

# Advanced Laser Fluorometry (ALF): New Technology for Oceanography and Environmental Monitoring

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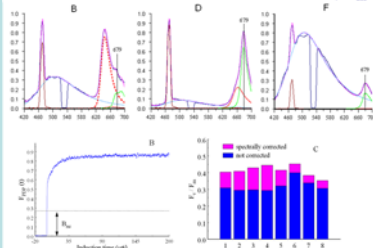
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## Abstract

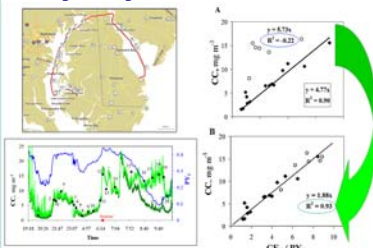
The Advanced Laser Fluorometry (ALF) has been recently developed for characterization of natural aquatic environments. It provides assessments of phytoplankton pigments, biomass, photophysiology, community composition, and chromophoric organic matter (COM). The environmental applications include oil/PAH detection and spectral discrimination from COM fluorescence. The ALF has been tested in the Pacific, Atlantic, and Arctic Oceans; Mediterranean, Arabian, and Bering Seas; Gulf of Mexico; Chesapeake, Delaware, and Monterey Bays; and Amazon and Congo River plumes. Its modular design allows flexible instrument configuration to optimize measurements in various water types. Several instrument modifications can be used for flow-through, fiber-probe, and in situ measurements. The commercial ALF instrument, Aquatic Laser Fluorescence Analyzer (ALFA) can be used for fully automated long-term underway measurements from various platforms. The recently developed ALF In Situ (ALFIS) prototype incorporates fiber-probe sampling. The probe will facilitate ALF technology in surface and submersible AUVs and gliders, vertical profilers, towed and stationary platforms (buoys, moorings, platforms, bridges, etc.). The fiber-probe sensor will allow sampling from remote locations and various depths. It is feasible to implement the ALF analytical capabilities in compact airborne LIDAR-fluorosensors.

## ALF Spectral Measurements Help to Improve Temporal Assessments of $F_v/F_m$



Non-Chl background in the spectral area of Chl fluorescence (upper panels) is quantified to subtract from Chl fluorescence induction (lower left) to spectrally correct the  $F_v/F_m$  ALF measurements (lower right) [1].

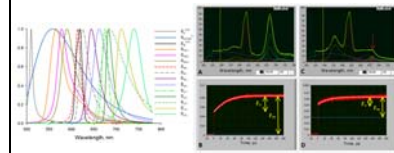
## ALF Temporal $F_v/F_m$ Measurements Help to Improve Spectral Assessments of Chl-a



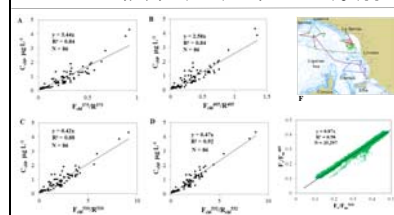
Normalization of Chl fluorescence to the concurrent underway ALF measurements of  $F_v/F_m$  eliminates the solar-induced non-photochemical quenching of both variables to yield high-accurate underway assessments of chlorophyll concentration [4].

## Advanced Laser Fluorometry

The ALF provides spectrally and temporally resolved measurements of the laser-stimulated seawater emission [1,2]. Various excitation wavelengths (e.g., 375, 405, 510 or 532 nm) can be used for the measurements [3]. Real-time spectral deconvolution (SDC) is used for assessment of Chl a, phycobiliprotein pigments and chromophoric organic matter (COM). The SDC provides detection and quantification of three spectral types of phycoerythrin (PE) for characterization of blue- and green-water types of autotrophic cyanobacteria and eukaryotic cryptophytes ( $F_{PE1}$ ,  $F_{PE2}$  and  $F_{PE3}$  with spectral maxima at 565, 578 and 590 nm, respectively) [1-3,5,7,8].

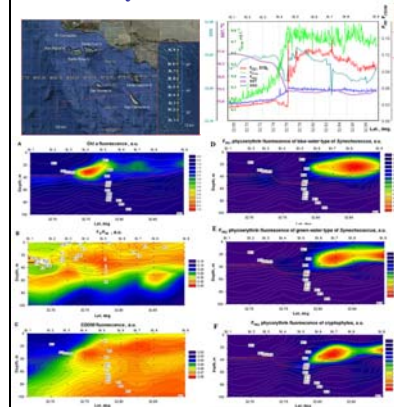


Left: A set of fifteen spectral components used for SDC analysis of emission spectra stimulated with 514 nm laser [2]. Middle & Right: Spectral (upper) and variable (lower) fluorescence measurements in diluted cultures of cryptophytes (middle) and cyanobacteria (right) [2].



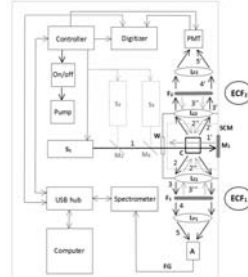
Left & middle: Correlations between Chl concentration and the ALFA fluorescence/Raman measurements using various excitation wavelengths. Right: Correlation between the ALFA  $F_v/F_m$  measurements using 405 and 514 nm excitation (see [3] for additional information).

## ALF: Studying Biogeochemical Variability Across the Oceanic fronts



An example of ALF measurements across the A-front in the Southern California Current Ecosystem. Three distinct autotrophic assemblages were identified. Northern waters were dominated by a blue-water type of *Synechococcus* cyanobacteria accompanied by green-water *Synechococcus* and cryptophytes. The highest phytoplankton biomass, dominated by diatoms and accompanied by elevated  $F_v/F_m$ , were found directly at the front. Strong structural frontal responses were also revealed by high-frequency underway ALF surface sampling (see [5]).

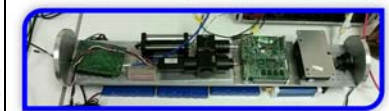
## Modular Design for Various Benchtop and In Situ ALF Configurations



A benchtop configuration of the ALF-T instrument [2,10] for spectrally and temporally resolved measurements of laser-stimulated emission in water. ECF1 and ECF2 are the emission collection-filtration units; C is a sample cell. The optical design provides four-fold increase in the emission signal vs. the traditional 90° scheme. The swappable sample compartment modules (SCM) can be used.



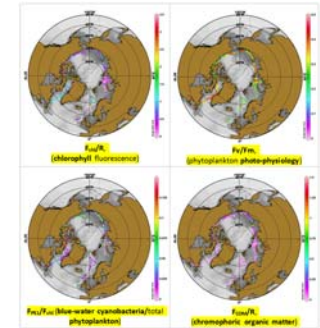
Above: An example of the ALF In Situ (ALFIS<sub>FP</sub>) instrument configuration for spectrally and temporally resolved in situ measurements of laser-stimulated emission in water via a fiber probe [10]. Below: The ALFIS<sub>FP</sub> prototype can autonomously operate in 4.5" aluminum case up to 12.5 hours powered by its rechargeable battery.



## ALF: Future Instruments & Platforms

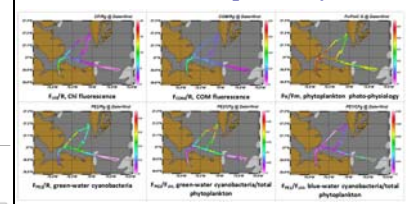


## ALFA Global Survey in the Arctic Seas



An example of the global-scale underway ALFA measurements (Dr. E. Boss, U. of Maine) to survey the impact of climate change on the bio-environmental situation in the Arctic Seas (May - Dec 2013, R/V Tara).

## ALFA Bio-Environmental monitoring in the Chesapeake Bay



The ALFA underway measurements in the Chesapeake Bay (Aug 2013; Dr. Gilerson, CUNY) provided rich information for bio-environmental characterization of the area using the new 514 nm laser for fluorescence excitation.

## References

- Chekalyuk, A.M. and M. Hafez. Advanced laser fluorometry of natural aquatic environments. *Limnol. Oceanogr. Methods*, 6:591-609 (2008)
- Chekalyuk, A. and M. Hafez. Next Generation Advanced Laser Fluorometry for Characterization of Natural Aquatic Environments: New Instruments. *Optics Express*, 21, 14181-14201 (2013)
- Chekalyuk, A. and M. Hafez. Analysis of spectral excitation for measurements of fluorescence constituents in natural waters. *Optics Express*, 21, 29255-29268 (2013)
- Chekalyuk, A. and M. Hafez. Photo-physiological variability in phytoplankton chlorophyll fluorescence and assessment of chlorophyll concentration. *Optics Express*, 19, 22643-22658 (2011)
- Chekalyuk, A.M., et al. Laser fluorescence analysis of phytoplankton across a frontal zone in the California Current ecosystem. *J. Plankton Res.* 34, 761-777 (2012)
- Ohman, M.D., et al. Autonomous ocean measurements in the California Current Ecosystem. *Oceanography* 18, 18-25 (2013)
- Goes, J.I., et al. Biogeography and ecophysiology of phytoplankton communities of the Amazon River Plume. *Progress in Oceanography* 120, 29-40 (2014)
- Goes, J. I., et al. Fluorescence, pigment and microscopic characterization of Bering Sea phytoplankton community structure and photosynthetic competency in the presence of a Cold Pool during summer. *Deep-Sea Research-II* (2013) doi:10.1016/j.dsr2.2013.12.004
- Chekalyuk, A.M. "Spectral and Temporal Laser Fluorescence Analysis such as for Natural Aquatic Environments", Patent application PCT/US2010/058891, Dec. 2010. (pending).
- Chekalyuk, A.M. "Optical Analysis of Emissions from Stimulated Liquids", Patent application PCT/US2013/024484, Feb. 2013 (pending).