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EARTH PHYSICS

REMOTE ESTIMATION OF FLUORESCENCE MARINE COMPONENTS DISTRIBUTION

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Abstract. This study combines fluorescence Lidar measurements with classical determinations in order to assess the type of correlation between them and the fluorescence characteristics of natural water and polluted water from Romanian Black Sea coast. A fluorescence Lidar system was used to estimate in real time the distribution of dissolved organic matter (DOM) and chlorophyll a. The levels of DOM concentration were characterized through fluorescence signature giving a picture of anthropogenic influences in the area. The fluorescence intensity for Black Sea coastal waters decreases with depth and with distance from the marine coast in the healthy areas. The bio-productivity of the marine environment, including algae blooming and oil pollution became more evident in the harbor areas.

Key words: fluorescence Lidar, dissolved organic matter, chlorophyll, petroleum.

1. INTRODUCTION

The marine environment can be affected by oil spills, harmful algae blooming and organic matter increase. Eutrophication is considered to be an important factor that contributes to habitat changes and to the blooming of harmful algal species [1].

The eutrophication effect is the changing in the structure of the coastal community due to the change into the ratio of individual nutrients relative to other nutrients. Causes of algae blooming and marine populations decreasing and the primary production at global scale can be estimated when is used the laser induced fluorescence method to evaluate the chlorophyll concentration.

The LIDAR (Light Detection and Ranging) systems use the Laser Induced Fluorescence (LIF) method to characterize in situ pollutants and organic matter. This technique is based on analysis of fluorescence signal induced in the target object by excitation with a laser beam.

Lidar signal is a composite of fluorescence responses of individual compounds; every component is identified and characterized by its spectral fluorescence fingerprint. The principal advantage of laser remote sensing is the possibility to obtain extensive information with high resolution from large water surfaces in real time.

Dissolved organic matter species represents a complex mixture of organic molecules. The most important DOM source are extra cellular release of organic matter by algae, release by zooplankton, lyses of bacteria and algae cells and release from sediments 0. The differences in molecular weight make to be difficult to characterize DOM using traditional chemical techniques, but Lidar technique can identify the mixing of different waters looking at DOM fluorescence signature.

Up to now measurements using Lidar induced fluorescence were carried out in Italy, Russia, Estonia, in the Atlantic Ocean, the Pacific Ocean and the Adriatic Sea, in the Baltic Sea, in the Mediterranean Sea, North Sea [3, 4, 5] and focused on the distribution and temporal evaluations of phytoplankton, pollution level estimation for marine waters and hydrographical parameters determination.

The aim of this paper is to reveal the contribution of a fluorescence LIDAR system on assessing the dissolved organic matter, petroleum and chlorophyll during august 2007 on Romanian Black Sea coastal zone and platforms area. The Lidar results are correlated with classical achievement of seawater parameters.

2. STUDY AREA AND METHODS

The system used for measurements is a monostatic ship borne fluorescence Lidar, able to detect and measure organic pollution, natural organic matter, and photosynthetic algae in water. The data used are achieved during the cruises performed on august 2007 onboard Mare Nigrum vessel along Romanian North-East Black Sea coast, between Cap Tuzla and Sf. Gheorghe Branch and on oil platforms proximity.

Continuous LIDAR measurements and physical-chemical, chlorophyll, zooplankton measurements were carried out. All physical-chemical parameters were quantified for surface water sample (0.5m). Three bathymetric profiles parallel with coast, starting from 20m depth waters and round circle around the platforms represents the areas evaluated continuous by fluorescence Lidar.

All ten sampling stations belong to the Lidar profiles (Fig.1): 1 represents the S5 Platform, 2 the Central Platform, 3 the S4 Platform, 4 the S7 Platform, 5 the S6 Platform, 6 the Danube, Sf. George branch discharge, 7 represents the Gura Portita area, 8 the Cap Midia area, 9 the Constanta area, 10 the Cap Tuzla area.

When is used a pulsed, monostatic system for water quality investigations, the intensity of the Lidar return signal is described by the Lidar equation [6, 7]:

$$\mathrm{d}I_{fl} = \mathrm{d}\Phi_{fl} R \frac{I_0}{x^2} \mathrm{e}^{-(x-x')(\alpha_l+\alpha_{fl})}, \tag{1}$$

where $\mathrm{d}\Phi_{\mathrm{fl}}$ represents the efficiency of the fluorescence process, R is a function which describes the system and medium characteristics, I_0 is the initial intensity, x-x' is the water depth where the signal has been excited, α is attenuation coefficient, indices l and fl describe the laser and fluorescence wavelengths.

The efficiency of the fluorescence process is given by [6]:

$$\mathrm{d}\Phi_{fl} = \mathrm{d}N_{fl}\sigma_{fl} = n_{fl}\sigma_{fl} S\mathrm{d}x, \tag{2}$$

where $\mathrm{d}N_{fl}$ represents the fluorescent molecules number in a given water volume $V = S\mathrm{d}x$; n_{fl} is the concentration and σ_{fl} the fluorescence cross-section of the investigated molecules.

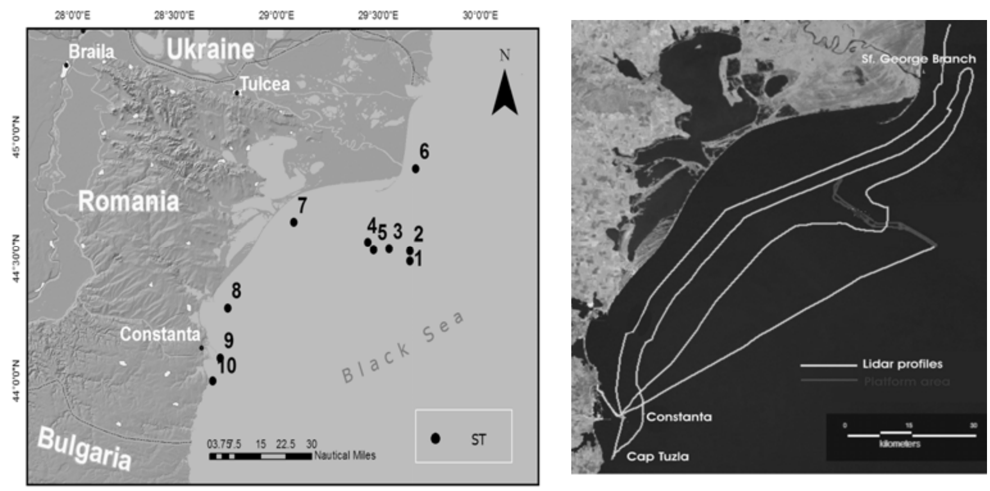

Fig. 1 – Maps of the field campaign (ST – sampling sites).

The fluorescence intensity corresponding to a water column between surface and depth z considered small (few cm) and $z \ll x'$ the fluorescence Lidar signal intensity can be calculated as:

$$I(z) = n_{fl,z}\sigma_{fl,z} \frac{RI_0}{x'^2} \frac{1}{\alpha_l + \alpha_{fl}} \left(1 - \mathrm{e}^{-z(\alpha_l+\alpha_{fl})}\right). \tag{3}$$

In the case of a homogeneous water column, where attenuation coefficient and fluorescence efficiency are constant, the intensity of returned Lidar signal became proportional with fluorescence molecular concentration, as it was considered in this paper.

3. RESULTS AND DISCUSSION

The physical-chemical parameters of surface seawater varied usually within the natural limits as can be seen in Table 1. The temperature had a 25.7°C average value and pH around 8.4. The minimum values of conductivity, pH and oxygen were observed on Danube Delta discharges area. Due to the intense photosynthetic process the seawater had an alkaline character (pH between 8.39 and 8.49). Important quantity of nutrients (phosphate – 2.7 mg·l^{-1}, nitrate – 0.06 mgl^{-1}) was the cause of phytoplankton blooming and dissolved oxygen important levels in the oil platforms area. The nitrite and dissolved oxygen reached the maximum values in the same zone and Gura Portita area, where the influence of Danube's water charged by nutrients is very important due to the surface cyclonal current, which facilitate mixing between river and sea water.

Table 1

Physical-chemical parameters

No	Salinity ‰	CND mS/cm	O_2 mg/l	Eh mV	NO_3 mg/l	PO_4^3 mg/l	HC mg/l
1	16.1	26.6	8.21	190	0.08	1.97	0.0
2	16.1	26.6	8.04	194	0.10	2.70	0.0
3	16.1	26.4	8.75	190	0.05	1.62	0.0
4	16.0	26.2	7.45	190	0.09	0.39	1.0
5	16.2	26.4	7.44	183	0.40	0.65	1.0
6	14.7	24.1	6.61	248	0.30	0.40	0.0
7	15.9	26.0	7.82	240	0.40	0.57	0.0
8	16.4	26.7	7.42	241	0.10	0.49	0.0
9	16.7	27.1	7.06	230	0.12	0.13	1.0
10	16.8	25.8	7.05	210	0.07	1.71	0.0

Water remote investigations were done with a fluorescence Lidar using as sounding radiation the beam of an excimer laser (308 nm) and of a tunable dye laser (367, 460 nm). For 308 nm water column investigations it can be usually detected three peaks: at 308 and 344 nm due to elastic scattering and water Raman scattering and an intense band with maxima around 450 nm corresponding to the DOM presence.

In Fig. 2 are presented the signals corresponding to the open sea water columns excited by 308 nm laser beam. Those three spectra show the DOM fingerprint for three profiles parallel with coast. It can be observed the difference of shapes and organic matter concentration: clean sea water presents an intense Raman signal and a broad organic matter fluorescence signature, unlike the narrow DOM fluorescence band and les intense Raman signal for human and river influenced water. These signals can be used to determine the organic matter components, the anthropogenic and rivers influences, the shape of signals being an indicator for water column nature. The DOM profiles estimated through remote method were in accordance with classic parameters evaluated in controlled medium (Table 1).

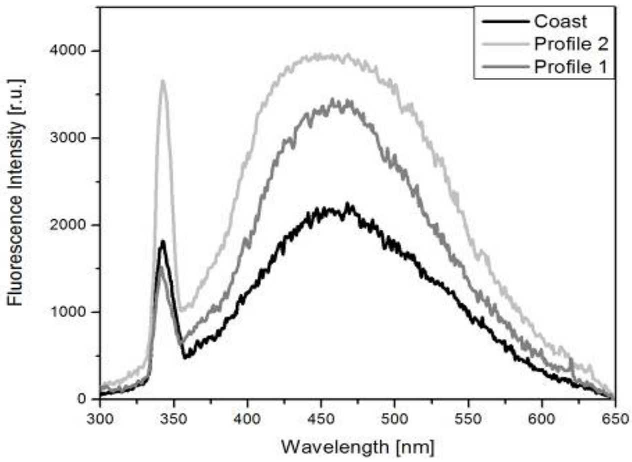

Fig. 2 – Lidar signals for Open Sea.

The chlorophyll distribution can be evaluated using 460 nm excitation wavelength. Two peaks can be seen in the fluorescence spectra: Raman band mixed with blue-green fluorescence and chlorophyll a (685 nm) (Fig. 3). The phytoplankton blooming was noticed during august 2007 campaign using fluorescence Lidar and classical determinations.

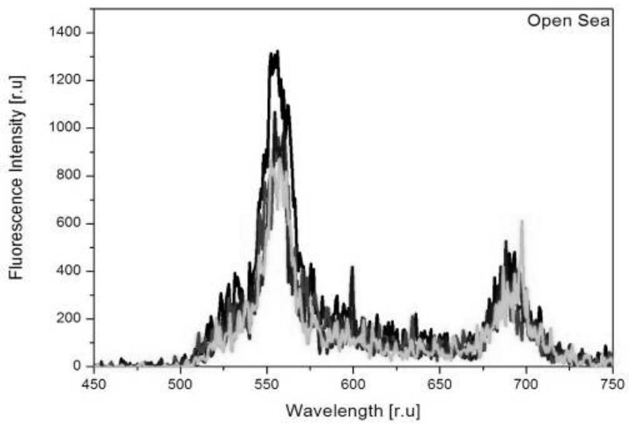

Fig. 3 – Lidar signal for 460 nm excitation wavelength.

Chlorophyll a concentration higher than 5 μg·dm^{-3} shows anthropogenic influence in accordance with coastal waters quality standards (table 2). Chlorophyll a concentration are minimal for oligotrophic media (5-10 μg·l^{-1} phosphor salt), increasing with the increase of nutrients (10–30 μg·l^{-1} total phosphor in mezotrophic media, 30–100 μg·l^{-1} in eutrophic media and higher than 100 μg·l^{-1}in hypertrophic media) as was observed by Grey [8]. The chlorophyll presence in Black Sea waters indicated the presence of diatom algae, while the chlorophyll b indicated the presence of the green unicellular algae, both of them the most important components of Black Sea phytoplankton.

For august 2007 the phytoplankton blooming was observed in some areas, with constant values on Romanian Black Sea coast and important values in Danube, Sf. George branch discharge area. In the proximity of oil platforms, the chlorophyll values were small comparing with areas under anthropogenic influence (Table 2). Lidar measurements on the parameters of seawater are in agreement with the results of laboratory measurements, the remote evaluation giving the possibility to detect punctual fluctuations.

Usually in late summer period are observed important phytoplankton quantities [9, 10]. During this campaign the unicellular algae were dispersed due to the surface and subsurface marine waters accentuate dynamics. The strong waves and currents in the oil platforms proximity distributed unequally the unicellular algae.

Table 2

Chlorophylls concentration

Sample No	Sample depth m	Chl. A μg/dm^3	Chl. B μg/dm^3	Chl. C μg/dm^3
1	0	0	0	0
2	0	0.43	0.15	0.27
3	0	0.40	0.56	0.12
4	0	0.87	0.30	0.53
5	0	0.40	0.51	0.60
6A	0	6.56	2.07	1.75
6B	5	6.15	1.45	2.11
6C	10	2.21	0.48	0.04
7A	0	1.74	0.59	1.07
7B	5	1.34	0.08	0.47
7C	10	0.87	0.30	0.53
8A	0	1.34	0.08	0.47
8B	5	0.87	0.35	0.05
8C	10	1.74	0.64	0.59
9	0	0.87	0.40	0
10A	0	1.34	0.08	0.47
10B	5	0.87	0.35	0.05

The Lidar system can be used to assess the oil type and spills area. The environmental effects of spilled oil can vary, depending upon the quantity and types of oils. The lighter refined petroleum products are mixing in the water column and are more toxic to aquatic species, but it is evaporating rapidly and do not persist long time in the ecosystem. The crude oil, which is less toxic, can remain on the water surface for a long time affecting the marine life 0. In the case of oil products presence along with DOM fluorescence band can be depicted another less intense band before 400 nm and after 550 nm corresponding to the light oil and respectively the heavy oil contribution (Fig. 4).

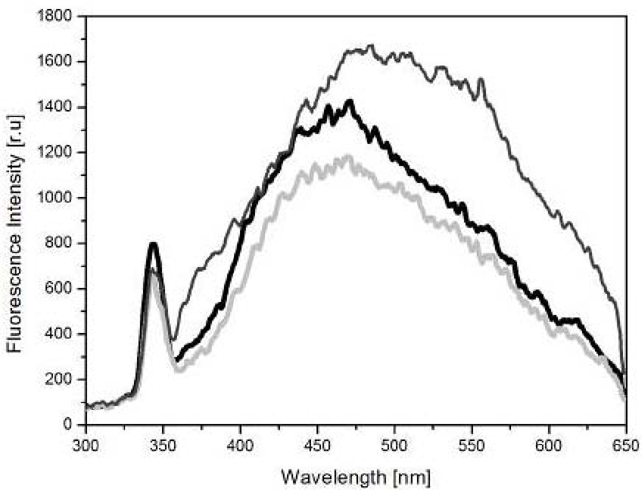

Fig. 4 – Platforms fluorescence spectra.

During august campaign all platform areas were evaluated in order to detect the oil spills. The Lidar measurements indicated the oil films around all platforms and near Midia and Constanta harbors, unlike the classic methods which indicated the oil presence around S6 and S7 platforms and near Constanta harbor.

The highest oil concentration was detected by Lidar near S5 platforms (9.81 relative units) and the spreader in central platforms proximity (Fig. 5). The petroleum products dispersion depended by wind direction and speed, resulting emulsions or big spills.

The cleanest platforms area corresponded to S3 platforms. The quantities of petroleum products were not significant and the areas are small, all the observations representing accidents or naval ruts.

Concerning the zooplankton from neritic waters of the Black Sea, it is characteristics for late summer to find populations of *Centropages kröyeri* var. *pontica* (maximum concentration 119 ex·m^{-3}).

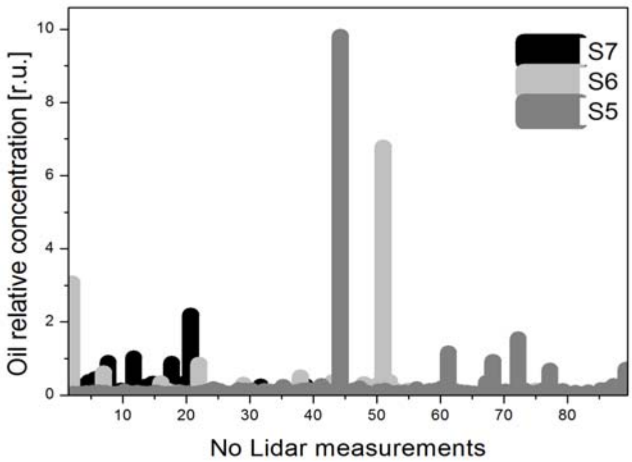

Fig. 5 – Petroleum products distribution around platforms.

The other thermopile species was depicted on the north sector, important densities of *Pseudonevadne tergestina*. The Rotifers, *Synchaeta littoralis* and *Synchaeta razelmii* had significant levels in platforms proximity where are rich trophic resources (DOM). Quantitatively the copepod *Acartia clausi* is the most important with maximum densities of 1137 ex·m^{-3}, meaning 64% from total amount of zooplankton (Fig. 6).

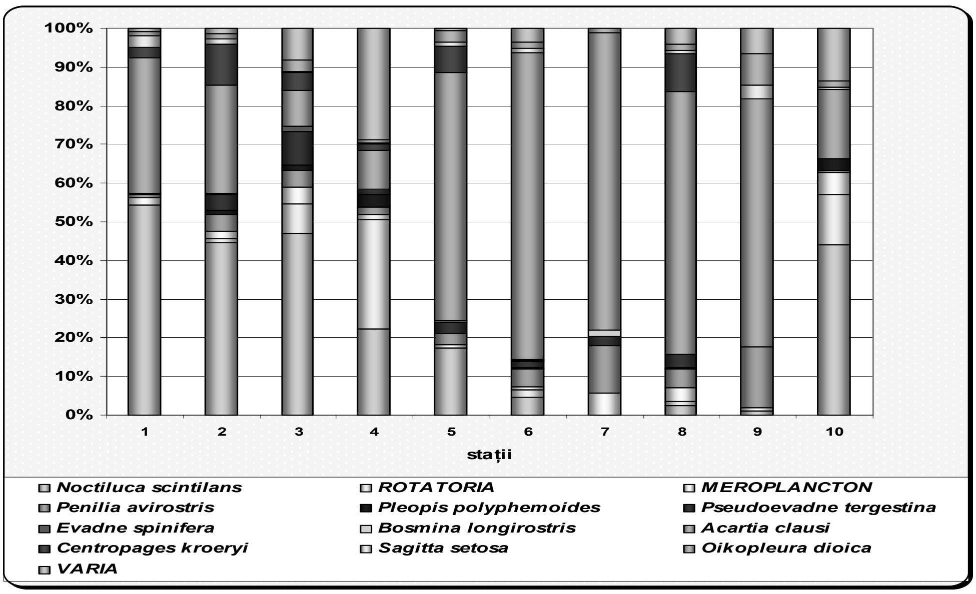

Fig. 6 – Percentage of zooplankton species in Cap Tuzla–Sf. Gheorghe branch area.

4. CONCLUSIONS

During the experiment period all physical-chemical parameters varied within the natural limits. The organic matter and chlorophyll distributions were influenced by river waters, the Danube delta discharge channel. The neritic water presented an alkaline character due to the intense photosynthetic process evidenced thought Lidar signals. The copepod *Acartia clausi* had a significant mean density (367 ex·m^{-3}), with maximum values around the oil platforms and in areas with nutrients, where phytoplankton and DOM were present.

The Romanian Black Sea waters had an oligotrophic character at the end of August. Oil spills were observed in the platforms proximity and near harbors. Good correlation was obtained between Lidar and classical measurements of organic matter, petroleum and chlorophyll. The most important advantage of the remote evaluation is the possibility to detect punctual fluctuations and small concentrations. Lidar systems can be very useful in environmental investigations, especially of the open water basins, due to the large covered area and the real time response.

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