

### **PSS fluorescence-chlorophyll metadata—Development of chlorophyll vs. fluorescence regressions for winter-spring transition (January-April 1998-2000)**

The PSS team (Vanderploeg, Johengen, Lang, Ruberg, Agy, Liebig) examined PSS fluorometer (Chelsea Aquatracka III, with logarithmic amplifiers) response with discrete chlorophyll samples taken at different depths at stations along the various transects during “pre-plume” (January-February), “plume” (March) and “post-plume”(early and late April) 1998-2000 to develop a set of chlorophyll *a* vs. fluorescence regressions that would be used to transform continuous fluorescence profiles to continuous chlorophyll profiles along the transects. Samples for chlorophyll *a* were sampled and analyzed by methods described in Vanderploeg et al. (2001). Linear regressions were developed from extracted chlorophyll *a* and antilog of PSS fluorometer volts for each cruise and combined cruises for different time periods (e.g. pre-plume) among years to come up with a set of as few as possible regressions to characterize the chlorophyll *a* vs. fluorescence response.

The horizontal distance from shore and sample depth were used to match the discrete grab samples with the corresponding PSS response. A search area of  $\pm 0.2$  km in the horizontal and  $\pm 0.5$  m in the vertical was established around the discrete sample. The PSS readings within this window were averaged to determine the PSS response. If no PSS readings were found, the search area was incrementally expanded. If no PSS readings were found within the maximum search area,  $\pm 2$  km in the horizontal and  $\pm 3$  m in the vertical, then the discrete grab sample was not used in the regression analysis. Over the three years, the average search window size was  $\pm 0.48$  km in the horizontal and  $\pm 0.59$  m in the vertical, and the average number of PSS values within the search window was 8.7. There were only 2 occurrences in 1998 where no PSS values were found within the maximum search window; 22 in 1999; and 8 in 2000. The distance between undulations are short in shallow water and longer in deeper water because of the standard method of raising and lowering the tow body at about 0.25 m/s. As a result, close match (small window) between grab samples and PSS recordings are highly probable nearshore. Since greater gradients in chlorophyll and TSM are found inshore rather than offshore, we believe the sampling window adequately captures the spatial pattern of chlorophyll and TSM.

During daylight hours (~ 09:00 – 16:00 EST) of high incident radiation, fluorescence response in surface waters (< 10 m deep) was often substantially less than that at greater depths, where photoinhibition of the fluorescence response is not a problem because of decrease in light intensity with depth (Kiefer 1973). To account for this artifact, surface data exhibiting photoinhibition were removed and regressions were rerun (Table 1). The photoinhibition response was not seen within the plume because of high light attenuation by suspended sediments. For some cruises with a lot of midday samples, there was a marked improvement (~ 20-30%) in  $r^2$  for chlorophyll vs. fluorescence regressions (Table 1). All further discussion refers to regression results without surface data exhibiting the photoinhibition response. Individual cruises and combined cruises for different time periods (January-February, March, early April, late April) generally gave similar regressions with a slope of ~ 0.03 (Table 1). During the March 1998 cruise following the intense storm event yielded a slope of 0.077. This very different response may be a result of photoadaptation of the phytoplankton to low light intensity during the event (Mitchell and Kiefer 1988).

During April 1999 there were a number of outliers in the chlorophyll vs. fluorescence response at nearshore river-mouth stations (J15, 20, and M15) during formation of a nearshore thermal bar (Fig. 1). We suspect this may be a response to the transition from large diatoms to smaller phytoplankton nearshore, which would have a higher fluorescence to chlorophyll *a* ratio (Alpine and Cloern 1985). We removed these outliers from the regression. Two regressions, therefore, were chosen to characterize the chlorophyll vs. fluorescence response. For all winter-spring PSS fluorometer output, except for March 1998, the following equation was applied:

$$\text{Chl (ug/L)} = 0.030 * (10^{\text{volts}} - 10^{0.486}) + 0.137,$$

where the term  $10^{0.486}$  is the blank correction term accounting for 0.486 volts obtained for 0.2 $\mu$ m filtered Lake Michigan water. Note the blank obtained for filtered lake water was not much greater than that for distilled water ( $10^{0.435}$ ). For March 1998, the following regression was obtained:

$$\text{Chl (ug/L)} = 0.077 * (10^{\text{volts}} - 10^{0.486}) - 0.772$$

Considering that the fluorescence to chlorophyll *a* ratio can change by a factor of 12 (Heaney 1978) depending on phytoplankton taxa, size, and physiology, the  $r^2$  for chlorophyll *a* vs. fluorescence regression was quite good. Part of the high correlation may result from the relatively homogeneous taxonomic status of the phytoplankton community during the winter-spring transition. **Note** that the predicted chlorophyll values from the regression equations can be an underestimate of measured chlorophyll *a* for surface samples for midday runs of the PSS and an overestimate at some nearshore river-mouth stations during April.

For the remainder of the year (May-Nov, 1998-2000), a third regression was used, based on preliminary analysis:

$$\text{Chl (ug/L)} = 0.021 * (10^{\text{volts}} - 10^{0.486}) - 0.683$$

When time permits, this regression will be replaced by one or more regressions that better characterize the summer/fall period.

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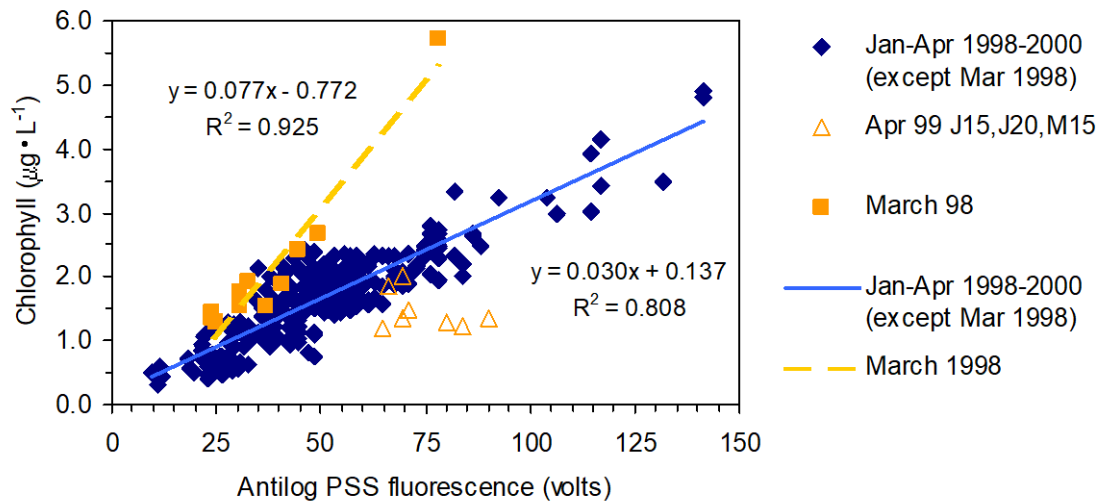
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Table 1. PSS Fluorescence-Chlorophyll Regressions Summary

Date	Using all data			Minus midday 1 & 5 m data		
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>
<b><u>1998</u></b>						
Jan/Feb 1998	0.033	0.353	0.698	0.034	0.248	0.715
<b>March 1998</b>	0.061	-0.014	0.753	<b>0.077</b>	<b>-0.772</b>	<b>0.925</b>
March 1998 [w/o St. Joseph transect]	0.049	0.108	0.880	0.049	0.108	0.880
Jan/Feb - March 1998	0.037	0.308	0.556	0.043	0.020	0.625
Jan/Feb - Mar [w/o St. Jo transect]	0.032	0.403	0.669	0.033	0.341	0.669
<b><u>1999</u></b>						
February 1999	0.034	0.066	0.827	0.036	-0.024	0.878
March 1999	0.026	0.435	0.734	0.029	0.123	0.898
April 7-8, 1999	0.020	0.649	0.472	0.025	0.264	0.706
April 7-8, 1999 [w/o J15 & J20]	0.023	0.568	0.580	0.029	0.168	0.855
April 26-27, 1999	0.012	0.516	0.422	0.019	-0.049	0.454
April 26-27, 1999 [w/o J15, M15]	0.020	0.218	0.658	0.037	-0.937	0.959
April 1999	0.015	0.725	0.344	0.019	0.452	0.474
April 1999 [w/o J15, J20, M15]	0.022	0.541	0.530	0.027	0.170	0.758
February - April 1999	0.025	0.434	0.623	0.028	0.179	0.747
Feb - Apr 1999 [w/o J15, J20, M15]	0.027	0.375	0.711	0.030	0.111	0.845
<b><u>2000</u></b>						
February 2000	0.034	0.210	0.752	0.040	-0.096	0.870
March 2000	0.035	-0.272	0.826	0.037	-0.409	0.905
April 2000	0.033	-0.101	0.836	0.033	-0.195	0.894
February - April 2000	0.031	0.075	0.799	0.032	-0.050	0.852
<b><u>1998-2000 (individual months)</u></b>						
Jan/Feb 1998-2000	0.032	0.283	0.778	0.034	0.170	0.818
March 1998-2000	0.028	0.281	0.589	0.031	0.039	0.706
March 1999-2000	0.030	0.108	0.765	0.032	-0.091	0.898
April 1999-2000	0.018	0.669	0.416	0.028	0.067	0.703
April 1999 [w/o J15, J20, M15] - 2000	0.022	0.538	0.579	0.031	0.012	0.854
Early April 1999-2000	0.020	0.624	0.528	0.030	0.017	0.834
Early Apr 99 [w/o J15, J20, M15] - 2000	0.022	0.593	0.601	0.031	0.031	0.885
<b><u>1998- 2000 (combined months)</u></b>						
Jan/Feb - March 1998-2000	0.029	0.327	0.645	0.031	0.160	0.719
Jan/Feb - Mar 1998-2000 [w/o Mar 98]	0.029	0.273	0.726	0.031	0.131	0.800
Jan/Feb - early Apr 98-00 [w/o Mar 98]	0.028	0.313	0.716	0.030	0.146	0.802
Jan/Feb - April 1998-2000	0.026	0.396	0.613	0.029	0.223	0.688
Jan/Feb - April 1998-2000 [w/o Mar 98]	0.027	0.347	0.673	0.029	0.188	0.753
<b>Jan/Feb - April 1998-2000 [w/o Mar 98 &amp; w/o Apr 99 J15, J20, M15]</b>	<b>0.028</b>	<b>0.303</b>	<b>0.723</b>	<b>0.030</b>	<b>0.137</b>	<b>0.808</b>

Fig. 1. Jan-Apr 1998-2000 [w/o Midday 5m & Apr 99 J15, J20, M15]



#### Literature Cited

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