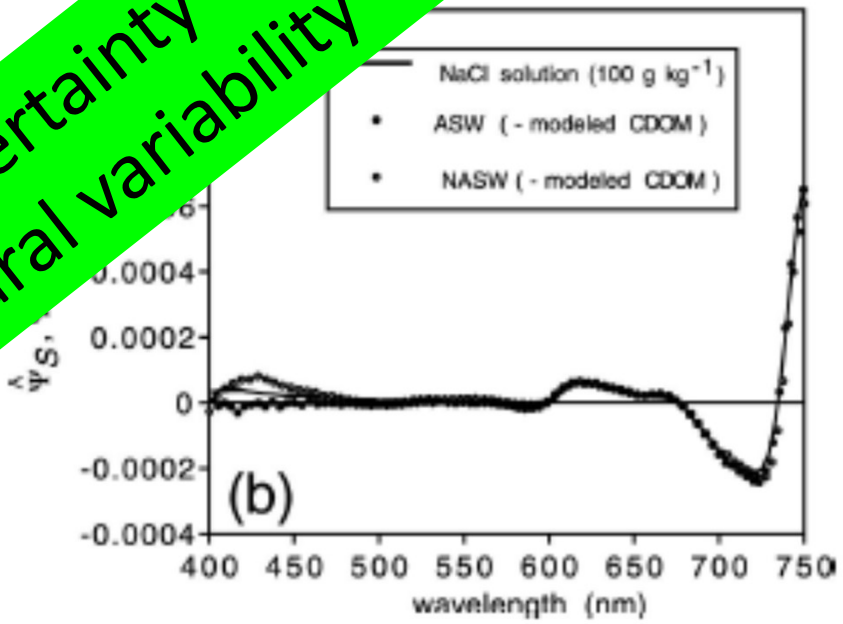


Fig. 3. Absorption coefficient from 550 to 800 nm adjusted at 685 nm to the value of Tam and Patel (1979). The curves represent absorption at temperatures of 5, 10, 15, 21, 25, and 30°C as read from bottom to top at 750 nm.

Pegau and Zaneveld 1993 Limnol Oceanogr.
Pegau et al. 1997 Applied Optics

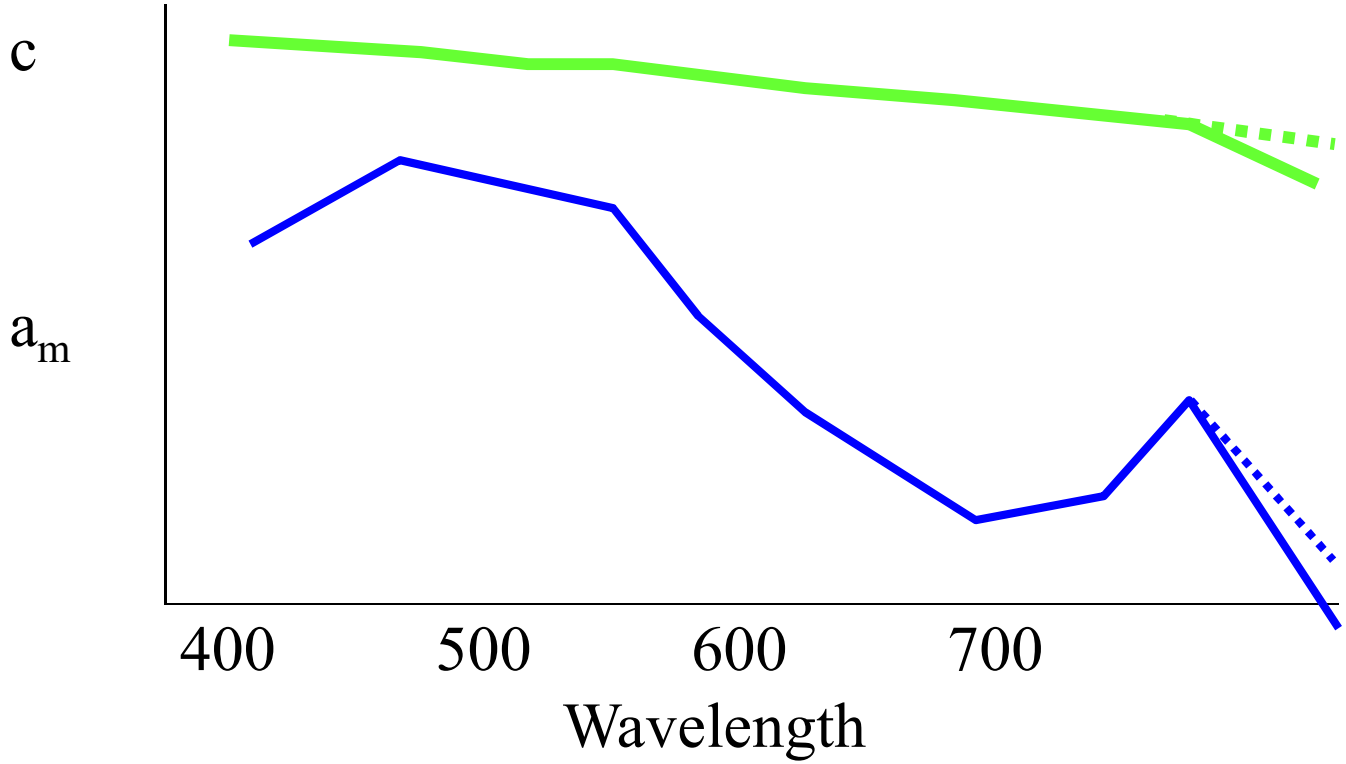
Sa

This is uncertainty due to natural variability



Sullivan et al. 2006 Applied Optics

Absorption from ac9



2. Temperature and salinity correction

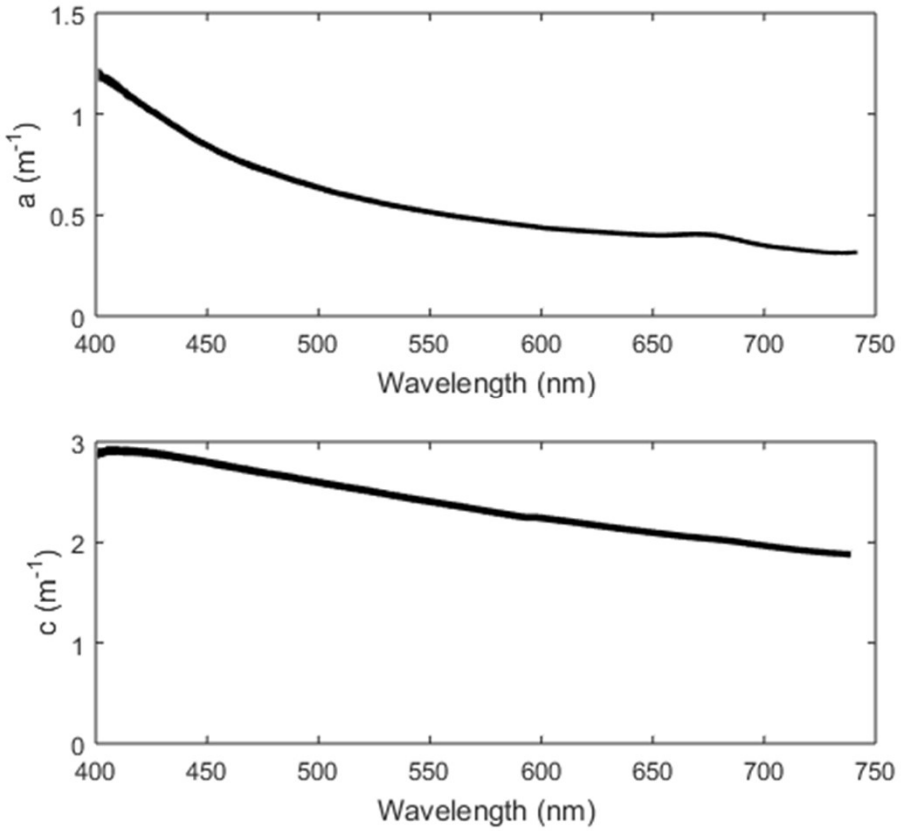
This is due to the fact that the in situ T and S are different than that of the calibration water

→ Requires measurement of T, S in situ

Bio-optical Sensors - Absorption

- Data Analysis and Interpretation – acs example
  - Collect sample scans

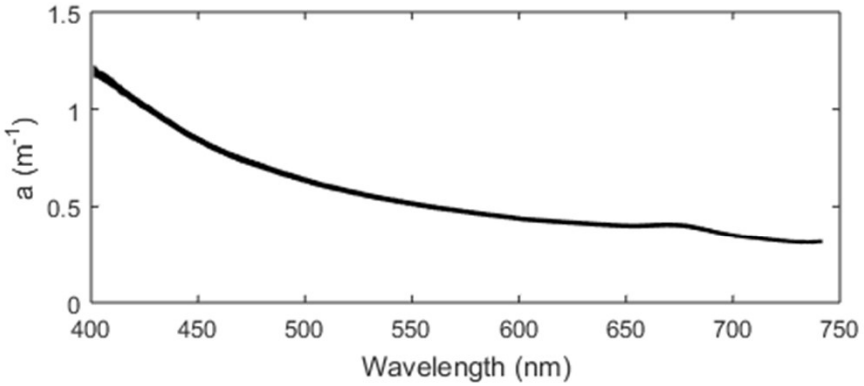
  1. correct for T, S

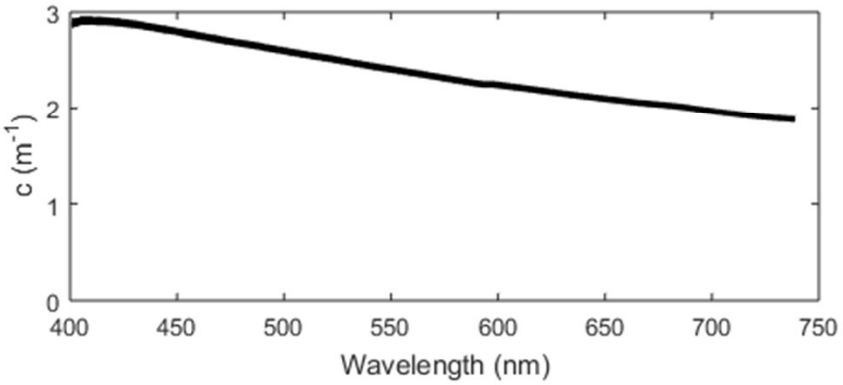


Bio-optical Sensors - Absorption

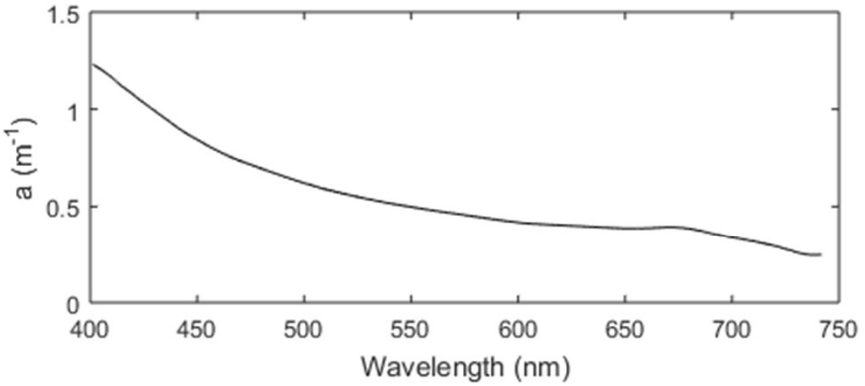
- Data Analysis and Interpretation – acs example
  2. Correct sample scans for pure water values (T, S corr)

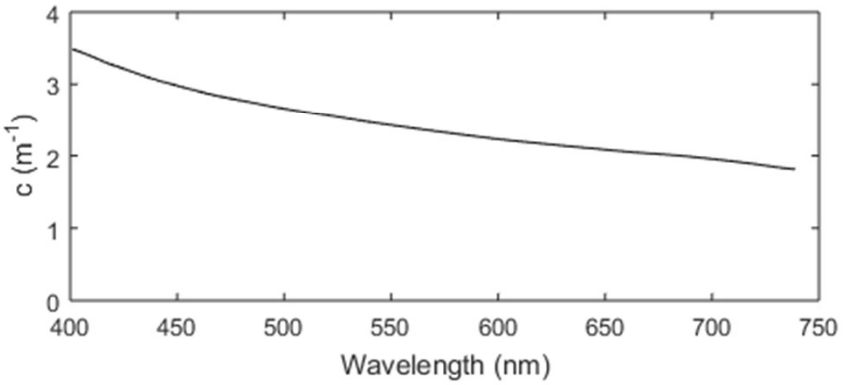
sample scan





corrected for pure water

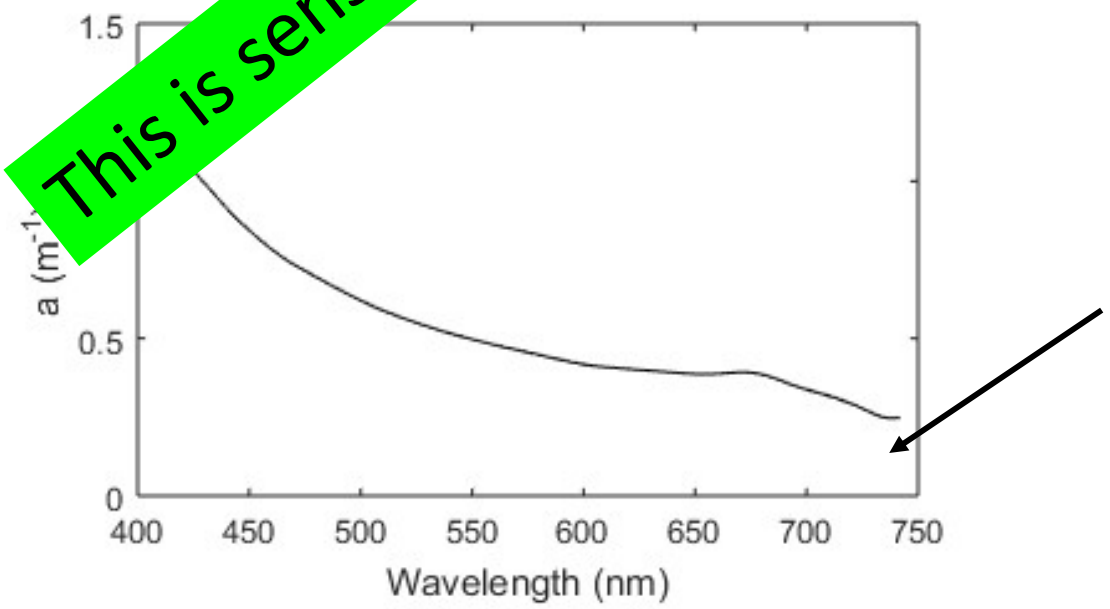




Bio-optical Sensors - Absorption

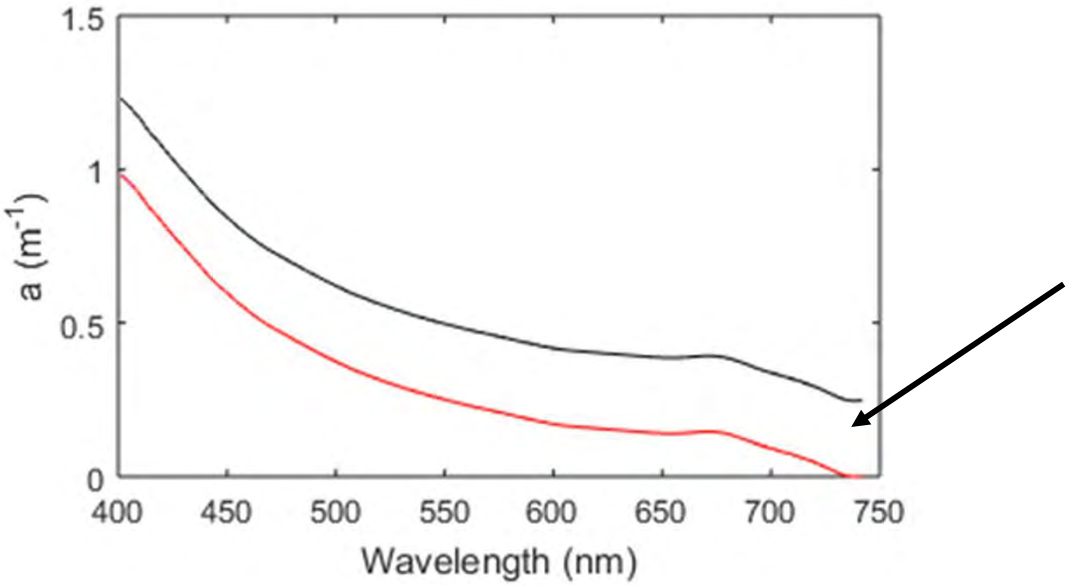
- Data Analysis and Interpretation – acs example
  - 3. Scattering correct the absorption spectra
    - find wavelength where absorption is negli
    - → measured *a* is actually **scattering e**
    - ***if*** T and S have been accurately co or

This is sensor uncertainty



Bio-optical Sensors - Absorption

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



Stramski and Babin 2002

Bio-optical Sensors - Absorption

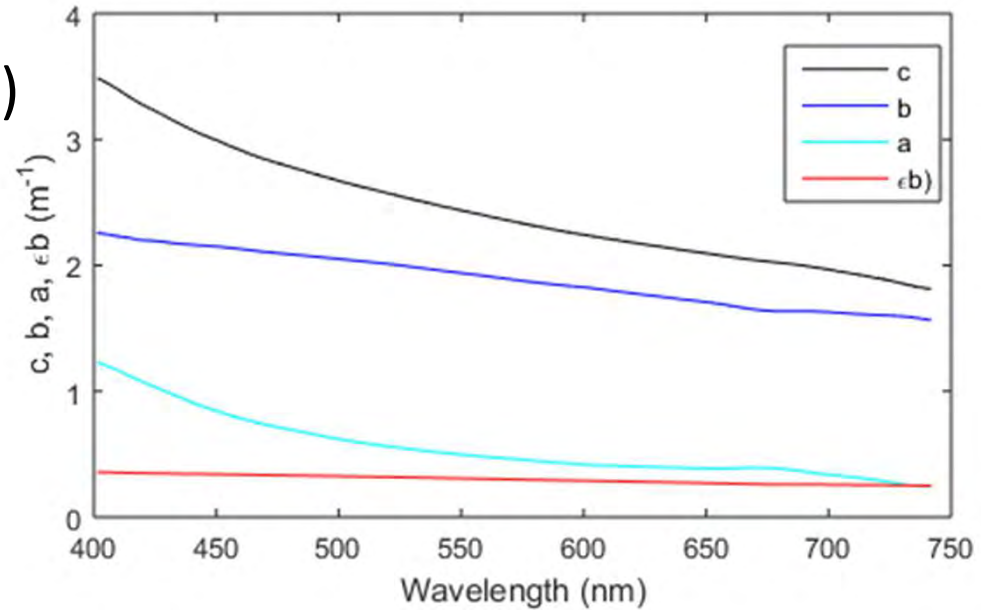
- Data Analysis and Interpretation – acs example
  - 3. Scattering correct the absorption spectra
    - b. Subtract spectral scattering contribution, fraction of b(λ)

      b(λ) = c(λ) – a(λ)

      if a(NIR) = 0 signal is due to scattering

      *f*b(λ) = a(NIR)/b(NIR)

$a_{corr}(\lambda) = a(\lambda) - (f b(\lambda) * b(\lambda))$

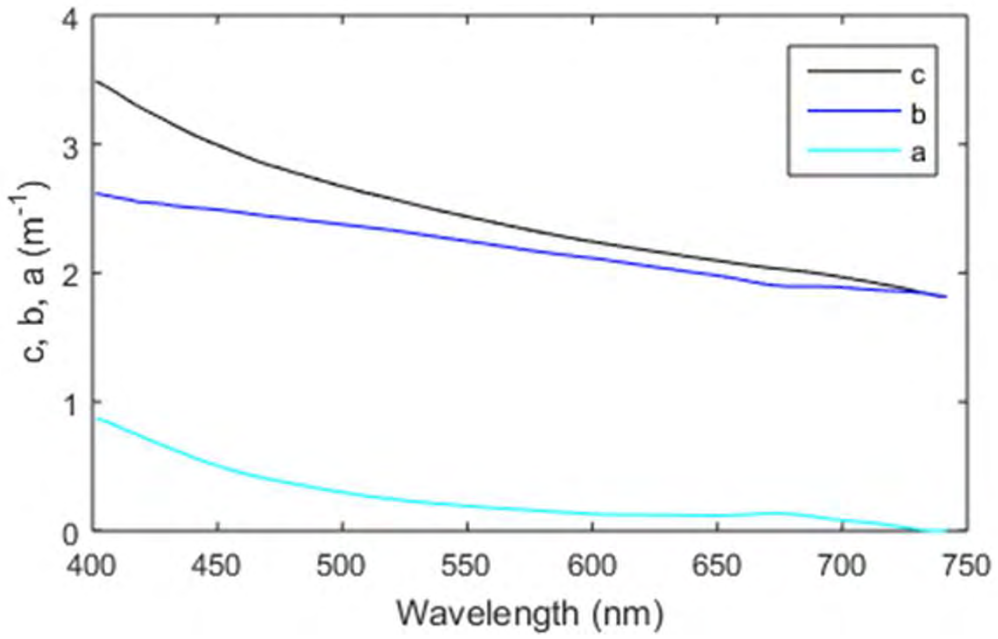


Roesler and Zaneveld 1993

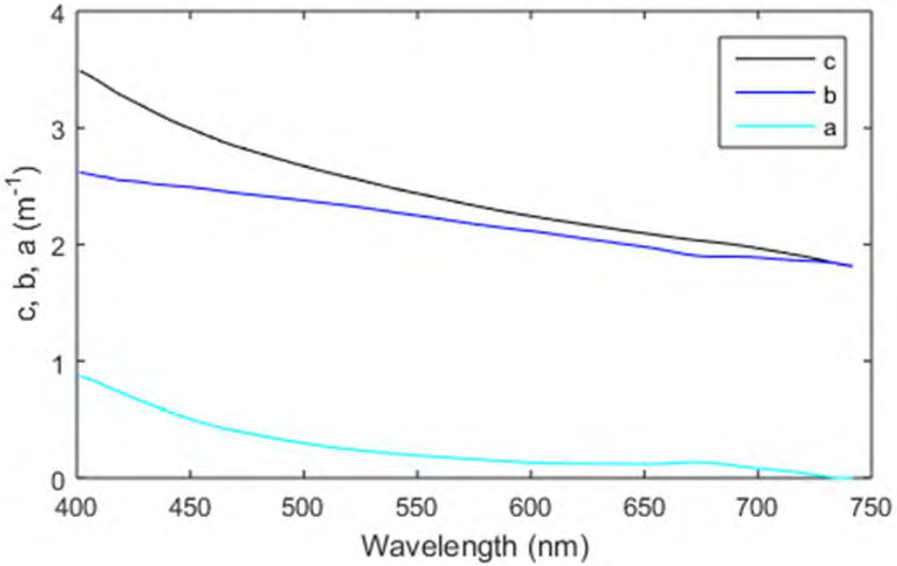
Bio-optical Sensors - Absorption

- Data Analysis and Interpretation – acs example
  4. Compute Scattering spectra

$$b(\lambda) = c(\lambda) - a(\lambda)$$



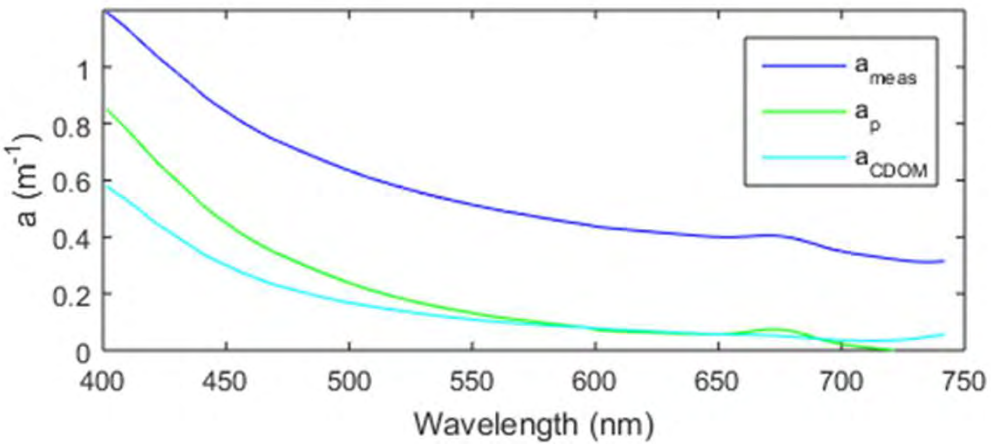
Best practices for obtaining Absorption/Attenuation from acs



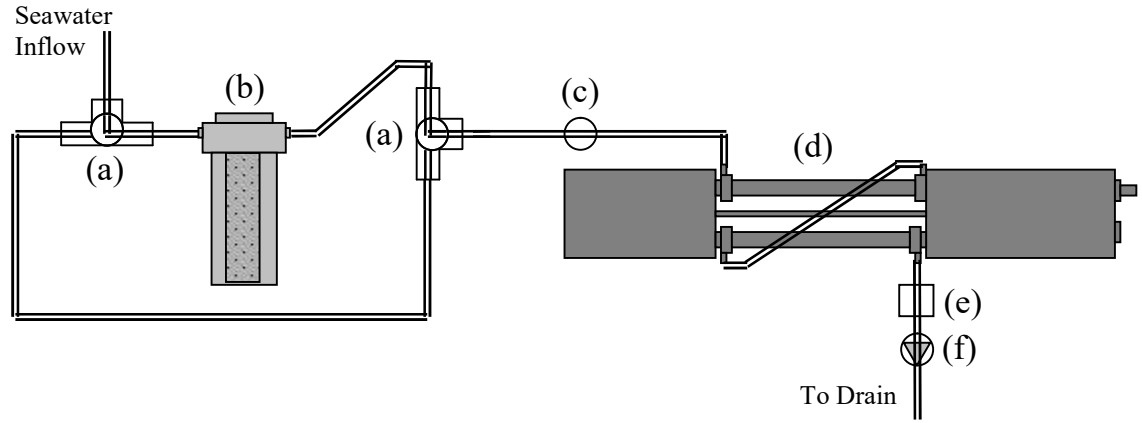
- Review Data processing
  - Temperature/Salinity correct a and c of sample and calibration data
  - Subtract T,S-corrected pure water calibration from sample scans
  - Apply spectral scattering correction to absorption
  - Compute scattering spectrum (b = c – a)

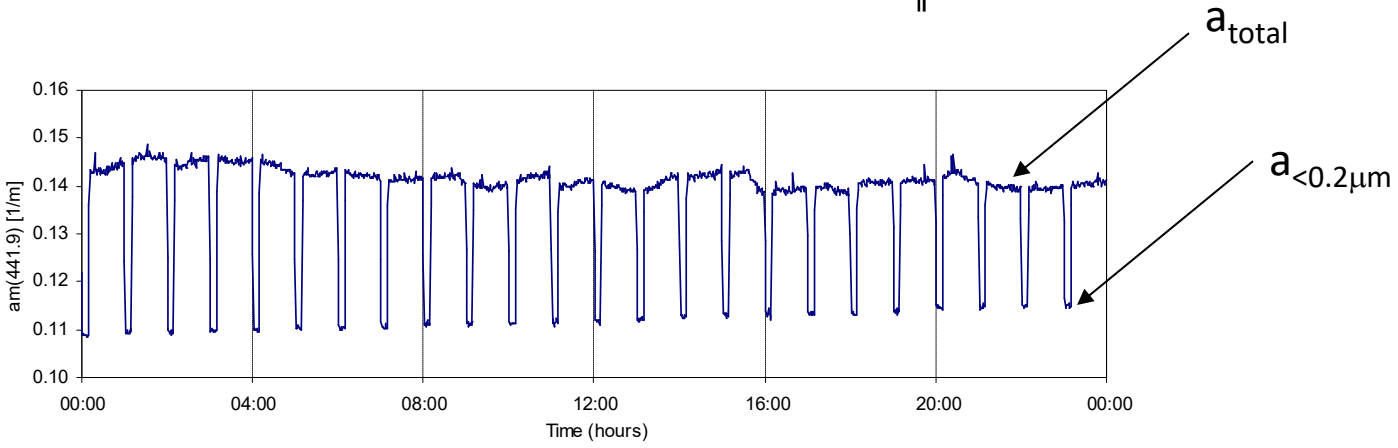
Bio-optical Sensors - Absorption

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



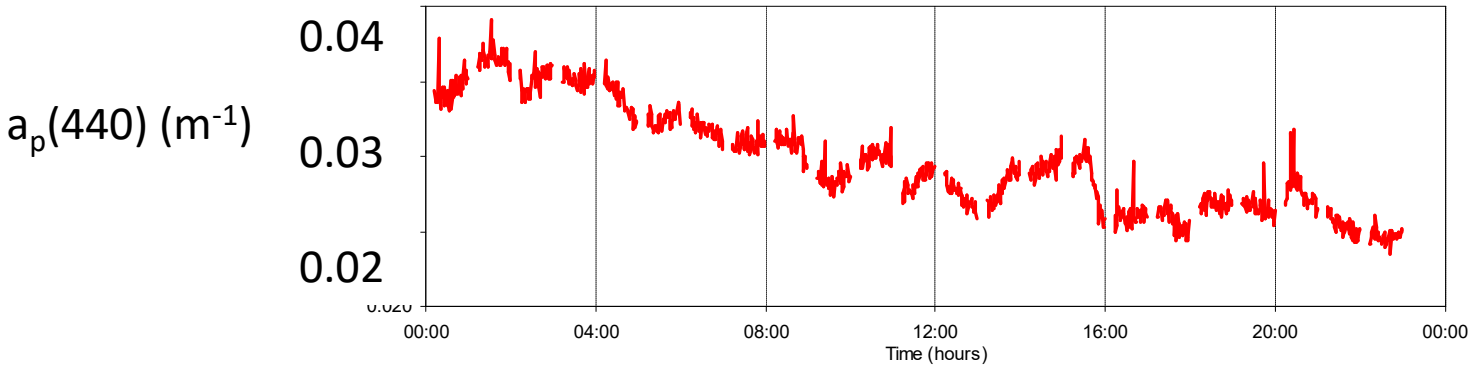
Automated shipboard flow-through method, calibration-independent

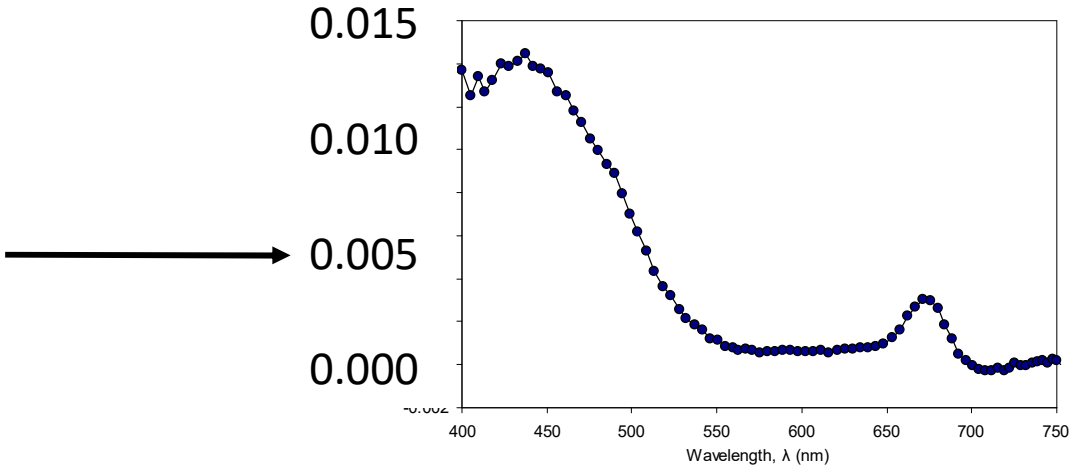




Slade et al., 2010

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





Slade et al., 2010

Let’s go play in the lab!