^{13}C as an indicator of sources of the settling and sedimentary organic matter in the Gulf of Lions (W Mediterranean)

^{13}C kot indikator izvora sedimentirajoče in sedimentirane organske snovi v Lyonskem zalivu (Z Sredozemsko morje)

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Abstract: The carbon isotopic composition of settling organic matter from sediment traps was determined on a seasonal basis in the Gulf of Lions (W Mediterranean). Isotopic variations reflected the dynamic nature of carbon input to continental shelf environments, which are influenced by phytoplankton blooms in spring and summer, and allochthonous (terrigenous) inputs in winter. The $^{13}C_{org}$ isotopic composition of organic matter in surface sediments suggests that the settling organic matter source was largely phytoplanktonic (marine).

Izvleček: V Lyonskem zalivu (Z Sredozemsko morje) smo določili izotopsko sestavo ogljika v sedimentirajoči organski snovi. Ugotovljene sezonske variacije odražajo spremenljive razmere, ki so posledica cvetenja fitoplanktona v pomladnem in poletnem obdobju ter kopenskega (terigenega) vnosa pozimi. Sedimentirajoči organski delci so pretežno fitoplanktonskega (morskega) izvora, kar se odraža tudi v izotopski sestavi $^{13}C_{org}$ v površinskih sedimentih.

Key words: stable carbon isotopes, settling material, organic matter, marine environment, sediments

Ključne besede: stabilni izotopi ogljika, sedimentacija, organska snov, morsko okolje, sedimenti

Introduction

The carbon isotope composition of organic matter ($\delta^{13}C_{org}$)[1] has been demonstrated in several cases to be a good indicator of the

[1]Carbon isotope composition is reported as $\delta^{13}C$ value in ‰, where

$$\delta^{13}C = \left[\frac{R_{sample}}{R_{std}} - 1\right] x\ 1000$$, $R = {}^{13}C/{}^{12}C$ and $R_{std} = 0.0112372$

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source material (ALTABET, 1996). Isotopic signals are produced when transformation processes cause isotopic discrimination between substrate and product. Organic C isotopic composition results from an integration of primary, secondary and allochthonous isotopic signal. Use of isotopic data involves either the recognition of ratios of characteristic of specific organic matter sources or transformations or exploitation of temporal or spatial variations as "natural" tracer experiments in which an isotopic signal propagates from one organic pool to another and from the surface into ocean's interior. Stable organic C isotope has been extensively used as a tracer for organic carbon cycling in particulate organic matter (POM), and for recent and ancient marine sediments with isotopically two or multiple distinguishable sources (FAGANELI ET AL., 1994; THORNTON AND MCMANUS, 1994; VOSS AND STRUCK, 1997; MIDDELBURG AND NIEUWENHUIZE, 1998; VOSS ET AL., 2000).

The objectives of the present work were to investigate the sources of settling POM and to evaluate the connection between the water column particles and sedimentary organic matter in the Gulf of Lions (W Mediterranean) using sediment trap experiment and ^{13}C isotope analysis. This study was performed in the frame of EUROMARGE-NB programme (CANALS ET AL., 1996).

MATERIALS AND METHODS

Samples

Settling particles were collected with a mooring devices (Figure 1) equipped with two time-series sediment traps (0.125 m^2 collecting area, 12 receiving cups, PPS3 Technicap) and two Aanderaa RCM7 current meters.

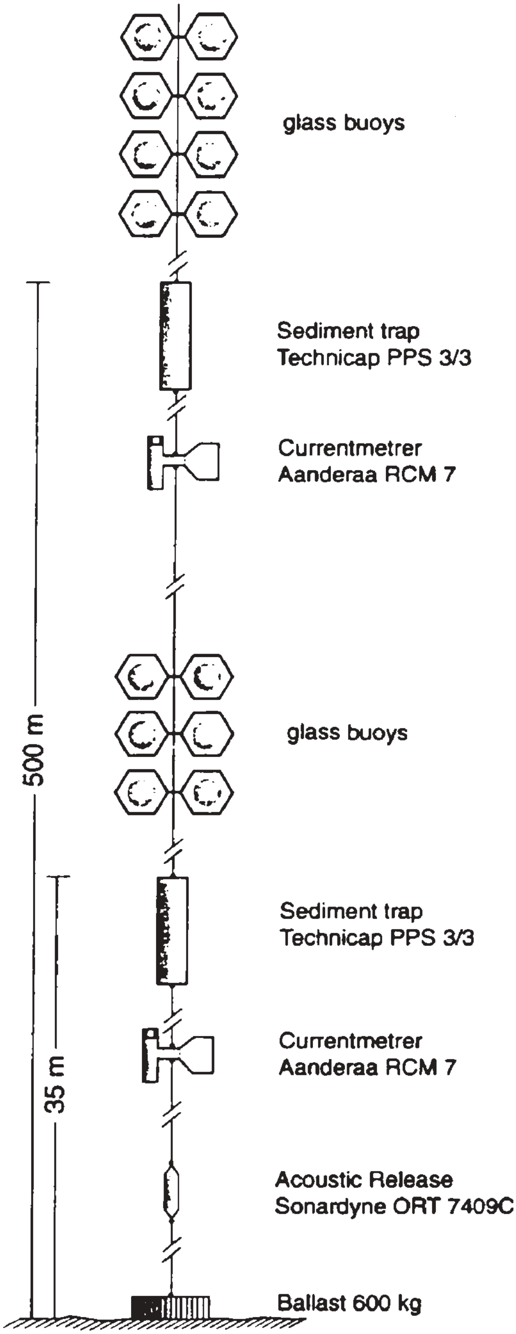

Figure 1. Sediment trap array configuration. The bottom trap was located 35 m above the bottom (mab) and the midwater one at 500 mab.

Slika 1. Kofiguracija lovilcev sedimentirajočih delcev, ki so bili postavljeni 35 m in 500 m nad dnom (mab).

They were deployed in the northwestern Mediterranean between Marseilles and the Balearic Island at the depths of 30 m and 500 m above the bottom (mab) (Figure 2). The $\delta^{13}C_{org}$ analyses were performed on sediment trap samples collected biweekly or monthly at seven sampling stations, US 22, US 23, US 24, US 30, EC 3, EC 8 and EC 9, from October 1993 to October 1994. Trap sample tubes were filled with 5 % formaldehyde solution buffered to pH = 7.5-7.8 in GF/F filtered seawater to prevent organic degradation during trap deployment.

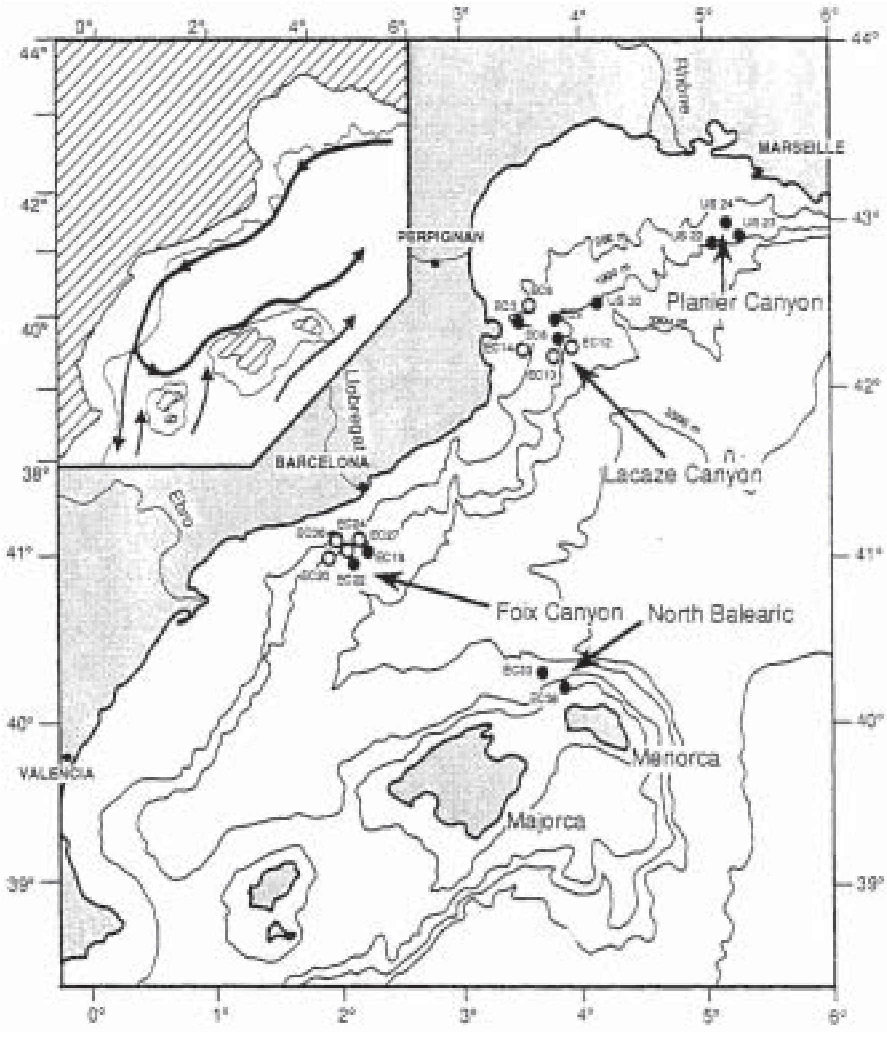

Figure 2. Locations of sampling stations with the main current system in the Gulf of Lions – North Balearic basin.

● Surface sediment and trap mooring

○ Surface sediment only

Slika 2. Lokacije postaj s prikazom smeri glavnega morskega toka v področju Lyonskega zaliva – S Balearski bazen.

Sediment samples, down to the depth of 20 cm, were collected using box corer at sampling stations indicated in Figure 2.

ANALYSES

In the laboratory, the nektonic organisms were removed from samples using wet sieving through 1 mm nylon mesh and the <1 mm organisms were eliminated by hand under microscope (HEUSSNER ET AL., 1990). The samples were then divided into several aliquots using a precision wet splitter.

Four subsamples were filtered through a 0.45 mm Millipore filters, rinsed with distilled water and dried at 40 °C for 24 hours to determine the dry weight. Organic carbon contents (% OC) were determined after decarbonation with 1 M HCl (HEDGES AND STERN, 1984) using Carlo Erba mod. 1108 CHNS analyzer. Weight percentages of total nitrogen (% TN) were determined similarly, but without acidification. Analyses of ^{13}C isotopic composition ($\delta^{13}C_{org}$) were performed with an Europa 20-20 mass spectrometer and the results expressed in ‰ from the V-PDB standard (COPPLEN, 1994). The precisions, based on replicate analyses were ±3 % for % OC and % TN, and ±0.2 ‰ for $\delta^{13}C_{org}$ values, respectively.

RESULTS AND DISCUSSION

^{13}C variations

The $\delta^{13}C$ values of settling organic matter in all studied traps revealed temporal variations (Figure 3a, b). Lower $\delta^{13}C$ values, around or below -22 ‰, were typical for late autumn and winter while higher values were characteristic for spring and late autumn – winter periods. These variations implied that the settling organic matter reflects planktonic marine (autochthonous) and terrigenous (allochthonous) imprints. Other interpretations, including temperature induced differences in C isotope fractionation (FONTUGNE AND DUPLESSY, 1981), differences in phytoplankton species and groups (CIFUENTES ET AL., 1988; FRY AND WAINRIGHT, 1991), aqueous CO_2 concentrations (RAU ET AL., 1992; OSTROM ET AL., 1997), seem less probable because $\delta^{13}C$ analyses in surface sediments in the study area revealed similar values (Table 1). The higher $\delta^{13}C_{org}$ values observed in spring and in late summer were a consequence of phytoplankton blooms (MONACO ET AL., 1999). Spring and summer phytoplankton blooms are mostly diatomaceous followed in autumn by enhanced grazing activity of zooplankton producing faecal pellets, and foraminifers (MONACO ET AL., 1999).

Variations in the C isotopic composition of phytoplankton have been attributed to changes in growth rates and in dissolved CO_2 (FRY AND WEIRIGHT, 1991; FRY, 1996; LAWS ET AL., 1995). Isotopic fractionation during phytoplankton production occurs during diffusion of CO_2 into the cell and especially during fixation by the photosynthetic enzyme RuBP carboxylase. Lower concentrations of aqueous CO_2 reduced the $\delta^{13}C$ values of algal tissue. Some phytoplankton species may actively use bicarbonate, which is enriched in ^{13}C by approximately 8 ‰ relative to dissolved CO_2. In general, higher $\delta^{13}C_{org}$ values are an imprint of higher biological produc-

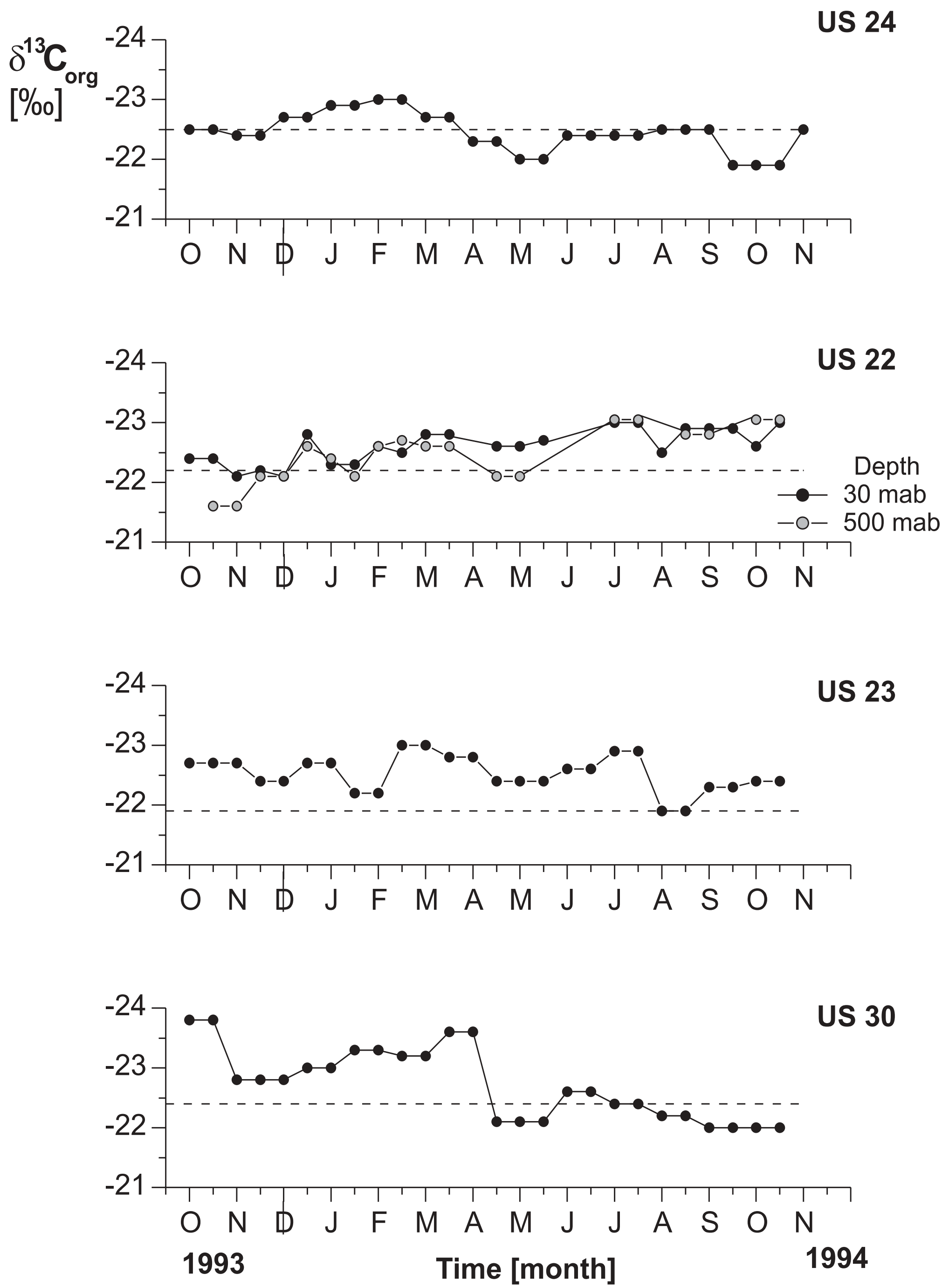

Figure 3a. Temporal variations of $\delta^{13}C_{org}$ values of settling particles at sampling stations (US).
Slika 3a. Sezonske variacije vrednosti $\delta^{13}C_{org}$ v sedimentirajočih delcih na vzorčevalnih postajah (US).

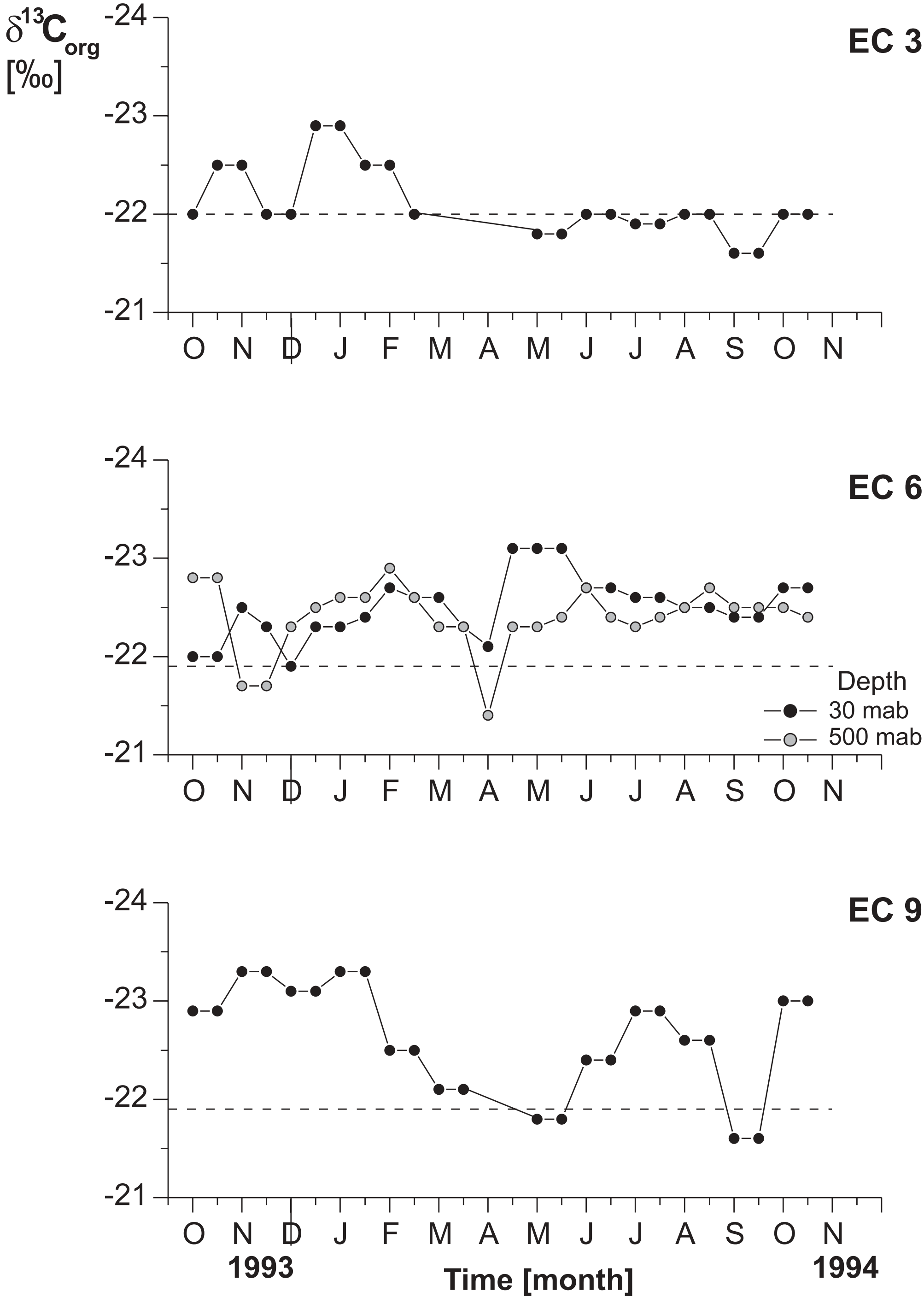

Figure 3. Temporal variations of $\delta^{13}C_{org}$ values of settling particles at sampling stations (EC).
Slika 3. Sezonske variacije vrednosti $\delta^{13}C_{org}$ v sedimentirajočih delcih na vzorčevalnih postajah (EC).

Table 1. Organic carbon, OC, and total nitrogen contents, TN, C/N = atomic organic carbon/total nitrogen (calculated directly from tabulated mean % OC and % TN) and $\delta^{13}C_{org}$ values in surface sediments (0-0.5 cm) at the sampling stations of the north Balearic basin.

Tabela 1. Koncentracije organskega ogljika, OC, in celokupnega dušika, TN, C/N = atomsko razmerje med organskim ogljikom/celokupnem dušiku (izračunano direktno iz povprečnih vrednosti % OC in % TN iz tabele) in $\delta^{13}C_{org}$ vrednosti v površinskem sedimentu (0-0.5 cm) na vzorčevalnih postajah v S Balearskem bazenu.

Station	Location	Depth (m)	OC (wt.%)	TN (wt.%)	C/N	$\delta^{13}C_{org}$ (‰)
EC 3	Lacaze Head (traps site)	600	0.94	0.07	15.7	-22.0
EC 6	Lacaze Axis (traps site)	1015	0.77	0.06	15.0	-21.9
EC 8	Lacaze North open-slope	315	0.39	0.05	9.1	-20.8
EC 9	Lacaze North open-slope (traps sites)	806	0.69	0.06	13.5	-21.9
EC 12	Lacaze Axis	1270	0.62	0.04	18.1	-20.3
EC 13	Lacaze South open-slope	760	0.74	0.06	14.4	-22.6
EC 14	Lacaze South open-slope	300	0.48	0.04	14.0	-22.6
EC 17	Foix East open-slope (traps site)	1105	0.79	0.08	11.6	-22.5
EC 19	Foix East open-slope (traps site)	1121	0.74	0.09	9.6	-22.4
EC 20	Foix East open-slope	850	0.84	0.08	12.3	-21.9
EC 22	Foix Axis (traps site)	1365	0.46	0.04	13.5	-22.5
EC 25	Foix Axis	1020	0.87	0.08	12.7	-23.0
EC 30	Foix Axis	656	0.86	0.07	14.4	-22.9
EC 34	North Balears Axis (traps site)	1230	0.68	0.06	13.3	-21.7
EC 36	North Balears open-slope (traps site)	653	0.56	0.07	9.4	-21.7
US 22	Planier Axis (traps site)	1098	0.62	0.23	3.2	-22.2
US 23	Planier open-slope (traps site)	727	0.71	0.10	8.3	-21.7
US 24	Planier Axis (traps site)	637	0.92	0.07	15.4	-22.5
US 30	Sete Axis (traps site)	1155	0.61	0.05	14.3	-22.4

tion in the water column, including faecal pellets and marine snow. Comparing the $\delta^{13}C_{org}$ values of settling POM at the station EC6 30 mab to that from 500 mab reveals similar temporal fluctuations, with a phytoplanktonic $\delta^{13}C_{org}$ signal of -21.5 ‰ observed about two weeks before at the shallower station.

Sources of organic matter

A simple two end-member mixing equation was used to calculate the terrigenous fraction of the settling POM (F_t)

$$\delta^{13}C_{org} = F_t\delta^{13}C_{org,t} + F_m\delta^{13}C_{org,m}$$

and

$$F_t + F_m = 1$$

where $\delta^{13}C_{org,t}$ and $\delta^{13}C_{org,m}$ are the isotopic values for terrestrial and marine end-members, respectively and F_m is marine fraction of the settling POM. The calculated F_t is highly sensitive to the selection of the end-member values. Despite the unknown $\delta^{13}C_{org}$ values of various planktonic sources, i.e.,

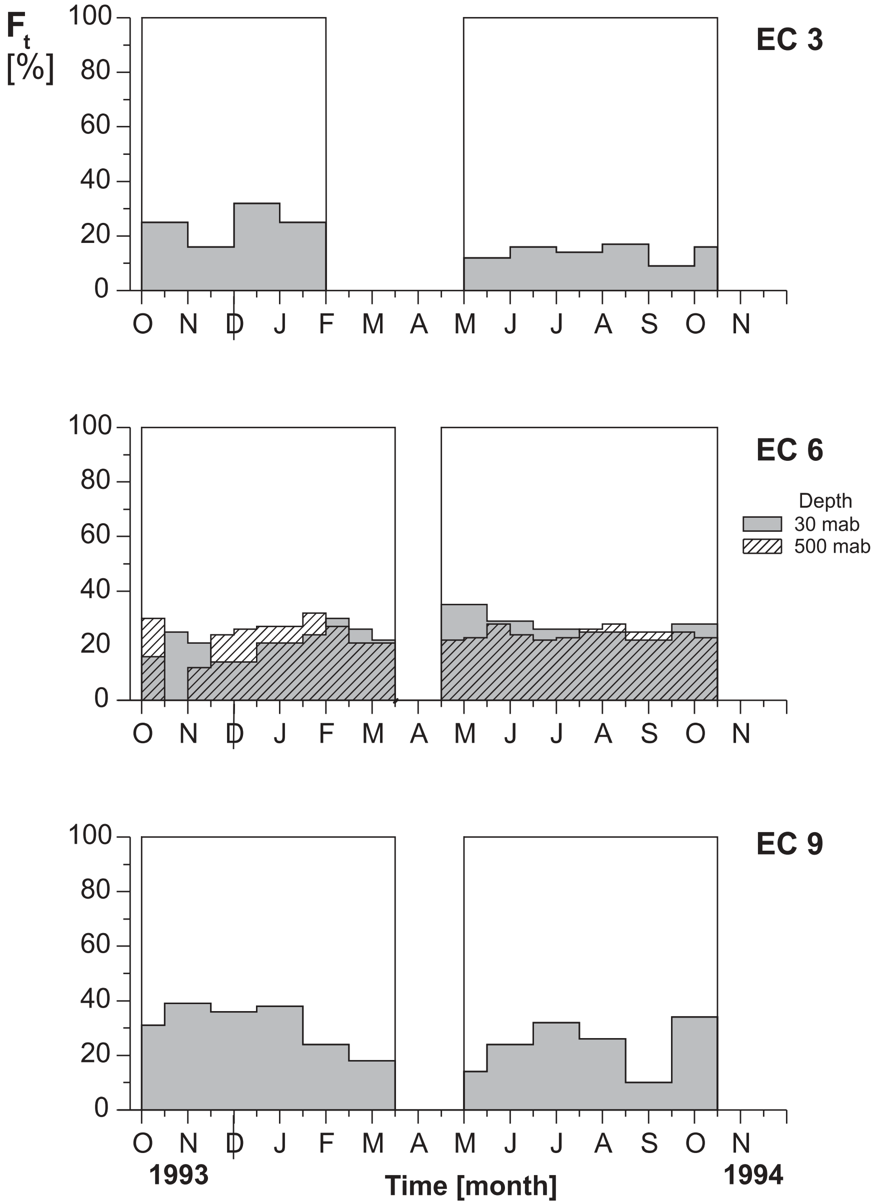

Figure 4a. Temporal variations of relative contribution of terrigenous (F_t) organic matter fraction in the settling matter at sampling stations (EC).
Slika 4. Sezonske variacije prispevka terigene organske snovi (F_t) k sedimentirajoči organski snovi na vzorčevalnih postajah (EC).

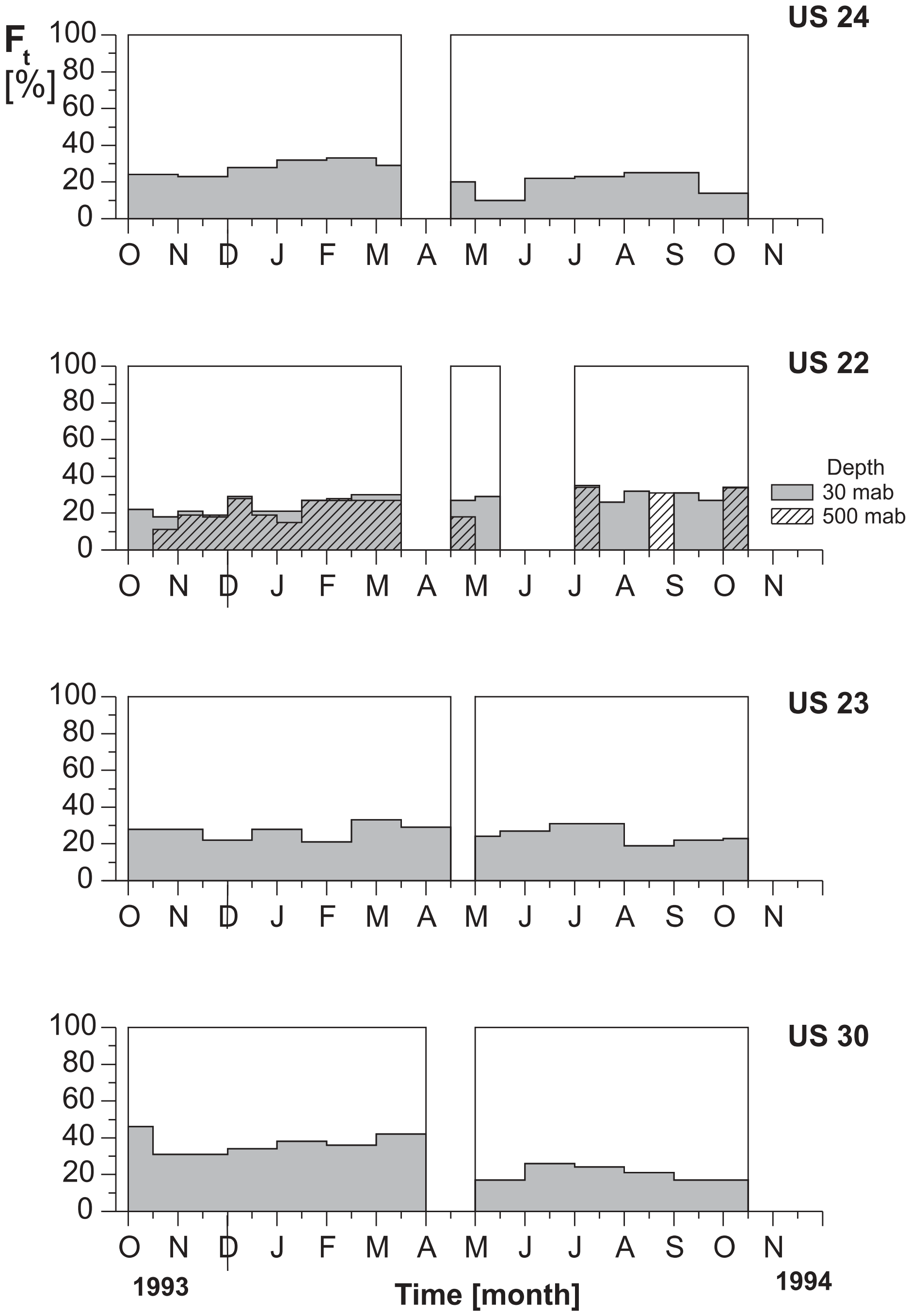

Figure 4b. Temporal variations of relative contribution of terrigenous (F_t) organic matter fraction in the settling matter at sampling stations (US).

Slika 4. Sezonske variacije prispevka terigene organske snovi (F_t) k sedimentirajoči organski snovi na vzorčevalnih postajah (US).

blooms, and terrestrial organic input in this area, it is reasonable to use an average $\delta^{13}C_{org}$ value of river POM of -27 ‰, and marine POM of -20 to -21 ‰, respectively. It emerges that the F_t in autumn-winter period would average about 1/3 but dropped down to < 20 % in other periods. Autumn and winter are characterized by higher river inflows (MONACO ET AL., 1990) reflected in a higher contribution of terrigenous POM and lower C_{org} flux (BUSCAIL ET AL., 1996). Comparing the data from different traps, it appears that the contribution of terrigenous settling POM was the highest at stations US30 and EC9 in the SW part of the Gulf of Lions.

This observation may be explained by the origin of the whole shelf, and its distribution, which is affected by the cyclonic circulation of the water, masses (Figure 2) in accordance with E-W gradient of the suspended particulate matter (MONACO ET AL., 1999). The reduced biogenic contribution observed in this area was mainly the consequence of dilution by the input of terrigenous material (BUSCAIL ET AL., 1996). However, in all periods, the settling POM was largely of marine origin. The prevailing presence of marine sedimentary organic matter in this area is supported by $\delta^{13}C_{org}$ values in surface sediments ranging between -20.3 ‰ and -23.0 ‰ (Table 1). On the other hand, the $\delta^{13}C_{org}$ values in settling particles in the Gulf of Lions across the continental slope off Marseilles in spring 1997 indicate higher, terrigenous contribution, approx. 50 % (KERHERVE ET AL., 2001) in the period of low nutrient input and no phytoplankton blooms. The comparison with the South Adriatic Pit (MISEROCCHI ET AL., 1999) shows that the terrigenous contribution is up to 2-fold higher in the southern Adriatic (in summer) than that in the Gulf of Lions. The marine contribution in the near-bottom samples collected in the trap NBI6 was higher than in the mid-water trap during the sampling period from December-February. This was probably due to differential settling patterns of particles dominated by lateral advection, which provides preferentially larger biogenic particles to the deeper trap (MONACO ET AL., 1990).

Additionally, stable carbon isotope compositions of the sedimentary organic matter provide information on the both origin and spatial uniformity of the associated organic matter. The organic mixtures in these sediments are remarkably uniform in their stable carbon isotope composition ($\delta^{13}C$ values ranged from -20.3 to -23.0 ‰), and hence in their percentage of marine and terrestrial organic matter. Given the values used for different end-members above, sediments appear to contain between 10 to 30 % of terrestrial organic matter.

To compare the magnitude of isotope discrimination between sinking particles and sediments in various regions, the isotopic change ($\Delta^{13}C_{org}$) between sinking particles and surface sediment at the same location was calculated. The $\Delta^{13}C_{org}$ showed relatively small variations, ranging between -1.4 and +0.6 ‰, in accordance with results from shallower marine areas reported by several workers (FISCHER ET AL., 1998; NAKANISHI AND MINAGAWA, 2003). The likely reason for observed differences may be the difference of trapping efficiency of different laterally transported allochthonous organic particles depending on the water condition and circulation.

Conclusions

1.) The $\delta^{13}C_{org}$ values of sediment trap samples suggest a seasonal cycle of phytoplankton production. During spring and summer, there was an input of phytoplanktonic organic matter. Phytoplanktonic organic matter was transported to bottom rather rapidly, in about two weeks time. Winter was more characterized by an input of terrigenous remains, however the settling organic matter throughout the entire year was largely of marine origin.

2.) The $\delta^{13}C_{org}$ values of surface sediments confirm the marine provenance of sedimentary organic matter in this area. $\Delta^{13}C_{org}$ are mainly controlled by bottom depth and the discrimination in the particle sinking process seems to be an optional factor depending on the water condition and circulation.

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^{13}C kot indikator izvora sedimentirajoče in sedimentirane organske snovi v Lyonskem zalivu (Z Sredozemsko morje)

Povzetek: V okviru raziskovalnega programa EUROMARGE-NB smo v obdobju oktober 1993 – oktober 1994 raziskovali izvore sedimentirajoče organske snovi v Lyonskem zalivu (Z Sredozemsko morje) s pomočjo lovilcev sedimentirajočih delcev in analiz $^{13}C_{org.}$ Posebej nas je zanimala povezava med izvorom sedimentirajočih organskih delcev in organsko snovjo v površinskih sedimentih.

Sezonske variacije vrednosti $\delta^{13}C_{org}$ v sedimentirajočih delcih so se približno ujemale z variacijami fitoplanktonske produkcije (biomase). V pomladnem in letnem obdobju smo opazili vnos fitoplanktonske organske snovi, ki se je dokaj hitro, približno v obdobju dveh tednov, sedimentirala na morsko dno. V zimskem obdobju je bil delež kopenske organske snovi večji, čeprav je bila sedimentirajoča organska snov vseskozi pretežno morskega izvora. Vrednosti $\delta^{13}C_{org}$ v površinskem sedimentu potrjujejo pretežno morski izvor sedimentirane organske snovi v raziskovanem področju. Razlike med vrednostmi $\delta^{13}C_{org}$ v sedimentirajočih delcih in površinskem sedimentu ($\Delta^{13}C_{org}$), so majhne in pretežno odvisne od globine vodnega stolpca, kjer prihaja do razlik v sedimentaciji različnih delcev.