The Hyper-Spectral Temperature and Salinity Dependent Absorption Coefficients of Pure Water

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INTRODUCTION

A series of laboratory experiments were run to determine the temperature and salinity dependent absorption coefficients of pure water using a new hyper-spectral absorption and attenuation meter (the AC-S) manufactured by WET-Labs (Philomath, OR - http://www.wetlabs.com). The AC-S (Figure 1) employs the same path-length and a similar absorption and attenuation optical configuration as the WET-Labs AC-9 (9 wavelength ac meter) however; the AC-S has hyper-spectral resolution with approximately 85 wavelength bands between 400-750 nm (~ 4 nm bandwidth). Understanding how the absorption of pure water is affected by temperature and salinity is vital to researchers making in-situ or laboratory optical measurements in a variable medium such as seawater.

Figure 1. The AC-S (left instrument) next to the AC-9.

AC-S MEASUREMENT STABILITY AND PRECISION

The calibration stability and precision of AC-S measurements are comparable to that of an AC-9 (Figure 2). Over 1 month of heavy use, the calibration drift in the AC-S was minimal, and except for a small drift in the absorption wavelengths < 410 nm, varied within the expected precision of the instrument (+/- 0.003 m^{-1}).

The shape of the water calibration curves above 550 nm in Figure 2 is not instrument drift, but an example of the sensitivity of the AC-S. This characteristic shape is from the temperature dependent absorption of pure water. The small difference between the temperature of the original factory water calibration and these later water calibrations was easily detected by the AC-S (< 1 °C difference). These temperature (and salinity) effects must be corrected for when making precise measurements of particulate or dissolved absorption/attenuation.

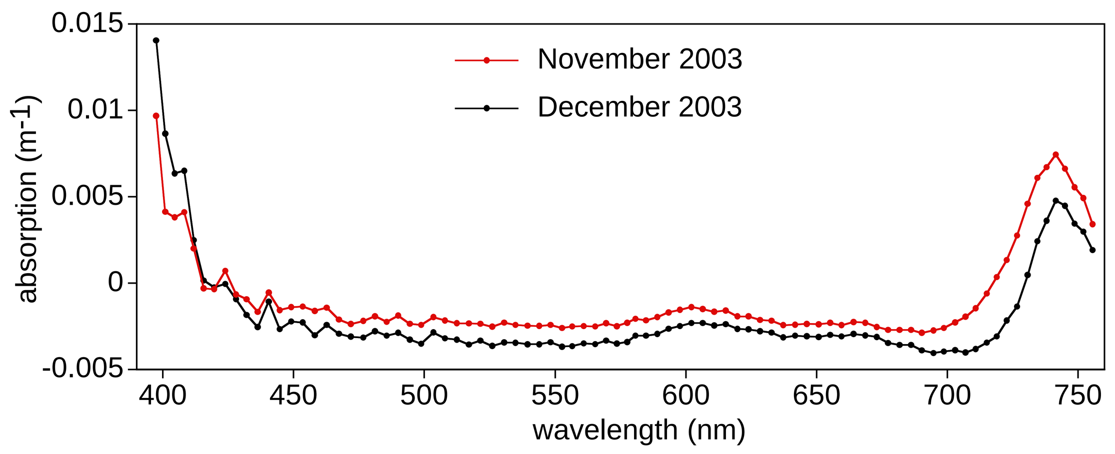

Figure 2 (left). The change in pure water laboratory calibrations of the AC-S in the absorption channel after one month of heavy use.

METHODS and RESULTS

TEMPERATURE COEFFICIENTS: The AC-S and a Seabird SBE-49 CTD were submerged in a clean, 50 L Nalgene tank that was filled with 18 ohm 0.2 µm filtered deionized water. Prior to using the AC-S and CTD for temperature coefficient experiments, the exteriors of the instruments were washed with laboratory detergent, thoroughly soaked and rinsed with deionized water. After filling the experimental tank, the water was allowed to degas and come to temperature equilibrium for 24 hours in a ~25 °C room. Just prior to starting each experimental run, the entire exterior of the 50 L tank was surrounded by crushed ice to gradually lower the temperature of the tank water from ~25 °C to ~5 °C. When the tank water reached ~5 °C the crushed ice was removed from the exterior of the tank and replaced with hot water to gradually raise the temperature of the tank water back to ~ 25 °C. The AC-S and CTD continually pumped and circulated the water and recorded absorption/attenuation and temperature during the temperature cycling. The AC-S had a 0.2 µm filter on its intakes to eliminate bubbles and any particles from contributing to the measurements. Least squares regressions of the differential change in absorption dependent on temperature were highly linear (Figure 3). The slopes of these relationships were used to calculate the temperature dependent absorption coefficients of water. No difference was found in the relationship slopes dependent on whether it was a heating or cooling cycle or between the absorption and attenuation channels of the AC-S.

SALINITY COEFFICIENTS: Salinity coefficients were determined using several dilutions of optical grade NaCl (99.99% pure) in 18 ohm deionized water. After adding salts to the pure water, the saltwater solution was 0.2 µm filtered. The different saltwater dilutions were run through the AC-S in a benchtop configuration and the absorption of pure water for the temperature of the saltwater was subtracted from the measurements. Least squares regressions of the differential change in absorption dependent on NaCl concentration were highly linear (Figure 4). The slopes of these relationships were used to calculate the salinity dependent absorption coefficients of saltwater. There was no difference in the slopes of the relationships between the absorption and attenuation channels of the AC-S.

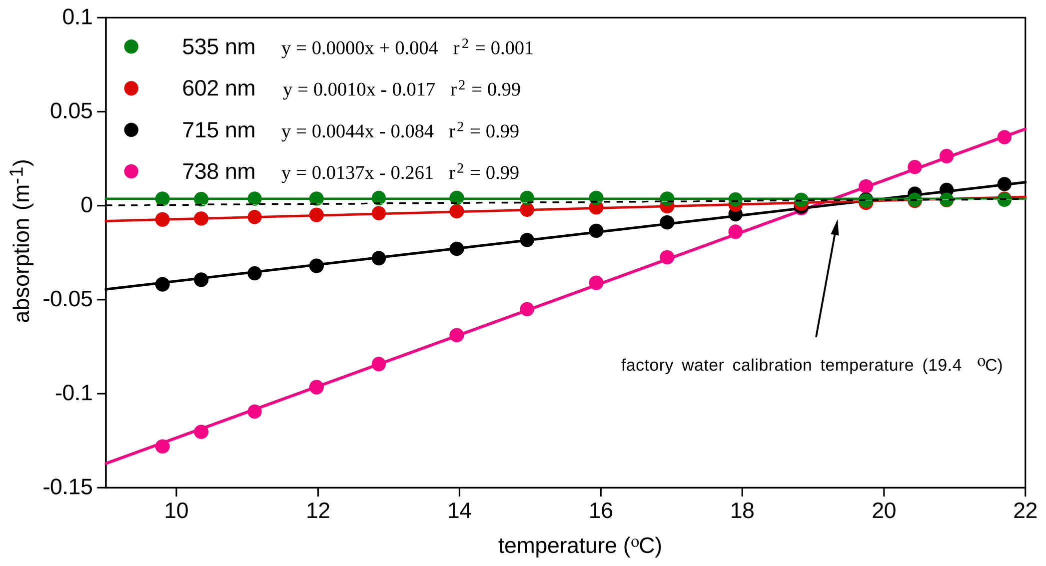

Figure 3. The change in absorption of pure water as a function of temperature for selected wavelengths of the AC-S. Lines and equations are least squares linear regressions of the relationships. As these relationships are differential in relation to the original factory water calibration temperature, they pass through zero at that temperature (~19.4 °C).

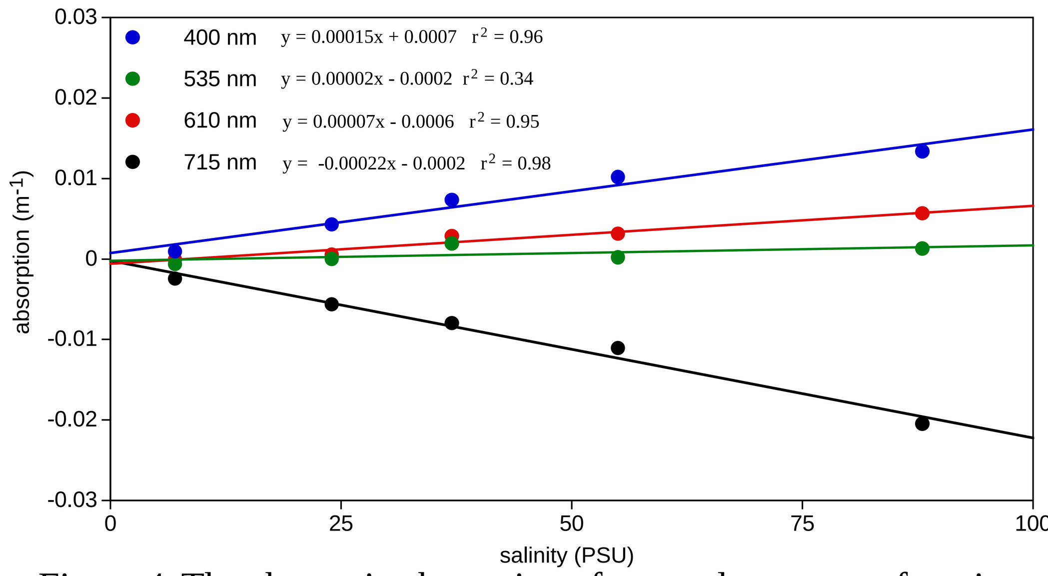

Figure 4. The change in absorption of pure saltwater as a function of NaCl concentration (PSU) for selected wavelengths of the AC-S. Lines and equations are least squares linear regressions of the relationships. As these relationships are corrected for temperature effects, the origins of the lines are zero.

The slopes of the linear relationships for the change in absorption as a function of temperature and salinity of water were calculated at all wavelengths of the AC-S and are plotted below (Figure 5).

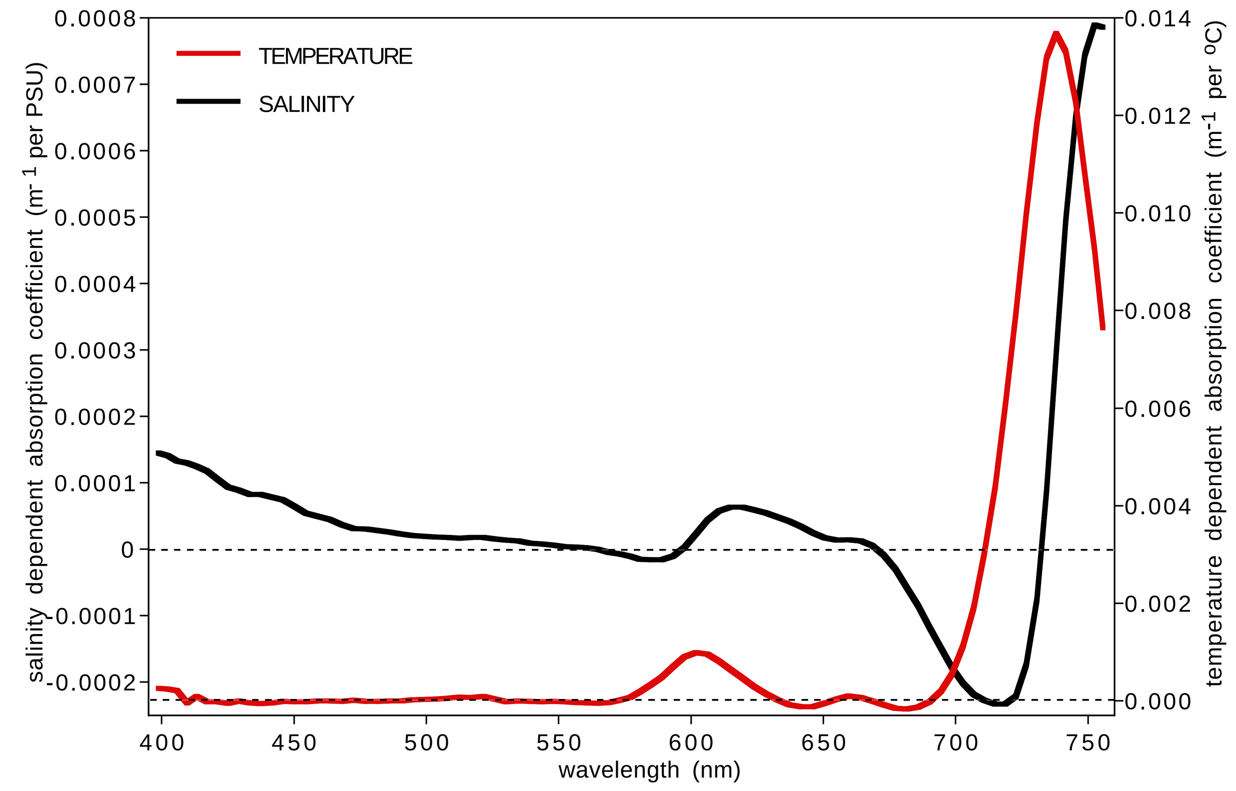

Figure 5 (left). The salinity (m^{-1} per PSU) (left axis, black line) and temperature dependent absorption coefficients (m^{-1} per °C) (right axis, red line) of pure water as a function of wavelength determined using the AC-S.

DISCUSSION and CONCLUSIONS

The spectral shape/location of the temperature coefficient peaks are correlated to locations of the O-H bond vibrational frequencies of water (the absorption of water being dependent on the temperature at these frequencies). The addition of salt ions appears to affect the ionic bonding of water to produce additional wavelength/frequency shifted absorption effects dependent on salt concentration.

The temperature coefficients measured in this study and those modeled by Pegau et al. 1997 (Applied Optics, 36: 6035-6046) and measured by both Trajberg & Højerslev 1996 (Applied Optics, 35: 2653-2658) and Buiteveld et al. 1994 (SPIE OOXII Vol. 2258) are shown in Figure 6. The measured values with the AC-S were very similar to those measured by Trajberg & Højerslev. The differences between the other two spectra and this study are likely due to measurement errors (Buiteveld et al. appeared to have background contamination) and/or instrument/model configurations (e.g. different bandwidth sizes for each discrete wavelength center).

We are unaware of any published hyper-spectral salinity coefficients in the visible and near-IR (but see presentation OOXVII-2-166 at this meeting). Pegau et al. 1997 reported salinity coefficients using the AC-9 and a comparison is shown in Figure 7. Unlike this study, Pegau et al. found different values for the attenuation and absorption channels of the AC-9. Our salinity coefficients are between the values found in the two channels of the AC-9. As the AC-S has a similar optical configuration, we suggest using a single set of salinity coefficients to correct in-situ AC-9 data.

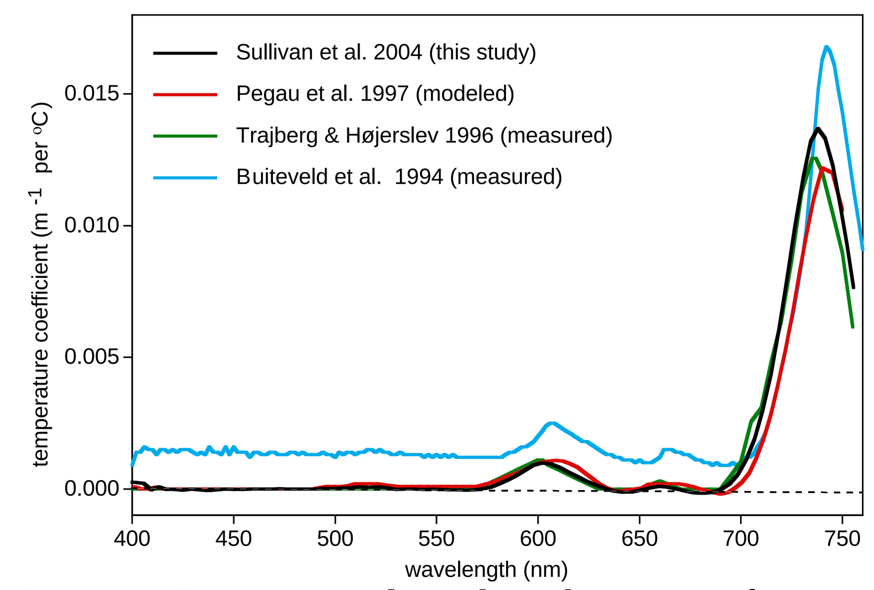

Figure 6. Temperature dependent absorption of pure water determined using the AC-S compared to the modeled values from Pegau et al. 1997 and the measured values of both Trajberg & Højerslev 1996 and Buiteveld et al. 1994.

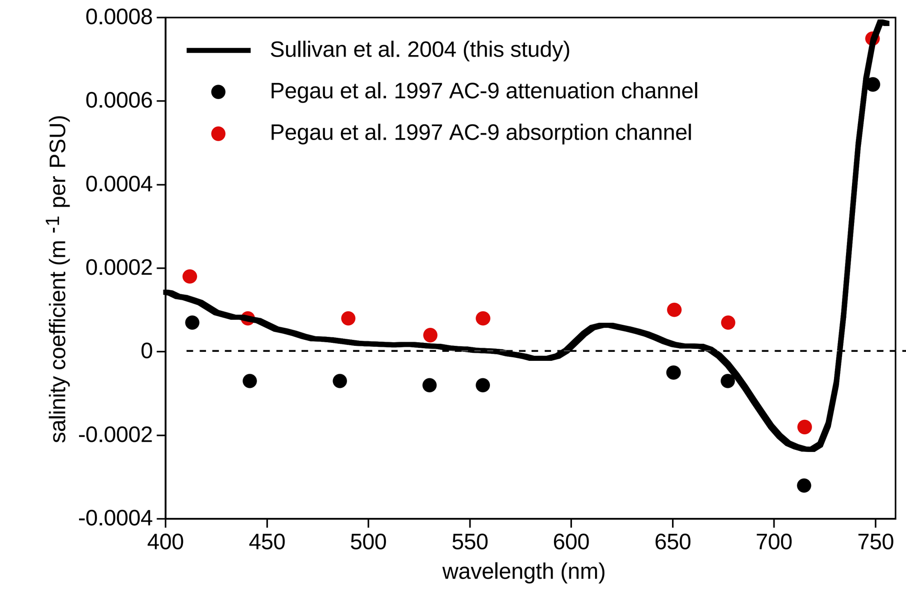

Figure 7. Salinity dependent absorption of pure saltwater determined using the AC-S compared to the measured values using an AC-9 from Pegau et al. 1997. Unlike this study, Pegau et al. found different values for the attenuation and absorption channels of the AC-9.

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