"*HPLC Fix Update*"

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OCRT
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Timeline of the events:

- Early-September 2006: HPL started analyzing the chlorophyll pigments for NASA. HQ ask me to coordinate the sample schedule between HPL and the ocean community.
- In response to my email of Sept 11, duplicate CHORS-HPL samples were identified:
  - 259 duplicate samples (Mannino)
    - ~100 were analyzed by HPL in July 2006
    - ~159 were sent to HPL for analysis with the highest priority
- End-September: the first set of duplicate HPL data were sent to Trees (in Italy) for match-up with CHORS samples.

- October: inquiries made about the status of the correction factor that CHORS was developing
  - An analysis document was requested from Trees
  - Started discussion with HQ about selecting independent HPLC scientists to review document
- Mid-November: remaining duplicate HPL sample data sent to Trees
- End-December: I reviewed the first draft report and provided comments
- Mid-January 2007: the revised document was sent to HQ and I contacted two scientists for the review

- Mid-end February: reviewers' comments were provided to Trees and all comments were addressed and integrated into document (2 formal reviews and 1 investigator email comments).
  - Document was sent to HQ
  - Trees could not attend the OCRT
- End-March: HQ arranged a meeting at GSFC where Trees presented results.
  - Invited participants: Hooker, Heukelem and Fargion
  - HQ decided to postpone the release of the document and to form a team (Hooker, Heukelem, Fargion, and Trees) to further investigate:
    - the cause of the bias by reviewing the implementation of the C8 method on the CHORS system, including system performance, reproducibility and uncertainty;
    - the best statistical approach to correct the CHORS data as well as assign uncertainty estimates for this correction.
- April 17: First team telecom planned

Investigators affected and numbers of samples

A. Mannino	414	G. Mitchell	802
A. Subramanian	143	H. Dierrsen	169
D. Clark	449	M. Moline	1,334
D. McGillicuddy	1,871	F. Muller-Karger	184
D. Siegel	467	N. Nelson	27
D. Stramski	307	R Letieler	210
F. Chavez	655	SeaHARRE 3	154
V. Hill/Cota	285		
TOTAL	7,471		

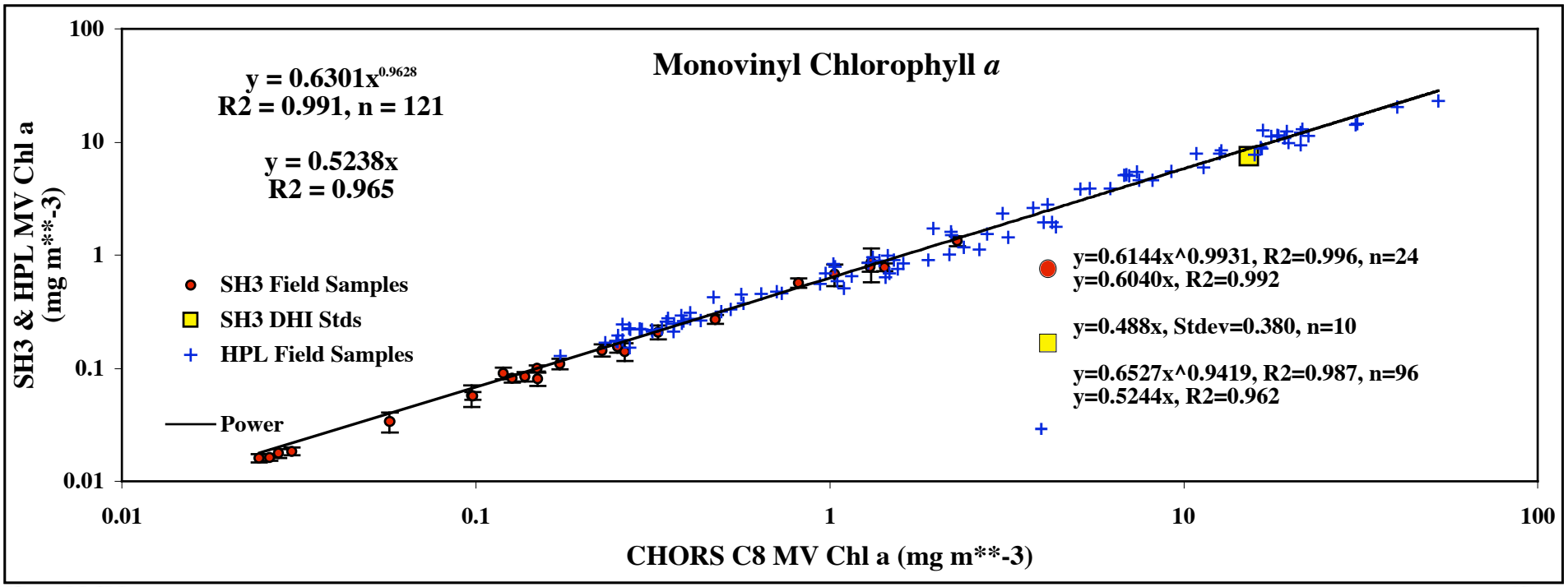
This data IS NOT in SeaBASS or NOMAD

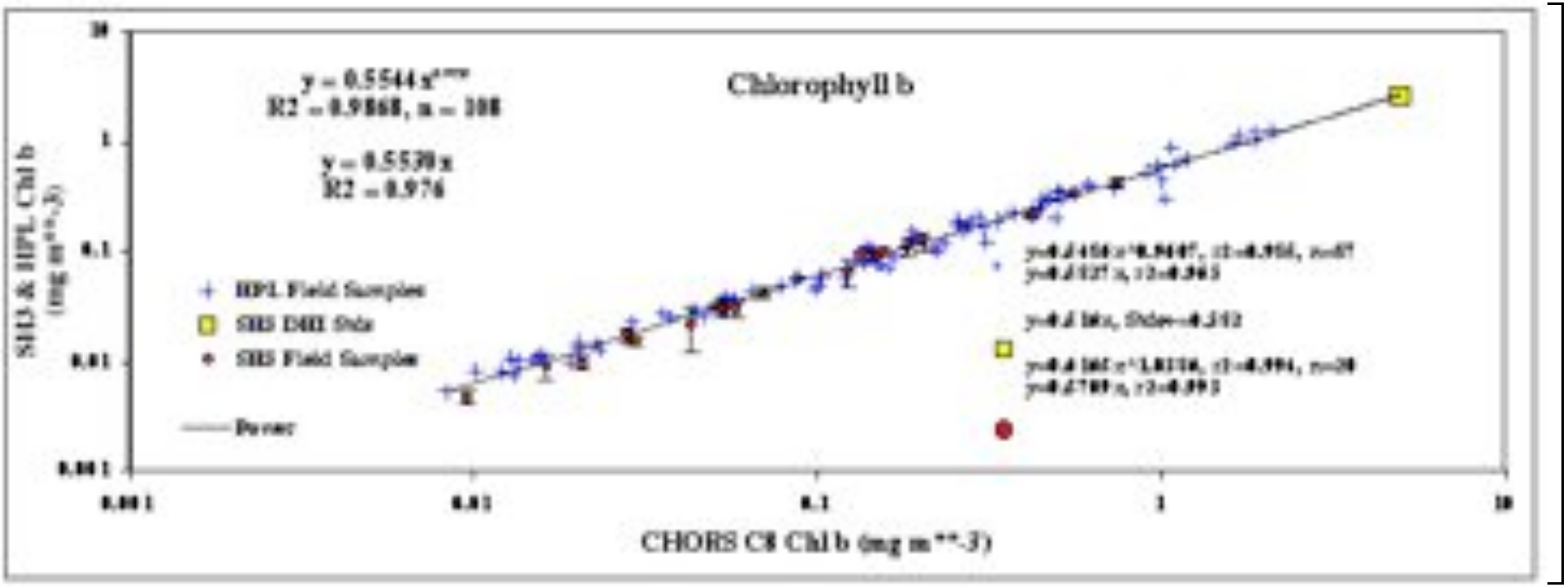
Available duplicate data set done by CHORS and HPL

- SH3 Field Samples (24 triplicate samples)
- SH3 Mixed Pigment Standard (10 duplicates)
- Mannino Samples (96 coastal samples)

-SH3 Field Samples and Standards were analyzed in Aug - Sep 2005.

- Mannino Samples
  - 24 analyzed in Aug - Sep 2005
  - 64 analyzed in Jan 2006


Monovinyl Chlorophyll a
y = 0.6301x^0.9628
R2 = 0.991, n = 121
y = 0.5238x
R2 = 0.965
SH3 Field Samples
SH3 DHI Stds
HPL Field Samples
Power
y=0.6144x^0.9931, R2=0.996, n=24
y=0.6040x, R2=0.992
y=0.488x, Stdev=0.380, n=10
y=0.6527x^0.9419, R2=0.987, n=96
y=0.5244x, R2=0.962
SH3 & HPL MV Chl a (mg m**-3)
CHORS C8 MV Chl a (mg m**-3)
100
10
1
0.1
0.01
0.01
0.1
1
10
100


Chlorophyll b
y = 0.5544x
R2 = 0.9868, n = 108
y = 0.5530x
R2 = 0.976
HPL Field Samples
SH3 DHI Stds
SH3 Field Samples
Power
SH3 & HPL Chl b (mg m**-3)
CHORS C8 Chl b (mg m**-3)
1
0.1
0.01
0.001
0.001
0.01
0.1
1

What Trees has found out:

1. The uncertainty in the results for the C_8 method seem not to be random (a linear/log-linear bias and constant throughout the year). Only for DV Chl a, MV Chl a and Chl b.
2. The reason for this constant overestimation could not be determined and will be further investigated by the team.
3. For all MODIS samples analyzed, Chl concentration was also determined using the standard fluorometric method. This method <u>does not</u> have the biases.

Joint analysis in the next few months

- A forensics activity to provide clear description of what was done to implement the C8 method;
- Analysis of the QA data for both the C8 and C18 methods as a function of time;
- Obtaining a detailed time line of what errors happened when, so the QA data can be used diagnostically; an analysis of whether or not what went wrong can be corrected using the principles or parameters of the problem and not just the statistics;
- An uncertainty analysis of the agreed upon correction scheme;
- This effort of the team will be reviewed by an expert in chromatography (perhaps from NIST).

Chuck Trees

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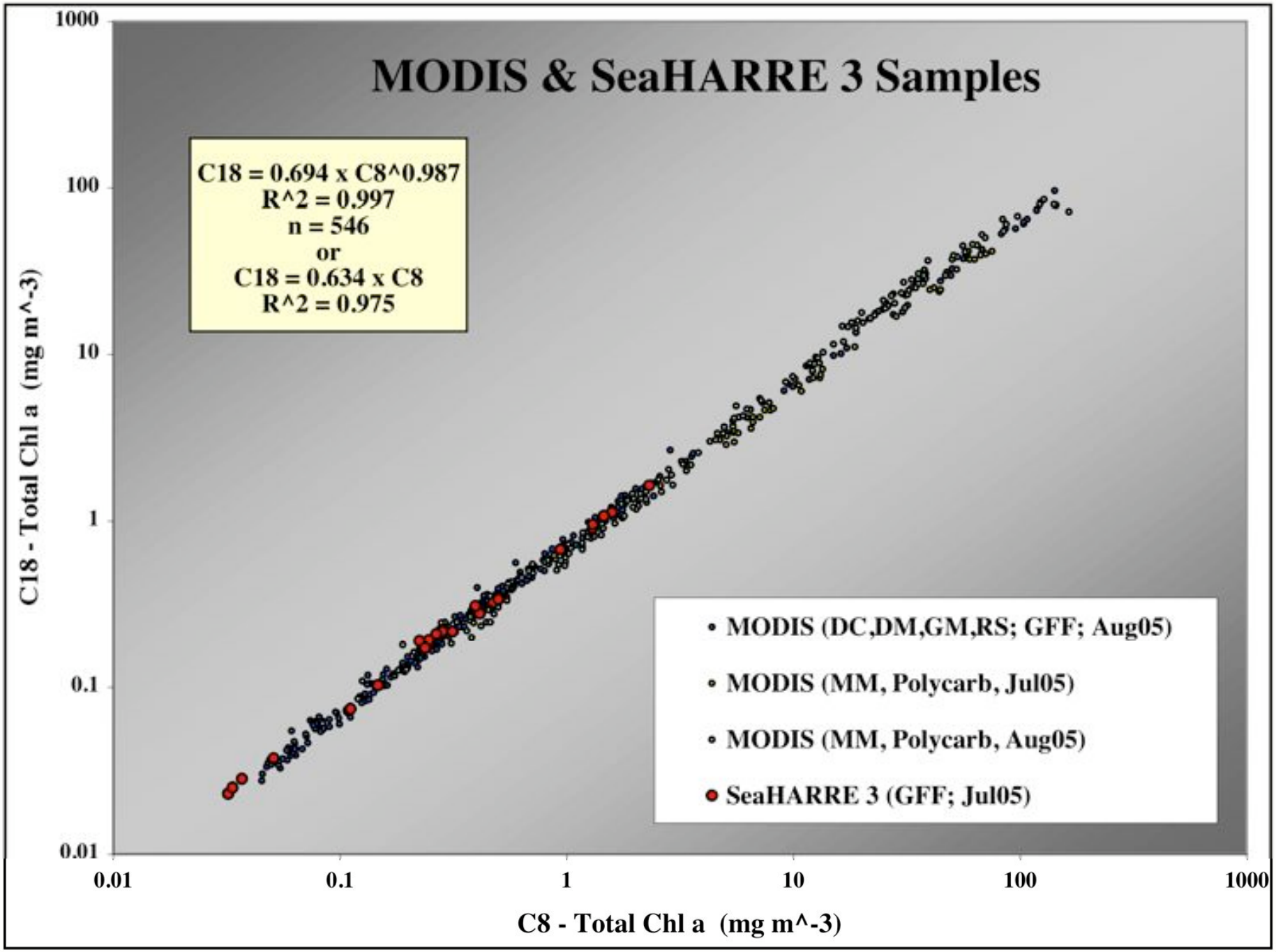
MODIS & SeaHARRE 3 Samples
C18 = 0.694 x C8^0.987
R^2 = 0.997
n = 546
or
C18 = 0.634 x C8
R^2 = 0.975
MODIS (DC,DM,GM,RS; GFF; Aug05)
MODIS (MM, Polycarb, Jul05)
MODIS (MM, Polycarb, Aug05)
SeaHARRE 3 (GFF; Jul05)
C18 - Total Chl a (mg m^-3)
C8 - Total Chl a (mg m^-3)
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000