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FLUORESCENCE OF AGEING EXTRACELLULAR PRODUCTS OF *SKELETONEMA COSTATUM*

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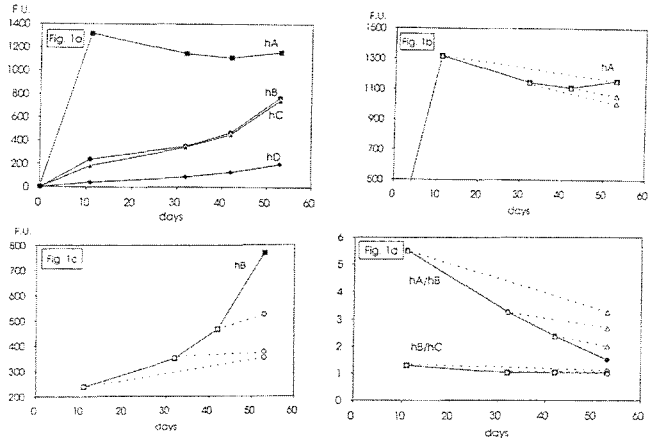
The extracellular organic matter (EOM) released in dissolved state in the water by phytoplankton was characterized using the synchronous fluorescence spectroscopy. This technique, due to its high sensitivity and selectivity, allows the spectral resolution of different compounds present in multicomponent mixtures of dissolved organic matter (VO-DINH, 1978; CABANISS and SHUMAN, 1987). The aim was to verify if quali-quantitative variations observed on the ageing EOM produced by algal cultures were related to changes in algal production rather than to chemical transformations of the released products. *Skeletonem costatum*, isolated from Adriatic Sea, was cultured in laboratory (EPA, 1974). The EOM produced was analyzed during a 53 days experiment, using a Spex-FluoroMax fluorimeter, scanning synchronously a wavelength range from 250 to 500 nm, with constant Δwl (25 nm) between ex and em monochromators. Samples were taken from the *S. costatum* culture at 11, 32, 42, 53 days of growth and filtered (0.45 µm). The filtered medium, containing the dissolved EOM, was kept ageing in the same light and temperature conditions of the producer culture. All samples were analyzed at the sampling time and at the 53rd day. The fluorimetric analysis provided spectra characterized by a main peak (A) at an excitation wavelength of 276 nm and a series of secondary peaks (B, C, D) located between 330 and 430 nm. Spectra of the differently aged culture-EOM (C-EOM) showed quantitative variations of the different components produced, as shown in Figure 1a (F.U.= fluorescence units). The fluorescence intensity of the first peak (hA), which reaches high values at the day 11, tends successively to decrease slightly, while the intensity of peaks >300 nm (hB, hC, hD) increase constantly during the 53 days (Fig 1a). The same trend in fluorescence was already described in previous ageing experiments made on a number of different algal species in culture (MINGAZZINI *et al.*, 1994; in press). In those cases, however, it was not clarified if the series of the higher wavelengths peaks, with respect to the first peak, may represent the fluorimetric response of different extracellular compounds produced in stationary growth phase, rather than a chemical transformation of the algal products already present in the medium.

The fluorescence values measured on the ageing filtered medium-EOM (M-EOM) are shown in Figure 1b and 1c. C-EOM and M-EOM are represented by uninterrupted and dotted lines, respectively. The decrease in fluorescence intensity of the first peak (Fig. 1b) is similar or even greater in the M-EOM compared to C-EOM. Conversely, the increase in fluorescence intensity of peaks >300 nm is constantly much lower in M-EOM than in C-EOM, as shown in Fig. 1c for hB. Since in M-EOM the decrease of hA is not accompanied by an increase of hB, hC, hD equal to that observed in C-EOM, the fluorescence enhancement is probably linked to the algal production in the stationary growth phase. The decrease of hA may be the result of slow photodegradation processes (CHEN and BADA, 1992) of products released by the actively growing culture.

The ratios hA/hB and hB/hC, calculated on C-EOM and on M-EOM in the 53-day experiment, are shown in Figure 1d. The ratio between the first two peaks (hA/hB), which decrease in time, was previously proposed (MINGAZZINI *et al.*, 1994; in press) to describe the quali-quantitative variation of the extracellular compounds released during the algal growth phases. The ratios between the last series of peaks (hB/hC in Figure 1d), which tend instead to remain constant in time, were used to describe the spectral features linked to the producer algal species. The comparison of the C-EOM and M-EOM supports the suggestions of MINGAZZINI *et al.*. The hB/hC ratio from both C-EOM and M-EOM remains in fact constant in time, indicating that the extracellular products released in the stationary phase from a monospecific culture do not vary qualitatively, while the decrease of the hA/hB ratio mostly reflects changes in production activity rather than chemical transformations of the released products. The differences observed comparing C-EOM to M-EOM hA/hB (Figure 1d) are in fact mainly related to the missing production in all M-EOM samples (from day 11 to 53), as shown in Figure 1c.



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VERTICAL CARBON FLUXES DURING SUMMER IN THE NORTHERN AND CENTRAL ADRIATIC SEA

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Within the framework of the EEC-sponsored ELNA (Eutrophic Limits of the Northern Adriatic) programme, vertical fluxes of particles and carbon were measured for short periods during mid-July 1993 in the Northern and Central Adriatic Sea. The central goal of ELNA is to assess the carbon assimilation capacity of the northern Adriatic in order to determine acceptable limits to its eutrophication. Besides studying particle export from the pelagic environment, the programme is oriented towards developing an oceanographic model to derive the mechanisms controlling nutrient and carbon budgets and fluxes for the northern part of the Adriatic.

A drifting sediment trap was deployed for two-24 hour periods in the Jabuka Pit and Po river plume areas during the ELNA3 cruise. The sediment trap used was a PPS5-Technicap model with a conical collection jar and a 1 m^2 surface opening fitted with a honey-comb baffle. The trap was positioned below the euphotic layer or a few meters above the bottom. The collection cup was filled with a 2% buffered formaldehyde solution before deployment to prevent grazing by swimmers. Before desalting and freeze-drying, the swimmers were removed by hand-picking under a dissecting microscope. During each deployment suspended particles were sampled near the drifter for analysis of carbon and nitrogen. Water samples were collected using Niskin bottles and filtered on precombusted fiberglass filters (Whatman GF/F). Particulate carbon and nitrogen were analyzed with a CHN Heraeus analyzer following protocols described by MIQUEL *et al.* (1994). POC samples were pre-treated with 1 M phosphoric acid prior to combustion to remove carbonate. Only total carbon was measured in the suspended particles.

A vertical profile in the Jabuka Pit showed a marked increase in particulate carbon between 50 and 70 m. The nitrogen content was also higher at these depths, especially at 50 m. This range corresponded with the CTD fluorescence maximum (50-70 m) associated to the highest phytoplankton biomass. In contrast, in the northern sector of the Adriatic suspended particulate carbon was very high in surface waters and then decreased with increasing depth. Particulate carbon concentrations were always higher than those measured at corresponding depths in the Jabuka Pit, and appeared to be of biological origin as indicated by the high nitrogen concentrations. The highest C and N content in central and northern Adriatic waters were 76 and 13 µg l^{-1}, and 438 and 59 µg l^{-1}, respectively. Integrated carbon values for the water column at both sites were 5.5 g m^{-2} (0-100 m, Jabuka site) and 4.1 g m^{-2} (0-27 m, Po outflow).

The downward particle, organic C, N and fecal pellet fluxes are reported in Table 1. Near the mouth of the Po river, mass flux was roughly 13 times higher than that measured in the oligotrophic waters over the Jabuka Pit. Carbon (total and organic) and nitrogen fluxes were also higher in the northern sector by a factor of 5 to 6 times. Furthermore, the sinking particles were different in nature at the two sites. Off the Po outflow, the particulate material was characterized by a large amount of amorphous, mucoid marine floc in which were suspended many small zooplankton fecal pellets (Table 1). In contrast, the sample from the Jabuka Pit was translucent and contained only few fecal pellets and detrital particles. In the north, large fish fecal pellets contributed significantly to the downward mass and carbon flux. Their numerical flux was only 36 pellets m^{-2} d^{-1} but because of their large size (mean length 3 mm, diameter 1.5 mm), they accounted for approximately 30% of mass flux and 60% of carbon flux. If fish pellets are not considered, then the remaining zooplankton fecal pellets represented only 6 to 10 % of the carbon flux at both sites.

Location (St. no.)	Lat.Long.	Date	Trap Depth	Bottom Depth	Mass	C.org. (mg $m^{-2}d^{-1}$)	Flux N	Fecal Pellets (No. $m^{-2}d^{-1}$)
Jabuka Pit (St. 3)	42°52.28'N 14°50.43'E	14-15/7	100	242	10	2.5	0.3	1.6×10^3
Po outflow (St. 172)	44°56.05'N 13°01.11'E	24-25/7	27	35	127	11.5	1.6	3.7×10^4

Table 1. Particle flux in the Adriatic Sea measured over 24 hours with a drifting sediment trap, July 1993.

Carbon flux in central Adriatic was, as for the other measured parameters, very low indicating the oligotrophic nature of these waters during summer. Furthermore, the total carbon sedimenting per day represented only 0.05% of the carbon pool in the water column above the trap, confirming that there was virtually no export from surface waters at that time. On the contrary, carbon flux in the northern Adriatic was much greater, although the fluxes are not particularly high for a coastal environment. Sinking particulate carbon represented 0.35% of the carbon standing stock per day in the water column suggesting a mesotrophic system was present during July.

Data obtained in 1993 will be complemented with similar results from a 1994 summer cruise. Both sets of data should help to understand interannual variations in carbon flux in the Adriatic. Given that one of the main objectives of ELNA is to construct a carbon budget for the northern Adriatic, it is also essential to understand long-term temporal changes in the downward flux of particle carbon. Thus, a time-series sediment trap has been moored in central Adriatic from which we expect to obtain at least one complete year of vertical particle flux data.

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