Lecture 3
IOPs: Absorption physics and absorbing materials

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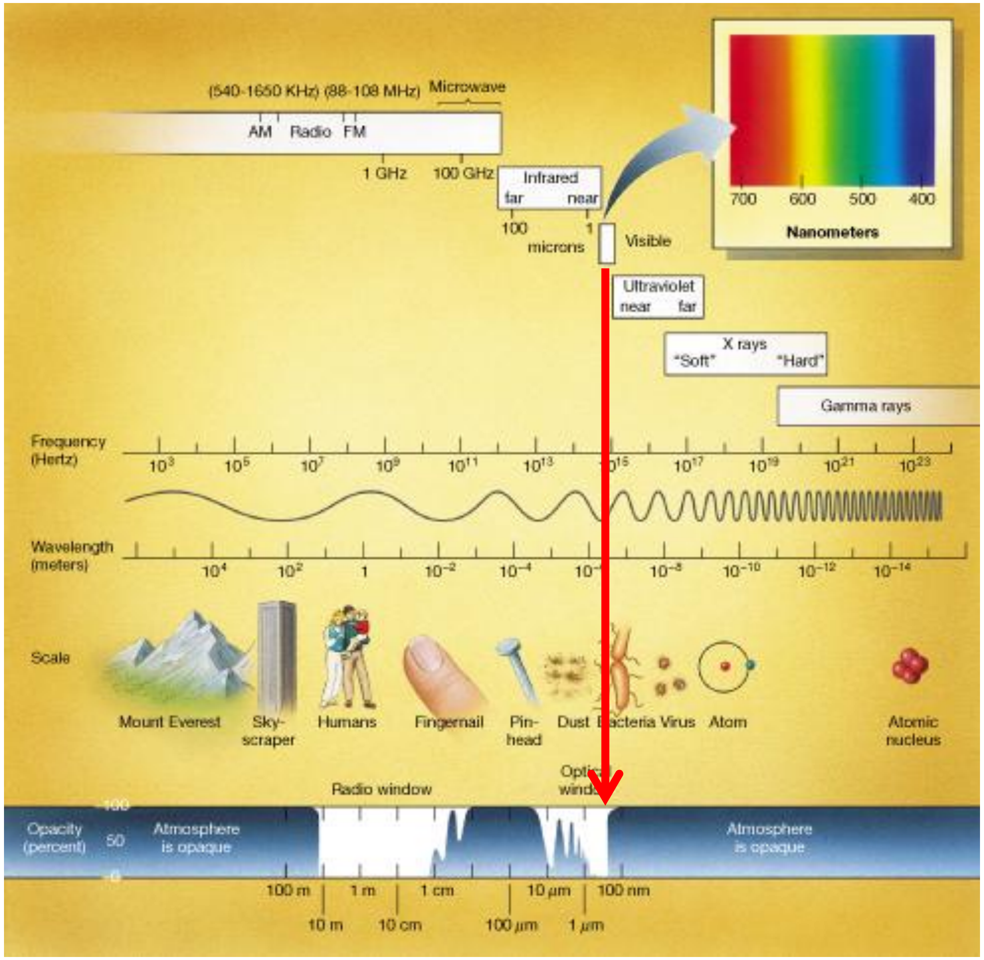
9 July 2013

Lecture Overview

- Overview of the electromagnetic spectrum
- What is absorption?
- Who are the absorbers?

Electromagnetic Spectrum

- Charged particles create electric fields (oscillation between +,-)
- When a charged particle moves, it creates a magnetic field
- The electromagnetic field oscillates as the energy propagates
- the range of oscillation frequencies is described by the EM spectrum

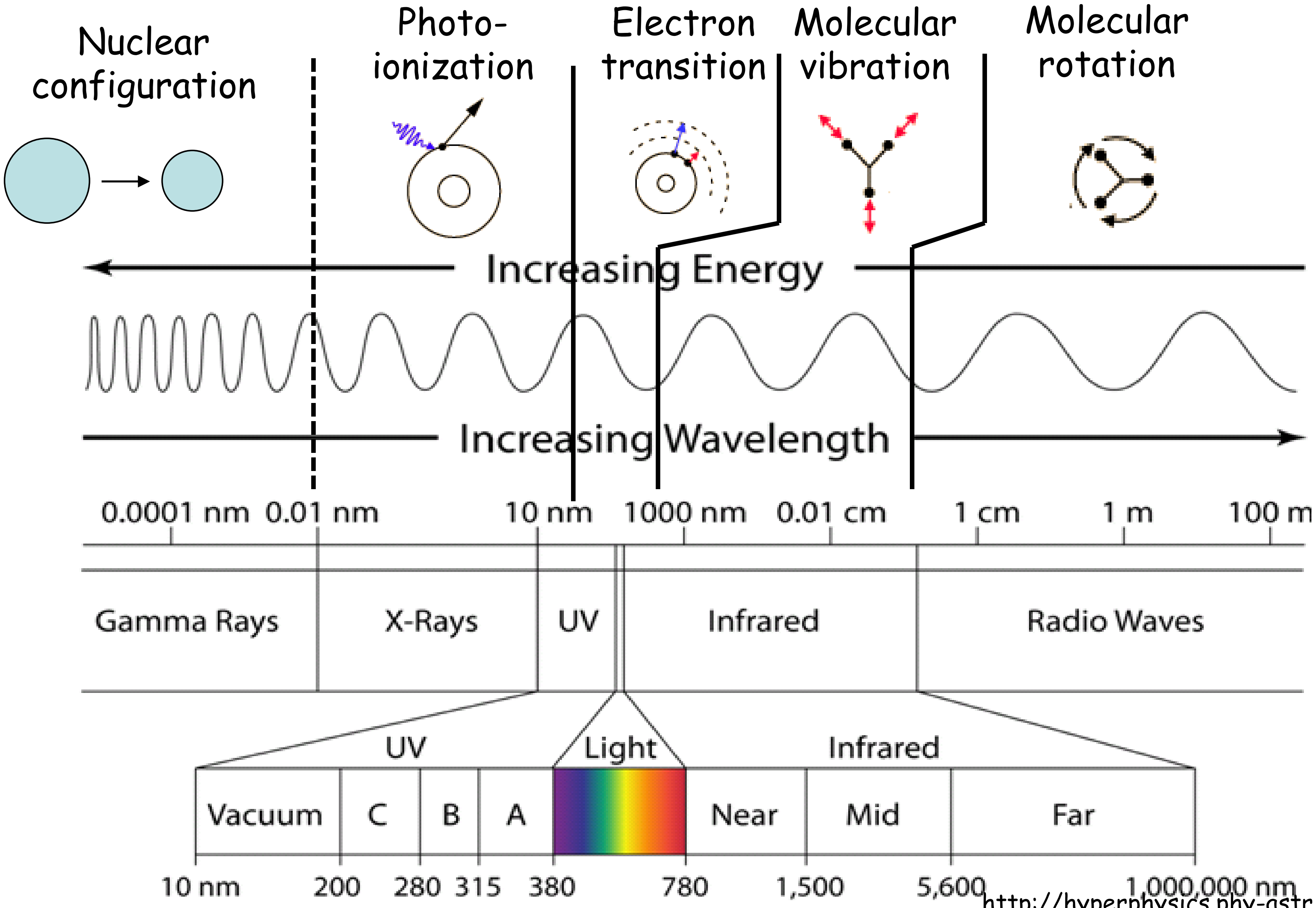


http://wps.prenhall.com/wps/media/objects/610/625137/Chaisson

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 given by hc/λ
- what happens to the molecule depends upon the energy, hence wavelength (frequency)

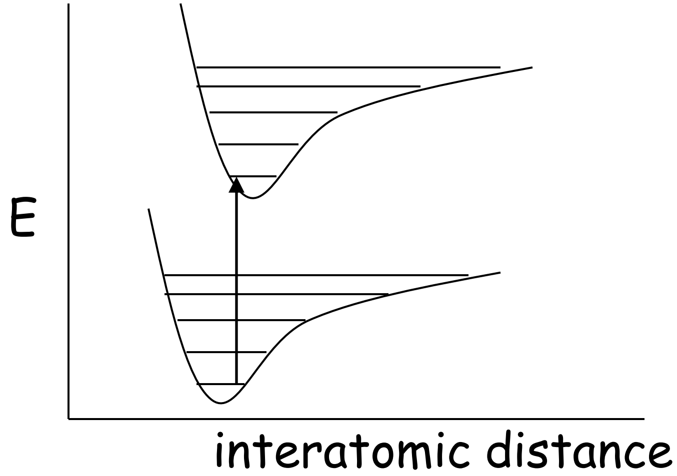
Interactions between energy and matter

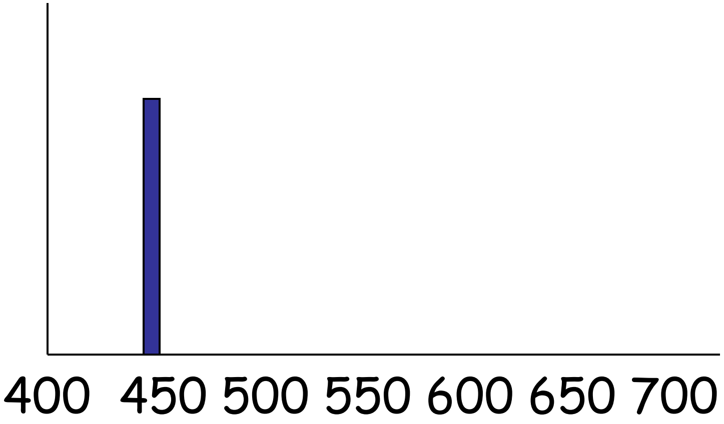


http://hyperphysics.phy-astr.gsu.edu

The amount of energy required to move an electron to another orbital shell is quantized

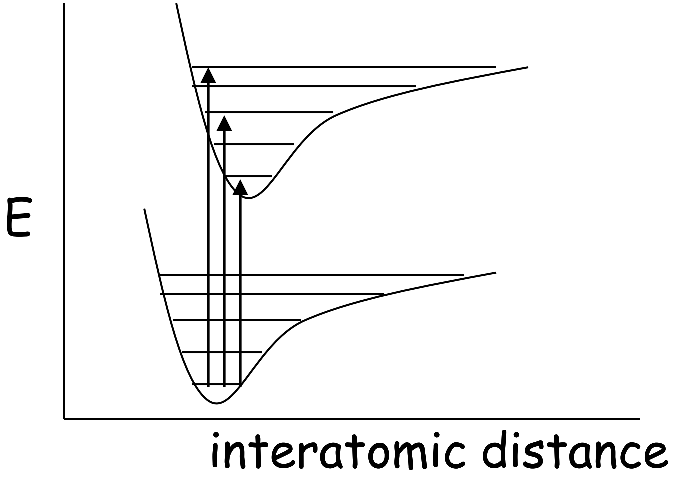
- The atom/molecule can **only** absorb visible radiation of this specific quantized energy or wavelength
- This determines the wavelength of the absorption peak

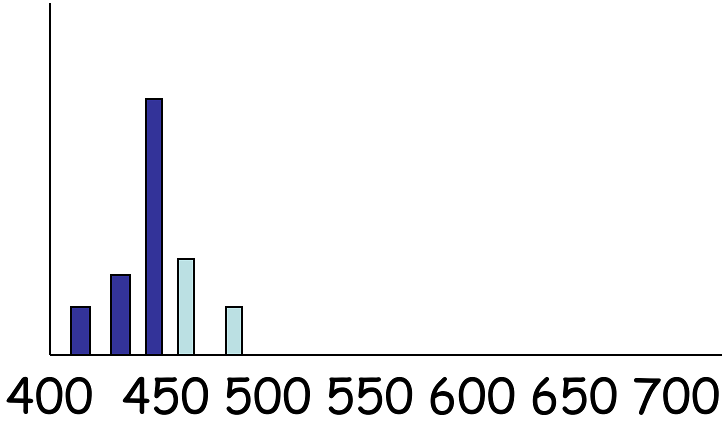




quantized energy states

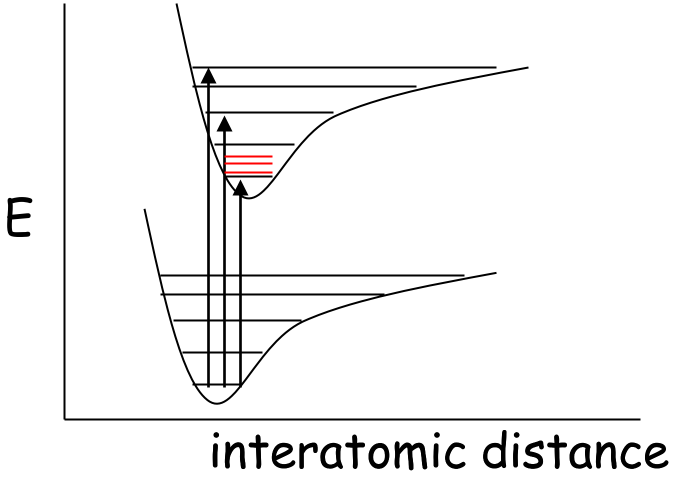
- Each orbital shell is associated with a series of higher excited states, which are also quantized
- These determine the wavelengths of the absorption side peaks which are higher (lower) energy but have a lower probability for absorption

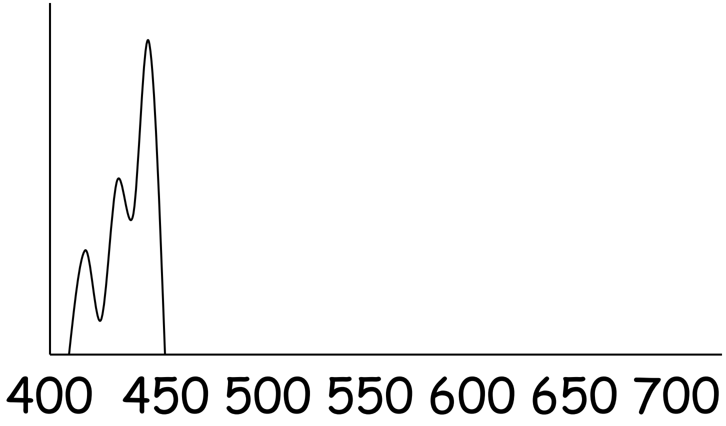




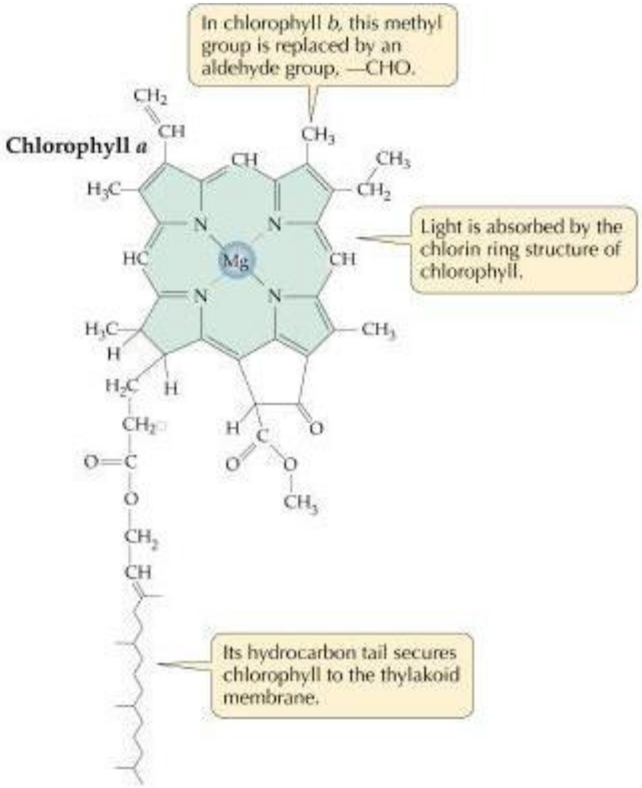
quantized vibrational states

- Each excited state, has vibrational and rotational states, also quantized
- These result in the smoothing of the absorption peaks





The chlorophyll *a* molecule has two higher energy orbital shells associated with the energy equivalent of a blue (443 nm) and a red (676 nm) photon

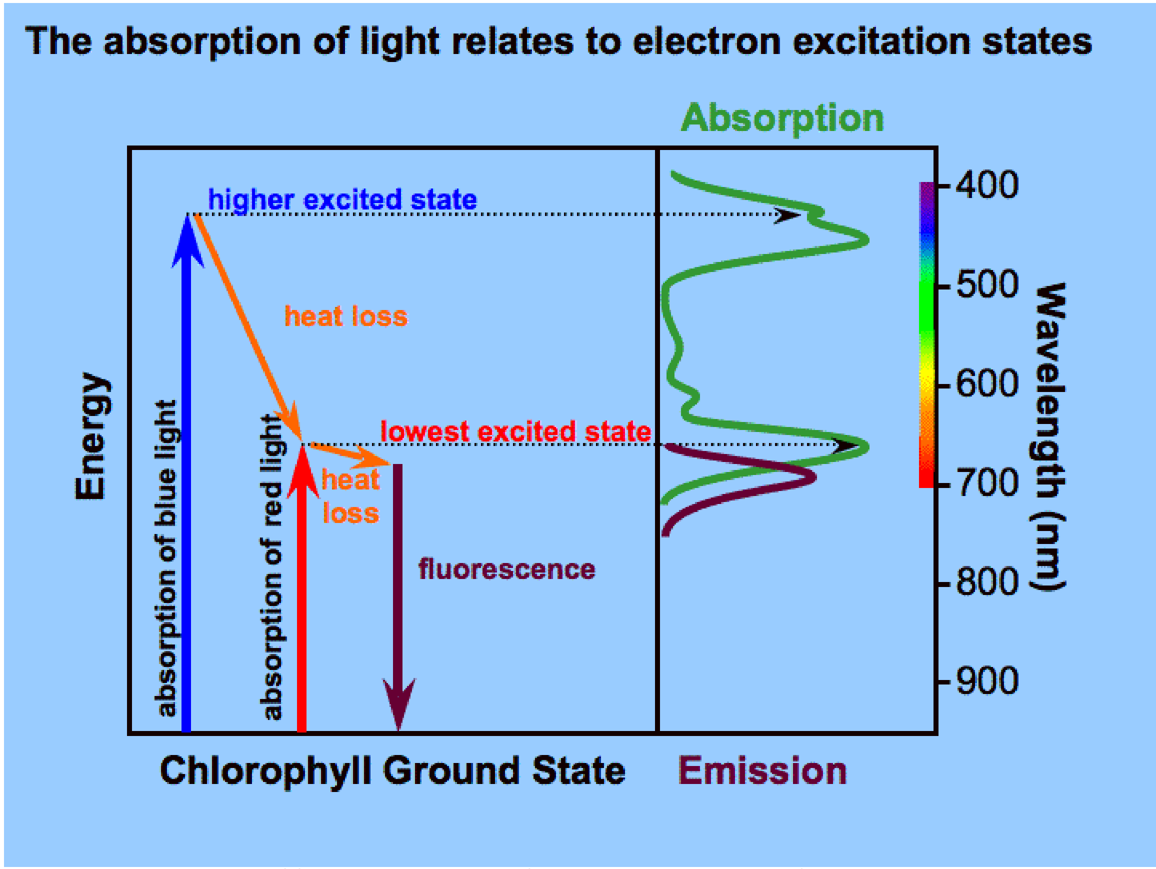


In chlorophyll *b*, this methyl group is replaced by an aldehyde group, —CHO.

Light is absorbed by the chlorin ring structure of chlorophyll.

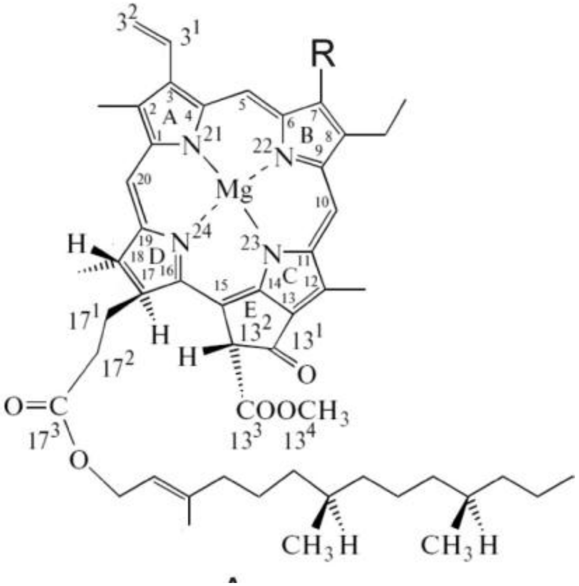
Its hydrocarbon tail secures chlorophyll to the thylakoid membrane.

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

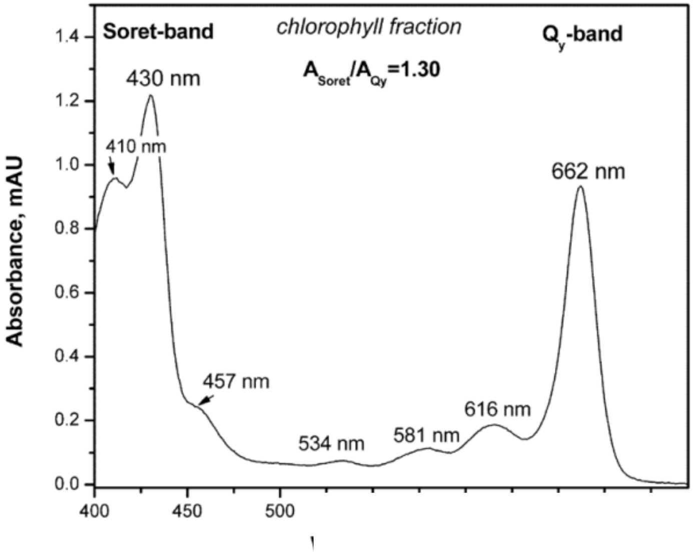


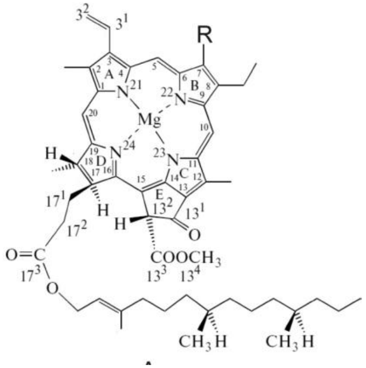
The absorption of light relates to electron excitation states

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

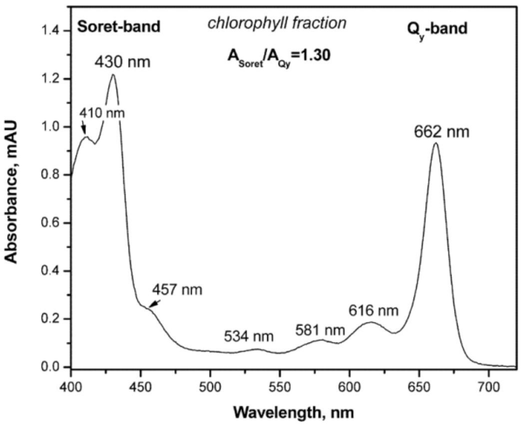


Chlorophyll



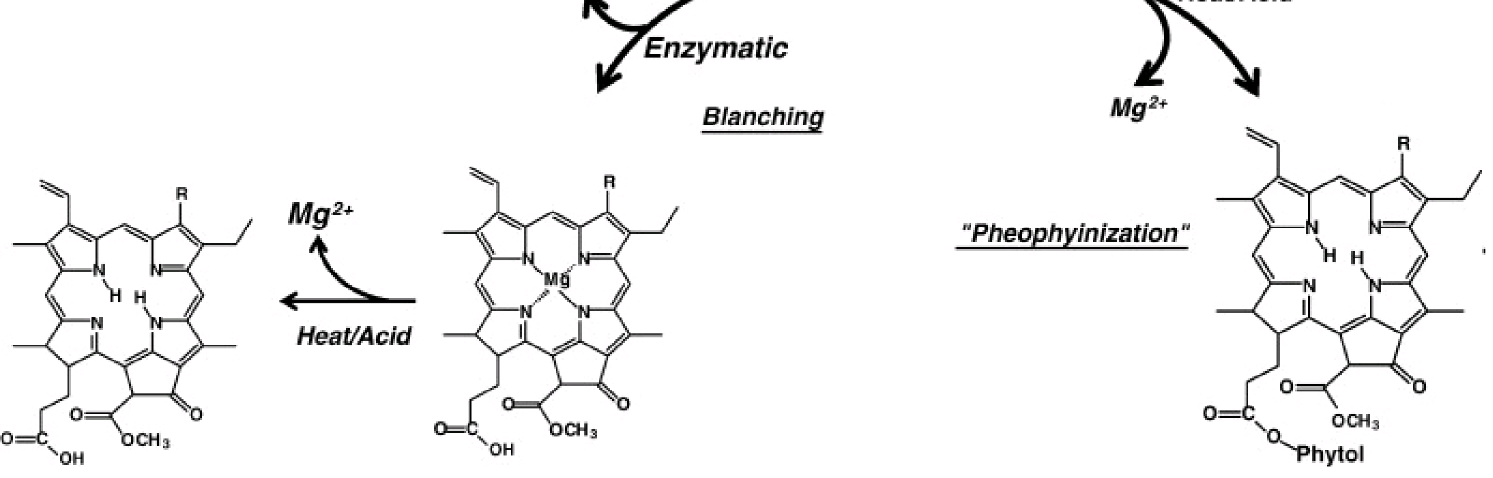


Chlorophyll



Phytol

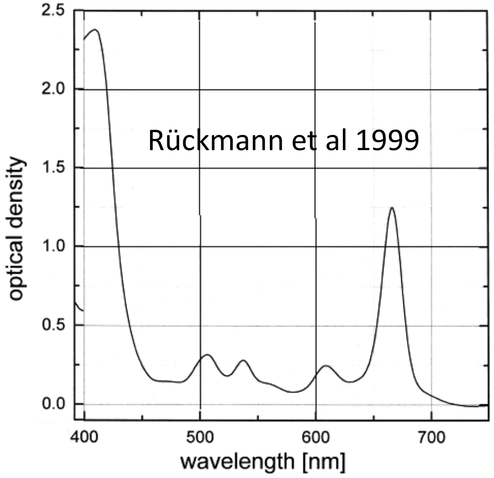
Heat/Acid



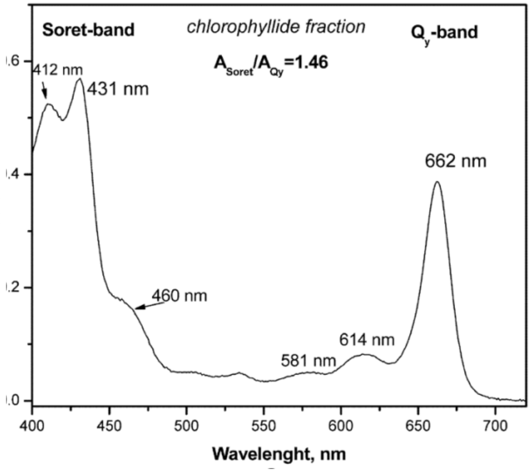
Pheophorbide

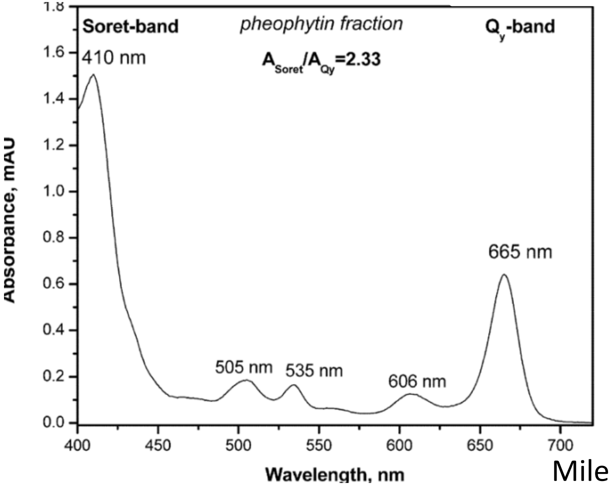
Chlorophyllide

Pheophytin



Rückmann et al 1999



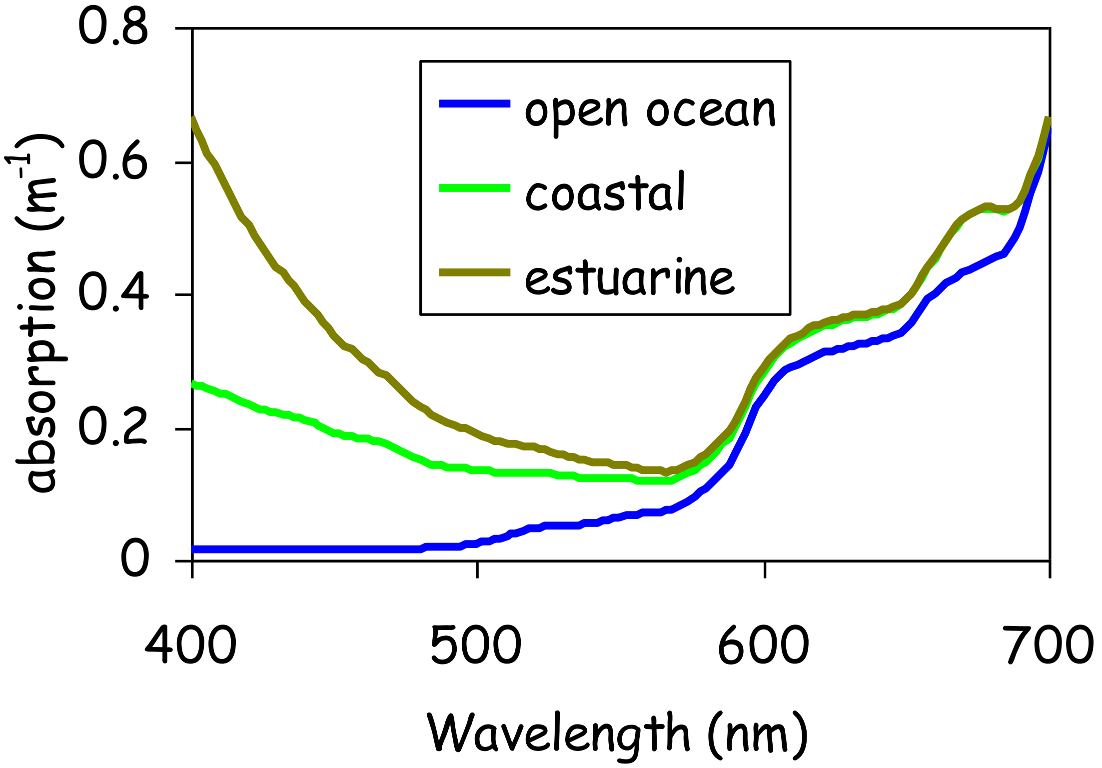


Milenković et al. 2012

Now that we know the physics of absorption

Let's meet the main absorbers in the ocean

Example of absorption spectra for three environments



- what do the spectra have in common?

all have strong red absorption

- How do they differ?

variable blue absorption

Absorption is a conservative property so total absorption is equal to the sum of the individual absorbing constituents

$$a_T = a_w + \Sigma a_{\text{dissolved compounds}} + \Sigma a_{\text{particles}}$$

And because of Beer's Law, the absorption coefficients are proportional to the concentration of absorbing matter, therefore absorption is a proxy for concentration

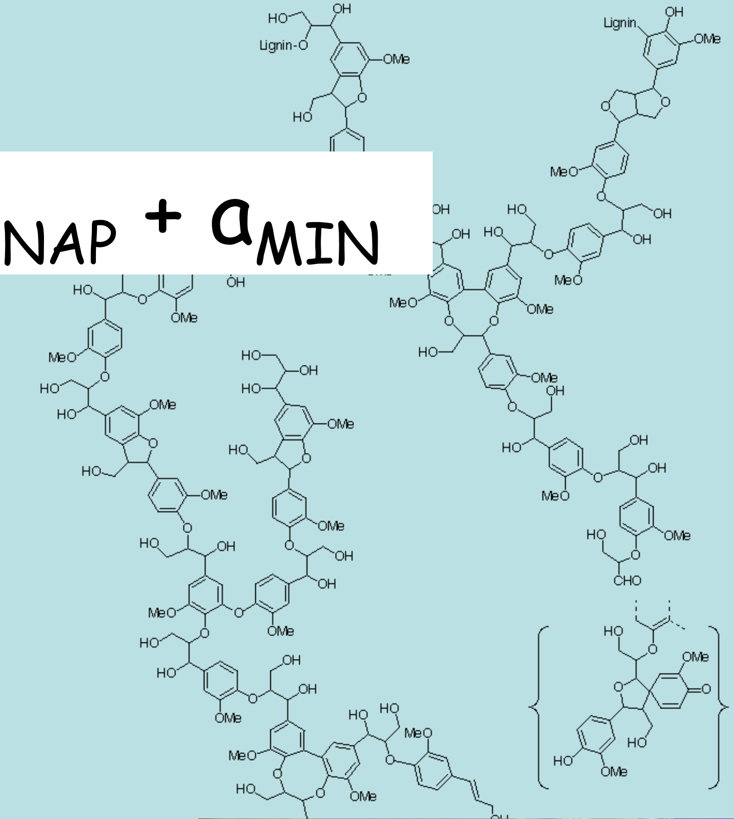
It is impractical to measure the absorption spectrum for each constituent

so we group components by their
common absorption properties
(and our inability to separate them)

Absorbing matter

Practically…

$$a_T = a_w + a_{CDM} + a_\phi + a_{NAP} + a_{MIN}$$



water
colored **d**issolved (**o**rganic) **m**atter
phytoplankton (in vivo pigments)
non-**a**lgal **p**articles (organic)
minerals (inorganic particulate matter)


© Clark Little / SWNS.COM

Absorbing Components: Water

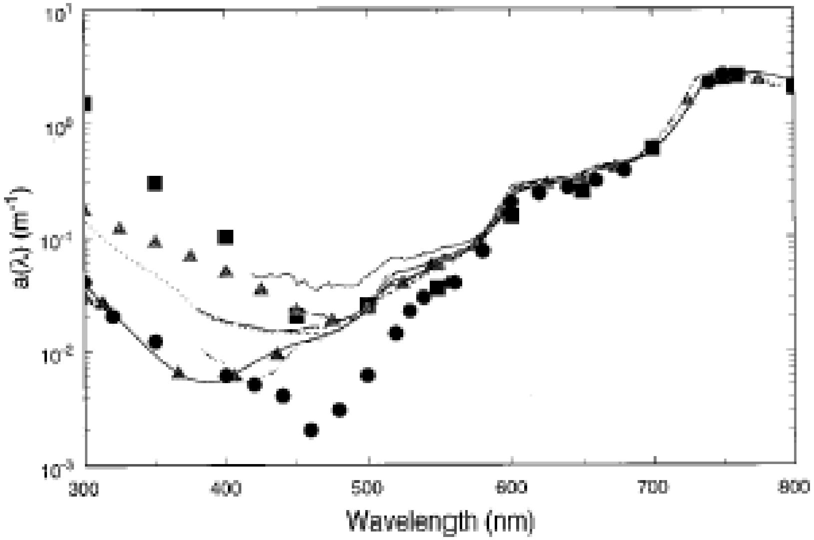


Fig. 1. Absorption coefficient of pure water as measured or compiled by several investigators.[1,2,11,18,19,21,26–33] The discrepancy in the estimated absorption coefficients is largest at short wavelengths where absorption by organic contaminants is significant. At wavelengths longer than 550 nm the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

Compendium and data
http://omlc.ogi.edu/spectra/water/abs/

Absorbing Components: Water

Temperature

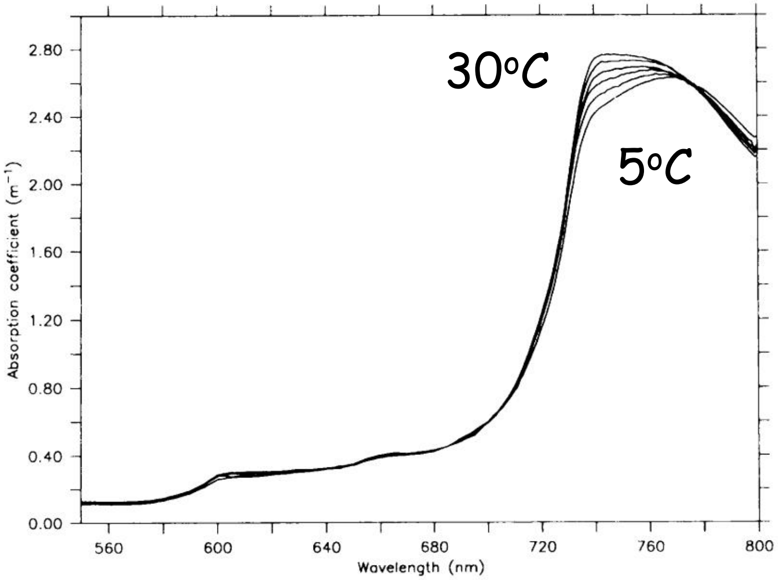
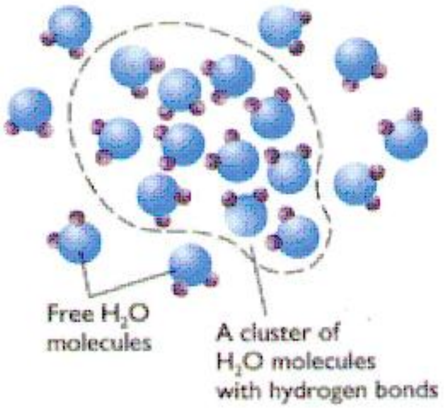
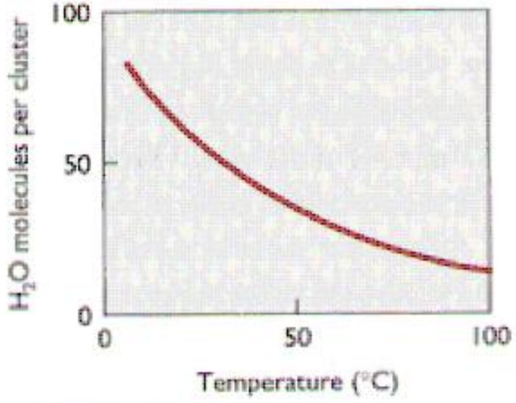


Fig. 3. Absorption coefficient from 550 to 800 nm adjusted at 685 nm to the value of Tam and Patel (1979). The curves represent absorption at temperatures of 5, 10, 15, 21, 25, and 30°C as read from bottom to top at 750 nm.

Pegau and Zaneveld 1993 Limnol Oceanogr.



(d) CLUSTERS OF WATER



(e) SIZE OF WATER CLUSTERS

natural variations

Absorbing Components: Water

Salinity

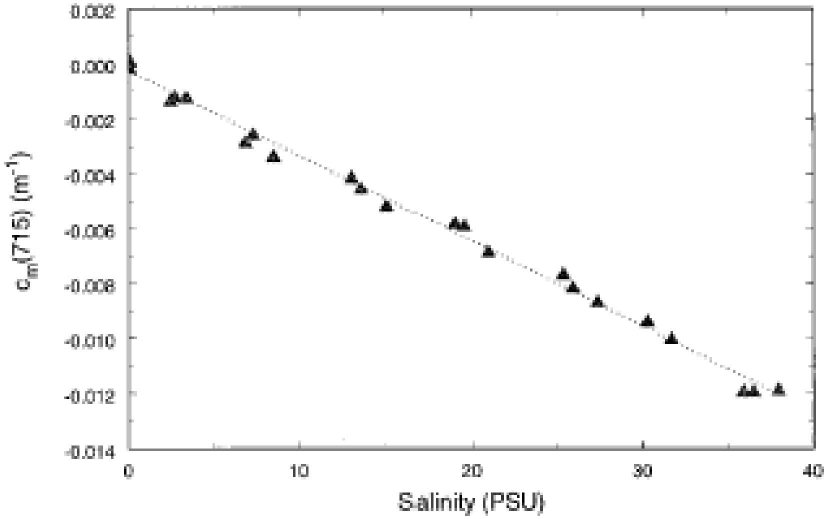
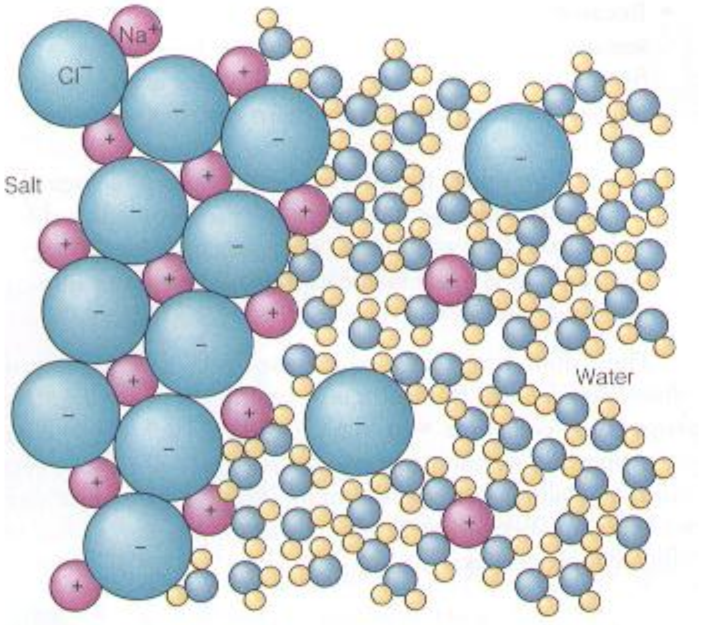


Fig. 6. Attenuation coefficient at 715 nm as a function of salinity. This figure illustrates the linear dependence of the attenuation coefficient on salinity.

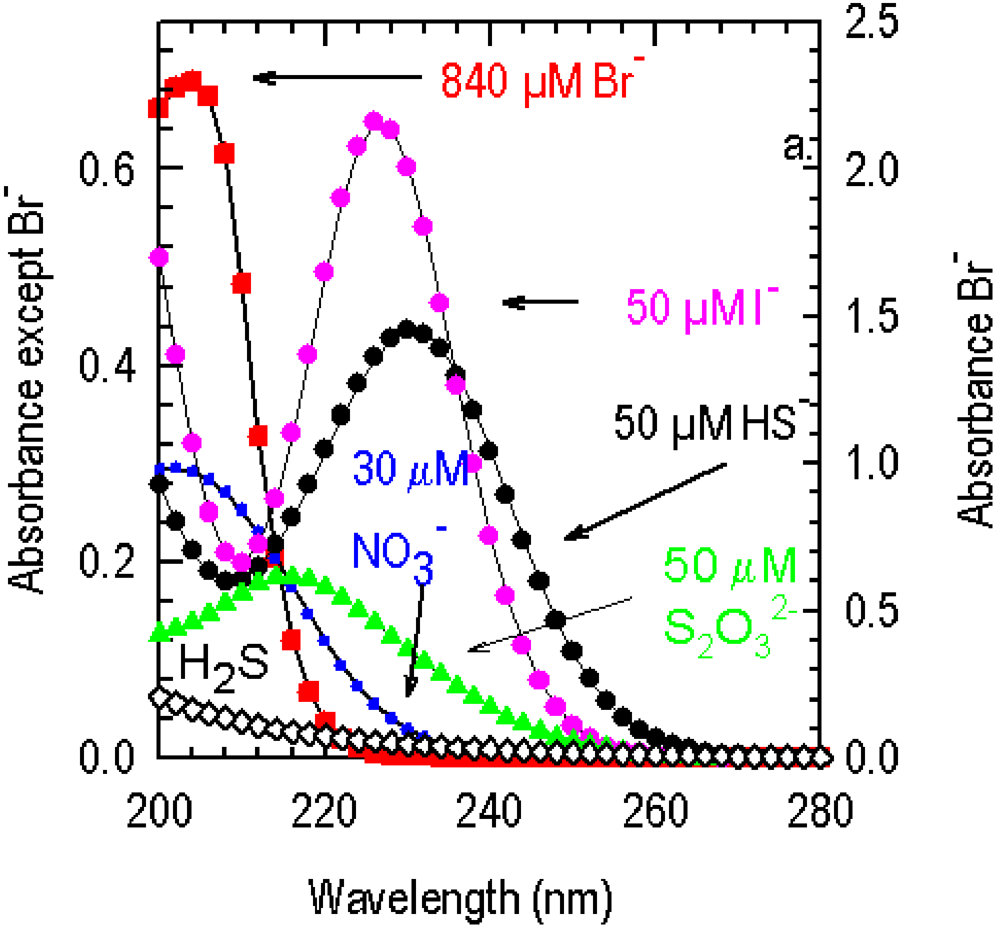
Pegau etal. 1997 Appl.Opt.



natural variations

Dissolved inorganic matter

- basis 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

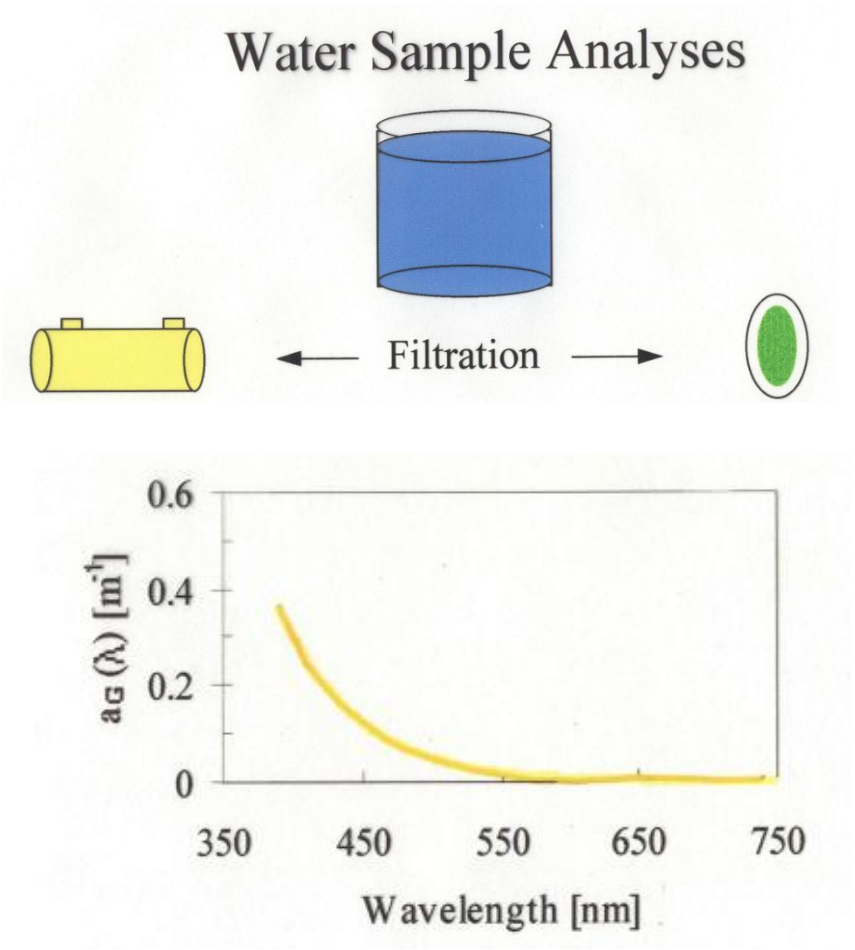
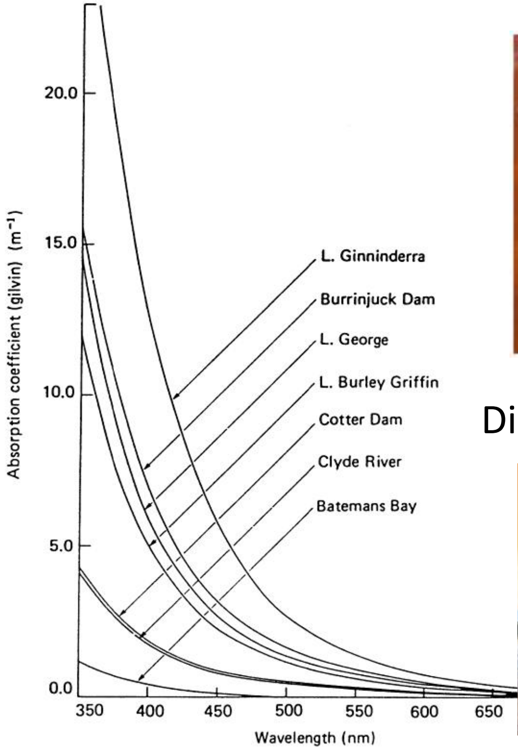
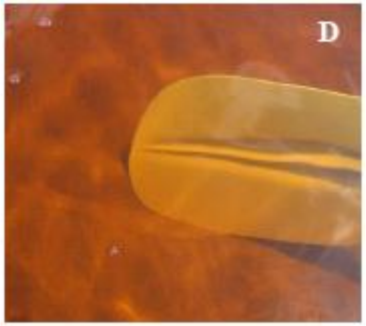


Fig. 3.5. Absorption spectra of soluble yellow material (gilvin) in various Australian natural waters (from Kirk, 1976*b*). The lowest curve (Batemans Bay, NSW) is for coastal sea water near the mouth of a river; the next curve (Clyde River, NSW) is for an estuary; the remainder are for inland water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

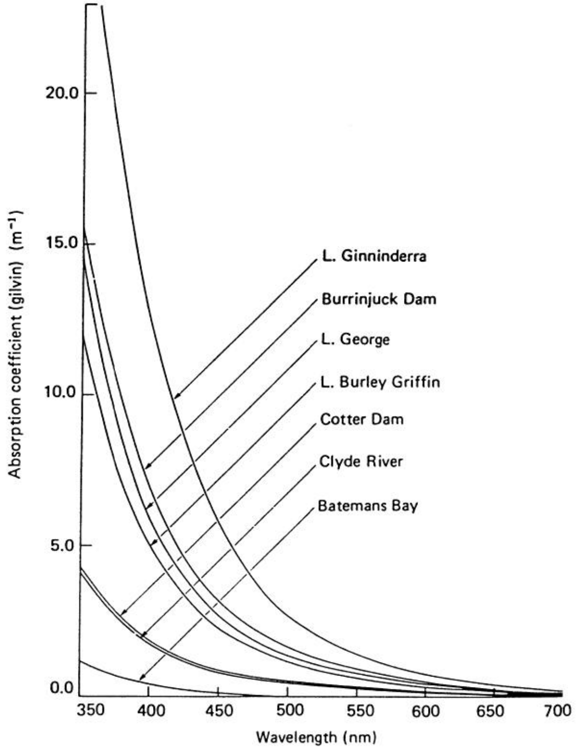


Dierssen et al. 2006

http://www.clarklittlephotography.com/

Absorbing Components:
Colored Dissolved (Organic) Matter

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

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

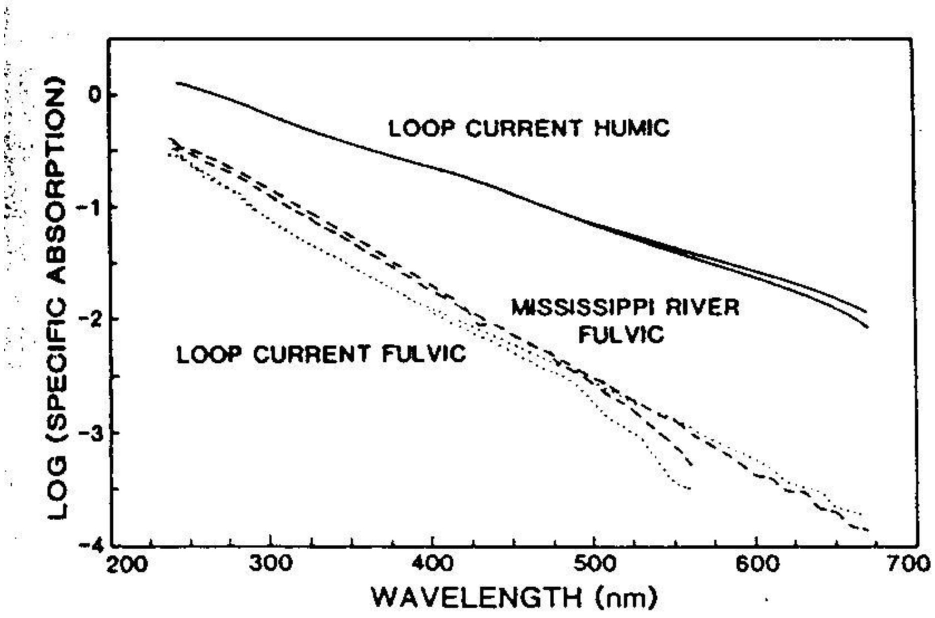
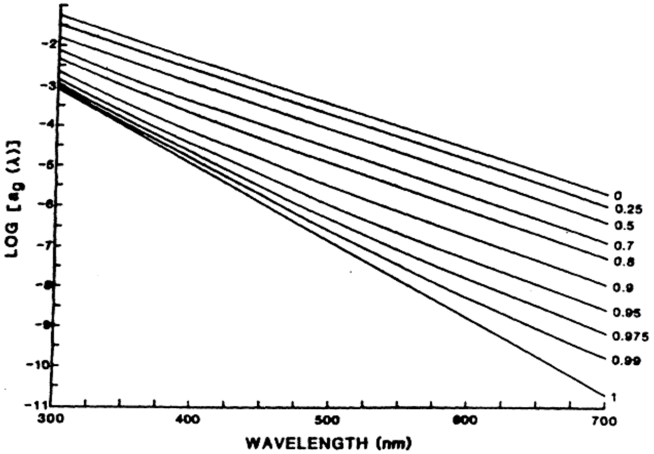


Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.

Carder et al. 1989 L&O

Absorbing Components:
Colored Dissolved (Organic) Matter

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



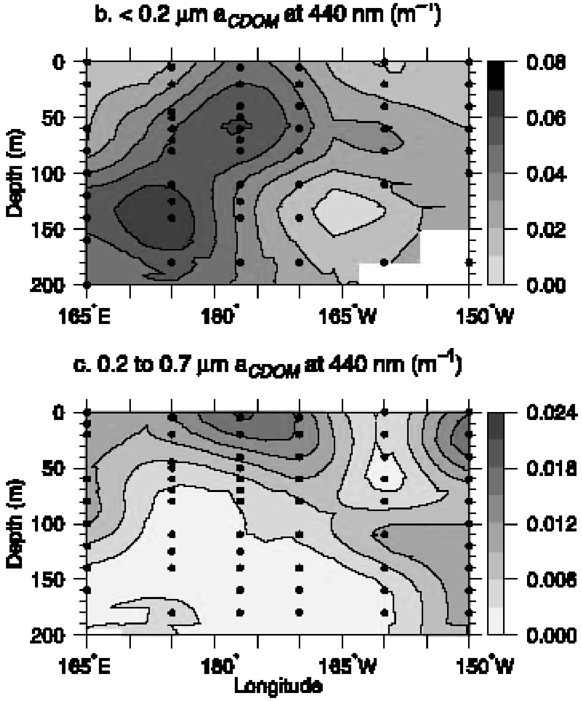
S
0.01

0.02

Fig. 3. Spectral variation of the absorption coefficient due to marine humus or Gelbstoff as a function of t 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



S=0.014

S=0.011

Simeon et al. 2003 JGR

Absorbing Components: Colored Dissolved Organic Matter

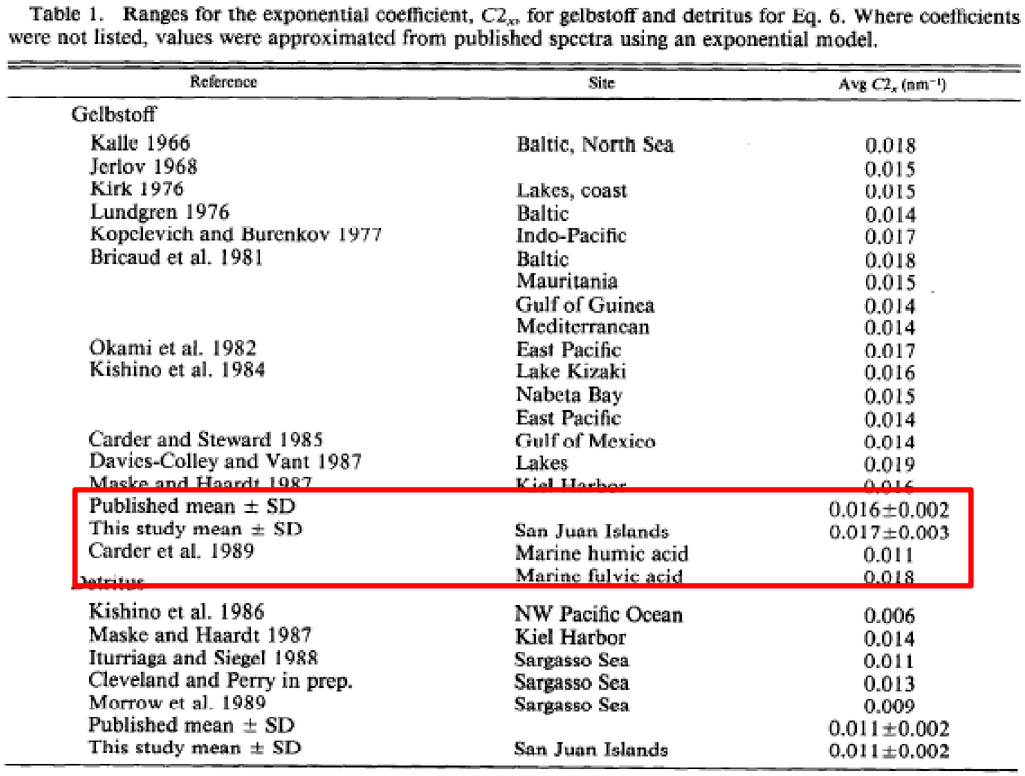
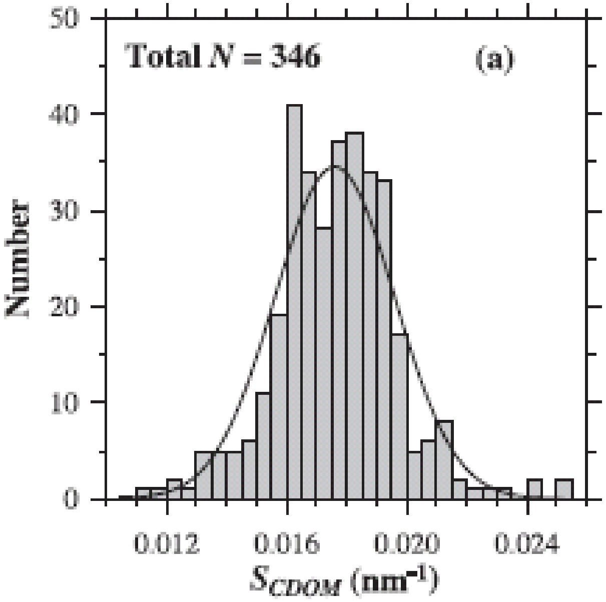


Table 1. Ranges for the exponential coefficient, $C2_x$, for gelbstoff and detritus for Eq. 6. Where coefficients were not listed, values were approximated from published spectra using an exponential model.

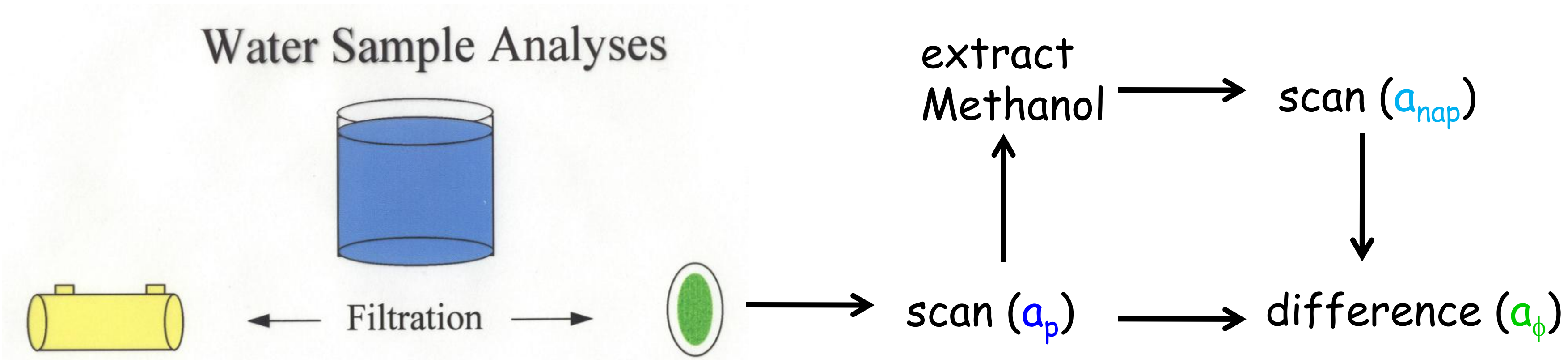
Reference	Site	Avg $C2_x$ (nm^{-1})
Gelbstoff		
Kalle 1966	Baltic, North Sea	0.018
Jerlov 1968		0.015
Kirk 1976	Lakes, coast	0.015
Lundgren 1976	Baltic	0.014
Kopelevich and Burenkov 1977	Indo-Pacific	0.017
Bricaud et al. 1981	Baltic	0.018
	Mauritania	0.015
	Gulf of Guinea	0.014
	Mediterranean	0.014
Okami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



Babin et al. 2003
European coastal waters

Absorbing Components: Particles

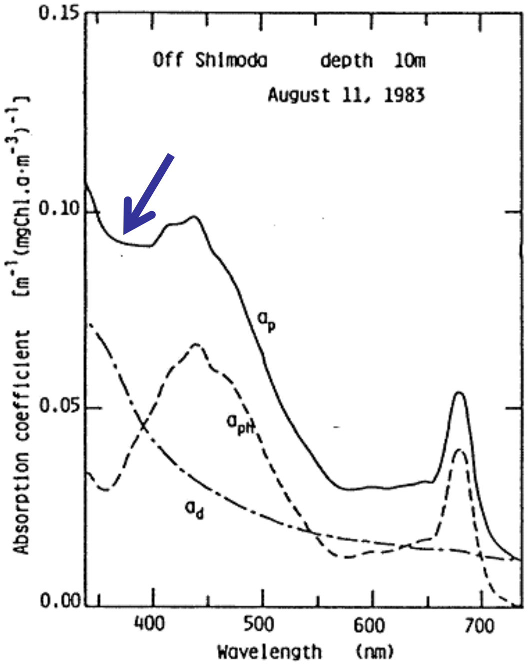


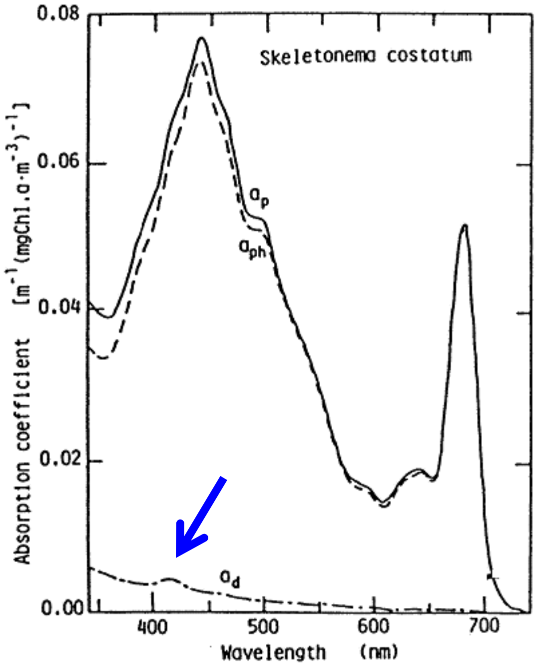
extract Methanol

scan (a_{nap})

scan (a_p)

difference (a_ϕ)



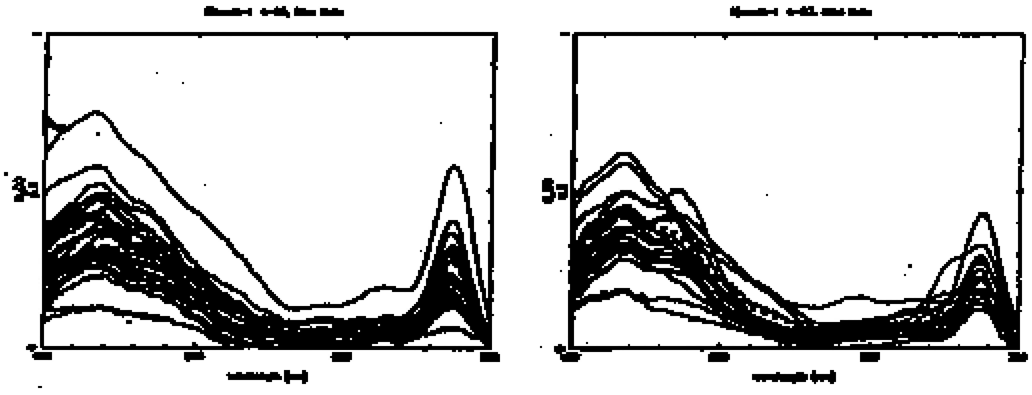


Kishino et al 1985

Absorbing Components: Phytoplankton

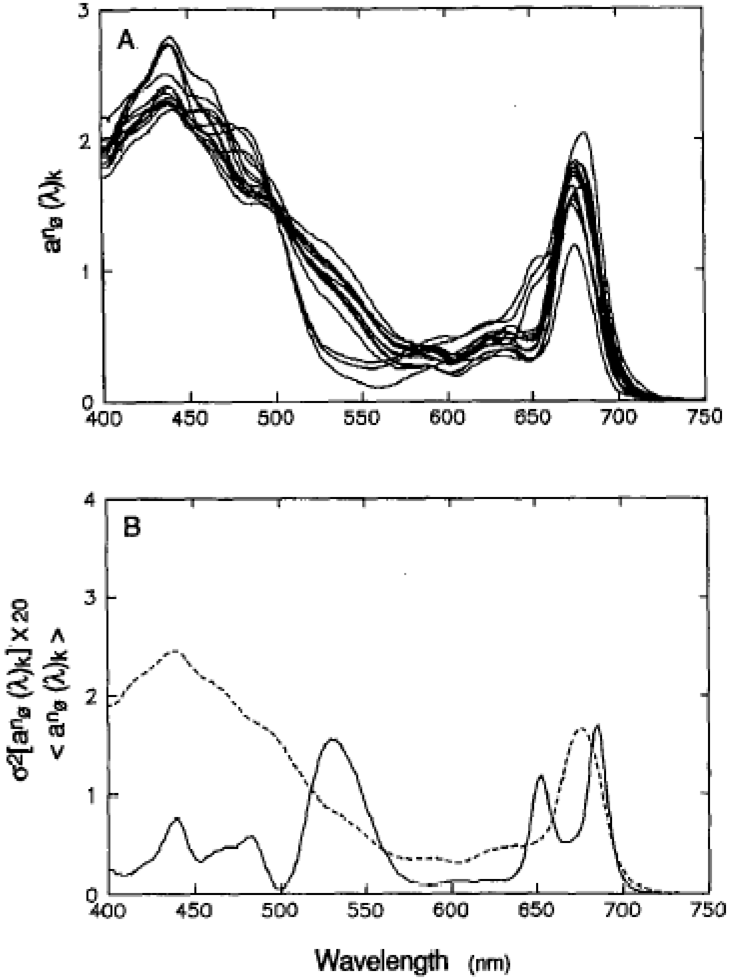
Individual cells, microphotometry

1710 *Iturriaga and Siegel* 1989 L&O

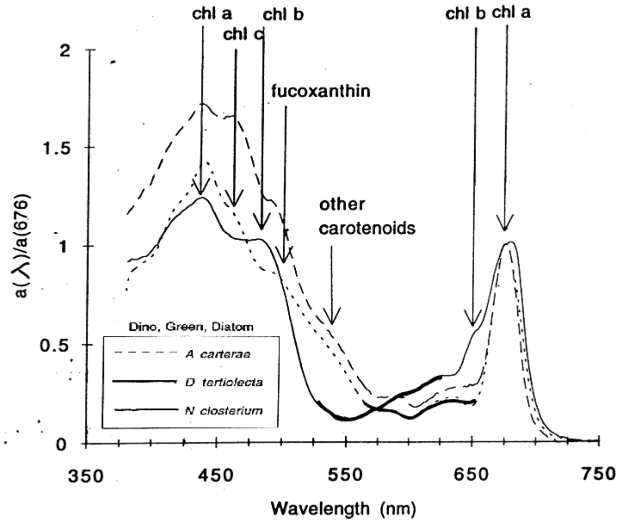


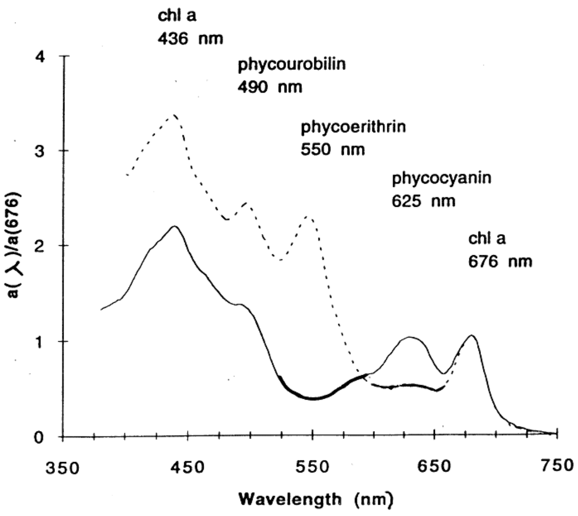
Absorbing Components: Phytoplankton

Species



Roesler et al. 1989 L&O





Absorbing Components: Phytoplankton

Pigment Packaging impact on absorption

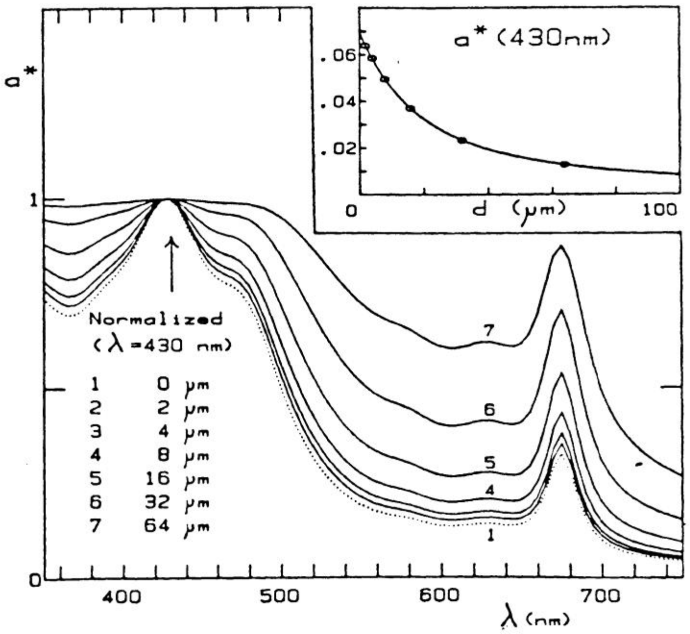
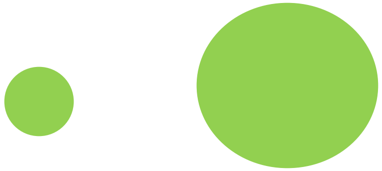


Fig. 2. Change in spectral absorption values with variable cell size (diameter, d, in µm) whereas the cell material forming the cells remains unchanged. The spectral absorption values of this material, somewhat arbitrarily adopted, are shown as the dotted curve. All curves are normalized, at $\lambda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

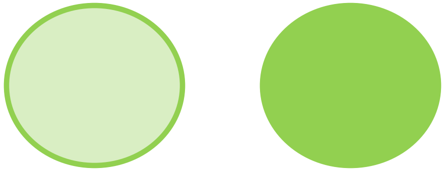
Morel and Bricaud 1981 DSR

(1) vary size, maintain constant intracellular pigment concentration



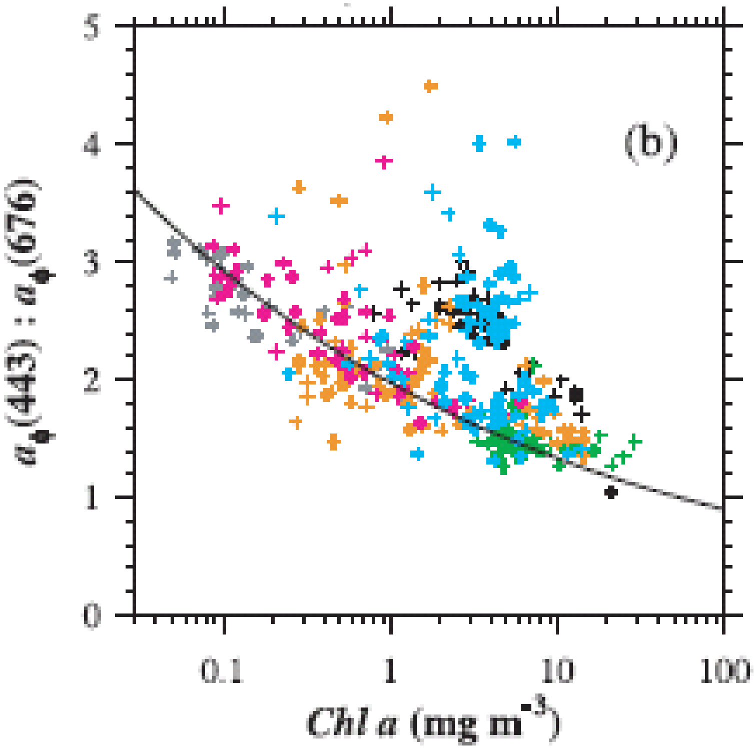
or

(2) maintain size, vary intracellular pigment concentration



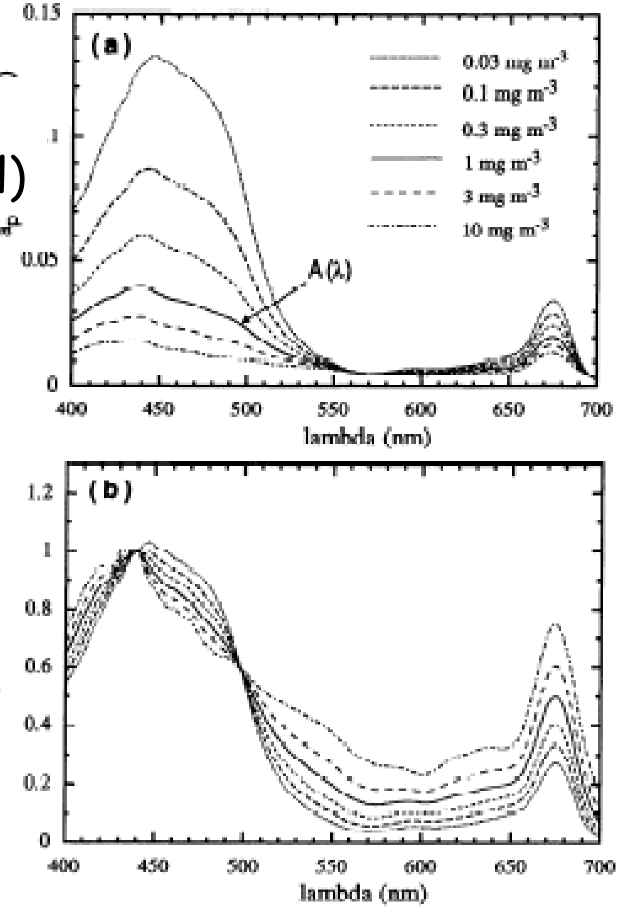
Absorbing Components: Phytoplankton

Babin et al. 2003



Bricaud et al. 1995

a*phi (m^2/mg chl)

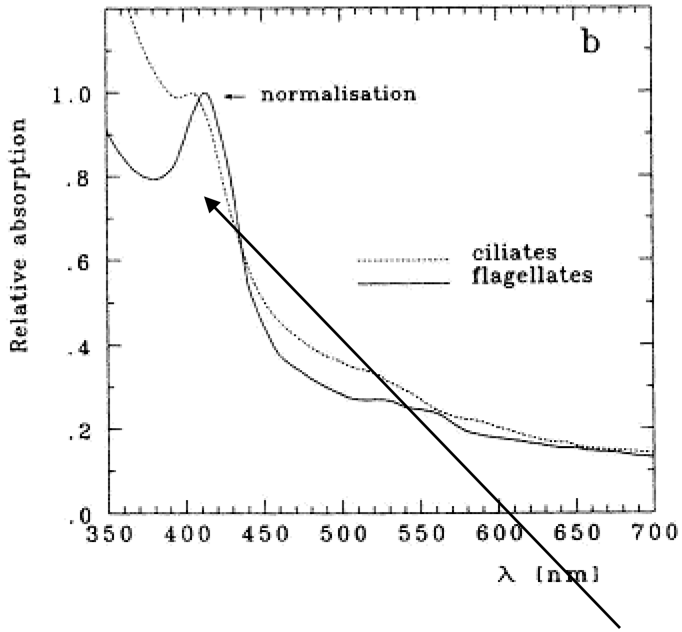


$\frac{\text{aphi}(\lambda)}{\text{aphi}(440)}$

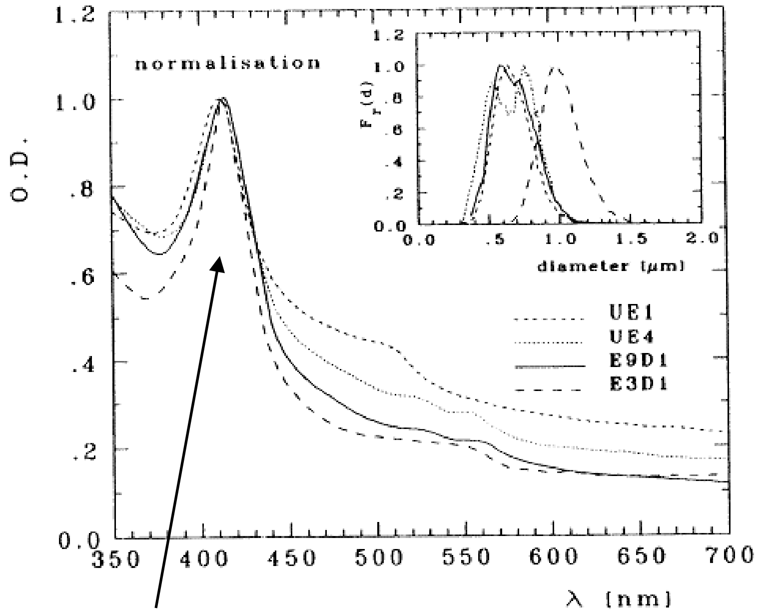
Global Relationships

Absorbing Components: other protists

ciliates and flagellates



heterotrophic bacteria

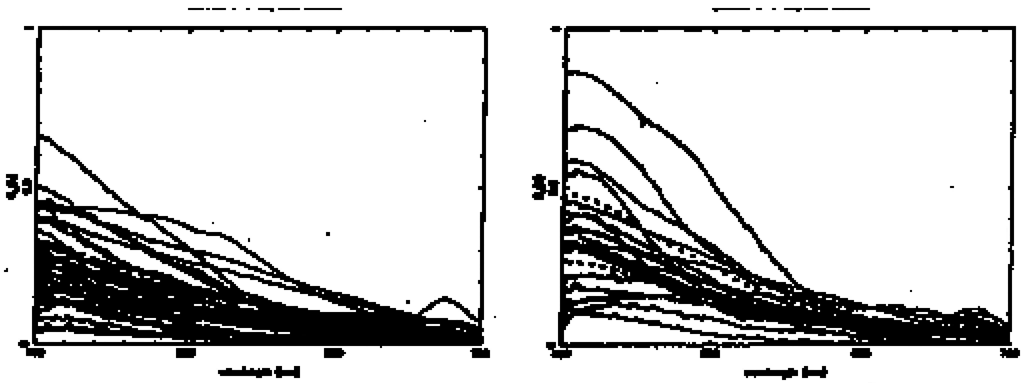


cytochrome 412

Morel and Ahn 1990 JMR

Absorbing Components:

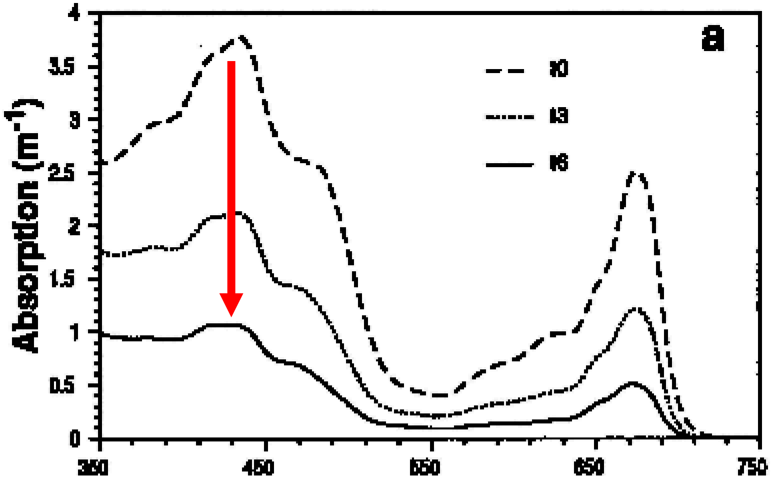
Non-algal Particles →organic detrital particles



Iturriaga and Siegel 1989 L&O

Nelson & Robertson: Detrital spectral absorption 1993]

JMR



photobleaching natural light levels

Absorbing Components:

Non-algal Particles

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

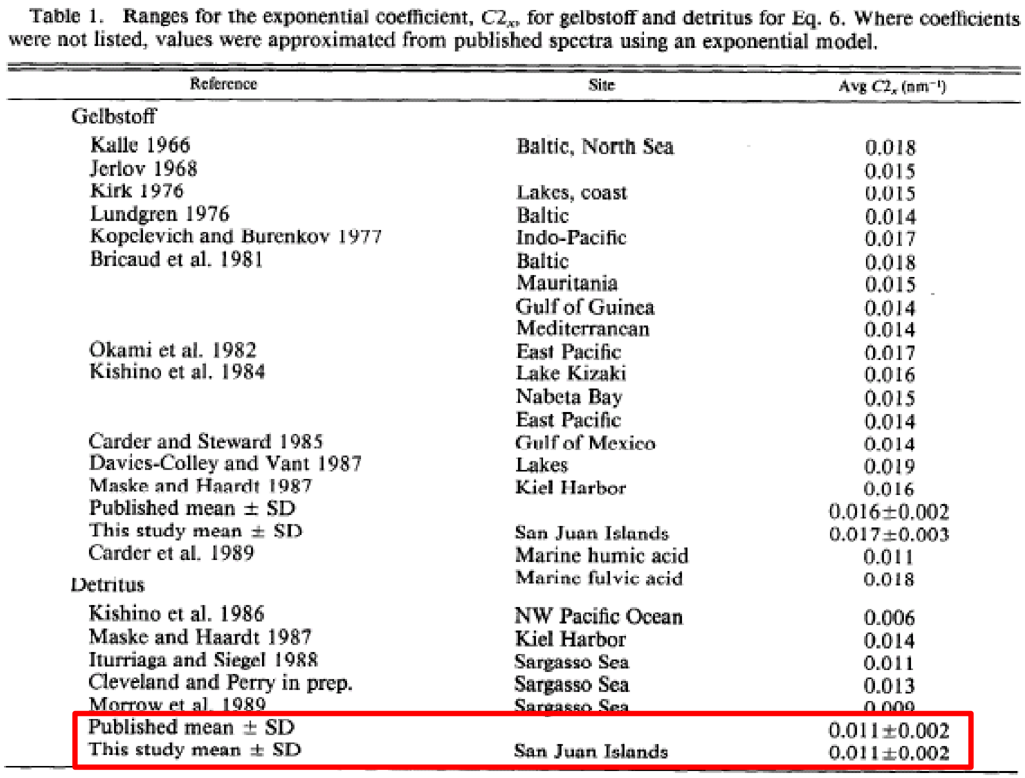
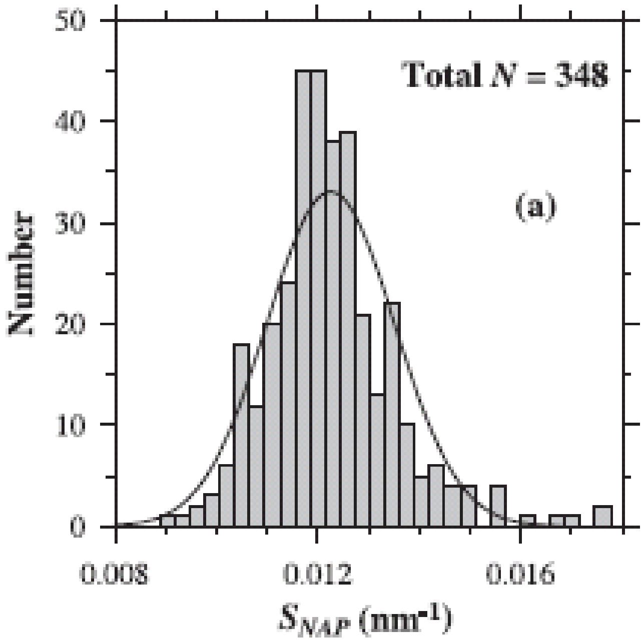


Table 1. Ranges for the exponential coefficient, $C2_x$, for gelbstoff and detritus for Eq. 6. Where coefficients were not listed, values were approximated from published spectra using an exponential model.

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



European coastal waters
Babin et al. 2003

Absorbing Components: non-algal or mineral particles

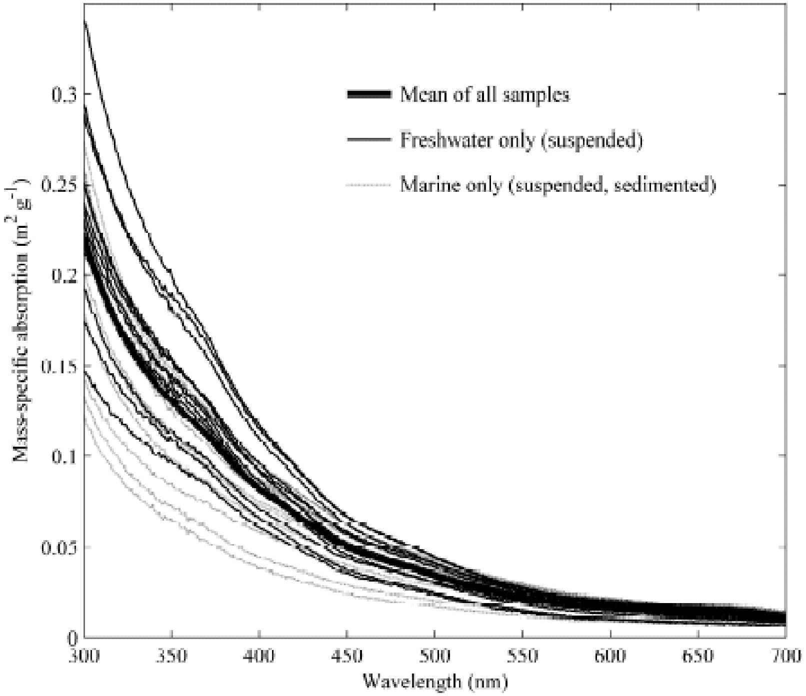


Figure 3.3. Mass-specific absorption spectra of all samples analyzed here (N = 25). Heavy black line shows the mean, thin solid lines show samples from freshwater sites on the Atchafalaya and Mississippi Rivers, and dashed lines show samples from marine sites at Freshwater Bayou and the Atchafalaya River delta. Marine samples include both sediments and suspended particulates; river samples are suspended particulates only.

iron oxide minerals

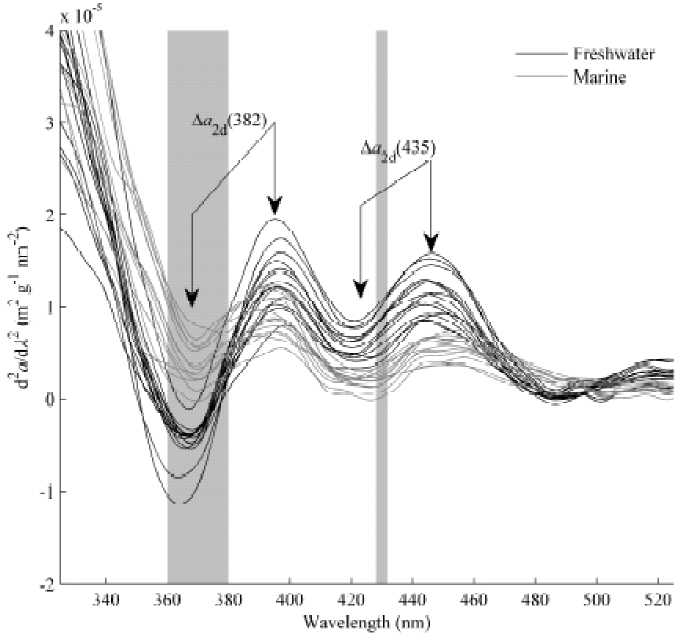


Figure 3.10. Second derivatives of mass-specific absorption spectra. Black lines denote freshwater samples and gray lines denote marine samples. Bracketed arrows labeled "$\Delta a_{2d}(382)$" and "$\Delta a_{2d}(435)$" show locations of second-derivative maxima and minima used to compute iron absorption peak heights plotted in Figure 3.11. Light gray vertical bars highlight approximate ranges for electronic transition bands of various iron oxide minerals (Sherman and Waite, 1985).

Estapa 2011

Absorbing Components: inorganic particles

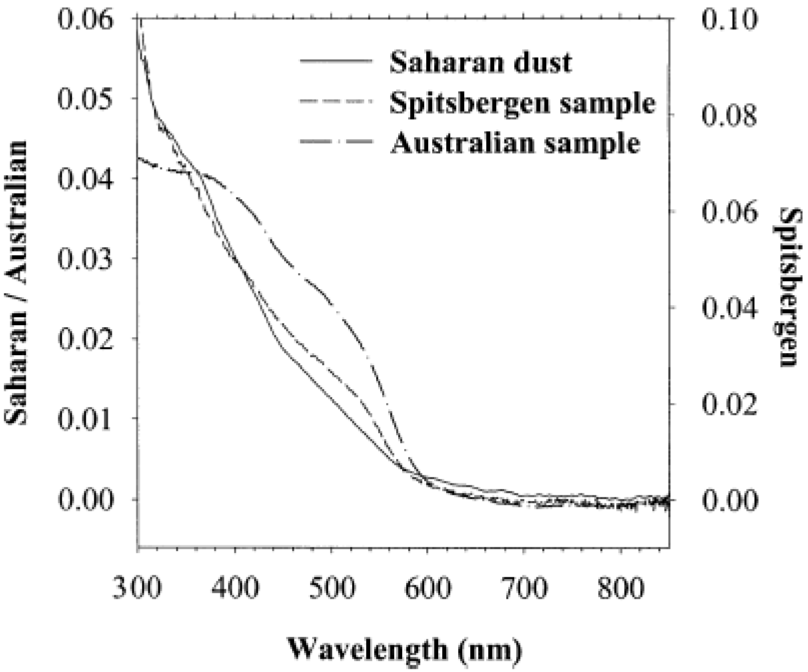


Fig. 5. Absorbance spectra of natural assemblages of mineral particles from three different environments.

Babin and Stramski 2003

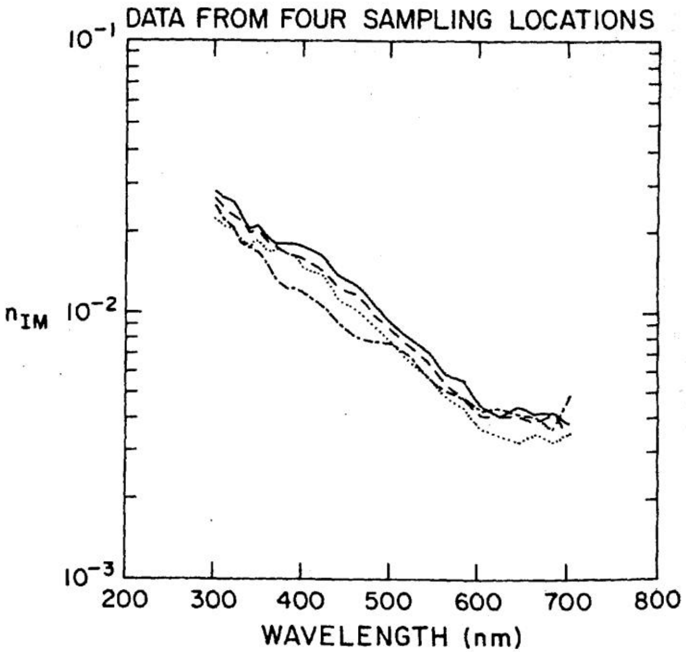
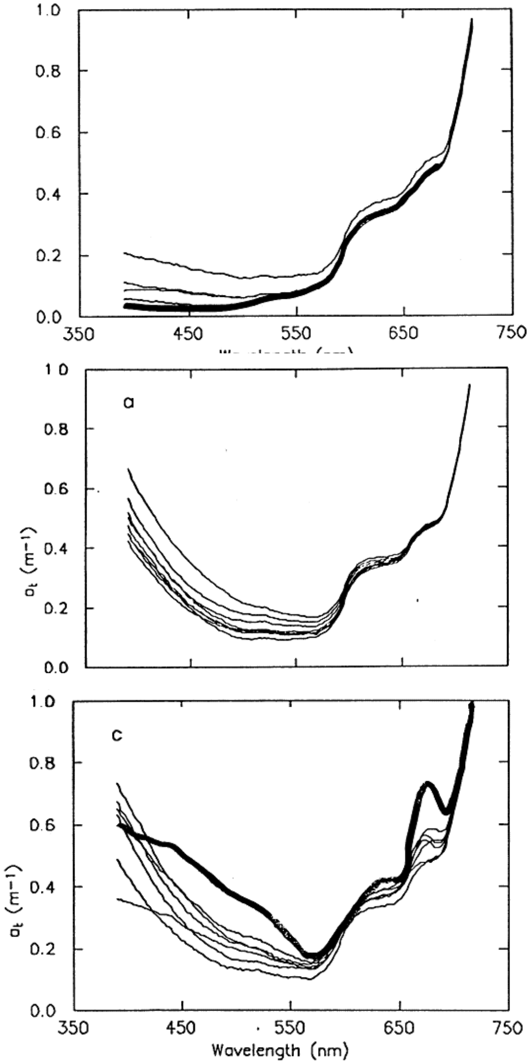


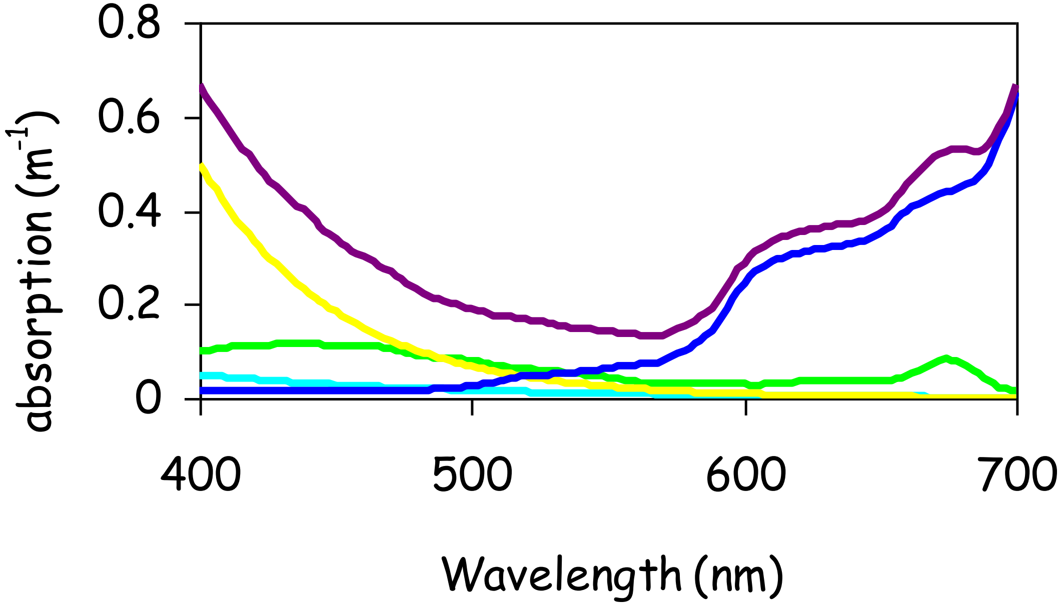
Fig. 8. Imaginary index of refraction for Saharan aerosols from each of the collection locations. The solid line represents the Tenerife sample; the dashed line, the *Meteor* sample; the dotted line, the Barbados sample; and the dashed-dotted line, the Sal Island sample.

Patterson et al. 1977 JGR

To model the impacts of absorbing constituents…add them up



Morel and Prieur 1977



- which component dominates?
  - blue waters
  - green waters
    - phytoplankton (V-type) case I
    - inorganic particles (U-type) case II

More on absorption

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