Colored Dissolved Organic Matter (CDOM) Absorption Workshop, Round Robins and Protocols

The goal of the CDOM absorption workshop and protocol activity was to update and develop new community consensus protocols for CDOM absorption measurements for various instruments with emphasis on the WPI UltraPath system, which is a relatively newer instrument not part of the NASA Ocean Optics Protocols[1] (Mueller, et al. 2003). Hereafter, these protocols will be referred to as NOOP. and essential for obtaining accurate CDOM absorption values for relevant visible wavelengths within oligotrophic ocean waters. One of the main objectives of the workshop was to reach consensus on how to accomplish the refractive index (salinity) correction. The CDOM absorption workshop was held at Goddard on Nov. 13-15, 2013. The participants included members from the U.S. and international ocean color community that are considered experts in CDOM absorption measurements, particularly with the WPI Ultrapath systems, and appropriate FSG staff (see Table 2). The workshop was organized into three elements: presentations and discussion on the protocols currently applied on the various instruments of interest by the participants, a laboratory intercomparison activity to reconcile differences in protocols and instrument to instrument variability, and discussions on recommendations for a standard protocol. The objectives of workshop and protocol activity were to:

1. Develop community consensus protocols for CDOM absorption using the WPI UltraPath
    a. Reach consensus on a salinity/refractive index correction
    b. Document variability between different UltraPaths.
    c. Define the causes of any revealed differences.
2. Compare results from double-beam spectrophotometers, UltraPaths, PSICAM, a-sphere, and ac-s instruments
3. Document precision and accuracy of CDOM measurements for each type of instrument.
4. Review and update the NOOP for CDOM absorption measurements including protocols on sample collection, storage and analysis from raw optical density to a_{CDOM} and CDOM spectral slopes.
5. Identify and recommend NIST-traceable calibration standards to confirm instrument performance for spectrophotometers and Ultrapaths.
6. Recommend or plan for a NIST-traceable CDOM standard material or community consensus reference material (similar to deep seawater DOC).
7. Develop a complete protocol document for discrete a_{CDOM} bench measurements

Table 2: List of participants in the CDOM absorption workshop and protocol activity.[1]

Participants	**Affiliation**
Mathias Belz	World Precision Instruments
Jean-Francois Bertrand	Joint Research Center, Ispra, Italy
Neil Blough	University of Maryland, College Park, MD
Emmanuel Boss	University of Maine, Orono, Maine

[1] Mueller et al. 2003. NASA Ocean Optics Protocols for Satellite Ocean Color Sensor Validation, Revision 4, Volume IV: Inherent Optical Properties: Instruments, Characterizations, Field Measurements and Data Analysis Protocols. NASA/TM-2003-211621/Rev4-Vol.IV.

Annick Bricaud*	Laboratoire d'Océanographie de Villefranche, France
Rossana Del Vecchio	University of Maryland, College Park, MD
Eurico D'Sa	Louisiana State University, Baton Rouge, LA
Atsushi Matsuoka	Universite Laval, Quebec, Canada
Rick Miller	East Carolina University, Greenvill, NC
Norm Nelson	University of California, Santa Barbara, CA
Rüdiger Röttgers	Helmholtz-Zentrum Geesthacht , Centre for Materials and Coastal Research, Germany
Teresa Serrano*	University of Granada, Granada, Spain
Maria Tzortziou	City College of New York, CCNY/GSFC
Joaquin Chaves	NASA Goddard Space Flight Center/SSAI
Carlos Del Castillo	NASA Goddard Space Flight Center
Scott Freeman	NASA Goddard Space Flight Center/SSAI
Antonio Mannino	NASA Goddard Space Flight Center
Aimee Neeley	NASA Goddard Space Flight Center/SSAI
Mike Novak	NASA Goddard Space Flight Center/SSAI
Jeremy Werdell	NASA Goddard Space Flight Center

* Did not participate in the workshop, but will participate in reviewing and editing the protocol document.

A primary activity of the workshop was to conduct a round robin intercomparison of CDOM absorption measurements using various instruments including two double-beam spectrophotometers, 6 UltraPath UPUV systems, one WPI liquid waveguide capillary system, one PSICAM and other spectrophotometers (WETLabs ac-s and HOBI Labs a-sphere) on a wide range of samples. Prior to the workshop Rick Miller prepared a series of CDOM dilution samples at various salinities that were distributed to the workshop participants so that we would have some results to share prior to the workshop to aid in reaching consensus on the salinity correction for the UltraPath. The results from the pre-workshop dilution round robin experiment were synthesized and presented to the group. The variability between instruments and researchers was greater than expected.

During the laboratory intercomparison, a recently developed cleaning procedure by WPI was demonstrated to the group, and various methods of instrument troubleshooting were discussed. Each participant demonstrated their protocols for making waveguide measurements to understand the sources of the measurement differences observed. A series of seawater samples were prepared for instrument comparisons during the workshop; however, there were issues with the functionality of some of the UltraPath systems. Consequently, many of the samples prepared for the round robin were not successfully measured by all of the instruments. Therefore, it was difficult to develop supportable conclusions on the most efficient method for measuring CDOM with the UltraPath technology. During the group discussions, a rough draft for a CDOM protocol was outlined. It was decided that the development of a consensus reference material (CRM) that could be used to assess the performance of the instruments used to make CDOM absorption measurements was a crucial initiative of the working group. One of the participants recommended the Suwannee River Fulvic Acid I (SRFA) available from the International Humic Substance Society (IHSS) as a potential CRM candidate. Many new insights were attained from the workshop activities including agreement on using NaCl solutions to

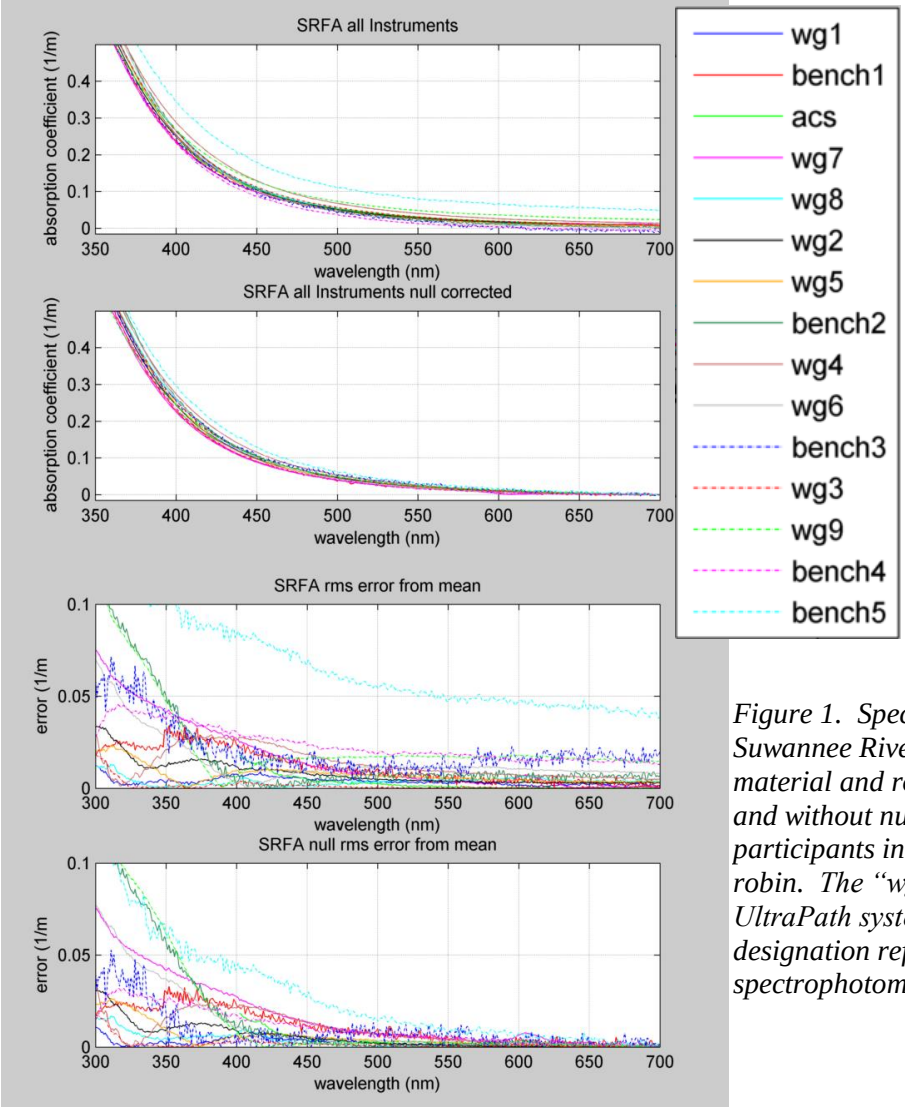

Figure 1. Spectral CDOM absorption of Suwannee River Fulvic Acid (SRFA) material and root mean square error with and without null correction from the various participants in the January 2014 round robin. The "wg" designation refers to UltraPath systems, and the "bench" designation refers to double-beam spectrophotometers.

correct for sample refractive index. To address some of the existing protocol issues and new questions that arose from the workshop, another round robin exercise was planned to measure seawater samples as well as various humic and fulvic acid materials from the (IHSS).

A CDOM absorption round robin was conducted in January 2014 to follow-up on the unresolved protocol topics discussed at the CDOM workshop. The FSG staff prepared the [2]various seawater samples and IHSS materials including SRFA and Pony Lake Fulvic Acid (PLFA) and shipped out the liquid samples and also dry samples of the SRFA IHSS material to each researcher for spectrophotometric analysis. Measurements of the reference materials and seawater samples were more variable between instruments than expected (but not unreasonable). However, the experiment was a good starting point to begin to characterize the SRFA (Fig. 1). Results from these activities were presented at the NASA Ocean Color Research Team meeting in May 2014 and also at the Ocean Optics XXII conference in October 2014.

The consensus of the CDOM protocol working group attained during a telecon in February 2014 was to conduct one additional round robin to resolve remaining protocol issues

and determine the uncertainty that can be achieved by a group of CDOM absorption experts. The group recommended that the FSG conduct a few experiments to resolve potential contamination issues with the various filter types used by the community. These experiments were completed in November 2014. We are also evaluating whether sample storage impacts CDOM absorption measurements, and it appears that filtered samples stored in amber bottles under refrigeration show no appreciable change in CDOM absorption (Fig. 2).

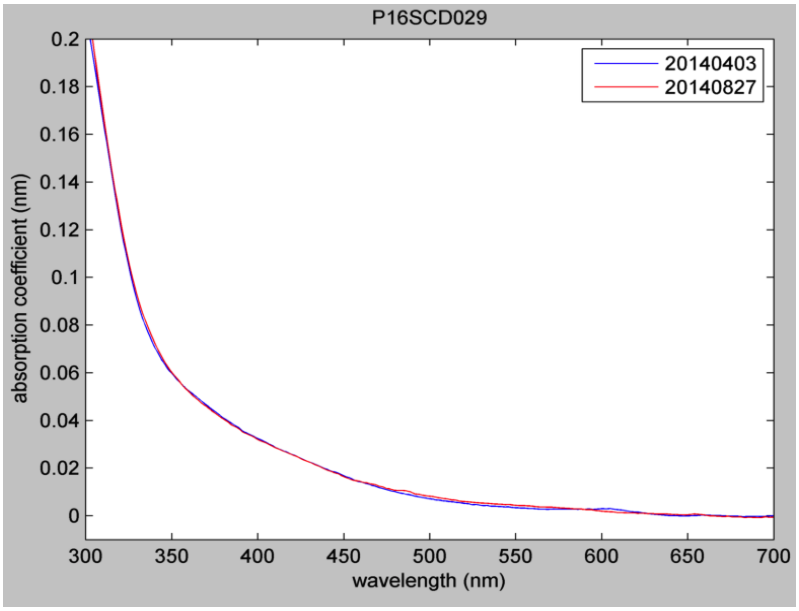

Figure 2. Spectral CDOM absorption of a surface sample analyzed fresh at sea (20140403) and nearly 5 months later in the lab (20140827) on the UltraPath instrument.

To further our understanding of factors that impact CDOM absorption measurements, an extensive analysis of over 800 CDOM samples measured at Goddard on both an UltraPath and a Cary 100 double-beam spectrophotometer was conducted. The results suggested that much of the uncertainty in UltraPath measurements was due to the salinity correction and/or wavelength dependent scattering. A protocol for preparing saltwater solutions, measuring them, and extrapolating a salinity correction curve from the measurements was developed with Norm Nelson and recent applications of this approach indicate that this procedure will reduce the variability between UltraPath instruments. During this process, we learned that the salinity reference (NaCl solutions) dilution curves, instrument drift, and laboratory environmental conditions, especially temperature, have a significant impact on the measured raw absorbance. Null correction of raw absorbance measurements is strongly recommended to resolve instrument drift, instrument-to-instrument variability, and small changes in environmental conditions. Such null corrections should be small on the order of ±0.003 absorbance units (AU). Raw absorbance values at red wavelengths much greater than ±0.003 AU suggest a problem with sample preparation.

A draft of the UltraPath and double-beam spectrophotometer CDOM absorption protocols has been written and distributed to the leads of the working group. The round robin exercises carried out in conjunction with the CDOM working group have been a valuable tool for developing a method for making CDOM measurements with UltraPaths. The final round robin of this protocol development activity will characterize the SRFA CRM and define what the acceptable variability is when measuring the CRM so that investigators can determine if their measurements are consistent with the community accepted values.