# Retrieving in situ particulate absorption spectra in optically clear waters: An example from the Equatorial Pacific

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A ship-board surface flow through system was equipped with a WET Labs ac9 configured with a switchable 0.2 μm filter cartridge to measure total and filtered absorption and attenuation. The filter was engaged routinely throughout each day. Observations were collected on three cruises (September 2005, January 2006 and September 2006) along an equatorial transect from approximately 8N to 8S along the 140W longitude then east to 125W and from 8S to 8N, completing 3 sides of a box. Discrete samples were collected from the flow through system and processed for spectrophotometric particulate absorption coefficients. The in situ absorption coefficients were of the order 0.005 to 0.01 $m^{-1}$, the same order as the resolution of the ac9. In these optically clear waters, instrument stability and calibration are of utmost importance for retrieving accurate absorption spectra. We experienced problems with instrument stability on one cruise and were plagued by pure water calibration issues on both. However, by computing the particulate absorption and attenuation spectra from the difference between temporally adjacent total and filtered water observations we were able to retrieve robust and accurate spectra, which compared well with those derived from filter pad absorption observations, on highly resolved spatial scales. We are able to quantify seasonal and spatial variations in particle optical properties across the equatorial upwelling zone. The particle absorption is dominated by phytoplankton exhibiting spectral shapes consistent with small cell sizes and high light acclimation. The slopes of particle beam attenuation spectra are likewise consistent with small particle sizes.

## INTRODUCTION

In situ measurements of inherent optical properties in clear open ocean waters brings attention to a number of instrumentation issues, foremost, that measurements are made relative to pure water. For example, instruments such as the WET Labs ac-9 reflective tube absorption and attenuation meter are calibrated to provide zero readings in clean fresh water. However, optically pure water, free of bubbles, particles, and dissolved organics, is difficult to generate in a well-equipped laboratory, let alone at sea. The stability of pure water is poor, and its absolute optical properties are not well known. Secondary problems include drift in instrument electronics or optics and fouling of optical windows.

The measured response, $a_m(\lambda)$, of a reflective tube spectral absorption meter such as the ac-9 can be described as

$$a_m(\lambda) = a_g(\lambda) + a_p(\lambda) - a_{offset}(\lambda) - \Delta a_w(\lambda, T, S)\,, \qquad (1)$$

where $a_g(\lambda)$ and $a_p(\lambda)$ are the dissolved and particulate material contributions to the measured absorption, $a_{offset}(\lambda)$ is a calibration value such that the instrument response is zero in pure water, and $\Delta a_w(\lambda, T, S)$ corrects for the temperature and salinity-dependent difference in absorption coefficient between pure water used in calibration and the waters in which the measurement is being made.

Calibration values are generally calculated by the manufacturer, in the users' laboratory, and in the field using an optically pure water source. Such calibrations are recommended when the instrument is shipped or transported, and periodically (ideally daily) while in the field, to account for changes in optical alignment, spectral filter response, and lamp and electro-optics drift. Calibrations are difficult to perform in the field due to the difficulty in generating optically clean water, and in clear ocean waters the uncertainty in the calibration (based on repeated calibrations) is substantial in comparison to the signal being measured. Furthermore, for instruments deployed in moored arrangements, or in shipboard flow-through systems, such frequent calibrations may not be an option.

Fortunately, many studies are primarily concerned with the optical properties of particulate material in the water. Using periodic filtered measurements, robust, accurate and calibration-independent particulate absorption and attenuation spectra can be calculated as the difference between temporally adjacent total and filtered water observations. Below, we discuss methods for making such measurements and compare particulate measurements made using the difference method with measurements made using the filter pad technique.

## METHODS

The WET Labs ac-9 is an in situ absorption and attenuation meter utilizing dual flow tubes (one for attenuation, one for absorption). The ac-9 provides absorption and attenuation measurements at 9 wavelengths in the visible, using a collimated source lamp and spectral bandpass filters arranged on a rotating wheel, producing complete spectra at a rate of 6 Hz. The ac-s provides measurements at greater than 80 wavelengths using a linear variable filter, producing complete spectra at approximately 3 Hz. Absorption is measured using a reflective tube and a wide-angle detector (with diffuser). Attenuation is measured using a non-reflective tube and collimated detector. Each instrument is available in 10 and 25 cm pathlength versions. In this work, we have used the 25 cm ac-s and ac-9. The ac-9 and ac-s are calibrated at the factory to produce zero output in clean fresh water. However, field calibrations are used to remove the effects of optical misalignment and instrument drift.

The absorption of pure water is dependent on temperature and salinity in the red and near-infrared portion of the spectrum. In situ measurements of absorption and attenuation therefore include not only the effects of particulate and dissolved materials, but also the difference between the absorption coefficient of the water being measured and the reference water used for instrument calibration, as in Eq. (1), where

$$\Delta a_w(\lambda, T, S) = (T - T_r)\Psi_T + (S - S_r)\Psi_S \,. \tag{2}$$

In Eq. (2), $T$ and $S$ are the in situ water temperature and salinity, $T_r$ and $S_r$ are the temperature and salinity of the water used for calibration, and $\Psi_T$ and $\Psi_S$ are the temperature and salinity-specific absorption coefficients of water [$\mathrm{m^{-1}\,{}^{\circ}C^{-1}}$] and [$\mathrm{m^{-1}\,PSU^{-1}}$] (Pegau et al., 1997; Sullivan et al., 2006).

Reflecting tube absorption meters such as the ac-9 do not collect light scattered from the incident beam, causing the instruments to overestimate the absorption coefficient. In most spectrophotometers, scattering correction is accomplished by subtraction of a baseline value around 750 nm, assuming that (1) absorption is negligible in this region of the spectra, and (2) that the scattering coefficient is spectrally flat. For the ac-9 and ac-s a more accurate scattering correction scheme can be employed since the instruments also measure spectral beam attenuation. Since the spectral scattering coefficient can be determined as the difference in attenuation and absorption, the assumption that the scattering coefficient is spectrally flat is not needed. Instead, a first-order scattering coefficient is calculated as the difference of attenuation and the uncorrected absorption,

$$b'(\lambda) = c(\lambda) - a_m(\lambda)\,. \tag{3}$$

This scattering coefficient will be slightly underestimated since the uncorrected absorption is overestimated. Absorption is corrected using the shape of the first-order scattering coefficient and by assuming that absorption in the NIR is negligible (Zaneveld et al., 1992):

$$a(\lambda) = a_m(\lambda) - a_m(715)\frac{b'(\lambda)}{b'(715)}\,. \tag{4}$$

Calibration-independent measurements are made by calculating the difference of total and filtered water measurements. We have used WET Labs absorption and attenuation meters (both ac-9 and ac-s) in concert with a switchable filter cartridge, usually a 0.2 μm nominal pore size, as is often used as an operational cutoff between particulate and dissolved material. Using a flow through system as in Figure 1, the valve is used to divert flow to the instrument through the filter. The periodic filtered measurements (5b) are subtracted from adjacent unfiltered samples (5a):

$$\text{(unfiltered)} \quad a_{m(1)}(\lambda) = a_g(\lambda) + a_p(\lambda) - a_{offset}(\lambda) - \Delta a_w(\lambda, T\,S) \tag{5a}$$
$$\text{(filtered)} \quad a_{m(2)}(\lambda) = a_g(\lambda) \qquad\qquad - a_{offset}(\lambda) - \Delta a_w(\lambda, T\,S) \tag{5b}$$

resulting in $a_{m(1)}(\lambda) - a_{m(2)}(\lambda) = a'_p(\lambda)$, where $a'_p(\lambda)$ is the particle absorption (uncorrected for the effects of scattering), thus eliminating dependence on clean water offsets as well as temperature and salinity absorption correction. Both the clean water offsets, and temperature corrections can be sources of uncertainty in post-processing absorption data. These uncertainties are of order 0.005 $m^{-1}$ and can be substantial in comparison to the absorption signals in optically clear waters, which are often $< 0.01\ \mathrm{m}^{-1}$. Uncertainty in clean water calibration (the stability of repeated calibrations and cleanings) is also typically of order 0.005 $m^{-1}$. An additional source of uncertainty arises from the temperature and salinity correction of water absorption. The variation in water absorption in the near infrared as a function of water temperature (Eq. (2)) is approximately 0.0035 $m^{-1}$ $°C^{-1}$ at 715 nm. Thus small uncertainties in in situ water temperature lead to significant uncertainty in near infrared absorption. This is two-fold problematic, not only because of the uncertainty in temperature-corrected absorption coefficient in the near infrared, but secondly, because the measured absorption signal in this wavelength region is used to correct absorption spectra for the effects of particle scattering within the sample volume.

Discrete water samples were collected periodically from the flow through system and processed for spectrophotometric particulate absorption analysis using the quantitative filter pad method (Mitchell, 1990; with modifications as in Roesler, 1998) for comparison with the particulate absorption data acquired from the ac-9. An average of 1000 ml of seawater from the on-board flow through system was collected and filtered through Whatman GF/F glass fiber filters (nominal pore size <0.7 μm). Filtered samples were stored in liquid nitrogen until shipped back to the laboratory for spectrophotometric analysis. A Cary 3E UV-VIS Spectrophotometer was used to measure optical density $D_p$ over the wavelength range of 300-800 nm. Initially particulate absorption was calculated as described in Roesler (1998), as

$$a_p(\lambda) = \frac{1}{\log_{10} e}\left(D_p(\lambda) - \left\langle D_p \right\rangle_{750-800}\right)\left(\beta V_{filt} / A_{eff}\right)^{-1}, \tag{6}$$

where $V_{filt}$, and $A_{eff}$ are the volume of sample filtered and effective area of the filter pad. The effects of scattering losses on the filter pad are accounted for by subtraction of a spectrally flat baseline, here the average of the optical density spectra over the wavelength range 750-800nm, $\left\langle D_p \right\rangle_{750-800}$. The pathlength amplification factor, $\beta$, accounts for the difference in photon pathlength through the sample on a filter pad versus in suspension, for which Roesler (1998) derived a theoretical value of 2. However, because the optical density reading on the filter pads were less than ~0.25, the $\beta$ correction factor derived by Roesler (1998) is not robust because the optical properties of the filter pad dominate the pathlength amplification factor. In this optical regime the multiple scattering correction factor of Mitchell (1990) is expected to be more robust. Thus the particulate absorption was also calculated as

$$a_p(\lambda) = \frac{1}{\log_{10} e}\left(D_{p,CORR}(\lambda) - \left\langle D_{p,CORR} \right\rangle_{750-800}\right)\left(V_{filt} / A_{eff}\right)^{-1}, \tag{7}$$

where $D_{p,CORR}(\lambda) = 0.392 \cdot D_p(\lambda) + 0.655 \cdot D_p^2(\lambda)$.

The difference method described above (e.g. Eq. 5) can also be used to produce calibration-independent particle beam attenuation spectra, $c_p(\lambda)$. Beam attenuation is often used to estimate the concentration of suspended particles by calibrating it against particle mass, volume, or particulate organ carbon (e.g. Bishop, 1999). Optical theory predicts that the beam attenuation spectra can be approximated well as a power-law function of wavelength,

$$c_p(\lambda) = A\lambda^{-\gamma}. \tag{8}$$

The exponent, $\gamma$, has been shown be related to the particle size distribution (Boss et al., 2001). For natural waters, a useful approximation is to assume a differential particle size distribution of the form

$$N(D) = N_0 (D/D_0)^{-\xi}, \tag{9}$$

where $N_0$ is the differential concentration $[\mathrm{m}^{-3}\ \mu\mathrm{m}^{-1}]$ of particles of reference diameter $D_0$ and $\xi$ is the size distribution slope. For a size distribution of this form, it has been shown that the size distribution and beam attenuation spectra are related by relationship

$$\xi = \gamma + 3. \tag{10}$$

## RESULTS

Underway flow-through ac-9 particulate absorption observations were collected on three cruises (Aug-Sep 2005, Jan-Feb 2006 and Aug-Sep 2006) along an equatorial transect from approximately 8N to 8S along the 140W longitude then east to 125W and from 8S to 8N, completing 3 sides of a box. During the September 2005 and January 2006 cruises, we used an ac-9 with the 0.2 μm filter engaged manually when on station and also occasionally while in transit. During the Aug-Sep 2006 cruise, a hyperspectral ac-s (measuring absorption and attenuation at 83 wavelengths between 400 and 750nm) and automated valve system were employed. The automated valve system, consisting of an electrically-actuated three-way valve and computer controller, yielded filtered measurements for 10 minutes at the start of every hour (Figure 2A). A 24-hour time sequence of ac-s measured particulate absorption (Figure 2B) demonstrates that the variability in particulate absorption over this segment from 5N 123.5W to 2.5N 125W is of order 0.01 $m^{-1}$. However, more interesting is the smaller scale absorption features of order 0.005 $m^{-1}$ observed over spatial scales of order 0.1°. These are features which are at the limit of the factory-specified resolution of the instrument because of calibration and correction uncertainties, yet are resolvable using this approach. These fine scale variations are attributed to small-scale patchiness in the surface phytoplankton distributions, as the derived particulate absorption spectrum is characteristic of a nearly pure algal suspension (Figure 3C). The absorption coefficient at the red chlorophyll peak (676 nm) is approximately 0.002 $m^{-1}$, which is equivalent to a chlorophyll concentration of 0.10 to 0.15 mg $m^{-3}$, depending upon the chlorophyll-specific absorption coefficient used, which is comparable to measured values.

To validate our flow-through particulate absorption measurements, we compared them with coincident discrete filter pad spectrophotometric measurements taken from the August 2005 and September 2006 Equatorial Pacific cruises. We compared the ac-9 measurements with particulate absorption from filter pad optical density measurements using two different formulae (Figure 3A,B). In both cases, correlation between the measurements was high ($R^2>0.81$) and the offset between ac-9 and filter pad absorption was zero within the precision of the ac-9. However, the regression between our ac-9 and filter pad absorption measurements did not exhibit a slope of one.

We suspect one or a combination of the following reasons for the disagreement: (1) differences in filtration efficiency between the ac-9 with cartridge filter and the spectrophotometric approach utilizing GF/F filters; or (2) selection of the pathlength amplification factor, $\beta$, in the conversion from spectrophotometer-measured optical density to absorption coefficient (in [$m^{-1}$]). The cartridges used with the ac-9 were 0.2 μm nominal pore size membrane filters (PALL AcroPak Supor Membrane during the 2005 cruise, and GE Osmonics Memtrex-NY during the 2006 cruises), having different retention characteristics compared with the GF/F, and each having a dependence on filtration pressure. Filtration pressure for the filter pad measurements is low, while flow rates and pressure for the ac-9 system are higher, and can vary over the course of filter fouling and as a function of the upstream flow-through supply. Many authors have discussed the pathlength amplification issue inherent in filter pad absorption measurements and devised solutions, both theoretical (Roesler, 1998) and empirical (e.g. Mitchell, 1990; Bricaud and Stramski, 1990). The problem is especially difficult at the low optical densities found in clear open ocean waters. We have attempted two different correction methods, neither of which agreed with the ac-9 measurements. Further research is needed to address these possible reasons for disagreement.

Particulate $a_p(440)$ and $c_p(\lambda)$ slopes along the 140W and 125W equatorial transects, for the Aug-Sep 2005 and Jan-Feb 2006 cruises, are shown in Figure 4. Both 125W transects show equatorial enhancement of absorption associated with upwelling. In comparison, at 140W the equatorial upwelling feature is generally less distinct, and more variable between cruises as is demonstrated by the higher $a_p(440)$ variability. The slope of particle beam attenuation, indicative of particle size distribution, indicates a trend of larger particles near the equator, while the 125W transects possess no clear pattern.

## CONCLUSION

Acquiring in situ particulate absorption data from a ship-board flow through system in clear open ocean waters proves difficult when absorption observations are of the same order of magnitude as pure water calibrations. Achieving proper pure water instrument calibrations at sea is a separate challenge and they are often not made as frequently as needed to correct for the effects of instrument fouling and drift. By taking the difference between temporally adjacent total and filtered absorption values when using a WET Labs absorption and attenuation meter configured with a switchable 0.2 μm filter cartridge, we are able to produce absorption spectra that are within the resolution of the instrument and that are independent of clear water calibrations, offsets due to drift in instrument electronics or optics, and fouling of optical windows.

We have shown that trends in continuous absorption data collected with an ac-9 using the difference method are consistent with those derived by discrete filter pad particulate absorption analysis calculated in the laboratory using a spectrophotometer. However, the filter pad measurements indicate higher absorption than the ac-9. While additional work is needed to understand the disagreement in absorption magnitude, the ac-9 differencing technique allows us to measure particulate absorption nearly continuously, over long periods of time, and at the limit of ac-9 accuracy. Having the ability to make such measurements in a wide range of waters, from optically clear to turbid nearshore, at high temporal and spatial resolution, will improve our ability to resolve small-scale structure in the open ocean.

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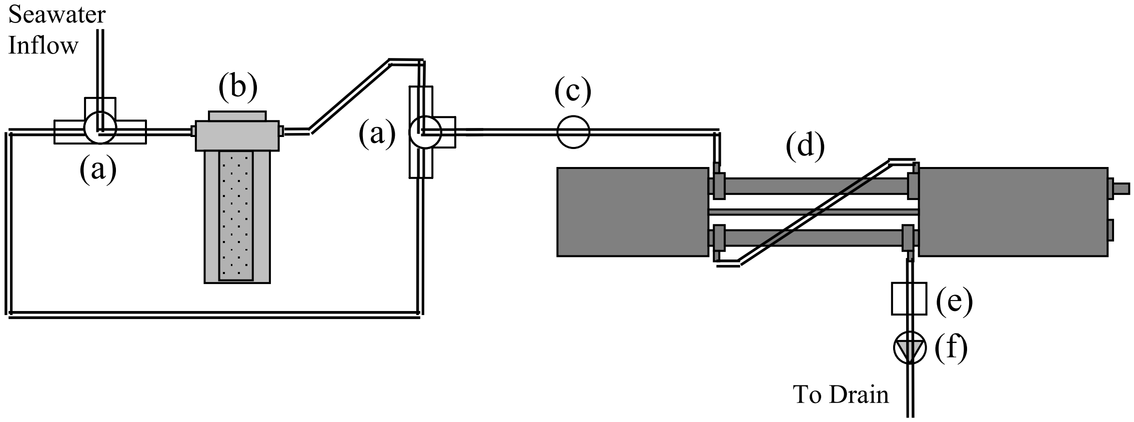

***Figure 1 – Example flow through system setup. Seawater inflow can be diverted using a pair of three-way ball valves (a) through a 0.2 µm filter (b) or directly to instrument. A stopcock or needle valve (c) with quick-disconnect fitting is used to control flow rates to the instrument (d) and facilitate its removal for cleaning. A volume flow sensor (e) is used to assess fouling of the filter. A check valve (f) ensures that no air is drawn into the instrument under a no-flow condition.***

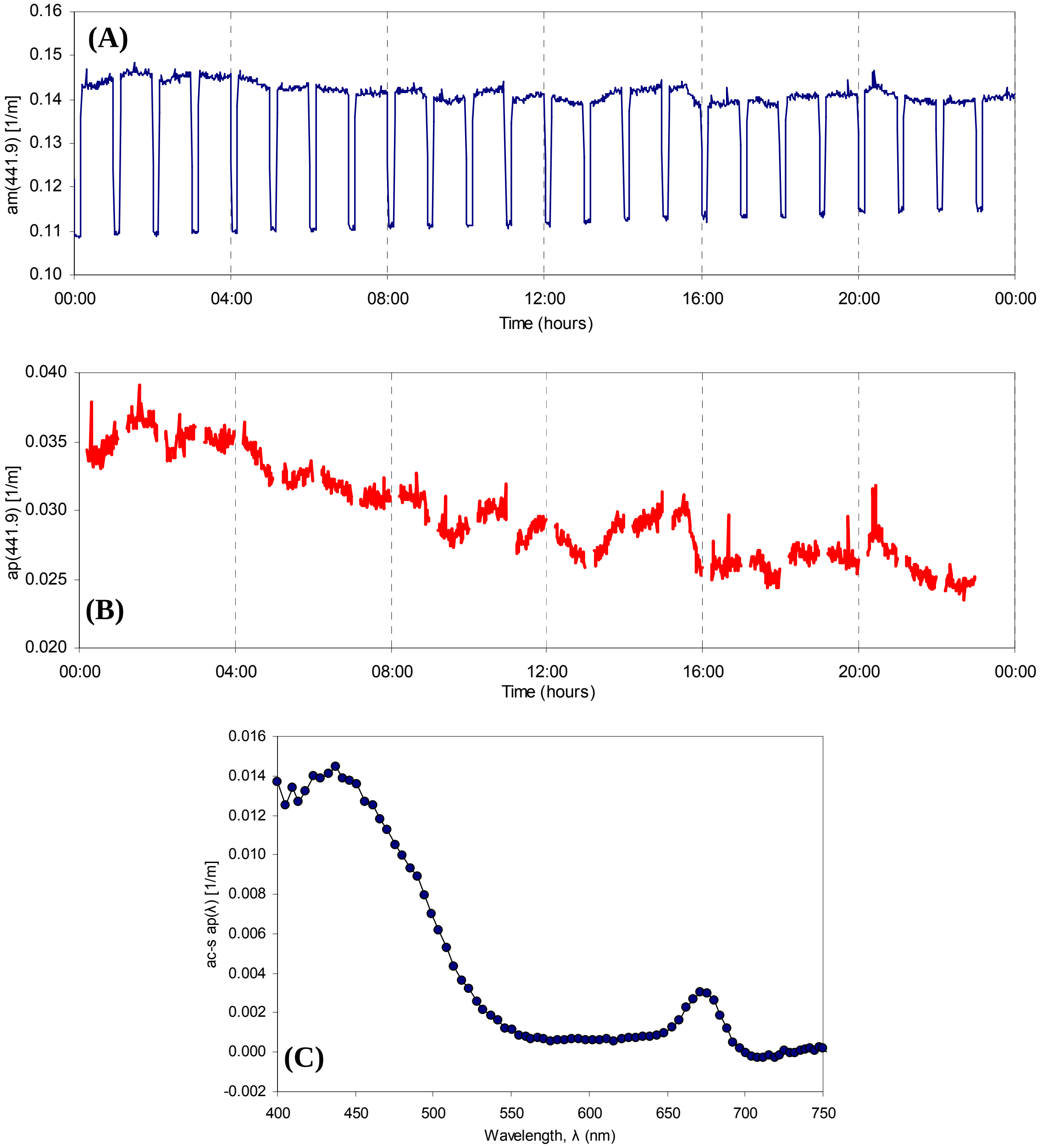

***Figure 2 – (A) Example uncalibrated, uncorrected, 1-min binned measured absorption data from the ac-s during the Aug-Sep 2006 equatorial cruise. Filtered measurements were made for 10 minutes at the start of each hour. Instrument drift or fouling over the course of the day is evident in the filtered measurements. (B) Calibration-independent ac-s particle absorption measurements for the same time period. (C) Example of particle absorption spectra from ac-s time series.***

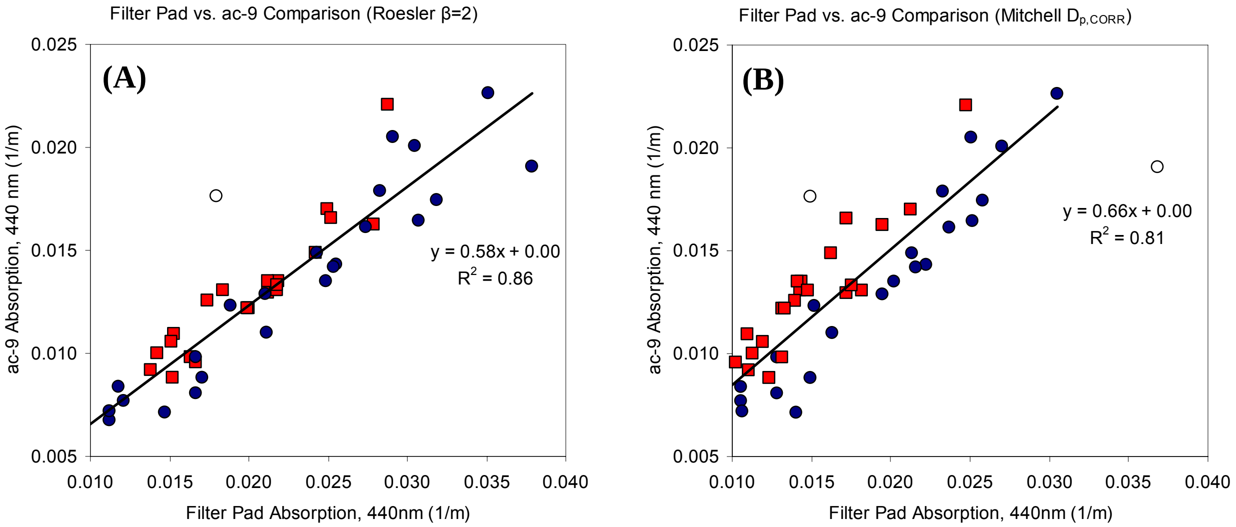

***Figure 3 – Observed relationship between coincident filter pad and flow-through ac-9 particle absorption from Aug-Sep 2005 (blue circles) and Jan-Feb 2006 (red squares) Equatorial Pacific cruises. Empty symbols denote exclusion from the linear regression. In (A) filter pad absorption was determined from optical density using Eq. (6) as in Roesler (1998). In (B) filter pad absorption was determined using Eq. (7) as described in Mitchell (1990).***

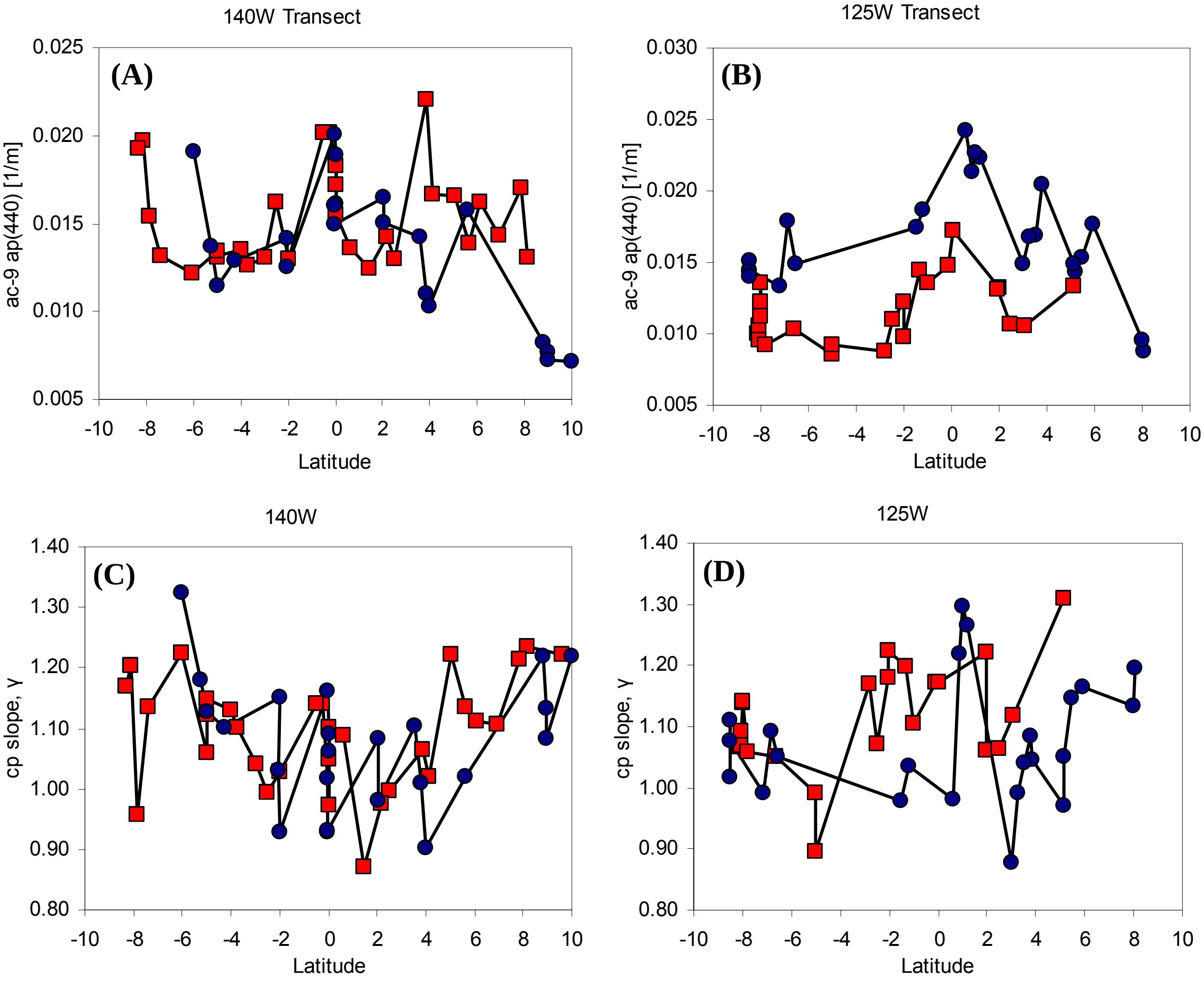

***Figure 4 – (A,B) ac-9 measured particulate absorption for repeat transects during the Aug-Sep 2005 (blue circles) and Jan-Feb 2006 (red squares) Equatorial Pacific cruises. Both 125W transects show equatorial enhancement of absorption associated with upwelling. In comparison, at 140W the equatorial upwelling feature is generally less distinct, and more variable between cruises, as is demonstrated by the higher $a_p(440)$ variability. (C,D) Slope of particle beam attenuation spectra for the repeat transects, indicative of particle size distribution. The 140W transect shows an apparent trend of larger particles near the equator, while the 125W transects possess no clear pattern.***