

# Variation in the composition of carbohydrates in the Dona Paula Bay (west of India) during May/June 1998

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**Abstract** – Suspended particulate material was analysed for particulate carbohydrate concentration and composition and for the bulk parameters: suspended particulate matter, chlorophyll *a*, particulate organic carbon, particulate organic nitrogen and particulate proteins. Chlorophyll *a* concentrations increased from May 7 to 15 due to the development of a small scale bloom of diatom *Navicula* sp. and decreased for the remaining period after the premonsoon rain on 16 and 17 May. Concentrations of particulate organic carbon, organic nitrogen, carbohydrates and proteins increased with the increase in chlorophyll *a* concentration. Together particulate protein–carbon and carbohydrate–carbon accounted for 10 to 30% of the organic carbon. Glucose contributed 26 to 81% to the total particulate carbohydrates. The decrease in glucose concentration was accompanied by the increase in mannose, galactose, xylose, arabinose, rhamnose and fucose. Chlorophyll *a* showed significant positive relationship with glucose and negative relationships with arabinose and xylose. Conversely, suspended particulate matter showed significant positive relationships with xylose and arabinose and negative relationships with chlorophyll *a* and glucose. The hexoses to pentoses ratio increased during 7 to 15 May and decreased thereafter. Relatively higher chlorophyll *a*, particulate protein–carbon plus carbohydrate–carbon, glucose, hexoses: pentoses ratio and lower rhamnose plus fucose suggested the presence of more fresh marine organic matter during May 8 to 15. Subsequently, chlorophyll *a*, contribution of particulate protein–carbon plus carbohydrates–carbon to organic carbon, hexoses to pentoses ratio, and weight percentage of glucose decreased whereas, weight percentage of rhamnose plus fucose, arabinose and xylose increased, reflecting highly degraded diagenetically altered particulate organic matter from May 16 to June 2. The carbohydrate content and composition as well as protein data suggest that the nature and source of organic matter varied within a few days at this tropical coastal site. Such variability in the nutritional quality of organic matter may have a strong influence on the metabolic activity of filter feeding organisms. © 2001 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

**Résumé – Variation de la composition en carbohydrates dans la baie de Dona Paula (ouest de l'Inde) en mai–juin 1998.** La concentration en chlorophylle *a* a augmenté du 7 au 15 mai (floraison de la diatomée *Navicula* sp.), avant de décroître après l'épisode pluvieux des 16 et 17 mai. Les concentrations de carbone et d'azote organique particulaires, ainsi que les hydrates de carbone et les protéines varient parallèlement à la chlorophylle *a*. Le carbone particulaire (protéines et hydrates de carbone) représente de 10 à 30% du carbone organique. Le glucose représente de 26 à 81% du total des hydrates de carbone dans le matériel particulaire. Sa décroissance est accompagnée de l'accroissement du mannose, du galactose, du xylose, de l'arabinose, du rhamnose et du fucose. La chlorophylle *a* présente une corrélation positive avec le glucose et négative avec l'arabinose et le xylose. La matière particulaire en suspension est positivement corrélée au xylose et à l'arabinose et négativement à la chlorophylle *a* et au glucose. Le rapport hexoses/pentoses s'élève du 7 au 15 mai et décroît après. Les concentrations relativement élevées en chlorophylle *a*, en carbone sous forme de protéines et d'hydrates de carbone, en glucose et le taux hexoses/pentoses élevé ainsi que les valeurs basses du rhamnose

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plus fucose suggèrent la présence de matière organique marine néoformée dans la période du 8 au 15 mai. Les tendances inverses s'observent du 16 mai au 2 juin. La teneur et la composition en hydrates de carbone, ainsi que les données de protéines suggèrent une variation de l'origine de la matière organique en peu de jours à ce site côtier tropical. Une telle variabilité de la qualité nutritive de la matière organique doit avoir une forte influence sur l'activité métabolique des filtreurs. © 2001 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

## **carbohydrates / India coast / nutrients / suspended particulate matter**

### **hydrates de carbone / côte de l'Inde / nutriments / matière particulaire en suspension**

#### **1. INTRODUCTION**

Carbohydrates are the structural and storage components of both marine and terrestrial organisms. Carbohydrates constitute an important fraction of dissolved, particulate and sedimentary organic matter (Mopper et al., 1980; Benner et al., 1992; Pakulski and Benner, 1994; McCarthy et al., 1996; Hernes et al., 1996; Borch and Kirchman, 1997; Skoog and Benner, 1998; Borsheim et al., 1999; Burdige et al., 2000). In particulate samples, the contribution of carbohydrate carbon to the particulate organic carbon (POC) may vary from 10 to 30% (Bhosle et al., 1992; Hernes et al., 1996; Sigleo, 1996). They are also central to many environmental processes such as formation of humic substances (Yamaoka, 1983), removal of dissolved metals (Geesey et al., 1986; Decho, 1990), flocculation of dissolved organic material (Mopper et al., 1995), mucilaginous macroaggregate production following eutrophication (Thornton et al., 1999) and the adhesion of microorganisms to soils and sediments (Cheshire, 1979; Decho, 1990).

It appears that some of the carbohydrates, such as storage polysaccharides (labile sugars), are rapidly utilized by the in situ organisms during its transport from the euphotic layer to greater depths (Handa and Tominaga, 1969; Ittekkot et al., 1982; Tanoue and Handa, 1987; Bhosle and Wagh, 1989; Bhosle et al., 1989). Such selective utilization of storage polysaccharides results in the accumulation of relatively less degradable structural polysaccharides (refractory sugars) as the major components of carbohydrates in particular organic matter of deep oceanic waters and marine sediments (Tanoue and Handa, 1987; Hamilton and Hedges, 1988; Cowie and Hedges, 1992; Cowie et al., 1992; Burdige et al., 2000). Further, the structural polysaccharides are relatively more refractory in nature and therefore, are more likely to leave an imprint on the geological record. Thus, carbohydrates are useful tools in elucidating sources and metabolic path-

ways of organic material in aquatic environments. Several studies have been carried out, wherein the spectral distribution of sugars in particulate matter, soil and sediments has been used as an indicator of the source in both marine and freshwater environments (Degens and Mopper, 1976; Cowie and Hedges, 1984; Preston and Prodduturu, 1992; Compiano et al., 1993). For example, the ratio of glucose:ribose may be used to distinguish inputs from marine and terrestrial sources, with a high ratio (> 20) indicating a terrestrial source (Degens and Mopper, 1976; Kemp, 1977; Liebezeit, 1986). However, the use of glucose:ribose was contested by others (Cowie and Hedges, 1984; Ittekkot and Arain, 1986). It was argued that a high ribose or glucose content in a sample might also result from its contribution from bacteria and phytoplankton. The arabinose to fucose ratio has been used to differentiate inputs from calcareous and siliceous sources in sediment trap materials (Ittekkot et al., 1984). Cowie and Hedges (1984) have suggested the use of several monomers to distinguish between terrestrial plant material, bacteria, phytoplankton and zooplankton. For example, they proposed the use of mannose to xylose ratio, the total percentage distribution of ribose plus fucose as well as of arabinose plus galactose in a sugar fraction (calculated on glucose-free basis) to distinguish plant material, bacteria, phytoplankton and zooplankton sources in suspended and sedimenting materials and in sediments. The total contribution from hexoses and pentoses in suspended material has also been employed for source identification, with low hexoses to pentoses (w:w) ratio being typical of soil organic matter derived from terrestrial plant material (Stevenson, 1982; Ittekkot and Arain, 1986).

In shallow coastal environment changes in organic matter may occur in much shorter time spans. Therefore, sampling at much shorter intervals is needed to understand the processes in shallow water environments. In order to evaluate nature and sources of organic matter,

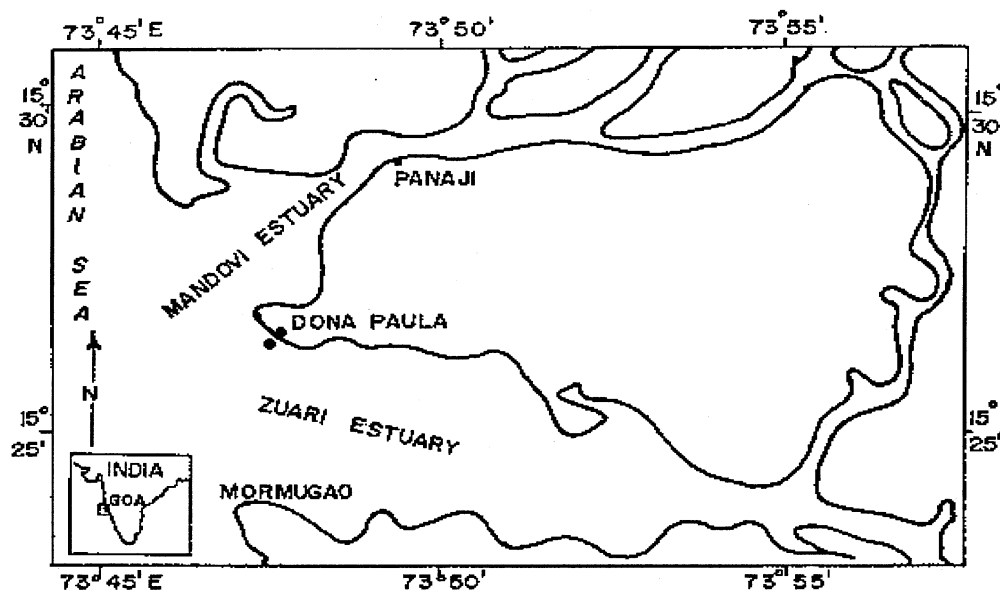


Figure 1. Location of the sampling station (●) in Dona Paula Bay, west coast of India.

suspended particulate material samples were collected from surface seawater (2 m) at one to three day intervals at a station in the Dona Paula Bay, west coast of India. The aims of the study presented here are: 1) to assess the changes in organic matter during the period of sampling, 2) to identify the variation in sources of organic matter, 3) to define the degradative changes in organic matter over a time scale of few days and, and 4) to study the effect of premonsoon rain on the nature of organic matter.

## 2. MATERIALS AND METHODS

### 2.1. Study area

The sampling station in the estuarine waters of the Dona Paula Bay was about 8 m deep (figure 1). Earlier works indicate that the surface water temperature ranges from 25°C to 35°C at the station. Salinity fluctuated from low of 10 during the southwest monsoon (June to September) to 35 during the summer months (February to May). The tidal range varied from neap tide of 0.25 m to spring tide of 2 m (Chandramohan et al., 1998). The current varied from a low of approximately 1 cm s<sup>-1</sup> in November–December, to a high of approximately 25 cm s<sup>-1</sup> in April–May (Jayakumar, personal communication). The mean significant wave height recorded in these waters was

0.93 ± 0.18 m, and the frequency of maximum height waves was approximately 10 s (Vethamony and Kumar, 1997). Nitrate concentrations at the station vary from 1 μM to 3 μM (Devassy and Goes, 1989). The site receives terrestrial organic inputs from the Zuari and Mandovi estuaries, which are fringed with thick mangrove coverage (Wafar et al., 1997). The average freshwater runoffs through the Mandovi and Zuari rivers are 300 m<sup>3</sup> s<sup>-1</sup> during monsoon (August) and 85 m<sup>3</sup> s<sup>-1</sup> in premonsoon (April) (Unnikrishnan et al., 1997). The primary production has been reported to be higher in postmonsoon than in premonsoon months (Devassy and Goes, 1988). The phytoplankton population in the study area is predominantly composed of diatoms with minor contributions from dinoflagellates and other algal forms (Bhaskar et al., 2000). The area experiences periodic blooms of diatoms during December–January and April–May (Devassy and Goes, 1988). The predominant diatom species are *Pleurosigma*, *Navicula*, *Nitzschia*, *Skeletonema*, *Chaetoceros*, *Rhizosolenia*, and *Coscinodiscus* (Garg and Bhaskar, 2000). The net zooplankton population is dominated by grazers like copepods, followed by chaetognaths larve (Padmavati and Goswami, 1996). The herbivore and carnivore zooplankton are most abundant in November–December and April–May, respectively (Padmavati and Goswami, 1996). The bottom sediment at the station was a mixture of fine sand and silt, and are poor in organic carbon (0.1%; Bhaskar et al., 2000).

## 2.2. Collection of samples

Surface seawater (2 m) samples were collected using a clean polyethylene carboy. Sampling was initiated on May 7, 1998 and completed on June 2, 1998. Samples were collected daily or after a gap of 2 to 3 days and the last sample on June 2 was collected after a gap of 7 days. Immediately after collection the samples were passed through 300  $\mu\text{m}$  nylon screens to remove zooplankton. Then duplicate aliquots were filtered through preignited and preweighed GF/F (450°C, 3 h) filters for the analysis of suspended particulate matter (SPM), particulate organic carbon (POC), particulate organic nitrogen (PON), chlorophyll *a*, particulate proteins (PP) and particulate carbohydrates (PCHO). Except for chlorophyll *a* and suspended particulate matter all the samples were stored at  $-20^\circ\text{C}$  until analyses.

Routine hydrographic observations including temperature, salinity and dissolved oxygen (DO) and nutrients nitrate and phosphate were carried out simultaneously during sampling. Temperature was measured using a thermometer. Salinity, DO, nitrate and phosphate were measured using the methods described by Parsons et al. (1984).

## 2.3. Analysis of bulk parameters

The SPM was determined after washing the particulate material on filter with distilled water and then drying the filter in an oven at  $50^\circ\text{C}$  for 24 h. The filter was then cooled and weighed on a Mettler microbalance (model At/20). POC and chlorophyll *a* were analysed using the methods described by Parsons et al. (1984). The PON was estimated following the method of Smart et al. (1983). Proteins were measured by the bicinchoninic acid method (Smith et al., 1985).

## 2.4. PCHO composition

The carbohydrate content and composition of the suspended particulate matter was determined by the capillary gas chromatographic technique described earlier (Bhosle et al., 1990; Bhosle et al., 1993). In brief, the GF/F filter containing particulate matter was treated with 72%  $\text{H}_2\text{SO}_4$  at room temperature ( $28 \pm 2^\circ\text{C}$ ) for 2 h. The sample was diluted to 1.2 M  $\text{H}_2\text{SO}_4$  using cold distilled

water, flushed with nitrogen, sealed and then hydrolysed for 3 h at  $100^\circ\text{C}$ . After cooling an internal standard (inositol) was added to the hydrolysate. Subsequently, the solution was neutralized with calcium carbonate. The  $\text{CaSO}_4$  precipitate was removed by centrifugation. The pH of the resulting solution was raised to 8–9 by adding 10% v:v triethylamine solution in water for hydrolysis of lactones. After about 30 min an excess of  $\text{NaBH}_4$  was added to reduce the monosaccharides to the corresponding alditols. The residual  $\text{NaBH}_4$  after 2 h in dark at room temperature was decomposed by addition of glacial acetic acid. After the effervescence had ceased the solution was evaporated to dryness under reduced pressure. Boric acid was removed by repeated addition of methanol and evaporation to dryness. The samples were desiccated over KOH in vacuo.

The acetylation was performed by addition of pyridine and acetic anhydride (1:1) and keeping it overnight at room temperature ( $28 \pm 2^\circ\text{C}$ ). The acetylation reagent was evaporated under reduced pressure and the resulting sample was desiccated overnight over KOH in vacuo. Subsequently, water (4 mL) was added and the solution was extracted 3 times with equal amount of dichloromethane. The combined dichloromethane extracts were dried on anhydrous sodium sulphate and concentrated.

## 2.5. Capillary gas chromatography

A capillary gas chromatograph (Chrompack model CP-9002) equipped with a fused silica capillary column coated with CPSil-88 (25 m, id = 0.32 mm) and a flame ionization detector was used to separate the alditol acetate mixture. Sample was injected (0.4  $\mu\text{L}$ ) using a programmable on-column injector when the initial oven temperature was  $70^\circ\text{C}$ . The oven temperature was then rapidly raised to  $150^\circ\text{C}$  and further programmed at  $3^\circ\text{C min}^{-1}$  to  $230^\circ\text{C}$  and maintained at this temperature for 10 min. Quantification of the components was achieved by peak area integration of the GC results using Maestro chromatographic data handling system installed in the instrument. In this study the PCHO has been defined as the sum of all the identified monosaccharides. Analytical reproducibility was better than  $\pm 6\%$ .

A simple regression analysis was employed to assess the relationships between various parameters (Sokal and Rohlf, 1981). Principal component analysis was per

formed on a personal computer using the Statistica Software package version 5.0 (Statsoft, Inc.). The data matrix used for principal component analysis consisted of the concentration of each sugars expressed in weight percentage and the particulate matter components *SPM*, chlorophyll *a*, *PP*, *PCHO* and carbon to nitrogen ratio. Factors were extracted after varimax rotation and when the eigenvalues were over 1.

### 3. RESULTS

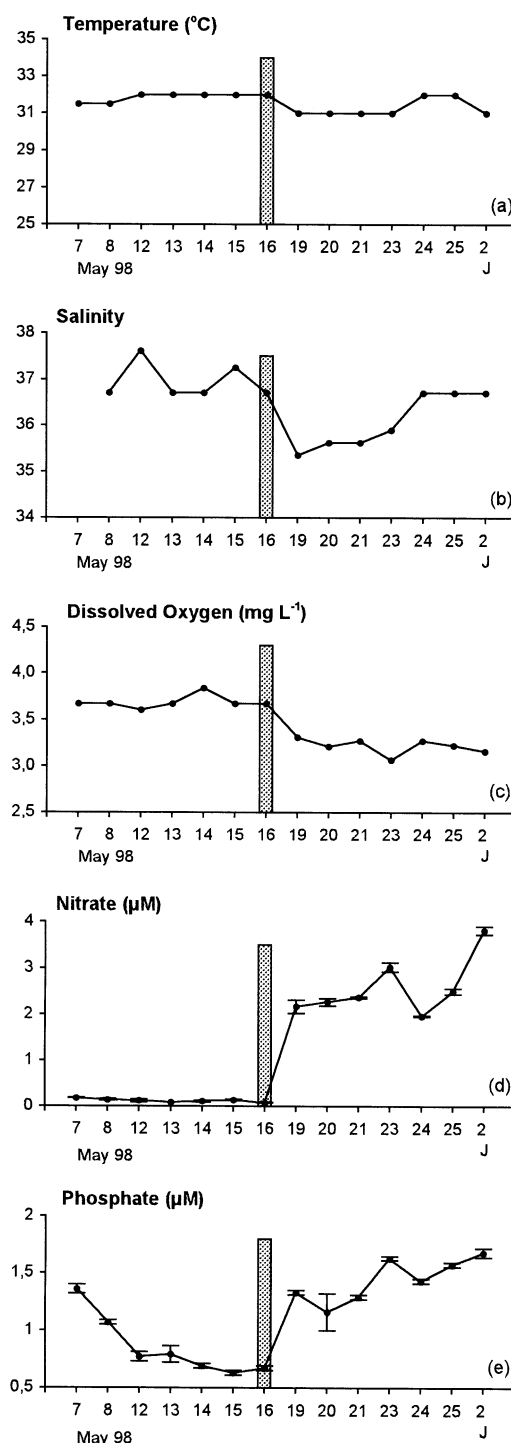
This study was carried out at a station in the Dona Paula Bay (figure 1) from May 7 to June 2, 1998. During the period of sampling the area received unexpected premonsoonal rain with strong winds ( $10$  to  $12 \text{ m s}^{-1}$ ) on 16 May (50 mm) and on 17 May (17 mm). These changes in meteorological conditions resulted in strong variation in the hydrography, nutrients and biochemical compositions of the particulate matter.

#### 3.1. Hydrography and nutrients

The changes in surface seawater temperature, salinity, dissolved oxygen and nutrients nitrate and phosphate during the sampling period are given in figure 2. Throughout the sampling period sea surface temperature remained fairly constant (average:  $31.5 \pm 0.5^\circ\text{C}$ ). After the rain, a small decrease in temperature was recorded from 19 to 23 May (figure 2a). Salinity and dissolved oxygen decreased on May 19 following the rain (figure 2b and c). Over the period of study salinity and dissolved oxygen varied from 35.09 to 37.61 and 3.07 to  $3.84 \text{ mg L}^{-1}$ , respectively. The nitrate concentration was initially low and showed a decreasing trend reaching a minimal value on 15 May and thereafter showed a sharp increase from 19 May onwards (figure 2d). A similar trend was observed for phosphate concentration (figure 2e). The nitrate and phosphate concentration varied from 0.05 to  $3.81 \mu\text{M}$  and 0.63 to  $1.68 \mu\text{M}$ , respectively.

#### 3.2. Bulk parameters

The *SPM* concentration varied from 51.1 to  $83.8 \text{ mg L}^{-1}$ . The *SPM* concentration was fairly constant until May 15 but increased thereafter, and a maximal value was ob



**Figure 2.** Variations in temperature (a), salinity (b), dissolved oxygen (c), nitrate (d) and phosphate (e) in the surface water of the Dona Paula Bay during the period of sampling from 7 May to 2 June 1998. Bars indicate mean  $\pm$  SD. Shaded bar indicates premonsoon rainfall.

served on June 2 (*figure 3a*). The average *POC* concentration was  $1857 \pm 182 \mu\text{g L}^{-1}$  and showed small fluctuations throughout the sampling period (*figure 3b*). The *PON* concentration varied from 73 to  $131 \mu\text{g L}^{-1}$  (*figure 3c*). The *PON* values generally decreased after the rain event of 16 May. The C:N ratio varied from 17.31 to 29.16 (*figure 3d*). The chlorophyll *a* concentration of the particulate matter varied from 0.26 to  $1.69 \mu\text{g L}^{-1}$  and the highest concentration (6.5 fold increase) was recorded on 15 May. This was followed by a sharp decrease in chlorophyll *a* concentration for the subsequent period of sampling (*figure 3e*). Concentration of *PP* varied from 257.3 to  $514.6 \mu\text{g L}^{-1}$  and exhibited a trend similar to that of chlorophyll *a* (*figure 3f*). *PCHO* concentration (sum of all identified monosaccharides) ranged between 101.5 to  $719.4 \mu\text{g L}^{-1}$ . The *PCHO* concentration increased over the period of sampling and reached a highest value on 15 May. This was followed by a sharp decrease on 19 May (*figure 3g*). In the later period of sampling there were small variations in *PCHO* concentrations. The pattern of increase in the *PCHO* was similar to that observed for chlorophyll *a* concentration. The *PP:PCHO* ratio showed a very wide variation (0.56 to 3.18) (*figure 3h*). In general the lowest ratio was associated with lowest nutrients and highest chlorophyll *a* concentration. After the rain event the ratio was relatively high. The *PCHO* yields (mg *PCHO* per 100 mg organic carbon) increased during 7 to 15 May and decreased for the remaining period of sampling (*figure 4a*). The contribution of *PCHO-C* and *PP-C* to the total *POC* varied between 9 to 29.6% (*figure 4b*).

### 3.3. Monosaccharides

The capillary gas chromatographic analyses revealed the presence of eight individual sugars in the hydrolysate of the suspended particulate matter of the surface seawater. The identified monosaccharides were rhamnose, fucose, ribose, arabinose, xylose, mannose, galactose and glucose (*table I*). Concentrations (as micrograms per liter and weight percentage) of these monosaccharides varied over the period of sampling. Of these, glucose was the most abundant monosaccharide in the particulate matter of the surface seawater. When the sampling was initiated on 7 May, the glucose concentration was 39%. With the increase in chlorophyll *a* concentration glucose contribution to the total *PCHO* also increased and reached a maximal value of 81% (*table I, figure 5*). Subsequently, glucose concentration declined to 26% on 23 May.

Thereafter no consistent trend was evident in the contribution of glucose to *PCHO*. On 2 June, the last sampling day, glucose contribution to the *PCHO* was 34.6%, which was similar to the value recorded on 7 May (39%). On the other hand, after the rain event, the abundance of other monosaccharides particularly rhamnose, fucose, xylose and arabinose, galactose and mannose increased, while that of glucose decreased (*figure 5*). Together these monosaccharides (excluding glucose) accounted for 65 to 74% of the total *PCHO*. Monosaccharides composition and especially glucose content (as weight percentage), clearly shows the presence of three types of particulate matter with different degradative histories (*figure 5*). For example, partially degraded organic matter with intermediate value of glucose (39%) was recorded on 7 May. Whereas, highly degraded organic matter containing 26.5% of glucose was present after the rain event, which took place on the night of 16 May. Conversely, relatively fresh organic matter was present on 15 May as evident from very high glucose content (81%).

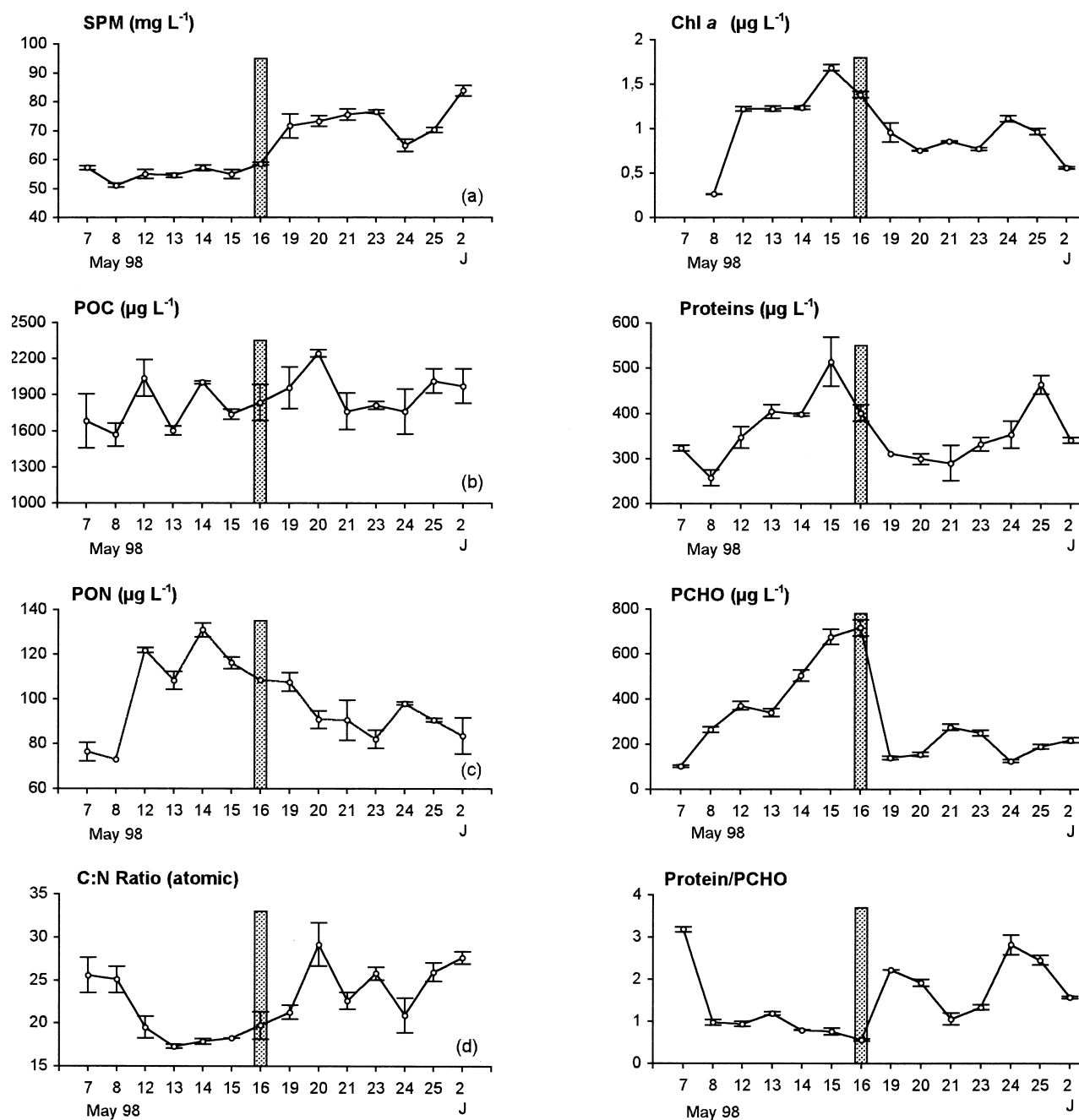
Classifying the different monosaccharides into hexoses (glucose, mannose and galactose), pentoses (ribose, arabinose and xylose) and deoxy sugars (rhamnose and fucose), their relative contribution to the total *PCHO* was: hexoses 71 to 91%, pentoses 2.71 to 15.42%, and deoxy-sugars 5.63 to 23.30% (*table I*). Hexoses were the major contributors, followed by deoxy sugars and pentoses to the total *PCHO* (*table I*). When the sampling was initiated on 7 May, the hexoses to pentoses ratio was low. The ratio increased with the increase in chlorophyll *a* concentrations until 15 May and thereafter the ratio declined rapidly (*figure 6a*).

### 3.4. Ratio of sugars and glucose-free weight percentages

The mannose to xylose ratio varied from < 1 to 3.5 over the period of sampling (*figure 6b*). Glucose-free weight percentages of arabinose plus galactose varied between 25.2 to 43.7% (*figure 6c*).

### 3.5. Relationships between particulate parameters

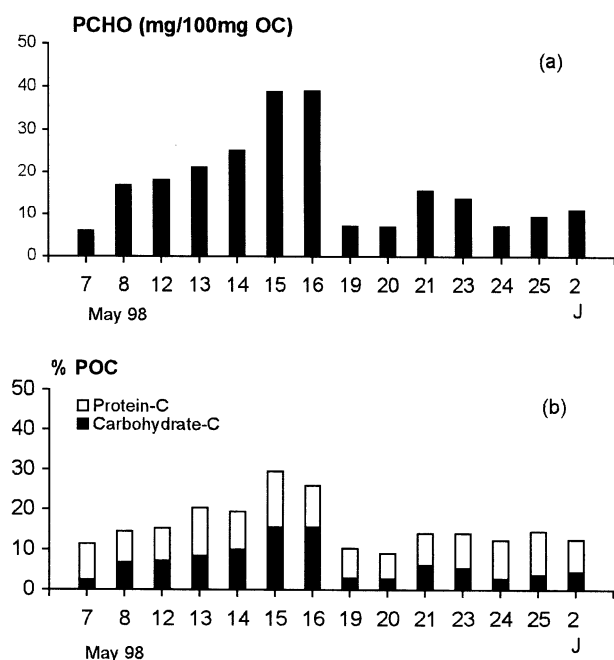
The suspended particulate matter showed a significant positive correlation with *POC* ( $r = 0.806$ ;  $P < 0.01$ ) and



**Figure 3.** Concentration of *SPM* (a), *POC* (b), *PON* (c), C:N ratio (d), chlorophyll *a* (e), proteins (f), total monosaccharides (g) and proteins:*PCHO* ratio (h) in the surface water of Dona Paula Bay during the period of sampling from 7 May to 2 June 1998. Bars indicate mean  $\pm$  SD. Shaded bar indicates premonsoon rainfall.

a negative correlation with *PON* ( $r = -0.861$ ;  $P < 0.001$ ). The *SPM* also showed negative correlations with chlorophyll *a* ( $r = -0.948$ ;  $P < 0.001$ ) and labile-C (*PCHO*-C

plus *PP*-C) ( $r = -0.767$ ;  $P < 0.01$ ). A moderate relationship was also observed between *POC* and *PON* ( $r = 0.754$ ;  $P < 0.01$ ). On the other hand, the chlorophyll



**Figure 4.** Variation in the carbohydrate yield (a), and in the contribution of protein-carbon and carbohydrate-carbon to POC (b).

*a* concentration of the particulate matter showed significant positive relationships with *PCHO* ( $r = 0.842$ ;  $P < 0.001$ ) and protein ( $r = 0.915$ ;  $P < 0.001$ ). A significant positive correlation was also observed between the concentrations of *PCHO* and *PP* ( $r = 0.849$ ;  $P < 0.001$ ). The *PCHO* concentration exhibited significant inverse correlations with nitrate ( $r = -0.786$ ;  $P < 0.01$ ) and phosphate ( $r = -0.864$ ;  $P < 0.001$ ).

### 3.6. Relationship between monosaccharides and particulate parameters

The *SPM* showed highly significant positive relationships with arabinose ( $r = 0.935$ ;  $P < 0.001$ ) and xylose ( $r = 0.914$ ;  $P < 0.001$ ), and a highly significant negative relationship with glucose ( $r = -0.910$ ;  $P < 0.001$ ). In contrast, chlorophyll *a* showed strong negative relationships with arabinose ( $r = -0.854$ ;  $P < 0.001$ ) and xylose ( $r = -0.909$ ;  $P < 0.001$ ), and a strong positive relationship with glucose ( $r = 0.893$ ;  $P < 0.001$ ). The glucose concentration was influenced by nutrients, as evidenced from strong negative relationships of glucose with nitrate ( $r = -0.888$ ;  $P < 0.001$ ) and phosphate ( $r = -0.912$ ;

$P < 0.001$ ). Concentrations of glucose also showed highly significant inverse relationship with deoxy sugars (rhamnose plus fucose) ( $r = -0.985$ ;  $P < 0.001$ ).

## 4. DISCUSSION

### 4.1. Bulk parameters

The main objective of the study was to assess the changes in the nature of particulate organic matter at short intervals of 1 to 3 days. During the period of sampling a small phytoplankton bloom mostly comprising of diatom *Navicula* sp. was recorded at the study site (qualitative microscopic observation). The bloom was disturbed by strong winds ( $12 \text{ m s}^{-1}$ ) and an unexpected premonsoon rain event on 16 May (50 mm) and May 17 (17 mm). The rain event changed the hydrography, nutrients and nature and sources of particulate organic matter (table II). When the sampling was initiated on 7 May, chlorophyll *a* concentration was low and gradually increased and reached a maximal value on 15 May. The observed increase in chlorophyll *a* indicates algal growth. This was also evident from the fact that the chlorophyll *a* concentrations showed inverse trends with the concentrations of nutrients.

After 16 May following the rain, the chlorophyll *a* concentration decreased. This decrease in chlorophyll *a* was perhaps due to the increase in *SPM* concentrations after the rain and/or reduction in the light penetration. This was evident from the significant negative relationship between the concentrations of chlorophyll *a* and *SPM* ( $r = -0.948$ ;  $P < 0.001$ ), indicating the dilution of chlorophyll *a* by the *SPM* material poor in chlorophyll *a*. The increase in *SPM* concentration after the rain was perhaps due to increased resuspension of bottom sediments because of the presence of stronger winds ( $10$  to  $12 \text{ m s}^{-1}$ ), atmospheric inputs of particles due to rain, and/or suspended material brought in by the river runoff. The latter seems likely, as there was a sudden decrease in salinity by 2 units and increase in *SPM* and nutrients after the rain indicating the river water discharge into the study area (table II).

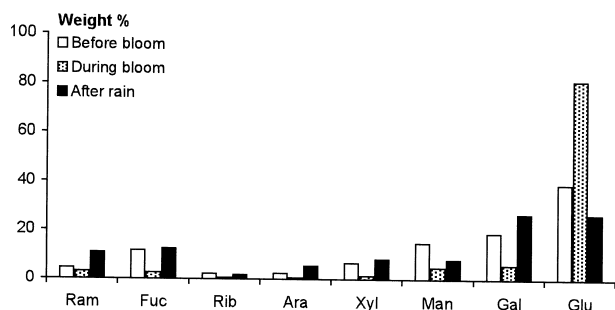
It was interesting to note that *SPM* showed positive and negative relationships with *POC* and *PON*, respectively, suggesting that the particulate material was fairly enriched in carbon relative to nitrogen. A significant



**Table I.** Monosaccharide composition of the particulate matter collected at the Dona Paula Bay, west coast of India during May/June 1998.

Sampling date	Rhamnose		Fucose		Ribose		Arabinose		Xylose		Mannose		Galactose		Glucose		Hexoses		Pentoses		Deoxy sugars	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
07/5/98	4.42	4.35	11.91	11.73	2.31	2.28	2.52	2.48	6.71	6.61	14.99	14.77	19.22	18.93	39.44	38.85	73.65	72.55	11.54	11.37	16.33	16.09
08/5/98	6.54	2.48	8.97	3.40	4.16	1.58	1.94	0.74	7.46	2.83	15.74	5.97	21.89	8.30	197.12	74.72	234.75	88.98	13.56	5.14	15.51	5.88
12/5/98	20.05	5.43	35.75	9.68	5.20	1.41	5.49	1.49	12.59	3.41	28.92	7.83	29.05	7.87	232.22	62.89	290.19	78.58	23.28	6.30	55.80	15.11
13/5/98	6.25	1.84	17.31	5.10	3.84	1.13	2.31	0.68	6.98	2.05	21.28	6.26	31.12	9.16	250.59	73.77	302.99	89.20	13.13	3.87	23.56	6.94
14/5/98	28.25	5.61	34.88	6.92	5.23	1.04	6.18	1.23	16.98	3.37	40.71	8.08	81.51	16.18	290.15	57.58	412.37	81.84	28.39	5.63	63.13	12.53
15/5/98	19.79	2.93	18.29	2.71	4.71	0.70	4.06	0.60	9.52	1.41	33.11	4.90	39.71	5.88	546.68	80.89	619.50	91.66	18.29	2.71	38.08	5.63
16/5/98	30.48	4.25	42.93	5.99	6.48	0.90	10.53	1.47	18.18	2.54	59.03	8.23	91.85	12.81	457.65	63.82	608.53	84.86	35.19	4.91	73.41	10.24
19/5/98	11.37	8.13	8.55	6.11	3.49	2.49	4.63	3.31	6.85	4.90	19.70	14.08	14.38	10.28	70.93	50.70	105.01	75.06	14.97	10.70	19.92	14.24
20/5/98	10.95	7.03	11.17	7.17	3.39	2.18	3.97	2.55	8.67	5.57	20.67	13.27	26.68	17.13	70.26	45.11	117.61	75.51	16.03	10.29	22.12	14.20
21/5/98	18.36	6.68	34.13	12.41	5.06	1.84	13.18	4.79	18.09	6.58	43.16	15.69	70.11	25.49	72.95	26.52	186.22	67.71	36.33	13.21	52.49	19.08
23/5/98	27.09	10.91	30.78	12.40	4.68	1.89	13.31	5.36	20.29	8.17	19.97	8.05	66.37	26.74	65.72	26.48	152.06	61.26	38.28	15.42	57.87	23.31
24/5/98	12.17	9.72	11.62	9.28	4.19	3.35	4.05	3.24	10.47	8.36	19.39	15.49	24.31	19.42	38.99	31.14	82.69	66.05	18.71	14.95	23.79	19.00
25/5/98	9.51	5.04	9.37	4.96	3.35	1.77	3.66	1.94	9.26	4.90	19.03	10.08	23.35	12.37	111.27	58.94	153.65	81.38	16.27	8.62	18.88	10.00
02/6/98	14.66	6.74	20.35	9.35	2.18	1.00	10.02	4.61	15.10	6.94	34.49	15.85	45.56	20.94	75.19	34.56	155.24	71.36	27.30	12.55	35.01	16.09

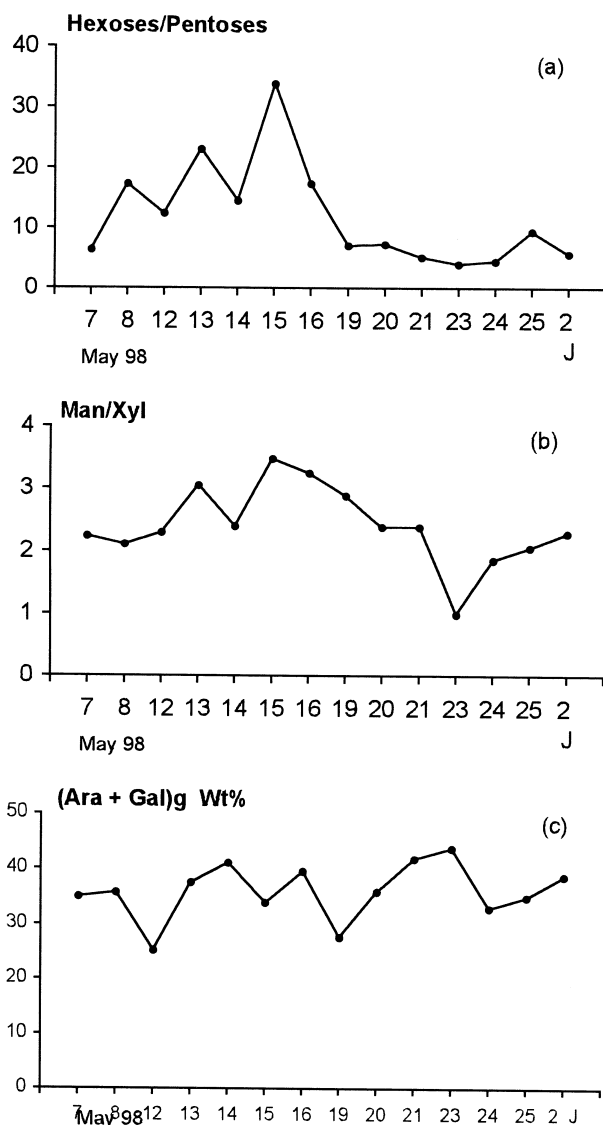
a: concentrations in micrograms per litre; b: percentage of weight.



**Figure 5.** Monosaccharides composition of the particulate matter before the bloom, during the bloom and after rain at the Dona Paula Bay during the period of sampling from May/June 1998.

positive relationship between the *POC* and *PON* indicates that these components concomitantly varied in these *SPM* samples. The carbon:nitrogen ratio (atomic) is one of the useful tools to assess the nature of organic matter. There were clear differences in the carbon to nitrogen ratio over the sampling period. When the sampling began on 7 May, this ratio was high (25), decreased to a lowest value of 17 on May 13, and increased again after May 15. Marine planktons have a ratio of around 5–6 (Hamilton and Hedges, 1988). In contrast, the ratios for vascular plant debris have been reported to fall in the range of 20–200 (Hedges et al., 1986). Thus the increasing chlorophyll *a* and decreasing trend in carbon:nitrogen ratio may indicate increasing contribution of the fresh marine organic matter during 7 to 15 May. However the observed high carbon:nitrogen ratio before the bloom and after the rain suggest the presence of either degraded marine organic matter or terrestrial organic matter in the study area. Degraded terrestrial material is enriched in nitrogen relative to carbon because of the colonization or adsorption by microorganisms. The presence of such material may be responsible for the observed trend in carbon:nitrogen ratio. Further adsorption of inorganic nitrogen by *SPM* may also influence the observed carbon:nitrogen ratio. Therefore, with the data at hand it is not possible to identify the exact reasons for the observed carbon:nitrogen ratio in our sample.

The *PCHO* and *PP* concentrations varied from 101.5 to 719.4  $\mu\text{g L}^{-1}$  and 257.3 to 514.6  $\mu\text{g L}^{-1}$ , respectively. These concentrations are in the range observed for the coastal and estuarine waters (Ittekkot et al., 1982; Ochiai et al., 1988; Sigleo, 1996; Jennerjahn and Ittekkot, 1999). The changes in *PCHO* and *PP* concentrations paralleled the distribution of chlorophyll *a*. Chlorophyll *a* was



**Figure 6.** Variation in the hexoses:pentoses ratio (a), mannose to xylose ratio (b) and weight percentage of arabinose + galactose (on a glucose-free basis) (c) of the suspended particulate matter of the Dona Paula Bay.

significantly related with *PP* ( $r = 0.915$ ;  $P < 0.001$ ) and *PCHO* ( $r = 0.842$ ;  $P < 0.001$ ). Similarly, we observed significant correlation between *PCHO* and protein ( $r = 0.849$ ;  $P < 0.001$ ). From these relationships it was evident that phytoplankton was the major source for these compounds in the *SPM* samples.

The observed increase in the contribution of *PCHO-C* and *PP-C* to the total carbon suggests that these com

**Table II.** Summary of the hydrography, nutrients and biochemical parameters at the Dona Paula Bay, west coast of India during May/June 1998.

	Before bloom	During bloom	After rain
Temperature (°C)	31.50	32.00	31.00
Salinity	36.71	37.25	35.90
Dissolved oxygen (mg L <sup>-1</sup> )	3.67	3.67	3.07
Nitrate (μM)	0.18	0.14	3.03
Phosphate (μM)	1.36	0.63	1.63
SPM (mg L <sup>-1</sup> )	57.20	55.00	76.50
POC (μg L <sup>-1</sup> )	1683.29	1736.79	1813.08
PON (μg L <sup>-1</sup> )	76.46	116.07	82.14
C:N ratio	25.58	18.25	25.79
Chl <i>a</i> (μg L <sup>-1</sup> )	0.26	1.69	0.77
PP (μg L <sup>-1</sup> )	323.14	514.62	332.11
PCHO (μg L <sup>-1</sup> )	101.52	675.87	248.21
PP:PCHO ratio	3.18	0.76	1.34
PCHO yield (mg per 100 mg OC)	6.03	38.91	13.69
PCHO-C + PP-C / POC (%)	11.43	29.49	14.09

pounds were produced during the growth of phytoplankton. The relative distribution of *PCHO* and *PP* however, appears to vary during the period of study. For example, during the initial period of sampling the *SPM* material contained a lower quantity of carbohydrate and a higher quantity of protein. Conversely, the *SPM* material collected during the later period of sampling had a lower protein and a higher carbohydrate content. Laboratory grown diatom cultures and natural phytoplankton populations are known to produce lower amount of carbohydrates and higher amount of proteins during the early logarithmic growth phase (Myklestad, 1977; Hitchcock, 1978), while diatom cells in the stationary growth phase produce higher amount of carbohydrate and lower amount of protein. It is possible that the relative distribution of *PCHO* and *PP* in our samples reflects the effect of growth phase of natural diatom populations.

Marine diatoms appear to have a relatively high production of carbohydrates in culture (Handa, 1969; Myklestad et al., 1989) and in natural waters (Ittekkot et al., 1981; Tanoue and Handa, 1987; Bhosle et al., 1989), especially during nutrient deficient condition (Myklestad, 1977; Hama and Honjo, 1987). This was also the case at the study site, as higher amounts of carbohydrate were produced by the natural phytoplankton population when nutrient deficient condition prevailed. This was substantiated by the inverse correlations between carbohydrate and nutrients nitrate ( $r = -0.786$ ;  $P < 0.01$ ) and phosphate ( $r = -0.864$ ;  $P < 0.001$ ). A further support for this can be obtained from the protein:carbohydrate ratio, which was

lowest ( $< 0.6$ ) when the nutrient concentration was lowest (Myklestad, 1974; Hitchcock, 1978).

The *PCHO-C* and *PP-C* contributed 2.7 to 15.6% and 6.3 to 14.0% to the total percentage of *POC*, respectively. Together the contribution of these compounds to the total *POC* varied from 9.0 to 29.6%. Their contribution to *POC* was high during 7 to 15 May (11.0 to 29.6) and low during 16 May to 2 June (9.0 to 14.0). Furthermore, the contribution of these compounds to *POC* decreased with the increase in *SPM* content of the seawater. This relationship between the nature of *POC* and *SPM* concentrations for individual samples may be either due to differences in the sources of organic matter or due to biodegradation processes. Thus the high contribution of *PCHO* and *PP* to *POC* may result from a predominantly autochthonous input of organic matter, for example from in situ primary production (Thurman, 1986). This is further supported by the strong correlations of *PCHO* and *PP* with the concentrations of chlorophyll *a*. In contrast to this, relatively less *PCHO* and *PP* were associated with high *SPM* concentrations, suggesting either the dilution of organic matter with inorganic material or contribution from extensively degraded soil organic matter. What is geochemically significant here is the relatively inert nature of the *POC* associated with high *SPM* concentration after the rain. This organic matter appears to have undergone significant biochemical degradation before reaching the sampling point. This biodegradation could have occurred in soils, from which a part of organic

matter is derived, within the rivers during the sediment storage and/or in flood plains.

It was interesting to note that the organic matter collected after the rain (19 May) showed some enrichment of ribose and protein but was depleted in *PCHO*. The relatively higher protein concentration after rain may reflect selective partitioning of dissolved organic material between water and negatively charged particles, such as clay minerals (Theng, 1979; Hedges et al., 1994). Basic amino acids and/or other nitrogenous compounds impart a positive charge on dissolved organic materials such as proteins and humic acids within the natural pH (Thurman, 1986; Hedges et al., 1994). Such a process may have facilitated the adsorption of protein on clay minerals and other particles, thereby enhancing the protein content of the *SPM* material after the rain. Further, the observed increase may also be due to the adsorption or colonization of bacteria and/or diatom onto the clay minerals.

#### 4.2. Monosaccharide spectra

Capillary gas chromatographic analysis revealed the presence of eight individual sugars, namely rhamnose, fucose, ribose, arabinose, xylose, mannose, galactose and glucose, in the *SPM* samples. These monosaccharides are of common occurrence in the carbohydrates of suspended particles collected from various marine environments (Cowie and Hedges, 1984; Tanoue and Handa, 1987; Bhosle et al., 1992). The contribution of individual sugars to the total *PCHO*, however, varied during the period of sampling. This temporal variability in carbohydrate composition may be due to changes in the growth phase of algae (Decho, 1990; Bhosle et al., 1995), sources and the nature of organic material in the suspended particulate matter.

Of the eight monosaccharides, glucose was the most abundant in the particulate matter over the period of sampling. This was not surprising since it is the dominant sugar in all forms of terrestrial and marine sources. Its concentration varied from 26 to 81%. A glucose contribution ranging from 20 to 80% to the total *PCHO* has been reported for the suspended particulate matter collected from other marine environments, particularly during phytoplankton blooms or for laboratory grown stationary phase diatom cultures (Handa and Yanagi, 1969; Ittekkot et al., 1982; Tanoue and Handa, 1987; Bhosle et al., 1990). In the present study, during the period of

phytoplankton bloom glucose contribution to the total *PCHO* increased from 39 to 81%, indicating the synthesis of glucose-rich polymers. This was further supported by the significant positive correlation between glucose and chlorophyll *a* ( $r = 0.893$ ;  $P < 0.001$ ), which also suggests that increase in concentration of glucose was due to the growth of phytoplankton. In addition, some of the *Navicula* sp. has been reported to produce polysaccharides rich in glucose (90%) when grown in the laboratory conditions (Bhosle et al., 1995). Further, in diatom cultures or natural populations, accumulation of glucose-rich polysaccharides  $\beta$ -1,3 glucan takes place under nutrient-limited conditions (Handa, 1969; Handa and Tominaga, 1969). Concentrations of glucose showed inverse correlations with nutrients nitrate and phosphate, suggesting the possible role of these nutrients in regulating the concentration of glucose containing polysaccharides in algae. Subsequently, after the rain (after 15 May) the weight percentage of glucose concentration decreased. This was also evident from the relative increase in other monosaccharides. Therefore, it is possible that the decrease in glucose content reflects the preferential utilization of the glucose-rich polymers. Alternatively, the observed decrease in glucose may indicate dilution due to glucose-poor material or decrease in phytoplankton biomass. We observed a significant inverse correlation between the concentrations of glucose and the concentrations of *SPM*. This implies that the decrease in glucose was also due to dilution by *SPM* poor in glucose.

The decrease in glucose content was associated with the increase in galactose, mannose, xylose, arabinose, rhamnose and fucose. These monosaccharides are major components of diatom cell wall (Hecky et al., 1973; Haug and Myklestad, 1976). The cell wall, i.e. structural polysaccharides, decomposes less rapidly than the glucose-rich polysaccharides in the ocean (Handa and Yanagi, 1969; Ittekkot et al., 1982). The increased abundance of these monosaccharides during the period of sampling thus indicates the relative stability of these compounds during the initial period of decomposition (Handa and Yanagi, 1969; Bhosle et al., 1992).

The *SPM* samples exhibited 2 to 4 fold increase in the absolute concentration as well as the weight percentage of deoxy sugars (rhamnose plus fucose) at the expense of glucose. An increase in the percentages of deoxy sugars and a corresponding decrease in glucose has been observed in more degraded riverine particulate organic

matter and decomposing vascular plant tissues (Hedges et al., 1994; Opsahl and Benner, 1999). However, elevated levels of deoxy sugars may also indicate the contribution from microbial biomass (Cowie and Hedges, 1984; Hamilton and Hedges, 1988; Hedges et al., 1994; Opsahl and Benner, 1999). In our samples the weight percentage contribution of ribose is inferior to 3%, implying that microbial biomass was not the major contributor to the elevated levels of deoxy sugars. Hedges et al. (1994) observed an increase in the percentages of deoxy sugars with a progressive increase in the degradation of natural particulate organic matter. Opsahl and Benner (1999) also reported a selective increase in deoxy sugars and a decrease in glucose and xylose in several types of mangrove tissues. In our samples, there was a significant inverse relationship between glucose and deoxy sugars ( $r = 0.985$ ;  $P < 0.001$ ) suggesting the selective utilization of glucose. These results suggest that the abundance of deoxy sugars relative to glucose indicate degradative state of organic matter (Hedges et al., 1994; Opsahl and Benner, 1999).

The mannose to xylose ratios varied from  $< 1$  to 3.5 during the period of sampling, suggesting the contribution from phytoplankton, angiosperm leaves and grasses to the *PCHO* of the *SPM* (Cowie and Hedges, 1984). This conclusion was further supported by the combined weight percentages of arabinose and galactose (calculated on a glucose-free basis), which together varied between 25 to 46%.

The concentrations of arabinose and xylose were low during 7 to 15 May and increased after 15 May following the rain. Both arabinose and xylose exhibit significant negative relationships with chlorophyll *a* suggesting that live algal material was not the major source for these sugars. In contrast to this, both these monosaccharides showed highly significant positive correlations with the concentrations of *SPM* indicating their association with detrital *SPM* derived from soil organic matter. A further evidence for the presence of soil organic matter can be obtained from the hexoses to pentoses ratio.

The study site was influenced by river inputs after the rain event on 16 May as was evident from the decrease in the salinity of surface seawater. Therefore, it is possible that the organic matter obtained after 15 May have been influenced by the presence of soil organic matter. The soil origin of organic matter transported after the rain is evident from the hexoses:pentoses ratio. The contribution

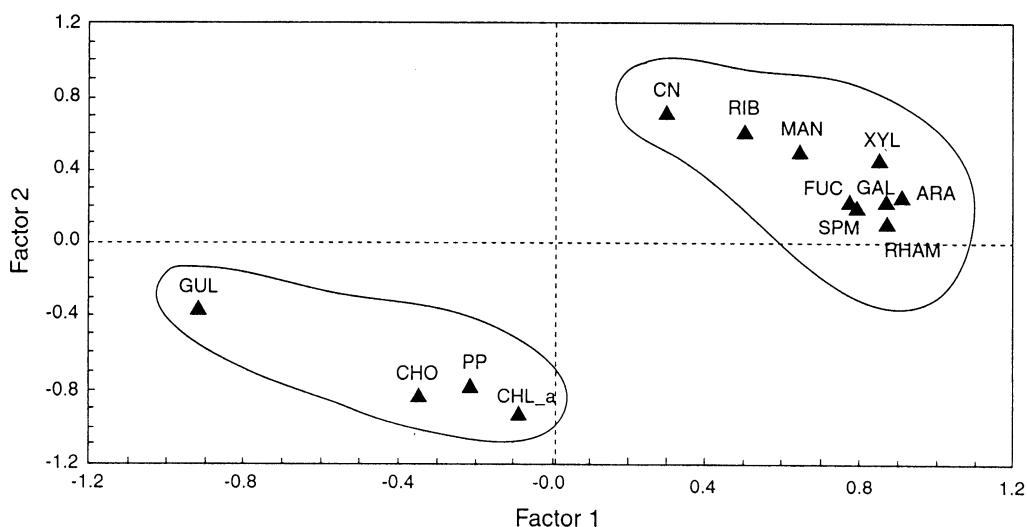
of pentoses to the *PCHO* increased, especially after 15 May. The increasing contribution from pentoses results in a lowering of the hexoses:pentoses ratio and the lowest value of 0.6 was observed on 23 May. Such a low hexoses:pentoses ratio is typical of soils with inputs from land plants (Stevenson, 1982; Ittekkot and Arain, 1986).

### 4.3. Principal component analysis

The observed trends in the particulate samples were further assessed using the principal component analysis (PCA). The particulate matter data matrix established two factors. The first factor was most effective and accounted for 63.7% of the variance. The cumulative variance among these two factors was 77.2%. These two factors refer to the two main events i.e. the bloom and the rain event that occurred during the period of sampling. The factor loadings for the two factors were obtained after the varimax rotation. The PCA factor loadings plot for factor 1 versus factor 2 are shown in *figure 7*. The plot clearly separated the variables into two clusters (two different quadrant) and it provides insight into the relationships that exist among the variables. *PP*, *PCHO* and glucose that are present in one cluster are closely associated with chlorophyll *a*, signifying their common origin (bloom period). On the other hand, the xylose, arabinose, fucose, rhamnose and galactose constitute a very compact cluster and are closely associated with *SPM*. These results differentiated the bloom and the rain event and also revealed the sources for the monosaccharides during the period of sampling.

### 4.4. Degradation of organic matter

Three parameters, the contribution of *PCHO-C* plus protein-C to the *POC*, the weight percentage glucose content and the percentages of deoxy hexoses (rhamnose plus fucose) in a sample, are potentially useful to evaluate the degradative state of organic matter (Ittekkot and Arain, 1986; Cowie and Hedges, 1984; Hedges et al., 1994; Cowie et al., 1995; Hernes et al., 1996; Opsahl and Benner, 1999). Carbohydrates and proteins account for 30 to 70% of the organic matter in all types of fresh marine and terrestrial sources, which appear to decrease during early degradation in the water column and newly deposited sediments (Degens and Mopper, 1976; Cowie and Hedges, 1994; Cowie et al., 1995; Pantoja and Lee,



**Figure 7.** Plot of PCA loading factors of the sugars and particulate matter components. The variables are labelled as follows: *SPM*, suspended particulate matter; *CHL a*, chlorophyll *a*; *PP*, protein; *CHO*, carbohydrates; *CN*, C:N ratio; *GUL*, glucose; *GAL*, galactose; *MAN*, mannose; *RIB*, ribose; *XYL*, xylose; *ARA*, arabinose, *RHAM*, rhamnose; *FUC*, fucose.

1999). It has been suggested that the decrease in the relative contribution of carbohydrate and protein (i.e. labile organic carbon) to organic carbon may reflect the nature of organic matter (Cowie and Hedges, 1994; Cowie et al., 1995). Therefore, the relative contribution from these two compound classes to the total *POC* may reflect the degree to which the biodegradation of organic matter has proceeded. Conversely, the contribution of *PCHO-C* plus *PP-C* to the total *POC* indicates the potential of degradation of organic matter within the water column and in sediments. The contribution of *PCHO-C* and *PP-C* to the total *POC* varied from 9.0 to 29.6% in our samples. As compared to the live marine and terrestrial material, these values are low, suggesting the degradation of organic matter and/or dilution by *PCHO* and *PP* poor organic or inorganic material. On 7 May the contribution of these compounds to the total *POC* was very poor (11%), which indicates the presence of extensively degraded organic matter. With the increase in chlorophyll *a*, the contribution of carbohydrate and protein to *POC* increased (14 to 29.6% of *POC*), especially from 8 to 15 May, implying a relative abundance of fresh biogenic organic matter. After the rain, the contribution of these compounds to *POC* ranged from 9 to 14% again, indicating the presence of highly degraded terrestrial organic matter at the study site. Alternatively, the decrease in *PCHO-C* plus *PP-C* contribution to *POC* may be due to dilution by inorganic material. The latter seems

also possible because of the inverse relationship between the *PCHO-C* plus *PP-C/POC* (%) and the concentration of *SPM*.

The neutral sugar profile provides additional indicators of degradative state of organic matter (Hedges et al., 1994; Hernes et al., 1996; Opsahl and Benner, 1999). For example, glucose content (as weight percentage) is another factor that indicates the degradative state of organic matter. Glucose contributes 58 to 90% to the total *PCHO* in fresh plankton and terrestrial tissues (Cowie and Hedges, 1984; Opsahl and Benner, 1999). Due to preferential utilization, weight percentages of glucose tend to decrease from marine planktonic source to benthic sediments (Hernes et al., 1996; Jennerjahn and Ittekkot, 1999). Similarly, a decreasing trend for weight percentage glucose has also been reported for the highly degraded terrestrial plant material (Hedges et al., 1994; Opsahl and Benner, 1999).

In our samples, weight percentage glucose (or absolute concentration) showed a decreasing trend over the period of sampling. During the phytoplankton bloom, the weight percentage glucose was very high (81% of the *PCHO*). After 15 May, the weight percentage glucose decreased to about 26%. Such a low weight percentage glucose is a typical characteristic of extensively degraded organic material (Hedges et al., 1994; Opsahl and

Benner, 1999), or may indicate a decrease in phytoplankton biomass. The observed changes in weight percentage of glucose thus suggest the extent of organic matter alteration in our *SPM* samples. An extensive alteration of glucose relative to other sugars was also evident from the inverse relationships of glucose with *SPM*, arabinose, xylose and rhamnose plus fucose.

The contribution of deoxy hexoses (rhamnose plus fucose) to the *PCHO* is yet another potentially useful parameter to assess the degradative state of organic matter in both marine plankton and in vascular plant materials (Cowie and Hedges, 1984; Cowie and Hedges, 1994; Hedges et al., 1994; Opsahl and Benner, 1999). Hedges et al. (1994) observed an increase in the percentage of deoxy sugars and the corresponding decrease in glucose in progressively more degraded particulate organic matter samples from the Amazon River, suggesting that the deoxy sugars may be relatively stable during decomposition. We observed that the contribution of deoxy hexoses was relatively low during the growth of plankton and increased after the rain event (*table 1*). The weight percentage of deoxy sugars increased from 5.6 (on 15 May) to 23.3% (on 23 May) during the period of study. The increased contribution of deoxy sugars was associated with a concomitant decrease in glucose content. It was also evident from the highly significant inverse relationship between deoxy sugars and glucose. It could be argued that the elevated levels of deoxy sugars were due to the presence of bacteria enriched in deoxy sugars (Cowie and Hedges, 1984; Hamilton and Hedges, 1988; Hedges et al., 1994). Since ribose was a minor component (< 3%) of the *PCHO* in our samples, elevated percentages of deoxy sugars in our samples indicate a degradative state of organic matter or a selective utilization of glucose.

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