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Christos Panagiotopoulos, Richard Sempéré. The molecular distribution of combined aldoses in sinking particles in various oceanic conditions. *Marine Chemistry*, 2004, 95 (1-2), pp.31-49. 10.1016/j.marchem.2004.07.005 . hal-04688929

**HAL Id: hal-04688929**

**<https://hal.science/hal-04688929>**

Submitted on 5 Sep 2024

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# The molecular distribution of combined aldoses in sinking particles in various oceanic conditions

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Received 7 January 2004; received in revised form 22 July 2004; accepted 22 July 2004  
Available online 29 December 2004

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## Abstract

Sinking particles were collected from different marine locations in the Southern Indian Ocean, Mediterranean Sea, and the upwelling (UPW) zone of Agadir Morocco using free-floating sediment traps set from 50 to 300 m. Aldose composition was determined using high-performance anion-exchange chromatography with pulsed amperometric detection following hydrolysis in 0.1 M HCl. Carbohydrate yields (PCHO-C/POC%) and C:N ratios were higher in the Mediterranean Sea samples (PCHO-C/POC=12.9±8.4%; C:N ratios=8.3±1.6; *n*=11) than in samples from the Southern Indian Ocean (PCHO-C/POC=3.6±0.94%; C:N ratios=5.7±0.59, *n*=7), indicating compositional differences in the bulk and sugar content of the collected particles. The molecular composition revealed that glucose was the most abundant monosaccharide in the Mediterranean Sea and upwelling zone samples (22–51 wt.% of the total aldoses), whereas ribose (17–39 wt.%) and galactose (10–27 wt.%) were the predominant aldoses in the Southern Indian Ocean samples. Similarly, deoxysugars (fucose+rhamnose) calculated on glucose-free basis were more abundant in particles from the Mediterranean Sea (18.8±5.6 wt.%, *n*=12) than those from the Southern Ocean samples (8.4±3.5 wt.%, *n*=7). These results suggest a non-uniform chemical composition of upper ocean sinking particles among oceanic provinces in terms of carbon, nitrogen, and sugar content. Such differences might be due to various biological species encountered in surface waters and/or to different status of degradation of recently produced sinking particles between Southern Ocean and Mediterranean Sea during the sampling periods. These results suggest that both high PCHO-C yields and high relative abundance of glucose do not necessarily reflect the presence of fresh material as hitherto assumed. A more extensive study at the molecular level is necessary in order to understand the distribution of sugars in different oceanic regimes.

*Keywords:* Sinking particles; Southern Indian Ocean; Mediterranean Sea; Morocco upwelling; Monosaccharides; C:N ratios; PCHO-C yields

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## 1. Introduction

Carbohydrates, like lipids and proteins, are common structural (chitin, mureine, chondroitin; Brock et al., 1994; Benner and Kaiser, 2003) and storage (glucans; Paiter, 1983) compounds, and they constitute a large part of marine biomass (Tanoue and Handa, 1987; Biersmith and Benner, 1998; Aluwihare and Repeta, 1999). Carbohydrates, in particular, comprise a significant fraction (5–20%) of the particulate material (Tanoue and Handa, 1987, Pakulski and Benner, 1994; Hernes et al., 1996; Panagiotopoulos et al., 2002) and dissolved organic matter (DOM; 30%; Pakulski and Benner, 1994), and moreover contribute to the formation of transparent exopolymer particles (TEP, Mopper et al., 1995; Zhou et al., 1998).

Some carbohydrates such as monomers (glucose, ribose) or polymers (glucans) are important food sources for heterotrophic bacteria, with rapid turnover rates ranging from hours to days (Rich et al., 1996; Skoog et al., 1999; Kirchman et al., 2001). However, other studies suggest that sugars are less labile and therefore can provide information about the biological source (Cowie and Hedges, 1984; Ittekkot et al., 1984; D'Souza and Bhosle, 2001) and metabolic pathways/fates of organic matter (Ittekkot et al., 1982; Tanoue and Handa, 1987; Cowie et al., 1992; Hedges et al., 1994; Hernes et al., 1996; Skoog and Benner, 1997; Opsahl and Benner, 1999). These results are consistent with studies indicating that combined carbohydrates are an important component of the semilabile DOM pool that comprises a large fraction of high molecular-weight DOM in surface waters (6–20%; McCarthy et al., 1996; Skoog and Benner, 1997; Benner, 2002; Repeta et al., 2002). Such results indicate that we still have a limited understanding of the relative lability of carbohydrates in marine systems.

Carbohydrates are actively removed from surface waters in sinking particles (Hernes et al., 1996; Skoog and Benner, 1997; Panagiotopoulos et al., 2002). Earlier studies reported that microbial degradation (Panagiotopoulos et al., 2002) and abiotic processes capable of aggregate destruction (Karl et al., 1988; Biddanda and Pomeroy, 1988; Jumars et al., 1989) may change the molecular distribution of particulate carbohydrates. Other investigators reported that

nutrient limitation may alter the composition of phytoplankton (Takeda, 1998; Hutchins and Bruland, 1998), and ultimately the elemental composition of exported particles (Brzezinski et al., 2003). On the other hand, uniform compositions have been observed among diverse oceanic regimes for the high molecular-weight fraction of DOM (McCarthy et al., 1993; 1996; Aluwihare et al., 1997; Skoog and Benner, 1997), total DOM (Borch and Kirchman, 1997), and some particulate organic matter (POM) and DOM samples measured simultaneously (Skoog and Benner, 1997). Indeed, most environmental applications using chromatographic techniques (either HPAEC-PAD or gas chromatography (GC)) for neutral sugar determination have focused on seawater (Rich et al., 1996; Borch and Kirchman, 1997; Skoog and Benner, 1997; Amon et al., 2001; Amon and Benner, 2003), sediments (Kerhervé et al., 2002), or vascular plant (Opsahl and Benner, 1999), whereas few reports have been published on the neutral sugar composition in sediment trap material (Hernes et al., 1996; Kerhervé et al., 1999). Thus, more information is still required on sugar composition in sinking POM, in order to make any generalization about their molecular distribution in this marine organic matter pool.

Here, we report results of sugar composition of large particles from different oligotrophic (Mediterranean Sea and Southern Indian Ocean) and eutrophic systems (coastal Atlantic Upwelling (UPW)). The Mediterranean Sea is considered a low-nutrient low-chlorophyll system (LNLC) limited by phosphorus (Zohary and Roberts, 1998, Turley et al., 2000; Moutin et al., 2002; Van Wambeke et al., 2002). In contrast, the Southern Indian Ocean system is a high-nutrient low-chlorophyll system (HNLC; Pondaven et al., 1999, and references therein; Boyd, 2002) which exhibits elevated productivity only in the Polar Front due to the entrainment of trace elements (de Baar et al., 1995). In this study the objectives were:

- (1) to contrast combined neutral sugar composition in settling particulate material collected from marine environments characterized by different productivity regimes at the time of sampling, and
- (2) to examine the combined neutral sugar distribution and to check whether neutral monosaccharides can be used as tracers of biological activities.

## 2. Materials and methods

### 2.1. Study area

Detailed information including geographic sampling location, primary production, bacterial production, and total organic carbon (TOC) stocks is presented in Table 1.

Briefly, particles were collected between January and February (1999) in the Southern Indian Ocean during the Antares-4 program, at two typical stations including the polar front zone (PFZ;  $\sim 46^\circ\text{S}$ ;  $62^\circ\text{E}$ ) and the subtropical zone (STZ;  $\sim 43^\circ\text{S}$ ;  $63^\circ\text{E}$ ; Fig. 1). Between 0 and 200 m, at the PFZ station, temperature

and salinity varied from 5 to  $10^\circ\text{C}$ , and from 33.69 to 33.94, respectively. Higher values of temperature and salinity were found in the first 200 m for station STZ (T:  $14\text{--}18^\circ\text{C}$ ; S: 35.42–35.52; Park et al., 2002). In the area studied, nitrate distribution was characterized by a South–North gradient with higher values in the PFZ ( $15.6\ \mu\text{M}$ ) than in the STZ ( $<1\ \mu\text{M}$ ; Leblanc et al., 2002). Notably, higher values of primary and bacterial productions integrated to the 1% surface irradiance were recorded in the STZ ( $40\ \text{mmol C m}^{-2}\ \text{day}^{-1}$  for PP and  $12\ \text{mmol C m}^{-2}\ \text{day}^{-1}$  for BP) than in the PFZ ( $28\ \text{mmol C m}^{-2}\ \text{day}^{-1}$  for PP and  $8\ \text{mmol C m}^{-2}\ \text{day}^{-1}$  for BP; Table 1; Leblanc et al., 2002; Sempéré et al., in preparation). TOC standing stocks showed similar

Table 1  
Summary of particle sampling conditions and seawater characteristics

Southern Indian Ocean			
Station	Polar front zone (PFZ)		Subtropical zone (STZ)
Location	$\sim 46^\circ 01.22'\text{S}$ ; $62^\circ 56.70'\text{E}$		$\sim 43^\circ 05.27'\text{S}$ ; $63^\circ 27.32'\text{E}$
Max. depth (m)	4300		5005
Sediment trap sampling depth (m)	200		200
Euphotic zone depth (m)	150		150
PP ( $\text{mmol C m}^{-2}\ \text{day}^{-1}$ ) <sup>a</sup>	28		40
BP ( $\text{mmol C m}^{-2}\ \text{day}^{-1}$ ) <sup>b</sup>	8		12
TOC ( $\text{mmol C m}^{-2}$ ) <sup>b</sup>	7474		9568
Mediterranean Sea			Atlantic Ocean
Station	Ligurian Sea (Med. Sea1)	Ionian Sea (Med. Sea2)	Upwelling (UPW)
Location	$\sim 43^\circ 25.41'\text{N}$ ; $007^\circ 51.20'\text{E}$	$\sim 33^\circ 59.54'\text{N}$ ; $022^\circ 00.91'\text{E}$	$\sim 31^\circ 00.99'\text{N}$ ; $010^\circ 02.14'\text{W}$
Max. depth (m)	2240	2140	90
Sediment trap sampling depth (m)	100	200	50
Euphotic zone depth (m)	90	130	50
PP ( $\text{mmol C m}^{-2}\ \text{day}^{-1}$ ) <sup>c</sup>	13	19	348
BP ( $\text{mmol C m}^{-2}\ \text{day}^{-1}$ ) <sup>d</sup>	5	5	89
TOC ( $\text{mmol C m}^{-2}$ ) <sup>b</sup>	5300	7912	3094

Primary production (PP, based on  $^{14}\text{C}$  assimilation technique (over a period  $>10\ \text{h}$ ), Moutin et al., 2002); bacterial production (BP, based on  $^3\text{H}$ -leucine incorporation technique, Van Wambeke et al., 2002) and total organic carbon (TOC, measured by HTOC technique (Sempéré et al. (2003))), stocks are integrated values to  $<1\%$  of light penetration (euphotic zone depth). The thermocline depth was 10 m at Agadir upwelling and ranged from 10 to 25 m in Mediterranean Sea stations, and from 50 to 70 m in southern Ocean stations.

<sup>a</sup> Leblanc et al. (2002).

<sup>b</sup> Sempéré et al. (in preparation).

<sup>c</sup> Moutin, personal communication and Moutin et al. (2002).

<sup>d</sup> Van Wambeke et al. (2002).

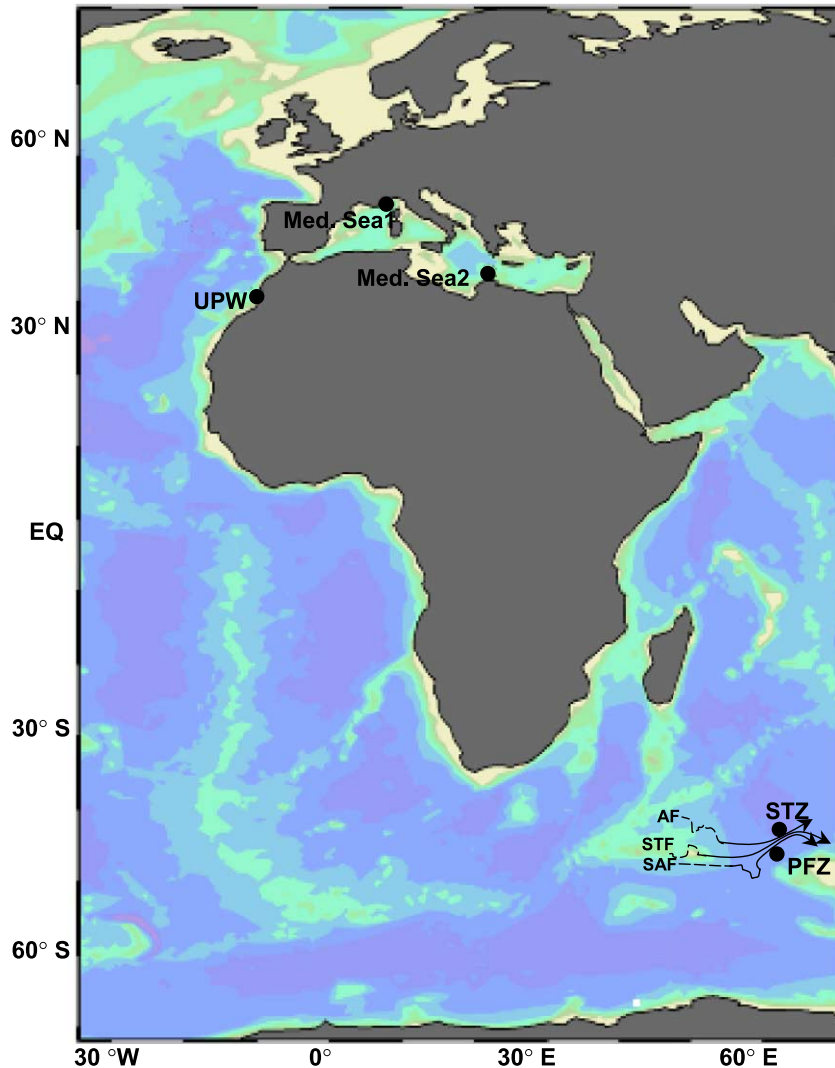


Fig. 1. Sampling locations during Antares 4 (Southern Indian Ocean, Jan. 1999) and Prosopé cruises (Mediterranean and Atlantic Ocean, Sept. 1999). Southern Indian Ocean currents according to Park et al. (2002). Notations: polar front zone (PFZ); subtropical zone (STZ); subantarctic front (SAF); subtropical front (STF); Agulhas return front (AF); Atlantic upwelling (UPW); Ligurian Sea (Med. Sea1); Ionian Sea (Med. Sea2).

trends being higher in the STZ ( $9568 \text{ mmol C m}^{-2}$ ) than in the PFZ station ( $7474 \text{ mmol C m}^{-2}$ ; Table 1).

Particles were also collected during September–October 1999, in the Northwestern Mediterranean Sea (Ligurian Sea) at the French time series station Dyfamed (Station ‘Med. Sea1’) and in the Eastern Mediterranean (Ionian Sea; Station ‘Med. Sea2’; Fig. 1). Temperature and salinity at the Med. Sea1 station (0–200 m) varied from 13 to 22 °C and from 38.31 to

38.53, respectively, whereas at Med. Sea2, the corresponding values (0–200 m) ranged from 15 to 26 °C and from 38.66 to 38.93. Nitrate concentrations were higher at Med. Sea1 than at the Med. Sea2 station, ranging from 0.02 to 8.33  $\mu\text{M}$  and from 0.012 to 4.08  $\mu\text{M}$ , respectively (Raimbault, unpublished results). Although the Ionian Sea (Med. Sea2) is usually considered the most oligotrophic area of the Mediterranean on an annual basis (Turley et al., 2000)

integrated (1% surface irradiance) primary and bacterial productions were similar for both sites (13–19 mmol C m<sup>-2</sup> day<sup>-1</sup> for PP and ~5 mmol C m<sup>-2</sup> day<sup>-1</sup> for BP; Table 1). TOC standing stocks were 7912 mmol C m<sup>-2</sup> over the 0–130 m layer at Med. Sea2, and 5300 mmol C m<sup>-2</sup> over the 0–90 m layer at Med. Sea1 (Table 1).

Particles were also collected in the Atlantic Ocean near the Moroccan coast, in the highly eutrophic area of the Agadir Upwelling (UPW) during the Prosope program (Sept. 1999; Fig. 1). Temperature and salinity at the UPW station (0–50 m) varied from 15 to 17 °C and from 36.14 to 38.15, respectively, whereas nitrate concentrations ranged from 1.21 to 10.4 µM. Integrated primary and bacterial productions values were 348 and 89 mmol C m<sup>-2</sup> day<sup>-1</sup>, respectively, whereas TOC stocks over the first 0–50 m (1% surface irradiance) were 3094 mmol C m<sup>-2</sup> (Table 1).

## 2.2. Sediment trap sampling

Sequential particle flux samples were collected for 6 hours using a free-drifting sediment trap (Technicap, PPS5) with a mouth of 1 m<sup>2</sup>, as described by Miquel *et al.* (1994). Prior to the deployment of the sediment traps into the Mediterranean Sea and Atlantic Ocean, HgCl<sub>2</sub> (final concentration of 10 mg l<sup>-1</sup>) was added to the bottom of the collection chamber. Previous study showed no bacterial activity at such HgCl<sub>2</sub> concentration (Sempéré *et al.*, 2000b). Salinity of water in the bottle was raised to 40‰ to prevent loss by diffusion. No fixative solution was added to the Southern Indian Ocean samples. The traps were located just below the euphotic zone (except for one trap deployed at 50 m depth at the Med. Sea2 site; Table 1), and thus, vertical fluxes of particulate matter represent exported production. After trap recovery, living or dead mesozooplankton trapped inside the sampling cups (250 ml) were carefully removed so that only detrital particles and organisms <1 mm were analyzed. Samples were split using a peristaltic pump (Perfill IQ 2000, Jencons) for the different analyses (POC, sugar determination, lipids etc). For carbohydrates, immediately after sampling, subsamples (20–25 ml) were filtered through 25-mm Whatman GF/F filters (precombusted at 450 °C for 6 h; nominal retention of 0.7 µm) at low vacuum pressure ( $P < 50$  mm Hg) and stored in the dark at -17 °C until analysis (approximately 3 months).

## 2.3. Particulate organic carbon (POC) determination

To remove inorganic carbon GF/F filters with collected particles were covered with a few milliliters of 2 N HCl and were evaporated until dryness. POC analysis for sediment trap filters were carried out using a Carlo Erba model N 1500 Analyzer (Southern Indian Ocean samples) according to Strickland and Parsons (1972), whereas those from the Mediterranean Sea (Med. Sea1, Med. Sea2) and Atlantic Ocean (UPW) were analyzed using a semiautomatic wet oxidation method and were assayed on a three-channel Technicon Auto-Analyzer (Raimbault *et al.*, 1999). The standard deviation of each method was about 2%. Previous comparison between wet oxidation method and CHN Leco 800 analyser using glycine as a standard indicated that recovery efficiency of wet oxidation for POC and PON were close to 100% (at the 95% confidence level; Raimbault *et al.*, 1999).

## 2.4. Sample preparation and acid hydrolysis for sugar determination

The collected particulate material on the GF/F filters (Section 2.2) was dried in a desiccator to constant weight, and then hydrolyzed under N<sub>2</sub> atmosphere with 0.1 M HCl at 100 °C for 20 h (Burney and Sieburth, 1977), in precombusted Pyrex vials (450 °C for 6 h). After cooling, the aqueous acid was evaporated in a rotary evaporator at ~30 °C, and the residue was washed with a small volume of water (200 µl) which was removed by a second evaporation (Cheng and Kaplan, 2001). The residue was dissolved in a 0.5- to 2-ml volume of Milli-Q water depending on the expected concentrations, resulting in a 5–10 times dilution. Finally, samples were filtered through quartz wool in duplicates and injected (20 µl) into the HPAEC-PAD system.

Initial laboratory tests with suspended POM collected on GF/F filters showed no significant differences (at the 95% confidence level, paired *t*-test  $P > 0.1$ ) in carbohydrate concentrations when hydrolyzed with 1 M H<sub>2</sub>SO<sub>4</sub> 95 °C for 4 h (Kerhervé *et al.*, 2002) or 0.1 M HCl 100 °C for 20 h (Burney and Sieburth, 1977). Similar results were also reported for dissolved carbohydrates (Borch and Kirchman, 1997; Witter and Luther III, 2002). However, our prelimi-

nary results showed that mild hydrolysis conditions (0.1 M HCl at 100 °C for 20 h) were better adapted to the HPAEC-PAD system yielding lower blanks and higher recovery (~20%) of some monosaccharides such as fructose and ribose.

## 2.5. Sugar determination

Aldose concentrations in hydrolyzed samples were measured by HPAEC-PAD according to Mopper et al. (1992) and were modified by Panagiotoopoulos et al. (2001, 2002). Briefly, monosaccharides were separated on an anion-exchange column (Carbopac PA-1, Dionex) by isocratic elution with 19 mM NaOH, a flow rate of 0.7 ml min<sup>-1</sup> at 17 °C (column temperature), and were detected by an electrochemical detector (Decade, Antec) using a gold working electrode and a Pd reference electrode. The NaOH mobile phase (20 mM) was prepared by

diluting low-carbonate NaOH (Baker) into Milli-Q water, which had been sparged with He for at least 10 min at a flow rate of 100 ml min<sup>-1</sup>. This working solution was kept in He-pressurized bottles. Column regeneration was carried using a 1M NaOH solution at a flow rate of 1 ml min<sup>-1</sup> for at least 35 min after each sample analysis. During this procedure, the detector was switched off and the column was reversed. This step was crucial in order to obtain similar retention times between successive injections. The minimum time of re-equilibration of the column after each cleaning was 30–45 min depending on the current of the detector (~90–120 nA). Assuming four injections per day including HPAEC-PAD run time, column regeneration, and equilibration of the system with 19 mM NaOH, the working solution (20 mM NaOH) was used for only 4–5 days. Procedural blanks were made with combusted GF/F filters hydrolyzed in 0.1 M HCl (100 °C, 20 h). The only

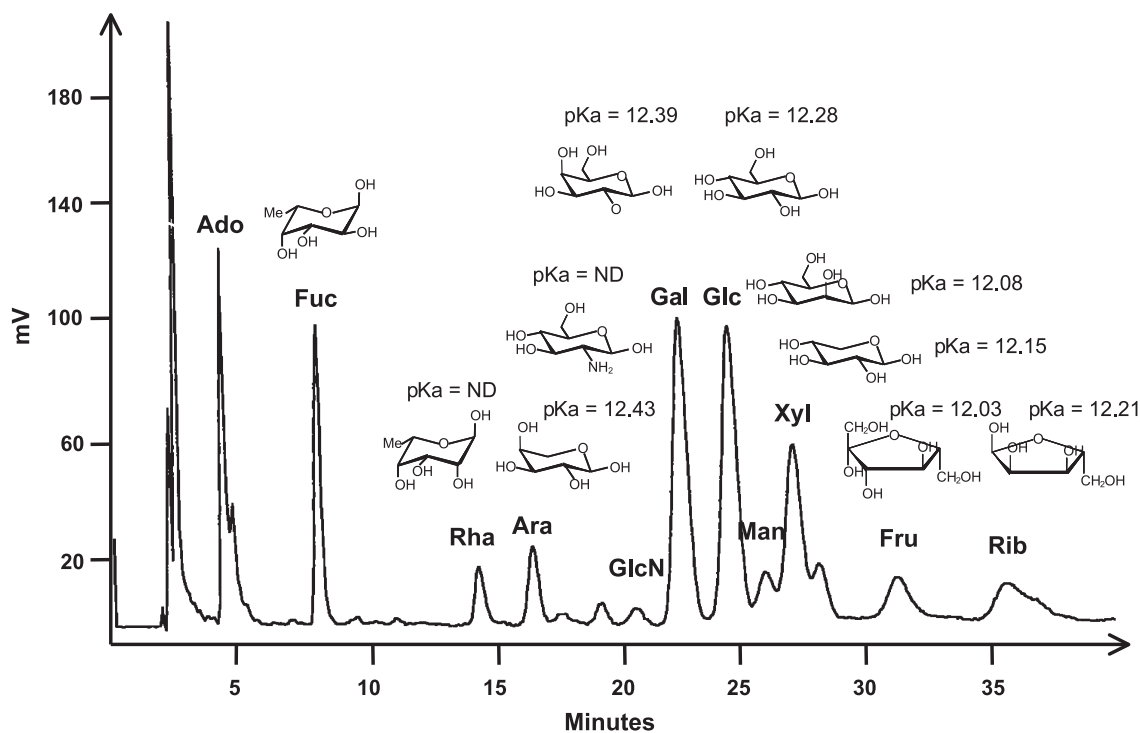


Fig. 2. Typical monosaccharide chromatogram of hydrolyzed Mediterranean Sea particles (200 m depth sediment trap, Med. Sea1 station) analyzed by HPAEC with integrated PAD using isocratic elution of NaOH at 19 mM at 17 °C. Analytical conditions were 1M NaOH-post-column addition (flow rate 0.2 ml min<sup>-1</sup>) with PAD and a total flow rate of 0.9 ml min<sup>-1</sup>; sample loop 20 µl. Abbreviations: Fuc., fucose; Rha., rhamnose; Ara., arabinose; GlcN., glucosamine; Gal., galactose; Glc., glucose; Man., mannose; Xyl., xylose; Fru., fructose; Rib., ribose. Adonitol (Ado.) is not present in natural waters and was used as an internal standard. Chair forms and dissociation constants (pKa) of sugars are also given in the chromatogram. ND: No data available in literature.

detectable sugar in blanks was glucose (7–10 nM). Because this value was negligible compared to the amount found in samples, data were not blank corrected. Analytical errors determined from twofold replicate analysis were better than 8% for all sugars except ribose (15%). Final particulate sugar concentrations (PCHO) are expressed as C-equivalents. Ten individual monosaccharides were detected in the hydrolysates of particulate material including deoxysugars (fucose, rhamnose), pentoses (arabinose, ribose, xylose), amino-sugar (glucosamine), hexoses (galactose, glucose, mannose), and keto-hexose (fructose). Fig. 2 depicts a typical HPAEC-PAD chroma-

togram of monosaccharides and their chemical structure.

## 2.6. Statistical analyses

Principal component analysis (PCA) was used in this study in order to reduce the multidimensional nature of the data set. This statistical approach can be used to evaluate interrelationships among a large number of variables and to get information about their similarities in terms of their underlying dimensions. Thus, the information in a large data set may be transformed into two smaller matrices that are linear

Table 2

Particulate combined aldoses (PCHO-C), POC 24 h fluxes and POC/PP, PCHO-C/POC ratios of particles collected with sediment traps in the polar front zone (PFZ), subtropical zone (STZ), coastal Atlantic Upwelling (UPW), Ligurian Sea (Med. Sea1), and Ionian Sea (Med. Sea2)

Site	Sampling interval (h)	POC	PCHO-C	PCHO-C/POC	POC/PP	PCHO-C/PP	C/N
		mg m <sup>-2</sup> day <sup>-1</sup>			(%)		
PFZ (200 m)	24	13.9	0.36	2.56	4.14	0.11	5.3
	24	18.3	0.42	2.31	5.45	0.13	6.4
	24	13.1	0.42	3.24	3.90	0.13	6.4
	av.	15.1	0.40	2.70	4.49	0.12	6.0
STZ (200 m)	24	4.45	0.18	4.07	0.93	0.04	5.0
	24	4.70	0.19	4.01	0.98	0.04	6.1
	24	5.11	0.19	3.70	1.06	0.04	5.8
	11	6.91	0.35	5.01	1.44	0.07	5.1
	av.	5.29	0.23	4.20	1.10	0.05	5.5
Med.Sea1 (100 m)	12	3.72	0.32	8.58	2.31	0.20	10.0
	24	8.96	0.47	5.20	5.57	0.29	9.4
	18	2.95	0.78	26.4	1.83	0.48	6.4
	12	3.47	0.42	12.2	2.16	0.26	8.2
	12	–	0.12	–	–	0.07	–
	av.	4.78	0.42	13.1	2.97	0.26	8.5
Med.Sea1 (200 m)	18	2.25	0.16	7.21	1.40	0.10	8.3
	24	3.88	0.44	11.4	2.41	0.27	5.9
	24	3.26	0.22	6.85	2.02	0.14	7.8
	12	2.99	0.65	21.8	1.86	0.40	11.3
	av.	3.10	0.37	11.8	1.92	0.23	8.3
Med.Sea2 (50 m)	24	6.01	0.63	10.5	2.61	0.27	8.9
	24	5.14	0.50	9.66	2.23	0.22	9.0
	12	4.19	1.06	25.3	1.82	0.46	9.3
	24	4.66	1.09	23.3	2.03	0.47	9.7
	av.	5.00	0.82	17.2	2.17	0.36	9.2
Med.Sea2 (250 m)	24	0.88	0.25	27.9	0.38	0.11	9.9
	24	1.10	0.14	6.47	0.48	0.06	7.4
	24	1.60	0.12	7.60	0.70	0.05	7.5
	av.	1.19	0.17	14.0	0.52	0.07	8.2
	24	10.8	0.27	2.50	0.26	0.01	9.5
UPW (50 m)	24	8.00	0.37	4.70	0.19	0.01	7.5
	24	9.40	0.32	3.60	0.23	0.01	8.5
	av.	9.40	0.32	3.60	0.23	0.01	8.5

PCHO-C/POC (%) is the carbon-normalized of particulate combined aldoses in the POC pool. All fluxes are normalized to 24 h and correspond to the sum of the flux of four samples, 6 h each. PP is the Primary production and PP data are in Table 1. Av. Average.



combinations of the original data set. The new “score” matrix contains information about the sample (sediment trap) patterns in the data while the loading reflects the influence of the variables (biomarkers) on the sample patterns. These two matrices, often called principal components (PC) are created in order of decreasing variance in data. This approach has been successfully used in earlier studies in order to assess the origin or the degradation status of the organic matter in terms of amino acids (Dauwe and Middelburg, 1998; Ingalls et al., 2003) and lipids (Wakeham et al., 2002). The number of observations in this study is 250 (10 sugars×25 samples) which clearly permits the use of this statistical approach. PCA was made by using biomarker/sugar fluxes ( $\mu\text{g m}^{-2} \text{day}^{-1}$ ) employing the statistical package SPSS 10.0 for Windows.

### 3. Results

#### 3.1. Bulk parameters

##### 3.1.1. POC and PCHO–C fluxes

Estimated POC fluxes greatly varied between the different areas. The highest POC fluxes were recorded at the PFZ and at the Atlantic UPW followed by the STZ station and the Mediterranean Sea sites (Leblanc, 2002; see also Table 2). For the Southern Indian Ocean samples,  $^{234}\text{Th}$ -based POC fluxes (Coppola, 2002) are in a good agreement with direct POC measurement results. Isotope-based estimates were not available for

the Mediterranean Sea. Below the euphotic zone, average PCHO–C fluxes ranged from  $0.17 \text{ mg C m}^{-2} \text{day}^{-1}$  (Med. Sea2-250 m) to  $0.42 \text{ mg C m}^{-2} \text{day}^{-1}$  (Med. Sea1-100 m), whereas values as high as  $0.82 \text{ mg C m}^{-2} \text{day}^{-1}$  were measured inside the euphotic zone at 50 m at the Med. Sea2 station (this sample is not representative of the exported PCHO–C or POC flux; Table 2). Estimated PCHO–C fluxes were comparable to those in the Bering Sea, Sargasso Sea, North and Eq. Pacific Ocean ( $0.04\text{--}3.6 \text{ mg C m}^{-2} \text{day}^{-1}$ , Tanoue and Handa, 1987, Ittekkot et al., 1984; Hernes et al., 1996).

##### 3.1.2. C:N, $\text{POC}\times\text{PP}^{-1}$ , $\text{PCHO}\text{--}\text{C}\times\text{PP}^{-1}$ ratios and PCHO–C yields

At the time of sampling, Southern Indian Ocean samples (PFZ and STZ stations) were characterized by low C:N ratios ranging from 5.1 to 6.4, whereas higher values were measured for the Atlantic UPW (7.5–9.5) and Mediterranean Sea samples (Med. Sea1: 5.9–11.3; Med. Sea2: 7.4–9.9) suggesting differences in the initial composition and/or in the degradation status of the particles studied (Table 2; Fig. 3). Highest  $\text{POC}\times\text{PP}^{-1}$  ratios were found in PFZ (4.5%) followed by the Med. Sea1 (1.9–3.0%), Med. Sea2 (0.52–2.2%), STZ (1.1%) and the Atlantic UPW (0.23%; Table 2). Basically, all values were the same order of magnitude previously reported for other open ocean settings including the Pacific Ocean, Arabian Sea, and the Mauritanian upwelling system (<10%; Buesseler, 1998; Bory et al., 2001; Ducklow et al., 2001). We found that the  $\text{PCHO}\text{--}\text{C}\times\text{PP}^{-1}$  ratios

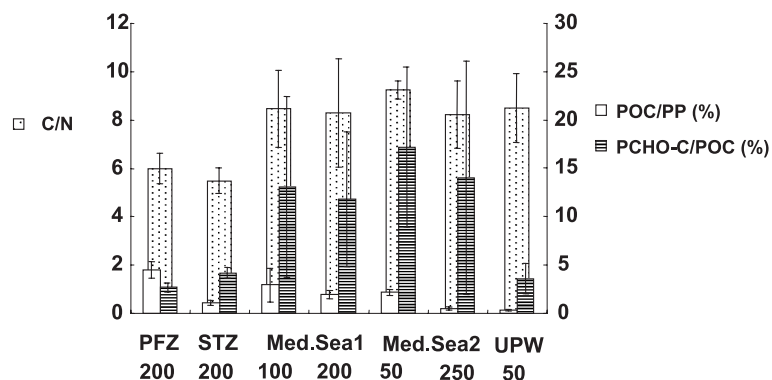


Fig. 3. Average C:N ratios, particulate organic carbon (POC)/primary production (PP) ratio (%) and total sugar yield of POC (PCHO–C/POC ratios (%)) from sediment trap particles of polar front zone (PFZ), subtropical zone (STZ) in Southern Indian Ocean, from Mediterranean Sea, e.g., Ligurian Sea (Med. Sea1) and Ionian Sea (Med. Sea2) and from the Upwelling of Agadir (UPW) in coastal (Morocco) Atlantic Ocean. PP data as in Table 1.

closely followed  $\text{POC} \times \text{PP}^{-1}$  ratios, being much higher in the Mediterranean Sea (range of 0.07–0.26%) and the Southern Ocean (range of 0.05–0.12%), than at the UPW system (~0.01%; Table 2).  $\text{PCHO-C} \times \text{PP}^{-1}$  ratios agree with other open ocean observations (0.20–0.40%; Hernes et al., 1996; Chavez et al., 1996), but were much lower than values found near the Japanese coast (22%; Hamanaka et al., 2002).

Carbohydrate yields, calculated as the percentage of organic carbon by dividing  $\text{PCHO-C}$  by the  $\text{POC}$  ( $\text{PCHO-C} \times \text{POC}^{-1}$  %), were two- and threefolds

higher for the Mediterranean Sea samples (Med. Sea1, Med. Sea2: 13–16%) than for the Atlantic UPW (4%) or the Southern Indian Ocean samples (PFZ, STZ: 3–4%).  $\text{PCHO-C}$  yields measured in UPW and Southern Ocean sites were in the low range for values reported in other areas including the central equatorial Pacific Ocean (5–18% Hernes et al., 1996), North Pacific (7–10%; Tanoue and Handa, 1987), Sargasso Sea (3–6%; Ittekkot et al., 1984), and eastern Mediterranean Sea (4–10%, Kerhervé et al., 1999).

Table 3

Elemental carbohydrate compositions of particles collected with sediment traps in the polar front zone (PFZ), subtropical Zone (STZ), coastal Atlantic Upwelling (UPW), Ligurian Sea (Med. Sea1), and Ionian Sea (Med. Sea2)

Site	Sampling interval (h)	Fuc.	Rha.	Ara.	GlcN.	Gal.	Glc.	Man.	Xyl.	Fru.	Rib.	Deox.	Hex.	Pent.
Carbohydrates (wt.% of particulate-combined aldoses)														
PFZ (200 m)	24	8.83	3.25	5.74	3.87	24.1	15.2	2.85	12.3	6.35	17.5	13.5	46.9	39.6
	24	5.57	3.58	4.49	3.16	26.4	15.2	3.01	13.4	8.13	17.1	10.3	50.2	39.4
	24	5.18	3.64	4.37	2.35	27.4	14.9	2.97	13.9	8.38	16.9	9.88	50.7	39.4
	av.	6.53	3.49	4.86	3.12	25.9	15.1	2.94	13.2	7.62	17.2	11.2	49.3	39.5
STZ (200 m)	24	5.38	–	1.22	9.57	11.3	15.5	14.6	6.54	–	35.9	5.95	45.8	48.3
	24	5.79	–	2.56	11.06	14.9	13.7	18.8	9.94	–	23.3	6.51	53.2	40.3
	24	4.05	–	2.03	9.97	15.6	15.0	13.9	4.59	13.3	21.9	5.28	57.6	37.1
	11	4.76	–	1.42	7.10	9.90	15.8	12.0	4.83	5.45	38.8	5.44	43.1	51.5
	av.	5.00	–	1.81	9.43	12.9	15.0	14.8	6.48	9.36	30.0	5.80	49.9	44.3
Med. Sea1 (100 m)	12	11.3	5.01	3.49	0.87	23.2	35.8	2.36	10.5	3.64	3.76	17.1	64.3	18.6
	24	6.94	3.48	2.45	1.83	17.9	51.0	1.92	5.01	6.53	2.90	11.4	77.3	11.3
	18	2.68	5.46	2.10	2.85	8.03	45.3	2.38	8.44	12.3	10.4	9.59	65.7	24.7
	12	11.7	5.02	4.59	1.63	15.5	27.2	–	7.90	0.77	25.7	17.1	43.7	39.1
	12	14.7	4.99	6.02	–	29.2	22.4	–	22.6	–	–	19.7	51.7	28.6
	av.	9.45	4.79	3.73	1.79	18.8	36.4	2.22	10.9	5.81	10.7	15.0	60.6	24.5
Med. Sea1 (200 m)	18	8.14	2.96	1.86	–	17.3	42.6	0.89	8.81	0.15	17.3	11.1	60.9	28.0
	24	5.86	6.92	1.28	1.34	13.7	39.5	–	4.65	1.48	25.3	13.2	54.8	32.1
	24	7.36	5.23	2.72	0.32	17.5	34.7	0.34	11.5	–	20.4	12.6	52.7	34.7
	12	12.9	3.80	4.61	0.49	23.2	22.9	3.81	15.6	1.62	11.1	17.1	50.9	32.0
	av.	8.57	4.73	2.62	0.72	17.9	34.9	1.68	10.1	1.08	18.5	13.5	54.8	31.7
Med. Sea2 (50 m)	24	3.95	8.89	2.24	2.35	11.0	39.0	2.31	2.55	11.0	16.8	14.8	60.3	24.9
	24	4.61	8.40	2.02	3.47	12.9	31.1	2.43	2.97	2.63	29.5	13.9	49.4	36.7
	12	4.03	15.8	1.85	4.92	14.5	29.5	4.73	3.87	2.18	18.7	21.3	52.4	26.3
	24	2.83	10.2	1.66	5.67	9.90	32.8	4.05	4.23	5.26	23.3	14.6	52.5	32.8
	av.	3.85	10.8	1.94	4.10	12.1	33.1	3.38	3.41	5.26	22.1	16.2	53.7	30.2
Med. Sea2 (250 m)	24	3.03	0.92	0.48	–	37.8	38.4	–	0.75	13.8	4.94	4.57	88.3	7.14
	24	7.26	2.13	2.91	–	22.7	30.1	1.92	8.06	11.0	14.3	10.6	61.0	28.4
	24	6.47	2.75	1.08	–	19.0	36.1	0.85	9.75	15.0	9.12	10.8	65.7	23.5
	av.	5.58	1.93	1.49	–	26.3	34.9	1.38	6.19	13.3	9.45	8.66	71.7	19.7
UPW (50 m)	24	3.85	2.21	1.81	1.76	11.1	30.5	3.41	6.03	36.8	2.46	9.86	73.4	16.8
	24	2.45	1.69	0.58	1.21	7.66	58.8	2.17	3.54	20.2	1.76	5.27	87.3	7.47
	av.	3.15	1.95	1.19	1.49	9.39	44.7	2.79	4.78	28.5	2.11	7.57	80.3	12.1

All fluxes are normalized to 24 h and correspond to the sum of the flux of four samples, 6 h each. The elemental composition of the deoxysugars (Fuc.+Rha), hexoses (Gal.+Glc.+Man.), and pentoses (Ara.+Xyl.+Rib.) is also given.

Abbreviations: Fuc., Fucose; Rha., Rhamnose; Ara., Arabinose; GlcN., Glucosamine; Gal., Galactose; Glc., Glucose; Man., Mannose; Xyl., Xylose; Fru., Fructose; Rib., Ribose; Deox., Deoxysugars; Hex., Hexoses; Pent., Pentoses.

Reported values of total lipids/POC ratios, based on floating sediment trap sampling deployed in the seasonal ice zone (SIZ) and permanently open ocean zone (POOZ), both in the Indian sector of Southern Ocean, were 5–20% and 6–38%, respectively (Cailiau et al., 1999). Total lipids/POC ratios and total amino acids/POC ratios were 7–28% and 5–30%, respectively, in the Mediterranean Sea at the Dyfamed site (Goutx et al., 2000). In the Equatorial Pacific Ocean, lipids and amino acids accounted for 10–30% and for 66% of the POC, respectively (Wakeham et al., 1997; Lee et al., 2000), whereas in the Sargasso Sea, amino acids contributed 9–25% of the POC pool (Ittekkot et al., 1984). Thus, sugars appeared to be the second or third most abundant class of exported particulate organic compounds.

### 3.2. Molecular composition of monosaccharides

#### 3.2.1. Distribution of combined aldoses in sediment traps

For the Mediterranean sediment trap samples (Med. Sea1 and Med. Sea2 stations), glucose was the major aldose (22–51%), followed by galactose and ribose which made up 8–38% and 4–30%, respectively of the carbohydrate pool. Xylose and fucose were consistently higher than the remaining aldoses, 1–23% and 3–15%, respectively, although at Med. Sea2 (50 m), rhamnose and glucosamine reached

values of 11% and 4.1%, respectively. By contrast, in the Southern Indian Ocean, ribose was either the first (STZ: 22–39%) or second (PFZ: 17–18% after galactose 24–27%) most abundant sugar (Table 3). Glucose (14–16 wt.%) was next, followed by mannose (3 wt.% in PFZ and 15 wt.% in STZ) or xylose (5–14%). The remaining aldoses represented 1–13% of the total aldoses. Although the STZ and PFZ trap samples were not poisoned during sampling, the molecular distribution averaged over subsequent 24-h periods did not change drastically (Table 3), i.e. ribose and galactose were the main monosaccharides followed by glucose whatever the position of the sample accumulator of the trap, indicating that this was a general trend at the time of sampling at the PFZ and STZ stations. Particulate material in the Atlantic Upwelling (UPW) was characterized by a high contribution of glucose (31–59%) and fructose (20–37%) followed by galactose (8–11%) and a small contribution of ribose (~2%).

#### 3.2.2. PCA

The grouping of samples by area and depth using principal component analysis (PCA), formed several clusters (sample scores; Fig. 4a). A plot of score group samples collected from the Mediterranean Sea falls to the right of the other samples. The Mediterranean samples Med. Sea1 (100–200 m) and Med. Sea2 (50–250 m) stations could not be separated further by

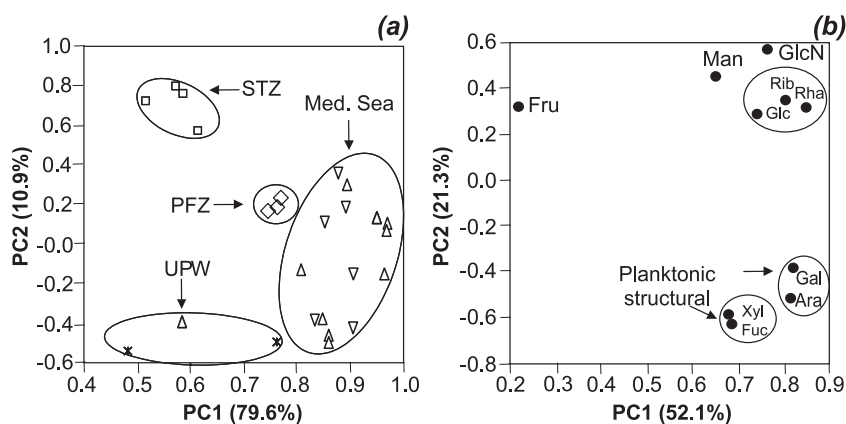


Fig. 4. Principal component analysis (PCA): (a) and (b) are sample scores and variable (biomarker) loadings, respectively for floating sediment traps at the polar front zone (PFZ), subtropical zone (STZ), Mediterranean Sea (Med. Sea1, Med. Sea2), and UPW stations. The variance accounted for by each principal component is shown in parentheses after the axis label. For each cluster in the Mediterranean Sea, data from Med. Sea1 and Med. Sea2 stations are pooled. Abbreviations of sugars are given in Table 3. Symbols:  $\diamond$ , PFZ 200 m;  $\square$ , STZ 200 m;  $\triangle$ , Med. Sea1 100, 200 m;  $\nabla$ , Med. Sea2 50, 300 m; \*UPW 50 m.

using their sugar composition. On the other hand, STZ (200 m) samples formed a well-identified compact cluster in the upper left quadrant, and the group of PFZ samples (200 m) were located in the center quadrant to the left of the Mediterranean Sea samples. UPW samples (50 m; lower left quadrant) also formed a cluster characterized by the high variability of the PC1 factor (range of 0.50–0.75%) and a contribution of one Med. Sea1 sample (100 m). Nevertheless, these results indicate that different particles from various locations could be characterized in terms of their monosaccharidic composition.

Grouping samples by area and depth also provided different information about the relationships of the individual compounds as seen from the sample loadings (Fig. 4b). These results indicate distinct contrasts in the origin of the organic matter that are not dependent on the sampling site. Of the biomarkers plotted, fucose, xylose, arabinose, and galactose project most positively on PC1 and most negatively on PC2, thus forming two compact clusters (lower left quadrant). Rhamnose, ribose and glucose cluster together in the upper right quadrant (most positively on PC1 and PC2 factors). Glucosamine and mannose were located quite close to the cluster of rhamnose, ribose, and glucose, whereas fructose is located to the upper left quadrant isolated from the other sugars (Fig. 4b).

## 4. Discussion

### 4.1. POC fluxes and $POC \times PP^{-1}$ ratios

POC fluxes and primary productivity measurements were obtained using daily values and must be considered as snapshots of the biological system. Nevertheless, all data were obtained during moderately productive periods in late summer for both the northern (Sept. 1999) and southern hemispheres (Jan.–Feb. 1999). Large variations of  $POC \times PP^{-1}$  values were found between locations, indicating that these parameters were poorly correlated each other (Table 2; Fig. 3). This variability may be due to the presence of different planktonic organisms (siliceous or calcareous). Highest  $POC \times PP^{-1}$  ratios were found in the PFZ, probably because of diatom blooms in the surface waters (Tréguer et al., 1995; Buesseler et al.,

2001; Nelson et al., 2002, and references therein). Estimated  $POC \times PP^{-1}$  values at the UPW site were surprisingly low (0.23%), whereas those found at the Mediterranean sites (Table 2; Fig. 3) are similar to those previously reported for the Dyfamed Site (Med. Sea1 site;  $POC \times PP^{-1}$ : 5.8–12.5%; Copin-Montégut and Avril, 1993), and in the central part of the Ionian Sea (1.4–3.4%, May–June) near the Med. Sea2 site (Moutin and Raimbault, 2002). Interestingly, our results indicated high fluxes of sugar-poor particulate material at the sites where higher primary production were measured ( $> 300 \text{ mg C m}^{-2} \text{ day}^{-1}$ ) as in the Atlantic Upwelling and in the PFZ (and to a less extent in the STZ; Fig. 5). Although horizontal speeds in Agadir upwelling are not available, maximum values of  $100 \text{ cm s}^{-1}$  have been reported South of the area studied (in the Mauritanian upwelling, Bory et al., 2001). It is likely that POC fluxes in the UPW were underestimated due to lateral export of particles reducing trap efficiency, a phenomenon normally observed in shallow waters (François et al., 2001).

### 4.2. PCHO–C yields in relation to the C:N ratios of the particles

Higher PCHO–C yields were associated with higher C:N ratios in Mediterranean Sea samples;

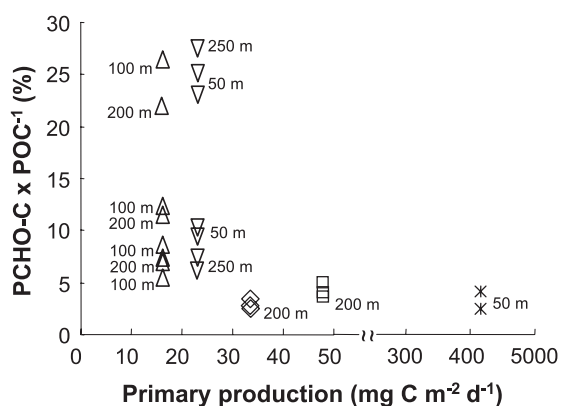


Fig. 5. PCHO–C/POC ratios (%) as a function of primary productions ( $\text{mg C m}^{-2} \text{ day}^{-1}$ ) from sediment trap particles of polar front zone (PFZ), subtropical zone (STZ) in Southern Indian Ocean, from Mediterranean Sea, e.g., Ligurian Sea (Med. Sea1) and Ionian Sea (Med. Sea2) and from the Upwelling of Agadir in coastal (Morocco) Atlantic Ocean. Primary productions data as in Table 1.

however, the opposite trend was found in Southern Ocean samples (Table 2; Fig. 3). Although very few data exist to date concerning the PCHO yields of sinking particles in the Southern Indian Ocean and Mediterranean Sea, we note from the literature significant differences in the C:N ratios of sinking particles between the Mediterranean Basin (C:N=7.8–13, Goutx et al., 2000; Boldrin et al., 2002) and the Indian sector of the Southern Ocean (C:N=5.7–7.3, Tréguer et al., 1988; Buesseler et al., 2001; Leblanc et al., 2002). C:N ratios close to the Redfield ratio (5.5–6.0) are typical of marine plankton and, thus, of fresh organic material (Redfield et al., 1963). Therefore, the differences we found in the C:N ratios of exported particles suggest either (1) an external input of material able to change the C:N ratio of the sinking particles, (2) qualitative differences in the relative abundance of the main organic compound classes for the living species (mainly phyto- and zooplankton) and, consequently, in the exported material between the Southern Ocean and the Mediterranean Sea sites at the time of sampling, or (3) a different degradation status of the exported particles.

Allochthonous input of material in the coastal Atlantic Upwelling and Mediterranean Sea sites could influence the composition of sinking particles since the C:N ratios of terrestrial organic matter and aerosols are sometimes >20 (Tyson, 1995; Sempéré and Kawamura, 2003). Additionally, marine planktons have lower sugar contents compared to terrestrial vascular plants that are rich in cellulose (Cowie and Hedges, 1984; Opsahl and Benner, 1999). Given that the Mediterranean Sea is a semienclosed basin surrounded by continents receiving significant continental aerosols and river particles (Copin-Montégut and Avril, 1993; Sempéré et al., 2000a), these external supplies possibly may increase the C:N ratios and PCHO–C yields of marine particles in the Mediterranean Sea when compared to remote areas of the Southern Ocean. Terrestrial influences are also likely to occur at the UPW station which is located a few kilometers from the coast. However, such an external particle source is likely to be two orders of magnitude lower than in situ production of particles (Copin-Montégut and Avril, 1993) and cannot simultaneously explain the high C:N ratios and PCHO–C yields in the particles in the Mediterranean Sea and the UPW-Atlantic.

Previous studies based on modeling  $^{13}\text{C}$ -NMR data (Hedges et al., 2002) reported higher yields of proteins (70–73%) to lipids (10–15%) or carbohydrates (15–17%), and lower C:N ratios (5.3–5.6) for Southern Ocean marine plankton samples compared to other oceanic regimes (Equatorial Pacific Ocean, C:N ratio: 7.1; proteins: 57%, carbohydrates: 21% and Arabian Sea, C:N ratio: 8.1; proteins: 51%, carbohydrates: 24%). Similarly, a recent study carried out across the PFZ indicated high concentrations of amino acids in sinking particles (collection depth 1000–1300 m) accounting for 17–28% of total organic carbon (Ingalls et al., 2003). Our low C:N ratios (5.5–6.0) for PFZ and STZ sinking particles are similar to those estimated by Hedges et al. (2002) for phytoplankton living in the same area clearly suggesting the export of fresh, protein-rich material in these areas. The lower PCHO–C yields (2.7–4.2%) in our Southern Indian Ocean samples compared to the results of Hedges et al. (2002) may be explained by the different analytical techniques ( $^{13}\text{C}$ -NMR versus 0.1 M HCl hydrolysis followed by HPAEC-PAD). We have no evidence to suggest that proteins were more abundant in the Southern Ocean than in the Mediterranean Sea plankton because we did not measure amino acids in our samples. Nevertheless, such scenario could explain the low C:N ratios and the low PCHO–C yields of exported particles.

On the other hand, the C:N ratios we found at the Mediterranean Sea and UPW sites were similar to previously reported values. As described above (see Introduction), the Mediterranean system is often limited by phosphorus (Zohary and Roberts, 1998, Turley et al., 2000; Moutin et al., 2002; Van Wambeke et al., 2002). According to Myklestad (1995) and Mingazzini et al. (1995), this limitation may induce extracellular release of sugar-rich material such as mucilage or transparent exopolymer particles (TEP) from phytoplankton, increasing the PCHO–C yields and C:N ratios. For example, a recent study carried out at the Dyfamed site (Med. Sea1) indicated that the C:N ratio of TEP produced from naturally occurring dissolved organic matter during the summer season is well in excess of the Redfield ratio, with an overall average C:N ratio of ~20 (Xavier et al., 2001). Alternatively, the different C:N ratios of the two systems may be due to different food web

interactions at the time of sampling. Earlier investigations indicated that zooplankton digestion of diatoms increased the C:N ratio (up to 10), and the relative abundance of mannose (up to 28% of the total neutral sugars) in zooplankton fecal pellets (Cowie and Hedges, 1996). The lower C:N ratios of sinking particles measured in the Southern Indian Ocean may suggest low grazing activity in this area compared to the Mediterranean Sea system. However, the relative abundance of mannose (1.4–3.4%) was comparable in all areas (except for STZ; Table 3), possibly indicating that grazing was similar in both systems.

Because proteins are generally considered as the most labile organic compounds in sinking particles (Smith et al., 1992; Wakeham and Lee, 1993), bacterial degradation of particles will give rise to an increase in the relative abundance of other classes of organics such as carbohydrates. This suggests that the C:N ratios in the Southern Ocean are lower than in Mediterranean Sea samples because the sinking particles are less degraded. Our water column measurement do not indicate which area is more bacterially active because bacterial to primary production ratios in the euphotic zone are similar in both areas, ranging between 0.28–0.30 and 0.26–0.38 for Southern Ocean and Mediterranean samples, respectively (Table 1). The overlap in this ratio suggests similar bacterial cycling of dissolved organic matter and probably similar density of bacteria on particles. Alternatively, organic matter in sinking particles from the Southern Ocean might be better protected than that of the Mediterranean Sea because of higher silica content and/or of the lower temperatures (Leblanc et al., 2002) which prevent silica dissolution (Nelson et al., 1995) resulting in lower PCHO–C yields. Such associations between organics and minerals have been proposed (Hedges and Keil, 1999) and were suggested for a study carried out across the PFZ (Ingalls et al., 2003).

#### 4.3. Possible associations between sugars based on the PCA

As previously indicated (Section 3.2.2), fucose and xylose as well as arabinose and galactose formed two compact classes (Fig. 4b). Among these compounds, galactose was the most abundant, in

agreement with earlier studies indicating that this sugar is the major sugar compound of diatom cell walls (Hecky et al., 1973). According to Handa and Yanagi (1969), this monomer also constitutes a large fraction of the insoluble carbohydrates detected in sinking particles. The association of arabinose-galactose, and xylose-fucose probably indicates that these sugars are bound together forming structural heteropolysaccharides (i.e., arabinogalactan, arabinoxylan, and fucoxylan) or homopolysaccharides (i.e., fucoidans, galactans, and xylans) that are abundant in the cell walls of different algae, including diatoms, and are released into seawater at the end of phytoplankton blooms (Handa and Yanagi, 1969; Haug and Mykkestad, 1976; Ittekkot et al., 1982; D'Souza and Bhosle, 2001). To date, no direct evidence (HPLC or GC measurements) exists for the presence of these polymers in marine environments. However, earlier investigations used these substrates to estimate potential hydrolysis rates by marine bacteria in bottom waters and marine sediments (Arnosti, 2000, and references therein). These studies also indicated the less labile-structural nature of these heteropolysaccharides.

Our results also indicated that rhamnose, glucose, and ribose cluster together (Fig. 4b). Rhamnose is generally found in the extracellular or cell wall polysaccharides of diatoms (Tanoue and Handa, 1987) and in bacteria (Haug and Mykkestad, 1976; Kennedy and Sutherland, 1987; Hicks et al., 1994). Glucose is derived from both structural (heteropolysaccharides) and storage ( $\beta$ -1,3 glucans) compounds of phytoplankton (Handa and Tominaga, 1969; Haug and Mykkestad, 1976; Cowie and Hedges, 1984; Tanoue and Handa, 1987; Hernes et al., 1996; Skoog and Benner, 1997; Kerhervé et al., 1999). Much less is known about the distribution of ribose in sinking or suspended particulate material. This is partly due to the degradation of this monosaccharide during strong acid hydrolysis (Borch and Kirchman, 1997; Bier-smith and Benner, 1998). Ribose is a common component of RNA and nucleotides of bacteria, whereas it is found in lower concentrations in phytoplankton and vascular plants (Cowie and Hedges, 1984; Hicks et al., 1994; Opsahl and Benner, 1999). The high relative abundance of ribose in sediment trap material in the PFZ, STZ and Med. Sea2-50 m clearly indicates the presence of non-

structural and labile compounds (RNA, or nucleotides) which may be rapidly degraded (Tanoue and Handa, 1987; Hernes et al., 1996). This is consistent with other observations that suggest that trapped materials were freshly produced. The association of rhamnose, ribose, and glucose may suggest that these sugars have a common origin but clearly cannot provide information concerning their source because these sugars are found in all planktonic organisms including bacteria.

Glucosamine, mannose, and fructose were not associated with other sugars. Glucosamine is contained in the polymer chitin (as *N*-acetylglucosamine) that constitutes the refractory structural homopolysaccharide of arthropods, fungi, and marine organisms (Muzzarelli, 1977). In marine bacteria, *N*-acetylglucosamine is often associated with amino acids (alanine, glycine, and glutamic acid) and *N*-acetylmuramic acid constituting the peptidoglycane (Brock et al., 1994; Hedges et al., 2000). Mannose generally occurs in the cell walls and/or extracellular polysaccharides of diatoms (Handa and Yanagi, 1969; Haug and Myklestad, 1976) as well as in bacteria exopolysaccharides (Umezawa et al., 1983; Kennedy and Sutherland, 1987). It has been suggested that fructose is a minor component of marine carbohydrates as it is generally destroyed by strong acid hydrolysis (Borch and Kirchman, 1997). Our results indicate that fructose was present in most of the particulate samples analyzed although higher concentrations (20–37%) were recorded at the UPW station (Table 3). The high abundance of fructose at this station may be due to the presence of Chlorophyceae species, which are known to produce significant quantities of food storage material such as fructans (Percival, 1968). The occurrence of these species at this station was confirmed by pigment analysis (Claustre, unpublished results).

#### 4.4. The influence of diagenesis on the carbohydrate content of sinking particles

A previous study showed a significant vertical gradient in PCHO-C yields throughout the water column of the Equatorial Pacific Ocean revealing the reactive nature of combined aldoses in particulate material (Hernes et al., 1996). Nevertheless, we still have a limited understanding about the

relative fate of particulate sugars compared to other classes of organic compounds. For instance, we found that glucose predominated Mediterranean Sea samples, possibly indicating the presence of fresher organic matter when compared to Southern Ocean samples. However, lower abundance of glucose associated with slightly higher abundance of ribose (STZ) and lower C:N may suggest the opposite conclusion. It is important to note that the low glucose abundance observed at the PFZ and STZ stations is consistent with the low glucosidase activity reported by Christian and Karl (1998) for Southern Ocean particles when compared to Pacific Ocean samples. Currently, we do not know whether glucose is a labile sugar or not because this monosaccharide appears to be the dominant sugar in highly degraded material as well as in fresh and labile DOM (Hama and Yanagi, 2001; Amon and Benner, 2003).

As indicated by Amon and Benner (2003), the lability of glucose-rich polymers depends on the origin of the polysaccharide. Glucose might be the dominant sugar in storage polysaccharides such as glucans (homopolysaccharide) but it is less abundant when associated with other sugars, such as xylose which forms structural polysaccharides (heteropolysaccharide). Glucose-homopolysaccharide is utilized preferentially to glucose-heteropolysaccharide, leading to a relative enrichment of structural polysaccharides (Amon and Benner, 2003). Because particles of the STZ and PFZ were characterized by a low relative abundance of glucose and a high abundance of intracellular and nonstructural sugars such as ribose, glucose in such material would be a component of both storage and structural polysaccharides. On the other hand, in Mediterranean Sea particles, the high abundance of glucose and low abundance of ribose probably reflects that structural heteropolysaccharides are predominant over intracellular homopolysaccharides (glucans), the latter being already degraded.

#### 4.5. Glucose+ribose and C:N ratios

The differences between the various locations including the Southern Indian Ocean, Mediterranean Sea and Atlantic Ocean can also be illustrated in a plot of wt.% of glucose plus ribose vs. the C:N ratio

(Fig. 6). In the same figure, we added the free floating trap (105 m), sediment results from the central Eq. Pacific Ocean (Hernes et al., 1996; Hernes et al., 2001) and sediment core results from the Mediterranean Sea (Gulf of Lyons, Buscail et al., 1995). To our knowledge, there are no available data related to sugars in sedimentary material from the Southern Indian Ocean. The overall results indicate that the wt.% contribution of glucose+ribose of the total carbohydrate pool in sediment trap material (range of 30–80%) was twofold higher than that in the sediment (range of 17–39%). This further suggests that these two monosaccharides were preferentially removed from the sedimentary carbohydrate pool. The C:N ratio and wt.% glucose+ribose were negatively correlated in sediment trap samples of the Southern Indian Ocean as well as sediment trap and sediment material of the Mediterranean Sea (Fig. 6). In the central Eq. Pacific, the correlation was not significant ( $r=-0.22$ ;  $p>0.05$ ;  $n=28$ ) because of similar values of C:N values in the traps and sediments. Fig. 6 also indicates that the association of the C:N ratio with wt.% glucose+ribose can help to assess the fate of the organic pool in the regions studied.

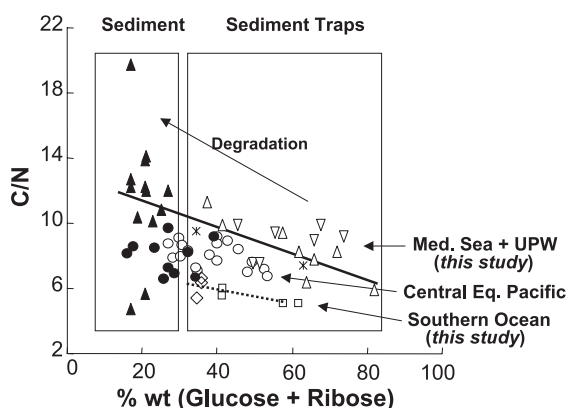


Fig. 6. C:N ratios versus wt.% (Glc+Rib). wt.% ribose were calculated on glucose free basis. For each line, the regression equations and the Spearman's correlation coefficient ( $r$ ) are as follows: black line, UPW and Med. Sea (traps+sed.)  $C/N = -7.53$  (wt.% glc+rib)+13;  $r = -0.53$ ;  $p < 0.01$ ;  $n = 30$ . dashed line: Southern Ocean (traps)  $C/N = -4.00$  (wt.% glc+rib)+7.46;  $r = -0.83$ ;  $p < 0.05$ ;  $n = 7$ . Floating sediment trap (105 m) and sediment data in the central Equatorial Pacific are from Hernes et al. (1996, 2001), respectively. Mediterranean Sea sediment data are from Buscail et al. (1995). Symbols:  $\diamond$ , PFZ 200 m;  $\square$ , STZ 200 m;  $\triangle$ , Med. Sea1 100, 200 m;  $\nabla$ , Med. Sea2 50, 300 m; \*UPW 50 m;  $\circ$  Eq. Pacific 105 m;  $\bullet$ , Sediment Eq. Pacific;  $\blacktriangle$ , Sediment Med. Sea.

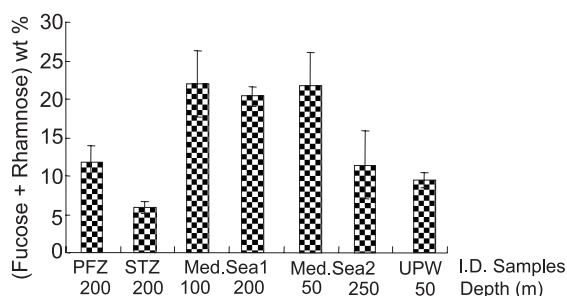


Fig. 7. Average relative abundances (wt.%) of deoxysugars (fucose+rhamnose) calculated on glucose-free basis in particles collected by sediment traps in polar front zone (PFZ), subtropical zone (STZ) in Southern Indian Ocean, from Mediterranean Sea, e.g., Ligurian Sea (Med. Sea1) and Ionian Sea (Med. Sea2) and from the Upwelling of Agadir in coastal (Morocco) Atlantic Ocean.

#### 4.6. Relative abundances (wt.%) of deoxysugars (fucose+rhamnose)

With the exception of Med. Sea2-250 m, our results showed a higher deoxysugar content in sinking Mediterranean particles than in Southern Ocean and coastal Atlantic particles at the time of sampling (Fig. 7). According to Cowie and Hedges (1984) elevated wt.% of deoxysugars are indicative of highly degraded organic material. This conclusion derives from the fact that sediment trap material is depleted in deoxysugars and is enriched in glucose, whereas the opposite is observed for sediment material. This consideration suggests that Mediterranean sinking particulate material is more degraded than that of Southern Ocean or the Atlantic UPW, consistent with C:N ratios and glucose and ribose relative abundances (see above). Alternatively, Haug and Myklesstad (1976) and Myklesstad (1995) indicated that in response to nutrient stress some *Chaetoceros* species (case of Mediterranean Sea) may excrete copious amounts of extracellular polysaccharides, mainly consisting of deoxysugars and galactose, which could explain in part the higher deoxysugar levels in the Mediterranean Sea during the period studied.

#### Acknowledgments

We are grateful to the captain and crew of the R.V. Marion Dufresne and R.V. Atalante for excellent



service at sea as well as Michel Denis and Hervé Claustre chief scientists during Antares-4 and Prosopé oceanographic cruises, respectively. We also thank C. Jeandel and C. Bournot-Marec for sediment trap deployments and particle collection. Our special thanks to L. Ignatiades who performed PCA analysis for sugars. We also acknowledge P. Raimbault, B. Charrière, and A. Masson for POC analyses, T. Moutin and B. Quéguiner for primary production data and R. Lafont for laboratory assistance. This manuscript benefited from advice and comments given by D. Delmas, P. Kerhervé, A. Momzikoff, A. Juhl, and K. Mopper. We are grateful to Peter Hernes and one anonymous reviewer for discussion and advice on the submitted version of the article. This research was supported by France-PROOF projects (Antares-4 and Prosopé). Financial support for C.P. PhD thesis came from the Alexander S. Onassis Public Benefit Foundation, Greece.

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