Lecture 3
Absorption physics and absorbing materials

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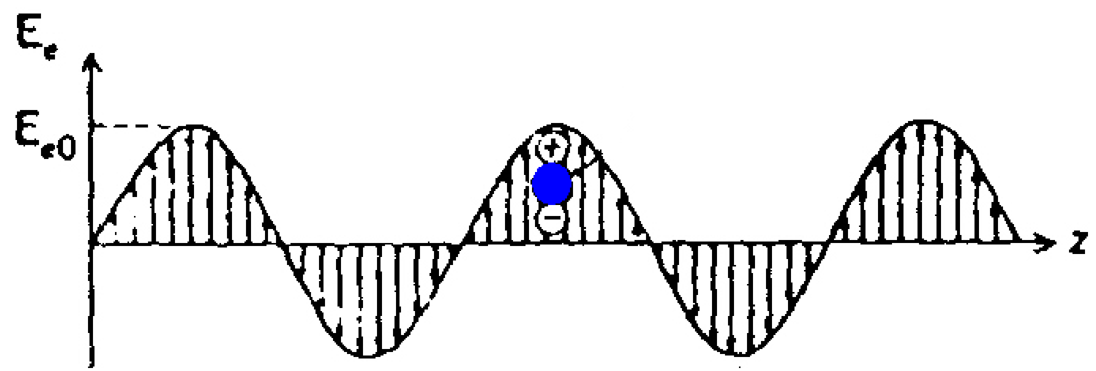
10 July 2017

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?

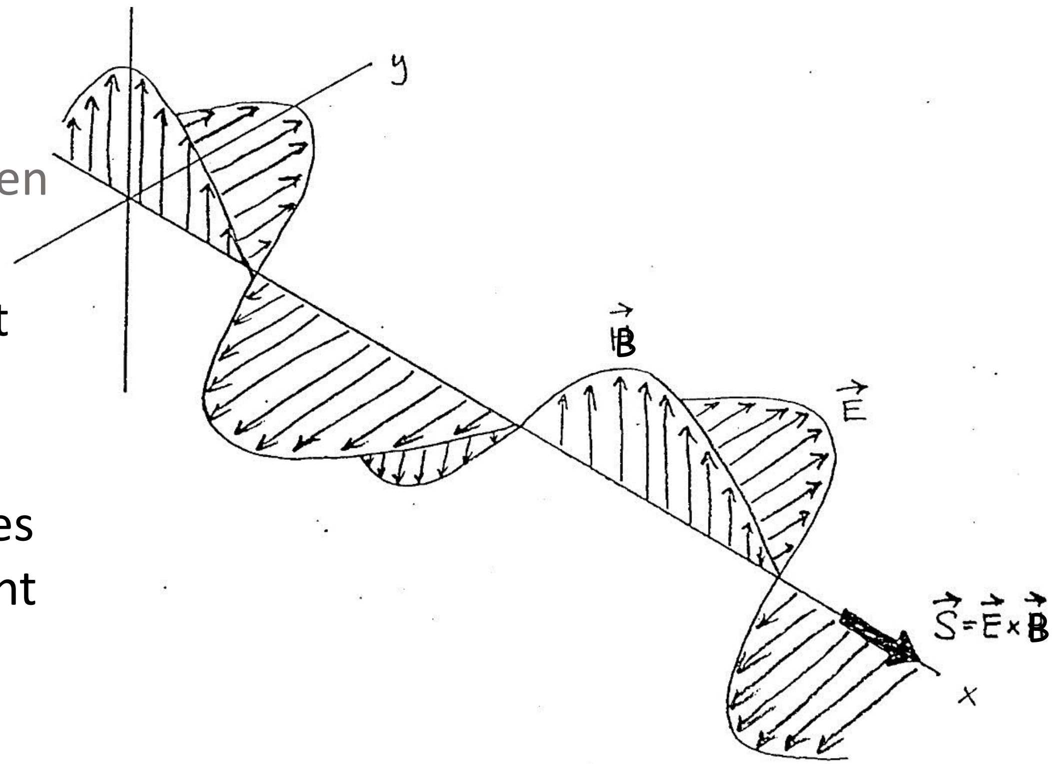
Electromagnetic Radiation

- Charged particles (dipoles) create electric fields **E** (oscillation between +,-)



Electromagnetic Radiation

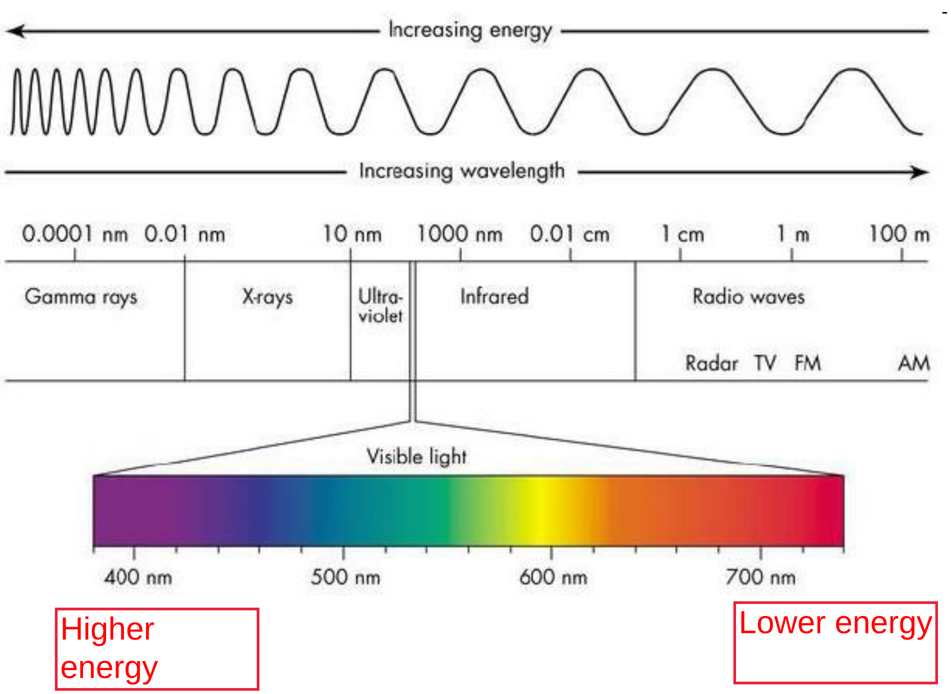
- Charged particles, dipoles, create electric fields **E** (oscillation between +,-)
- When a charged particle moves, it creates a magnetic field, **B** (or H depending on book)
- The electromagnetic field oscillates as the energy propagates **E**x**B** (right hand rule)



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 **ExB** (right hand rule)

- the range of oscillation frequencies is described by the EM spectrum

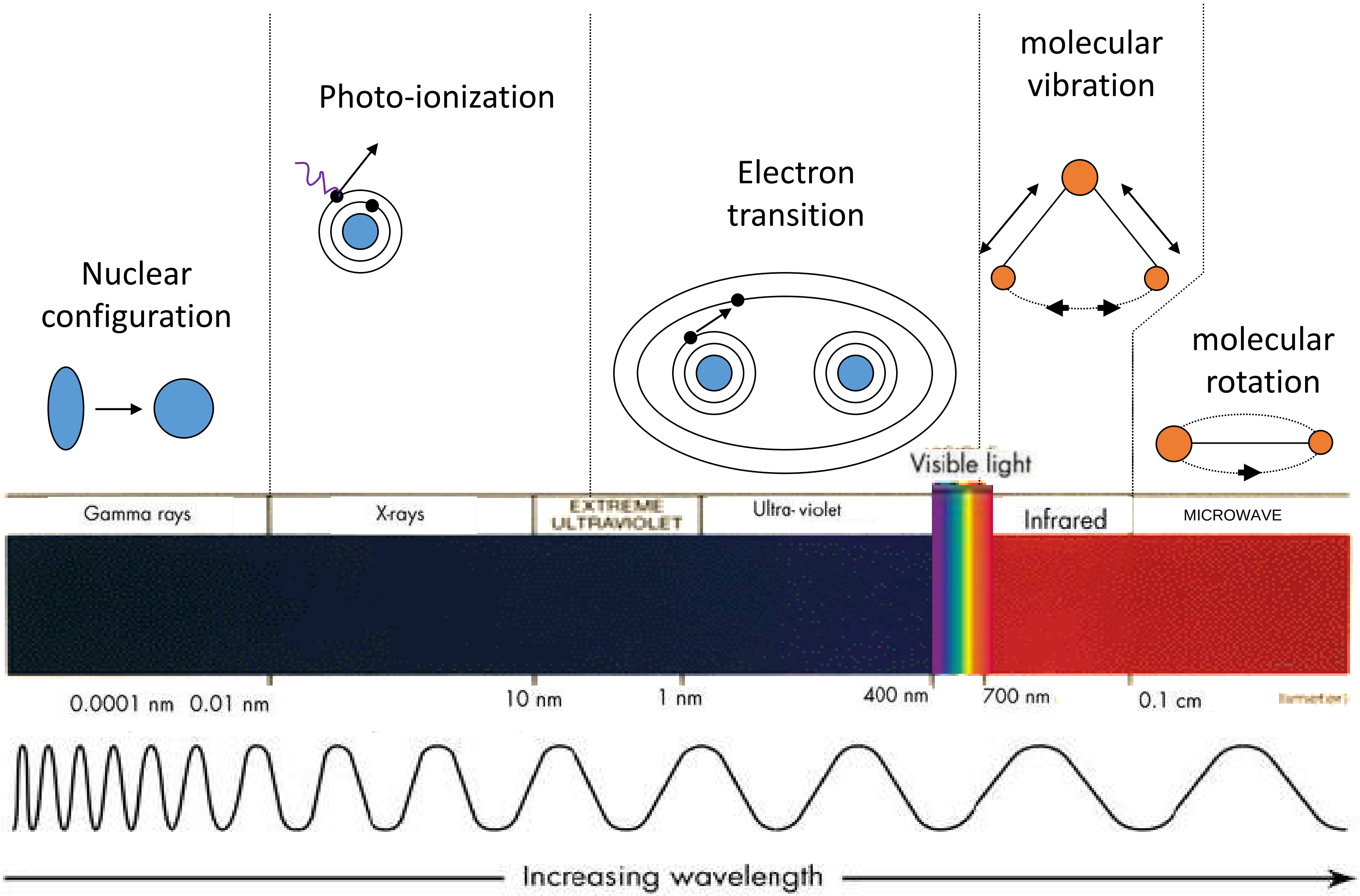


http://www.antonine-education.co.uk/physics_gcse

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

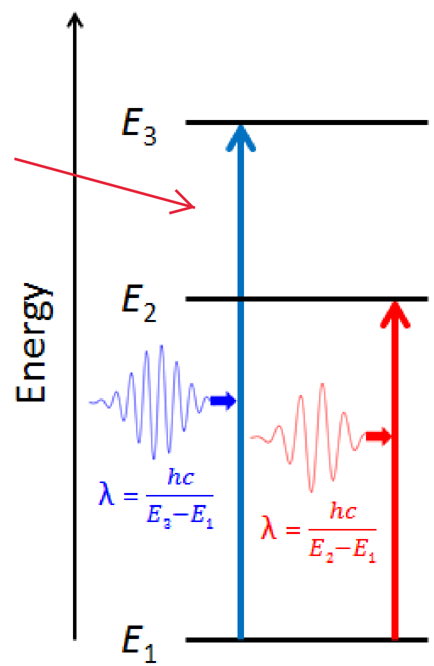
Interactions between energy and matter

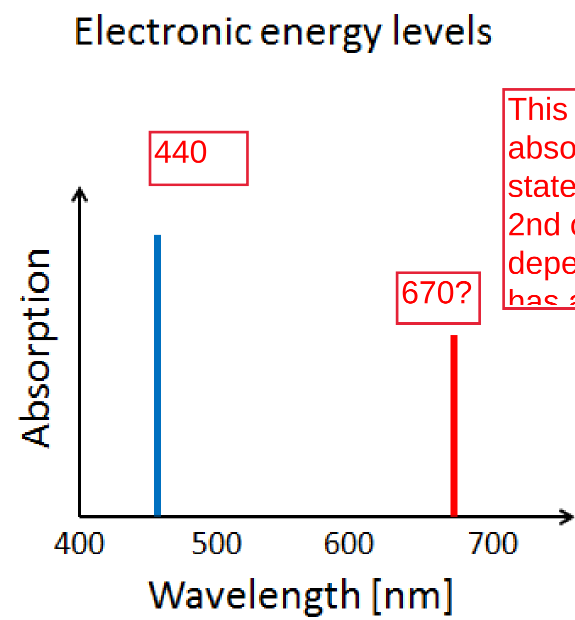


Quantized electronic states

- 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

allowable quantized energy difference



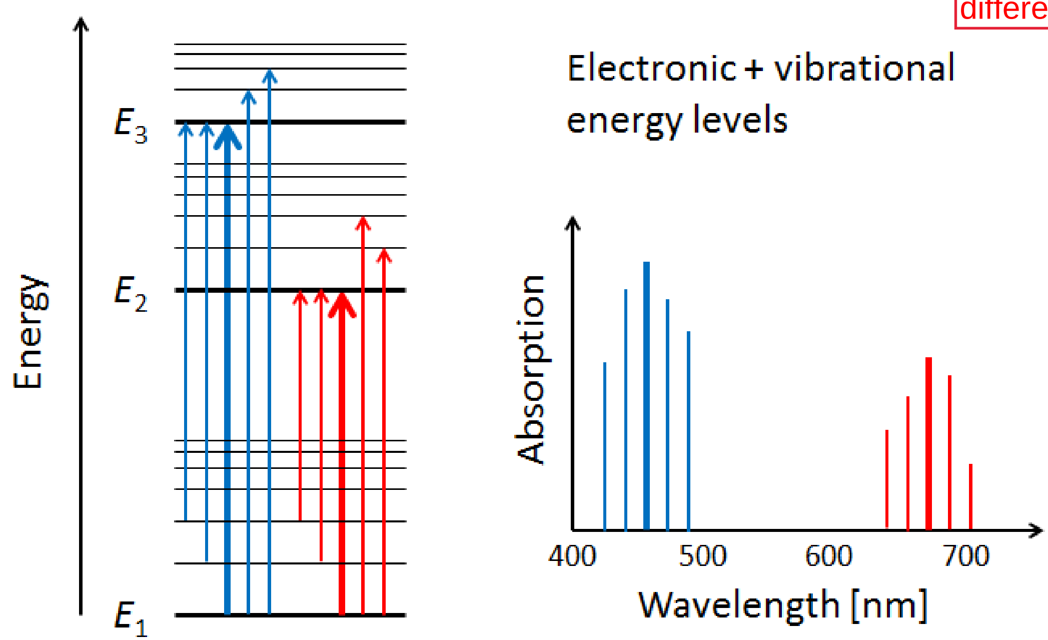


This is chlorophyll- it can absorb energy at two different states
2nd or 3rd electronic state depending on which energy it has absorbed

Quantized vibrational states

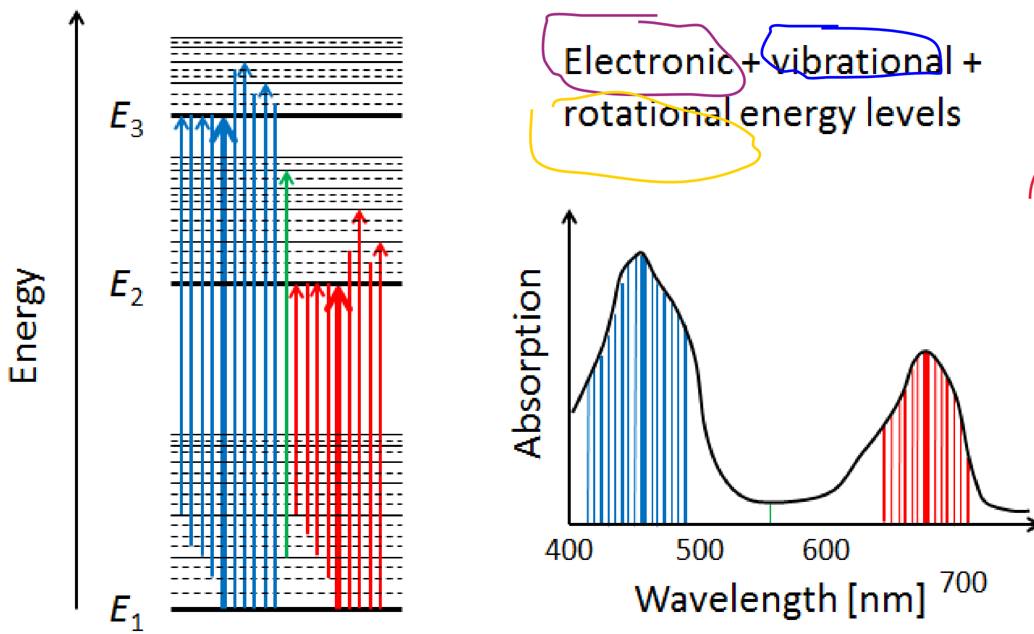
- Each orbital shell is associated with a series of higher excited states, associated with vibrational energy, which are also quantized
- These determine the wavelengths of the absorption side peaks which are higher (lower) energy but have a lower probability for absorption

Those curves are the vibrational levels with the different electron states.

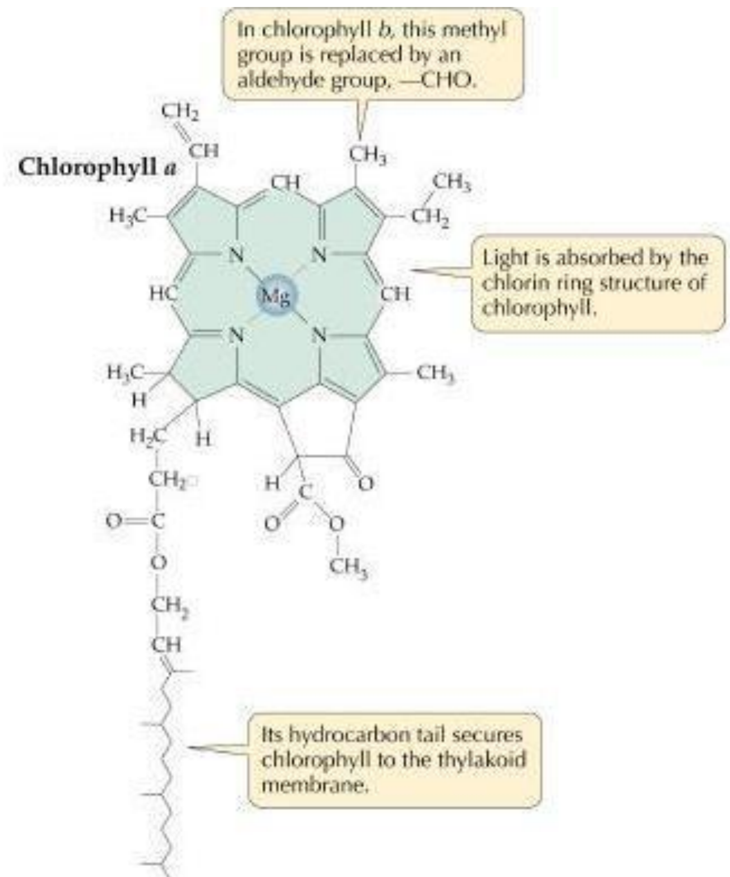


Quantized rotational states

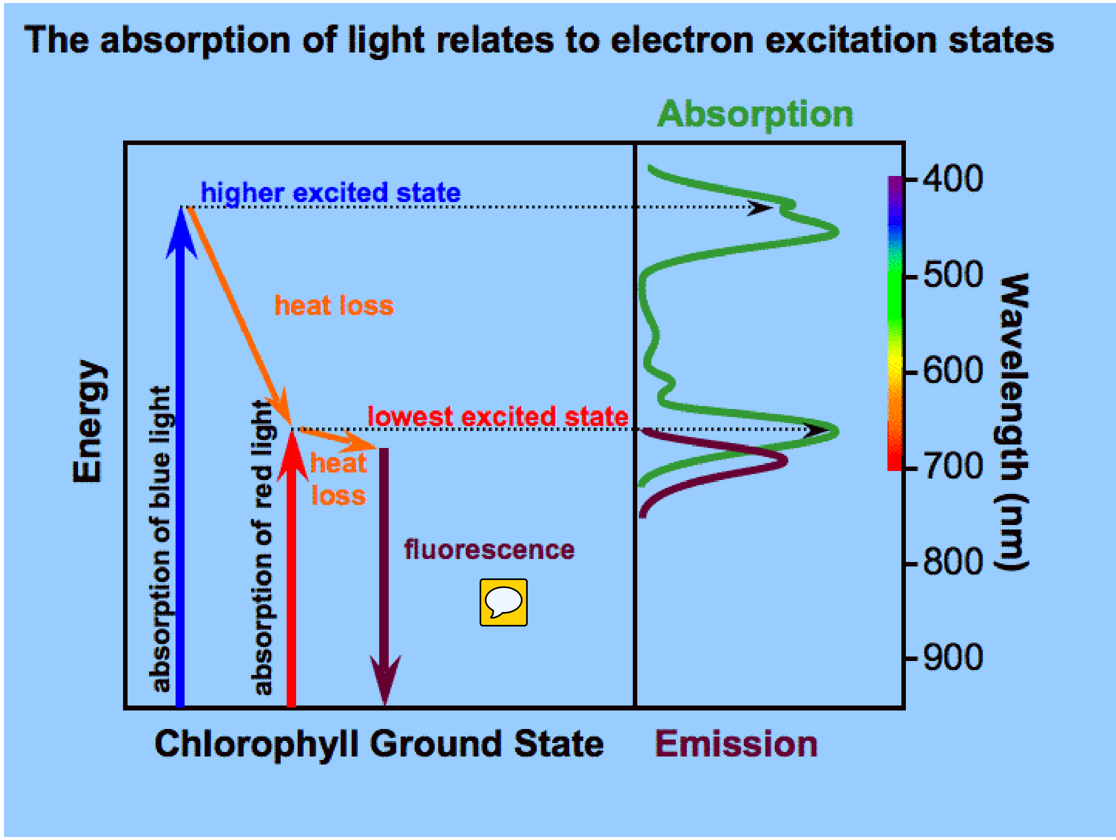
- Each vibrational state is associated with a series of higher rotational states, which are also quantized
- These determine the wavelengths of the absorption that smooth the absorption peaks



Chlorophyll *a* has two electronic states associated with the energy equivalent of blue(443 nm) and red (676 nm) photons

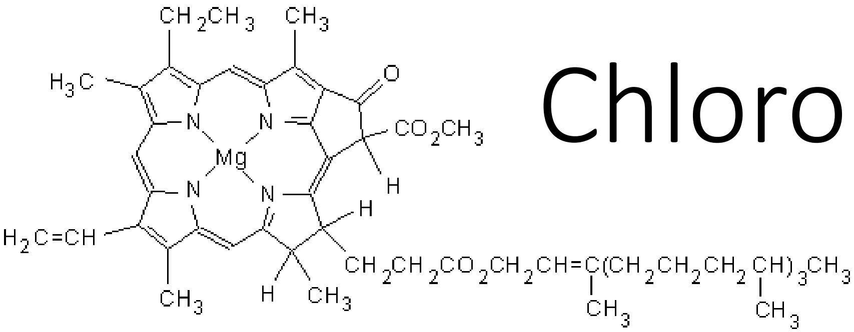


http://www.mie.utoronto.ca/labs



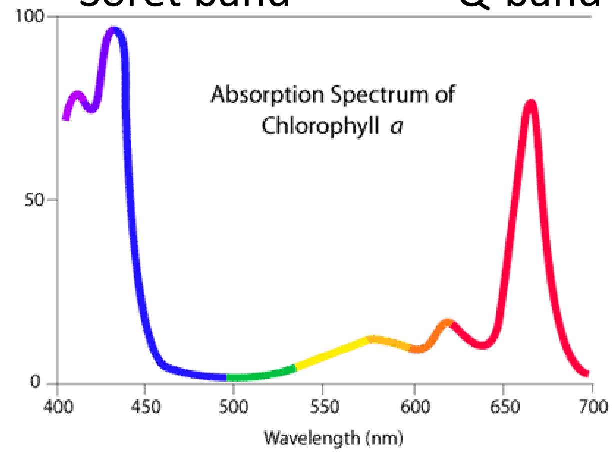
http://plantphys.info/plant_physiology/light.shtml

Chlorophyll *a*



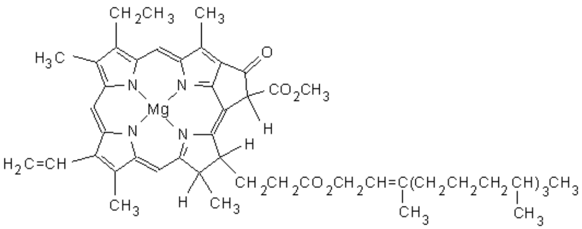
http://scifun.chem.wisc.edu/chemweek/chlrphyl/chlrphyl.gif

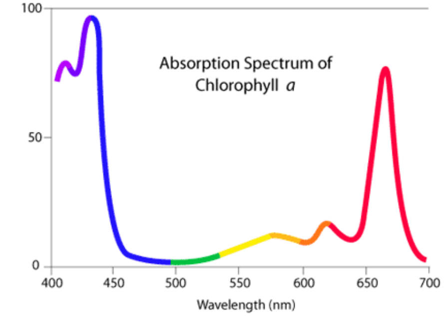
Soret band Q-band

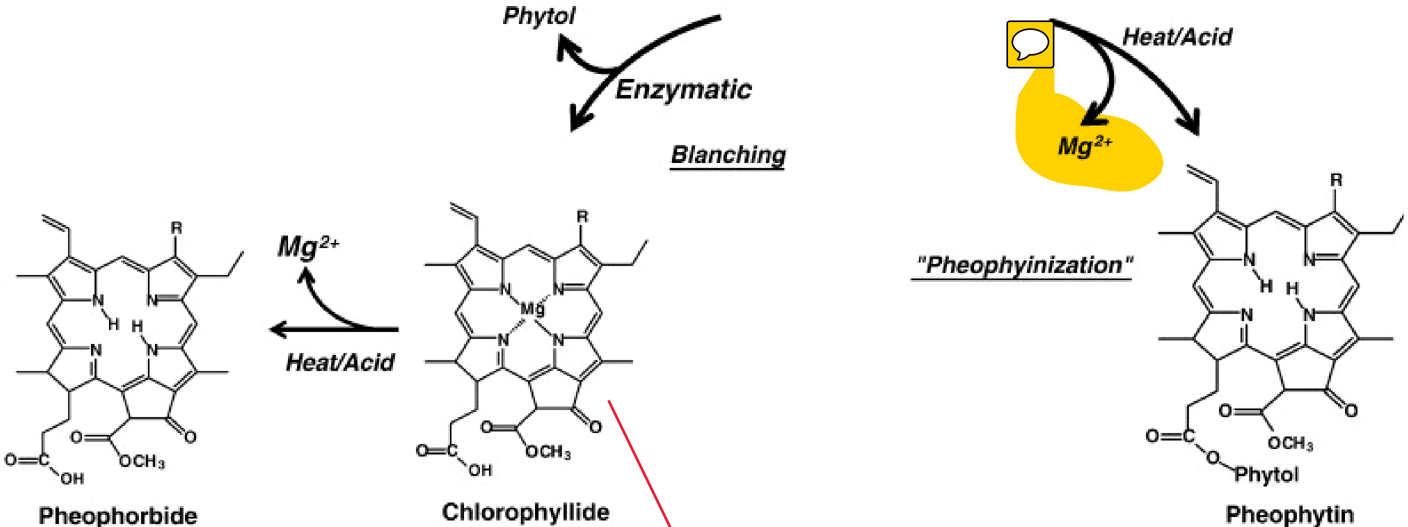


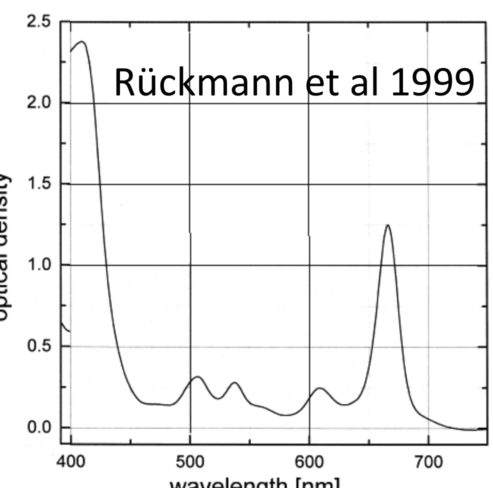
http://www.photochembgsu.com/assets/images/graph2.gif

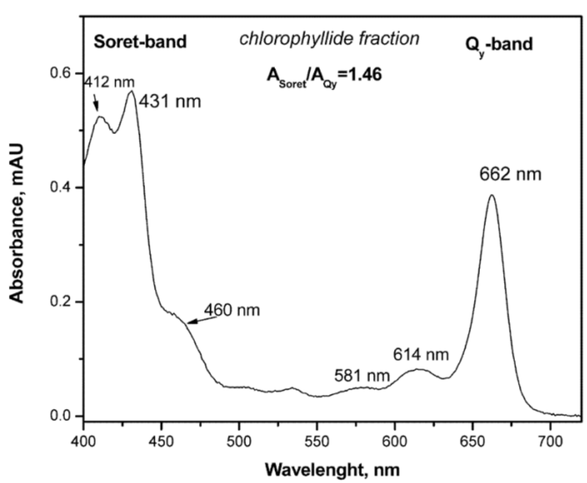
Chlorophyll

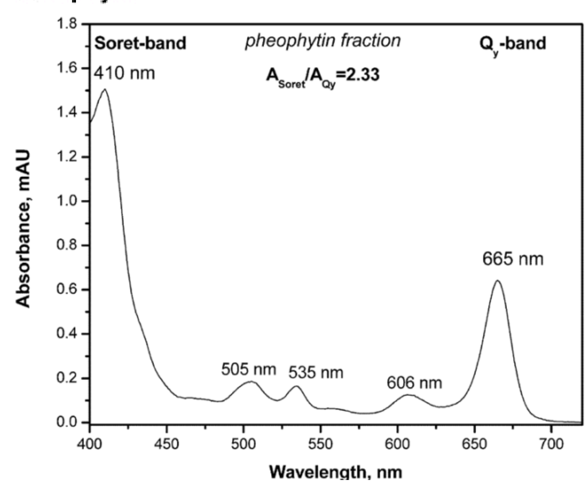










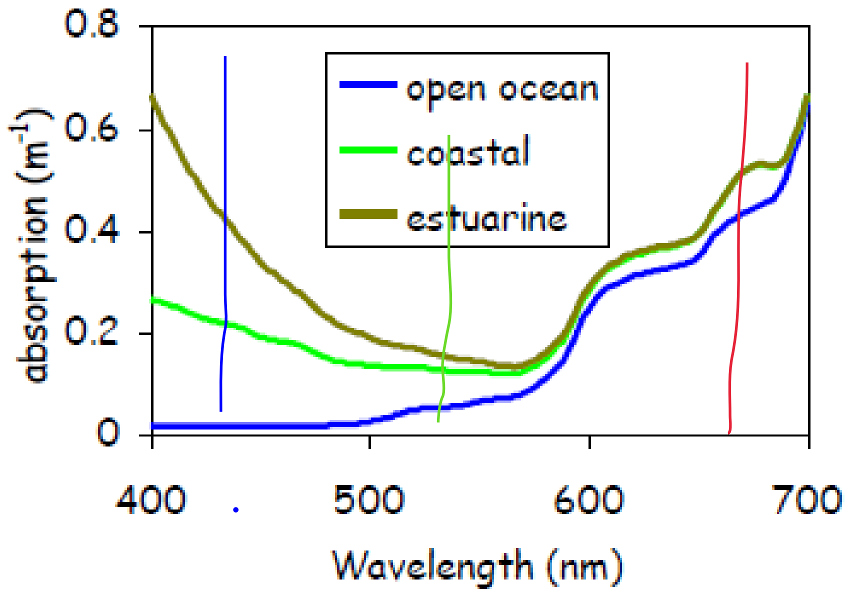


Milenković et al. 2012

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

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

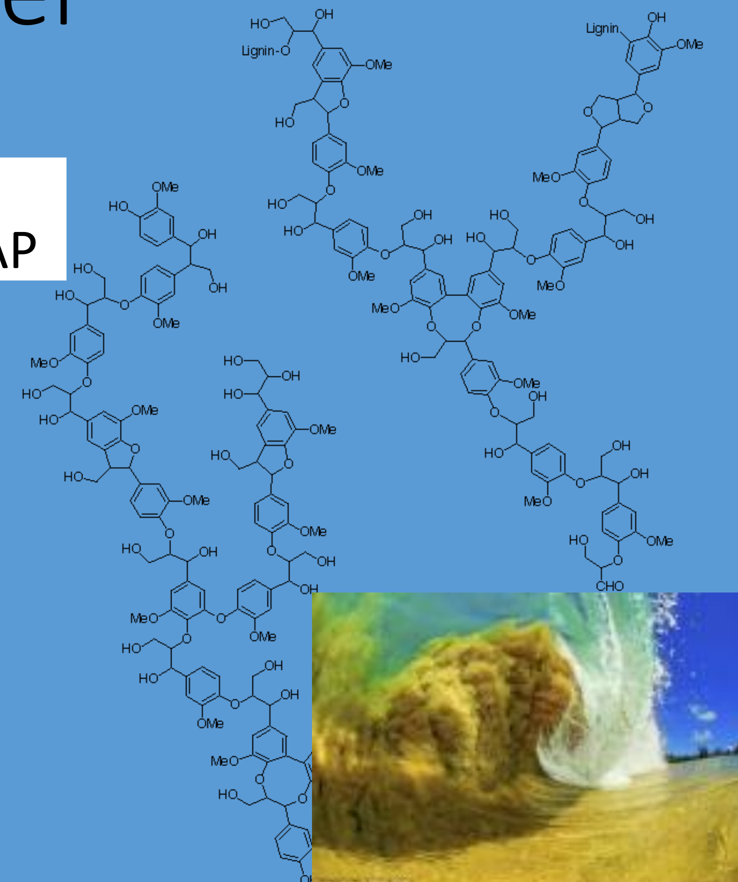
- Absorption is proportional to the concentration (Beer's Law)

$$a_{chl}(m^{-1}) = [chl](mg/m^3) * a^*_{chl}\ (m^2/mg)$$

It is impractical to measure absorption spectrum for each absorber

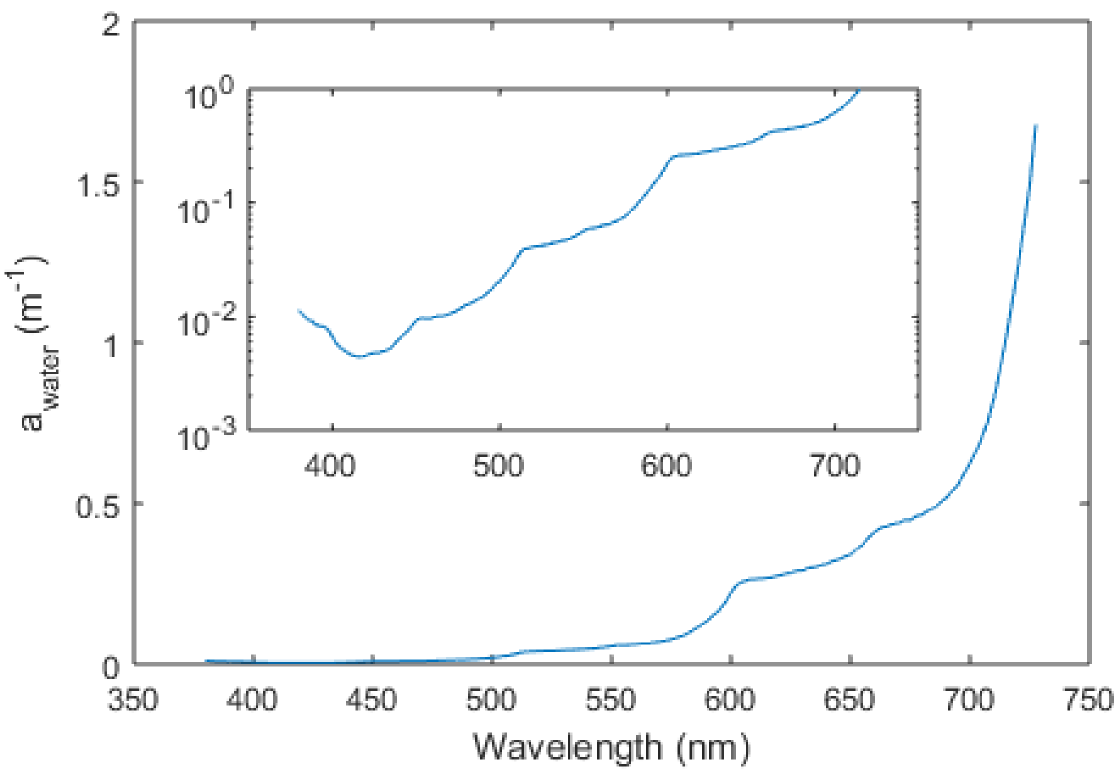
phytoplankton

$$a_T = a_w + a_{CDOM} + a_\phi + a_{NAP}$$



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

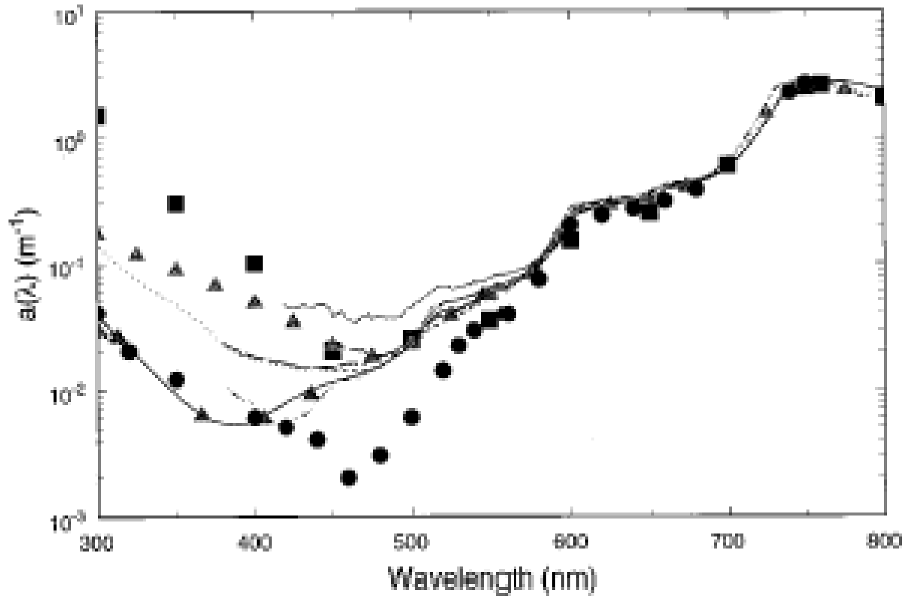


Fig. 1. Absorption coefficient of pure water as measured or compiled by several investigators.[1,2,11,18,19,21,26–33] The discrepancy in the estimated absorption coefficients is largest at short wavelengths where absorption by organic contaminants is significant. At wavelengths longer than 550 nm the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

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

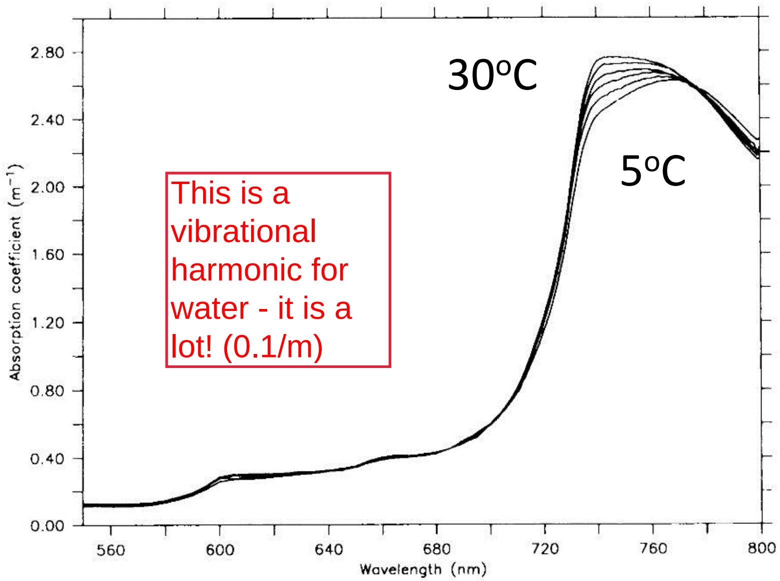
variations are **methodological**

This is important because we use "pure water" as a reference but the T of the sample and blank can also cause huge differences. Colder = more tight clusters, warmer = smaller clusters with fewer particles

Absorbing Components: Water

Absorption is lower when it is cold and higher when it is warm. It vibrates more when it is warmer which changes it ability to absorb quantized energy

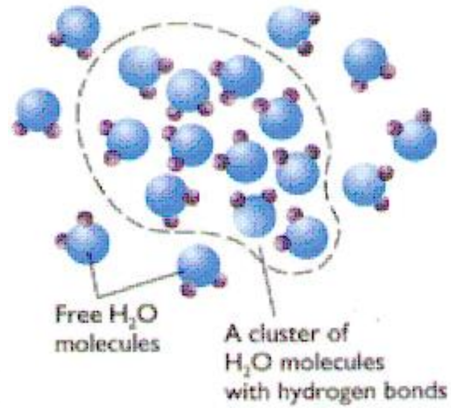
Temperature



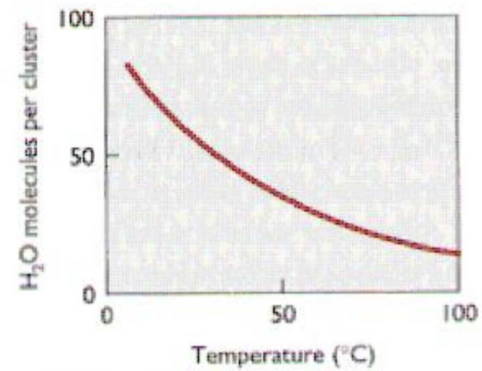
This is a vibrational harmonic for water - it is a lot! (0.1/m)

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.

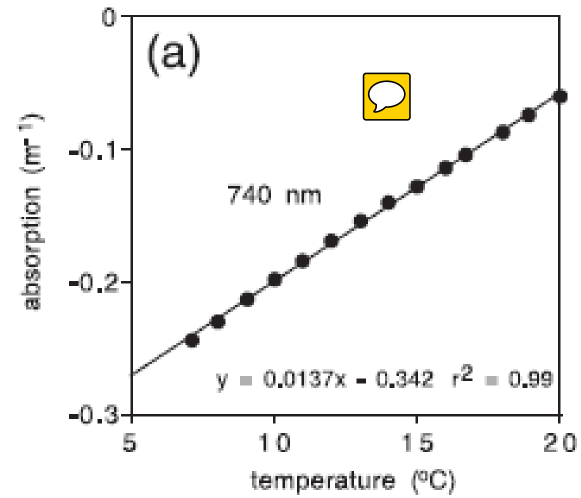
Pegau and Zaneveld 1993 Limnol Oceanogr.



(d) CLUSTERS OF WATER



(e) SIZE OF WATER CLUSTERS



natural variations

Sullivan et al. 2006 Appl Opt

Absorbing Components: Water

CDOM is everything that passes through a filter
But it isn't just organics, it is also inorganics:
Bromine, Hydrogen sulfate

Salinity

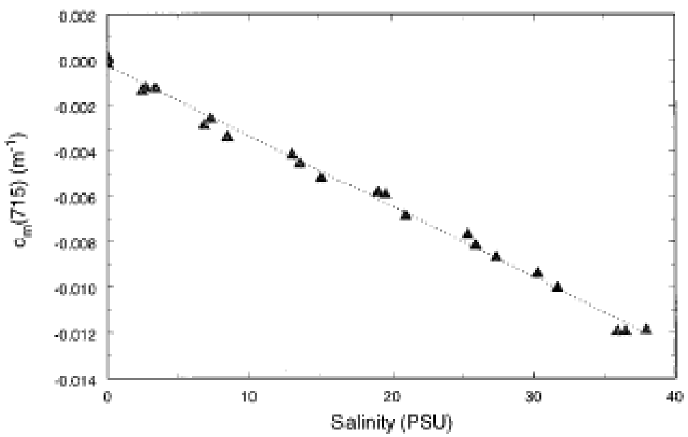
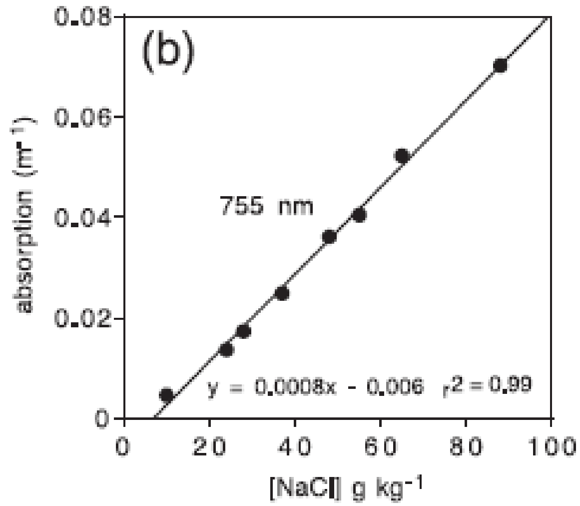
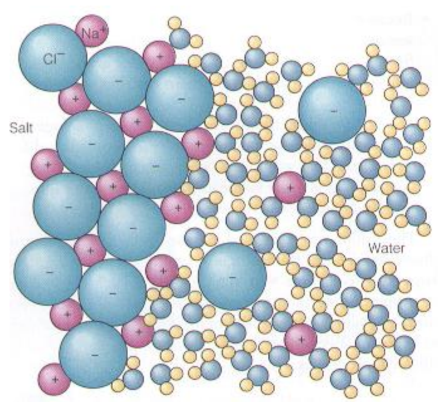


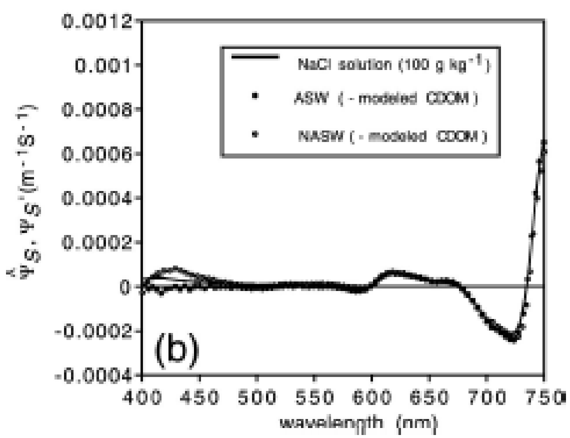
Fig. 6. Attenuation coefficient at 715 nm as a function of salinity. This figure illustrates the linear dependence of the attenuation coefficient on salinity.

Pegau etal. 1997 Appl.Opt.



Sullivan et al. 2006 Appl Opt



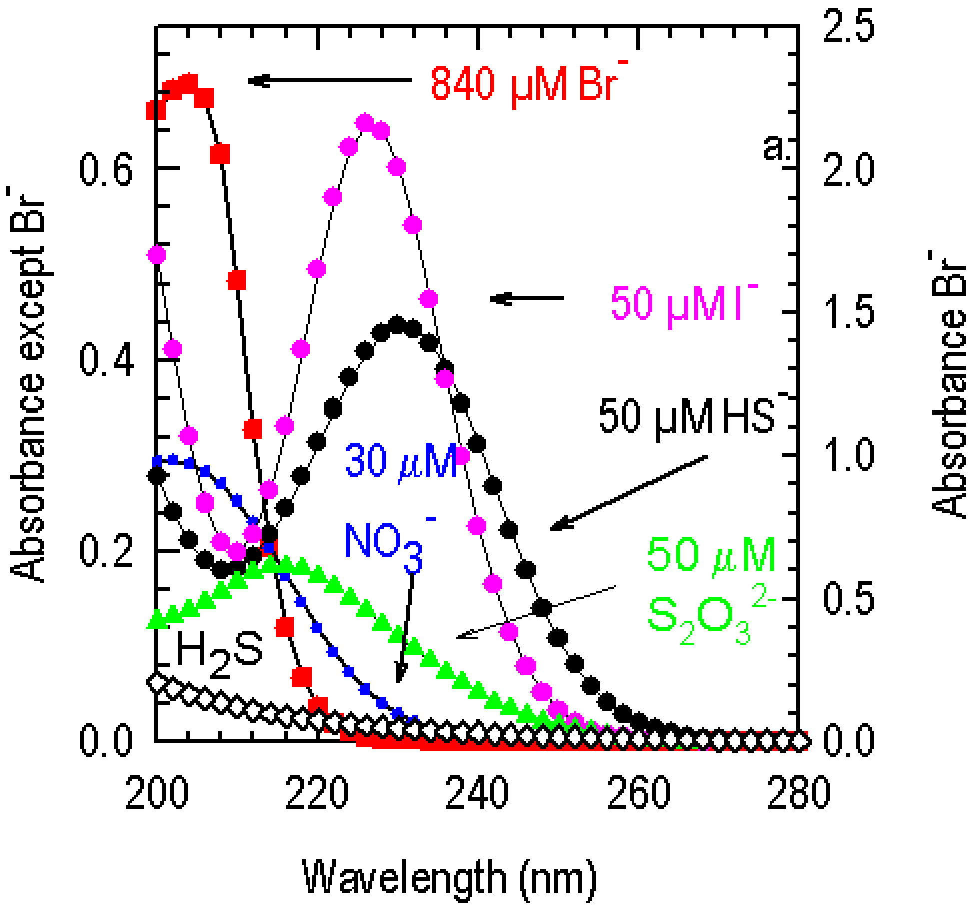


natural variations

Absorbing Components: Dissolved inorganic matter

- Basic for UV detection of nitrate, ISUS

- Johnson, K. S. and L. J. Coletti. 2002



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

Absorbing Components:
Colored dissolved organic matter (CDOM)

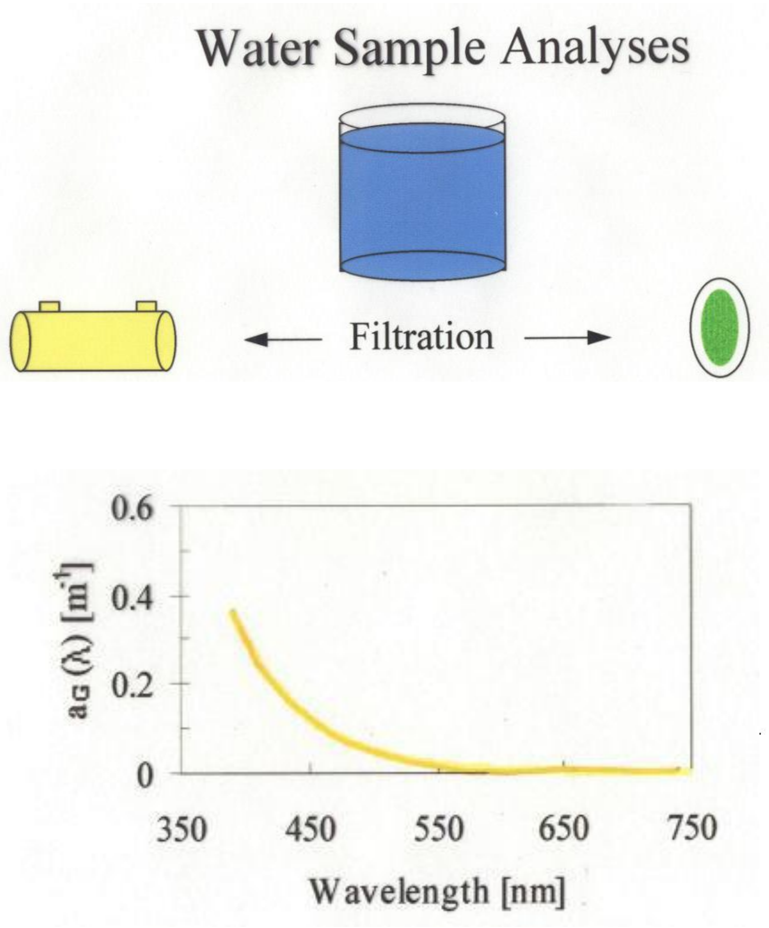
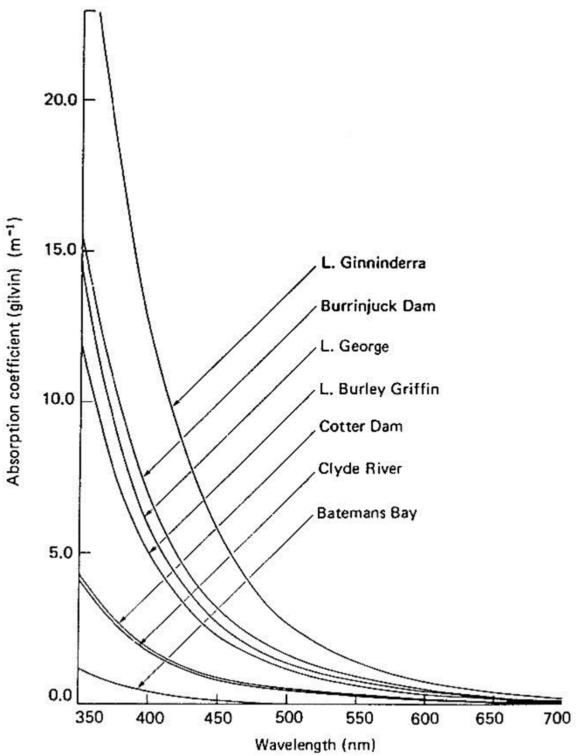


Fig. 3.5. Absorption spectra of soluble yellow material (gilvin) in various Australian natural waters (from Kirk, 1976*b*). The lowest curve (Batemans Bay, NSW) is for coastal sea water near the mouth of a river; the next curve (Clyde River, NSW) is for an estuary; the remainder are for inland water 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

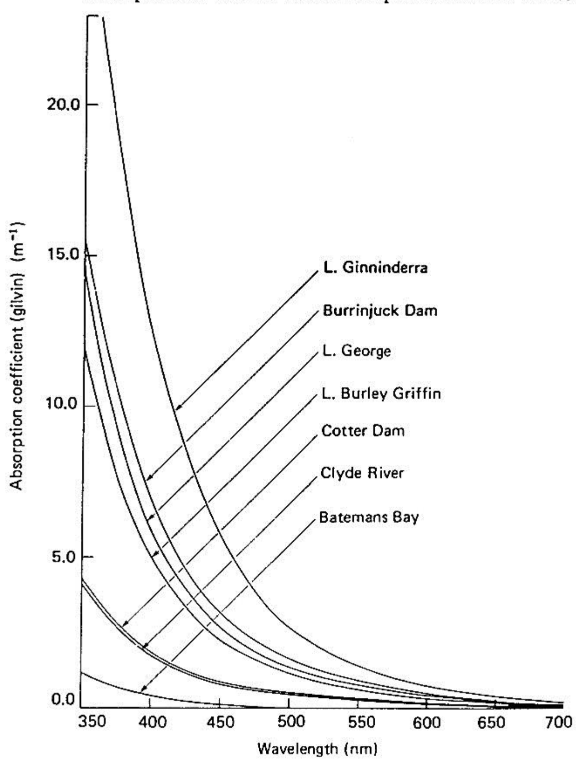
Strong blue absorption shifts light into the red - paddle is white

Dierssen et al. 2006

http://clarklittlephotography.com

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*b*). 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

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

People model this spectrum exponentially - know value at X and know slope you can predict the absorbance anywhere

Can use variability in absorbance to trace different water masses

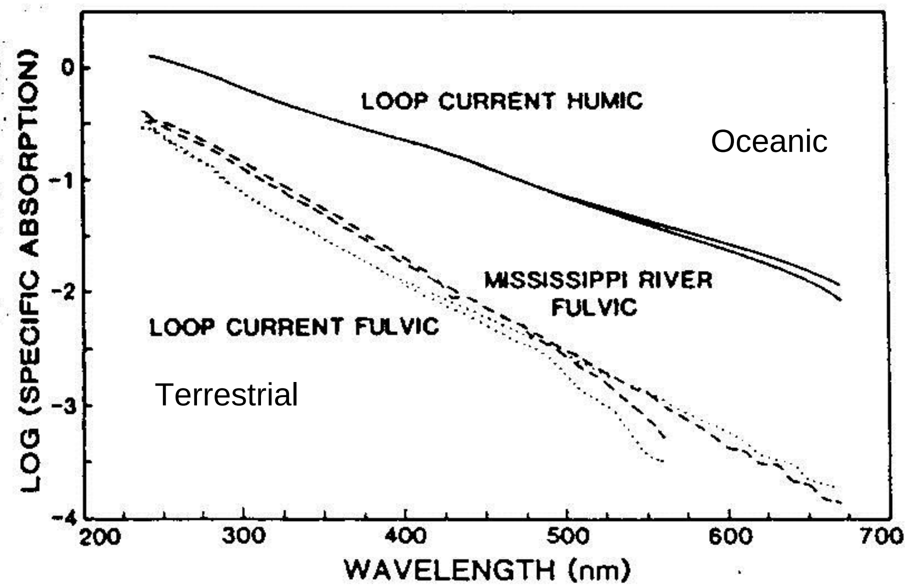


Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.

Carder et al. 1989 L&O

Absorbing Components: Colored dissolved organic matter (CDOM)

Measure CDOM at 412 very carefully to get spectral slope,

What wavelenght do you use to derive the slope? There are different windows = closer to UV is more sensitive to nucleic acid. (400=600, 220-300)

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

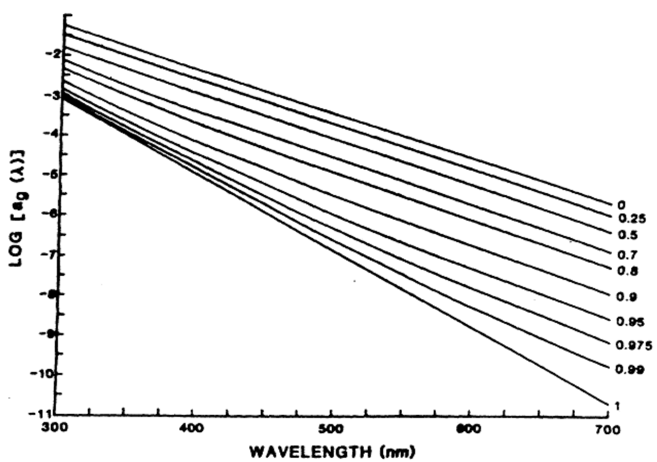


Fig. 3. Spectral variation of the absorption coefficient due to marine humus or Gelbstoff as a function of the fulvic acid fraction of Gelbstoff for $a^*_f = 0.00732$ m² g⁻¹, $a^*_h = 0.131$ m² g⁻¹, $B_f = 0.0186$ nm⁻¹, and B 0.0110 nm⁻¹. The fulvic acid fraction is shown beside each curve.

S

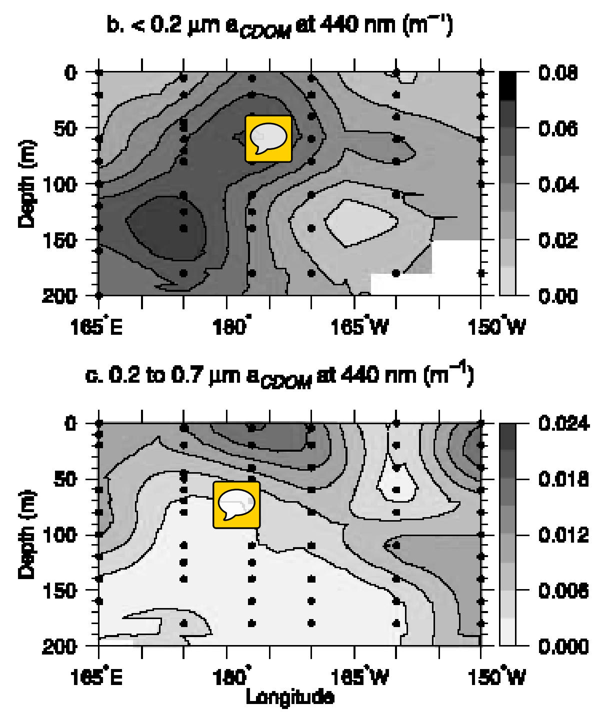
0.01

0.02

Carder et al. 1989 L&O

Using different slopes will allow you to compare to marine chemists using slope to measure benzene, etc

Equatorial Pacific



S=0.014

S=0.011

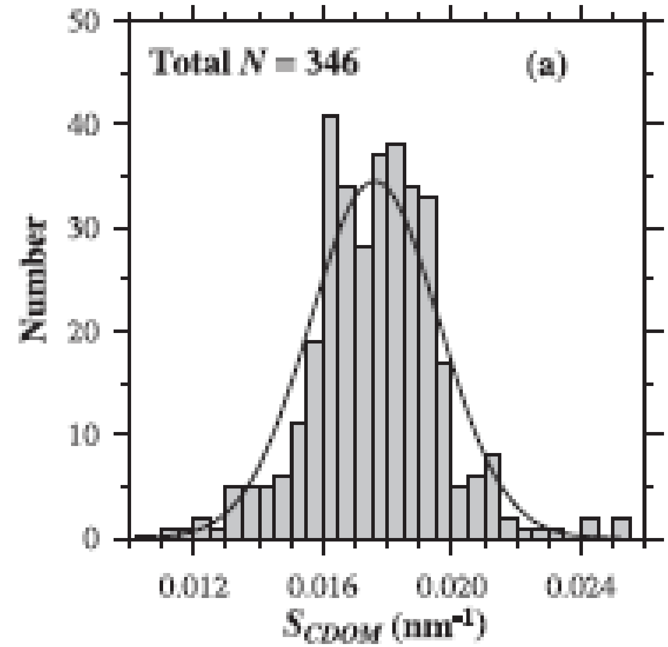
Simeon et al. 2003 JGR

Absorbing Components:
Colored dissolved organic matter (CDOM)

Table 1. Ranges for the exponential coefficient, $C2_x$, 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 $C2_x$ (nm^{-1})
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 Haardt 1987	Kiel Harbor	0.016
Published mean ± SD		0.016±0.002
This study mean ± SD	San Juan Islands	0.017±0.003
Carder et al. 1989	Marine humic acid	0.011
	Marine fulvic acid	0.018
Detritus		
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
Published mean ± SD		0.011±0.002
This study mean ± SD	San Juan Islands	0.011±0.002

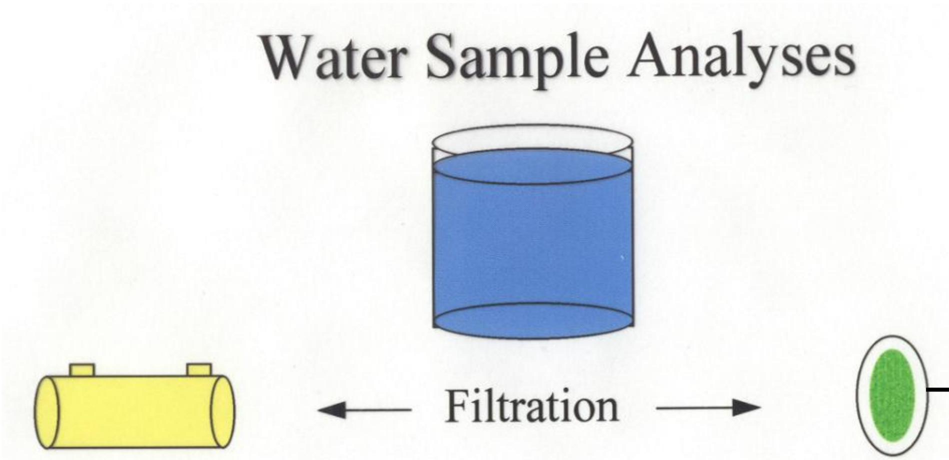
Roesler et al. 1989
(global synthesis)



Babin et al. 2003
(European coastal waters)

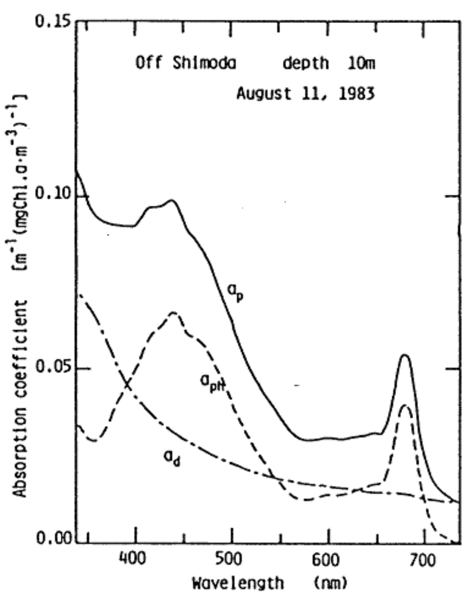
Absorbing Components: Particles

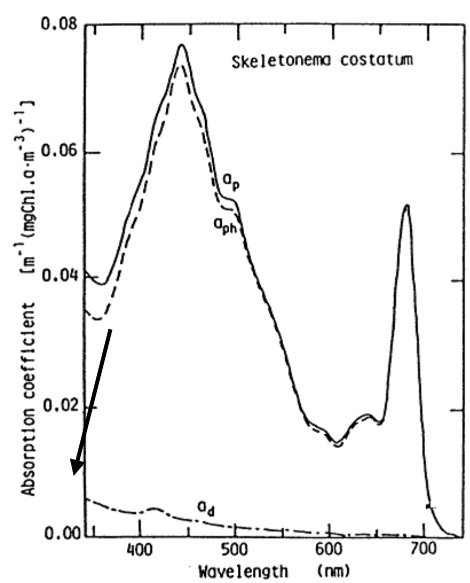
NAP: any particulate matter minus the pigments. Absorbance spectrum looks like CDOM but is in fact dead cells, bacteria, viruses, polysaccharides,



Methanol extraction → Scan (a_{nap})

Scan (a_p) → difference (a_{phyt})





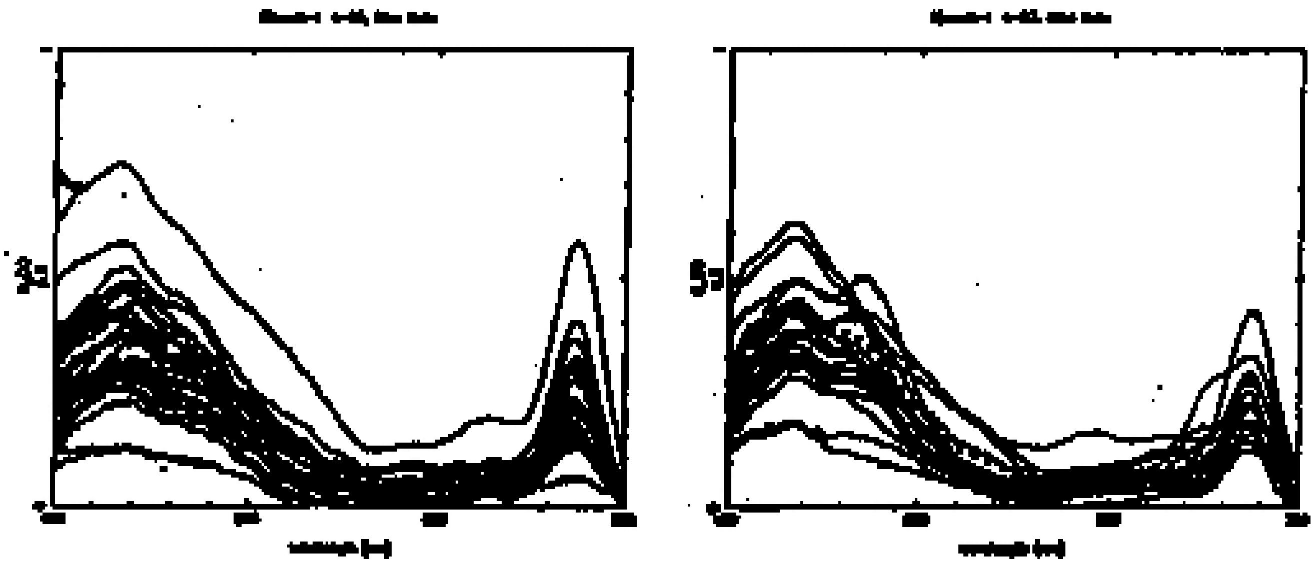
Kishino et al. 1985

Absorbing Components: Phytoplankton

If you add up the phytoplankton and the detritus - there is variability in individual cells

Individual cells, microphotometry

1710 *Iturriaga and Siegel* 1989 L&O



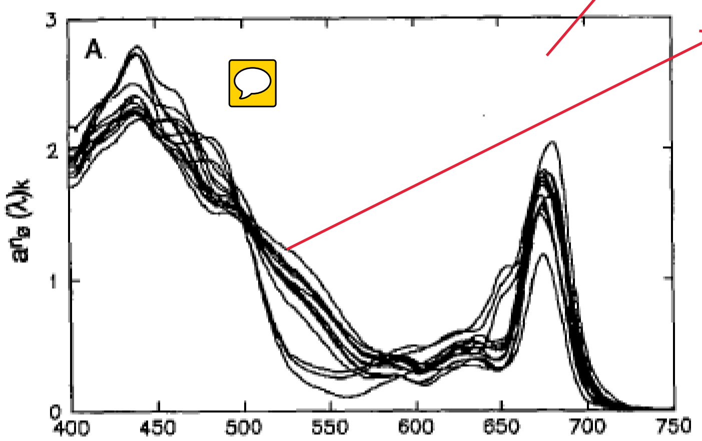
Wider peak means more pheophyton

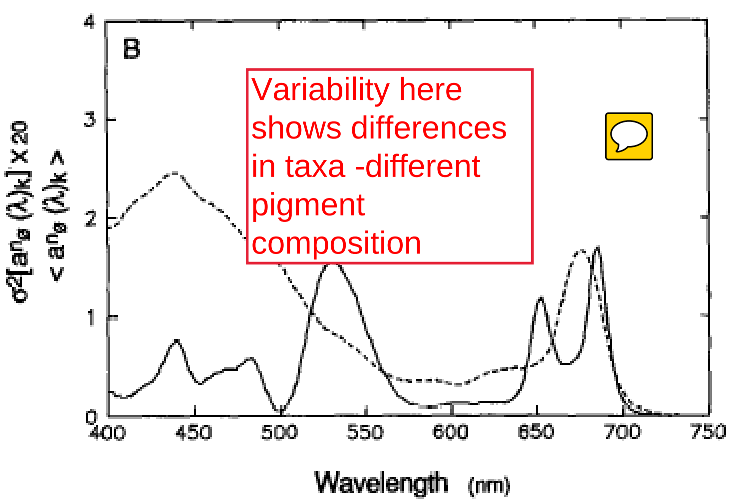
Absorbing Components: Phytoplankton

Variance in shape

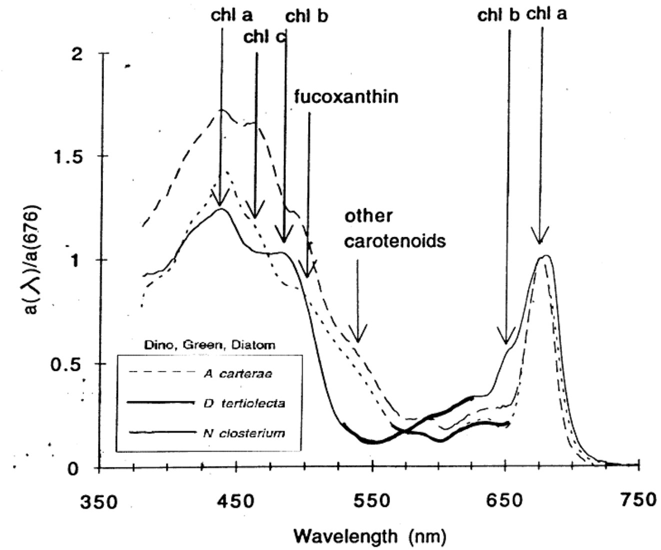
Species

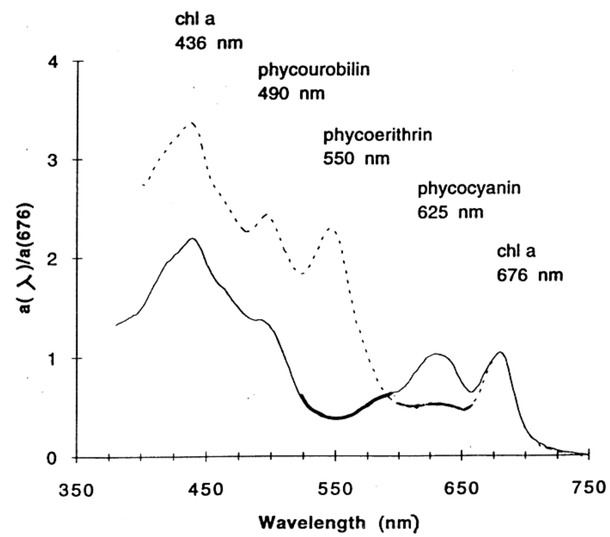
carete
noids





Variability here
shows differences
in taxa -different
pigment
composition





Roesler et al. 1989 L&O

Absorbing Components: Phytoplankton

Pigment Packaging impact on absorption

absorption about the same in blue and purple

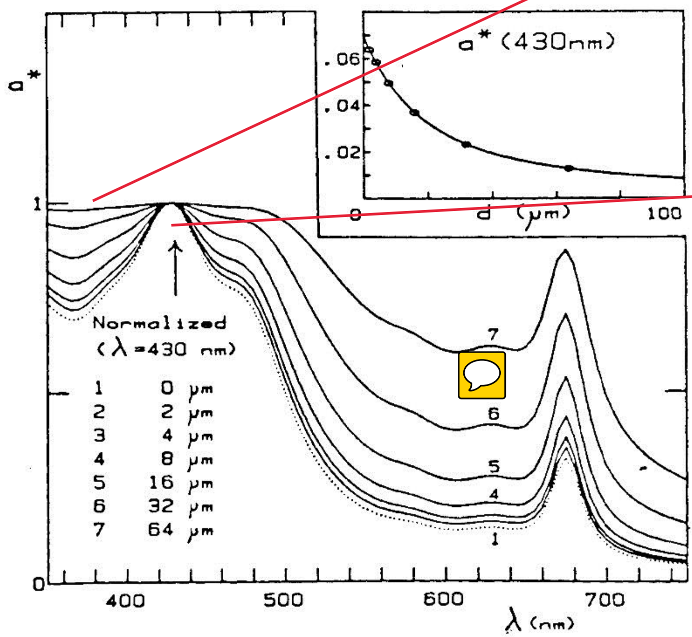


Fig. 2. Change in spectral absorption values with variable cell size (diameter, *d*, in μm) whereas the cell material forming the cells remains unchanged. The spectral absorption values of this material, somewhat arbitrarily adopted, are shown as the dotted curve. All curves are normalized, at $\lambda = 430$ 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}).

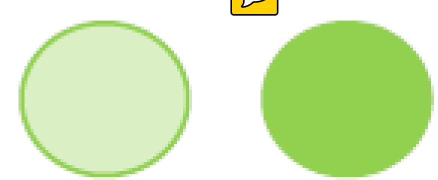
Morel and Bricaud 1981 DSR

(1) vary size, maintain constant intracellular pigment concentration

High absorption in UV but not blue

or

(2) maintain size, vary intracellular pigment concentration

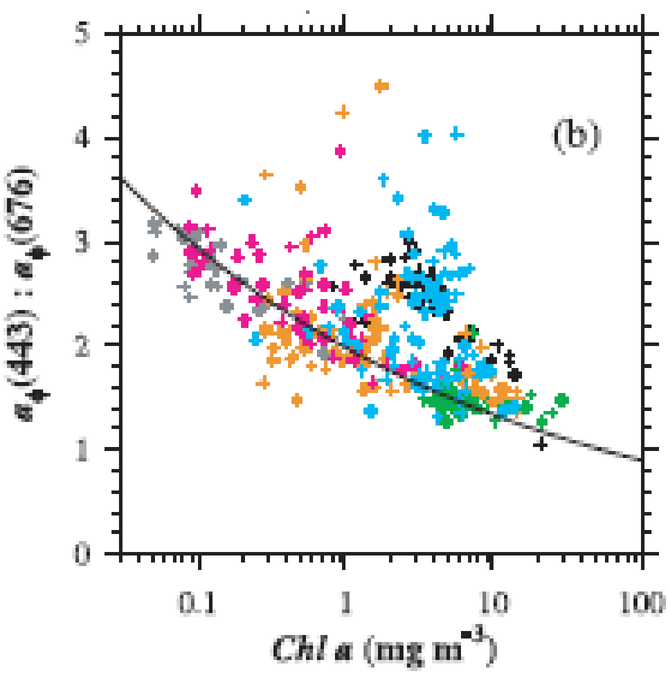


Absorbing Components: Phytoplankton

High nutrients = large cells = less peakedness

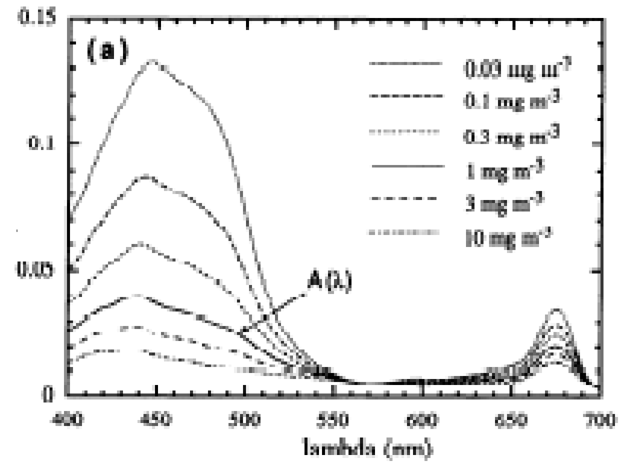
we would predict Mississippi would have less peakedness

Bricaud et al. 1995

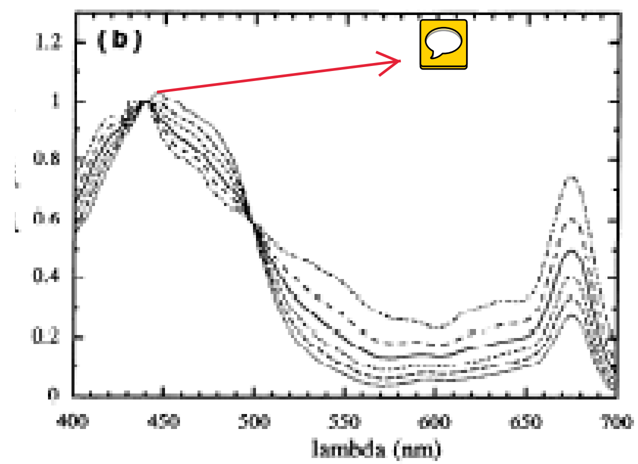


Babin et al. 2003

a^*_{phyt}
(m^2/mg chl)



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

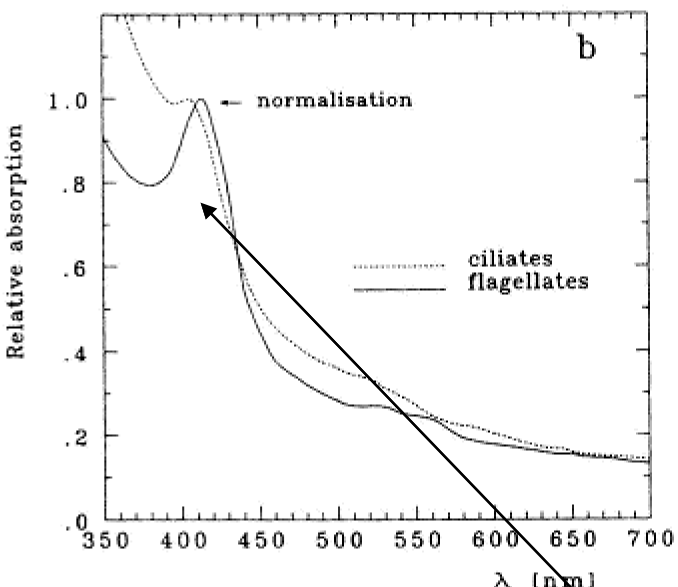


low chla doesn't ALWAYS mean small cells

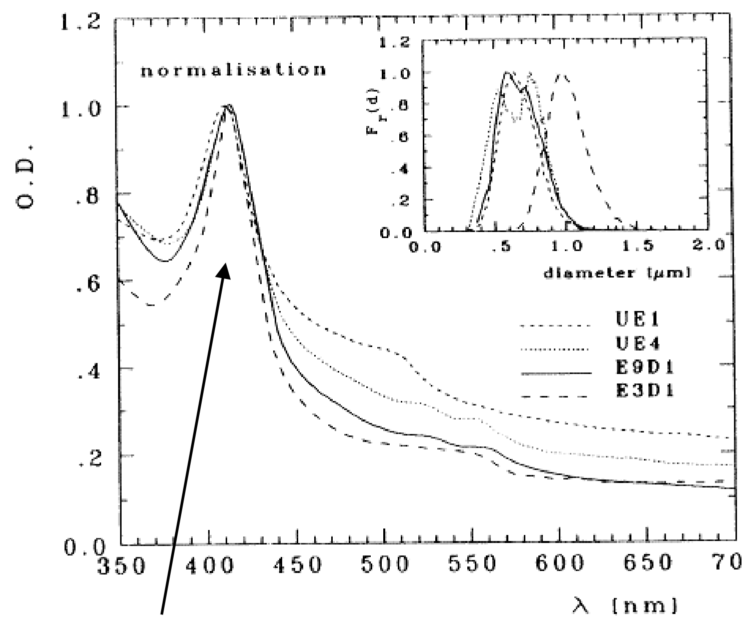
Global Relationships

Absorbing Components: other protists

ciliates and flagellates



heterotrophic bacteria



cytochrome 412

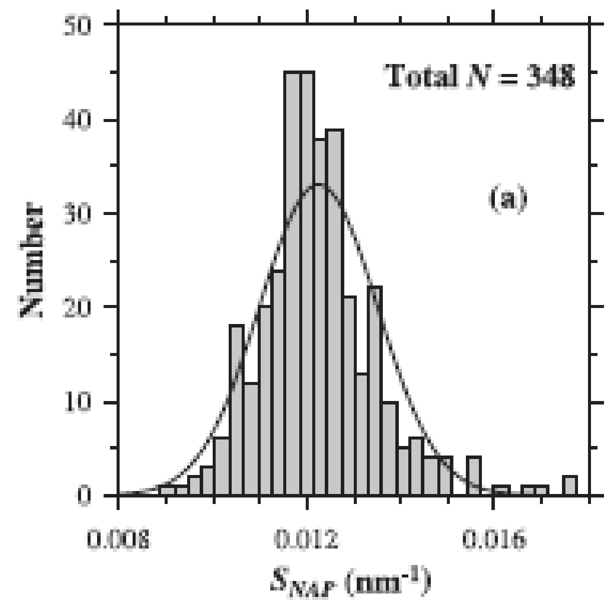
Morel and Ahn 1990 JMR

Absorbing Components: Non-algal particles

Table 1. Ranges for the exponential coefficient, $C2_x$, for gelbstoff and detritus for Eq. 6. Where coefficients were not listed, values were approximated from published spectra using an exponential model.

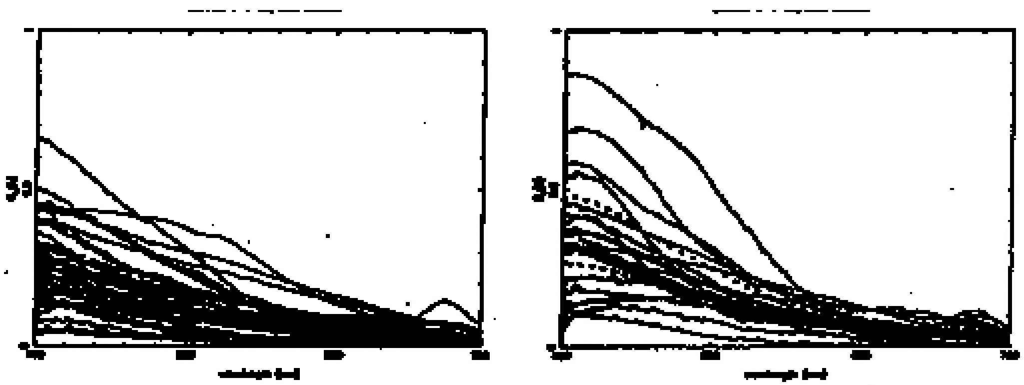
Reference	Site	Avg $C2_x$ (nm^{-1})
Gelbstoff		
Kalle 1966	Baltic, North Sea	0.018
Jerlov 1968		0.015
Kirk 1976	Lakes, coast	0.015
Lundgren 1976	Baltic	0.014
Kopelevich and Burenkov 1977	Indo-Pacific	0.017
Bricaud et al. 1981	Baltic	0.018
	Mauritania	0.015
	Gulf of Guinea	0.014
	Mediterranean	0.014
Okami 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 Haardt 1987	Kiel Harbor	0.016
Published mean ± SD		0.016±0.002
This study mean ± SD	San Juan Islands	0.017±0.003
Carder et al. 1989	Marine humic acid	0.011
	Marine fulvic acid	0.018
Detritus		
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
Published mean ± SD		0.011±0.002
This study mean ± SD	San Juan Islands	0.011±0.002

Roesler et al. 1989
(global synthesis)



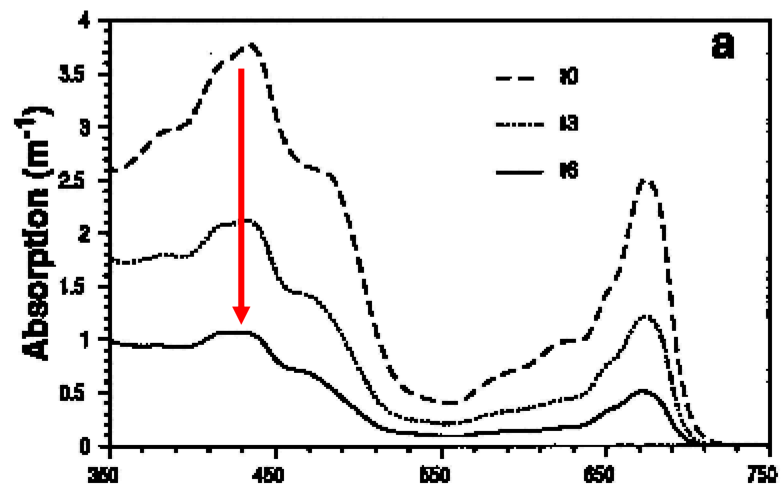
Babin et al. 2003
(European coastal waters)

Absorbing Components: Non-algal particles → what are they?



Iturriaga and Siegel 1989 L&O

Nelson & Robertson: Detrital spectral absorption 1993] JMR



Photobleaching natural light levels

Absorbing Components: inorganic particles

inorganic particles have strong blue absorption and weak red absorption just like the organic particles

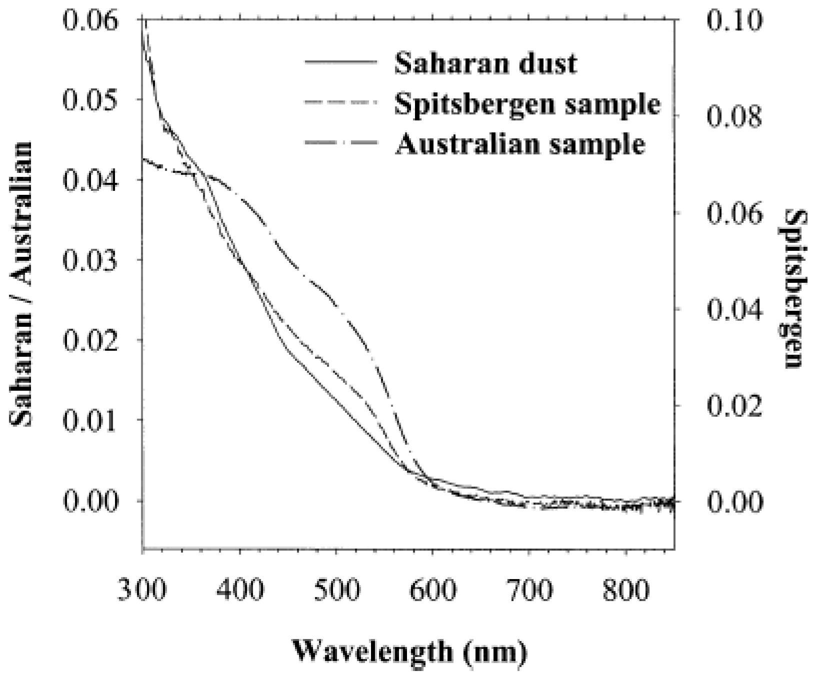


Fig. 5. Absorbance spectra of natural assemblages of mineral particles from three different environments.

Babin and Stramski 2003

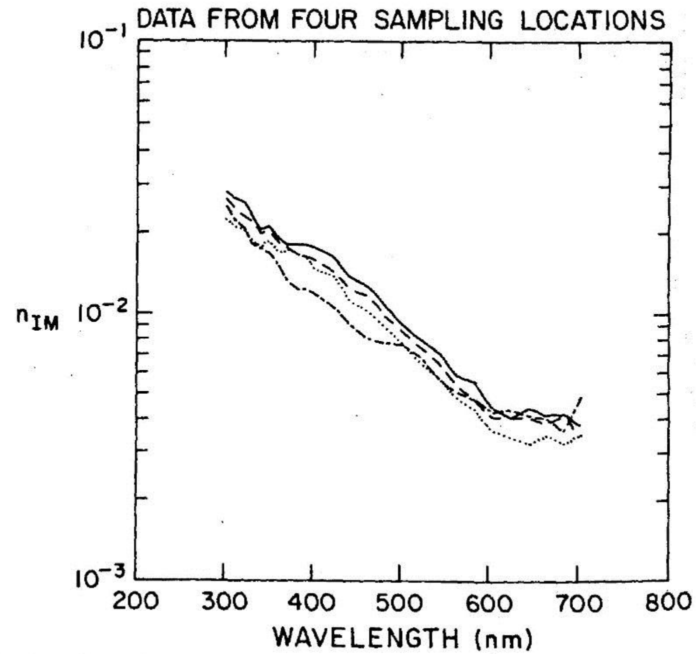


Fig. 8. Imaginary index of refraction for Saharan aerosols from each of the collection locations. The solid line represents the Tenerife sample; the dashed line, the *Meteor* sample; the dotted line, the Barbados sample; and the dashed-dotted line, the Sal Island sample.

Patterson et al. 1977 JGR

NAPs ARE NOT DEAD DETRITUS

Absorbing Components: inorganic particles

difference shows different electron states and can be used to estimate iron concentrations

Measured spectra

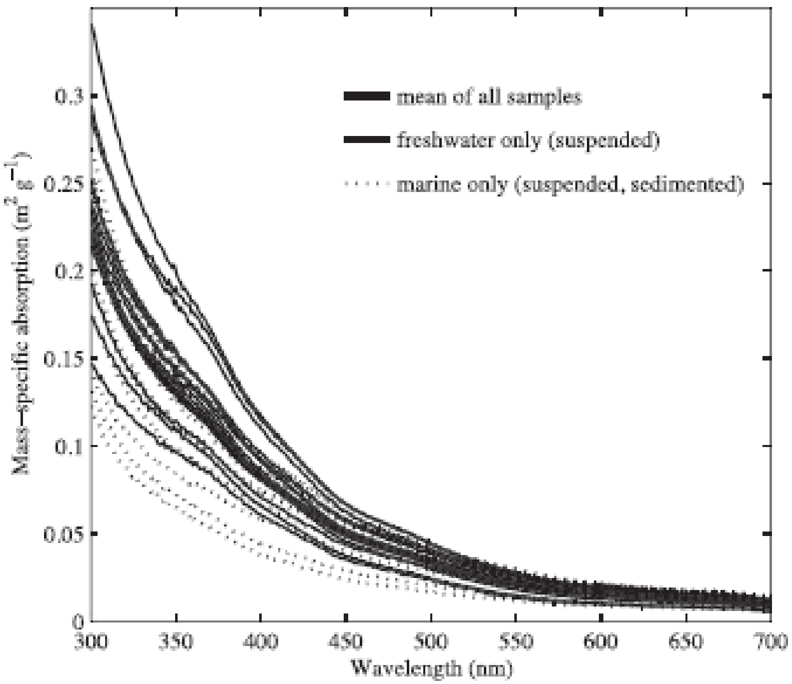


Fig. 3. Mass-specific absorption spectra of all samples analyzed here (n = 25). Heavy black line shows the mean, thin solid lines show samples from freshwater sites on the Atchafalaya and Mississippi Rivers, and dashed lines show samples from marine sites at Freshwater Bayou and the Atchafalaya River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

2nd Derivative used to quantify concentration of iron oxide minerals

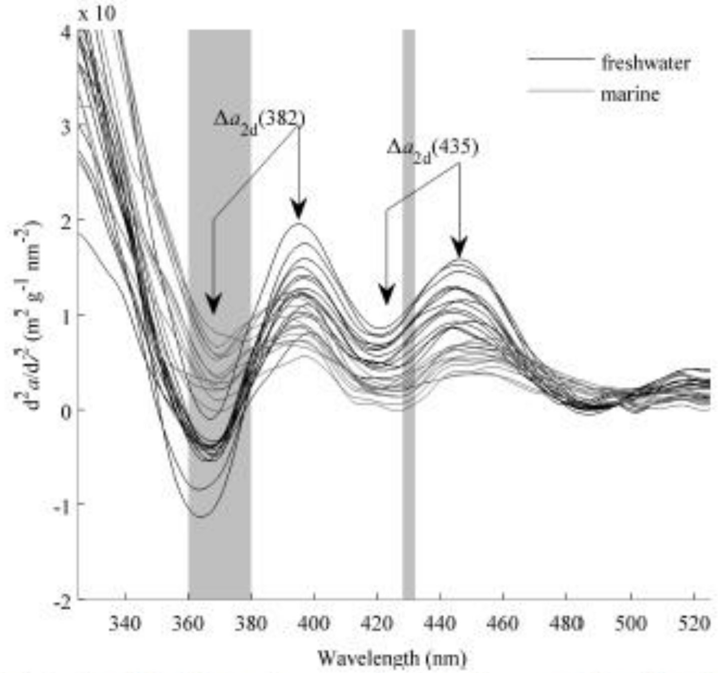
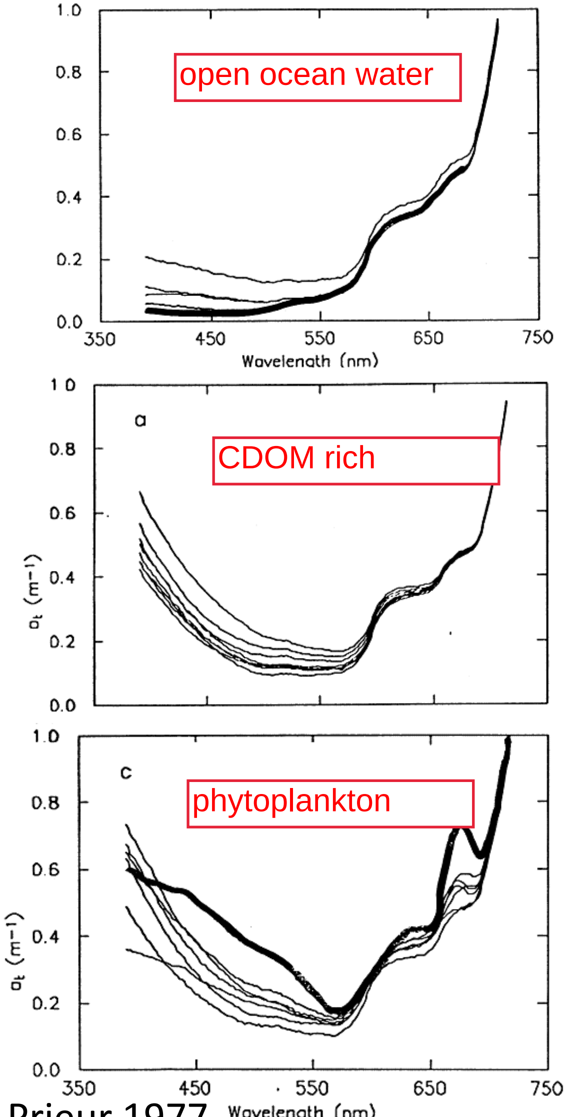


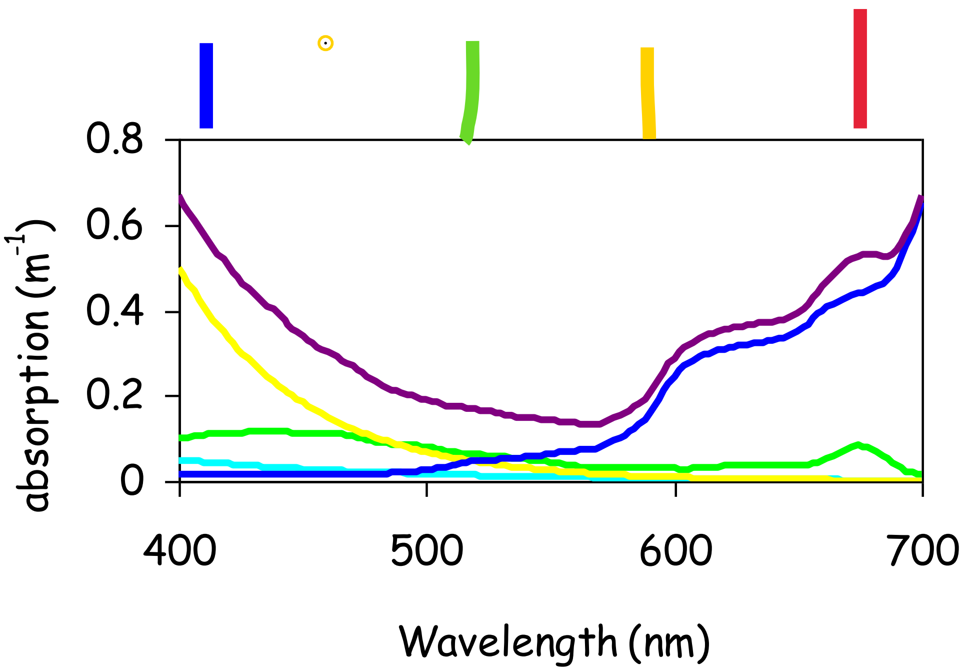
Fig. 10. Second derivatives of mass-specific absorption spectra. Black lines denote freshwater samples, and gray lines denote marine samples. Bracketed arrows labeled $\Delta a_{2d}(382)$ and $\Delta a_{2d}(435)$ show locations of second-derivative maxima and minima used to compute iron absorption peak 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).

Estapa et al. 2012

To model the impacts of absorbing constituents → add them up



Morel and Prieur 1977



Which component dominates?

- blue waters
- green waters
  - phytoplankton (V-type)
  - inorganic particles (U-type)

More on absorption

- Phytoplankton absorption
  - Lecture tomorrow
- Measuring absorption
  - Lecture tomorrow
- CDOM absorption methods
  - Lab tomorrow
- Particulate absorption methods
  - Lab Wednesday