

Carbohydrates, uronic acids and alkali extractable carbohydrates in contrasting marine and estuarine sediments: distribution, size fractionation and partial chemical characterization

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Abstract

Concentration, size fractionation and monosaccharide composition of carbohydrates and uronic acids were investigated in contrasting sediments of the Mandovi estuary (ME), Arabian Sea (AS) and the Bay of Bengal (BOB). Concentrations and monosaccharide composition of carbohydrates and uronic acids varied spatially. Average yields of carbohydrates and uronic acids were higher for the estuarine compared to marine sediments. Interestingly, yields of carbohydrates and uronic acids increased in sediments with water column depth, implying preferential removal of other constituents, selective preservation and/or lateral input of carbohydrate rich material. Analysis of monosaccharide biomarkers indicates that carbohydrates were derived from terrestrial plants, bacteria and phytoplankton, however, the influence of the former was relatively greater in sediments of the ME and BOB, as well as in residual sediments of ME. Approximately 11-21% of total carbohydrates could be extracted using hot alkali extraction followed by sonication. Irrespective of the depositional environment, carbohydrates and uronic acids were greater in the very high molecular weight size fraction (> 30 kDa). The abundance of glucose increased with the decrease in molecular size of extracted organic matter. This probably indicates its association with less degradable carbohydrates.

1. Introduction

In the biosphere, carbohydrates are the major organic compounds produced photosynthetically by autotrophic organisms. They account for a substantial amount of the dissolved and particulate organic carbon in the water and sediments of marine environments. For example, they may account for 10-85% of the dissolved organic carbon (DOC) in seawater (Pakulski and Benner, 1994) and sediment pore waters (Arnosti and Holmer, 1999; Burdige et al., 2000), 3-16% and 2-13% of the particulate organic carbon (POC) of the suspended (D'Souza and Bhosle, 2001), and sedimenting particles, respectively (Hernes et al., 1996; D'Souza et al., 2003; Panagiotopoulos and Sempere, 2005), and 3-20% in marine sediments (Cowie and Hedges, 1994; Burdige et al., 2000; Jensen et al., 2005). They serve as an important energy source for heterotrophic organisms (Decho, 1990), and are a potential precursor of refractory organic matter (OM) in sedimentary rocks (Sinninghe Damsté et al., 1998). Carbohydrate composition and concentration varies with the type and abundance of microorganisms, nutrient availability, growth stage and other environmental parameters (Decho, 1990).

Carbohydrates are classified as storage and structural. Storage carbohydrates are labile and are rapidly utilized by the *in situ* heterotrophic organisms. This results in the accumulation of relatively inert carbohydrates in marine particulate matter of deep sea oceanic waters (Handa and Tominaga, 1969; Bhosle and Wagh, 1989; Hernes et al., 1996; Panagiotopoulos and Sempere, 2005), and marine sediments (Bhosle and Dhople, 1988; Cowie et al., 1992; Burdige et al., 2000, Jensen et al., 2005). The abundance of relatively inert carbohydrates may result in depth invariant profiles and low yields of particulate carbohydrates, indicating the inert nature of some of the sedimentary carbohydrates (Hamilton and Hedges, 1988; Jensen et al., 2005).

Monosaccharide composition of neutral carbohydrates is a useful tool for identifying the sources of carbohydrates (Cowie and Hedges, 1984; Ittekkot et al., 1984; D'Souza and Bhosle, 2001; D'Souza et al., 2003, 2005; Panagiotopoulos and Sempere, 2005). The relative abundance of individual sugars and sugar ratios in a sample has been used to distinguish terrestrial, marine and siliceous and carbonaceous inputs to the suspended particulate matter and sediments (Cowie and Hedges, 1984; Ittekkot et al., 1984). Moreover, contribution of neutral carbohydrate carbon to organic carbon defined as yield provides information on degradation state

of OM, where high yield typically indicates fresh OM (Cowie and Hedges, 1994; Skoog and Benner, 1997)

In addition to neutral carbohydrates, many microorganisms, vascular plants, algae and other organisms produce acidic carbohydrates such as uronic acids (TURA). TURA differ from simple sugars because they contain a carboxylic acid group in place of methanolic carbon opposite the carbonyl carbon. Production of TURA is influenced by season, growth phase, levels of nutrient and metal ion (Whistler and Richards, 1970; Bergamaschi et al., 1999). Although present as a minor constituent of total carbohydrates, they are involved in humic acid production, detoxification of toxic chemicals, removal of metal ions, production of macroaggregates, adsorption of dissolved organic carbon and microbial adhesion (Yamaoka, 1983; Decho, 1990; Mopper et al., 1995; Leppard, 1997; Santschi et al., 1998; D'Souza et al., 2003).

A large part of the sediment organic carbon is loosely or tightly associated with mineral particles or held together by interaction between organic molecules. A combination of treatments such as heating with alkali followed by sonication appears to be more effective in extracting organic carbon from bulk sediment particulate organic carbon (POC). This extractable organic carbon is defined as mobile organic carbon (Miyajima et al., 2001). Characterization of this extractable OM for size fractions, carbohydrate concentration and monosaccharide composition provides useful information on the reactivity and origin of extractable OM in marine sediments (Miyajima et al., 2001).

There is little information available about the distribution and biochemical composition of OM in sediments from the northern Indian Ocean (Rao, 1960; Romankevich, 1984; Bhosle and Dhople, 1988; Paropkari et al., 1992; Unger et al., 2005), and the Mandovi estuary (ME). Moreover, most previous studies have focused their attention on bulk parameters such as total organic carbon (TOC), total nitrogen (TN) and bulk biochemical components of the OM, so the molecular level biochemical characterization of the OM has been poorly addressed. Therefore, the aims of the present study were to evaluate the spatial distribution of the TCHO and TURA, concentration and composition of the total neutral monosaccharides (TNMCHO) and the hot alkali extractable carbohydrates (ASCHO) in surface sediments collected from contrasting geographic areas and depths of the Bay of Bengal (BOB), Arabian Sea (AS) and the Mandovi estuary (ME).

2. Materials and methods

2.1. Study area

The northern Indian Ocean consists of the AS, BOB, and Andaman Sea. There are some major differences in the physical, chemical and biological characteristics of the AS and BOB. The AS receives river run off ($0.3 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$) from relatively smaller rivers such as the Tapti and Narmada, and is characterized by high rates of evaporation that exceed precipitation and river run off. This results in the formation of high salinity water masses. Biannual reversal of surface circulation is associated with the southwest monsoon (SWM) and northeast monsoon (NEM). During the SWM, the area experiences intense coastal and Open Ocean upwelling as a result of strong southwesterly winds blowing along the Somali and Arabian coasts. Upwelling and winter cooling pump nutrients into the surface waters, resulting in high primary production in the AS during the SWM and winter monsoon. As compared to these two seasons, both primary production and chlorophyll *a* content are relatively low in the spring inter-monsoon (SPIM) from mid March to early June. The northern AS has coarse grained sediment. The carbonate content is low ($< 10\%$) on the continental shelf off India. However, the continental slope is relatively rich in carbonate. The inner shelf sediments consist of silt clay, while sand and clayey silt are present on the outer shelf and in the deep sea, respectively.

The BOB receives large quantities of freshwater ($1.6 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$) from the major rivers: the Ganges, Brahmaputra, Irrawady, Godavari, Krishna, Pennar and Cauvery (Rao, 1985). These rivers, flowing through the various geological formations of the Indian subcontinent, introduce $2.0 \times 10^{15} \text{ g}$ of suspended particulate matter annually, i.e. 15% of the contemporaneous global discharge of fluvial sediment into the world's oceans (Rao, 1985). Warm sea surface temperature (SST) and low salinity lead to strong stratification that prevents transport of nutrients into the surface waters. Moreover, weak winds are unable to break the thermocline. Cyclones are frequent in the Bay, and can pump nutrients into the surface waters. This results in localized algal blooms (Vinaychandran and Mathew, 2003). Upwelling has been observed along the western boundary of the BOB (Shetye et al., 1991). Clastic sediments are recorded at the inner shelf and continental slope, while calcareous relict sediments are present at the outer shelf. Off the river mouth the

shelf is covered by fine grained terrigenous sediments (Rao, 1964). Gauns et al. (2005) compared various physical, chemical and biological properties of the AS and the BOB and concluded that the biological production is several fold lower in the BOB than in the AS.

The ME is an interstate river basin. The basin lies between 15° 15' 24" N and 15° 42' 00" N, and 73° 45' 46" E and 74° 24' 54" E. The total length of the main river is 87 km, of which the initial 35 km are in Karnataka and the remaining 52 km in Goa. The river has about 1580 sq km drainage area in Goa. The climate is humid tropical with a moderate temperature. Annual average rainfall is about 300 to 350 cm. The average depth of the estuary is about 5 m. Sediments near the mouth of the estuary are rich in montmorillonite, whereas kaolinite plus chlorite are abundant in the up stream region of the estuary. The ME is used for transport of public goods and iron and manganese ores.

2.2. Sample collection

A gravity corer was used to collect cores. Six cores were collected during the SK-182, and one during the SK-191 cruises of the ORV Sagar Kanya in the BOB in September/October, 2002, and April/May, 2003, respectively (Fig. 1). Similarly, five cores were collected in September, 1996 during the SK-117 cruise of the ORV Sagar Kanya in the AS (Fig. 1). Immediately after collection, the cores were sectioned at 2 cm intervals, and the sectioned sediments were stored at -20 °C.

A Van Veen grab sampler was used to collect surface sediment samples from various locations in the ME (Fig. 1). Surface sediments from the ME and top layer (2 cm) samples from the cores were lyophilized, except for BOB sediments that were dried at 40 °C in an electrical oven. Sediments were ground to a fine powder using an agate pestle and mortar, and stored at -20 °C until analysis.

2.3. Total organic carbon (TOC) and total nitrogen (TN)

Dry combustion was employed to estimate total carbon using a Shimadzu TOC 5000-A analyzer. In order to estimate inorganic carbon a known quantity (100 mg) of the sample was treated with 0.5 ml orthophosphoric acid and heated to 200 °C in the presence of oxygen. The evolved CO₂ was measured using the Shimadzu TOC 5000-A analyzer. Total organic carbon (TOC) was calculated as the difference between total carbon and inorganic carbon. Total nitrogen (TN) content was

estimated following the method of Raimbault and Gerd (1991). Samples were treated with alkaline potassium peroxydisulfate ($K_2S_2O_8$) in an autoclave for 90 min. The nitrate produced was reduced to nitrite by passing through a cadmium column. The nitrite concentration was measured spectrophotometrically at 543 nm following the procedure described by Parsons et al. (1984). EDTA was used as a standard.

2.4. Total carbohydrates (TCHO)

TCHO was analyzed using the phenol-sulfuric acid method (Dubois et al., 1956). A known amount of sediment was added to two clean test tubes. To each was added 1 ml of 12 M H_2SO_4 . The test tubes were incubated for 2 h at room temperature (28 ± 2 °C). To one, 2 ml of 2.5% phenol followed by 5 ml of concentrated H_2SO_4 were added, this being considered a sample; to the other test tube 2 ml distilled water (in place of phenol), followed by 5 ml concentrated H_2SO_4 were added, this being considered a blank. Samples were allowed to cool and the absorbance was measured at 490 nm. Glucose was used as a standard. TCHO is expressed as mmol C. The unit mmol C is obtained by multiplying mmol values by 6 assuming 6 mol of carbon per mol of hexoses.

2.5. Total neutral monosaccharides (TNMCHO)

TNMCHO concentration and composition were determined using a capillary gas chromatographic (GC) method (D'Souza et al., 2005). Briefly, the sample was treated with 12 M H_2SO_4 at room temperature for 2 h. It was diluted to 1.2 M H_2SO_4 using cold distilled water, flushed with N_2 , sealed and hydrolyzed for 3 h at 100 °C. After cooling, an internal standard (inositol) was added. The sample was neutralized, treated with $NaBH_4$, acetylated and analyzed using a Chrompack GC model CP-9002 or a HP model 6890 equipped with a flame ionization detector (FID), a programmable on column injector and a fused silica column coated with CPSil-88 (25 m, i.d. 0.32 mm). Both the detector and injector were maintained at 300 °C. The oven temperature was programmed as follows: 70 to 150 °C at 30 °C /min and then at 3 °C /min to 230 °C, at which it was maintained for 10 min. Identification of the monosaccharide was done by comparing the retention time of the unknown monosaccharide with that of the standard monosaccharide. Identification was further confirmed by co-injection of the standard monosaccharides. Quantification was achieved by peak area integration using the data handling system installed in the

instrument. The TNMCHO concentration is defined as the sum of all the identified monosaccharides. The contribution of individual monosaccharides to TNMCHO is expressed as mole%. Analytical variability of the GC method was $\pm 6\%$ and $\pm 10\%$ for the GC plus sample preparation method.

2.6. Total uronic acid (TURA)

Acidic carbohydrate such as TURA was analyzed according to the method of Filisetti-Cozzi and Carpita (1991), as reported in Hung et al. (2003). In short, a known amount of sample was placed in a test tube and 0.4 ml Milli-Q-UV-treated distilled water followed by 40 μl of 2 M sulfamic acid added, and the solution stirred with a vortex mixer; 2.4 ml 75 mM sodium tetraborate in concentrated H_2SO_4 was added and the mixture heated for 10 min in a boiling water bath. After cooling, 80 μl of 0.15% *m*-hydroxydiphenyl was added and the absorbance measured at 525 nm. Blanks were run in the same way as for the sample except that 80 μl 0.15% *m*-hydroxydiphenyl was replaced by 80 μl 0.5% NaOH. For each sample a separate blank was used. Using this method > 90% of the added uronic acid standard (glucuronic acid) could be recovered (data not shown). The unit used is mmol C, and is obtained by multiplying mmol values by 6 assuming 6 mol of carbon per mol of glucuronic acid. Analytical variability of the method based on 3 replicates was less than 10%.

2.7. Extraction and molecular size fractionation of alkali soluble carbohydrates (ASCHO)

ASCHOs were extracted following the method of Miyajima et al. (2001). Briefly, to a sediment sample (10 to 15 g), 20 ml of 0.5 M NaCl and 1 ml of 0.5 M Na_2CO_3 were added. The sample was autoclaved at 121 $^\circ\text{C}$ for 60 min, cooled and ultra-sonicated for 20 min. The sample was centrifuged at 2000 g for 20 min, and the supernatant was recovered as the extract. The extraction procedure was repeated twice. The extracts were pooled, and filtered through a 0.22 μm filter. Both the extract and the residual sediments were analysed for TCHO, TNMCHO and TURA following the methods described above.

ASCHOs were size fractionated into very high molecular weight (VHMW, > 30 kDa to 0.22 μm), high molecular weight (HMW, >10 kDa to 30 kDa), and low molecular weight (LMW, >1 kDa to 10 kDa) size fractions using an Amicon stirred

cell equipped with either 30 kDa, 10 kDa and 1 kDa MW cut off cellulose membrane ultra filter, respectively. Accuracy of the MW cut off was tested using 10 kDa dextran as a standard carbohydrate. Moreover, mass balance was also determined by measuring total carbohydrates in the AHS extract and each of the size fractions obtained from the stirred cells, and comparing the sum to the total. Polysaccharides were dialyzed against distilled water using dialysis bags and precipitated using ice cold isopropanol with samples incubated at 4 °C overnight (Bhosle et al., 1995). Before use, the dialysis bags were cleaned following the procedure described earlier (Bhosle et al., 1995). Efficiency of isopropanol precipitation was evaluated by estimating the total carbohydrates in each of the size fractions before and after precipitation. Polysaccharides were lyophilized, and analyzed for TOC and TNMCHO following the methods described above. Sulphate was measured following the method of Dodgson (1961). Pyruvate was estimated by the method of Slonecker and Orentas (1962).

3. Results and discussion

3.1. Total organic carbon (TOC) and total nitrogen (TN)

Generally, no particular trend was evident in the distribution of TOC and TN with respect to the sampling locations and depths, however a small increase was recorded for sediments sampled at 3500 m in the BOB (Table 1). Concentrations of TOC and TN in the sediments of the BOB and the AS were generally consistent with those reported previously (Bhosle et al., 1978; Bhosle and Dhople, 1988; Paropkari et al., 1992; Suthhof et al., 2000). For the residual sediments TOC decreased from upstream station (ME-15) of the estuary to mouth of the estuary (ME-7), and from upper to lower slope sediments, whereas TN did not show any particular trend (Table 1). Relatively higher concentrations of TOC and TN in the sediments of the ME were probably due to higher primary production and higher input of allochthonous OM compared to the offshore oceanic waters of the northern Indian Ocean (Madhupratap et al., 2003; Gauns et al., 2005).

The C/N ratio is a useful tool to assess the nature of sediment OM. Marine microalgae and bacteria have values of 4 to 6 (Hamilton and Hedges, 1988). Moreover, as degradation progresses, the ratio increases. The C/N ratio of all the sediment samples was higher than that observed for marine OM derived from fresh

microalgae and bacteria. Low values (8 to 9) were recorded at BOB-3, AS-2, ME-7 and ME-10, indicating the presence of relatively fresh OM at these stations. On the other hand, relatively high (>9) values were recorded at BOB-1 and AS-4, suggesting the presence of degraded OM at these locations. Higher values recorded at some of these stations may also reflect a possible terrestrial OM influence, since C/N ratios of freshwater OM are generally much higher than those recorded for marine OM (Lobbes et al., 2000). The C/N values for the remainder of the samples fall between these two ranges, indicating intermediate degradation status of sediment OM at these locations. Relatively higher C/N ratios were recorded for the residual sediments, suggesting selective removal of nitrogen.

3.2. Total carbohydrates (TCHO)

TCHO varied with respect to the sampling locations without exhibiting any particular distribution trend. TCHO concentrations for the BOB sediments (0.09-0.19 mmol C g⁻¹ dry sediment) were lower than those measured for the AS sediments (0.08-0.33 mmol C g⁻¹ dry sediment), and the ME (0.13-0.38 mmol C g⁻¹ dry sediments) (Table 1). These values are in the range of values earlier reported for sediments of the BOB and AS (Bhosle and Dhople, 1988; Bhosle et al., 1978), and from other marine environments (Romankevich, 1984). There was a significant positive correlation ($r = 0.705$; $n = 22$; $p = 0.001$) between the concentrations of TCHO and TOC in the sediments from these contrasting environments suggesting common origin of these compounds. Concentrations of TCHO in residual sediments decreased from the estuary (# ME-15) to the deep AS sediments #AS-2.

3.3. Total neutral monosaccharides (TNMCHO)

TNMCHO ranged between 0.03 and 0.05 mmol C g⁻¹ dry sediment and from 0.02-0.14 mmol C g⁻¹ dry sediment for the BOB and the AS sediments, respectively, and accounted for ~28-48% of TCHO (Table 1). For the ME, TNMCHO varied between 0.05 and 0.11 mmol C g⁻¹ dry sediment, accounting for ~18-47% of the TCHO. TNMCHO showed a significant positive correlation with TOC ($r = 0.678$; $n = 22$; $p < 0.001$) and TCHO ($r = 0.780$; $n = 22$; $p < 0.001$). Concentrations of TNMCHO reported here are in the range of values recorded earlier for the sediments from other marine environments (Cowie and Hedges, 1984; Steinberg et al., 1987; Hamilton and Hedges 1988; Cowie et al., 1992; Martens et al., 1992; Burdige et al.,

2000; Kerherve et al., 2002; Jensen et al., 2005). For the residual sediments TNMCHO concentrations decreased from the estuary to the deep sea stations, and accounted for 3.1-7.3% of TOC (Table 1).

TNMCHO represented ~18-48%, and ~21-47% TCHO in sediments and residual sediments, respectively (Table 1). Kerherve et al. (2002) did not find any correspondence between TNMCHO and TCHO for the sediments of the northern Mediterranean Sea. Similar trends have been recorded for other types of samples. For example, for pore water samples from the mid-Atlantic, the contribution of TNMCHO to TCHO varied from 30-50% (Burdige et al., 2000). Similarly, for the water column, the contribution of TNMCHO to TCHO showed large variations (7-50%; Borch and Kirchman, 1997; Skoog and Benner, 1998). This suggests that the TNMCHO accounted for variable proportions of the TCHO. The observed differences between TCHO determined using the spectrophotometric method, and those measured with the GC method may be due to several factors, including the importance of non-aldose carbohydrates such as amino sugars, uronic acids and sugar alcohols (Burdige et al., 2000). Moreover, the differences also may be due to structural changes to individual aldoses incorporated into refractory DOC molecules that may allow them to still be recognized with the phenol-sulfuric acid method but not with the GC method.

3.4. Alkali soluble carbohydrates (ASCHO)

A part of organic carbon extractable from bulk sediment POC using alkali, heating and sonication (AHS) is defined as the mobile fraction of sediment POC (Miyajima et al., 2001). It appears that such treatment will release carbohydrate molecules bound to sediment mineral particles by heat sensitive hydrogen and van-der Waals bonds, and alkali hydrolyzable ester and *O*-glycosidic bonds. This extracted organic carbon contained large amount of ASCHO that accounted for ~12-22% of the TCHO (Table 2a). The contribution of ASCHO to the TCHO increased in sediments from upstream (# ME- 15) to the mouth of the estuary (# ME-7), and from upper slope (AS-4, 1000 m) to lower slope (AS-2, 2775 m) of the AS (Table 2a). These spatial variations in the ASCHO probably were due to differences in molecular size, hydrophobicity, electrical charge and mechanisms of organic–mineral and organic-organic interactions.

ASCHO was size fractionated into VHMW (> 30 kDa to 0.22 μ m), HMW (>10 kDa to 30 kDa) and LMW (>1 kDa to 10 kDa) size fractions using stirred cells equipped with ultra-filters. A standard solution of 10 kDa dextran gave a recovery of ~80% when processed using HMW ultra-filter (10 kDa MW cut off). Similarly, the sum of the carbohydrates in VHMW, HMW and LMW size fractions accounted for 68 to 87% ($X = 80 \pm 8\%$) of the extracted ASCHO (Table 2b). This means contamination or losses were minor during the ultra-filtration process (Fernandes et al., 2007). When precipitated using isopropanol ~68-98% and 67-94% of VHMW and HMW carbohydrates, respectively of the ASCHO could be recovered (Table 2c). This suggests that the amount of isopropanol precipitated carbohydrates was almost identical to the carbohydrates in the VHMW ($r = 0.9732$; $n = 5$; $p < 0.001$) and HMW ($r = 0.9818$; $n = 5$; $p < 0.001$) fractions of the ASCHO. However, when precipitated with isopropanol recovery of LMW carbohydrates was relatively low (20-72%), particularly for stations ME-7 and AS-2 (Table 2c).

AHS extractable organic carbon of the bulk sediment POC is relatively rich in high MW carbohydrates. The presence of many monosaccharides, TURA, sulfate and pyruvate in the VHMW, HMW and LMW size fractions indicates that these are high MW sulfated acidic hetero-polysaccharides (Fig. 2, Table 3). Highest yields of TCHO, TNMCHO and TURA were recorded for the VHMW fraction of the ASCHO, and the yields decreased with the decrease in molecular size (Fig. 2, Table 3). This is in line with the size continuum model suggesting that reactivity decreases with size (Burdige and Gardner, 1998; Burdige et al., 2000).

It is suggested that high MW AHS carbohydrates are early intermediary products of re-mineralization of bulk sediment POC, and are one of the important organic substances that connect POC of the bulk sediments to pore water DOC and DOC of the overlying water column (Burdige and Gardner, 1998; Burdige et al., 2000; Miyajima et al., 2001). High MW carbohydrates are degraded by hydrolytic and fermentative processes to monomeric low molecular compounds (mLMW) that are then rapidly oxidized by terminal respiratory organisms in sediments (Burdige and Gardner, 1998; Arnosti and Holmer, 1999; Burdige et al., 2000). At the same time, a part of the HMW-DOC is only partially oxidized, leading to the production of polymeric LMW-DOC (pLMW-DOC). Geopolymerization of mLMW compounds may also be involved in the production of pLMW organic matter. It is suggested that pLMW organic matter may gradually undergo, chemical, biochemical and structural

modifications producing pLMW refractory organic matter that is depleted in labile compounds like carbohydrates.

3.5. Carbohydrate yields

Carbohydrate yield is a useful tool to assess degradation state of OM. The yield is high for the freshly derived OM, and low for the degraded OM (Handa and Tominaga, 1969; Cowie and Hedges, 1992; Skoog and Benner, 1997; Hernes et al., 1996; Burdige et al., 2000). TCHO and TNMCHO yields varied from 9-26%, and 2.3-11%, respectively (Table 1). Average carbohydrate yields in the sediments were highest for the ME and lowest for the BOB, whereas intermediate values were recorded for the AS (Fig. 3). For many coastal and offshore marine sediments, TCHO yields varied between 3 and 25% (Cowie and Hedges, 1984; Cowie et al., 1992; Martens et al., 1992; Hernes et al., 1996; Burdige et al., 2000; Jensen et al., 2005). Overall, the yields were higher (> 5%) at stations BOB-3, AS-1, AS-2, AS-3, ME-7, ME-10, ME-13 to 15, implying recent deposition of carbohydrate rich organic matter at these stations. In contrast, carbohydrate yields were low (< 5%) for the other stations indicating the presence of highly degraded organic matter at these stations (Table 1). However, such low yields can also be obtained due to dilution of organic matter with carbohydrate poor inorganic or organic material. In residual sediments carbohydrate yields did not produce any consistent trend (Table 1).

TNMCHO yields generally decrease with water column depth, sediment core depth, and with the degradation of OM (Cowie and Hedges, 1994; Skoog and Benner, 1997; Opsahl and Benner, 1999; Jensen et al., 2005). In the present study yields of TCHO and TNMCHO were higher in sediments of greater water depths (>2170 m), and lower in sediments from shallower water depths (86 m and 1000 m) (Fig. 4). This is in contrast with the general observation that TNMCHO yield is a robust indicator of OM degradation state. The observed increase probably indicates lateral input of carbohydrates rich material and/or preferential removal of other organic constituents resulting in the enrichment of carbohydrates in these sediments. Moreover, sediment refocusing may be another factor that may have influenced the carbohydrate yields. It appears that sampled locations in the AS experience sea level transgression since the Holocene. As a result, sediments on the outer shelf were reworked and deposited on the upper slope. Evidence of such slumping has also been acquired all along the western margin of India. Faster deposition of sediment

leaves little time for degradation resulting in better preservation of organic fraction (Rao, 1989; Rao and Wagle, 1997; Guptha et al., 2001). Yet another reason for high carbohydrate yields in the AS is the abundance of coccolithophorids and foraminifers in biogenic flux to the surface sediments in the study area (Ramaswamy and Gaye, 2006). It has been pointed out that TNMCHOs are well preserved in calcareous plankton material (Hernes et al., 1996; Kerherve et al., 2002). High mole % abundance of rhamnose plus fucose plus ribose in sediments of these locations suggests that the OM was mostly derived from marine sources (Fig. 5).

Interestingly, with exception of one station (2300 m deep station BOB-3), yields of both TCHO and TNMCHO were fairly constant for the BOB sediments. Station BOB-3 is located in the deep channels connecting the peninsular rivers Godavari, Cauvery and their tributaries to the deep BOB, and also receives sediments from the Ganga-Brahmaputra systems by equatorward dispersal (Chauhan and Vogelsang, 2006). The dispersal of sediment in the deep sea, delivered by the rivers is due to slumping turbidity current transport along these channels and valleys. Such a river supply of carbohydrate rich terrigenous material at station BOB-3 deep in the mid-ocean depth may be responsible for the observed increase in carbohydrate yield. Terrestrial plant origin for the carbohydrates at this station was evident from high mole % (26 mole %) of arabinose plus xylose as well as low (<0.5) rhamnose plus fucose to arabinose plus xylose ratio (Table 4). From our data it was evident that the utility of TNMCHO yield as an indicator of degradation state probably depends on several factors including sources, degradation during transport and in sediments, and hydro dynamical conditions characterizing the continental margin.

3.6. TNMCHO composition

TNMCHO composition was variable in the sediments of the AS, BOB and the ME (Table 4). The observed variations in the monosaccharide composition may be due to changes in the sources of OM and selective utilization by heterotrophic organisms. Glucose was the most abundant monosaccharide (29-43.9 mole %), especially in ME (Fig. 6), and its abundance decreased in sediments from the ME to the deep AS (Fig. 5). For both the AS and BOB sediments, glucose accounted for 12.7-21.8 mole % (Fig. 6). Glucose is present at higher levels in vascular plants. In diatoms glucose is a major constituent of storage polysaccharide β 1, 3-glucan, which

is easily degraded by *in situ* aquatic organisms and/or metabolized during diatom cell sinking (Tanoue and Handa, 1987; Hama and Yanagi, 2001). Cowie and Hedges (1996) reported selective utilization of intracellular material rich in glucose by herbivorous copepod zooplankton *Calanus pacificus* when fed on ¹⁴C labeled cells of the diatom *Thalassiosira weissflogii* under laboratory conditions. During the degradation, glucose and xylose were selectively removed from vascular plant tissues by heterotrophic microorganisms (Opsahl and Benner, 1999). Such selective removal of glucose may be responsible for the low abundance of glucose in the sediments of the AS and the BOB (Moers et al., 1989; Opsahl and Benner, 1999).

Galactose was the most abundant monosaccharide in the sediments of the BOB and AS, and was also fairly abundant in the sediments of the ME (Table 4, Fig. 6). Galactose is present in terrestrial plants (Cowie and Hedges, 1984), and is one of the major constituents of the mineral matrix of some phytoplankton cell walls and bacteria (Handa and Yanagi, 1969; Hecky et al., 1973; Cowie and Hedges, 1984). Moreover, the contribution of galactose to the TNMCHO increased during phytoplankton bloom (Ittekkot et al., 1982). Therefore, it is possible that this monosaccharide may have been derived from a mixed source consisting of phytoplankton, marine bacteria and/or terrestrial plants.

Rhamnose, fucose and ribose are abundant in bacteria, fungi and phytoplankton (Cowie and Hedges, 1984; Moers et al., 1989; Hicks et al., 1994; D'Souza, 2004). These monosaccharides were abundant in sediments of the AS (Fig. 6), and their contribution to total TNMCHO increased in sediments from the ME (# ME-15) to the deep AS (AS-1) (Fig. 5). From the distribution profiles of these sugars, it was evident that the contribution from phytoplankton and bacteria to the sediment OM increased from the estuary to the deep AS.

Arabinose and xylose together accounted for ~14-31 % of the TNMCHO, and were particularly more abundant in sediments of the ME and the BOB (Table 4, Figs. 6 & 7). Both these sugars were abundant in shallow water (< 600 m) and deep water (> 2300 m) sediments of the BOB (Fig.7). Such high abundance of these sugars is not observed in the OM derived from phytoplankton because neither of these sugars contributes much to the whole cell or cell wall material of diatoms. However, both are abundant in terrestrial plants as constituents of arabinoxylan and arabinoglucuronoxylan (Cowie and Hedges, 1984; Oades, 1984; Ogier, 2001; Guggenberger et al., 1994). Moreover, a ratio of rhamnose plus fucose to arabinose

plus xylose of 0.5 or less indicates the presence of plant derived carbohydrates (Guggenberger et al., 1994; Biersmith and Benner, 1998). Therefore, high abundance of these sugars in shallow (< 600 m) and deep water (> 2300 m) sediments of the BOB indicates the presence carbohydrates derived from plant material. This conclusion also was further supported by low rhamnose plus fucose to arabinose plus xylose ratios (0.4 to 0.7) observed for these sediments (Table 4). As discussed above, these deep water stations (BOB-1, BOB-2 and BOB-3) of the BOB are influenced by the run off from the peninsular and Himalayan rivers. Moreover, the increase in mole % arabinose and xylose at these deep water stations of the BOB was accompanied by an increase in mole % ribose (Fig. 7). This may indicate the presence of terrestrial OM with immobilized microbial biomass in the sediments at these stations. Tremblay and Benner (2006) reported that 60-75% of the N and 20-40% of the C in highly decomposed detritus were not from the original plant tissues but were mostly derived from heterotrophic bacteria.

All the monosaccharides observed for the sediments (Table 4), were also present in various size fractions of the ASCHO (Table 3). However, differences in the depositional environments and molecular size did not influence monosaccharide composition except glucose (Table 3). Glucose mole %, however, increased with the decrease in molecular size except one station in the ME (Table 3). This probably suggests its association with less degradable glucose rich polysaccharides (Tanoue and Handa, 1987).

Residual sediments of the AS (# AS-2 and # AS-4) were enriched in rhamnose and fucose (14.4-20.6 mole %) and depleted in arabinose plus xylose (15.0-18.5 mole %) (Table 4). In contrast, residual sediments of the ME (#ME-7, ME-10 and ME-15) were enriched in arabinose plus xylose (21-22.8 mole %) and depleted in rhamnose and fucose (6.2-9.2 mole %) (Table 4). As discussed above, this difference in the monosaccharide composition implies that the residual sediments were influenced by terrestrial OM.

3.7. TURA

TURA are carboxylated acidic polysaccharides. They appear to be involved in immobilization, detoxification of toxic compounds, removal of metal ions, etc. (Decho, 1990; Tang et al., 2001). However, little is known about their distribution and cycling in marine environments. In the present study, TURA varied from 0.02-0.04

mmol C g⁻¹, 0.03-0.09 mmol C g⁻¹, and 0.02- 0.10 mmol C g⁻¹ dry sediments, and accounted for 1.4-4.6%, 2.3-8.8% and 1.8-7.1% of the TOC in the BOB, AS and ME, respectively (Table 1). TURA contributed from 16.2-27.9%, 21.3-43.9%, and 14.8-36.5% of TCHO in sediments of the BOB, AS and the ME, respectively. No particular gradient was evident in the contribution of TURA to TOC and TCHO along a transect extending from the ME to the deep AS (Table 1). TURA concentrations showed fairly good relationship with the concentrations of TOC ($r = 0.561$; $n = 22$; $p = 0.01$) and TCHO ($r = 0.900$, $n = 22$, $p < 0.001$), suggesting their common origin. TURA concentrations and yields in the sediments of the north Indian Ocean and the ME are relatively higher than those recorded for the sediments of the Dabob Bay, Saanich Inlet, Black Sea and the Baltic Sea (Mopper, 1977; Mopper and Larsson, 1978; Bergamaschi et al., 1999). However, a direct comparison may not be advisable because of the differences in the analytical methods used. Similarly, as compared with BOB, concentrations and yields of TURA are higher for the AS sediments probably because Chlorophyll *a*, primary production, bacterial production and zooplankton abundance are several fold higher in the Arabian Sea (Gauns et al., 2005).

Concentrations and yields of TURA in particulate matter rapidly declined with water depth probably suggesting utilization by *in situ* organisms (Hung et al., 2003; Khodse et al., 2007). In contrast, TURA yields generally increased in sediment with water depth for both the AS (up to 2750 m) and the BOB (2300 m; Fig. 4). TURA yields increased with sediment core depth for both the Dabob Bay and Saanich Inlet due to *in situ* production by bacteria (Bergamaschi et al., 1999). For both the AS and the BOB, the TURA/TCHO ratio in sediment did not show any consistent trend with water depth suggesting that TURAs were not accumulated due to preferential utilization of TCHO (Table 1), Therefore, *in situ* production by bacteria, additional inputs and/or selective preservation may be responsible for the observed increase in the TURA yields in sediments of both the AS and the BOB (Bergamaschi et al., 1999).

Irrespective of the depositional environments TURA concentrations and yields were relatively high for VHMW, intermediate for HMW and low for LMW fractions of the ASCHO (Fig. 2). The progressive decrease suggests their bio-reactive nature. Similarly, for the residual sediments, TURA concentrations, yields

and contribution to TCHO are higher in ME as compared with the AS probably due to the influence of terrestrial OM in the former (Table 1).

TURAs are derived from several sources including bacteria, phytoplankton, benthic organisms, and terrestrial plants etc. (Bergamaschi et al., 1999; Hung et al., 2003; Khodse et al., 2007). Contribution from these sources will be of interest in controlling TURA concentrations in marine environments. Moreover, TURA production by microorganisms is influenced by concentrations of nutrients and metal ions in the growth medium or in the natural waters. Similarly, adsorption by particles due to their surface active nature, and microbial utilization and degradation are the other factors that may have influenced concentrations of TURA in the study area (Bergamaschi et al., 1999; Hung et al., 2001, 2003). With the data at hand, it is not possible to determine exact factors controlling TURA abundance in our sediments, however, some of the above factors may have been involved.

4. Summary

Concentrations and carbon normalized yields of TCHO, TNMCHO, and TURA showed strong spatial differences, and were highest for the ME, intermediate for AS and lowest for the BOB. This may be due to differences in biological production, sources, terrestrial inputs and microbial degradation.

Carbohydrates yields generally decreased with water column depth. However, for our sediments, yields of TCHO, TNMCHO and TURA were higher in deep water (>2000 m) compared with relatively shallow water (< 1000 m) sediments. These contrasting results indicate that for our deep sea sediments, TNMCHO yield was not a useful indicator of degradation state probably due to lateral input of carbohydrate rich material, selective utilization of other organic constituents and/or preservation of carbohydrates.

Extractable OM was removed from bulk sediment POC using AHS. ASCHO accounted for 11-22 % of TCHO. TCHO and TURA were enriched in VHMW fraction of the ASCHO. As the molecular size decreased, the yields of these compounds decreased. VHMW carbohydrates are considered to be initial intermediary products of POC mineralization in sediments, and thus may play an important role in connecting sediment POC to pore water DOC and DOC of the overlying water column (Burdige et al., 2000; Miyajima et al., 2001).

Monosaccharide composition and ratios indicate that OM in sediments of the ME, BOB and the AS was derived from bacteria, phytoplankton and terrestrial material. The impact of terrestrial material, however, was more evident for the ME and the BOB sediments, and residual sediments of ME. Differences in depositional environments and molecular size of ASCHO did not influence monosaccharide composition, except glucose which increased with the decrease in molecular size of OM suggesting its association with refractory organic matter.

TURA although accounted for a small proportion of TOC, are likely to play important roles in many environmental processes. However, more data are required on their dynamics, monomeric composition and factors regulating concentrations so as to better explain their role in carbon cycling.

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Captions

Figure Captions

Fig.1. Locations of the stations sampled during various cruises of (a) ORV Sagar Kanya in the northern Indian Ocean and (b) Mandovi estuary (Goa).

Fig.2. The contribution (%) of TCHO-C (a) and TURA-C (b) to organic carbon in different size fractions of organic matter.

Fig.3. The average yields of TCHO, TNMCHO and TURA in the sediments collected from various sampling regions. Bar represent the standard deviation. ME = Mandovi estuary, AS = Arabian Sea, and BOB = Bay of Bengal.

Fig.4. Effect of sediment sampling depth on the yields of TCHO, TNMCHO, and TURA in the Bay of Bengal (a), and Arabian Sea (b).

Fig.5. Variation in the mole % of rhamnose (Rhm) plus fucose (Fuc) plus ribose (Rib) (a) arabinose (Ara) (b), and glucose (Glu) of the sediments collected along a transect extending from the Mandovi estuary to the deep Arabian Sea.

Fig.6. Variation in the average monosaccharide composition (as mole %) of the sediments of the Arabian Sea (AS), the Bay of Bengal (BOB) and the Mandovi estuary (ME) (Rhm, rhamnose; Fuc, fucose; Rib, ribose; Ara, arabinose; Xyl, xylose; Man, mannose; Gal, galactose; Glu, glucose) of the surface sediment collected from different region. Bar represent the \pm SD.

Fig.7. Effect of sediment sampling depth on the monosaccharide composition of the sediments of the Bay of Bengal (a) and the Arabian Sea (b).

Table Captions

Table 1

Distribution of TOC, TN, C/N ratio, TCHOs, TURAs, TNMCHOs, contribution of TCHO- C, TURA- C and TNMCHO- C to TOC, and TCHO/TURA ratio in surface and residual sediments from Bay of Bengal, Arabian sea and Mandovi estuary

Table 2a

Concentration of ASCHOs and contribution (%) to TCHOs of Mandovi estuary and Arabian Sea sediments

Table 2b

Recovery of ASCHOs after size fractionation

Table 2c

Recovery of ASCHOs after isopropanol precipitation

Table 3

Composition of isopropanol precipitated polymers of various molecular size from sediments of Arabian Sea and Mandovi estuary

Table 4

Monosaccharide composition (mole %) of surface and residual (after alkali extraction) sediments from Bay of Bengal, Arabian Sea and Mandovi estuary

Table 1

Station	Depth (m)	TOC	TN	C/N	TCHO			TURA			TNMCHO			TCHO/ TURA	Ratio	
					a	SD	ratio	a	SD	b	c	a	SD			b
Bay of Bengal																
BOB-1	3500	1.48	0.06	21.0	0.14	±0.00	9.2	0.02	±0.00	1.4	19.0	0.03	-	2.3	25.0	7.0
BOB-2	2700	0.89	0.05	14.8	0.09	±0.01	10.2	0.02	±0.00	2.0	24.1	0.03	-	3.4	33.3	4.5
BOB-3	2300	0.71	0.06	9.4	0.18	±0.01	25.0	0.04	±0.00	4.6	22.5	0.04	-	5.9	23.5	4.5
BOB-4	1300	1.30	0.08	14.4	0.14	±0.01	11.0	0.03	±0.01	2.1	23.3	0.05	-	4.2	37.7	4.7
BOB-5	980	1.39	0.08	14.8	0.15	±0.01	10.5	0.03	±0.00	2.1	25.1	0.05	-	3.6	34.6	5.0
BOB-6	600	1.63	0.09	16.2	0.19	±0.01	11.5	0.03	±0.00	1.5	16.2	0.05	-	2.9	25.1	6.3
BOB-7	70	1.13	0.04	25.6	0.10	±0.01	9.0	0.03	±0.01	2.0	27.9	0.03	-	2.6	28.3	3.3
Arabian Sea																
AS-1	3140	0.50	0.04	10.3	0.10	±0.00	20.1	0.04	±0.00	7.0	42.5	0.04	±0.00	8.5	42.5	2.5
AS-2	2775	0.44	0.05	8.2	0.11	±0.00	26.2	0.04	±0.00	8.8	40.8	0.04	±0.01	9.2	35.0	2.8
AS-3	2170	0.69	0.05	12.9	0.15	±0.01	21.3	0.03	±0.00	3.7	21.2	0.07	±0.00	10.2	47.7	5.0
AS-4	1000	3.41	0.10	28.7	0.33	±0.01	9.7	0.09	±0.00	2.3	28.5	0.14	±0.01	4.2	43.7	3.7
AS-5	86	0.85	0.05	14.0	0.08	±0.00	9.0	0.03	±0.00	3.3	43.9	0.02	-	2.6	28.3	2.7
Mandovi estuary																
ME-6	-	1.24	0.06	17.4	0.18	±0.01	14.5	0.02	±0.00	1.8	14.8	0.05	±0.00	4.3	29.9	9.0
ME-7	-	0.84	0.09	8.0	0.13	±0.00	15.9	0.02	±0.00	2.6	19.7	0.06	±0.00	6.7	42.3	6.5
ME-8	-	1.07	0.07	12.9	0.17	±0.00	15.9	0.03	±0.00	2.3	17.4	0.05	±0.00	4.4	27.4	5.7
ME-9	-	2.12	0.10	17.8	0.38	±0.01	17.9	0.08	±0.01	3.4	22.8	0.08	±0.00	3.9	21.6	4.8
ME-10	-	0.90	0.10	7.9	0.14	±0.00	15.6	0.03	±0.00	2.7	20.8	0.07	±0.00	7.3	46.8	4.7
ME-11	-	1.40	0.09	13.2	0.27	±0.02	19.1	0.07	±0.00	4.5	28.7	0.07	±0.01	5.2	27.1	3.9
ME-12	-	1.68	0.11	13.0	0.34	±0.01	20.3	0.10	±0.00	5.4	32.0	0.06	±0.00	3.6	17.9	3.4

Continued

ME-13	-	1.29	0.09	11.7	0.30	±0.01	23.6	0.10	±0.00	7.1	36.5	0.08	±0.01	6.2	26.4	3.0
ME-14	-	1.88	0.09	19.0	0.36	±0.00	19.1	0.09	±0.00	4.2	26.9	0.11	±0.02	5.9	30.9	4.0
ME-15	-	1.01	0.06	15.7	0.26	±0.02	26.2	0.07	±0.00	6.1	28.0	0.11	±0.03	11.0	41.9	3.7
Residual sediment																
AS-2	2775	0.35	0.01	22.0	0.06	±0.00	17.5	0.01	±0.00	2.5	17.5	0.01	±0.00	3.6	20.8	6.0
AS-4	1000	2.36	0.05	40.2	0.21	±0.00	9.1	0.03	±0.00	1.1	15.1	0.07	±0.02	3.1	34.1	7.0
ME-7	-	0.46	0.03	15.7	0.08	±0.00	17.1	0.01	±0.00	1.9	13.2	0.03	±0.00	6.2	36.3	8.0
ME-10	-	0.55	0.01	72.3	0.10	±0.00	17.5	0.02	±0.00	2.5	17.3	0.03	±0.00	4.8	27.4	5.0
ME-15	-	0.80	0.01	67.5	0.13	±0.00	15.6	0.05	±0.00	5.5	42.3	0.06	±0.00	7.3	46.9	2.6

a = concentration m mol C g⁻¹ dry sediment.

b =% TOC.

c =% TCHO.

d = concentration m mol N g⁻¹ dry sediment.

SD = standard deviation.

- = No data

Table 2a

Station	TCHO mg/g	ASCHO mg/g	ASCHO/TCHO %
AS-2	3.4	0.72	20.9
AS-4	9.9	1.52	15.5
ME-7	4.0	0.86	21.6
ME-10	4.2	0.74	17.6
ME-15	7.9	0.94	11.9
Ave.	-	-	17.5
SD ^a	-	-	4.0

^a Standard deviation

Table 2b

Stations	ASCHO before size fractionation (mg/g)	ASCHO after size fractionation (mg/g)			Total ASCHO after size fractionation (mg/g)	Recovery %
		VHMW	HMW	LMW		
AS-2	0.72	0.16	0.18	0.29	0.63	87.6
AS-4	1.53	0.48	0.41	0.28	1.16	76.0
ME-7	0.86	0.22	0.23	0.27	0.72	83.9
ME-10	0.74	0.27	0.08	0.16	0.50	68.1
ME-15	0.94	0.32	0.19	0.30	0.80	85.1
Average	-	-	-	-	-	80.1
SD ^a	-	-	-	-	-	8.0

VHMW = >30kDa to 0.2 μ m; HMW = >10 kDa to 30 kDa; LMW = >1 kDa to 10 kDa; ^a Standard deviation

Table 2c

Stations	Total ASCHO before precipitation (mg/g)			VHMW			HMW			LMW			Total ASCHO after precipitation (mg/g)	Total recovery %
	a	b	c	a	b	c	a	b	c	a	b	c		
AS-2	0.63	0.16	0.11	67.9	0.18	0.15	81.2	0.29	0.11	40.1*	0.37	59.2		
AS-4	1.16	0.48	0.43	88.4	0.41	0.39	94.7	0.28	0.13	49.1*	0.94	81.1		
ME-7	0.72	0.22	0.15	68.5	0.23	0.16	67.2	0.27	0.06	20.5*	0.36	50.0		
ME-10	0.50	0.27	0.27	98.1	0.08	0.07	91.4	0.16	0.10	63.1	0.43	86.0		
ME-15	0.80	0.32	0.25	78.7	0.19	0.15	81.9	0.30	0.22	72.2	0.61	77.0		
Average	-	-	-	-	-	-	-	-	-	-	-	71.0		
SD ^a	-	-	-	-	-	-	-	-	-	-	-	15.4		

a = ASCHO after size fractionation (mg/g); b= ASCHO after precipitation (mg/g); c = % Recovery (% Recovery = b/a*100)
^a Standard deviation, * = poor recovery after isopropanol precipitation.

Table 3

Station	Fraction	Monosaccharide composition (mole %)										OC	TNMCHO		TNMCHO-C		Sulfate		Pyruvate	
		Rhm	Fuc	Rib	Ara	Xyl	Man	Gal	Glu	a	a		% Yield	b	b	b	b			
AS-2	VHMW	8.7	6.0	2.8	8.2	14.9	14.2	27.7	17.6	12.3	1.7	14.2	0.8	0.3						
	HMW	7.1	8.7	1.8	6.6	10.1	15.1	26.7	23.8	30.4	3.3	11.0	0.6	0.2						
	LMW	4.7	6.1	1.3	4.5	5.9	18.9	30.3	28.3	37.3	3.5	9.5	0.7	0.2						
AS-4	VHMW	3.1	8.8	19.3	18.1	14.1	11.5	14.7	10.3	26.6	9.1	34.0	0.8	0.2						
	HMW	2.4	4.7	3.2	15.1	12.7	15.1	28.7	18.1	27.4	2.3	8.5	1.1	0.2						
	LMW	4.9	0.6	2.5	7.8	8.0	22.4	30.9	23.0	23.1	1.7	7.4	1.1	0.3						
ME-7	VHMW	9.1	9.2	0.9	10.7	9.3	14.8	19.8	26.2	52.1	3.4	6.6	nd	nd						
	HMW	8.1	5.7	1.1	6.7	9.6	15.7	21.7	31.4	50.2	2.9	5.7	1.0	0.2						
	LMW	1.9	5.5	0.2	4.8	1.3	15.8	10.7	59.8	62.3	3.2	5.1	nd	Nd						
ME-10	VHMW	5.1	4.7	0.0	8.1	2.1	17.7	16.1	46.3	26.7	2.3	11.8	1.1	0.3						
	HMW	6.0	11.1	0.0	12.8	2.4	19.5	13.7	34.5	29.8	1.8	6.0	1.0	0.2						
	LMW	11.4	9.8	0.0	9.8	2.5	20.7	14.6	31.1	34.8	1.3	3.8	1.5	0.3						
ME-15	VHMW	8.5	8.0	1.5	9.1	9.4	13.9	24.1	25.5	67.4	3.8	5.6	1.4	0.2						
	HMW	7.0	4.4	0.5	6.0	8.1	15.6	27.2	31.1	63.5	3.4	5.4	1.3	0.2						
	LMW	8.0	3.4	0.6	6.5	9.5	15.1	26.7	30.2	58.6	2.9	4.9	1.9	0.2						

a = μ mol C mg^{-1} of polymer; b = μ mol mg^{-1} of polymer
VHMW = > 30 kDa to 0.2 μm ; HMW = > 10 kDa to 30 kDa; LMW = > 1kDa to 10 kDa

Table 4

Station	Monosaccharide composition (mole %)											Rhm+Fuc/Arb+Xyl					
	Rhm ^a	SD ^b	Fuc ^c	SD ^b	Rib ^d	SD ^b	Ara ^e	SD ^b	Xyl ^f	SD ^b	Man ^g	SD ^b	Gal ^h	SD ^b	Glu ⁱ	SD ^b	Ratio
Bay of Bengal																	
BOB-1	5.0	- ^m	4.5	-	6.3	-	14.8	-	12.9	-	15.1	-	23.6	-	17.9	-	0.40
BOB-2	10.7	-	4.7	-	4.2	-	12.2	-	11.1	-	15.2	-	20.1	-	21.8	-	0.78
BOB-3	5.4	-	4.6	-	5.8	-	13.4	-	12.5	-	14.4	-	24.8	-	19.1	-	0.45
BOB-4	11.4	-	7.1	-	4.0	-	8.7	-	8.4	-	16.4	-	23.5	-	20.4	-	1.27
BOB-5	9.4	-	6.8	-	4.8	-	9.1	-	12.4	-	15.8	-	23.2	-	18.6	-	0.88
BOB-6	5.8	-	5.3	-	6.1	-	13.7	-	12.8	-	15.7	-	25.0	-	15.6	-	0.48
BOB-7	8.4	-	5.5	-	7.9	-	17.8	-	13.0	-	13.1	-	21.6	-	12.7	-	0.52
Arabian Sea																	
AS-1	11.8	-	8.6	±0.5	3.5	±1.3	9.3	±0.1	9.8	±2.2	17.4	-	19.9	±0.5	19.7	±3.3	1.2
AS-2	11.3	-	8.4	±0.2	4.3	±0.1	9.3	±0.5	11.9	±0.7	18.1	±0.3	19.9	±0.6	16.9	±0.2	1.1
AS-3	10.0	-	8.3	-	5.1	±0.3	10.1	±0.4	13.8	±0.1	16.7	±0.6	18.7	±0.1	17.2	±0.2	0.9
AS-4	9.9	-	9.6	-	5.1	-	8.3	±0.2	13.8	±0.1	15.4	±0.1	19.5	±0.1	18.5	±0.1	1.0
AS-5	10.9	-	9.1	-	4.9	-	8.6	-	12.8	-	15.0	-	19.5	-	19.3	-	1.1
Mandovi estuary																	
ME-6	11.2	±1.1	7.3	±0.6	2.1	±0.1	11.3	±0.5	5.9	±1.2	14.4	±0.1	18.7	±0.4	29.0	±0.6	1.3
ME-7	8.5	±0.7	5.1	±0.3	1.6	±0.3	15.5	±1.0	7.9	±0.2	10.2	±0.3	13.7	±0.5	37.4	±1.2	0.7
ME-8	8.0	±0.5	3.3	±0.1	1.0	±0.1	15.9	±1.0	7.2	±0.1	8.7	±0.5	11.9	±0.2	43.9	±1.0	0.6
ME-9	9.1	±1.3	6.2	±1.5	1.3	±0.9	9.7	±0.6	5.8	±0.2	13.0	±1.7	17.3	±1.4	37.4	±6.1	1.2
ME-10	7.5	±0.1	3.8	±0.2	1.0	±0.1	17.8	-	6.7	±0.2	11.7	±0.3	16.1	±0.1	35.4	±0.2	0.5
ME-11	9.2	±0.1	4.9	±0.2	1.0	-	12.1	±0.2	6.3	±0.5	11.6	±0.5	14.8	±0.1	40.1	±1.2	0.9

Continued

ME-12	8.8	-	4.3	±0.2	1.0	±0.3	9.1	±0.4	5.2	±0.1	13.9	±0.3	14.6	±0.1	43.2	±0.5	1.1
ME-13	9.6	±0.4	5.5	-	0.8	±0.3	12.1	±1.2	5.7	±0.7	12.6	±1.1	15.0	±0.1	38.7	±1.4	1.0
ME-14	10.0	±0.1	5.7	±0.2	1.2	±0.2	11.9	±0.5	7.5	±0.1	12.2	±0.2	14.7	±0.2	36.8	-	0.9
ME-15	5.6	±0.9	2.7	±0.3	0.8	±0.1	17.3	±0.7	10.7	±0.6	9.4	±0.2	14.1	±0.4	39.3	±2.6	0.3
Residual sediment																	
AS-2	7.9	±0.4	6.5	±0.1	2.4	±0.3	10.2	±0.8	8.3	±0.4	19.4	±0.1	23.0	±0.7	22.1	±1.4	0.9
AS-4	10.4	±0.1	10.2	±0.1	2.7	±0.4	8.1	±0.3	6.9	±0.7	18.3	±0.9	22.4	±0.5	21.0	±0.6	1.6
ME-7	5.7	±0.9	2.7	±0.2	1.0	±0.3	14.7	±0.8	6.3	±0.9	8.0	-	11.4	±0.1	50.3	±1.2	0.5
ME-10	6.5	±0.5	2.7	±0.2	0.8	±0.2	15.9	±0.5	6.2	±0.3	9.3	±1.1	14.0	±0.6	44.8	±2.3	0.5
ME-15	4.2	±0.3	2.0	±0.4	0.7	±0.4	12.7	±1.2	10.1	±0.3	6.6	±0.6	10.2	±0.9	53.5	±4.2	0.3

^a Rhamnose; ^b Standard deviation; ^c Fucose; ^d Ribose; ^e Arabinose; ^f Xylose; ^g Mannose; ^k Galactose; ^l Glucose
^mSD < 0.1

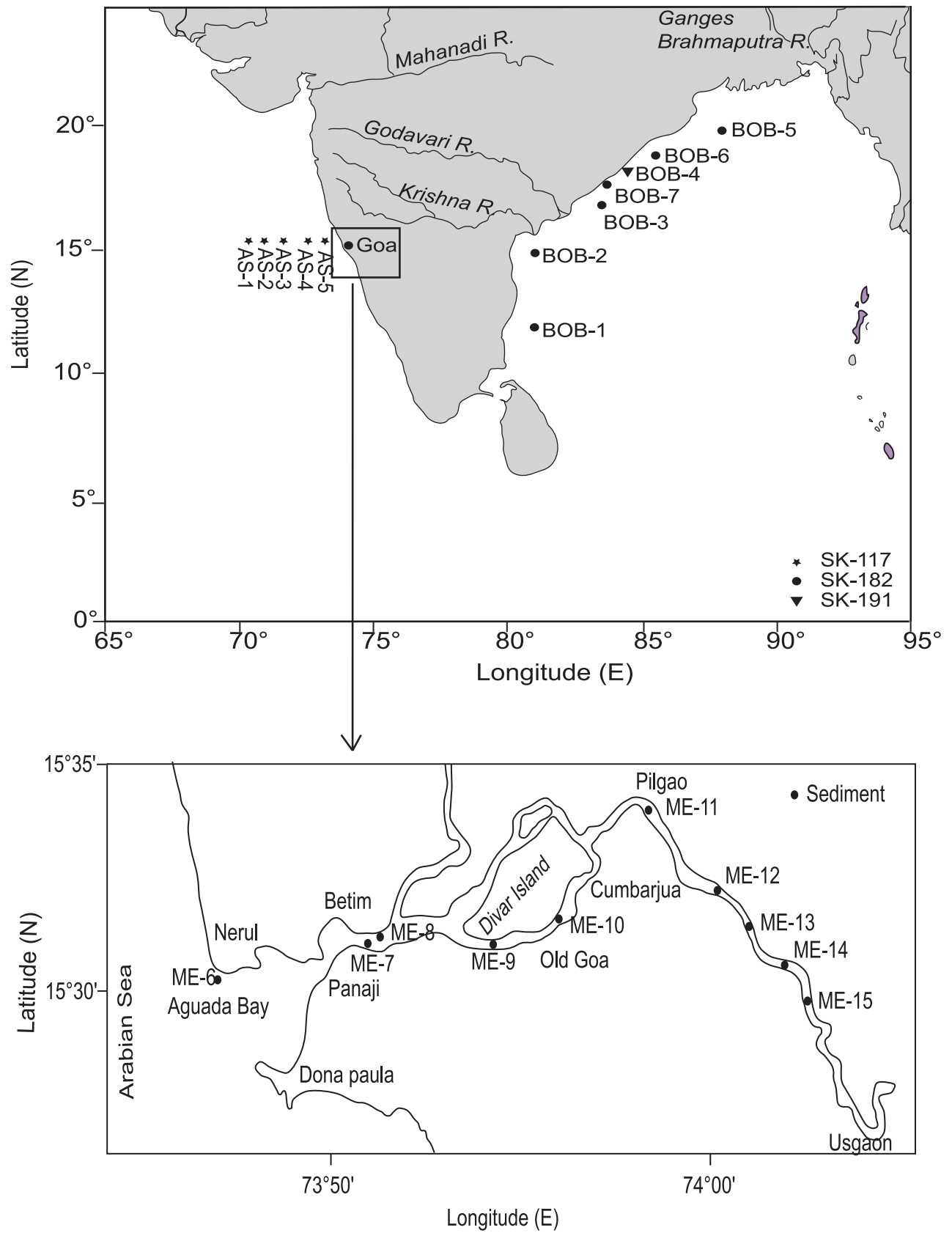


Fig.1

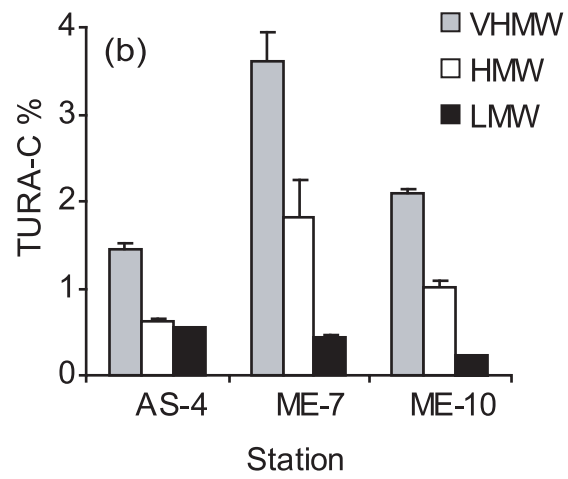
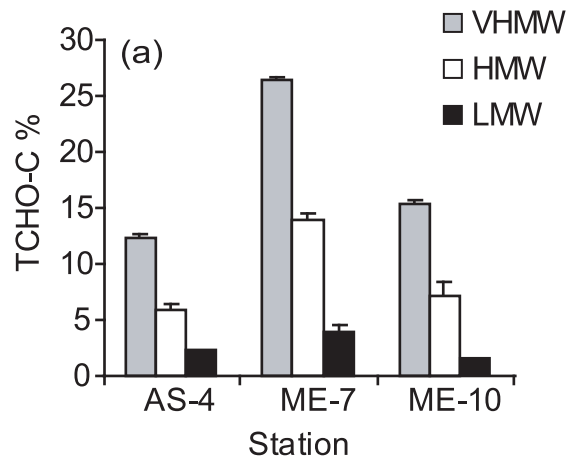


Fig.2.

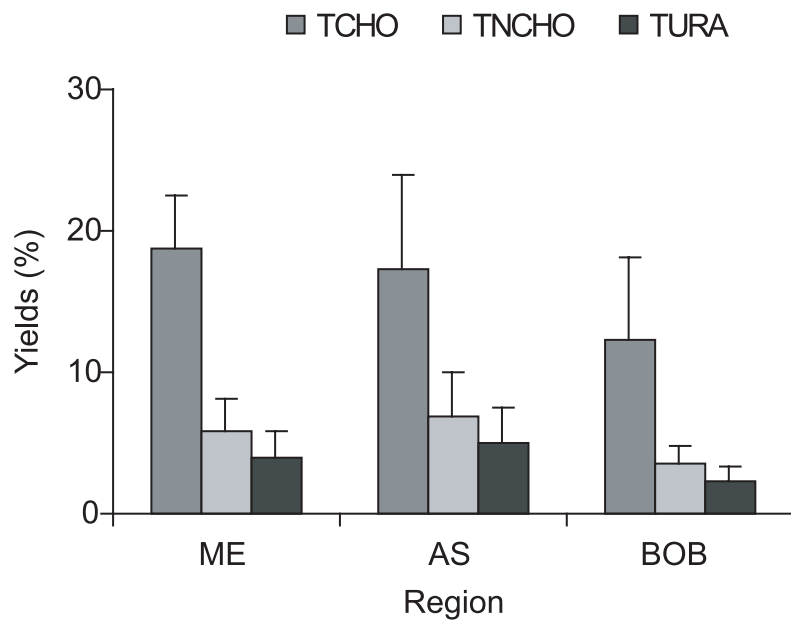


Fig.3.

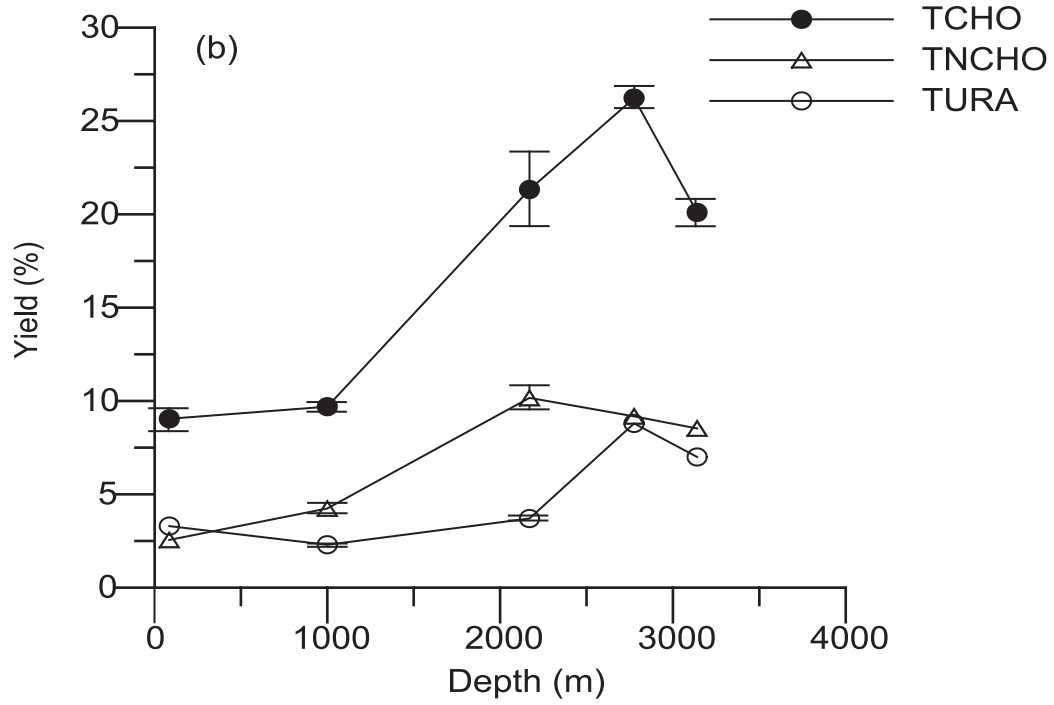
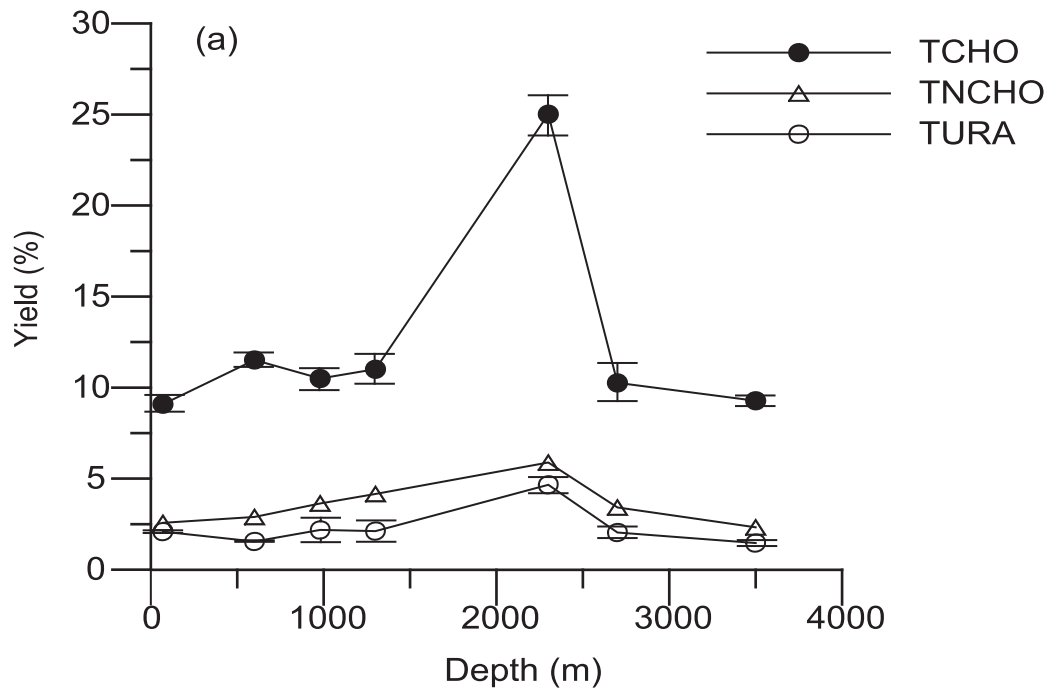


Fig.4.

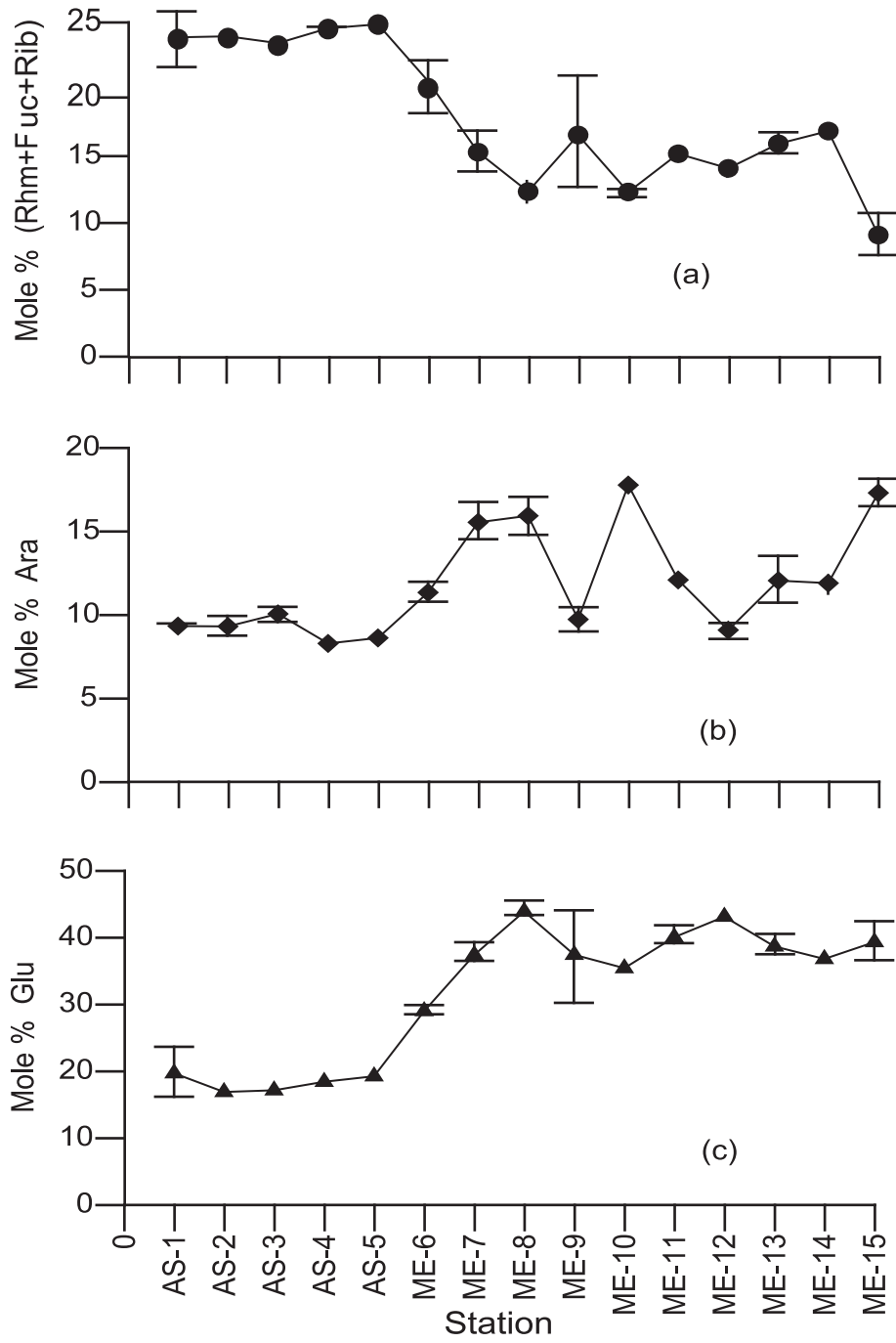


Fig.5.

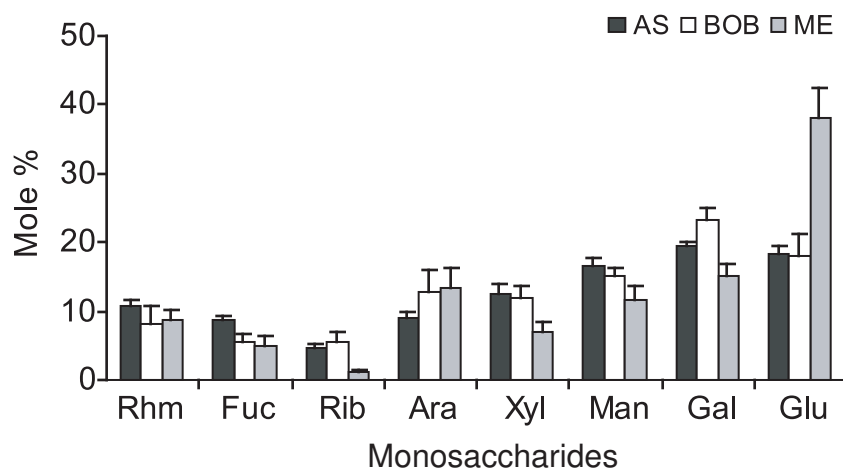


Fig. 6.

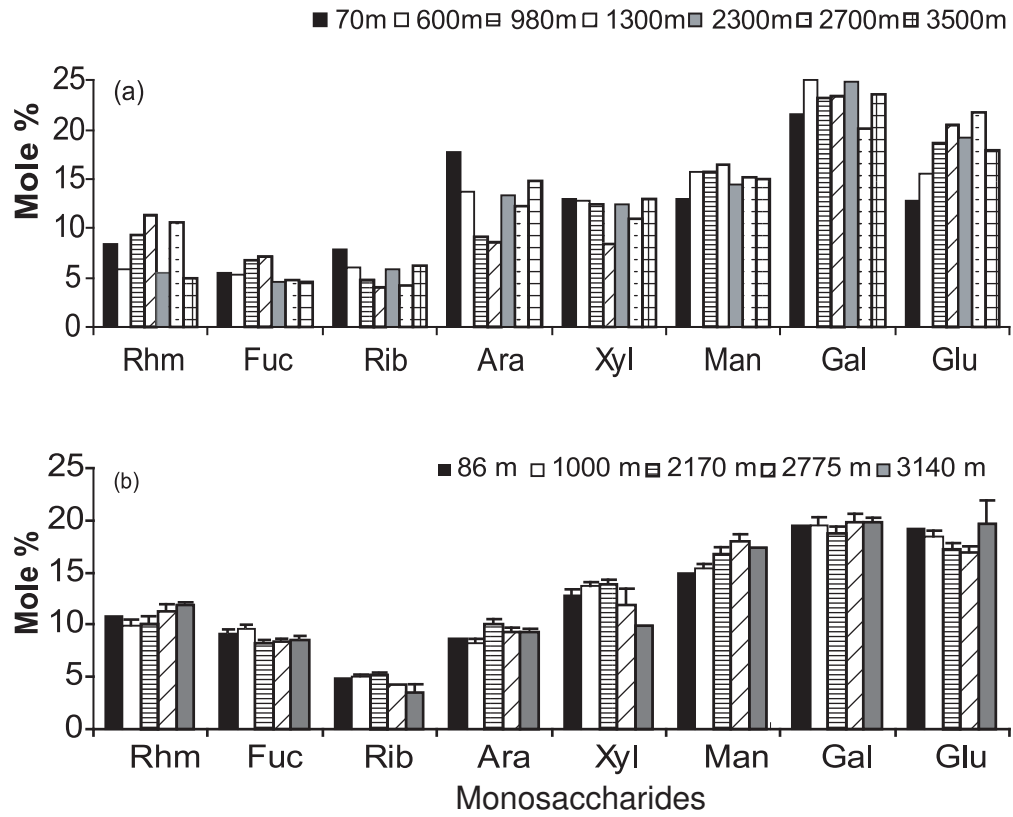


Fig. 7.