Lecture 4

Absorption Part 1 – theoretical basis of absorption, absorption by individual particles, bulk absorption

Collin Roesler

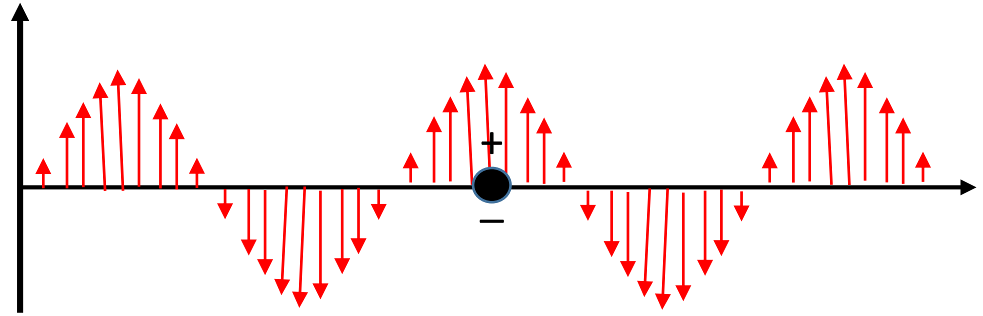
20 July 2021

Lecture Overview

- Overview of the electromagnetic spectrum
- Absorption on molecular scales
- Major absorbers in the ocean
- Lecture 5: Measuring absorption in the ocean
- Lab 2: Absorption by solutions
- Lab 3: Absorption by particles

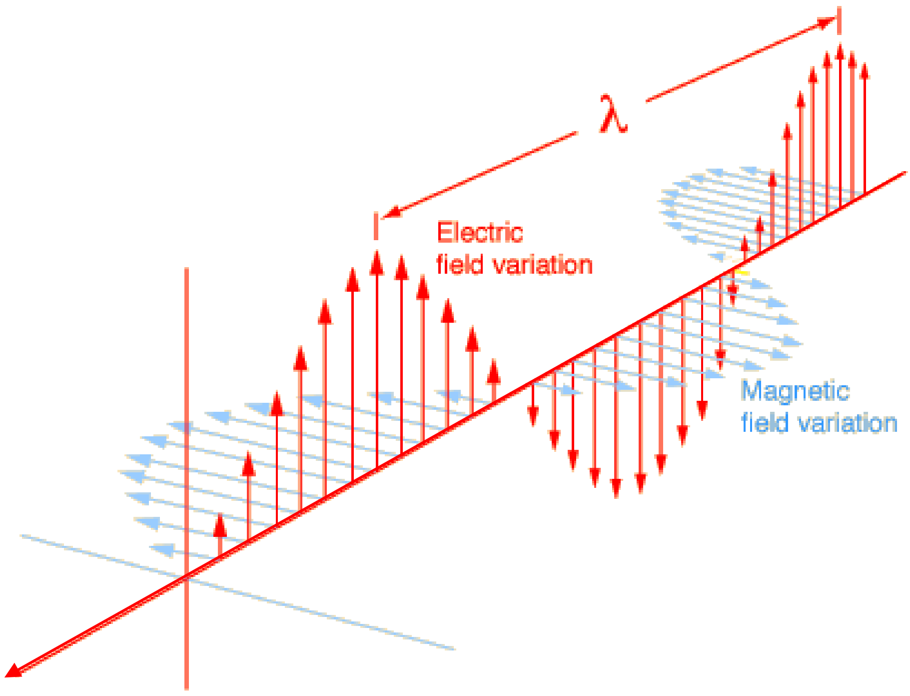
Electromagnetic Radiation

- 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**
- The electromagnetic field oscillates as the energy propagates **E**x**B** (right hand rule)



Electromagnetic Radiation

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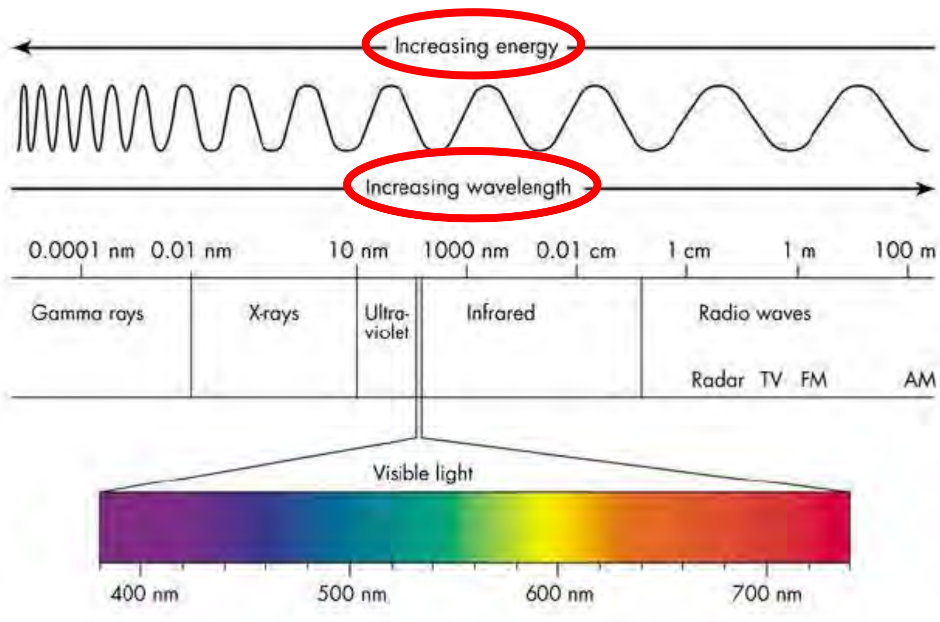
- the range of oscillation frequencies is described by the Electro-Magnetic (EM) spectrum

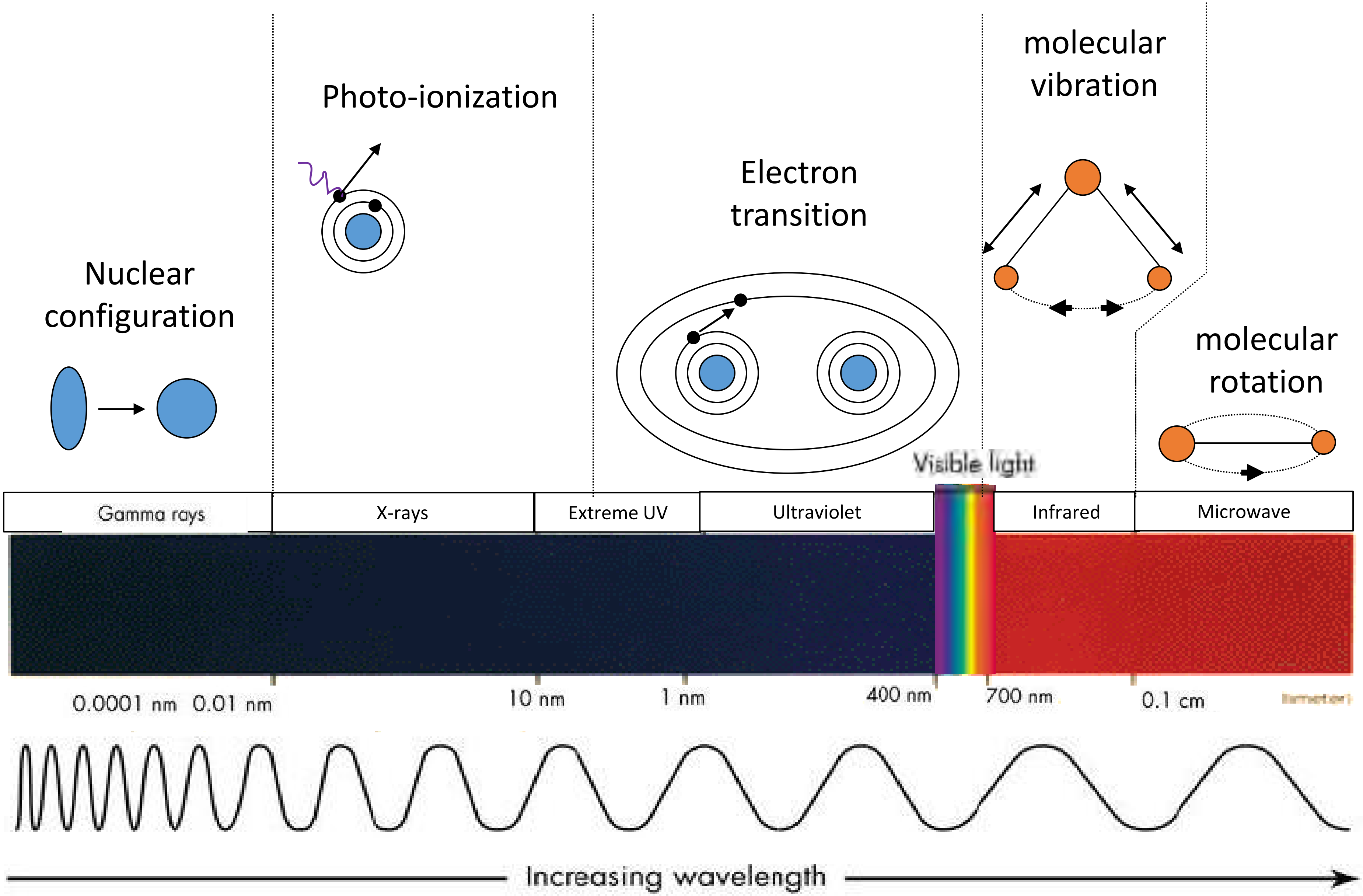


http://www.antonine-education.co.uk/physics_gcse

What is absorption?

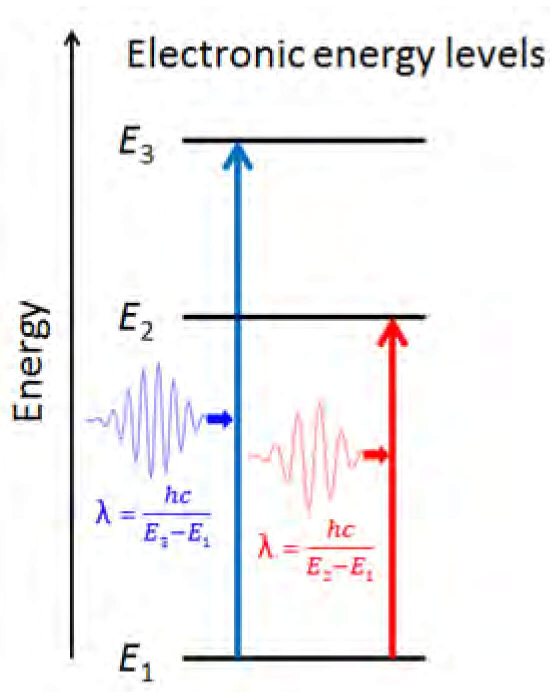
- Since electromagnetic radiation is energy propagation, when molecules absorb radiation, they absorb *energy*
- The energy associated with each part of the spectrum is given by $E = hc/\lambda$
  - *h Planck's constant*
  - *c speed of light in a vacuum*
  - λ *wavelength*
- What happens to the molecule depends upon the amount of energy, and therefore the wavelength

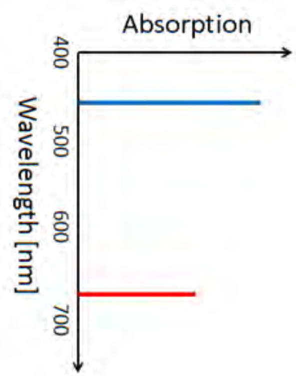
Interactions between energy and matter



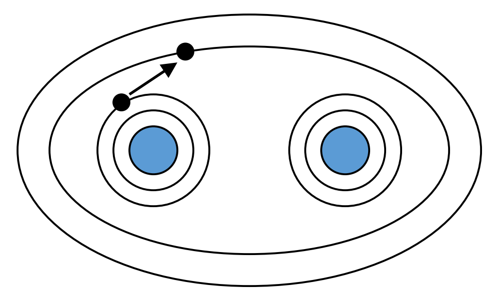
Quantized electronic states

- Amount of energy required to move an electron to a higher orbital (electronic state transition) is *quantized*
- A molecule absorbs radiation **only** of this specific quantized energy
- The quantized energy determines the absorption peak wavelength
- This example shows a molecule with two higher energy levels (E2 and E3) and thus two absorption peaks



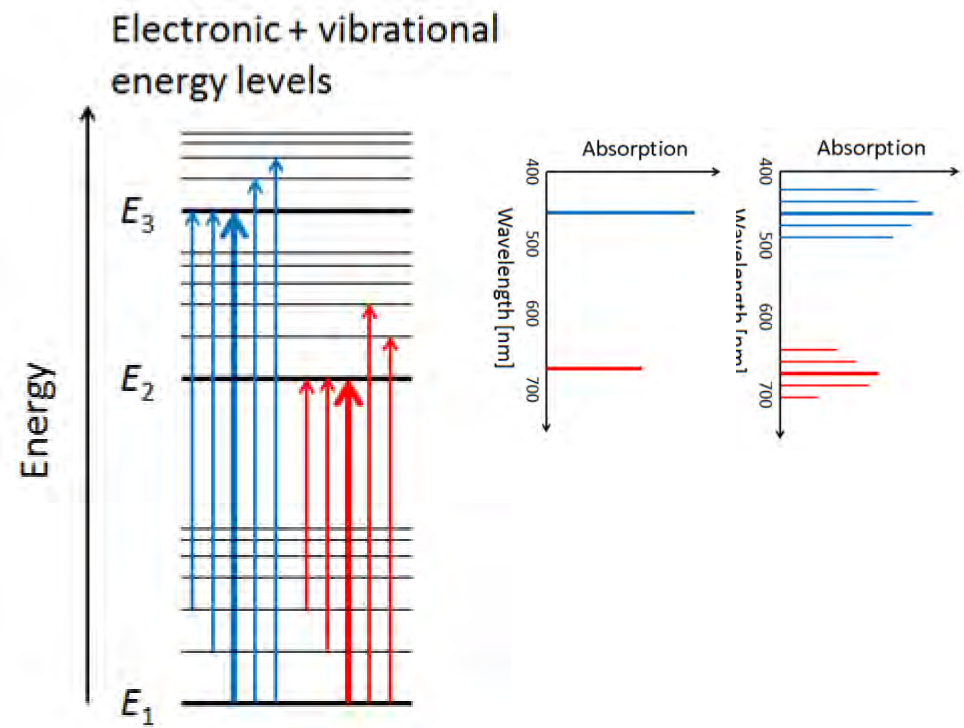


Electron transition

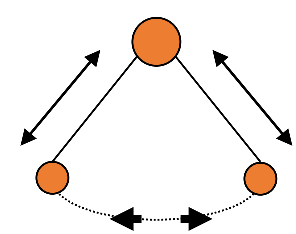


Quantized vibrational states

- Each orbital 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 that have higher or lower energy, but have a lower probability for absorption

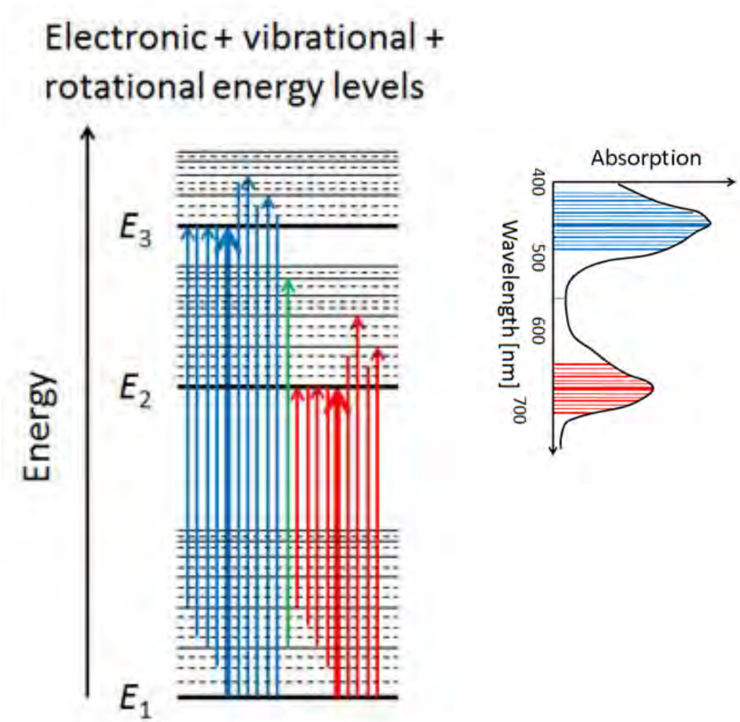


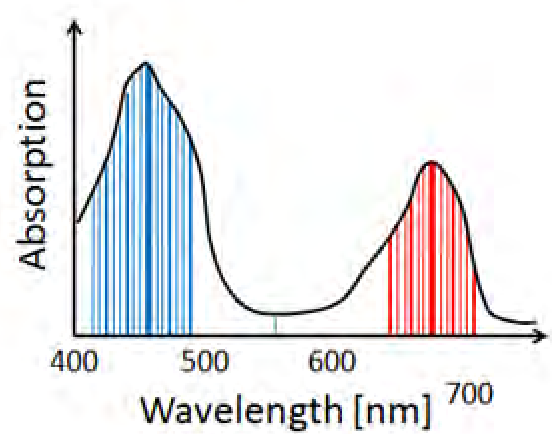
molecular
vibration



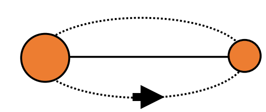
Quantized rotational states

- 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



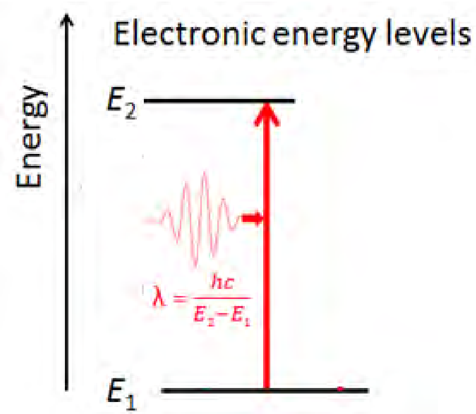


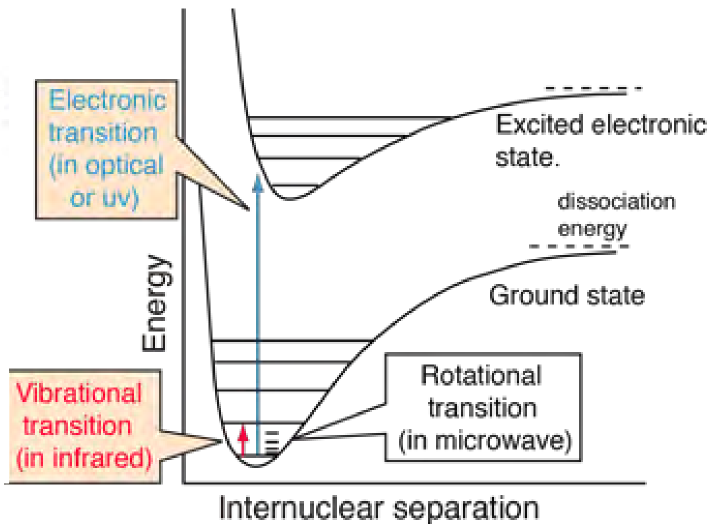
molecular rotation

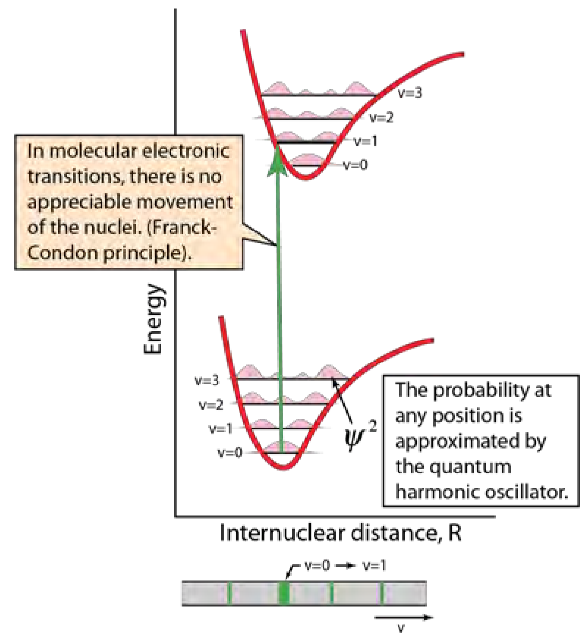


Quantized states

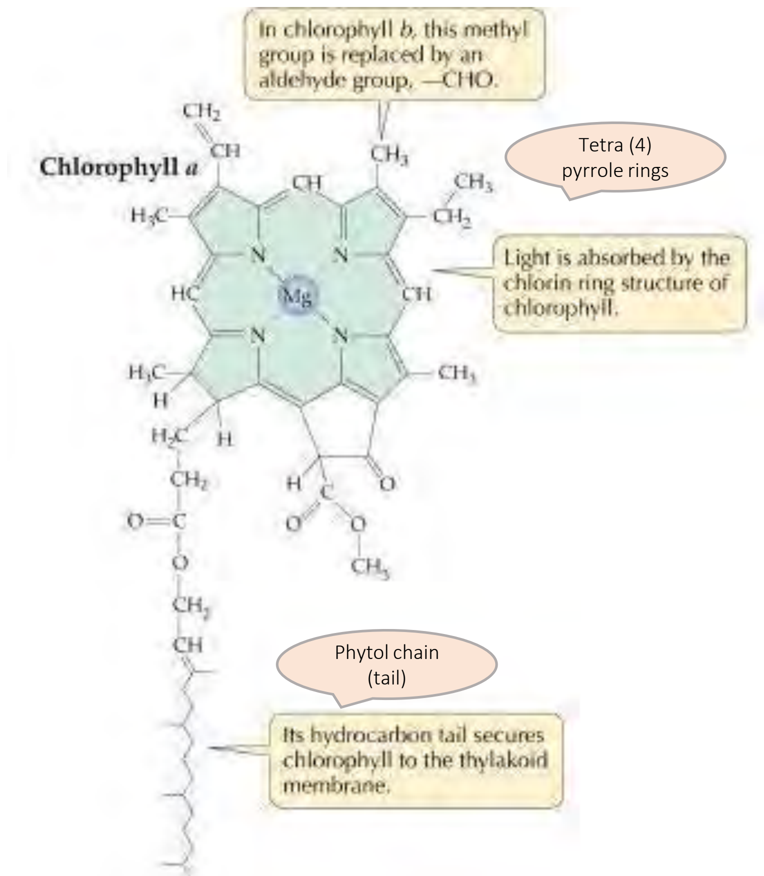
- Each level is really a distribution as a function of internuclear separation
- With probabilities (likelihoods of occurrence)
- Higher probability of transition → higher absorption coefficient



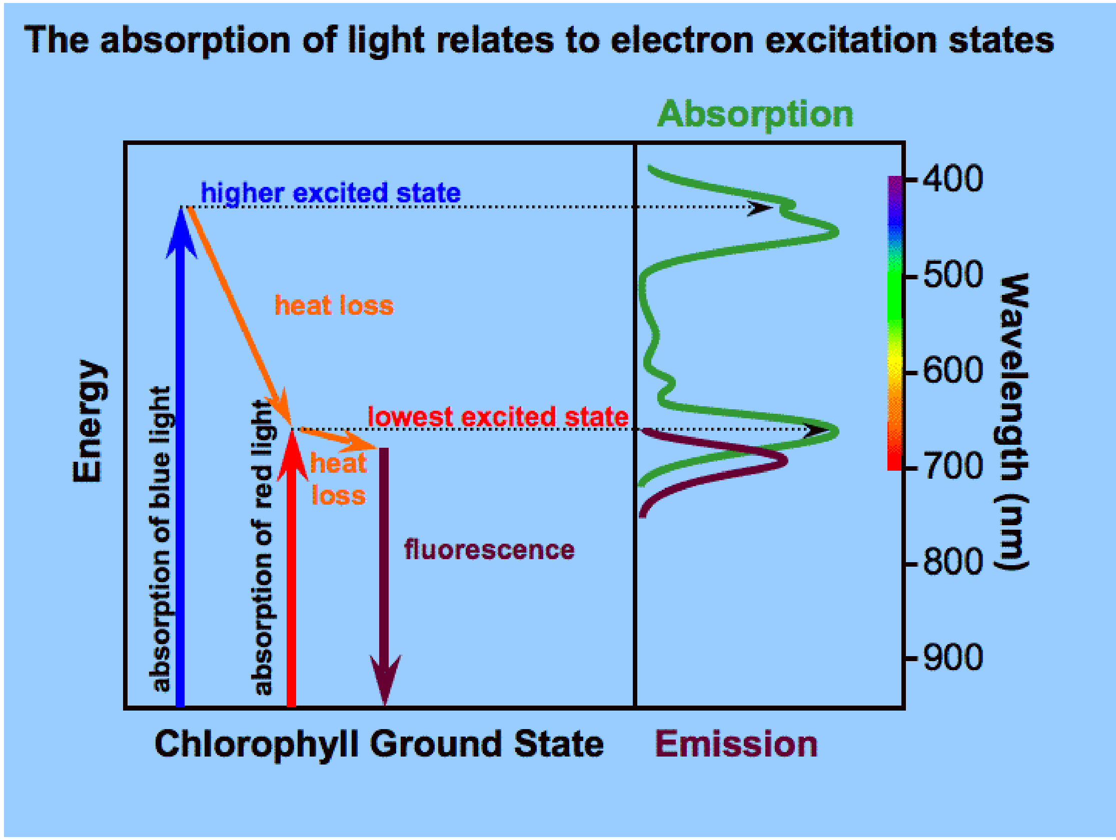




Chlorophyll *a* has two electronic states associated with the energy equivalent of blue (443 nm) and red (676 nm) wavelengths

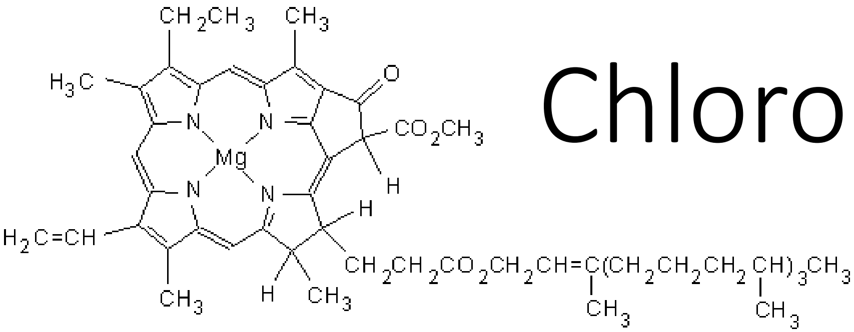


http://www.mie.utoronto.ca/labs



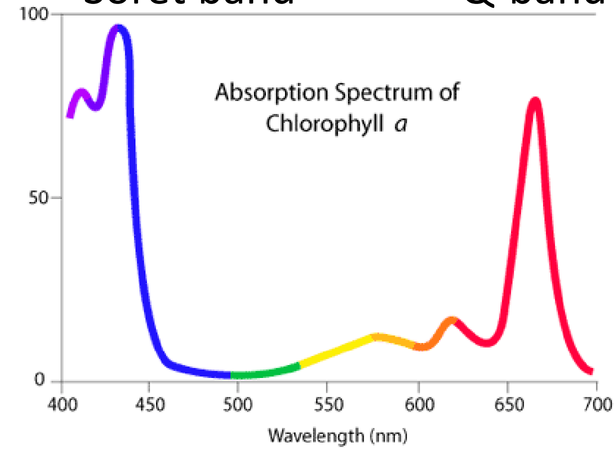
http://plantphys.info/plant_physiology/light.shtml

Chlorophyll *a*

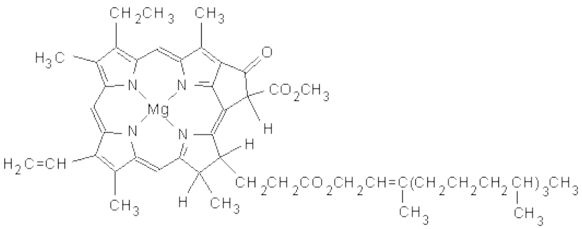


http://scifun.chem.wisc.edu/chemweek/chlrphyl/chlrphyl.gif

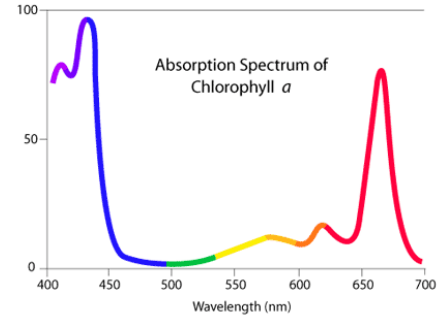
Soret band Q-band

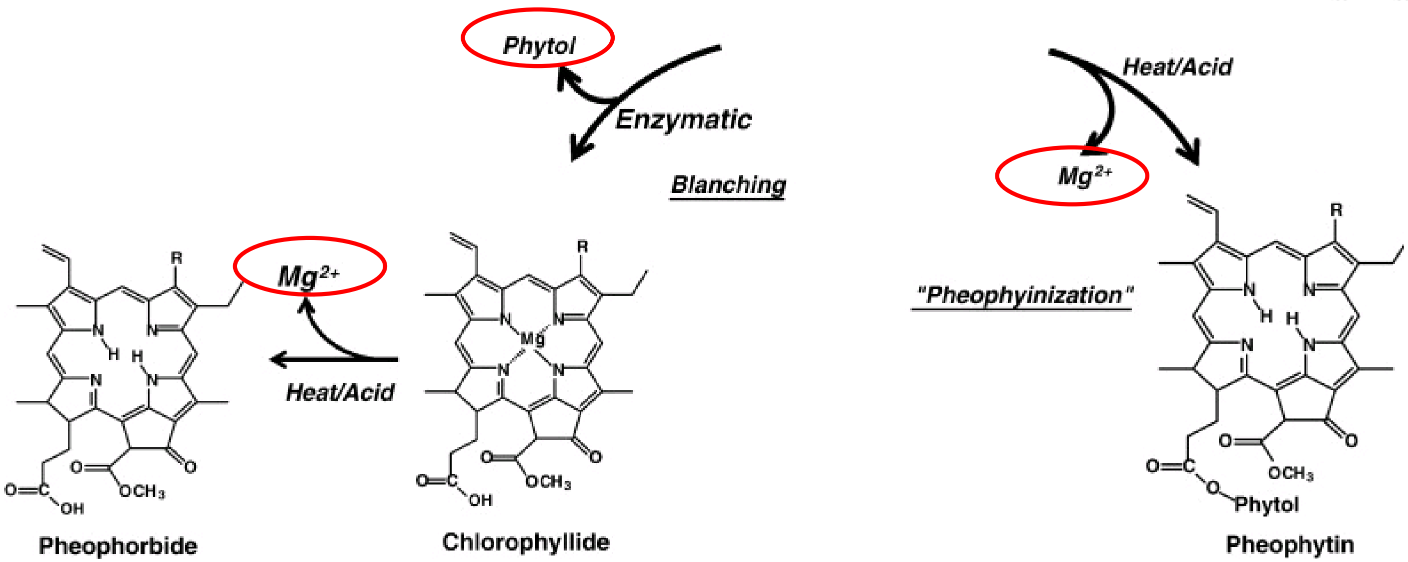


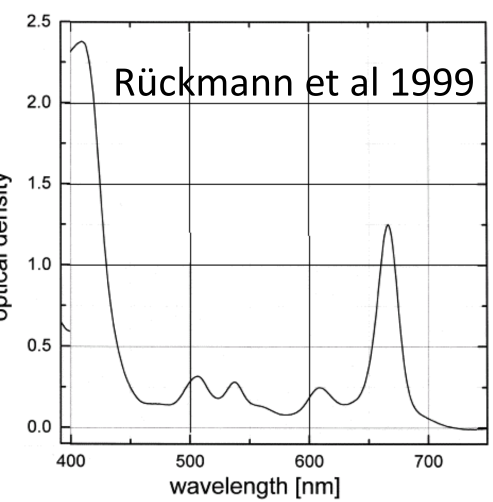
http://www.photochembgsu.com/assets/images/graph2.gif

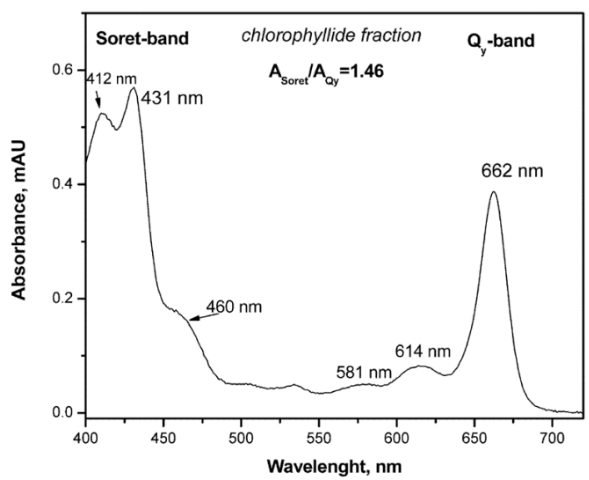


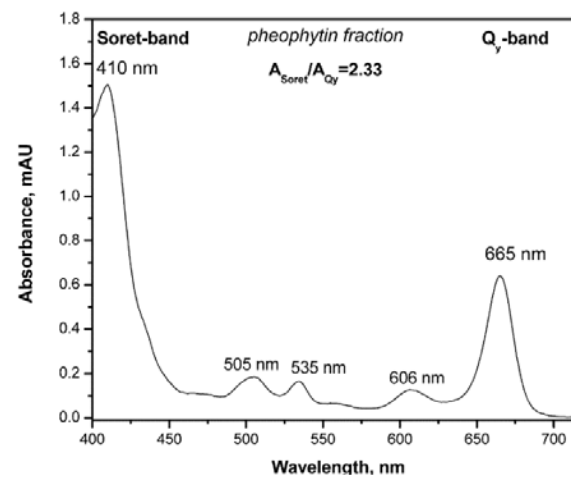
Chlorophyll









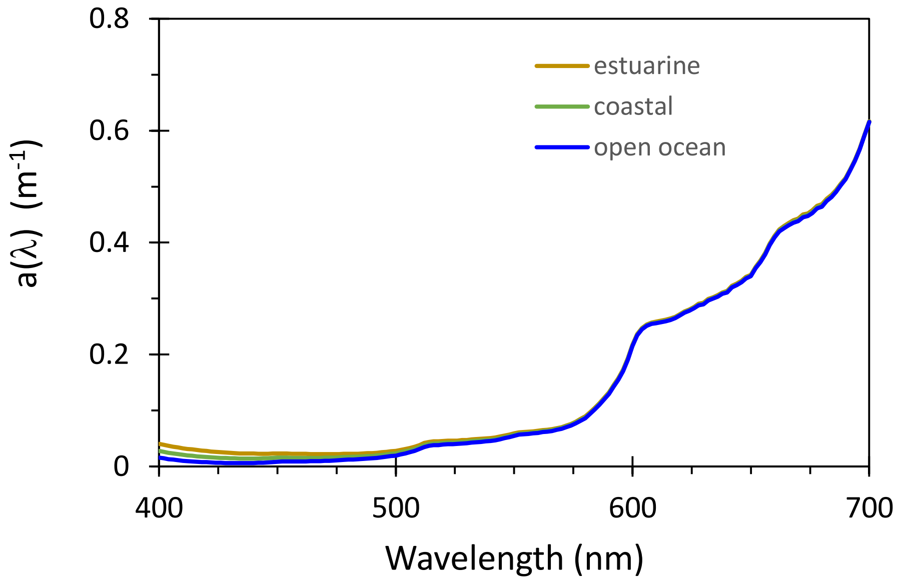


Milenković et al. 2012

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

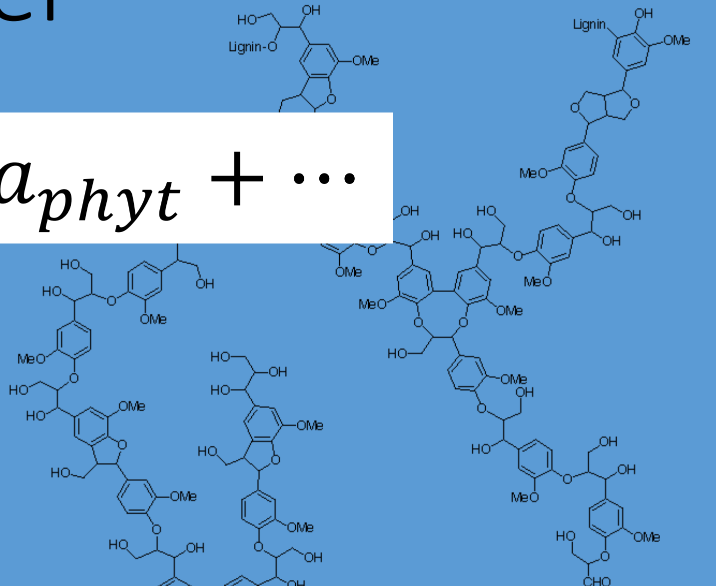
$$a_{total} = a_{water} + \sum a_{dissolved} + \sum a_{particles}$$

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

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

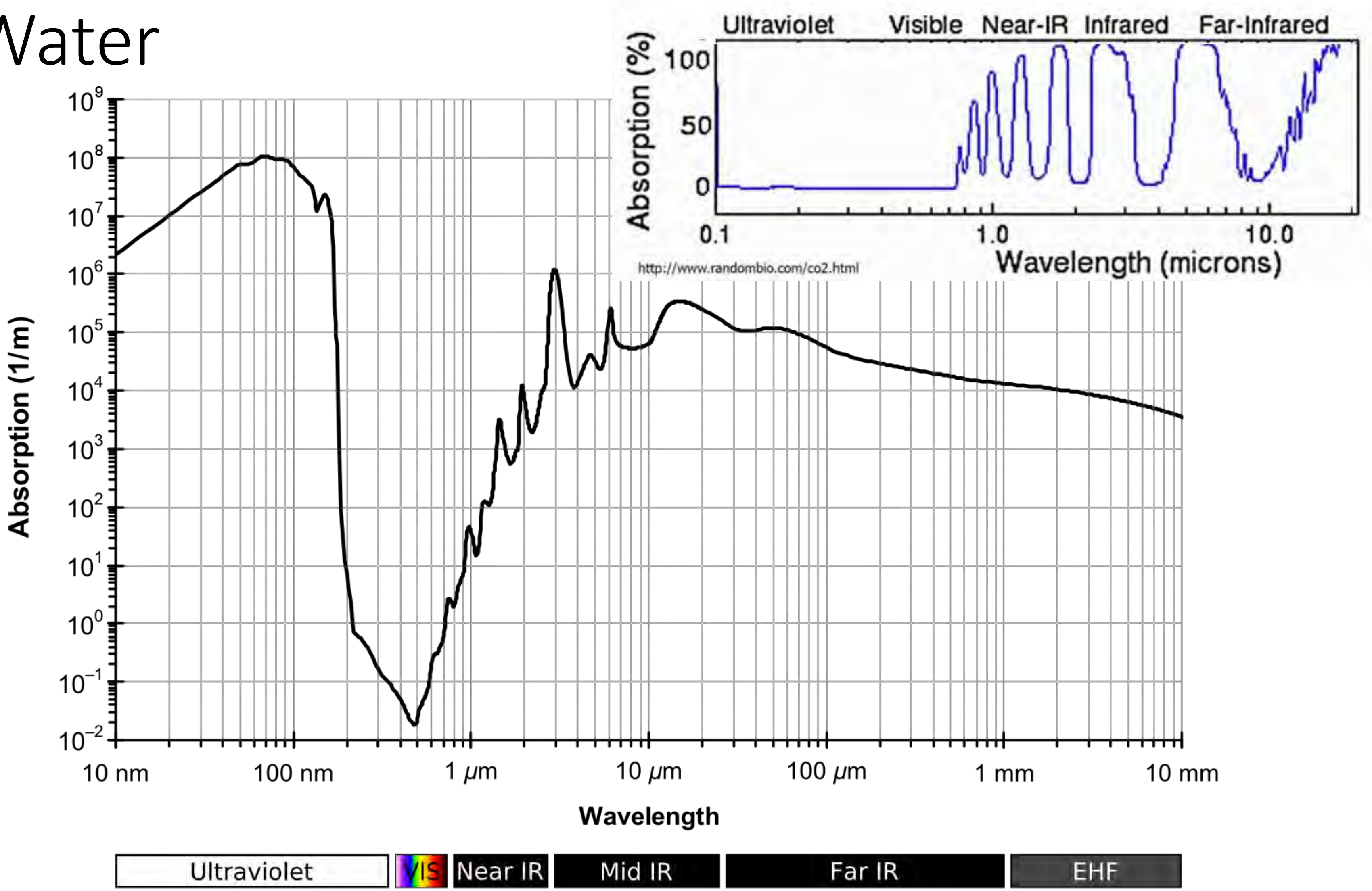
It is impractical to measure absorption spectrum for each absorber

$$a_T = a_w + a_{CDOM} + a_{nap} + a_{phyt} + \cdots$$

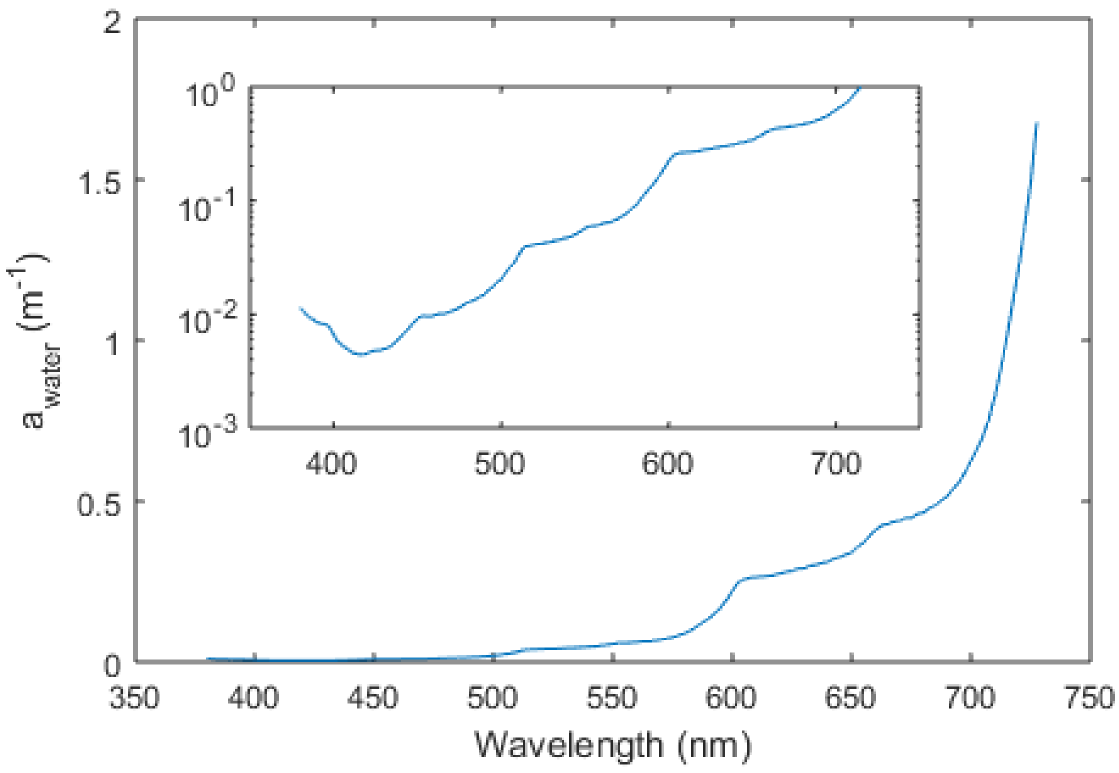


Group components by their common absorption properties
(an our inability to separate them operationally)

Absorbing Components: Water



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

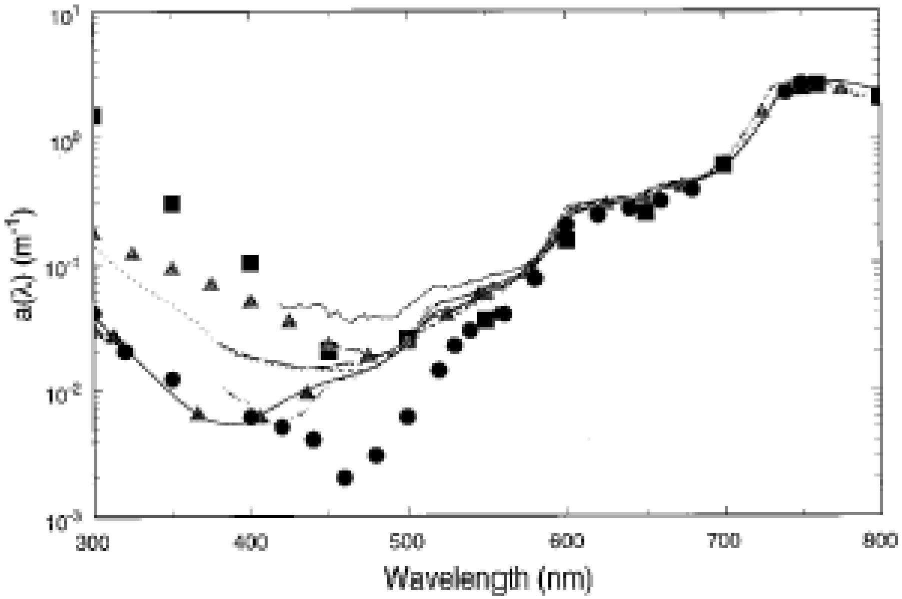


Fig. 1. Absorption coefficient of pure water as measured or compiled by several investigators.[1,2,11,18,19,21,26–33] The discrepancy in the estimated absorption coefficients is largest at short wavelengths where absorption by organic contaminants is significant. At wavelengths longer than 550 nm the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

Absorbing Components: Water

Temperature

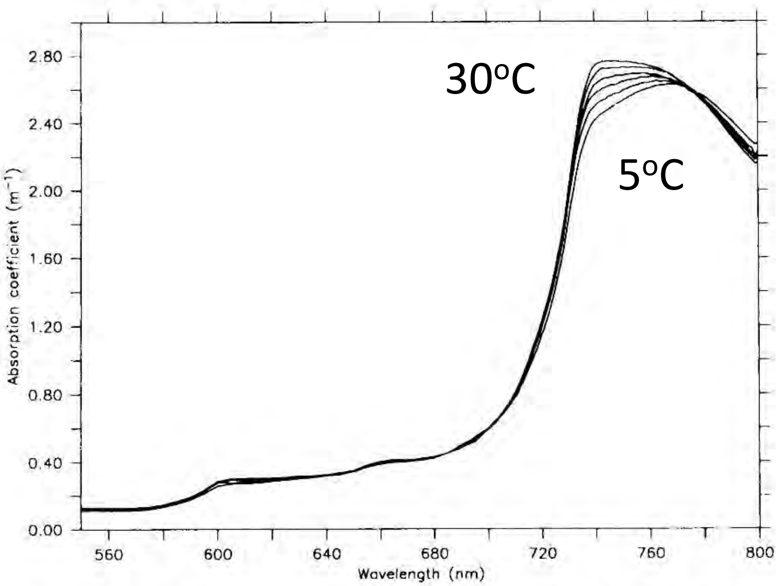
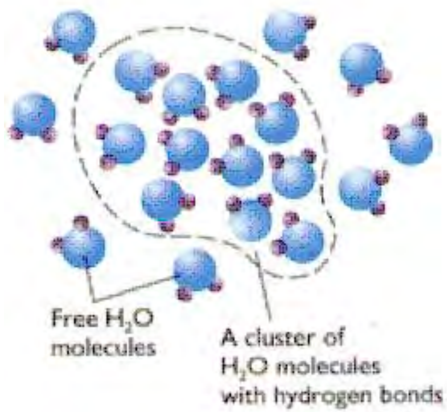
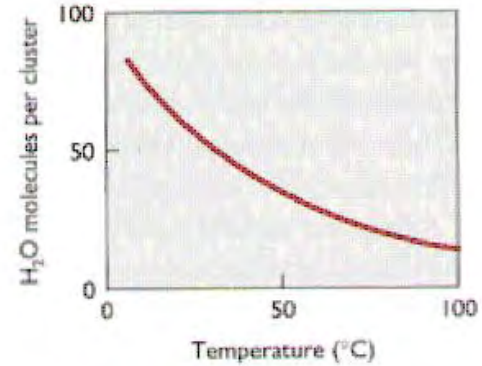


Fig. 3. Absorption coefficient from 550 to 800 nm adjusted at 685 nm to the value of Tam and Patel (1979). The curves represent absorption at temperatures of 5, 10, 15, 21, 25, and 30°C as read from bottom to top at 750 nm.

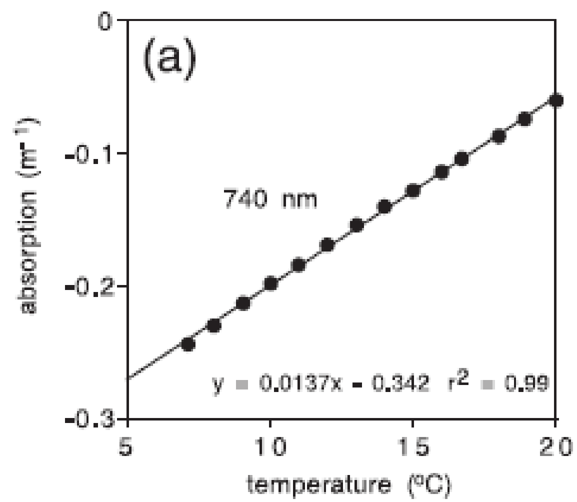
Pegau and Zaneveld 1993 Limnol Oceanogr.



(d) CLUSTERS OF WATER



(e) SIZE OF WATER CLUSTERS



natural variations

Sullivan et al. 2006 Appl Opt

Absorbing Components: Water

Salinity

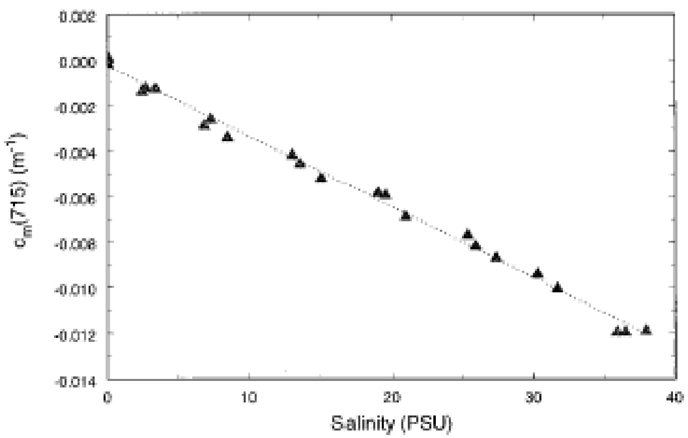
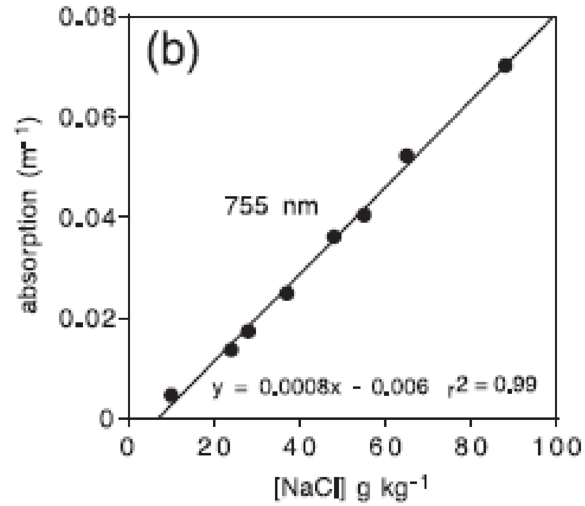
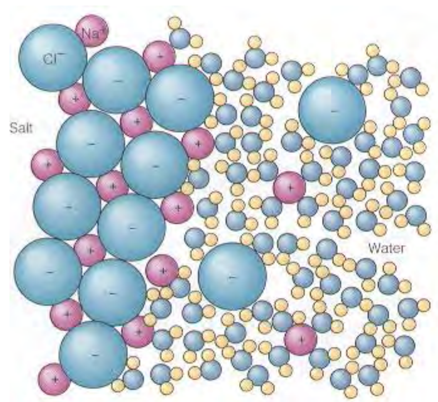


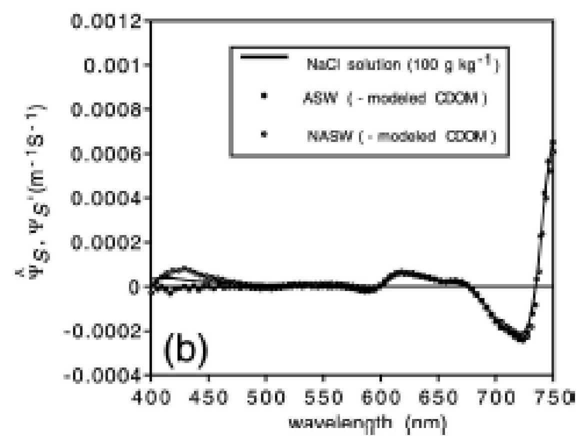
Fig. 6. Attenuation coefficient at 715 nm as a function of salinity. This figure illustrates the linear dependence of the attenuation coefficient on salinity.

Pegau etal. 1997 Appl.Opt.



Sullivan et al. 2006 Appl Opt



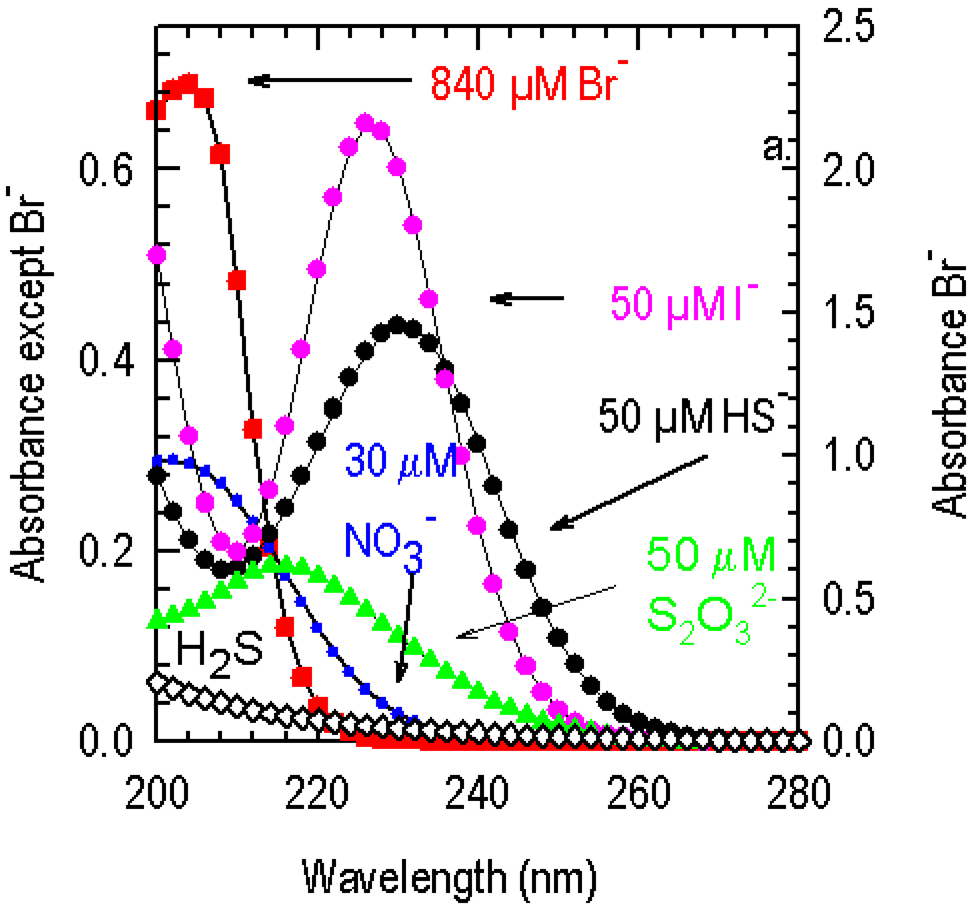


natural variations

Absorbing Components: Dissolved inorganic matter

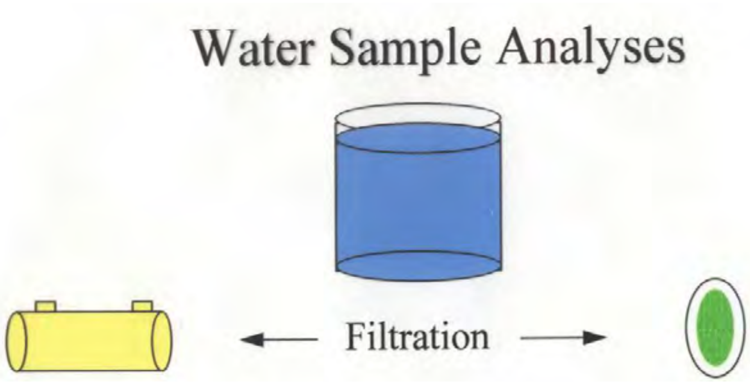
- Basic for UV detection of nitrate, ISUS

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



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

Absorbing Components:
Colored dissolved organic matter (CDOM)



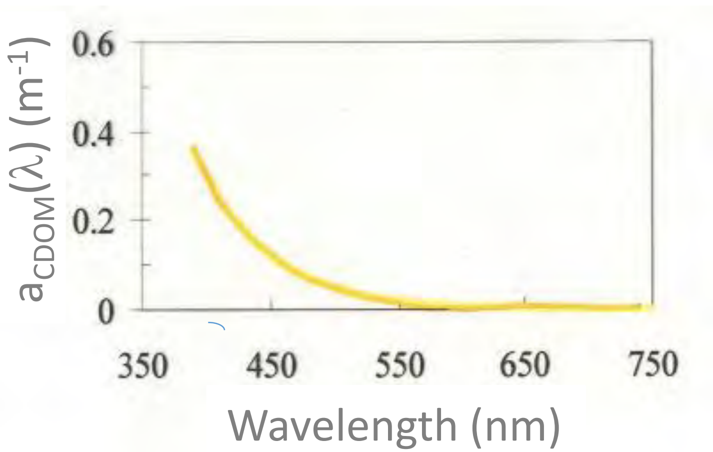
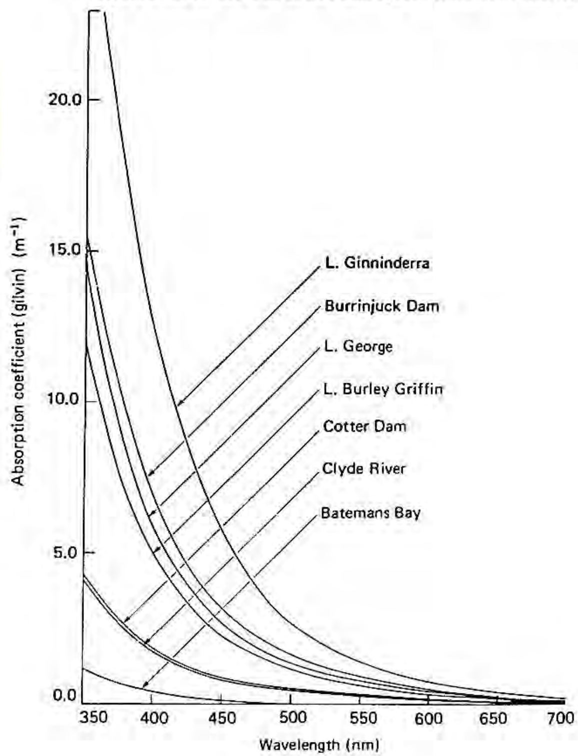


Fig. 3.5. Absorption spectra of soluble yellow material (gilvin) in various Australian natural waters (from Kirk, 1976*b*). The lowest curve (Batemans Bay, NSW) is for coastal sea water near the mouth of a river; the next curve (Clyde River, NSW) is for an estuary; the remainder are for inland water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

Dierssen et al. 2006

http://clarklittlephotography.com

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Colored dissolved organic matter (CDOM)

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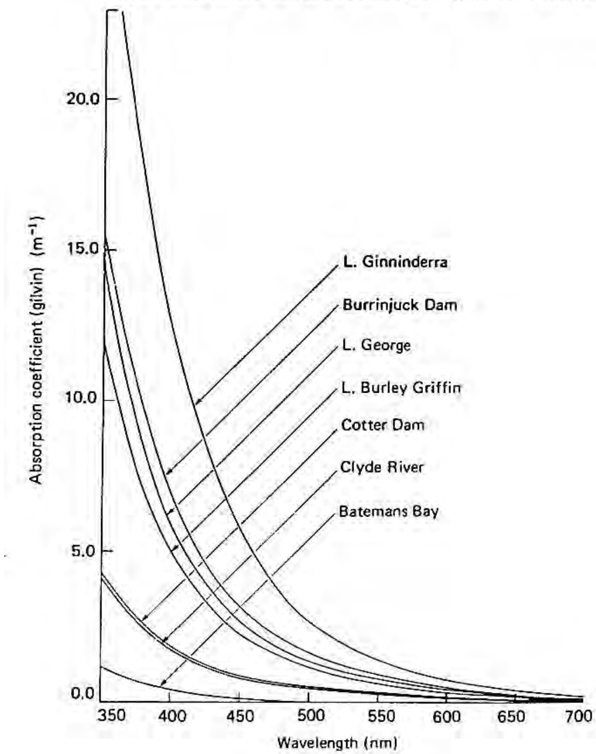


Kirk 1983

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

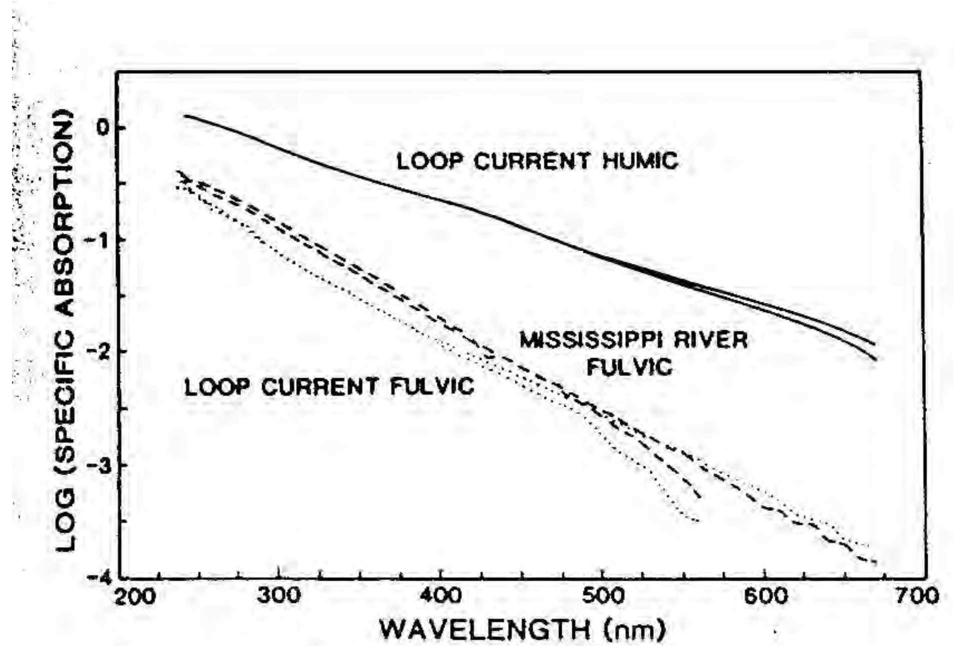
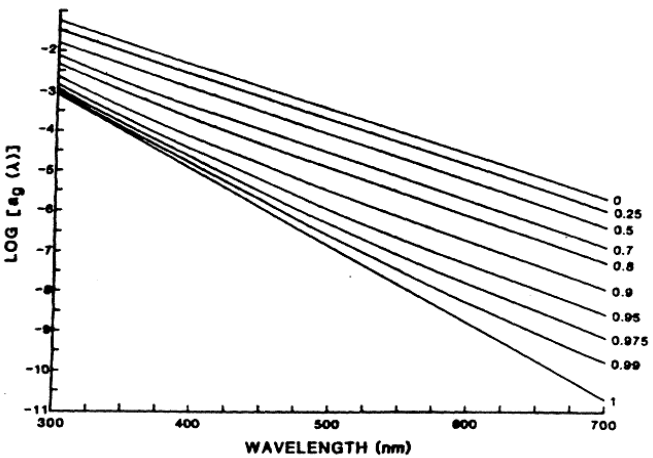


Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.

Carder et al. 1989 L&O

Absorbing Components: Colored dissolved organic matter (CDOM)

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

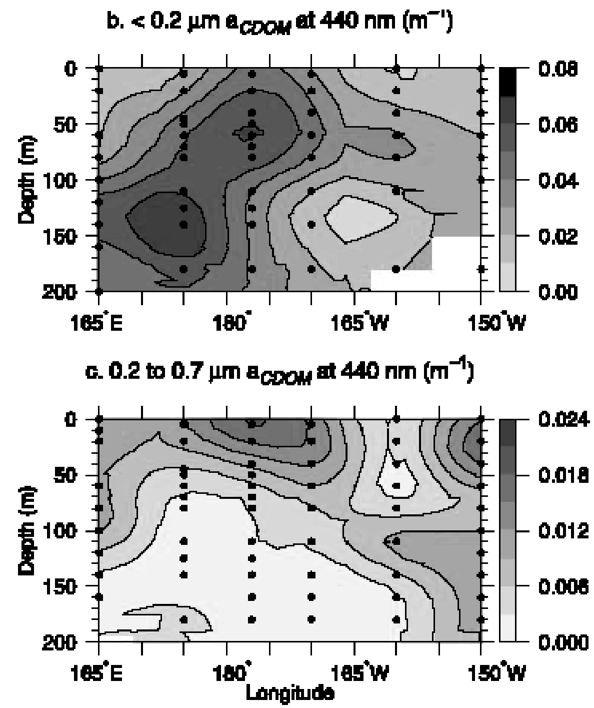


S
0.01-humic
0.02-fulvic

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 $a^*_f = 0.00732\ m^2\ g^{-1}$, $a^*_h = 0.131\ m^2\ g^{-1}$, $B_f = 0.0186\ nm^{-1}$, and B $0.0110\ nm^{-1}$. The fulvic acid fraction is shown beside each curve.

Carder et al. 1989 L&O

Equatorial Pacific –
filtrate pore size and spectral slope



S=0.014

S=0.011

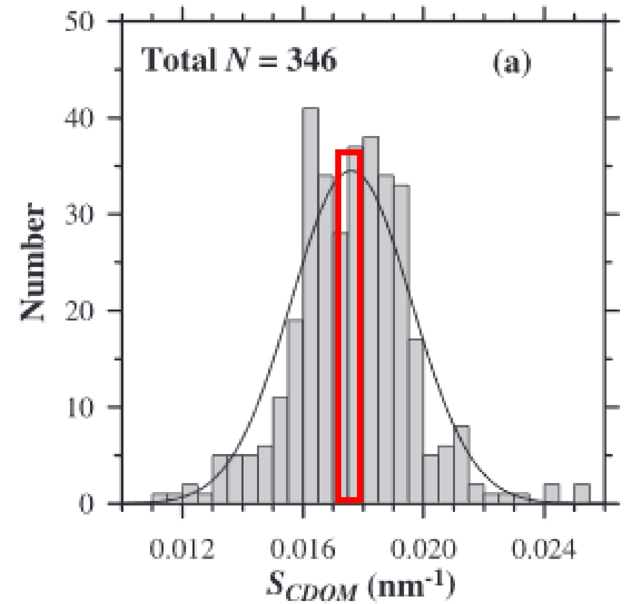
Simeon et al. 2003 JGR

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.

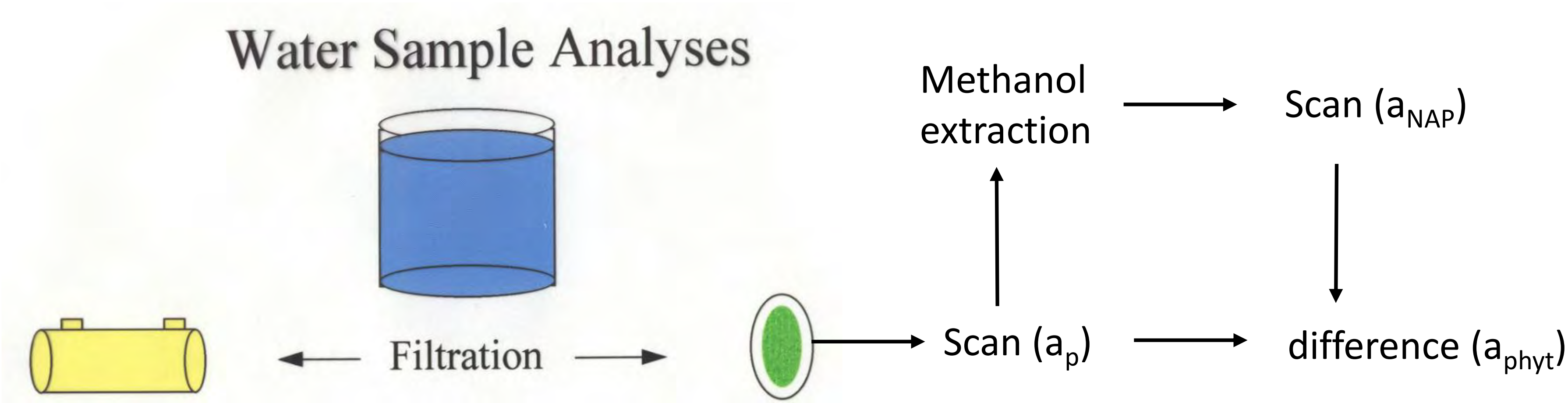
Reference	Site	Avg $C2_x$ (nm^{-1})
Gelbstoff		
Kalle 1966	Baltic, North Sea	0.018
Jerlov 1968		0.015
Kirk 1976	Lakes, coast	0.015
Lundgren 1976	Baltic	0.014
Kopelevich and Burenkov 1977	Indo-Pacific	0.017
Bricaud et al. 1981	Baltic	0.018
	Mauritania	0.015
	Gulf of Guinea	0.014
	Mediterranean	0.014
Okami 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

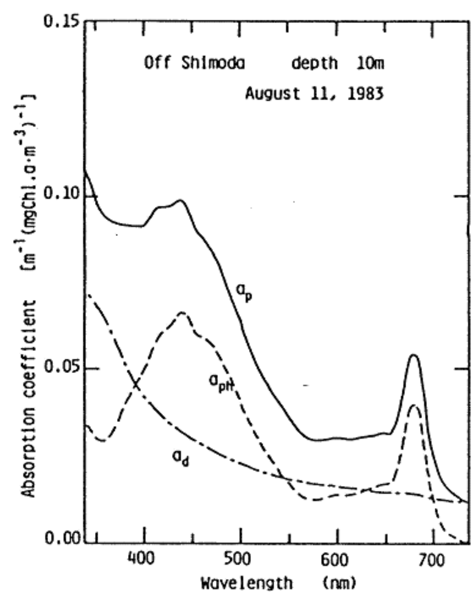
Roesler et al. 1989
(global synthesis)

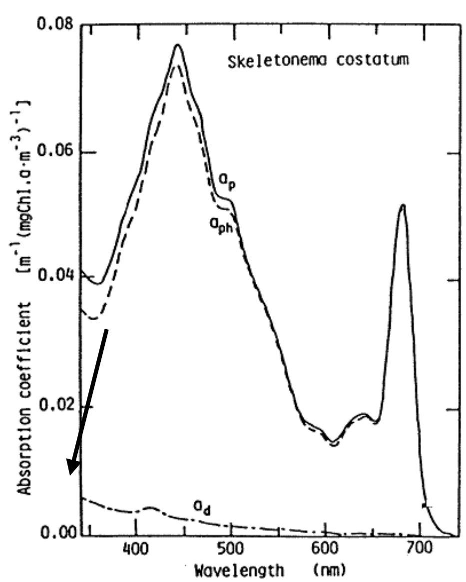


Babin et al. 2003
(European coastal waters)

Absorbing Components: Particles





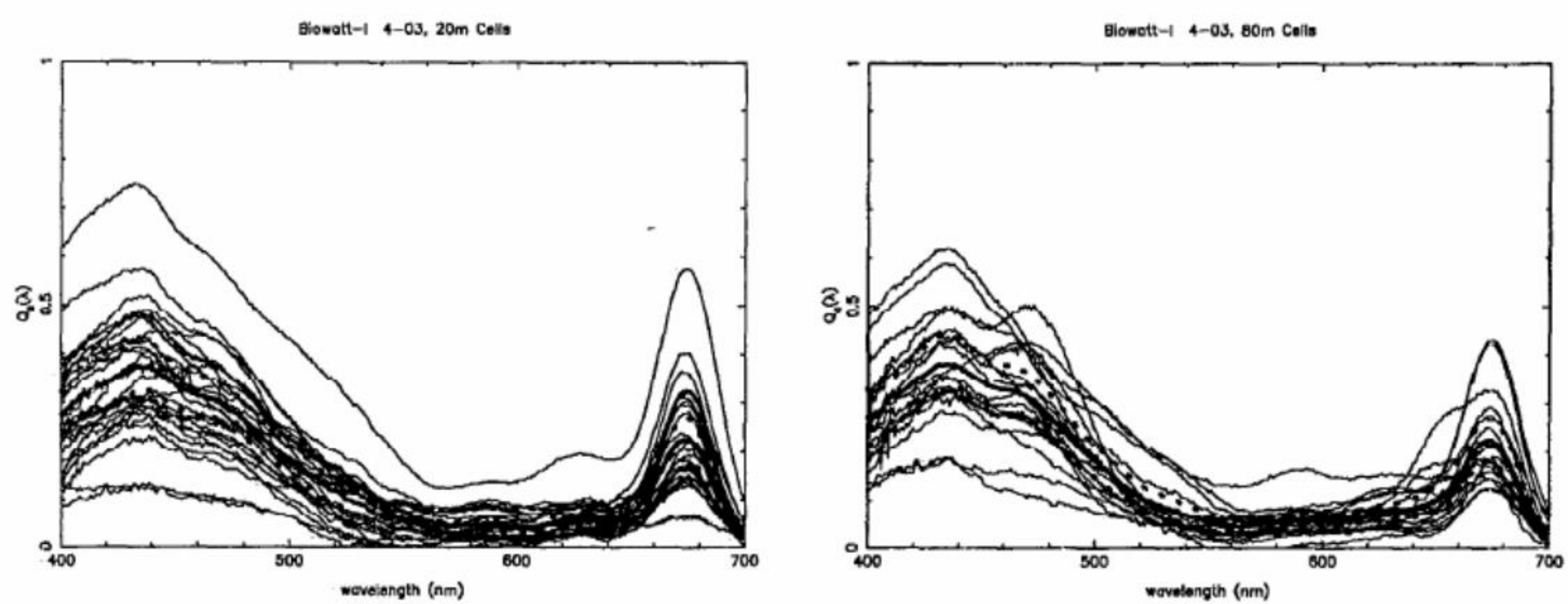


Kishino et al. 1985

Absorbing Components: Phytoplankton

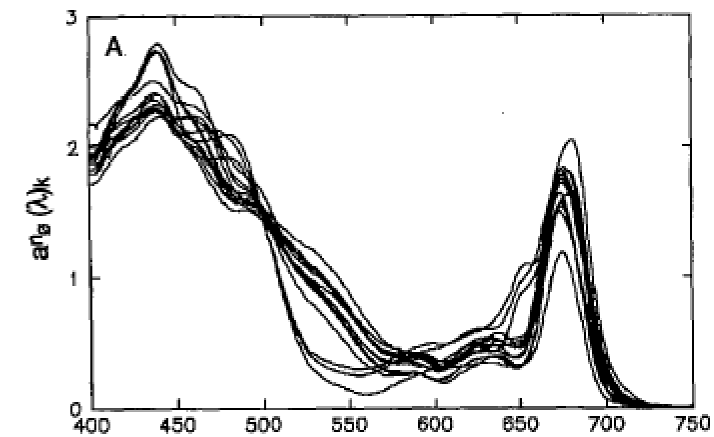
Individual cells, microphotometry

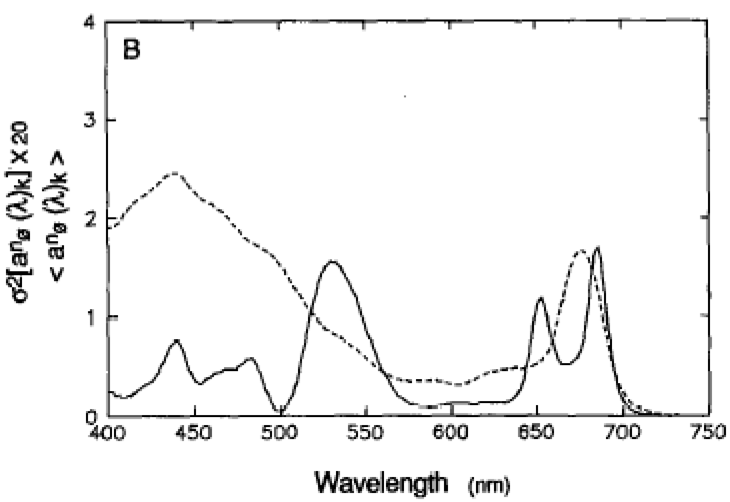
1710 *Iturriaga and Siegel* 1989 L&O

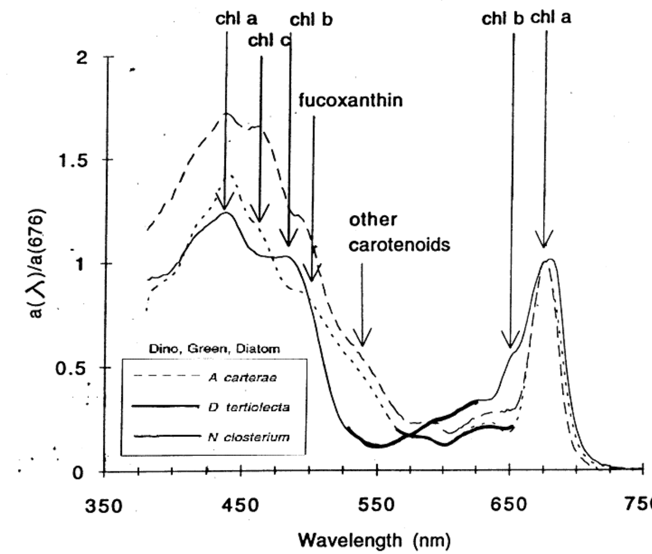


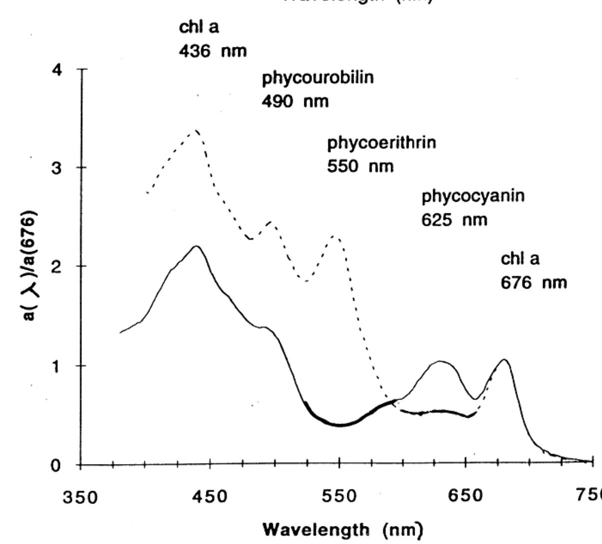
Absorbing Components: Phytoplankton

Species



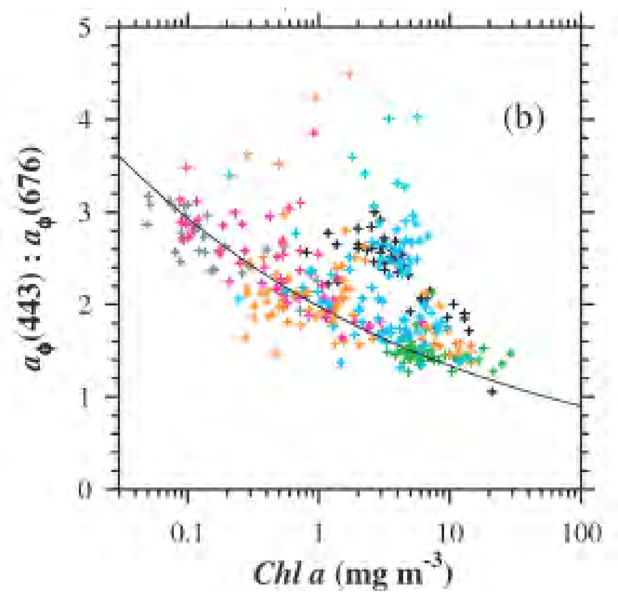






Roesler et al. 1989 L&O

Absorbing Components: Phytoplankton

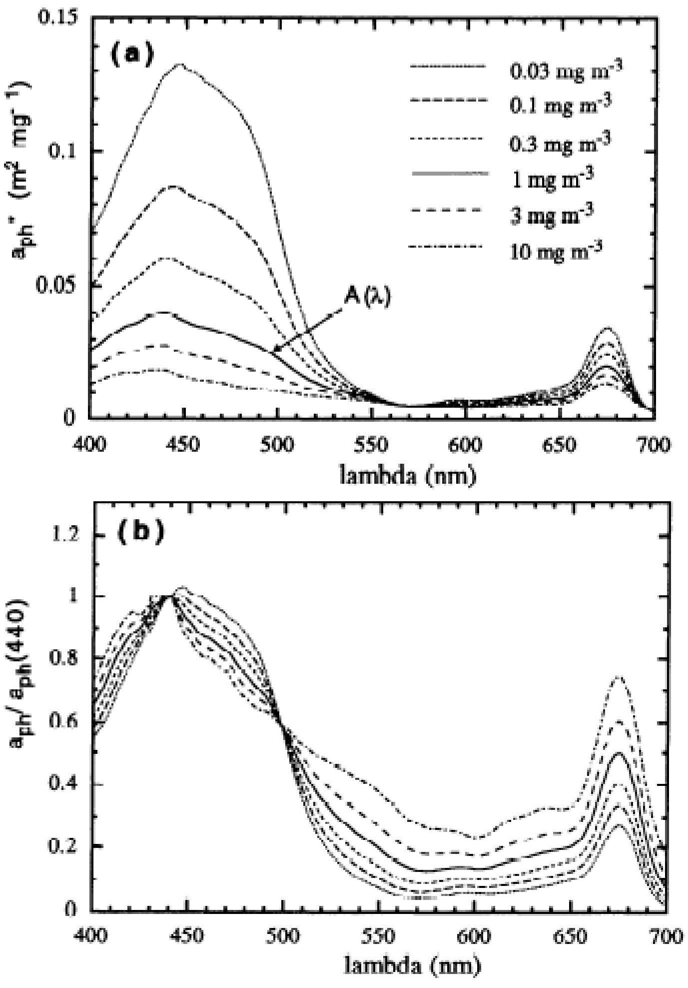


Babin et al. 2003

Bricaud et al. 1995

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

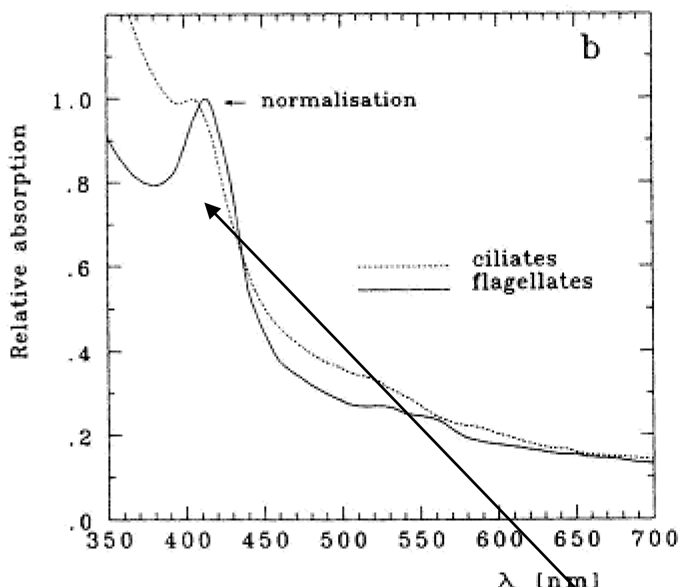
$\frac{a_{phyt}(\lambda)}{a_{phyt}(440)}$



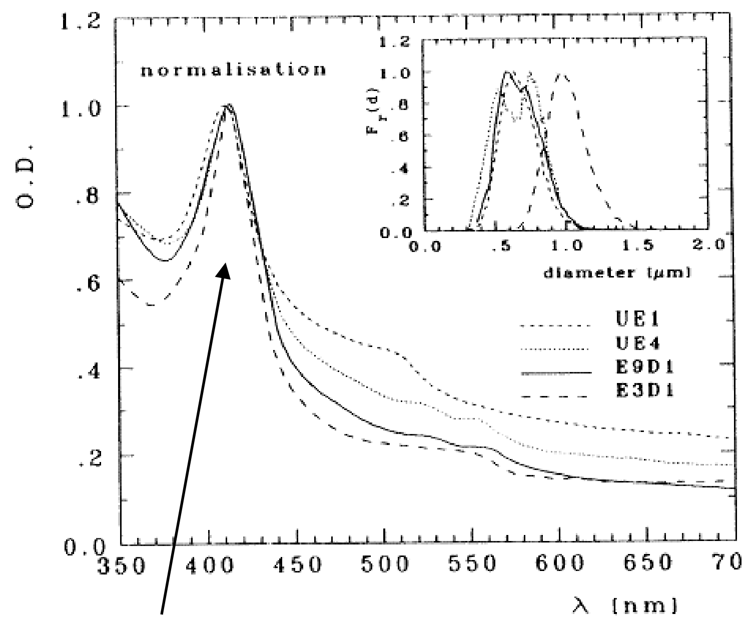
Global Relationships

Absorbing Components: other protists

ciliates and flagellates



heterotrophic bacteria



cytochrome 412

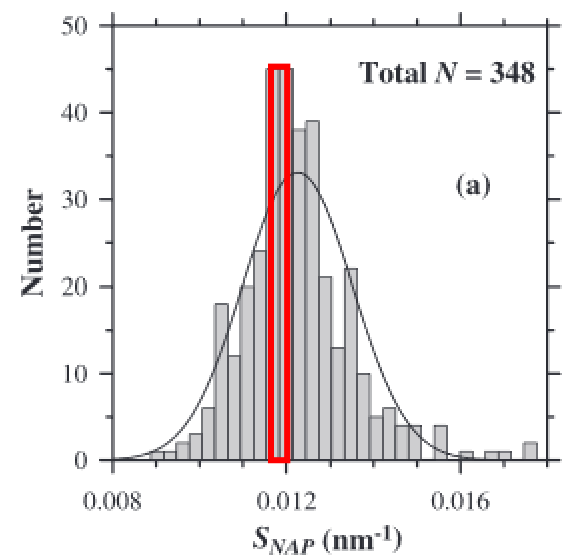
Morel and Ahn 1990 JMR

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.

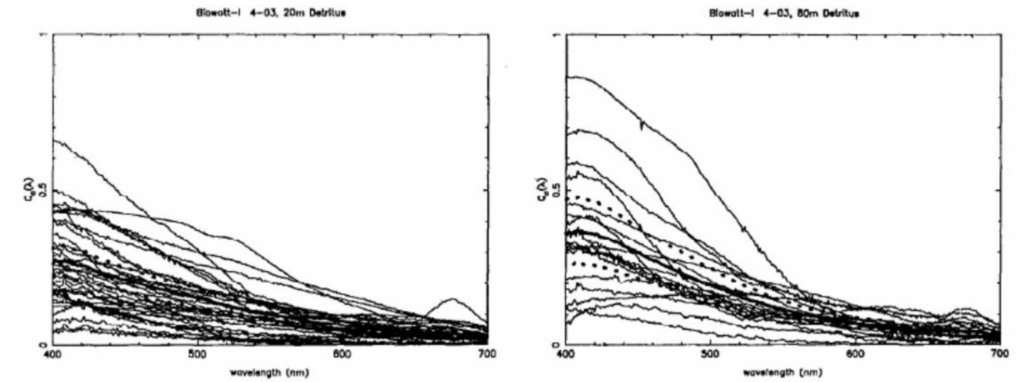
Reference	Site	Avg $C2_x$ (nm^{-1})
Gelbstoff		
Kalle 1966	Baltic, North Sea	0.018
Jerlov 1968		0.015
Kirk 1976	Lakes, coast	0.015
Lundgren 1976	Baltic	0.014
Kopelevich and Burenkov 1977	Indo-Pacific	0.017
Bricaud et al. 1981	Baltic	0.018
	Mauritania	0.015
	Gulf of Guinea	0.014
	Mediterranean	0.014
Okami 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)



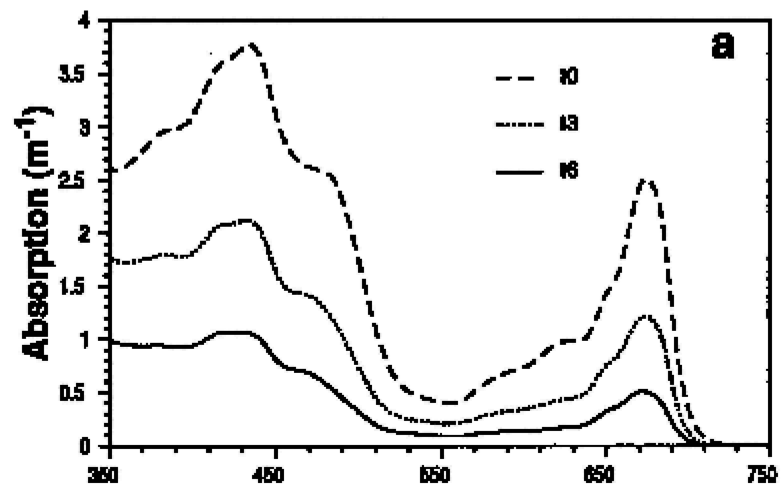
Babin et al. 2003
(European coastal waters)

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

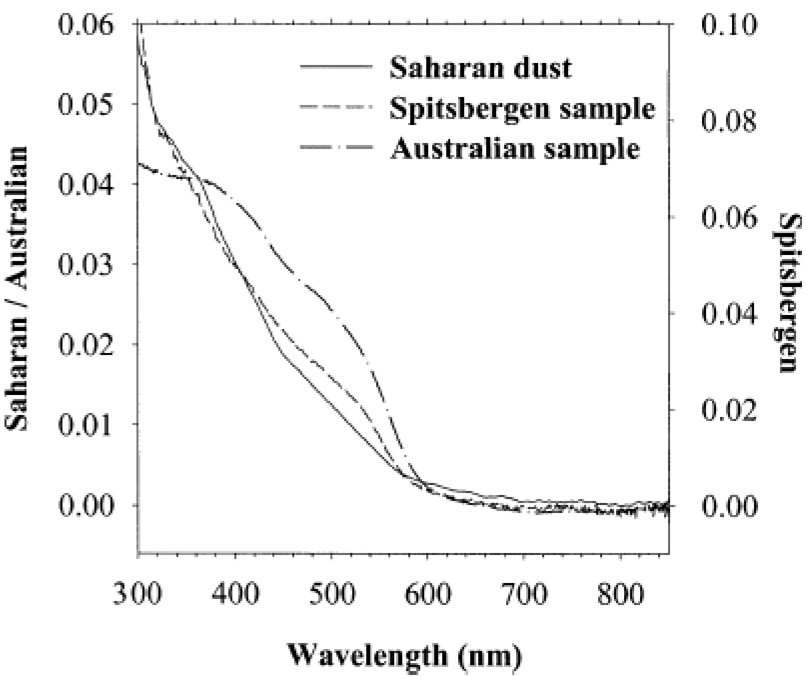


Fig. 5. Absorbance spectra of natural assemblages of mineral particles from three different environments.

Babin and Stramski 2003

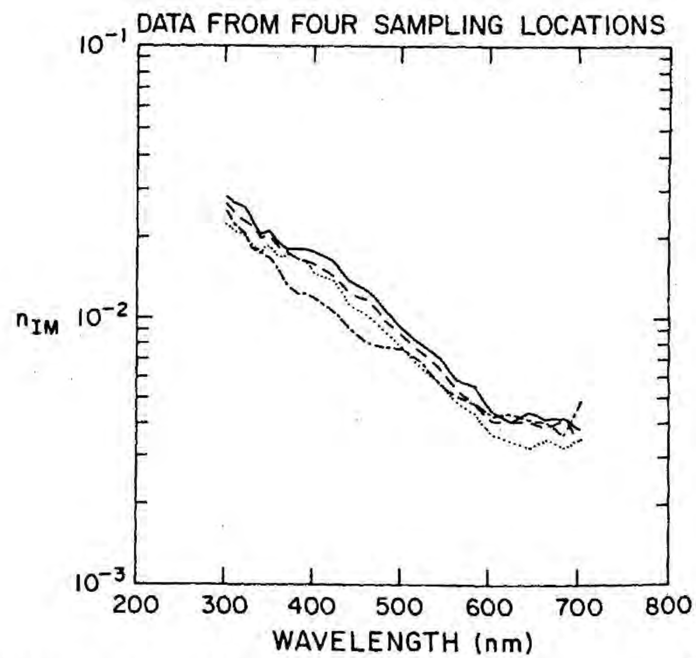


Fig. 8. Imaginary index of refraction for Saharan aerosols from each of the collection locations. The solid line represents the Tenerife sample; the dashed line, the *Meteor* sample; the dotted line, the Barbados sample; and the dashed-dotted line, the Sal Island sample.

Patterson et al. 1977 JGR

Absorbing Components: inorganic particles

Measured spectra

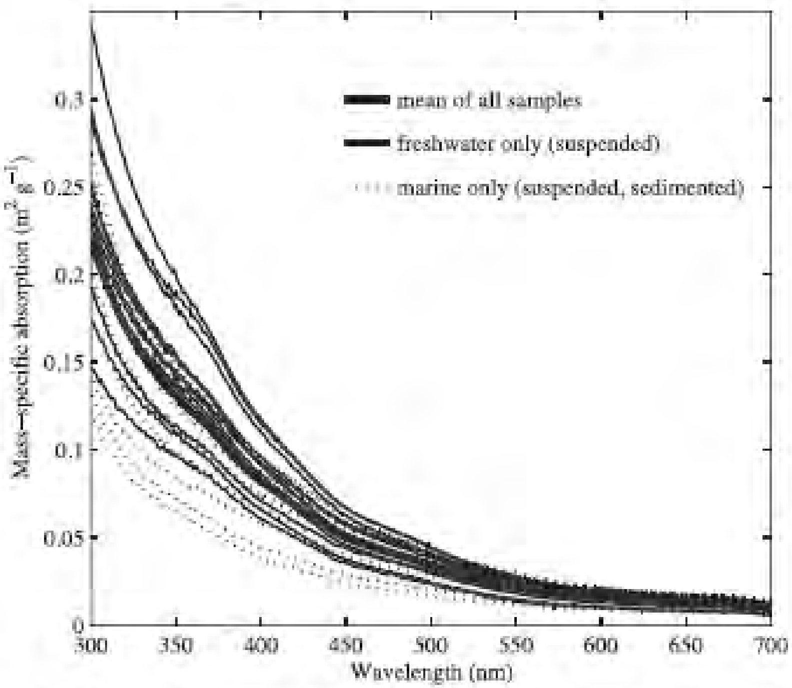


Fig. 3. Mass-specific absorption spectra of all samples analyzed here (n = 25). Heavy black line shows the mean, thin solid lines show samples from freshwater sites on the Atchafalaya and Mississippi Rivers, and dashed lines show samples from marine sites at Freshwater Bayou and the Atchafalaya River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

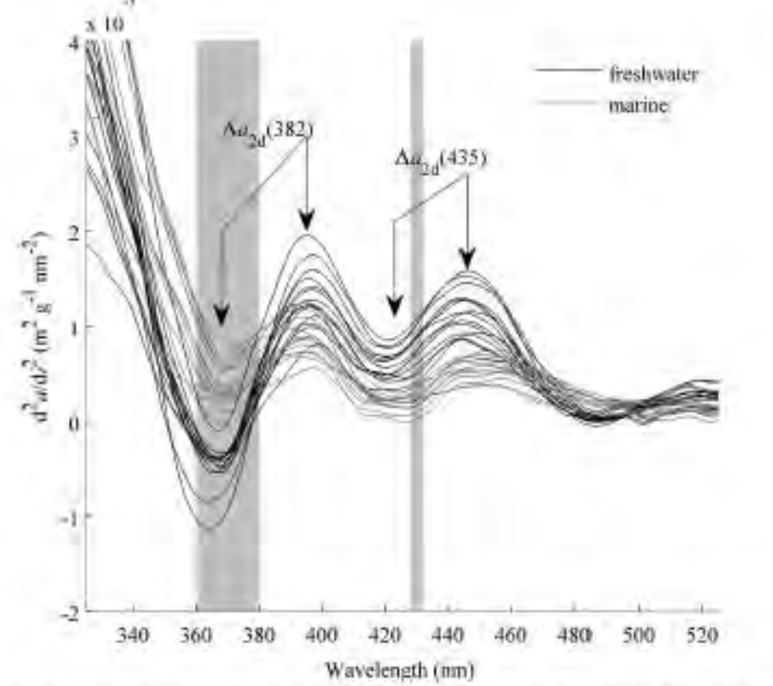
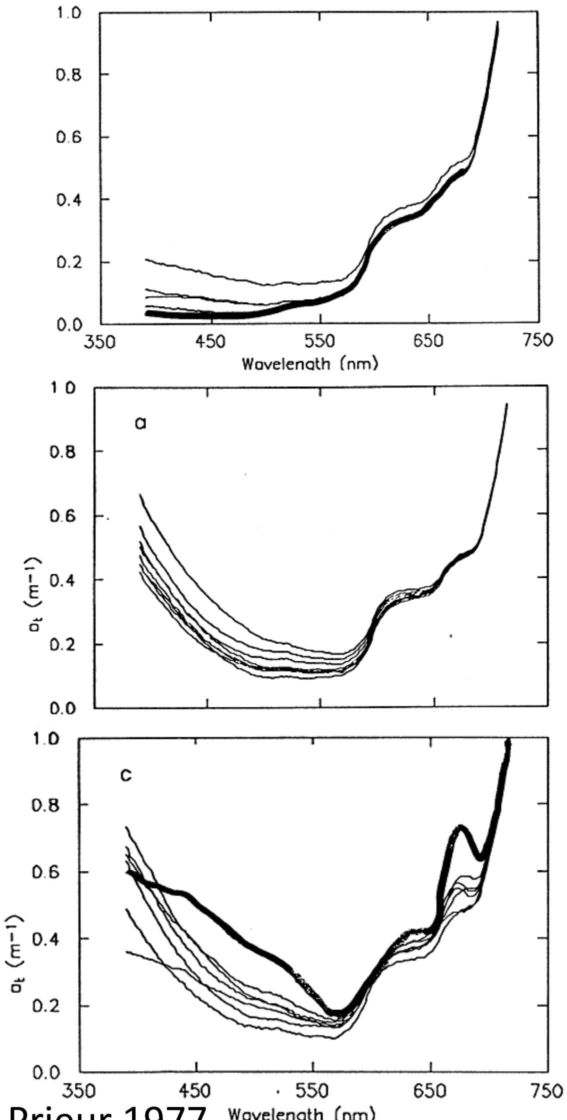


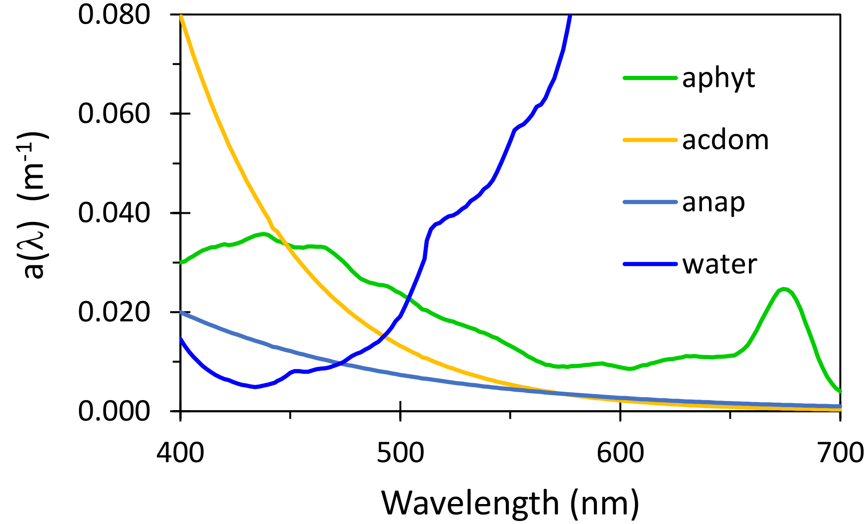
Fig. 10. Second derivatives of mass-specific absorption spectra. Black lines denote freshwater samples, and gray lines denote marine samples. Bracketed arrows labeled Δa_{2d}(382) and Δa_{2d}(435) show locations of second-derivative maxima and minima used to compute iron absorption peak heights plotted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

- Today
  - Lecture 5: Measuring absorption (Collin)
  - Lab 2 CDOM absorption methods
- Wednesday
  - Lab 3 Particulate absorption methods