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Stable isotopes ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) in settling organic matter of the northwestern Mediterranean Sea: biogeochemical implications

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Abstract − Within the framework of the High Frequency Flux (HFF) experiment (MATER programme), time-series sediment traps have been deployed for two months on the continental slope off Marseilles to measure downward particle fluxes at a high frequency sampling rate (two and six days). Combined isotopic analyses of carbon and nitrogen have been performed on selected samples. Both isotopic tracers have been used for the first time on organic material of the Mediterranean Sea (Gulf of Lions) to determine the main biological sources and to address the biogeochemical processes that affected this material. Settling particles were characterised by very low values of $\delta^{15}N$ (near 0‰) and $\delta^{13}C$ (near –24.5‰) that indicate the existence of a mixed material with two sources that differ according to the considered element (C or N). The terrestrial source slightly dominates the carbon pool because of its higher C:N ratio, whereas the nitrogen pool may mostly originate from N_2-fixing cyanobacteria ($\delta^{15}N \simeq 0$‰, low C:N ratio). These preliminary data suggest that dissolved atmospheric N_2 may act as a significant new nitrogen source in the Mediterranean Sea.

Résumé − Les isotopes stables ($^{13}C/^{12}C$ et $^{15}N/^{14}N$) du matériel organique en Méditerranée occidentale: implications biogéochimiques. Dans le cadre de l'expérience '*High Frequency Flux*' (HFF, programme MATER), des pièges à particules ont été déployés sur la pente continentale au large de Marseille pendant deux mois (16 mars–2 mai 1997) afin de mesurer avec une fréquence d'échantillonnage élevée les flux descendants de particules. Des analyses isotopiques combinées du carbone ($^{13}C/^{12}C$ ou $\delta^{13}C$) et de l'azote ($^{15}N/^{14}N$ ou $\delta^{15}N$) ont été effectuées sur les échantillons comportant suffisamment de matériel. Ces deux isotopes stables sont utilisés pour la première fois sur du matériel organique collecté par piège à particules en Méditerranée, afin de déterminer les principales sources biologiques qui le composent et de mieux cerner les processus biogéochimiques qui l'affectent. Le matériel collecté se caractérise par de faibles valeurs de $\delta^{15}N$ (proches de 0‰) et $\delta^{13}C$ (proches de –24‰) qui s'écartent des distributions typiques rencontrées en milieu tempéré et se rapprochent de celles observées en Antarctique. Les processus responsables d'une telle distribution isotopique sont cependant différents entre ces deux écosystèmes. Dans le Golfe du Lion, les résultats semblent indiquer deux sources prépondérantes, distinctes selon l'élément considéré (C ou N). Ainsi, la source biologique terrigène dominerait légèrement dans le pool de carbone du fait de sa forte proportion en carbone (rapport C:N élevé), tandis que le pool d'azote serait essentiellement constitué de cyanobactéries ($\delta^{15}N \simeq 0$‰, faible rapport C/N) fixatrices d'azote atmosphérique dissous. Ces données préliminaires suggèrent ainsi un rôle important de cette

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source azotée inorganique (N_2) dans le fonctionnement d'un écosystème oligotrophe tel que la Méditerranée.

stable isotopes / isotopic tracers / settling particles / nitrogen fixation / Gulf of Lions

isotopes stables / traceurs isotopiques / particules en sédimentation / fixation d'azote / Golfe du Lion

1. INTRODUCTION

Continental margins play an important role in the global carbon cycle and focussed the attention of several international programmes over the last decade (Biscaye et al., 1994; Martin and Milliman, 1997; Monaco et al., 1999). These coastal areas, acting as a transit zone between land and open ocean, show more complex and variable processes than other oceanic systems. The northwestern Mediterranean Sea in particular has been the site of a continuous experimental and modelling effort to understand the circulation and the biogeochemical processes occurring along its continental margin. In this context, the studies carried out during the ECOMARGE and EUROMARGE programmes highlighted the importance of particle transfer and its seasonal and interannual fluctuations (Heussner et al., 1990b; Monaco et al., 1990, 1999a).

Within the framework of the European MTP II–MATER project (MAST 3), a multidisciplinary High Frequency Flux (HFF) experiment was carried out off the continental shelf edge in the northwestern Mediterranean Sea for a period of two months. This experiment aimed at recording particle fluxes over short periods of time (days) and at a small spatial scale (km). It also provided an opportunity to simultaneously study natural variations of $^{15}N:^{14}N$ and $^{13}C:^{12}C$ ratios. These stable isotopes have been widely used to trace sources of particulate organic matter (POM) and its biogeochemical transformation through the water column (Altabet, 1996; Voss and Struck, 1997; Waser et al., 1997; Middelburg and Nieuwenhuize, 1998). Isotopic signals are produced when transformation processes cause isotopic fractionation between substrate and product. Variations of the carbon isotopic ratio in organic particles may result, among principal causes, from changes in the ambient temperature which affect the CO_2 content (Fontugne and Duplessy, 1981; Rau et al., 1997), from the type of autotrophic species (marine or terrestrial) or from the number of degradation processes that particles undergo through the successive trophic levels (Rau et al., 1983). However, in the case of our small-scale survey, it can be easily assumed that the CO_2 level and sea surface temperature remained quite constant. Therefore, $^{13}C:^{12}C$ ratios should be essentially affected by the biological source of the particles and the transformation processes they underwent during their transfer. Regarding nitrogen, isotopic changes in a marine system are mainly explained by the dynamics of inorganic nitrogen compounds (NO^{3-}, NH^{4+}, N_2) in surface waters (Wada et al., 1987; Altabet, 1988; Liu et al., 1996; Jinping et al., 1997) and, to a lesser extent, by the trophic structure of the ecosystem (Montoya et al., 1990; Rau et al., 1983; Minagawa and Wada, 1984). Most isotopic variations in marine POM first consist in a depletion of ^{13}C and ^{15}N that is imparted during the initial formation of organic matter from inorganic precursors (primary production). Then, a stepwise enrichment of ^{13}C and ^{15}N occurs in particles along the food chain (Altabet, 1996).

So far, no nitrogen isotopic analyses have been performed on the contemporaneous organic material from the Mediterranean Sea, and the few existing carbon isotopic data are restricted to the Adriatic Sea (Faganelli et al., 1988). This preliminary work represents therefore the first study on both carbon and nitrogen stable isotopes in particulate matter of the Mediterranean Sea. It aims at describing the set of isotopic data obtained from samples collected within two of the three radials investigated during the HFF experiment. It also intends to highlight some major biogeochemical features that occurred during this two-month survey.

2. MATERIALS AND METHODS

Time-series sediment traps (Technicap model PPS3, 12 receiving cups) were moored along three parallel transects of three stations each across the continental slope off Marseilles (*figure 1*). According to the water depth, each mooring line was equipped with one to three traps, from subsurface to near-bottom (*figure 2*). Sampling intervals were set at two days for the first six samples of the time series (16–27 March 1997) and at six

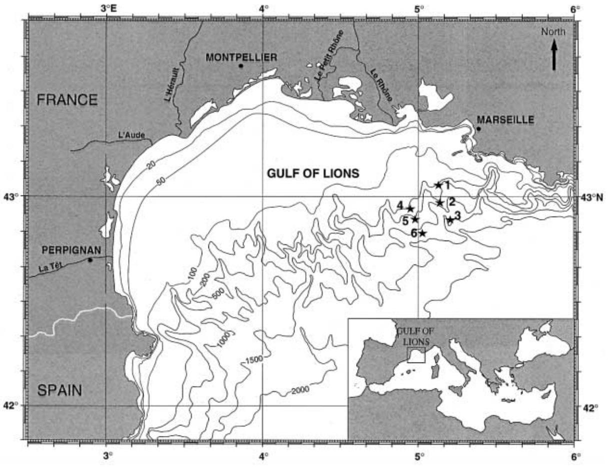

Figure 1. Study site and location of sediment traps in the Gulf of Lions.

days for the last six samples (28 March–2 May 1997). Results presented here concern more or less complete series, resulting from low sample quantities, obtained in traps from the eastern and middle transects.

All trap samples were collected in polyethylene cups filled with a buffered 5% formaldehyde solution. After recovery, the pH in the supernatant of the receiving cups was checked and if necessary corrected. Samples were then stored at 2 °C until processing. A detailed description of the preliminary treatment (removal of swimmers and subsampling) is given in Heussner et al. (1990a). Settling particles were separated from solution by filtration on precombusted GF/F filters (47-mm diameter). They were dried and pre-treated with 1 N HCl to remove carbonate before isotopic analysis. Carbonate-free samples were converted to gases by combustion in an Elemental Analyser (Fisons) connected to a Finnigan MAT-252 mass spectrometer by a ConFlo II interface (Finnigan). Organic carbon and total nitrogen elemental and isotopic abundance were determined from the residues of CO_2 and N_2 gases. The reference gases were pure N_2 and CO_2 from cylinders respectively calibrated against air nitrogen and PDB carbonate. Isotope abundance of ^{13}C and ^{15}N were conventionally expressed as per mil deviations from standards:

$$\delta^{13}\,\mathrm{C}(\text{‰}) = (R_{\mathrm{sample}}/R_{\mathrm{PDB}} - 1) \times 1\,000;$$

$$\delta^{15}\,\mathrm{N}(\text{‰}) = (R_{\mathrm{sample}}/R_{\mathrm{atm.N2}} - 1) \times 1\,000;$$

$$\text{and } R = {}^{13}\mathrm{C}:{}^{12}\mathrm{C} \text{ and } {}^{15}\mathrm{N}:{}^{14}\mathrm{N}$$

The analytical precision (standard deviation) of these measurements was $\simeq$ 0.1‰ for both δ^{13}C and δ^{15}N.

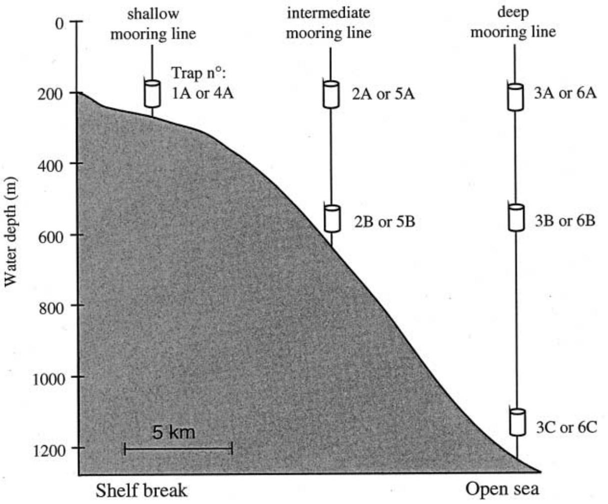

Figure 2. Deployment configuration of HFF sediment traps within a cross-slope transect.

3. RESULTS

Time-series mass fluxes, C:N ratios and carbon and nitrogen stable isotopes from samples collected at stations 1, 2, 3 (eastern transect) are presented as an example to show the overall temporal variability (*figure 3*). Total mass fluxes varied between 9 and 1 983 mg·m^{-2}·day^{-1} but the low values (< 1 000 mg·m^{-2}day^{-1}) largely dominated. No significant temporal and depth trends in mass fluxes were observed during the experiment, and traps fluctuated independently from each other. However, our data showed that total mass fluxes did not significantly decrease with depth, which implies the occurrence of lateral transport of particles, as it has been described for most trap experiments on continental margins (Monaco et al., 1990; Iseki et al., 1995; Heussner et al., 1999). C:N ratios were comprised between 6.1 and 12.3. In computing the average C:N ratio of sinking particles at each trap position, the C:N ratio for individual samples was weighted both for mass flux and for the duration of sample collection (*table I*). Contrary to mass fluxes, time and flux-weighted mean ratios showed a slight but significant vertical trend with higher means (> 9) in deep and near-bottom traps. Temporal variations of C:N were quite homogeneous (*figure 3*) and, moreover, the rare C:N changes were not related with fluctuations in mass fluxes. These results suggest that the collected material remained quite constant in nature throughout the experiment despite the large mass flux variations observed.

Isotopic values of trapped material ranged from –26.2 to –22.4‰ for δ^{13}C and from –2.7 to +3.3‰ for δ^{15}N. Most data varied, however, within a narrower range (–24.5 to –23.5‰ and –2 to +2‰, respectively) as exemplified by the time-series from the first transect (*figure 3*). Temporal variations of isotopic ratios in settling particles, recorded at various stations and depths, were further characterised by their independent evolution. As for the C:N ratios, isotopic variations were not concomitant with variations of mass fluxes. The spatial trend was roughly marked by the relative homogeneity of the isotopic values in deep traps, especially for δ^{13}C. The highest time and flux-weighted means of δ^{13}C were recorded in surface traps and towards the open-sea, although the difference between means was low (*table I*). On the other hand, the averaged δ^{15}N values did not show pronounced spatial trends.

4. DISCUSSION

The nitrogen isotopic ratios presented here are the first values ever obtained from settling particles of the Mediterranean Sea. Our δ^{13}C and δ^{15}N data were characterised by low ratios of nitrogen and carbon isotopes. When plotted against a compilation of values obtained from particulate organic matter collected throughout the world ocean (*figure 4*), they reveal an unusual distribution of Mediterranean samples, which makes them very close to ratios observed in Antarctic samples.

4.1. Nitrogen origin

So far very low values of δ^{15}N were found in Antarctic waters, although the environmental conditions of this marine system are totally different from the Mediterranean. In the Antarctic, the low δ^{15}N values were explained by intense and steady inputs of upwelled nutrients, generating high contents of nitrate in surface waters (Tréguer and Jacques, 1992). In general, light isotopes (^{14}N and ^{12}C) are more easily assimilated by living organisms than heavier isotopes (^{15}N and ^{13}C). Therefore, the preferential incorporation of light ^{14}[N]-NO_3^- by phytoplankton entrains a depletion of ^{14}[N]-NO_3^- in seawater and an increase in δ^{15}N of the residual nitrate. The constant and abundant supply of nutrients in Antarctic surface waters compensates the δ^{15}N increase of the residual nitrate and thus induces the low values of δ^{15}N found in organic particles. Moreover, the isotopic fractionation during the NO_3^- assimilation by phytoplankton (corresponding to the difference in δ^{15}N between the inorganic source and the organic product) is highest for diatoms that dominate the Antarctic ecosystem (Montoya and MacCarthy, 1995).

The oligotrophic Mediterranean ecosystem does not receive such strong nutrient inputs. The chemical surveys, performed on a weekly basis during HFF, showed nitrate contents < 1 μM in surface waters, rising to a maximum of 6 μM below the nitracline (Diaz et al., 2000). According to this study, NH_4^+ availability is much lower than that of NO_3^-, although the NH_4^+ uptake rate (ρNH_4^+) by phytoplankton generally represents more than 60% of the total (NO_3^- + NH_4^+) integrated nitrogen uptake in surface waters. Excreted NH_4^+ has been shown to be depleted in ^{15}N (Checkley and Miller, 1989), and the low values of δ^{15}N found in settling particles may consequently be induced by the preferential use of ammonium as nitrogen source by the phytoplankton (Dortch, 1990). However, several points could refute this hypothesis of NH_4^+ assimilation. First, NH_4^+-uptake rate (ρNH_4^+) calculations should be cautiously regarded due to the presence of interfering bacteria which may strongly overestimate ρNH_4^+ values (Kirchman et al., 1994). Second, the isotopic fractionation occurring during NH_4^+ assimilation is variable and decreases with NH_4^+ depletion to tend towards 0‰ (Pennock et al., 1996). Ammonium contents were found to be very low (< 20–240 nM) during the HFF survey (Diaz et al., 2000). Therefore, the resulting extreme low fractionation in ammonium uptake by phytoplankton is unlikely to explain our low δ^{15}N values in trapped material. Finally, NH_4^+ contents were heterogeneous in time and space during the experiment whereas all δ^{15}N values of trapped material remained extremely low (close to 0‰).

Therefore, an alternative process responsible for such low δ^{15}N values could be nitrogen (N_2) fixation by diazotrophic organisms such as cyanobacteria, as it has been found in the oligotrophic East China Sea (Minagawa, unpublished data). This picoplanktonic group has been ignored for a long time and its study in marine

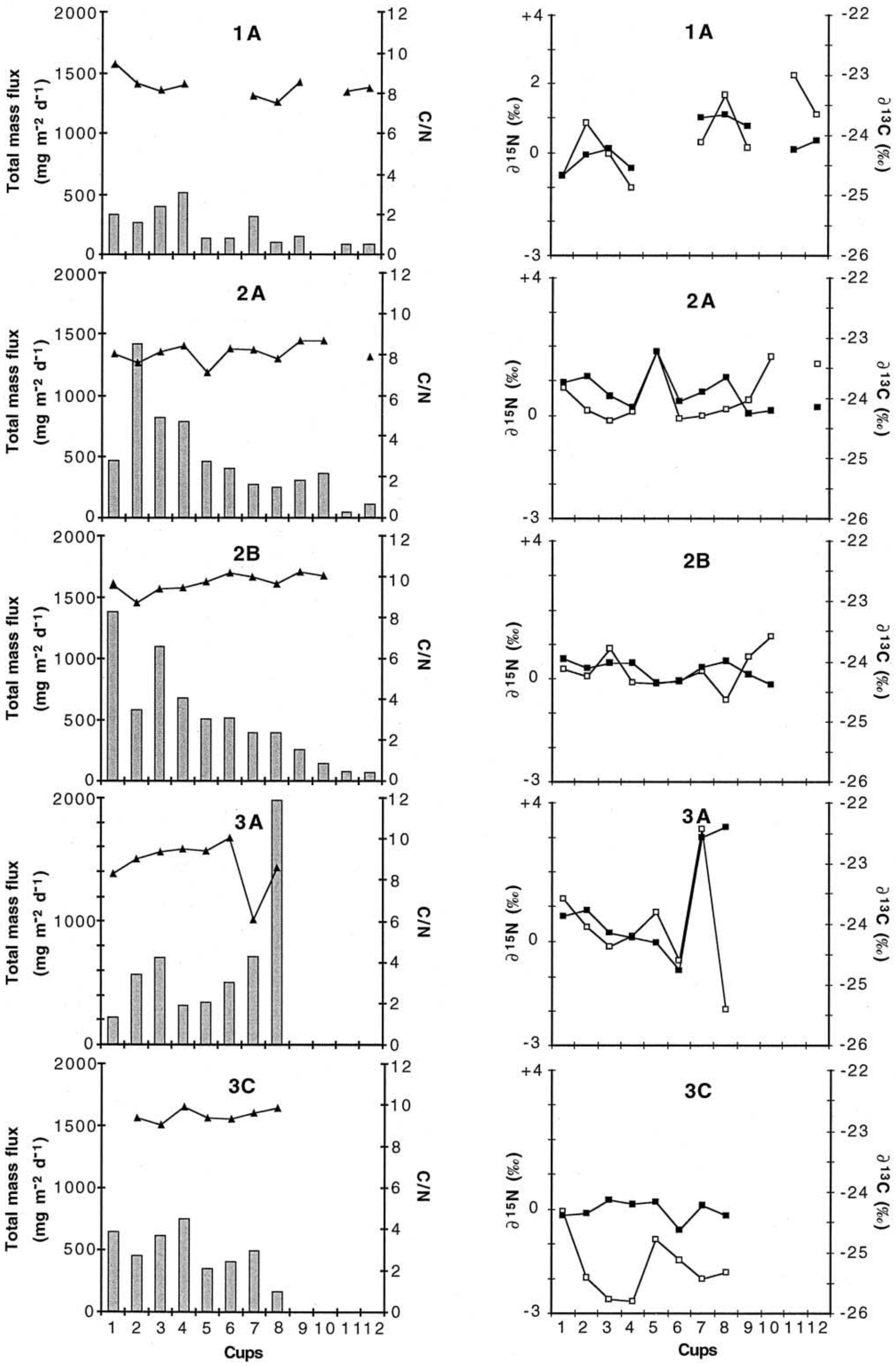

Figure 3. Time-series plots of a) total mass flux (histogram) and C:N ratio (curve) and b) carbon (δ^{13}C, black squares) and nitrogen (δ^{15}N, open squares) isotopic ratios for the easternmost HFF transect (lines 1 to 3). Sampling period was from 16 March 1997 to 2 May 1997, with the first six cups collecting material at a sampling rate of two days and the last six cups at six days.

Table I. Means of total mass fluxes, and time and flux-weighted means of C:N ratios, $\delta^{15}N$ and $\delta^{13}C$.

				Time and flux-weighted mean		
No.	Water depth (m)	Trap depth (m)	Total mass flux mean ($mg \cdot m^{-2} \cdot day^{-1}$)	C:N ratio	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
1A	242	213	167	8.3	+0.3 (n = 9)	–24.1 (n = 9)
2A	662	225	316	8.1	+0.5 (n = 11)	–23.9 (n = 11)
2B		633	350	9.7	+0.2 (n = 10)	–24.1 (n = 10)
3A	1279	293	895	8.3	–0.4 (n = 8)	–22.9 (n = 8)
3C		1250	430	9.5	–1.9 (n = 8)	–24.3 (n = 8)
4A	279	250	250	8.2	+0.6 (n = 6)	–23.6 (n = 6)
5B	651	565	595	10.3	–0.3 (n = 11)	–25.0 (n = 7)
6C	1237	1213	399	9.3	–0.1 (n = 11)	–24.5 (n = 8)

(*n* = number of samples)

ecology started with the recent introduction of epifluorescence microscopy. N_2 fixation is accompanied by little or no isotopic fractionation and thus, combined inputs of nitrogen by this pathway have $\delta^{15}N$ values close to those of atmospheric N_2 (–2 to +1‰) (Liu et al., 1996; Minagawa and Wada, 1986). The seasonal occurrence of cyanobacteria in the Gulf of Lions has been previously reported (Lantoine, 1995). Cyanobacteria are essentially abundant during spring and represent up to 60–80% of the total picoplankton. However, diatoms usually dominate during spring and picoplankton contributions account for less than 30% in this area (Lantoine, 1995).

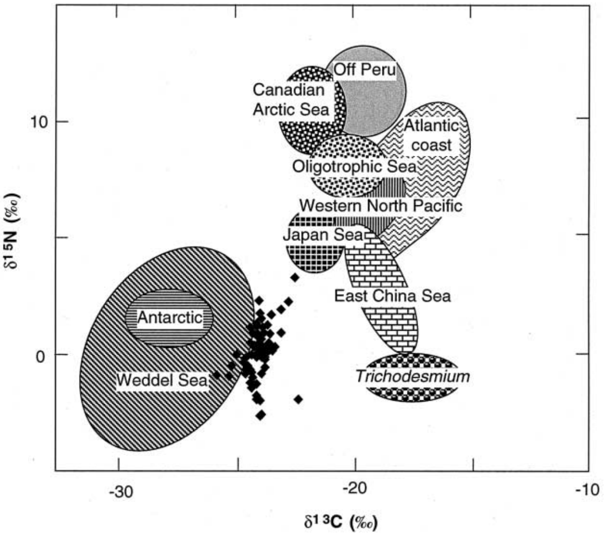

Figure 4. Isotopic distribution ($\delta^{13}C$ and $\delta^{15}N$) of the settling organic matter from the Gulf of Lions (black diamonds) and particulate organic matter from various study areas (from: Minagawa, 1995).

During the HFF experiment, no high nutrient inputs were upwelled and no phytoplankton blooms occurred in the study area (Diaz et al., 2000). The relative abundance of picoplankton and thus of bacteria was therefore supposed to be higher than expected at this season, which may explain our $\delta^{15}N$ values close to 0‰. This result argues in favour of a new nitrogen source (dissolved atmospheric N_2) introduced by cyanobacteria into the euphotic zone of the Gulf of Lions. Because cyanobacteria are more abundant in typical Mediterranean oligotrophic waters (Lantoine, 1995), we suggest that this new nitrogen source could reach a high relative proportion in the Mediterranean Sea, as it has been suggested by Grüber and Sarmiento (Grüber and Sarmiento, 1997) at a global scale from their quasi-conservative tracer study.

4.2. Carbon origin

Unlike nitrogen isotopes, most of the variation in $\delta^{13}C$ of POM in the ocean results from variations in the fractionation factor for carbon fixation and not through changes in the isotopic composition of nutrients. The low $\delta^{13}C$ values recorded in Antarctic waters might be explained by effects on C-fixation processes at low water temperature and the related high CO_2 availability to phytoplankton (Rau et al., 1982; Wada et al., 1987). The average water temperature (around 13.5 °C) observed at the HFF sites was obviously higher than that of Antarctic waters and thus could not induce our observed low $\delta^{13}C$ values.

So far, only limited investigations have been carried out on the carbon isotopic composition of organic particles in the Mediterranean Sea. Data obtained in the Northern Adriatic Sea displayed 1‰ higher δ^{13}C means than those recorded in this present study (Faganelli et al., 1988). Assuming a system with two main sources (marine and terrestrial) and using the same end-members as for the Adriatic sea (–21‰ and –28‰ for marine and terrestrial, respectively), we deduce that the trapped material collected during the HFF experiment is equally composed by these two sources.

Several studies (Wada and Hattori, 1976; Minagawa and Wada, 1986; Carpenter et al., 1997); reported that *Trichodesmium*, the most common diazotrophic cyanobacterium, has the lowest δ^{15}N (near 0‰) and the highest δ^{13}C (15–20‰) values among marine phytoplankton. Our δ^{13}C results, displaying lower values (mean δ^{13}C = –24.2‰ + –0.7‰), seem to contradict the assumption of a predominance of cyanobacteria during the experiment. However, *Trichodesmium* is not a common species in the Mediterranean. The ability to fix atmospheric nitrogen has been found in other marine cyanobacteria, such as, for instance, *Synechococcus* sp. (Mitsui et al., 1987), a major Mediterranean species (Lantoine, 1995). Therefore, unlike *Trichodesmium*, the δ^{13}C signature of the N-fixing cyanobacteria present during the HFF experiment may range within the normal δ^{13}C signature of phytoplankton (–18 to –22‰). The difference between the observed δ^{13}C values in trap samples and the δ^{13}C signature of Mediterranean N-fixing organisms would be thus reduced. It becomes then possible to explain this distance in δ^{13}C values by the difference in carbon and nitrogen contributions of both sources, marine and continental. The large contribution to phytoplankton of cyanobacteria in the Alboran Sea (Western Mediterranean) has been associated with low C:N ratios (Dachs et al., 1998). In the same way, the carbon contribution of cyanobacteria to the carbon biomass has been noticed as the lowest among picoplankton classes (Lantoine, 1995). Thus, low carbon contribution of cyanobacteria and high carbon contribution of terrestrial sources could result in the dilution of the δ^{13}C signature of cyanobacteria by material of terrestrial origin. The C:N ratios, mainly comprised between 8 and 10 in trap samples, support this idea of a mixing between two distinct sources. In this study, isotopic tracers (δ^{15}N and δ^{13}C) did, therefore, not necessarily corroborate with each other but brought complementary information on the main biological sources in both carbon and nitrogen cycles.

4.3. Spatial variations of δ^{15}N and δ^{13}C

The lowest weighted means of δ^{15}N were located in open-sea stations, especially at station 3. Most of this seaward trend could result principally from changes in the isotopic composition of the inorganic nitrogen source, suggesting that the contribution of N_2-fixing organisms is slightly enhanced for open-sea stations. This result is in accordance with previous observations in open-sea stations of the Gulf of Lions (Lantoine, 1995). With regard to δ^{13}C and C:N variations, weighted means showed a low horizontal and vertical gradient, which may be the result of a low shift in the composition of organic settling particles. The near-bottom transfer of terrigeneous particles (lowest δ^{13}C, highest C:N) could be superposed to the rising marine contribution (highest δ^{13}C, lowest C:N) in surface and seaward traps, as it has been previously observed in the same area during the ECORHONE survey (Monaco et al., 1999).

Trophic transfer of nitrogen leads to an approximate 3.5‰ upward shift between the food source and the consuming organisms. On the other hand, δ^{13}C seems to rise by a more modest 1‰ among the trophic chain. However, these changes, especially between phytoplankton and herbivores, are not yet fully known (Rau et al., 1983; Fry and Sherr, 1984; Minagawa and Wada, 1984). As the isotopic means did not show increased values in near-bottom traps but rather a low decrease, we suggest that transformation processes through the water column did not occur or at a lesser extent than shifts in the biological origin of the sinking particles. Thus, the diazotroph organisms rich in nitrogen compounds may quickly settle from the surface and induce the very low δ^{15}N for all traps during the duration of the experiment.

5. CONCLUSIONS

The preliminary isotopic analyses of carbon and nitrogen presented here suggest some interesting features regarding the biogeochemistry of organic particles in the northwestern Mediterranean Sea. The potential importance of N_2 fixation, suggested by the unexpectedly low δ^{15}N values observed during this high-frequency trap experiment, supports previous hypotheses based on the nitrogen budget of the Mediterranean Sea (Béthoux and Copin-Montegut, 1986; Béthoux et al., 1992, 1998). If the Mediterranean Sea is likely to represent a preferential site for atmospheric N_2 fixing, then future investigations focussing on the nitrogen cycle in this oligotrophic environment should take N_2 fixing into account. Our assumptions should, however, be confirmed by investigations on carbon and nitrogen isotopes within the other compartments of this marine system (nutrients, suspended matter, dissolved matter, sediments) and extended to larger scales.

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