# From Inherent Optical Properties to Biogeochemical Properties

Emmanuel Boss, U. of Maine

- Forward and inverse problems.
- The basis for the relationship (theoretical, empirical, hybrid).
- Concept of a 'proxy'.
- Bulk vs. single particle property (FCM).
- Supportive lab studies (controlled compared to ocean).
- Extensive vs. intensive properties.
- Some intensive proxies involve ratio of proxies.
- Uncertainties…

Remember: this is the major reason the field of Oceanography cares about optics!!!

IOP's: absorption, scattering, attenuation and fluorescence.

Why use optics?

Provides ability to observe oceans with high spatial and temporal resolution.

a. From space: global view of the ocean surface on a ~daily time scale.

b. In situ: sub-meter and sub-second.

Challenge: need to qualify the relationship between optical properties and the parameter of interest (including uncertainties).

# Laundry list of optical proxies from IOPs:

Nitrate, Sulphides – UV absorption.

DOM, Hydrocarbons – fluorescence (UV-ex, VIS-em), absorption.

PM, POC, $C_{phyto}$ – attenuation, scattering.

Phytoplankton pigments – fluorescence, absorption.

Particulate size tendencies or distribution – spectrum of attenuation and backscattering, near forward scattering, spikes.

Particulate composition (index of refraction) – back-scattering to scattering ratio, degree of polarization.

Particulate packing – attenuation + near-forward scattering.

Bubbles– angular scattering.

What is a proxy?

What are the hallmark of a good proxy?

What should YOU do before you decide to use a proxy?

How do you estimate the uncertainties associated with a proxy?

Be careful about 'extrapolating' proxies in space and time.

# Direct and inverse approaches in optics:


(a) ⇨ ? Tracks

e.g. Given particles → angular scattering

'well' posed


(b) ⇨ ? Dragon

Angular scattering → Type of particles present

'ill' posed

Bohren and Huffman, 1987

What kind of approach is the use of an optical proxy?

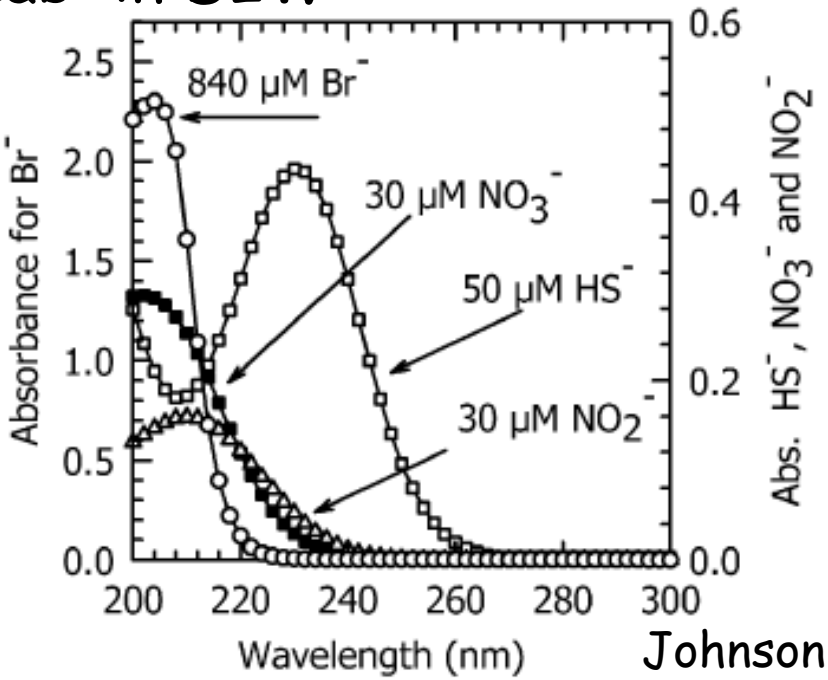
# Dissolved materials

- Scattering in weak -> attenuation ~ absorption.
- Operational definition -> smaller than a specific pore size.

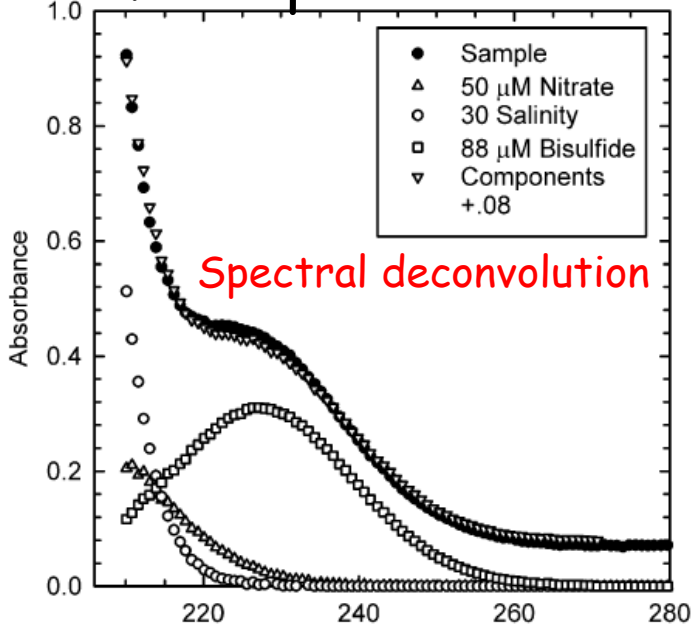
Dissolved absorption depends on:

- Dissolved organic materials (e.g. Tea, Urea).
- Ions ($Br^-$, $HS^-$, $NO_3^-$, $NO_2^-$).

Lab: in DIW



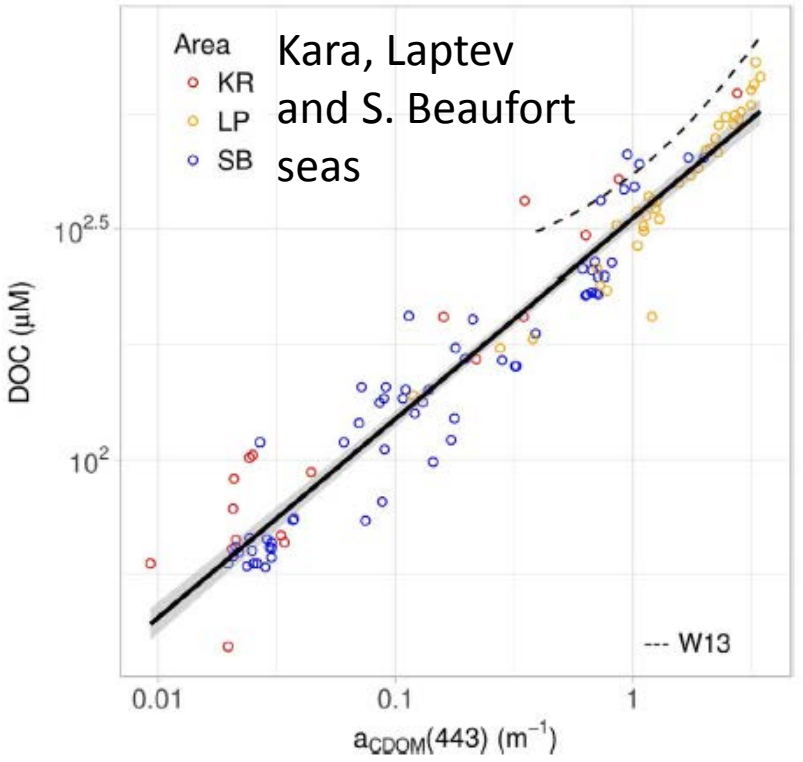

Field: 970m deep



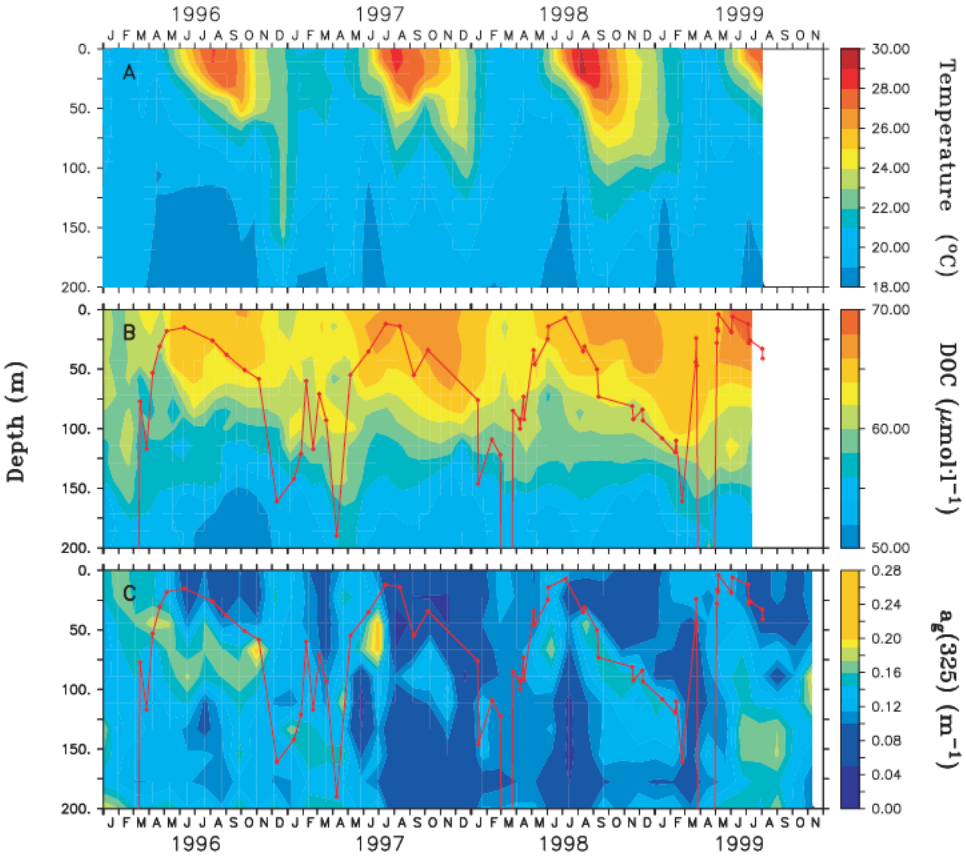

Johnson and Coletti, 2002, DSR

# Dissolved materials (largest C pool!)

- Colored (chromophoric) dissolved organic material (CDOM, gelbstoff, gilvin, yellow substances)
- Most often organic in origin (NB: dissolved iron oxides has a similar visible spectrum).
- Relation to DOC varies:




Matsuoka et al., 2017, RSE




Siegel et al., 2002, JGR

# Dissolved materials - composition

- Most often absorption spectrum is approximated by an exponential (other models apply, e.g. Twardowski et al., 2004). Exponent depends on [λ] and fitting method.
- Theoretical explanation – continuum of carbon (π)-bonds of different lengths (Shifrin, 1988). The larger (more atoms) the molecules the flatter the absorption spectrum.

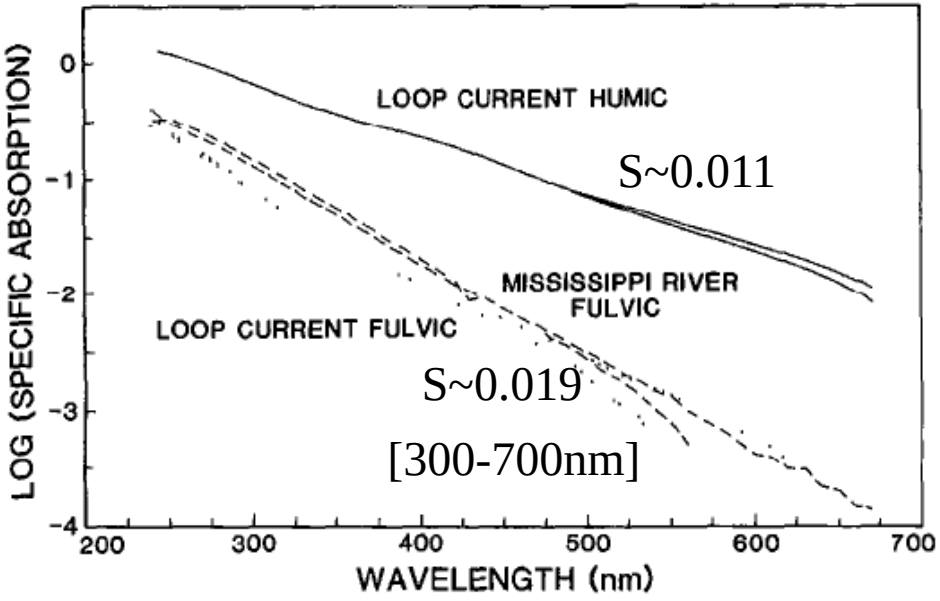
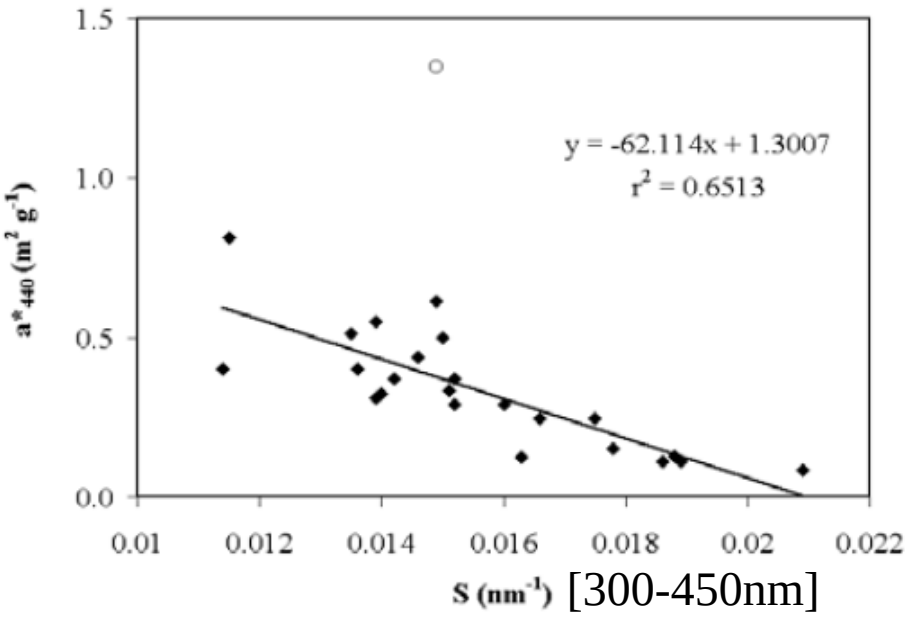



Fig. 1. Specific absorption curves vs. wavelength for marine humic acid and marine fulvic acid.

Carder et al., 1989



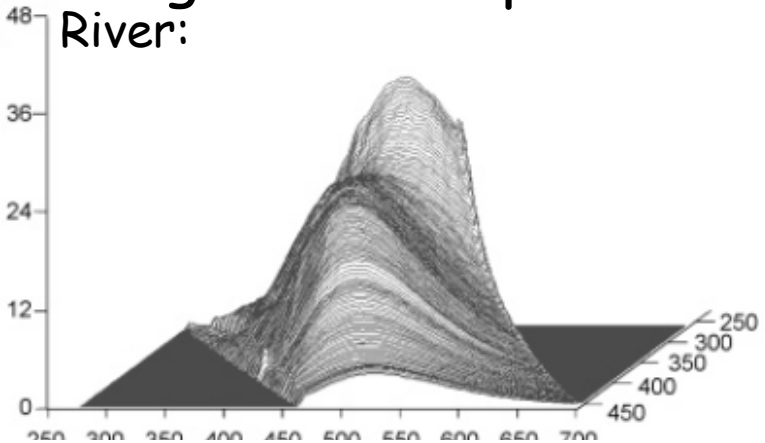

Georgia rivers, US

Yacobi et al., 2003

# Dissolved materials - Fluorescence

- FDOM quantified by fluorescence. Does not require filtration.
- Excitation-emission matrices are used to characterize the FDOM – signature of processes and pools.

River:




New marine productivity:

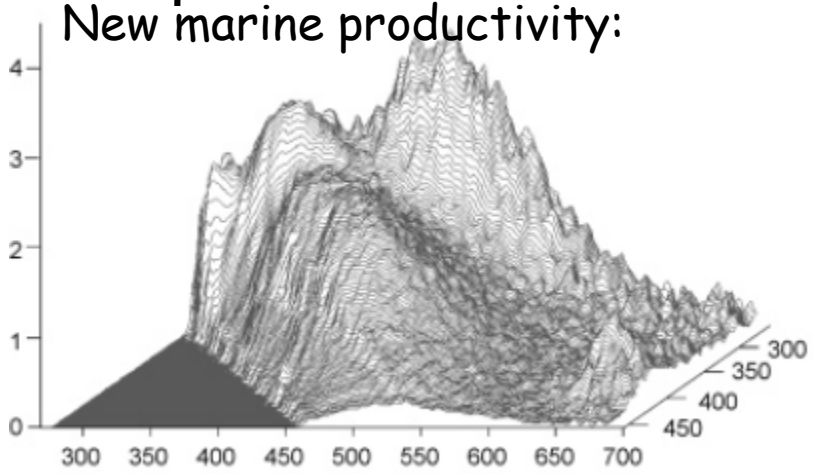


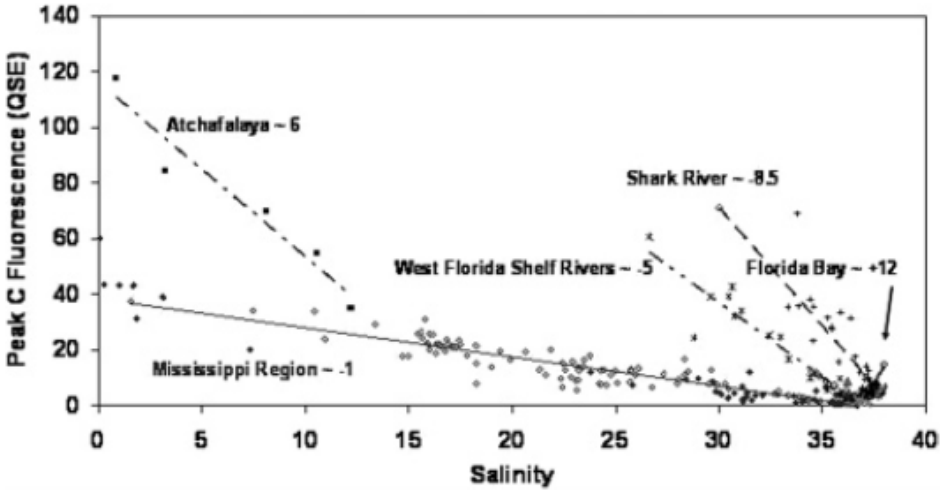

**Table 1.**

Coble, 2009:

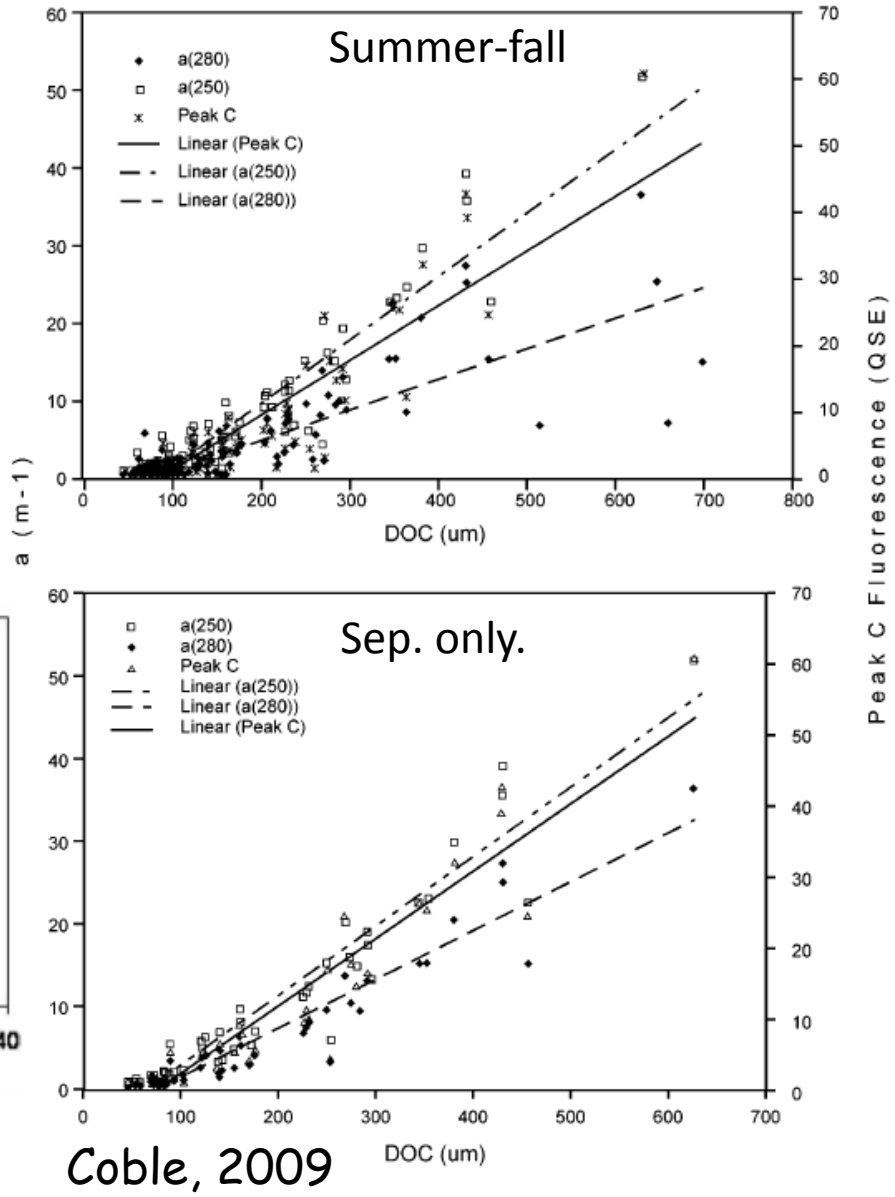
| component | peak name[43] | Ex/Em | peak number[25,49] | source[25,49] | peak[47,48] |
|---|---|---|---|---|---|
| tyrosine-like, protein-like | B | 275/305 | 8 | autochthonous | $\gamma$ |
| tryptophan-like, protein-like | T | 275/340 | 7 | autochthonous | $\delta$ |
| unknown | N | 280/370 | | | |
| UVC humic-like | A | 260/400−460 | 4 | fulvic acid, autochthonous, terrestrial | $\alpha'$ |
| UVC humic-like | A | 260/400−460 | 1 | humic, terrestrial, allochthonous | $\alpha'$ |
| UVC humic-like | A | 260/400−460 | 3 | humic, terrestrial, allochthonous | $\alpha'$ |
| UVA marine humic-like | M | 290−310/370−410 | 6 | anthropogenic from wastewater and agriculture | $\beta$ |
| UVA humic-like | C | 320−360/420−460 | 5 | terrestrial, anthropogenic, agriculture | $\alpha$ |
| pigment-like | P | 398/660 | | | |
| UVA humic-like | | 250 (385)/504 | 2 | fulvic acid, terrestrial, autochthonous | |

# Dissolved materials - Fluorescence

- FDOM and CDOM are predictors of DOC in coastal environments.
- In coastal environment both are linked to salinity through a dilution curve (which varies).




West Florida shelf:




Coble, 2009

# An aside: how do we fit? How do we determine goodness of fit?

Lets assume that we have a model

$$y = y(\lambda; \boldsymbol{a})$$

Try to minimize a merit function, e.g.:

$$\tilde{\chi} = \sum_{i=1}^{N} \left| \frac{y(\lambda_i) - y(\lambda_i; \boldsymbol{a})}{\sigma_i} \right|$$

# Regressions of type I and type II

Uncertainties in $y$ only:

$$y(x) = ax + b$$

$$\chi^2 = \sum_{i=1:N} \left( \frac{y_i - a - bx_i}{\sigma_i} \right)^2$$

Minimize $\chi^2$ by taking the derivative of $\chi^2$ wrt $a$ and $b$ and equal it to zero.

What if we have errors in both $x$ and $y$?

$$y(x) = ax + b$$

$$\chi^2 = \sum_{i=1:N} \frac{(y_i - ax_i - b)^2}{\sigma^2{}_{yi} + a^2\sigma^2{}_{xi}}$$

$$Var(y_i - ax_i - b) = \sigma^2{}_{yi} + a^2\sigma^2{}_{xi}$$

Minimize $\chi^2$ by taking the derivative of $\chi^2$ wrt $a$ and $b$ and equal it to zero.

# An aside: How do we determine goodness of fit?

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(M_i - O_i)^2}{n}}$$

Issues:

- Treatment of oultiers
- Sensitivity to dynamic range
- Parametric vs. non-parametric

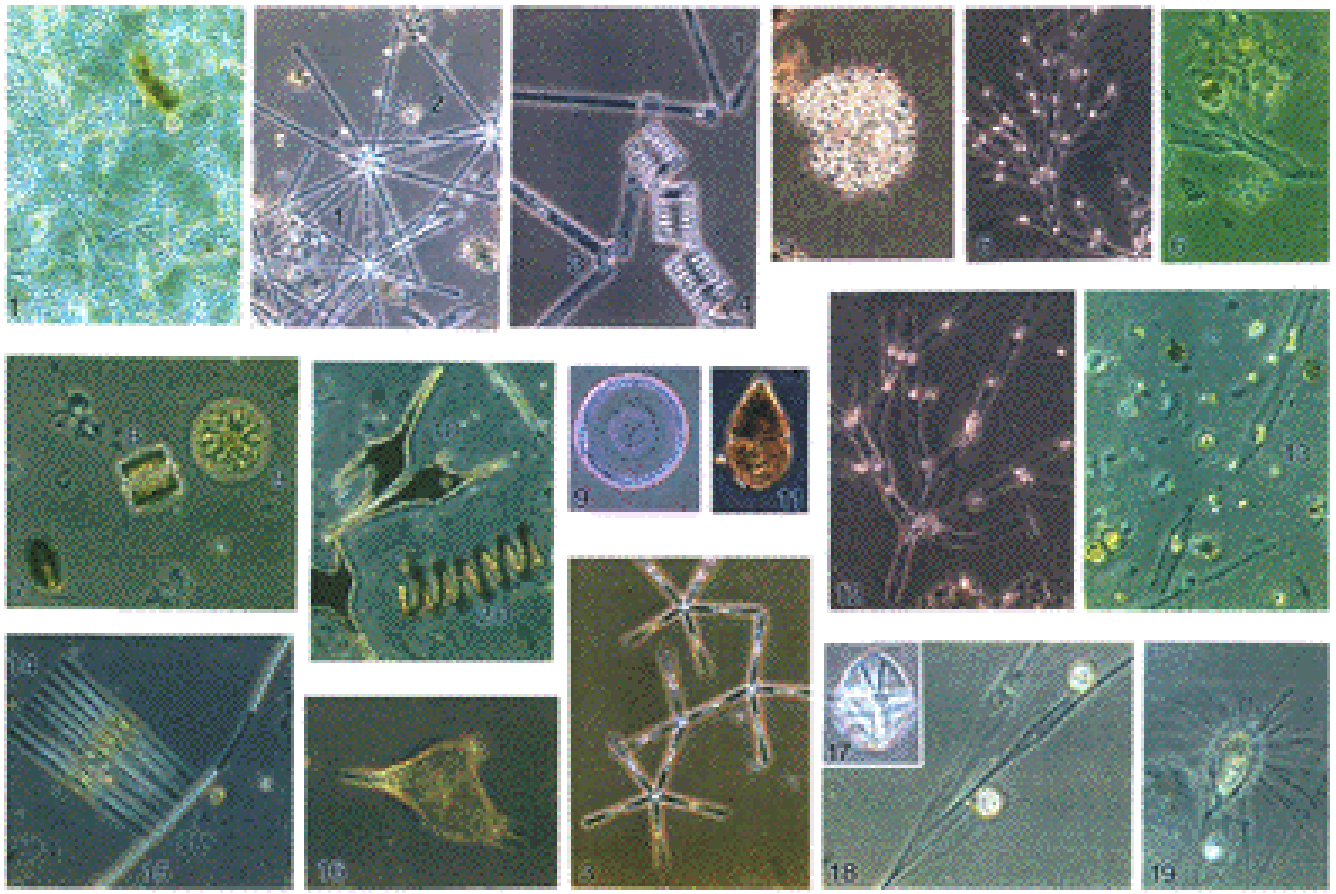
$$\mathrm{MAE} = \frac{\sum_{i=1}^{n}\left|M_i - O_i\right|}{n}$$

| Measurement | Frequently Used Metrics | Why or Why Not for Ocean Color | Notes |
|---|---|---|---|
| **Accuracy** | RMSE | • Distribution sensitive (assumes Gaussian)<br>• Often misinterpreted to be a simple estimate of average error<br>• No consistent relationship with average error magnitudes | Other Sum of Squares based measures have same problems, such as standard deviation, standard error. |
| **Goodness of fit** | $r^2$ | • Can be misinterpreted if not given in context, because it lacks a response to bias and is sensitive to outliers<br>• Can misrepresent error when the range is small<br>• Can overstate variable relationships even with apparently random error | |
| | Slope | • Can be misinterpreted, by reporting a good value for strongly-biased, low-precision models.<br>• Leverages (biased errors on either end) produce meaningless slopes<br>• Cannot address non-linear error<br>• Can allow tuning of a model to fit a particular region | Common least squares regression gives biased slope when the x variables contain errors [9] |
| | **Suggested Metrics** | | |
| **Bias** | Bias | • Quantifies the average difference between this estimator and expected value<br>• Estimates systematic error | Often based on mean, however median error can also be used if a more robust metric is needed |
| **Accuracy** | MAE | • Does not amplify outliers<br>• Accurately reflects error magnitude | Compared to mean, median absolute estimates are less sensitive to outliers. Similar metrics include mean/ median absolute percent error |
| | **New Approaches** | | |
| **Point by point accuracy** | % wins (Residuals) | • Considers model failures<br>• Provides consistent head-to-head comparison of algorithms | Pairwise comparison Decision support metric |
| **Temporal stability** | CV Intra-pixel | • Estimates imagery pixel stability.<br>• Estimates algorithm spatial and temporal performance.<br>• Does not require satellite-to-*in situ* match-ups | |

Seegers et al., 2018, OE

# What particles do we have in the ocean?

Phytoplankton

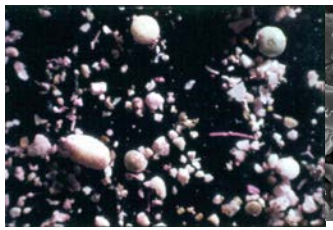



Variable in shape, size, pigment/cell and pigment composition.

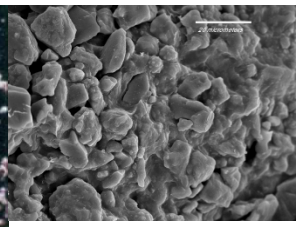
→ Variable in scattering and absorption properties

# What particles do we have in the ocean?

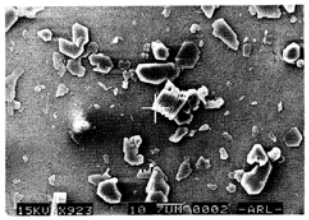
## Non-algal particles: Organic and inorganic.



Sand

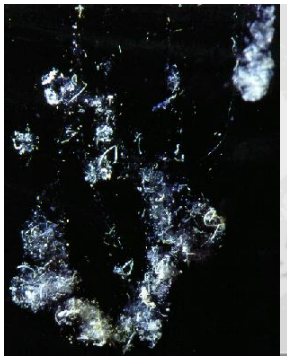


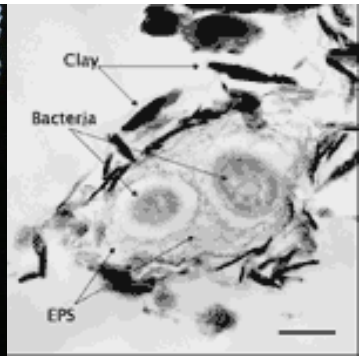
Silt



clay

## Aggregates <- packing



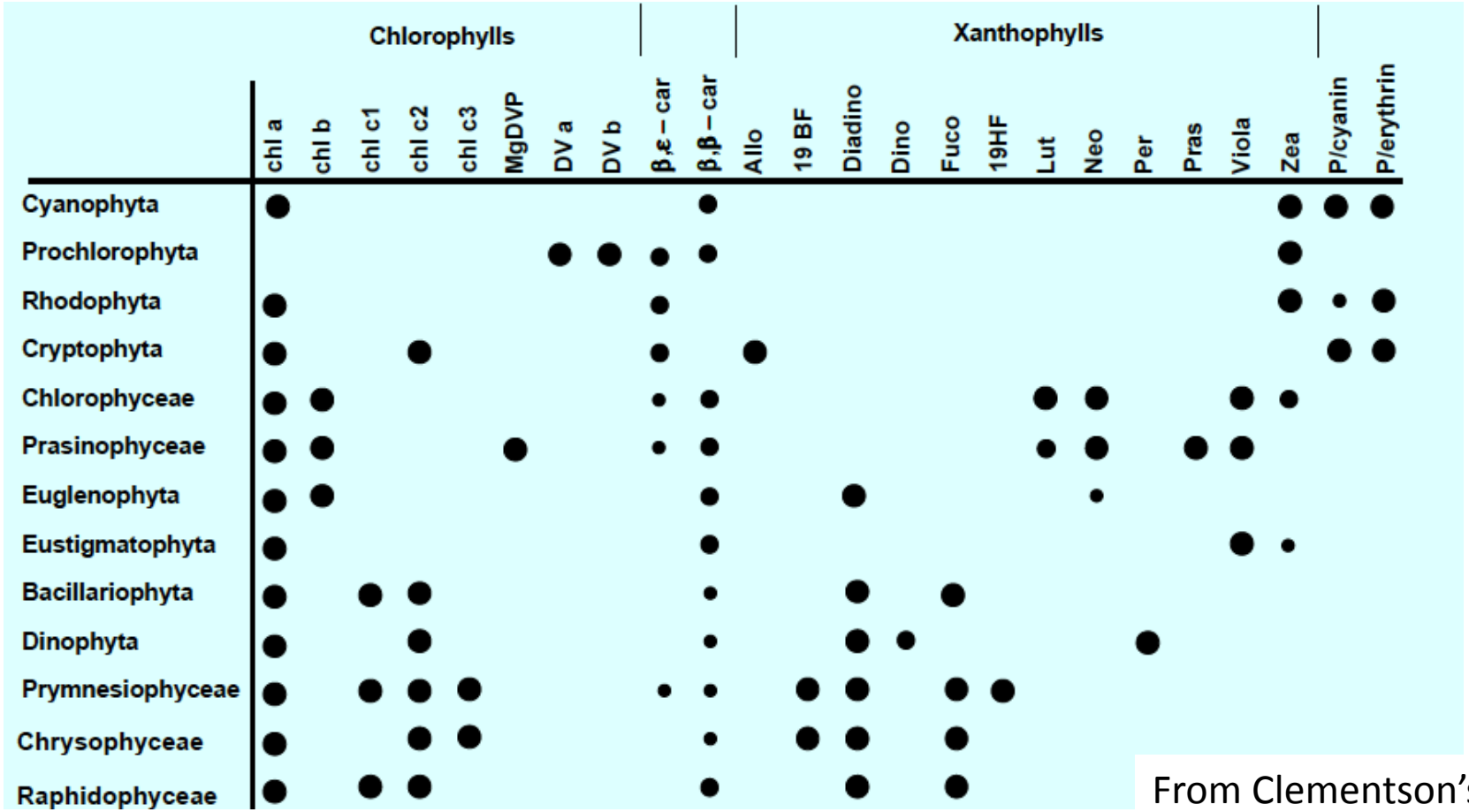



http://www.aad.gov.au/default.asp

→ Variable in scattering and absorption properties

# Particulate materials - Pigments

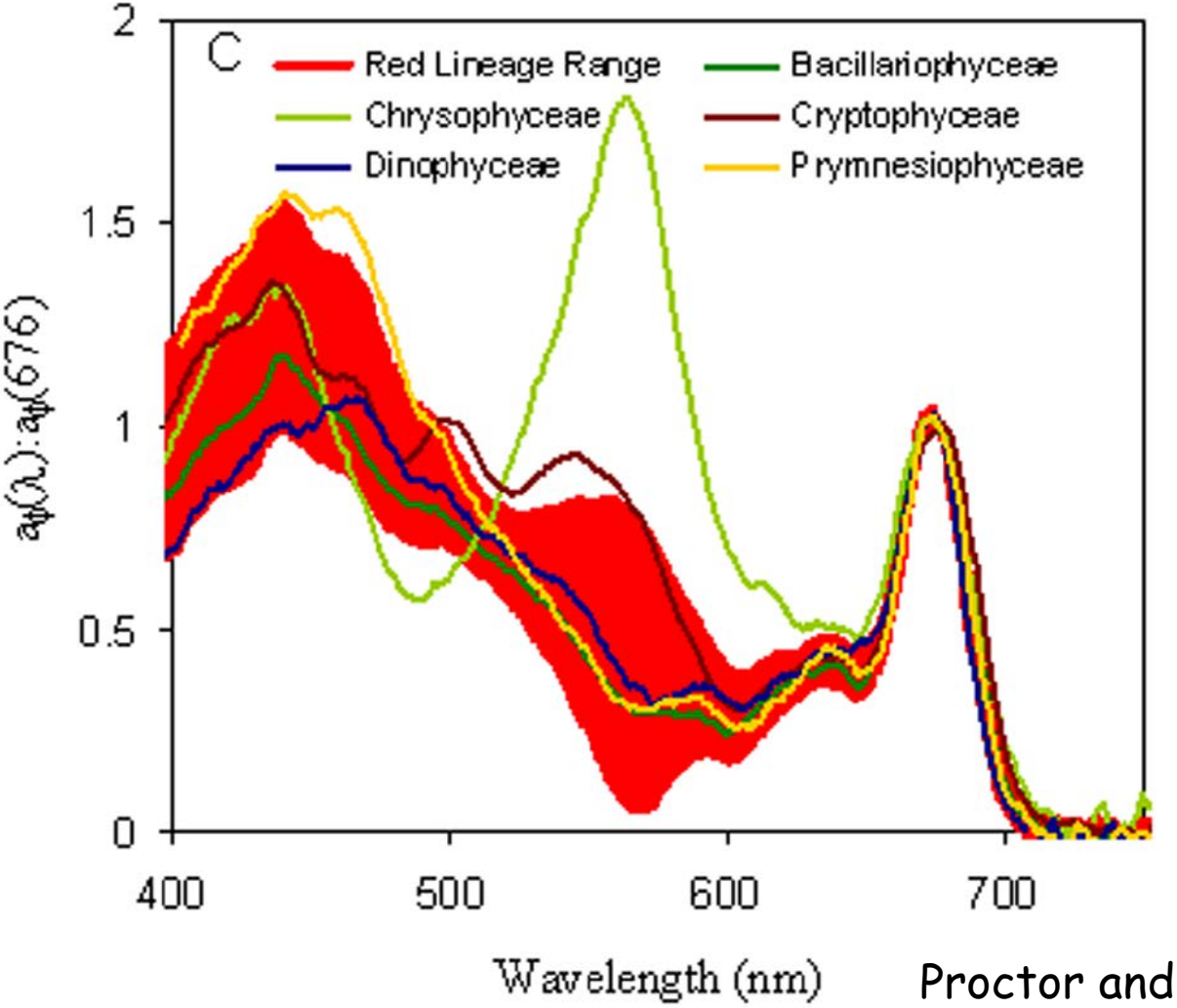
- More/less specific to certain life forms.
- Pigment have more/less specific absorption and fluorescence signatures.




From Clementson's 2000

# Pigments - Absorption

Variability between species (good if you want to study 'who is there?'):

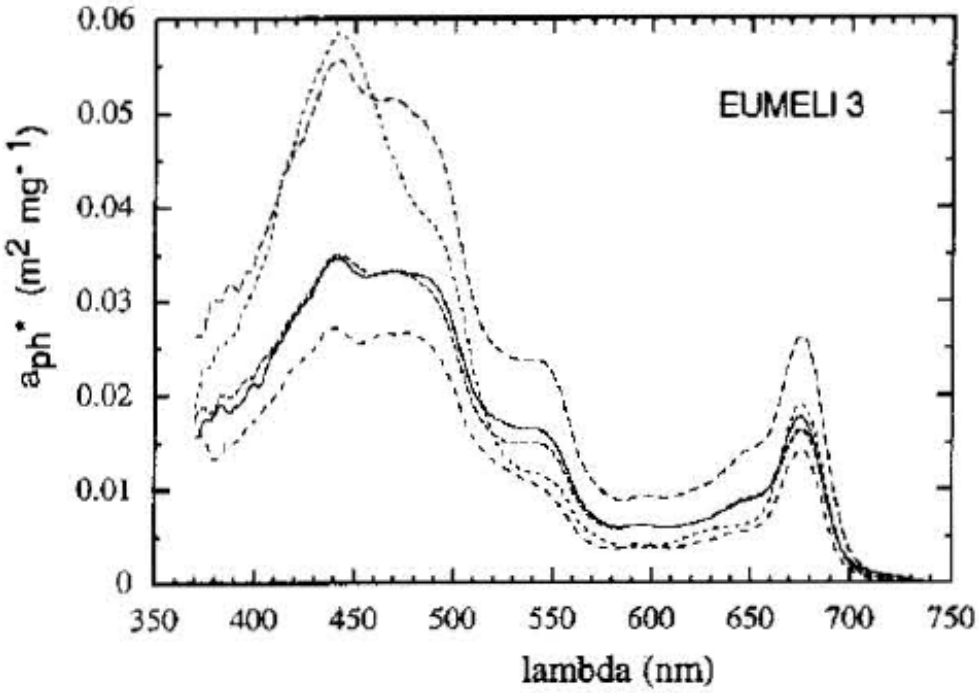



Proctor and Roesler, 2010

# Pigments - Absorption

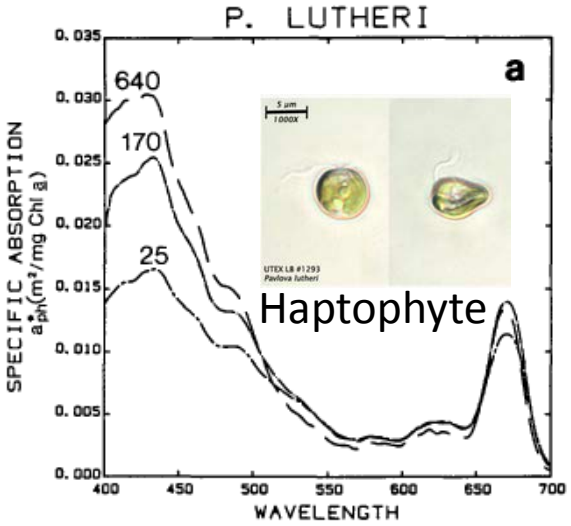
**BUT**, Variability due to growth conditions (light, nutrients):

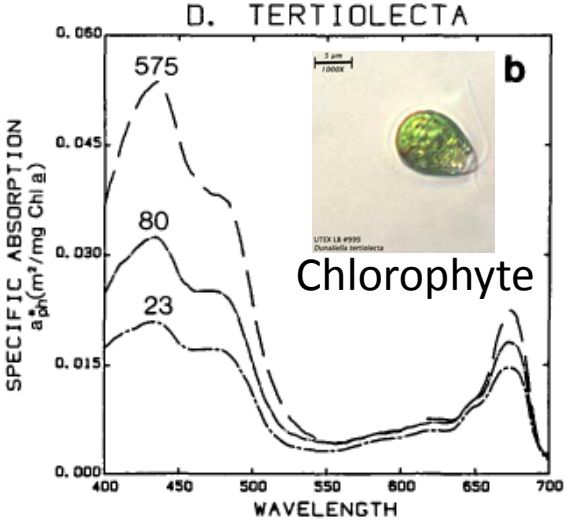
Field:




Bricaud et al., 1995

Lab:




Mitchell and Kiefer, 1988

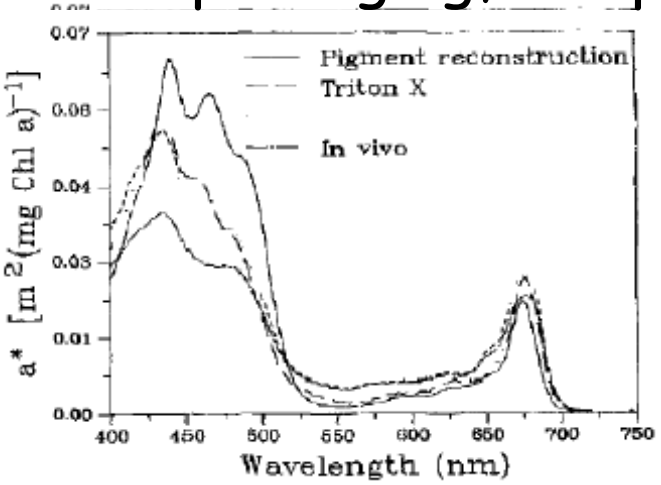
- In the lab: controlled environment.
- In the field: No control, varied species.

Which is more relevant?

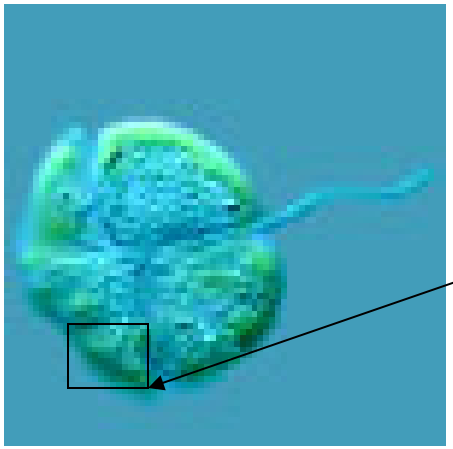
Low nutrients?

# Pigments - Absorption

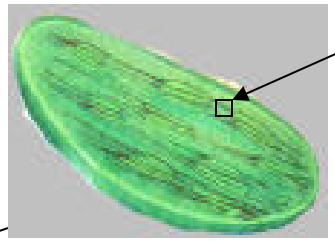
Pigment in a cell absorb differently than when out of the cell – packaging, complexing, solvent effect.



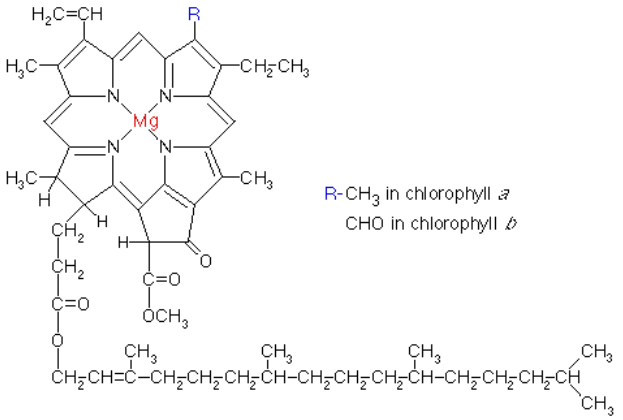

Sosik & Mitchell 1991



cell



chloroplast




The structure of chlorophyll

http://chaitanya1.wordpress.com/2007/07/09/strawberries/

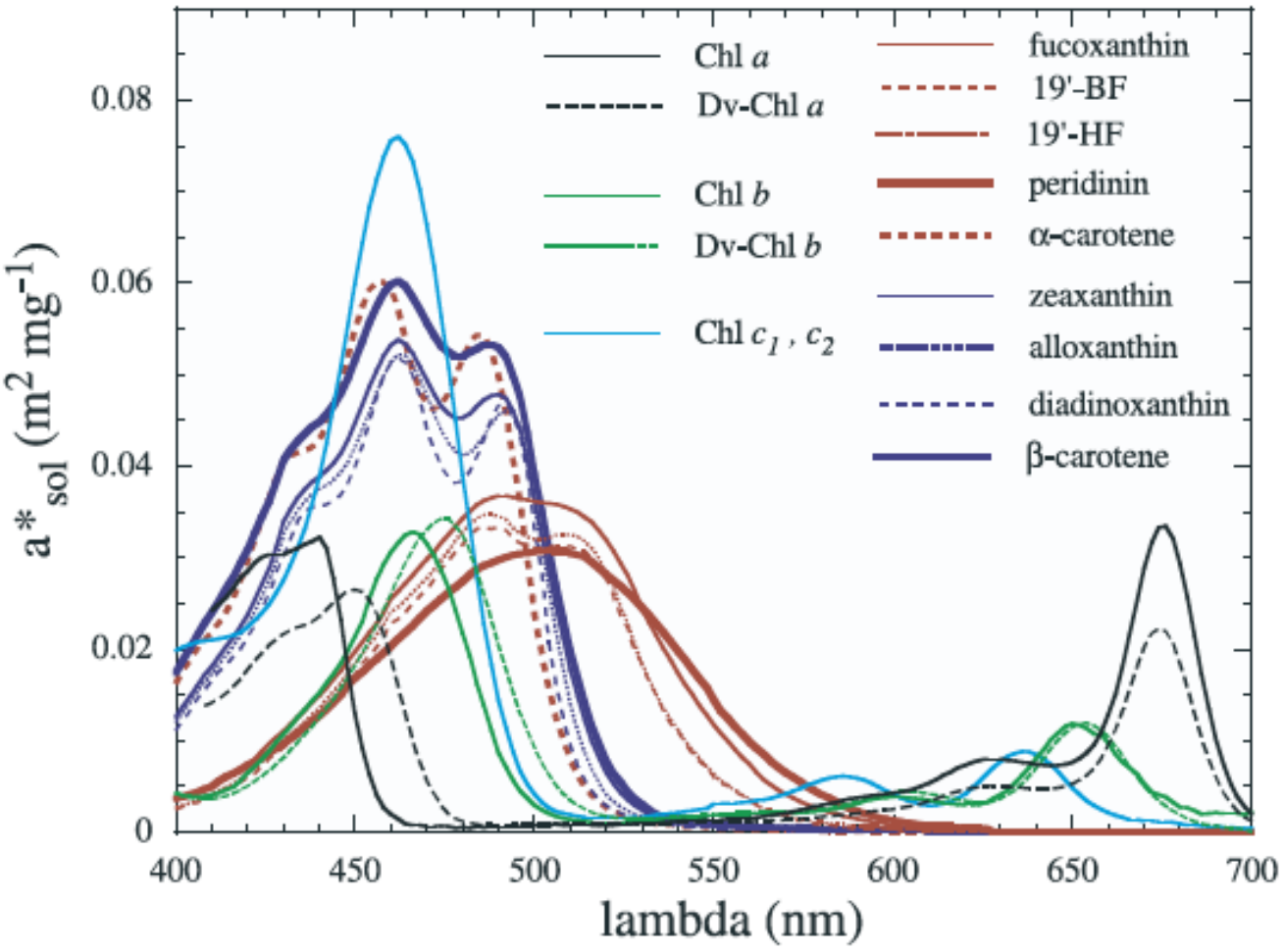
chlorophyll

Packaging: *a*/[chl] is function of size and [chl]

Duysens (1956)

# Pigments - Absorption

Richness of peaks → spectroscopic techniques.

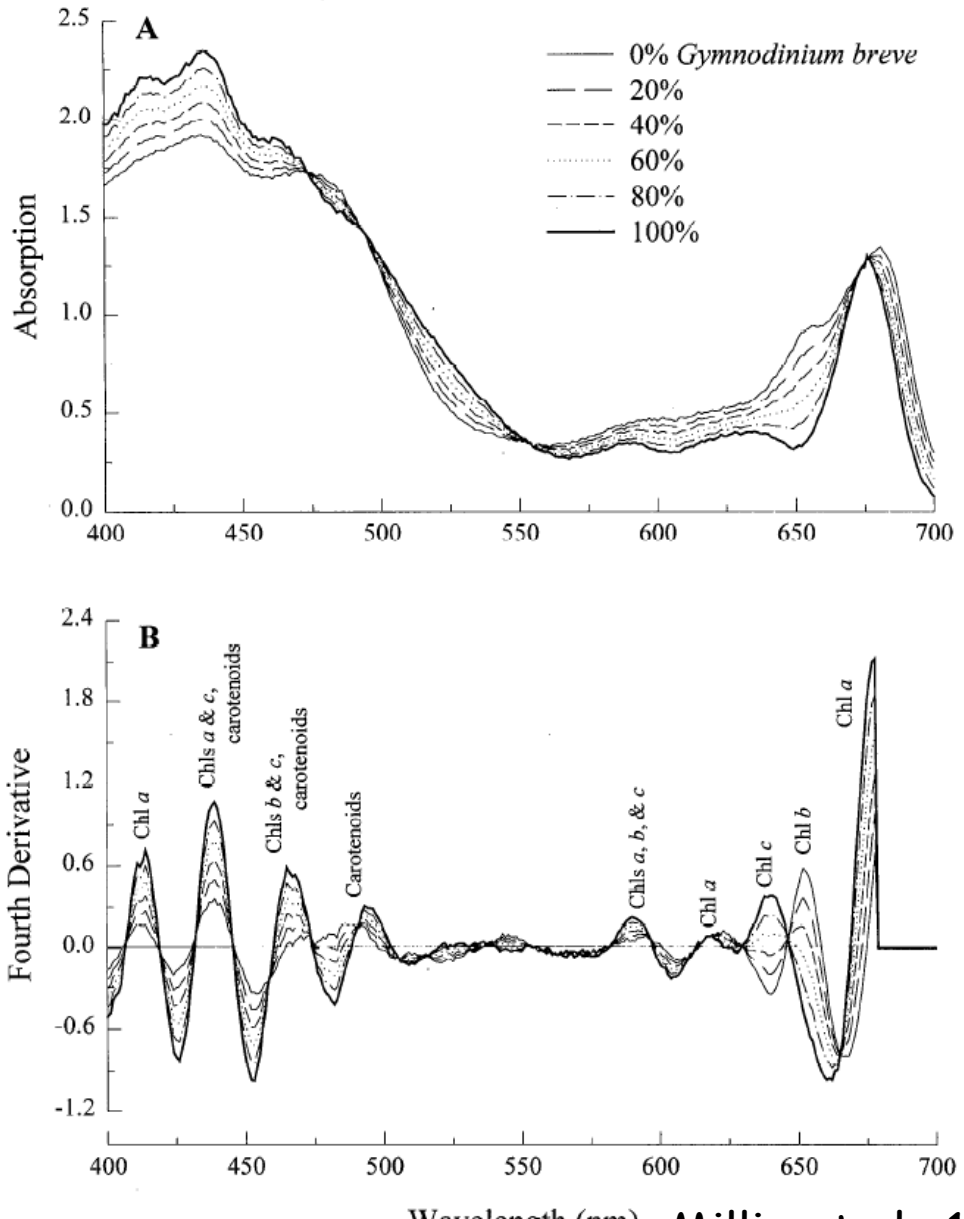



Bricaud et al., 2004, JGR

# Pigments - Absorption

Derivative analysis →

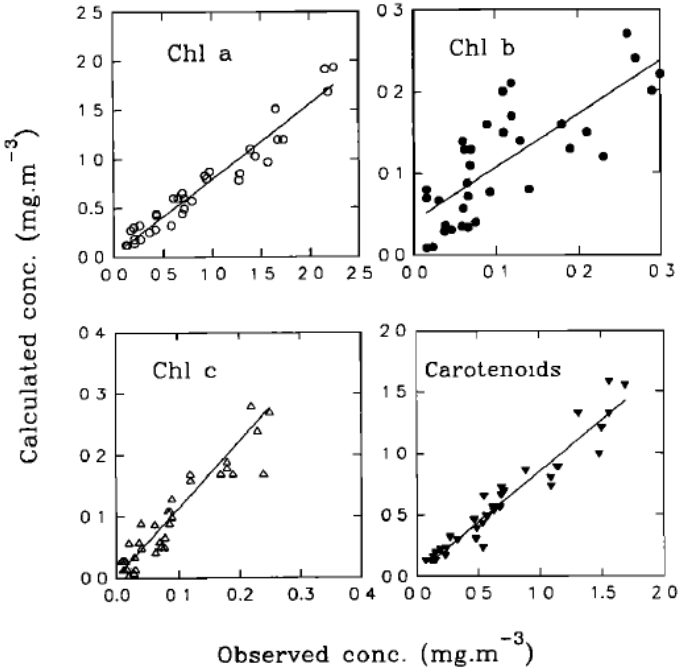
Similarity index used for HAB detection

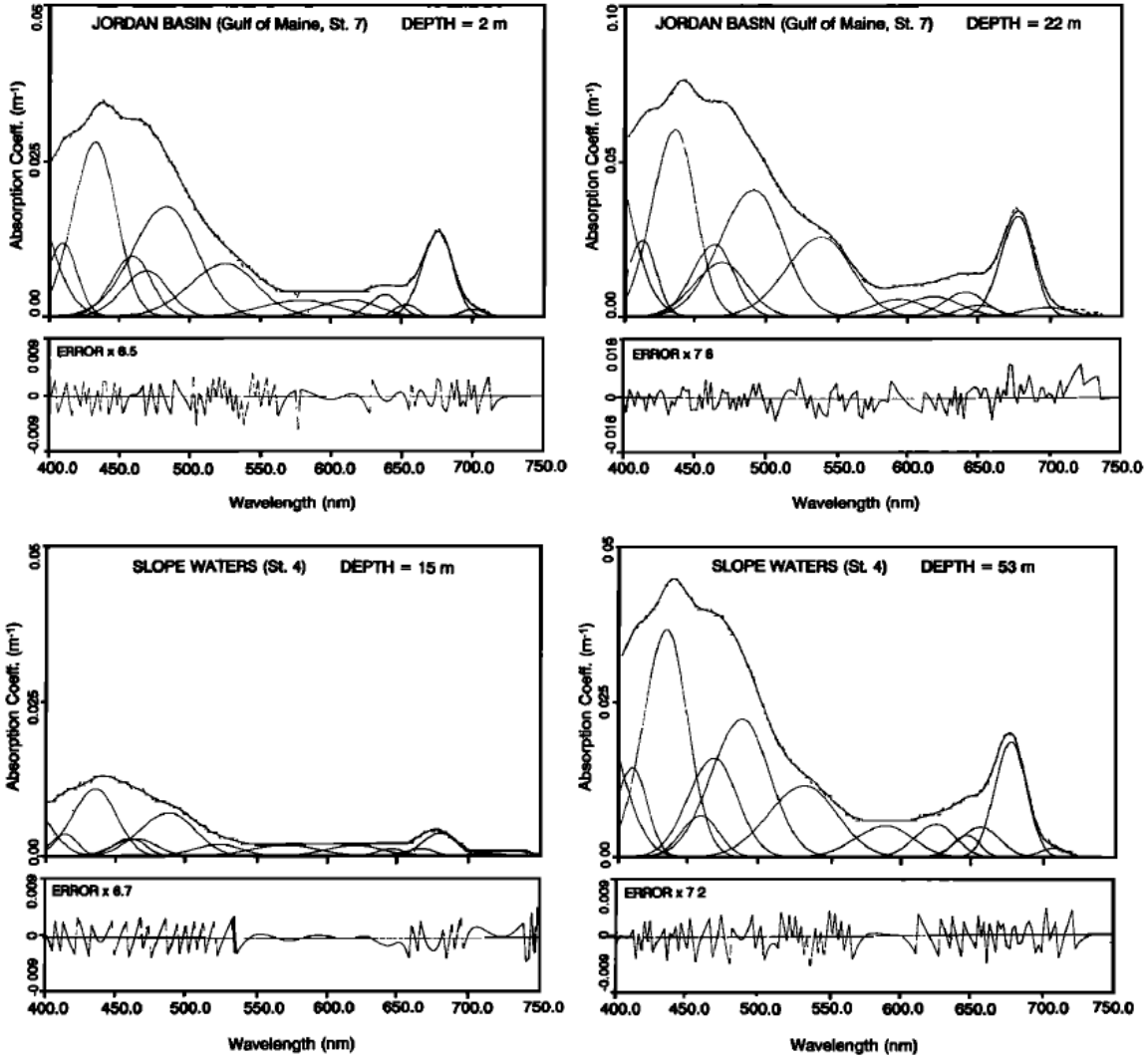



Millie et al., 1997

# Pigments - Absorption

Decomposition into Gaussian → PFTs




Hoepffner and Sathyendranath, 1991, 1993.

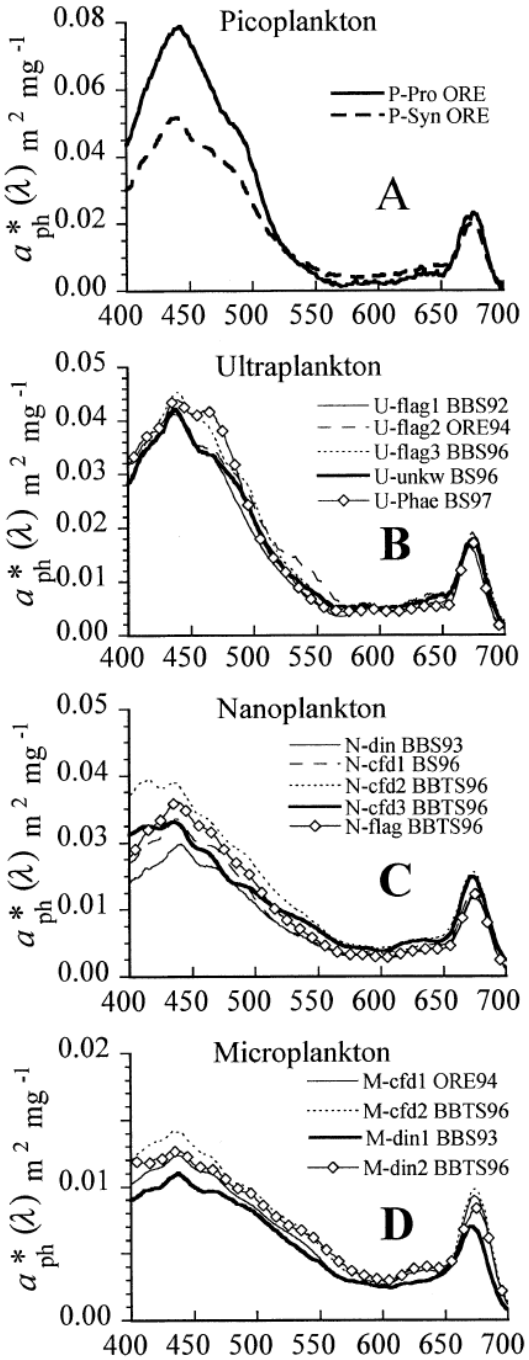
# Pigments - Absorption

Decomposition into "size"-based irical empspectra → PFTs

$$\hat{a}_{\langle ph \rangle}(\lambda) = [S_{\langle f \rangle} \cdot \bar{a}_{\langle pico \rangle}(\lambda)] + [(1 - S_{\langle f \rangle}) \cdot \bar{a}_{\langle micro \rangle}(\lambda)]$$

| Community | $S_{\langle f \rangle}$ | $r^2$ | No. of samples | $\langle a^*_{ph} \rangle$ ($m^2$ $mg^{-1}$) |
|---|---|---|---|---|
| P-Pro | 1.000 | nr | 7 | 0.0259 |
| P-Syn | 0.663 | 0.993 | 9 | 0.0195 |
| U-flag1 | 0.598 | 0.979 | 20 | 0.0160 |
| U-flag2 | 0.369 | 0.992 | 4 | 0.0180 |
| U-flag3 | 0.558 | 0.995 | 14 | 0.0181 |
| U-unkw | 0.491 | 0.992 | 9 | 0.0170 |
| U-Phae | 0.664 | 0.982 | 12 | 0.0175 |
| N-din | 0.287 | 0.987 | 7 | 0.0111 |
| N-cfd1 | 0.370 | 0.981 | 8 | 0.0126 |
| N-cfd2 | 0.266 | 0.963 | 5 | 0.0169 |
| N-cfd3 | 0.151 | 0.954 | 3 | 0.0138 |
| N-flag | 0.442 | 0.995 | 11 | 0.0136 |
| M-cfd1 | 0.002 | 0.989 | 8 | 0.0067 |
| M-cfd2 | 0.014 | 0.993 | 15 | 0.0076 |
| M-din1 | 0.025 | 0.987 | 2 | 0.0059 |
| M-din2 | 0.000 | 0.990 | 2 | 0.0072 |

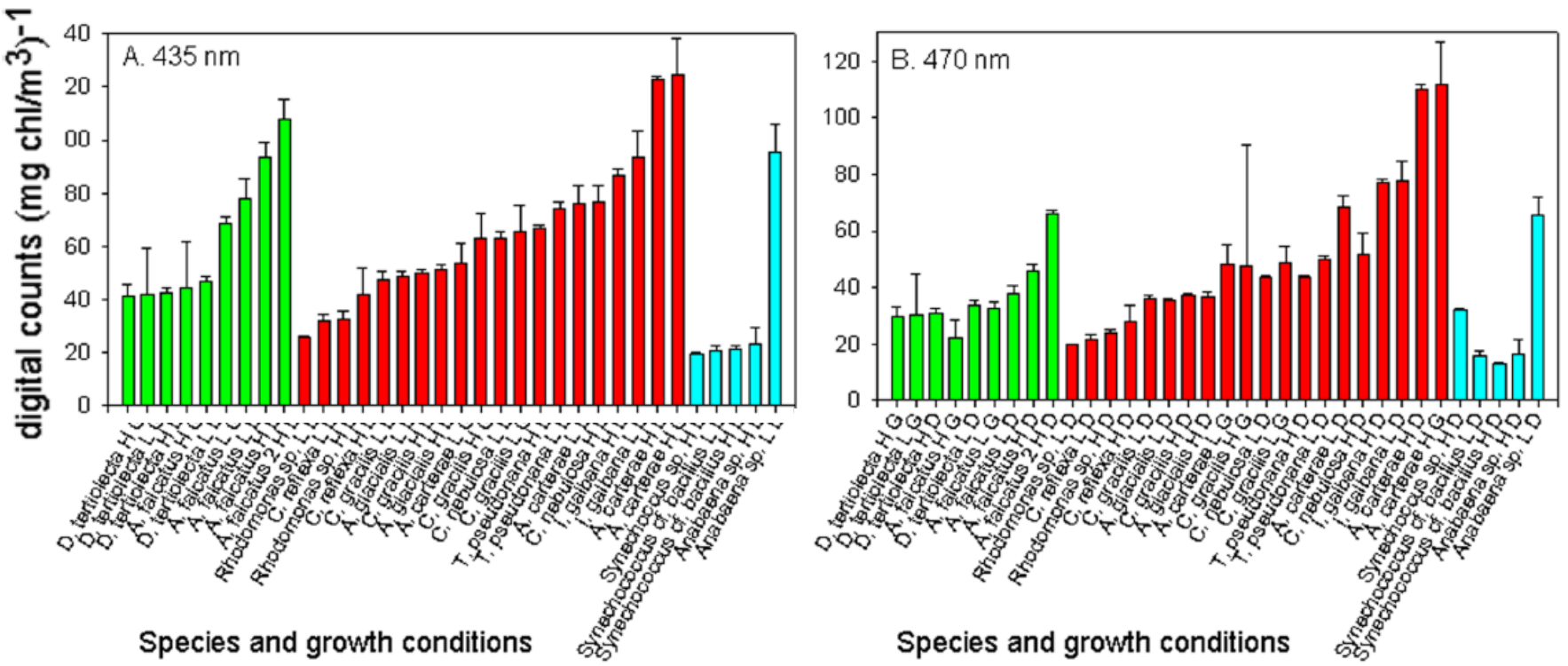
Ciotti et al., 2002



# Pigments - Fluorescence

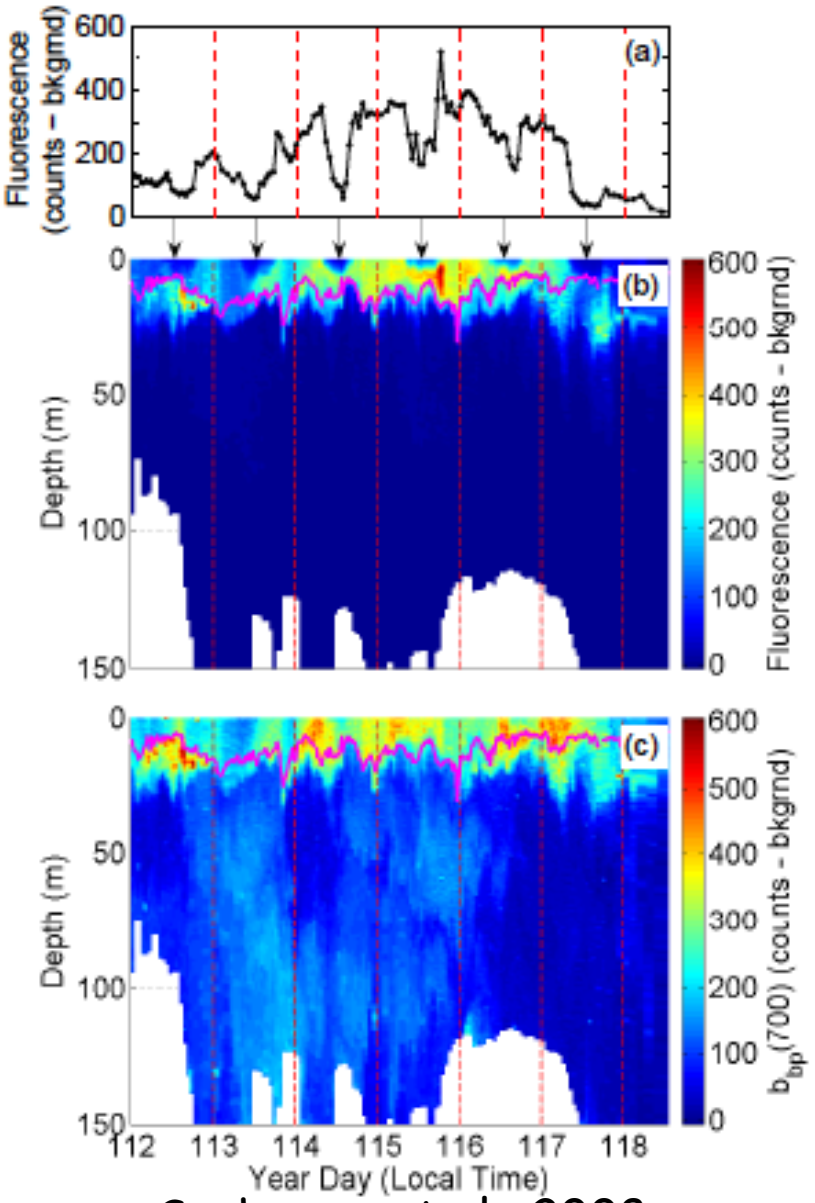
Once absorbed, some photon are emitted at a different wavelength.

Strength and wavelength of fluorescence depends on species, growth condition and light exposure (NPQ).

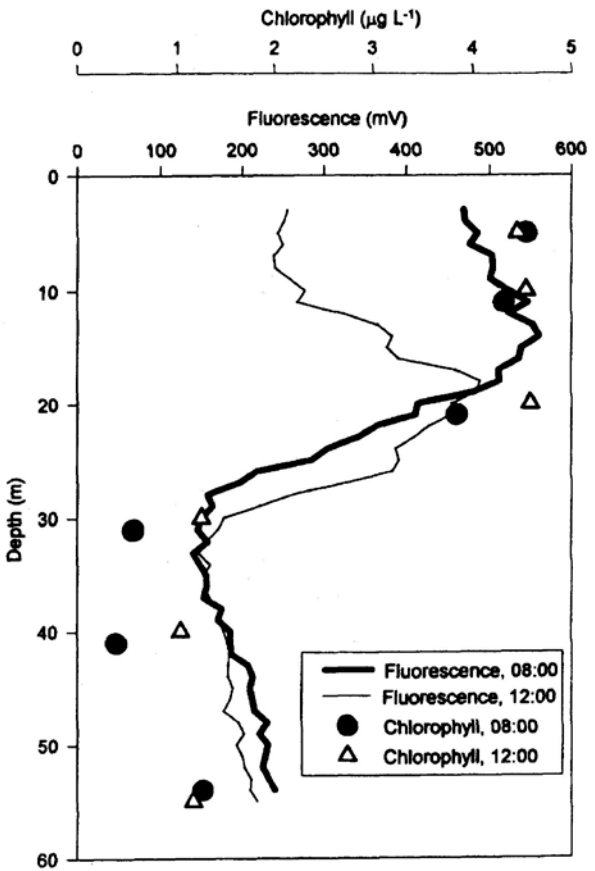



Proctor and Roesler, 2010

# Pigments - Fluorescence



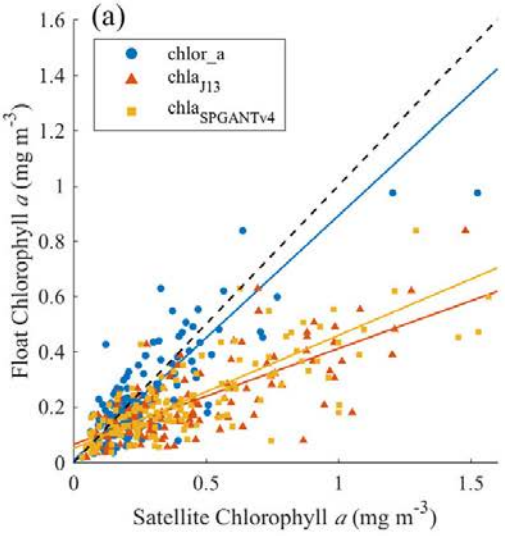

Sackmann et al., 2008

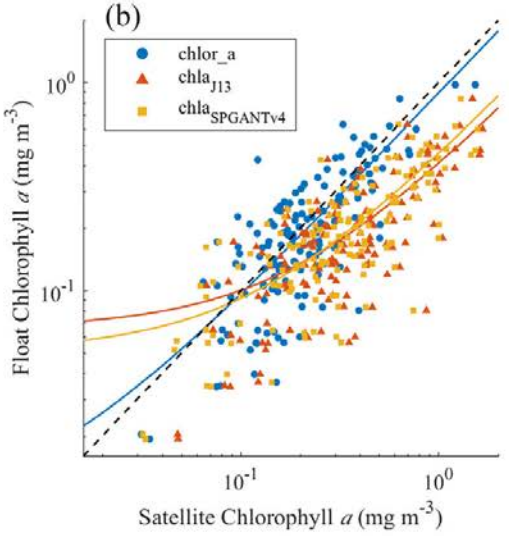


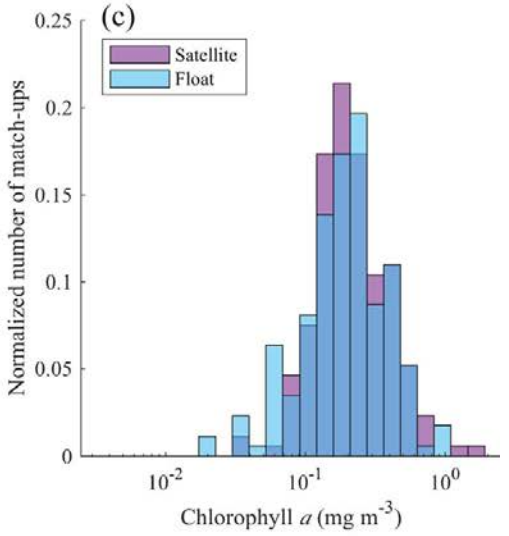

Falkowski and Raven, 1996

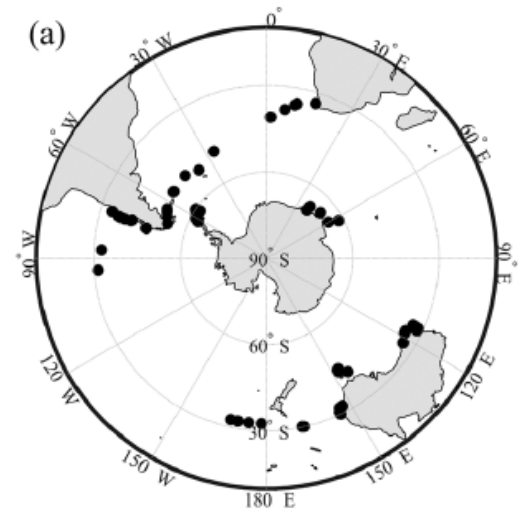
# Pigments - Fluorescence

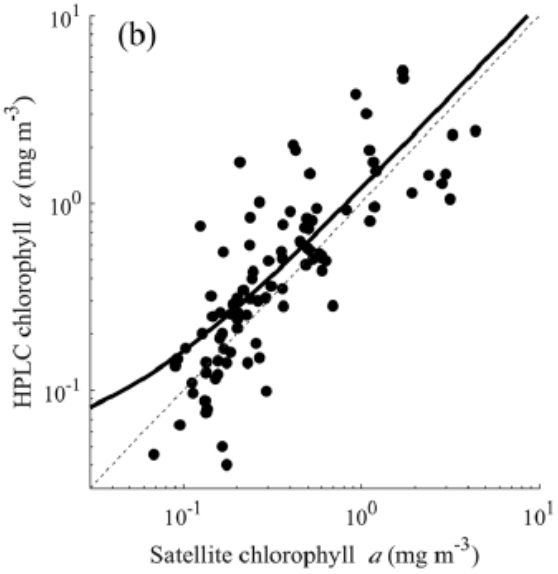
Despite these issues, can be very useful:

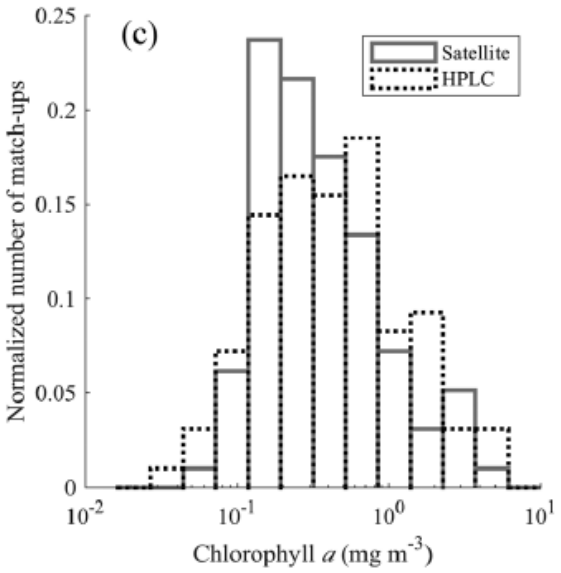



Haentjens et al., 2017

# From Inherent Optical Properties to Biogeochemical Properties
## Summary of first lecture

- In this lecture we looked at absorption and fluorescence (CDOM and particles) and the proxy derived by them.
- Utility of a proxy is application dependent (tolerance for uncertainties varies).
- Always test the applicability of a proxy before/while you use it (particularly for those derive with a large degree of empiricism – many of our sensors measure proxies!).
- Tomorrow – scattering and attenuation.