JAXA 4th Joint PI Workshop of Global Environment Observation Mission

Highly frequent and accurate observations of marine phytoplankton pigments and light regimes using state-of-the-art technologies

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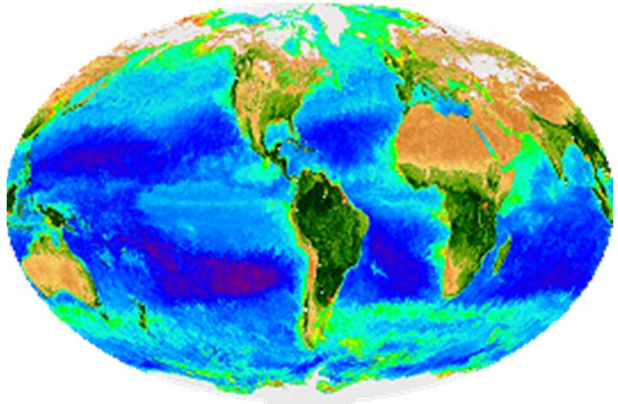
Because ocean color remote sensing with SGLI sensor requires high calibration accuracy, a large number of in situ observation data are required.



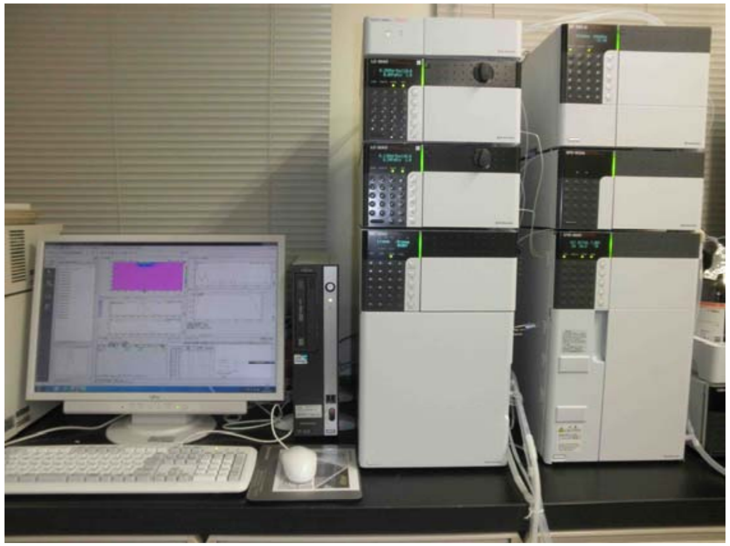
Our Main Cal/Val Activities During FY2013–2015

- Establish the methodology of UHPLC algal pigment analysis as a routine technique for estimating the biomass and community composition of phytoplankton in the sea.
- Obtain highly frequent and accurate data of phytoplankton pigments with an automated, continuous filtration system for surface seawater and UHPLC.
- Acquire high-quality AOP oceanic data with C-OPS (or C-PrOPS, which uses small digital thrusters to steer C-OPS).
- Discriminate optical properties between Case 1 and 2 waters.

State-of-the-art pigment analysis using UHPLC

- Ultra-high performance liquid chromatograph (UHPLC) is the instrumentation capable of delivering pressures above 40 MPa (= 408 kgf/cm^2) with a < 2 µm particle-size analytical column.

- UHPLC enables us to reduce the runtime by 1/4 to 1/10 as compared with conventional HPLC techniques.



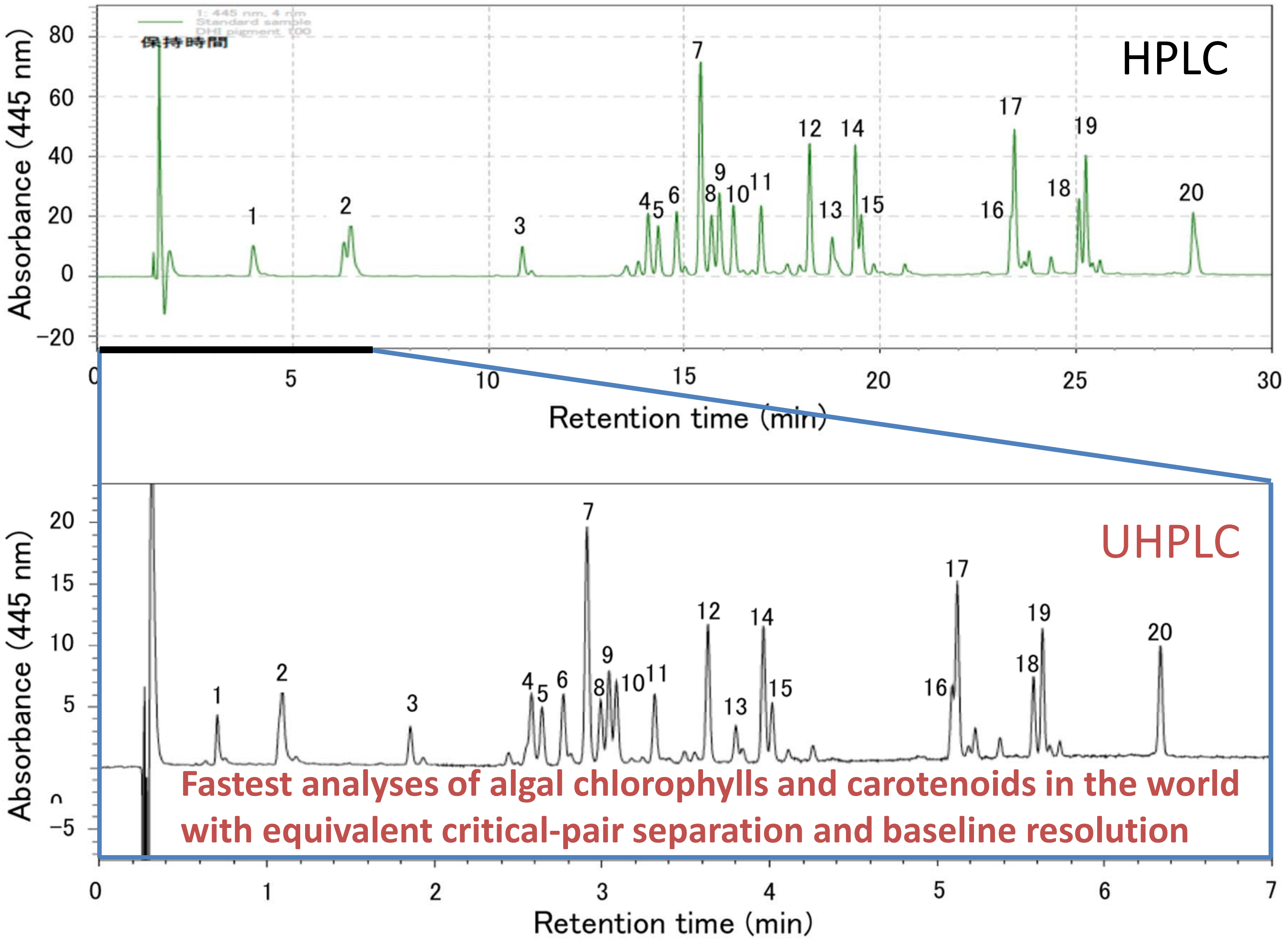
No paper has been published on the methodology of phytoplankton pigment analysis with UHPLC.

Shimadzu UHPLC Nexera system

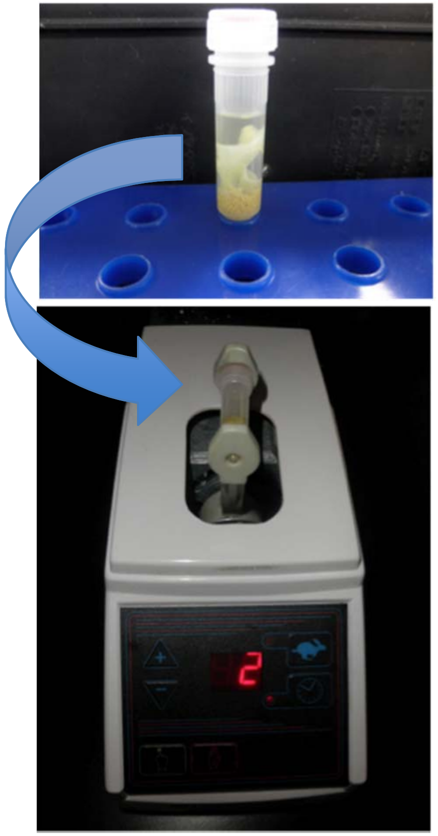
Main differences in pigment analysis between HPLC and UHPLC

	HPLC	UHPLC
Equipment	Shimadzu CLASS-VP system	Shimadzu Nexera system
Eluents and gradient method	Van Heukelem and Thomas (2001)	Modified Van Heukelem and Thomas (2001)
Analytical column	Agilent Eclipse XDB-C8, 3.5 μm particle, 4.6 × 150 mm	Agilent Eclipse XDB Plus C8, 1.8 μm particle, 4.6 × 50 mm
Inner Diameter (mm) of tubing	0.25	0.1
Flow rate（$mL\ min^{-1}$)	1.2	2.0
Maximum injection volume（μL）	500	50
Maximum column pressure（MPa）	~20	~60
Runtime（min）	30	7

HPLC and UHPLC chromatograms with phytoplankton pigment standards

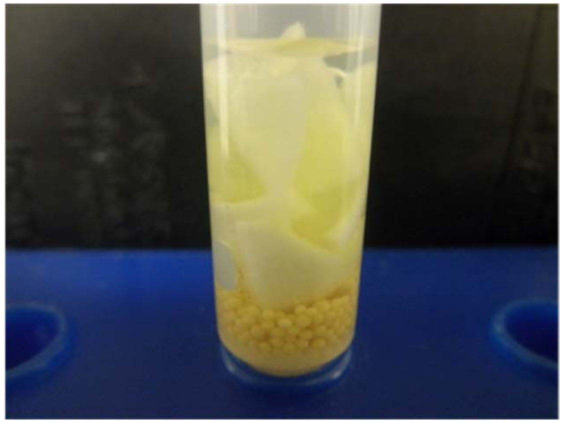


Development of DMF-bead-beating pigment extraction technique

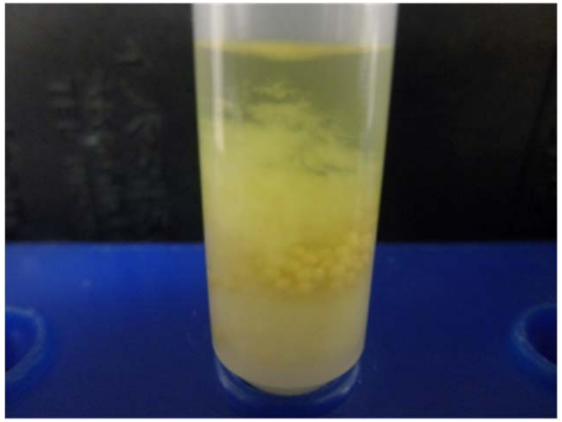


Biospec Mini-Beadbeater-1

Before



After



Extraction volume can be reduced from **3 ml** used in our conventional DMF-sonication method down to **700 µl** in the DMF-bead-beating technique.

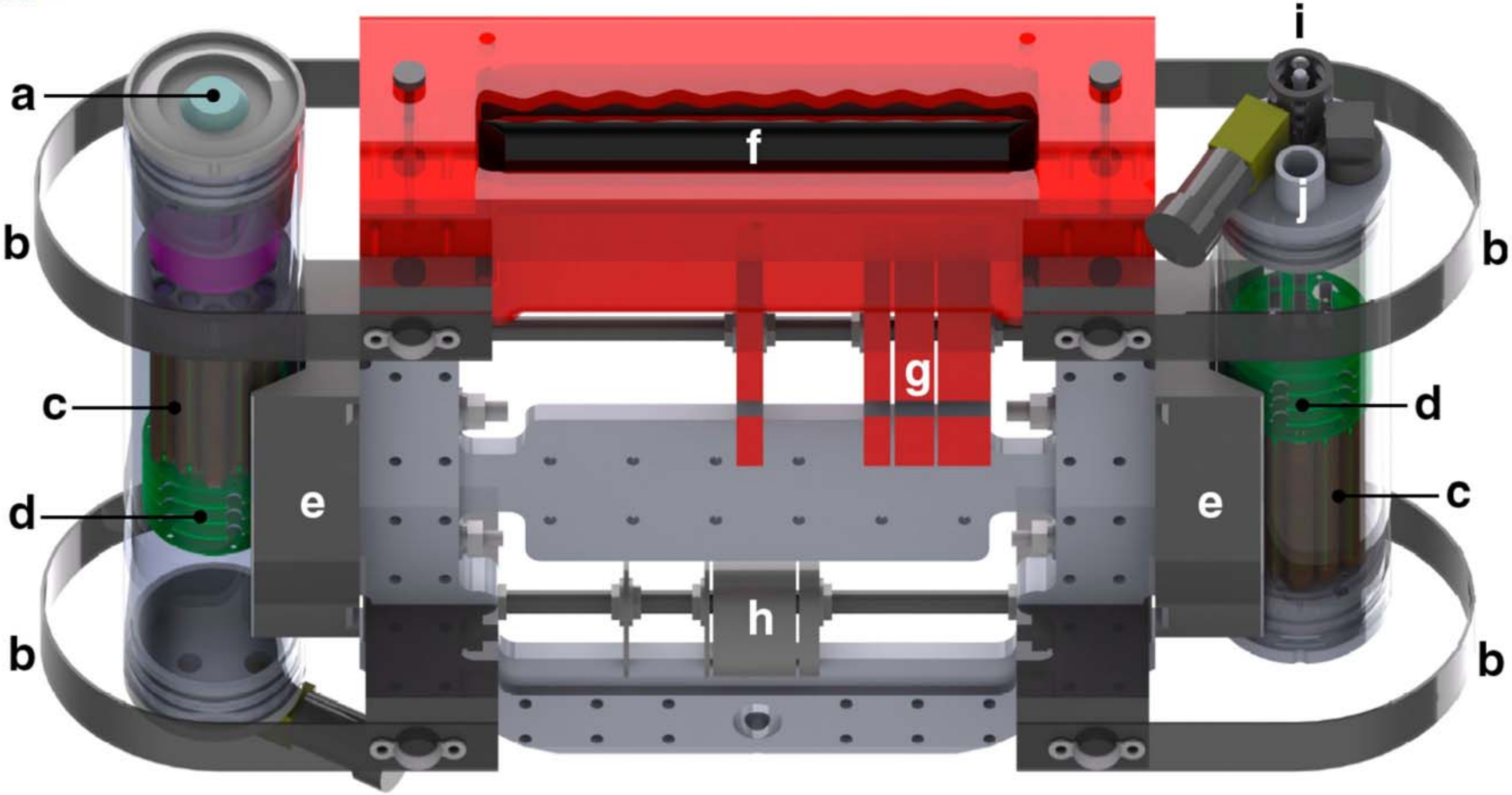
$$[\mathrm{Chl}\ a]_{\mathrm{bead\text{-}beating}} = 0.942 \times [\mathrm{Chl}\ a]_{\mathrm{sonication}}$$

$R^2 = 0.990$, $n = 36$

Acquiring high quality AOP oceanic data with C-OPS or C-PrOPS

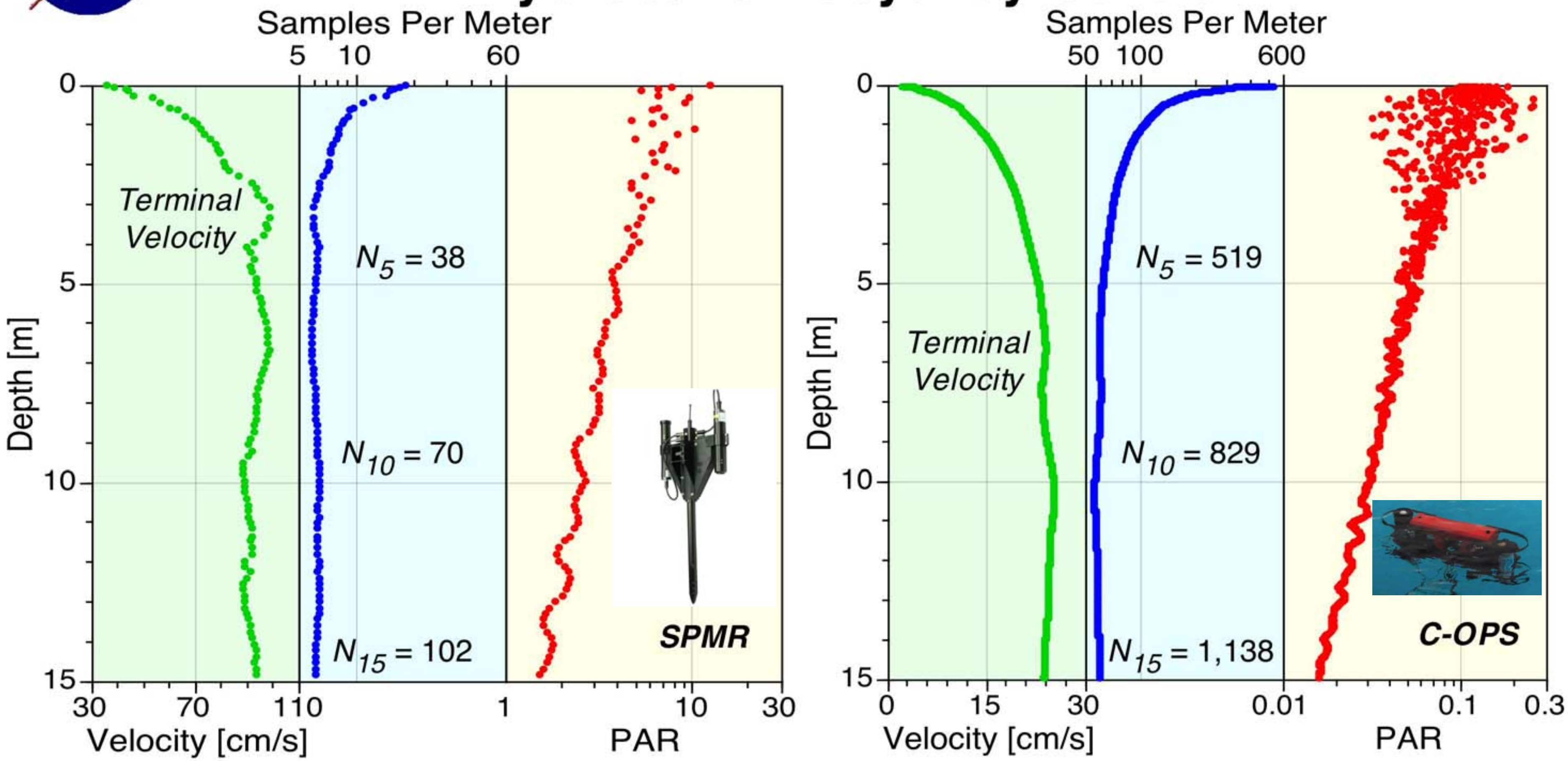
Dr. Stanford B. Hooker (NASA) with his C-OPS

The Biospherical Compact-Optical Profiling System (C-OPS): *Free-Falling 19-Channel XTRA Sensors*



C-OPS uses 7 cm (OD) sensors: a) cosine collector; b) side bumpers; c) 19 microradiometers cluster; d) new compact aggregator; e) adjustable v-blocks counter pitch biases; f) hydrobaric buoyancy (compressible bladders) allows near-surface loitering; g) adjustable flotation counters roll biases; h) weights (and floats) set terminal velocity and; i) temperature probe and j) pressure transducer.

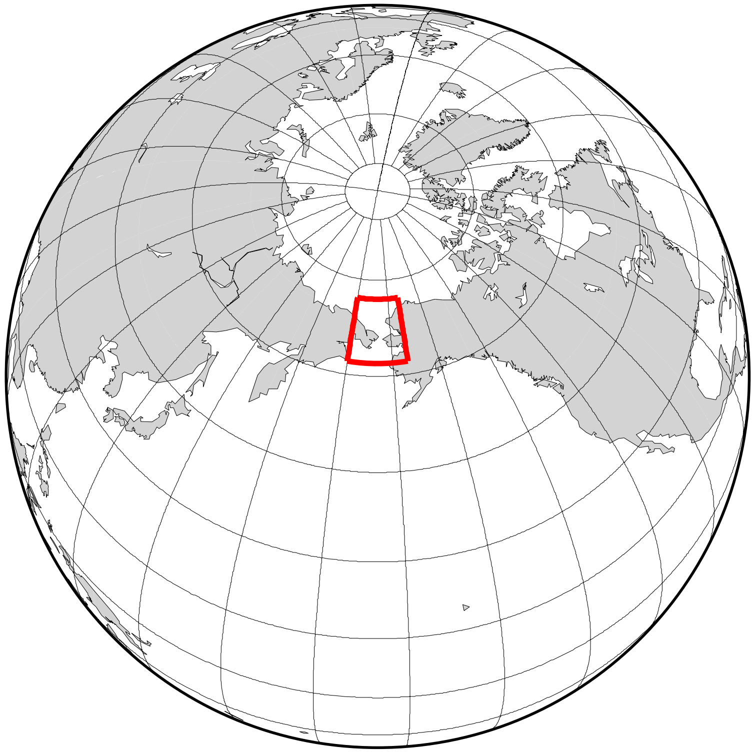
Sampling Improvements as a Result of the C-OPS Hydrobaric Buoyancy Control

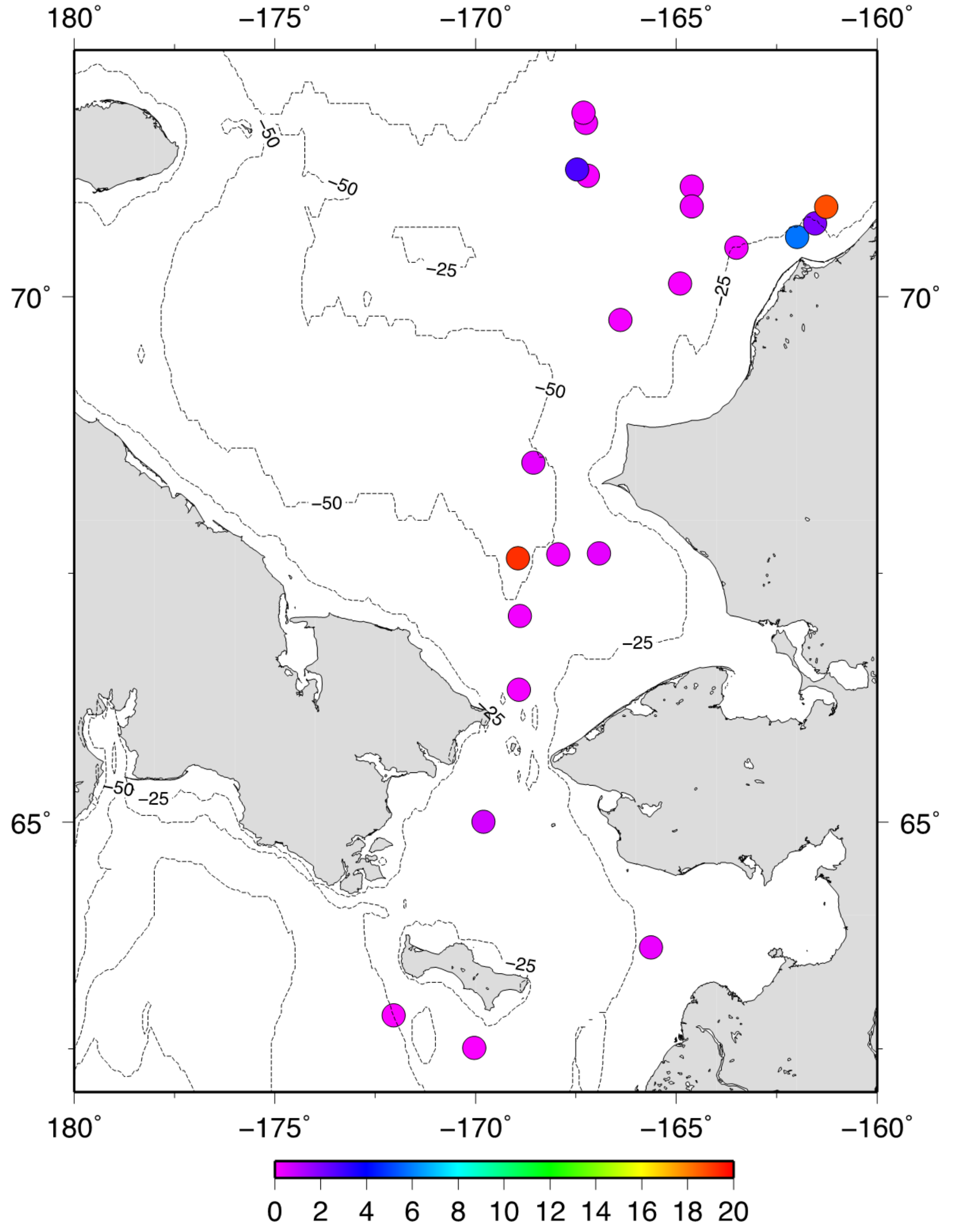


The buoyancy control enhancements to C-OPS result in an order of magnitude (or more) improvement in sampling resolution with respect to legacy instruments (N_z is the number of samples acquired by depth z, regardless of the tilt of the profiler). A noticeable consequence of the improved sampling resolution is a significant reduction in the aliasing of wave-focusing effects during clear-sky conditions.

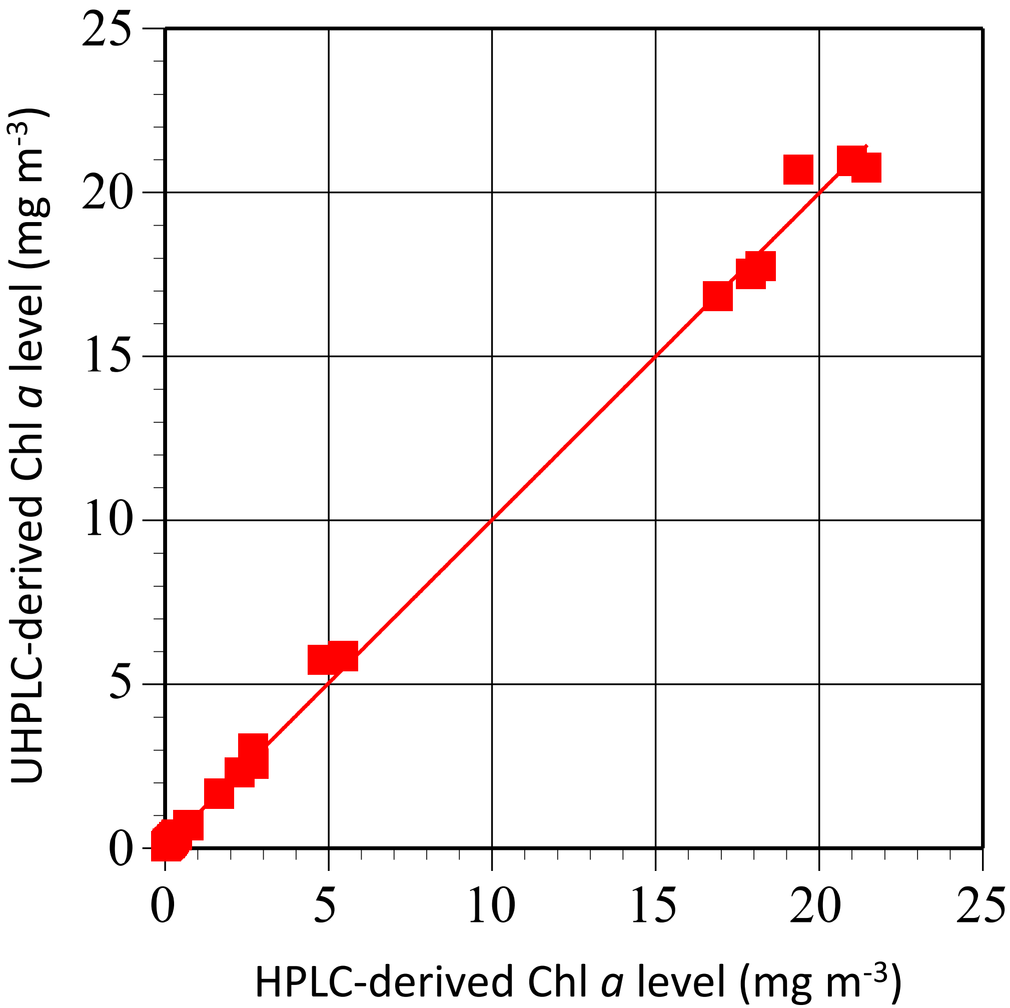
SPMR: SeaWiFS Profiling Multichannel Radiometer, a Satlantic free-falling optical profiler.

Field campaign in the Chukchi Sea during July 1 – 23, 2013 onboard the TR/V *Oshoro Maru* (Hokkaido Univ.)





Comparison of Chl *a* levels between HPLC and UHPLC during the TR/V *Oshoro Maru* cruise

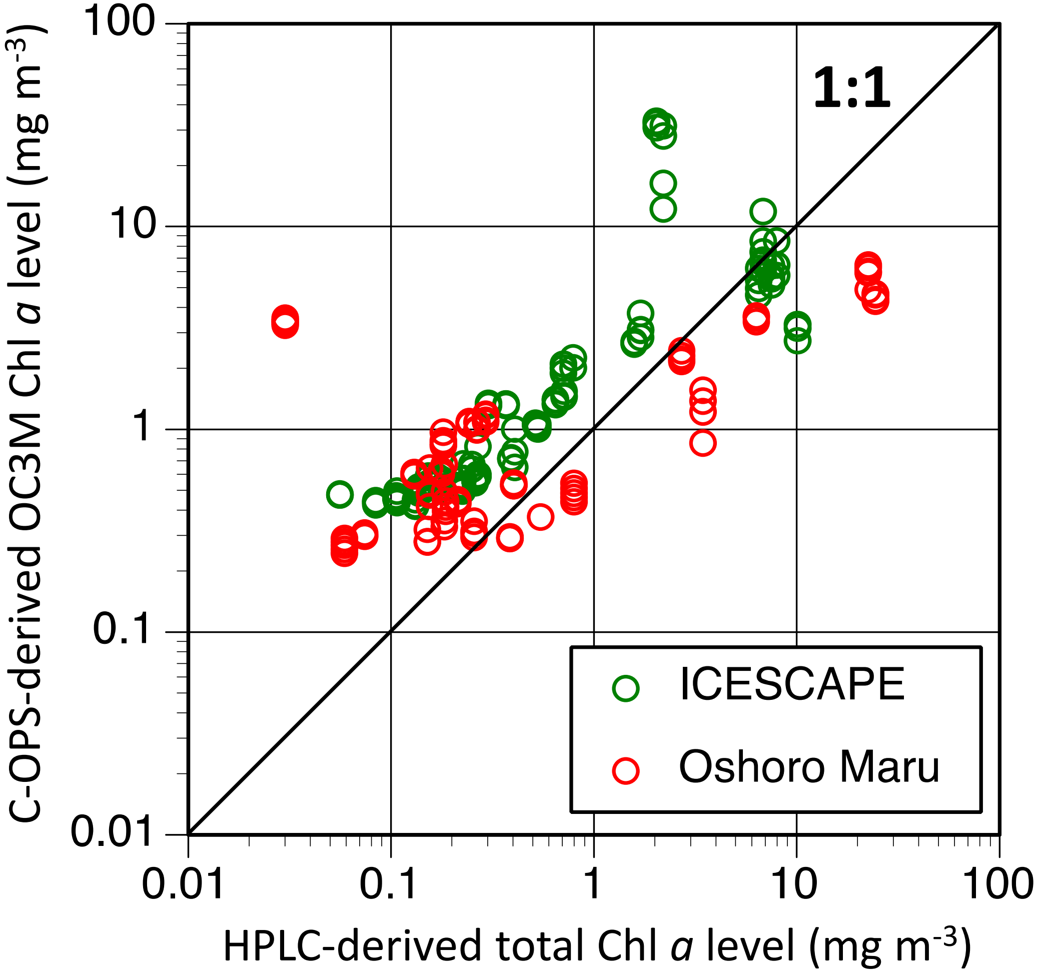


[Chl *a*]$_{UHPLC}$ = 1.00 × [Chl *a*]$_{HPLC}$

$R^2 = 0.998$, $n = 46$

For the determination of Chl *a* concentration, HPLC can be replaced with UHPLC.

Comparison of Chl *a* levels in the Chukchi and Bering Seas between HPLC and C-OPS OC3M algorithm



Total Chl *a* is the sum of Chl *a* and its derivatives (i.e., chlorophyllide *a*, Chl *a* allomer and epimer) which have the same absorption spectra as Chl *a*.

MODIS OC3Mv6 algorithm:

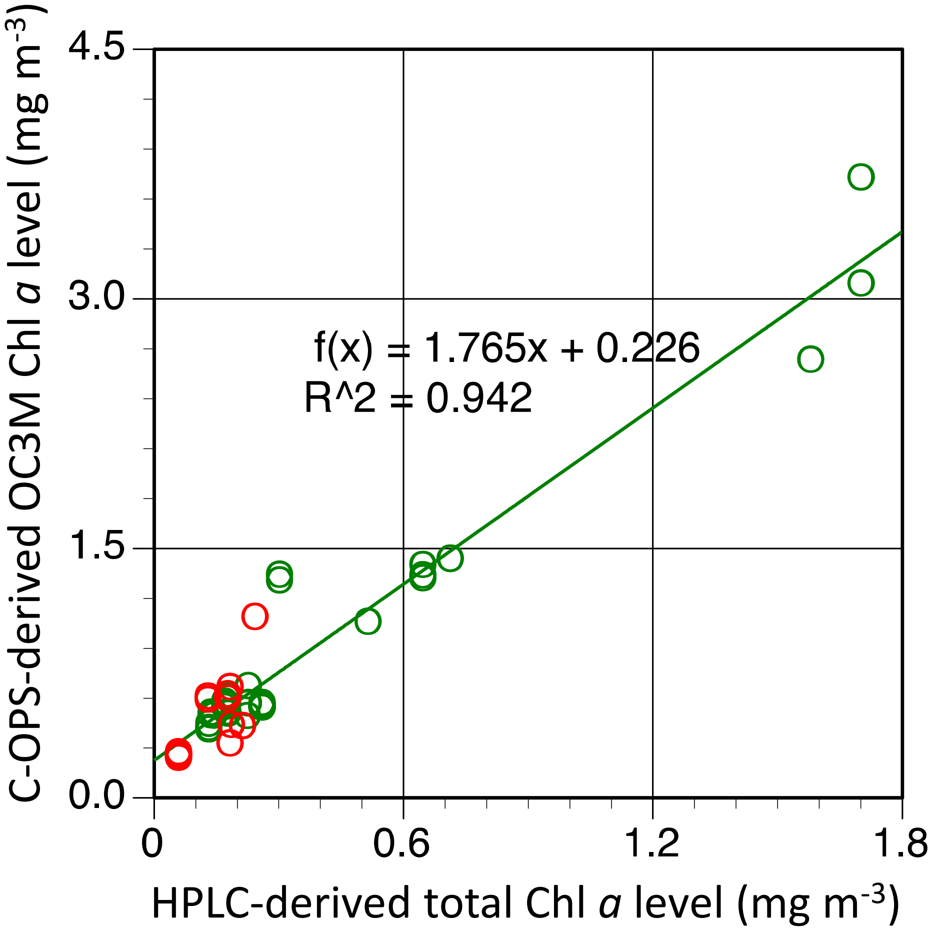
$\log_{10}[\text{Chl } a] = a_0 + a_1 R_L + a_2 R_L^2 + a_3 R_L^3 + a_4 R_L^4$

$a_0 = 0.2424$, $a_1 = -2.7423$, $a_2 = 1.8017$, $a_3 = 0.0015$, $a_4 = -1.2280$

$R_L = \log_{10}[\max(R_{rs}(443)/R_{rs}(547), R_{rs}(488))/R_{rs}(547)]$

R_{rs} is remote-sensing reflectance.

Comparison of Chl *a* levels in "Case 1 waters" of the Chukchi and Bering Seas between HPLC and C-OPS OC3M algorithm



We empirically characterized Case 2 waters with spectral end members for $K_d(320) > 0.9$ and $K_d(780) > 3.1$ as estimated with C-OPS.

$K_d(\lambda)$ is the diffuse attenuation coefficient of downward irradiance at λ nm.

Summary

- Our UHPLC pigment analytical technique can yield reliable validation data for ocean color remote sensing more rapidly than HPLC, which has been the validation "standard" for pigment measurements.

- MODIS OC3M algorithm did not reproduce well *in situ* Chl *a* in Arctic waters during the *Oshoro Maru* and ICESCAPE cruises.

- Optical (end-member) classification produces a more "coherent" validation scheme wherein new algorithm coefficients can be determined for Arctic (Case 1 and Case 2) waters.