Aquatic Calibration and Validation Activities and Future Needs
HPLC Uncertainties: *A Case Study for Establishing Guidelines and Review Procedures for Essential Climate-Quality Data Record (CDR) Analyses*

Stanford Hooker (NASA/GSFC), Laurie Van Heukelem and Crystal Thomas (UMCES/HPL)

The Aquatic Calibration and Validation breakout session was tasked with two responsibilities: a) after receiving an update from the session co-chairs concerning two sources of nonlinearity in the CHORS HPLC system, determine the future course of the correction of the aberrant pigment data set produced with this system (which spans 1998–2007 and is comprised of approximately 24,000 samples), and b) discuss and answer the four meeting questions associated with aquatic calibration and validation activities.

The main difficulty with the CHORS data is each attempt to peel back a layer of the problem has exposed a new problem. Options for any future effort are as follows:

1. The easiest option—suggested by more than one PI — is to ignore the problem and leave the data as is.
2. Classify the data as being unsuitable for calibration and validation activities, remove them from SeaBASS (already done), and do no additional work. In a few years many sampling holes in the dynamic range of the problem set will be filled by ongoing research. In addition, unsampled, but important, geographical areas could be resampled with targeted field campaigns. Individual PIs would have to determine the applicability of existing CHORS data to their research objectives (past and present).
3. Attempt to characterize the nonlinearities for Chl *a* (the most extensively calibrated CHORS pigment and probably the most important), establish a correction scheme, and correct the data. This will require new resources and personnel (CHORS stops working on this problem 31 May 2008).
4. Attempt to characterize the nonlinearities for the primary pigments, establish a correction scheme, and correct the data. This will require substantial new resources (reintegration of some pigments is likely).
5. Attempt to characterize the nonlinearities for all the pigments CHORS reported, establish a correction scheme, and correct the data. This will require very significant new resources (reintegration of many pigments).

The assembled scientists rejected option 1 and were not enthusiastic about option 2. Most of the discussion centered around options 3 and 4, with some minor support for option 5. Many scientists expressed concern about the amount of resources needed for options 3 and 4, particularly given that there is currently

no way of unequivocally assessing the absolute quality of the heretofore undescribed corrections. (The correction process cannot be described, because all the sources of uncertainty have not been characterized and may not be capable of being characterized.) Another aspect of the problem that was discussed was the effect of losing so much Chl a data (about 60% of the data in SeaBASS is affected) on the OC series of algorithms.

An unwanted and unnecessary source of uncertainty that all HPLC data, including a corrected CHORS data set, will still have is the variance from a nonuniform set of absorption coefficients used in pigment calibrations. In fact, many absorption coefficients being used by HPLC analysts today are not the most recent, or the most reliable, or even supported by the peer-reviewed literature. Although citations exist, the endpoint is not always a laboratory experiment.

What does the carbon cycle and ecosystems community expect of this effort?

1. Round robins and workshops focused on understanding the sources of uncertainties and their magnitudes are essential (including a recurring assessment and evolution of the protocols being used especially as the remote sensing focus changes from the open ocean to optically-complex coastal waters).
2. Performance metrics need to be established for all analyses important to CDRs.
3. All analyses for CDRs must have a quality-assurance plan (QAP) that is approved by the program manager or cognizant project office.

What are our biggest challenges in this area, and how do we address them?

1. Establishing calibration and validation capabilities for parameters other than Chl *a* and apparent optical properties (e.g., IOPs, DOC, DIC, etc.) will require a significant investment in time and resources.
2. An oversight capability with specific guidelines (at the program or project office level) is needed to a) ensure inspections and compliance with the QAP, and b) strengthen the peer-review process. The FDA and EPA recognized these problems 25 years ago and have designed and debugged many control procedures that can be transferred into the NASA program, which would also allow the procedures to be thoroughly discussed before they were implemented.

Is our list of identified data records complete, or is something missing?

1. Future science questions associated with the coastal ocean and near-shore processes are going to require a greater diversity of data products

than are being produced now. Many of the measurements involved do not have calibration standards, so the calibration and validation of many future data products is going to require an investment in establishing certified reference materials and traceability.

2. The ensuing data products should be archived in or linked with SeaBASS (especially metadata), because it is a unique repository of calibration and validation data.

Does the carbon cycle and ecosystems community need to establish priorities for these and other activities, and, if so, how should they be established?

1. It was recognized that limits need to be placed on the amount of data to be archived in SeaBASS, but a prioritization scheme was not agreed to.

2. Everyone agreed the radiometric data need to be at the highest quality possible; the additional data products needed for interpreting near-shore imagery must also be prioritized at a similar level of data quality.