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Chapter 9

Refinement of Protocols for Measuring the Apparent Optical Properties of Seawater

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9.1 INTRODUCTION

Ocean color satellite missions, like the Sea-viewing Wide Field-of-view Sensor (SeaWiFS), the Moderate Resolution Imaging Spectroradiometer (MODIS), or the Medium Resolution Imaging Spectrometer (MERIS) projects, are tasked with acquiring a global ocean color data set, validating and monitoring the accuracy and quality of the data, processing the radiometric data into geophysical units using a set of atmospheric and bio-optical algorithms, and distributing the final products to the scientific community. The long-standing objective of the SeaWiFS Project, for example, is to produce water-leaving radiances to within 5% absolute (Hooker and Esaias 1993). The accurate determination of upper ocean apparent optical properties (AOPs) is essential for the vicarious calibration of ocean color data and the validation of the derived data products, because the sea-truth measurements are the reference data to which the satellite observations are compared (Hooker and McClain 2000).

Water-leaving radiances can be derived by extrapolating in-water measurements taken close to the sea surface, or they can be obtained directly from above-water measurements. Although it has not been as extensively validated as the in-water approach, above-water methods for vicarious calibration remain nevertheless attractive, because a) the data can presumably be collected more rapidly and from a ship underway, and b) the frequently turbid and strongly absorbing waters in shallow coastal (Case-2) environments impose severe limitations on in-water measurements, particularly because of the instrument self-shading effect. One of the difficulties with above-water measurements, however, is the instruments involved cannot be floated away to prevent any reflection or shading perturbations associated with the measurement platform, which is easily accomplished with an in-water system.

Another problem within the general perspective of ocean color calibration and validation activities is the paucity of data at high chlorophyll *a* concentrations, particularly in Case-1 waters—the peak in the distribution of the data being archived is in a chlorophyll *a* range of 0.1–1.0 mg m³ (O'Reilly et al. 2000), i.e., the so-called mesotrophic regime. This deficiency influences not only the higher order products, because the algorithms being used are not as robustly determined at high concentrations, but also much of the lower order understanding of uncertainty budgets, because the various experiments used to determine uncertainties also do not include high productivity waters.

Whether for biogeochemical studies or ocean color validation activities, high performance liquid chromatography (HPLC) is an established reference technique for the analysis of chlorophyll *a* and associated phytoplankton pigments. For example, the SeaWiFS Project requires agreement between the *in situ* and remotely sensed observations of chlorophyll *a* concentration to within 35% over the range of 0.05–50.0 mg m³ (Hooker and Esaias 1993). This value is based on inverting the optical measurements to derive pigment concentrations using a bio-optical algorithm, so the *in situ* pigment observations will always be one of two axes to derive or validate the pigment relationships. Given the already established emphasis on understanding the uncertainties associated with the AOP measurements, it seems appropriate to also investigate the uncertainties in determining pigment concentrations using HPLC methods, so an understanding of the total uncertainty budget can be produced. The latter was the rationale behind the first SeaWiFS HPLC Analysis Round-Robin Experiment (SeaHARRE-1)