

# Phytoplankton UV-VIS spectral absorption in the Southern Ocean: preliminary results from the SO-GASEX Cruise

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## Introduction

### Southern Ocean Gas Exchange (SO-GASEX)

#### Cruise Objectives

- Improve parameterization of gas flux models using injection and tracking of dual deliberate tracer gases ( $^3\text{He}$  &  $\text{SF}_6$ ) with high winds and supporting physical, optical and biological measurements.
- Improve bio-optical models and remote sensing for spectral absorption and scattering of phytoplankton and CDOM and for photosynthesis in Southern Ocean where anomalous reflectance may be caused by calcareous skeletons of coccolithophore algae or by wind-driven bubbles.
- Better understanding of Southern Ocean ecosystem processes will help to predict global climate change.



SO-GASEX Cruise—29Feb-12Apr08 on NOAA ship R/V Ronald Brown north of South Georgia Island

### Southern Ocean Gas Exchange (SO-GASEX)

#### My Objectives

- Characterize the phytoplankton community during the SO-GASEX field campaign to help determine its contribution to underwater  $\text{pCO}_2$ .
- Test an improved method for measuring spectral absorption of particles and phytoplankton pigments by comparison with other methods for phytoplankton that vary in pigment composition and skeletal material.
- Explore alternate methods for detecting protective versus photosynthetic pigments (UV-VIS absorption versus HPLC) and relationship with measured photosynthetic efficiency.

## Methods

- **Solar PAR.** A pair of LI-COR cosine PAR sensors mounted on roof of radiation van near stern; LI-1000 datalogger recorded 5-second data at 15 minute averages and highest values per record used to minimize impact of periodic sensor shading during the rare sunny days.
- **Chlorophyll-a.** Extracted pigment determined from discrete samples (via Niskin bottles; 200-500 mL filtered on GFF filters with nominal  $0.7\mu\text{m}$  retention; extracted in 100% methanol in freezer for 24hr and fluorescence determined with Turner Designs fluorometer). *In vivo* fluorescence determined in depth profiles, 0-500m (Turner Designs C6 profiling fluorometer and Cyclops chl-a sensor).
- **UV-VIS Spectral absorption of particles and pigments** measured in samples on GFF filters (1-2 liters) shortly after collection. An improved version of the Transmission-Reflectance-bleaching method of Tassan & Ferrari (1995) was used (Hargreaves 2007) with the inherent benefits of universal calibration and pigment & detritus separation from total absorption by brief period of bleaching, and with the following improvements:

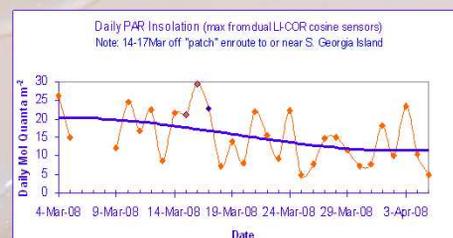
- Diode array spectrometer & lamp system offer portability (compact size, battery powered) & rapid measurement.
- UV-VIS signal with 2.7nm bandwidth (FWHM)
- Minimal handling of sample
- Correction for fluorescence artifacts

## Acknowledgements and references

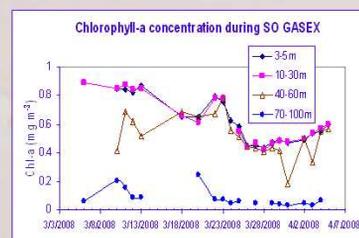
- **Funding** to BRH from NASA (grant NNX07AV23G, "Optical Properties in the Southern Ocean: In Situ measurements of Phytoplankton Absorption Using the pQFT\_TR Instrument in Support of the Southern Ocean Carbon Program" and ship support for cruise from NOAA.
- **Special thanks** to colleagues Veronica Lance for extracted chlorophyll-a analysis, to VL & Bob Vaillancourt for help before & during the cruise, & to John Marra for guidance during preparation of the proposal.
- **Preliminary phytoplankton absorption at 440nm modeled from above-water reflectance** provided by Bertrand Lubac and Zhong Ping Lee.
- **References:** Tassan & Ferrari (1995), *Limnology & Oceanogr.* 40: 1358-1368. Hargreaves (2007), AGU abstract, Fall Meeting. Lee, Carder & Arnone (2002), *Applied Optics* 41(27): 5763-5772.

## Study Site Characteristics

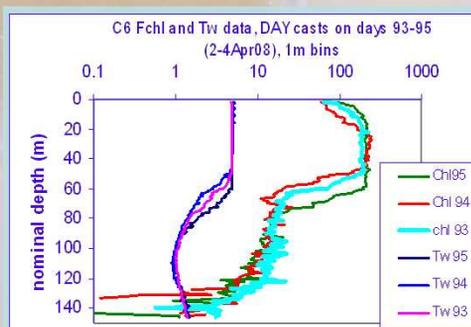
- **Site location** near South Georgia Island (see map at right, ca.  $51^\circ\text{S}$ ,  $38^\circ\text{W}$ , bottom depth ca 4000m, chosen for predictable high winds, strong  $\text{pCO}_2$  gradient, shallow mixed depth, stable water mass, and deep enough to minimize bottom effects.
- **Solar PAR** record shows large daily variation with gradual decline.
- **Mixed layer depth** ca 50 m; **surface temperature**  $3-5^\circ\text{C}$ .
- **Chlorophyll-a** in the mixed layer declined during March ( $0.9 \Rightarrow 0.4 \text{ mg/m}^3$ ) and rose slightly during early April.
- **Chl-a fluorescence** shows non-photochemical quenching in upper 10-20m during day; abrupt drop to lower [chl-a] below mixed layer. Constant ratio (390) for Fchl:[chl-a] for night and below 20m during day.



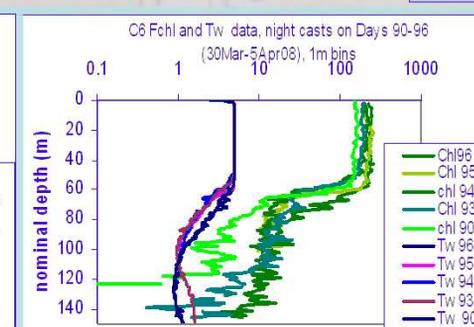
Daily insolation varied widely with few sunny days & general downward trend during March & April leading into Austral fall.



Methanol-extracted chl-a from Niskin bottle samples; Mixed layer (0m to 40-50m depth) declined in March, rose in April.

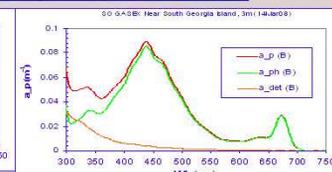
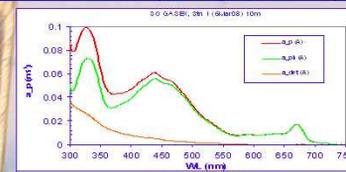
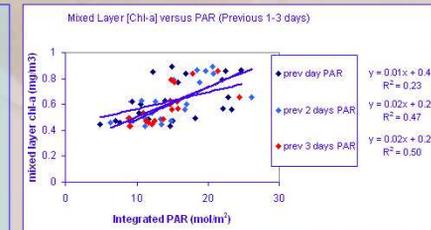


Day & Night depth profiles of temperature & chl-a fluorescence (Fchl) in early April using Turner Designs C6 profiling fluorometer. Note non-photochemical quenching above 20m in daytime profiles (Left) & uniform mixed layer at night (Right). Ratio of Fchl to methanol-extracted chl-a averaged 390 for all samples except daytime <20m.

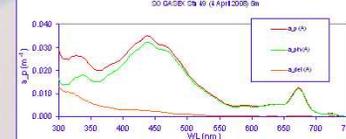
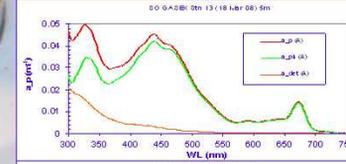


## Results & Discussion A.

Chl-a in mixed layer appears to respond within 1-2 days to solar radiation (graph at right), suggesting rapid turnover of pigment and possibly biomass. Absorption spectra (graphs below) demonstrate feasibility of shipboard analysis of spectral absorption. The temporal change in height of UV peaks (330-340nm, typical of MAA photoprotective compounds) relative to blue and red peaks also suggests that PAR waveband pigments will also have variable mix of photosynthetic and photoprotective roles.



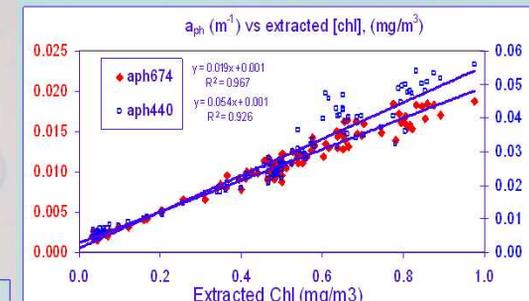
(above) Spectral absorption of surface particles, bleachable phytoplankton pigments, & detritus at South Georgia Island (mid-March). Note small UV peak.



(above) Spectral absorption of surface particles, bleachable phytoplankton pigments, & detritus at tracer injection patches (Mar-Apr).

## Results & Discussion B.

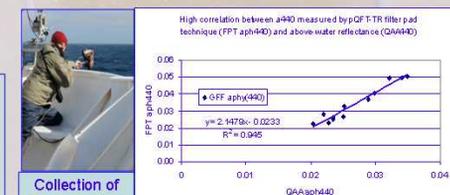
Graph at right shows strong fit between measured pigment absorption at red peak and extracted chl-a concentration. Slope is Chlorophyll-specific absorption; at 674nm 0.02 is common value. Slightly reduced fit for blue peak suggests variable pigments (possibly for photoprotection).



Regression of 674nm red peak ( $r^2=0.97$ ) and 440nm blue peak ( $r^2=0.93$ ) of spectral absorption versus extracted [chl-a]

## Results & Discussion C.

Graph at right compares measured pigment absorption at 440nm & value for 440nm absorption derived from above-water hyperspectral reflectance measurements using the QAA model of Lee et al 2002. While absolute values from remote sensing model do not rise as rapidly as values from filter pad measurements, there is excellent agreement in the low range & a strong regression ( $r^2=0.95$ ).



High correlation between  $a_{440}$  measured by pQFT-TR filter pad technique (FFT a<sub>ph440</sub>) and above water reflectance (QAA a<sub>ph440</sub>)

Collection of hyperspectral reflectance data by Bertrand Lubac

Regression of FFT  $a_{ph440}$  from measured spectral absorption of particles versus QAA  $a_{ph440}$  modeled from above-surface spectral reflectance

## Conclusions

Preliminary analysis of data from the SO-GASEX cruise that ended just two weeks ago suggest that

- We have begun to **characterize phytoplankton community optical properties** and its spatial and temporal trends the during the Southern Ocean Gas Exchange field campaign;
- The **improved filter pad technique worked well** for shipboard analysis of spectral absorption;
- **UV-VIS absorption appears to reveal phytoplankton variations in pigment composition** possibly related to photoprotection. We will compare data with HPLC pigments & photosynthetic efficiency.
- The **strong correlation of the red absorption peak with extracted chlorophyll-a** is promising given the likelihood that samples varied in abundance of calcite skeletal material from coccolithophore algae, a situation that would cause calibration problems for the traditional filter pad method. Data on calcite abundance will be available from another SO-GASEX project.
- **Accurate remote sensing** of phytoplankton absorption and photosynthesis appear feasible.