LOCAL AND REMOTE LASER SENSING OF BIO-OPTICAL PARAMETERS IN NATURAL WATERS

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Мониторинг природных вод (водоносных горизонтов, рек, озер, морей и океанов) является ключевым для защиты окружающей среды, безопасности экосистем и жизнеобеспечения. Лазерное зондирование может быть очень эффективным способом для измерений биооптических параметров природных вод. В статье представлены три системы: две локальные (CASPER и CLASS) и одна дистанционная (ELF). Их применение в полевых исследованиях углубило наши знания различных видов биоты: от лабораторных образцов до родников, от речных бассейнов Сицилии до регионов Антарктики.

Introduction

Hydrosphere plays an important role in sustaining life on Earth. Significant biogeochemical cycles take place on it. A complete understanding of such complex processes requires powerful systems. Laser sensing can assist a thorough investigation of natural processes, anthropogenic effects and their interactions. Although the revolutionary capabilities offered to environmental monitoring by laser have been firstly exploited in the atmospheric field, quite soon laser has been successfully used also in the hydrosphere for bathymetric surveys in shallow waters, turbidity measurements, pollution detections, especially in case of oil spills, and phytoplankton mappings. Laser sources, because of high intensity, small divergence, good monochromaticity and the possibility of short pulse emission, are ideal tools for non-contact sensing of natural constituents like dissolved organic matter, algal pigments and phytoplankton cells. Laser sensing can be local, if the object under study has to be sampled, or remote, if it can be investigated from a considerable distance, without removing it from its location.

1. CASPER

CASPER (Compact and Advanced laser SPEctrometer for Riade) (fig. 1) [1] has been realized for the project RIADE (Integrated research for applying new technologies and processes for combating desertification) [www.riade.net] and has been patented. It is based on double filtration ($30 \mu m$ and $0.22 \mu m$) and double excitation (frequency quadrupled Nd: YAG laser

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Fig. 1. CASPER.

emitting at 266 nm and diode laser emitting at 405 nm) in order to detect both dissolved and particulate components of waters coming from aquifers, rivers and lakes.

After the first filtration $(30 \ \mu m)$, that eliminates unwanted materials, the sample contains both dissolved and particulate components and it is introduced in the first cuvette, where it can be irradiated by both wavelengths separately. The second filtration $(0.22 \ \mu m)$ allows only the dissolved matter to pass into the second cuvette that, once more, can be crossed by a beam either at 266 nm or 405 nm.

The double excitation extends the range of detectable components: the fluorescence yield of oils, polycyclic aromatic hydrocarbons, and proteins is higher if excited at 266 nm, while that of chromophoric dissolved organic matter, chlorophyll-a and other algal pigments is higher if excited at 405 nm.

Eventually, the emission spectra give information on the chemical composition of the samples: e.g. phycoerythrin and chlorophyll-a, if excited at 405 nm, will emit at about 580 nm and 680 nm, respectively. Once calibrated with known samples, CASPER reaches remarkable accuracies in absolute concentrations: $0.1 \,\mu\text{g/l}$ for chlorophyll-a and $0.1 \,\text{mg/l}$ for dissolved organic matter.



Fig. 2. Contour plot of chlorophyll-a concentrations in the aquifer near Licata (Sicily) based on CASPER measurements during the RIADE Campaign (May 22–25, 2005).

CASPER is a good candidate for field campaign because it is battery operated, fully controlled by a portable computer and one measurement takes less than one minute. Figure 2 shows an example of contour plot of chlorophyll-a concentrations in the aquifer near Licata (Sicily) based on CASPER measurements during the RIADE Campaign (May 22–25, 2005). CASPER data have been used be ecologists and have improved our understanding of salinization and desertification

2. CLASS

CLASS (Laser scanning flow cytometer) [2] has been developed for the project MIAO (Microsensor systems for extreme and hostile applications) [wwwrob.brindisi.enea.it/miao]. It has been designed to characterize marine phytoplankton morphology and composition from the observation of Mie scattering, fluorescence and depolarization.

CLASS consists of three main subsystems: hydrodynamics, optics and electronics. Hydrodynamics is quite conventional except that it embeds two closed loop electronic pressure regulators, the first one for the sheath fluid and the second one for the sample fluid. The optical layout is shown in fig. 3. Its heart is the cuvette where particles flow in an on axis capillary (diameter: 250 μ m) from the bottom. The beam delivered by the diode laser emitting at 405 nm is focused by the lens L_1 in the capillary where it is scattered by the particle after going through the mirror with hole. The beam diameter in the interaction region is nearly constant (FWHM: $25\,\mu\mathrm{m}$). The forward scattered light is reflected by the spherical mirror constituting the bottom wall of the cuvette. The light coming out from the cuvette is reflected by the mirror with hole, filtered spatially by the iris, filtered spectrally by the interference filter and detected by the photomultiplier measuring the scattering as a function of angle (indicatrix). The scattering angle is related to the particle position along the capillary axis, and thus to the detection time. A reference particle position is fixed by the side scattered light focused by the lens L_2 , spatially filtered by the pinhole and detected by the photomultiplier measuring the trigger. The main parts of electronics are two preamplifiers (one after each photomultiplier) and a two-channel analog-to-digital converter with 14 bit resolution and 50 MS/s sampling.



Fig. 3. CLASS. Sizes in mm. IF: interference filter, L_1 and L_2 : lenses, PMT: photomultiplier tube.



Fig. 4. Size (a) and refractive index (b) measurement of Synechocystis cells by CLASS. In (a) two Gaussian fits are performed (the first with the points 1–5, labeled from left to right, and the second with the points 7–15) and two peaks at 1.0 and 1.7 μ m are obtained corresponding to single cells and two-cell aggregates, respectively. The Gaussian fit of the refractive index distribution (b) provided n = 1.53.

The light scattering inversion scheme used here to retrieve size and refractive index of spherical particles is a parametric solution of the inverse light scattering problem. This scheme is an evolution of the flying light scattering indicatrix method [3], based on the spectral decomposition of the detected angular light scattering. In fact, the features of the Fourier spectrum of experimental signals can be related to the particle characteristics. The inversion scheme, that was proved to be more robust in case of noisy data, is thoroughly described elsewhere [4] and the reader is referred to that reference for algorithm details. An example of CLASS results is given in fig. 4. Those measurements were carried out on August 2, 2005 and are to our knowledge the first application of laser scanning flow cytometry to marine particles.

3. ELF

ELF (ENEA Lidar Fluorosensor) (fig. 5) [5] is a technological product of PNRA (Italian Antarctic research program) [www.pnra.it]. The main parts of the system are a frequency tripled Nd:YAG and a telescope detecting Raman scattering by water, laser induced fluorescence by chlorophyll-a and chromophoric dissolved organic matter, and in vivo phytoplankton

fluorescence yield (with the pump-and-probe technique). ELF operates aboard the research vessel Italica and participated to oceanographic campaigns in the Mediterranean Sea, Indian Ocean, Pacific Ocean and Southern Ocean.

Thanks to narrowband filtering and electronic gating, laser induced fluorescence signals do not need corrections for radiometric and spectral characteristics of solar irradiance and surface reflectance. Furthermore, due to the short distance from the target, atmospheric effects are negligible. This explains why ELF data can be regarded as sea truth and have been provided to WOOD (Worldwide Ocean Optics Database) of ONR (Office of Naval Research) and SeaBASS (SeaWiFS Bio-optical Archive and Storage System) of NASA (National Aeronautics and Space Administration). Moreover, ELF data have been used for the calibration of the bio-optical algorithms of the ocean color satellite radiometers [6]: the ELF-calibrated bio-optical algorithm



Fig. 5. ELF consists of a transmitter: frequency-tripled Nd:YAG laser (1), a receiver: Cassegrain telescope (2) and a detector: optical fibers (3), bandpass filters (4) and photomultiplier tubes (5).



Fig. 6. Simultaneous measurements of chlorophyll-a by ELF (grey) and SeaWiFS (black) during a New Zealand — Italy transect.

of a given radiometer is based on the linear fit of the log-log plot of the ELF chlorophyll-a concentration versus the radiometer 490–560 band ratio, i.e.:

$$\log_{10} C = a_0 + a_1 R,$$

where C is the chlorophyll-a concentration measured by ELF in mg m⁻³ and:

$$R = \log_{10} \frac{Rrs(490)}{Rrs(560)},$$

Rrs(490) and Rrs(560) are the remote sensing reflectance at 490 and 560 nm, respectively, retrieved by the radiometer and R is called the 490–560 band ratio. An example of comparison between ELF and the satellite radiometer SeaWiFS [7] data is given in fig. 6.

4. Conclusions

Three advanced laser systems for local and remote sensing of bio-optical parameters in natural waters have recently been developed at ENEA.

CASPER, an innovative laser spectrofluorometer, operated during a field campaign in Sicily. Its data will improve our understanding of salinization and desertification.

CLASS applied for the first time laser scanning flow cytometry to marine particles. Very recently, fluorescence and polarization channels have been implemented and in the near future multiple excitations will be added, thus enlarging the characterizing capabilities of marine particles by CLASS.

ELF merged the accuracy of in situ samplers and the coverage of satellite radiometers. Its data demonstrate that present estimates of chlorophyll-a and primary productivity should be reviewed in the Antarctic coastal environment.

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References

- ARISTIPINI P., DEL BUGARO D., FIORANI L. ET AL. Mobile laser spectrofluorometer for natural waters monitoring in Sicily // Proc. of SPIE. 2004. Vol. 5880. P. 190–195.
- [2] BARNABA F., FIORANI L., PALUCCI A., TARASOV P. First characterization of marine particles by laser scanning flow cytometry // J. of Quantitative Spectroscopy and Radiation Transfer. 2006. Vol. 102. P. 11–17.
- [3] MALTSEV V.P. Scanning flow citometry for individual particle analysis // Review of Sci. Instruments. 2000. Vol. 71. P. 243-255.

- [4] SEMYANOV K.A., TARASOV P.A., ZHARINOV A.E. ET AL. Single-particle sizing from light scattering by spectral decomposition // Appl. Optics. 2004. Vol. 43. P. 5110-5115.
- [5] BARBINI R., COLAO F., FANTONI R. ET AL. Remote sensing of the Southern Ocean: techniques and results // J. of Optoelectronics and Advanced Materials. 2001. Vol. 3. P. 817–830.
- [6] BARBINI R., COLAO F., FANTONI R. ET AL. Lidar fluorosensor calibration of the SeaWiFS chlorophyll algorithm in the Ross Sea // Intern. J. of Remote Sensing. 2003. Vol. 24. P. 3205–3218.
- HOOKER S.B., ESAIAS W.E., FELDMAN G.C. ET AL. An overview of SeaWiFS and ocean color // SeaWiFS Technical Report Series, NASA Technical Memorandum 104566. 1992. Vol. 1 / Ed. by S.B. Hooker, E.R. Firestone (Greenbelt: NASA).

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