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# Sources and fluxes of particulate organic matter in shallow coastal waters characterized by summer macroaggregate formation

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**Abstract.** The origin and temporal variation in composition of sedimented particulate organic matter (POM) in the Gulf of Trieste (northern Adriatic) was studied over the year with special reference to the composition and sedimentation of macroaggregates in summer of 1991 using sediment traps.

Suspended and sedimented POM, comprising a minor part of the largely inorganic total particulate matter, was prevalently of marine origin and composed mostly of humic substances followed by carbohydrates and proteins. Seasonal variations of particulate proteins and carbohydrates were correlated with variations of phytoplankton biomass. 'New' production, occurring in late spring as a consequence of massive riverine inputs of N, Si and P nutrients in the surface layer of the Gulf, produced high particulate carbohydrate and protein concentrations. Subsequent depletion of introduced nutrients caused the decrease of particulate protein concentration but not that of particulate carbohydrate. The prolonged plankton biosynthesis of carbohydrates successively produced marine snow and later macroaggregates. The macroaggregates were characterized by $\delta^{13}C$ value of $-19.9‰$ and their carbohydrates were mostly composed of glucose followed in decreasing order by mannose, fructose, galactose, arabinose, ribose, xylose and fucose, suggesting a prevalent origin from phytoplankton structural heteropolysaccharides. Sedimentation of particulate organic constituents in the summertime, characterized by the massive presence of macroaggregates in the surface layer above the pycnocline, was the highest at a depth of 10 m at the end of this phenomenon, about six weeks after its first appearance. Sedimented macroaggregates were clearly traced by a characteristic $\delta^{13}C$ signal and higher carbohydrate concentrations. The monosaccharide composition was influenced by selective degradation in the water column. Sedimented POM in the bottom layer was, on the other hand, more affected by sediment resuspension. The mean yearly decrease of particulate protein-C and carbohydrate-C by 40–50% in the water column between the depths of 10 and 20 m indicates the preferential utilization of these constituents by microorganisms. The decrease of particulate humic-C is probably more the result of the export of particulate matter from the Gulf. This study also indicates that the macroaggregate formation has little impact on the annual C and N budget in such coastal areas.

## Introduction

Particulate organic matter (POM) in coastal waters originates from organic matter synthesized by marine organisms, mostly by phytoplankton, and from terrigenous sources, mostly by riverine inflows. This organic matter of different origin, composition and reactivity is successively transported to the sea floor as sedimented POM, forming sedimentary organic matter of markedly different composition to that in the surface layer of the water column (Wakeham & Lee 1989). POM is transformed and degraded within the entire water column during sedimentation before reaching the sediment-water interface. Only larger particles such as faecal pellets, phytodetritus, marine snow or marine snow-like macroaggregates and 'swimmers' can reach sediments with unaltered or little altered chemical composition. The degree of these biogeochemical transformations is now clearly recognized to be related to the hydrological properties and variations of biological activity in the water column (Lee & Wakeham 1992).

Marine snow and marine snow-like macroaggregates, representing a group of extremely fragile but fast-moving and therefore chemically little altered particles during sedimentation, are a frequent phenomenon in the northern Adriatic in summertime, and they have occasionally an important role in the summer vertical flux (Posedel & Faganeli 1991). Marine snow and macroaggregates are also known to be an important site of accumulation and degradation of organic matter within the water column, contributing to the patchy distribution of POM in sea water. Despite the episodic appearance of marine macroaggregates in the northern Adriatic their occurrence is known for more than 250 years (Fonda-Umani et al. 1989). However, little is known about their causes and mechanism of formation. High abundances of marine snow appeared recently in the summers of 1988 and 1989, due to diatomaceous blooms (Fanuko & Turk 1990), and in the summer of 1991, apparently due to a dinoflagellate bloom (Herndl 1992). All macroaggregates also contain various entrapped phytoplankters, microzooplankters, bacteria, detrital and mineral particles (Stachowitsch et al. 1990).

The aim of the present work was to study the origin and temporal variations of chemical composition of suspended and sedimented POM in the southern part of the Gulf of Trieste (northern Adriatic) over the year (October 1990 – November 1991), a year characterized by the presence of masses of mucous macroaggregates in the summer period. Analyses of organic C, its $^{13}C$ composition, total N, total carbohydrates, monosaccharides, total proteins and humic substances at suspended and sedimented POM were determined. Special attention was paid to the period of massive occurrence of macroaggregates in the summertime of 1991. An annual budget for all constituents studied was constructed and compared to those from a period apparently not affected by any planktonic bloom (Faganeli 1989).

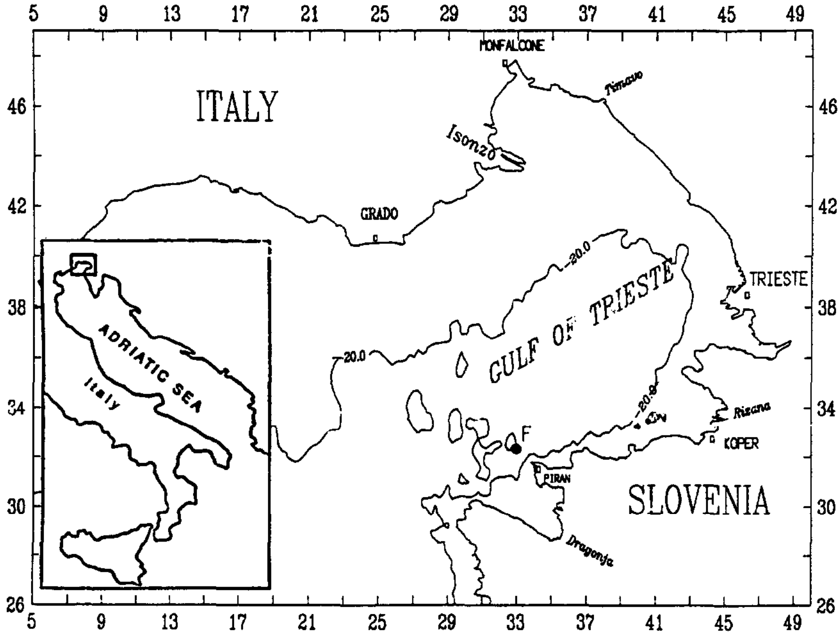

*Fig. 1.* Location of the station F in the Gulf of Trieste (northern Adriatic).

## Materials and methods

### *Samples*

Samples for analysis of POM were taken approximately biweekly from October 1990 to November 1991 at a fixed sampling station, F, located in the south eastern part of the Gulf of Trieste (Fig. 1). Samples were collected from depths of 0.5 and 20 m using 5 l Niskin bottles. Macroaggregates were collected in July 1991 at the sea surface using polyethylene bottles.

The sedimentation rates of POM were also measured from October 1990 to November 1991 at station F (Fig. 1) approximately biweekly over a period of 24 hours using moored sediment traps. The deepest sediment trap, similar to that described by Blomqvist & Kofoed (1981), was designed to collect 4 samples simultaneously, and was situated approximately 1 m above the bottom to reduce the bottom sediment resuspension. The other trap was located at the depth of 10 m and designed to collect 2 samples simultaneously. Both traps consisted of small plastic cylinders, each 50 cm$^2$ in the area. The height/width ratio of the cylinders was 5.

Samples of POM (2 l) and sedimented POM were filtered through Whatman GF/F glass-fibre filters precombusted for 3 hours at 480 °C to eliminate organic contaminants. The material collected on the filters was rinsed several times with distilled water to remove salts. All samples were freeze-dried for 24 hours and weighed. Dried samples were used for analysis of C, H, N contents, $^{13}C$ content of POM, and protein, total carbohydrate and humic contents, and analysis of monosaccharide composition. Macroaggregates were centrifuged at 15,000 rpm for 15 min at ambient (20 °C) temperature and the supernatant discarded. The sediment was rinsed with distilled water to remove salt and then freeze-dried to dryness.

### *Analyses*

Total particulate matter was determined gravimetrically. Total C and N contents were determined directly with a commercial CHNS elemental analyzer (Carlo Erba mod. EA 1103) and organic C after pretreatment of samples with 2 N HCl to remove carbonates. Analysis of $^{13}C$ isotopic composition of the $CO_2$ produced by ignition of samples in an oxygen atmosphere (Craig 1953), previously treated with 2 N HCl, was performed with a Varian MAT 250 mass spectrometer. The results were expresses as deviations in °/oo from the $^{13}C/^{12}C$ ratio of the Chicago PDB standard ($\delta^{13}C$).

Protein contents in samples were determined in 0.5 N NaOH homogenates (Rausch 1981) colorimetrically, using a slightly modified Coomassie Brilliant Blue protein assay (Bio Rad, USA) method of Setchell (1981) with casein as standard (Mayer et al. 1986). Casein, like bovine $\gamma$-globulin and albumin, seems to be an appropriate standard for this protein assay in plankton in general (Faganeli et al. 1989). Interferences from ligninosulphonate and sedimentary fulvic acid are negligible, while sedimentary humic acids exhibit approximately 1/3 of the absorbance of that of casein in the same concentration range (Posedel & Faganeli 1991). It seems possible that the humic acids contain some larger polypeptide residues bonded onto the structure of the humics (Tegelaar et al. 1989). Humic substances were determined in 0.5 N NaOH homogenates fluorimetrically at $\lambda$ex.=340 nm and $\lambda$em.=450 nm (Plechanov et al. 1983). Purified humic acid, isolated from coastal sediments along the W. coast of Sweden, was used as a standard. Total carbohydrate contents were analyzed colorimetrically using the MBTH procedure of Burney & McSeiburth (1977) after hydrolysis of samples in 1 M $H_2SO_4$ at 100 °C for 3.5 hours (Mopper 1977) in sealed ampoules and neutralization with NaOH, similar to that described by Pakulski & Benner (1992). In parallel, total carbohydrates in hydrolysates were also determined by the phenol-sulphuric acid method of Dubois et al. (1956), and no significant differences were found between the two methods (paired t-test $p \leq 0.01$, n=87).

For determination of monosaccharide composition the freeze-dried macroaggregates were extracted twice with diethyl ether to remove lipids and pigments, and the residue evaporated to dryness. The samples of sedimented POM were first treated with 72% $H_2SO_4$, left overnight at room temperature and the acid successively diluted to 1 M $H_2SO_4$. These samples were hydrolysed in sealed ampoules at 100 °C for 3.5 hours as previously described. The hydrolysates were successively neutralized with an equivalent amount of $Ba(OH)_2$ and $Na_2CO_3$ to pH=6.5–7. The $BaSO_4$ precipitate was removed by filtration using a precombusted Whatman GF/C glass-fibre filter. The hydrolysates were finally desalted by passing through columns of cation and anion exchange resins (Dowex 50WX8, Dowex 1X8). The desalted hydrolysates were spiked with phenyl-$\beta$-D-glucopyranoside as internal standard. The dried macroaggregate sample, with added phenyl-$\beta$-D-glucopyranoside as an internal standard, were hydrolysed with 4N trifluoroacetic acid at 125 °C for 1 hour under a stream of nitrogen. All samples were successively freeze-dried. For determination of neutral monosaccharides in macroaggregates and sedimented POM, including ketoses, derivatization to N-methyl-oxime acetates (Willis 1983; Neeser & Schweizer 1984) was applied. The dried samples were reacted with N-methylhydroxylamine hydrochloride in methanol/acetic anhydride (1:2) at 70–80 °C for 20 min. and then dried again by blowing nitrogen over the solution at room temperature. Acetylation of the dried residue was performed adding pyridine/acetic anhydride (1:3) and heated at 70–80 °C for 1 hour. The solution was dried under a stream of nitrogen and the dry residue dissolved in 1 ml of dichloromethane, washed with 1N HCl and distilled water, filtered through a precombusted Whatman GF/C glass-fibre filter and dried with $Na_2SO_4$. The solution was concentrated by evaporation in a stream of nitrogen. Gas-chromatographic analysis of N-methyloxime acetates was performed with a Hewlett-Packard (Mod. 5840A) GLC equipped with a FID using a split-type injector. Separation was achieved on a fused silica capillary column (25 m, 0.20 mm i.d.) coated with Carbowax 20 M. The temperature program was from 140 to 200 °C at a rate of 4°/min. and finally kept isothermal at 200 °C for 25 min. Helium was used as carrier gas. Gas chromatographic – mass spectrometric analysis was performed under the same conditions using an AutoSpec EQ (VG Analytical) mass spectrometer.

Basic hydrographic and nutrient analyses were performed by the Marine Biological Station Piran in the frame of the Alpe-Adria project 'Reasons and consequences of the formation of amorphous aggregates in the northern Adriatic sea' using standard methods (Grasshoff et al. 1983).

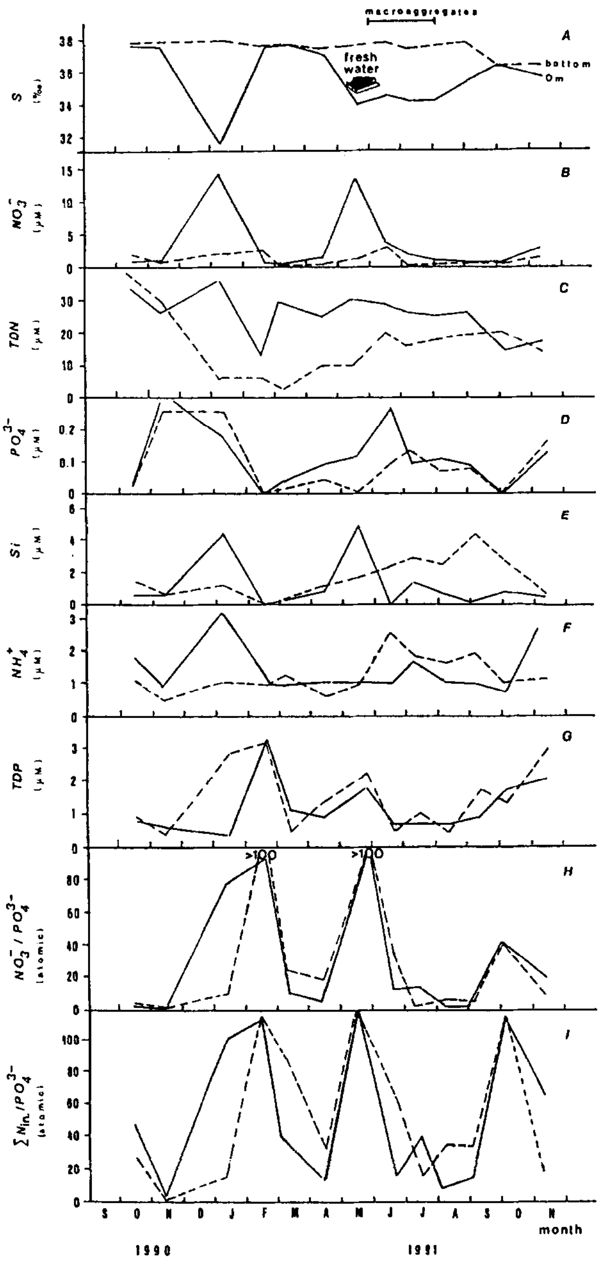

*Fig. 2.* Variations of salinity (A), concentrations of nitrate (B), total dissolved nitrogen (TDN; C), phosphate (D), silicate (E), ammonia (F), total dissolved phosphorus (TDP; G), and $NO_3^-/PO_4^{-3}$ (H) and $\Sigma N_{in.}/PO_4^{-3}$ ($\Sigma N_{in.} = NO_3^- + NO_2^- + NH_4^+$; I) ratios in the surface (0 m; solid line) and bottom (20 m; dashed line) layers at the station F. Horizontal line at the top indicates the occurrence of macroaggregates.

## Results and discussion

### *Composition of POM*

The composition of POM in terms of POC, particulate proteins and particulate carbohydrates, depicted in Fig. 2, showed wide temporal variations. Lower values of all particulate constituents appeared in wintertime (January –March). Similar or even somewhat higher results were reported previously as typical for the southern part of the Gulf of Trieste studied at a more inshore sampling point (Posedel & Faganeli 1991). We found no clear differences between surface and bottom layer concentrations of the constituents analyzed, probably due to extension of the euphotic zone to the bottom. The exception was the late spring and summer (in the period May–August 1991), during the formation and subsequent development of physical, chemical and biological stratifications with higher concentrations in the surface layer (Fig. 2).

'New' nutrients massively introduced into the surface layer of the Gulf of Trieste, especially by the river Isonzo in late spring, as indicated by a considerable decrease of salinity and increase of $NO_3$, $PO_4$, and Si concentrations (Fig. 2), promote 'new' phytoplankton production and the formation of a bloom (High Chl a concentrations; Fig. 3). This bloom was clearly reflected in the occurrence of the highest particulate carbohydrate and protein concentrations. The subsequent gradual decrease of $NO_3$ in the surface layer drastically reduced the particulate protein concentrations due to slower cellular protein biosynthesis. On the other hand, a lower decrease of particulate carbohydrate concentration was found in the presence of rather stationary $PO_4$, total dissolved phosphorus (TDP), $NH_4$ and total dissolved nitrogen (TDN) concentrations (Fig. 2). This would indicate that the particulate protein and carbohydrate contents were a function of $NO_3/PO_4$ ratios during that stage. This observation confirmed the suggestion of Kiφrboe et al. (1990) that nutrient (in our case nitrate) limitation of phytoplankton growth might occur after the bloom, induced by previous input of 'new' (riverine) nutrients (in our case nitrate) into the euphotic zone. The nitrate N – stressed cells subsequently produced extracellular polysaccharides with colloidal characteristics, making the phytoplanktonic cells sticky. These colloids, ranging between dissolved and particulate size fractions, were observable as higher particulate carbohydrate and POC concentrations in the subsequent ('mature') stage (August 1991; Fig. 3). Polysaccharide exudates are attractive energy rich media for bacterial growth, hydrolysing polymers. These polymers also contain dissolved organic nitrogen and dissolved organic phosphorus produced by the decay of phytoplanktonic cells and scavenged from sea water column. The regenerated nutrients could support vigorous phytoplankton growth within

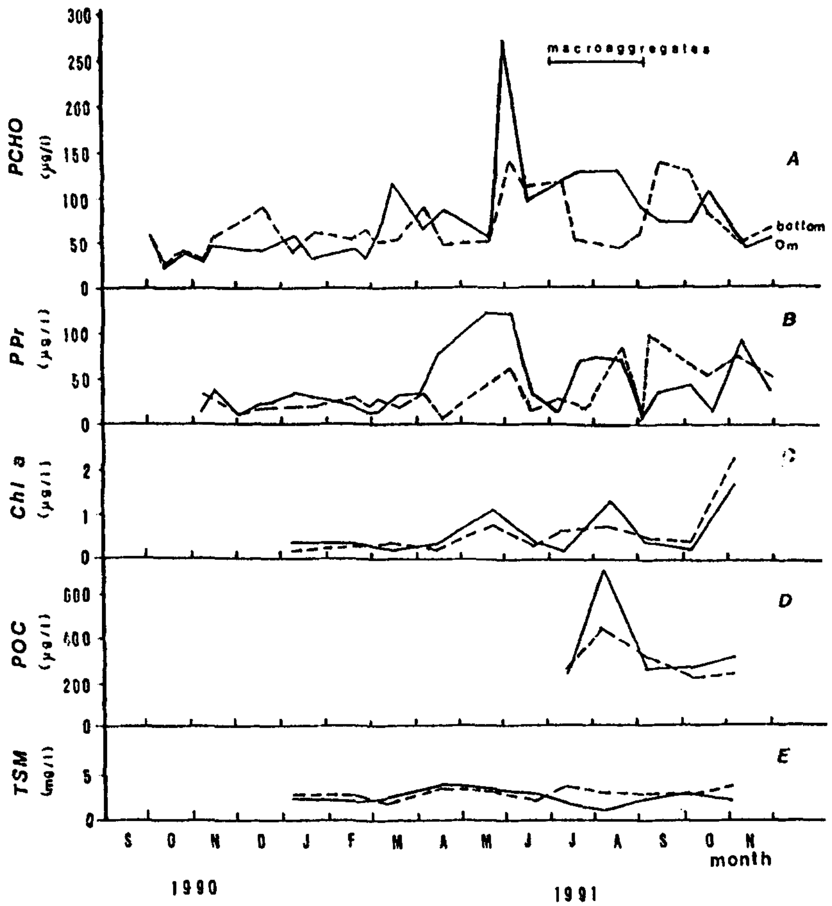

*Fig. 3.* Variations of particulate carbohydrates (A), particulate proteins (B), chlorophyll a (C; coutesy of P. Mozetič), particulate organic carbon (D) and total suspended matter (E) in the surface (0 m; solid line) and bottom (20 m; dashed line) layers at the station F. Horizontal line at the top indicates the occurrence of macroaggregates.

the aggregates, as suggested by the higher Chl a concentrations found in mid August of 1991, in parallel with higher particulate protein concentration in the presence of approximately stationary concentrations of $NH_4$, TDN, $PO_4$, TDP and Si in the ambient surface waters of the Gulf (Fig. 2, 3). Excreted polysaccharides make phytoplanktonic cells sticky, producing even denser aggregates (e.g. in August 1991) by collision through bacterial colonization of mucous and the gluing of aggregates into macroaggregates (Azam & Smith 1991).

*Table 1.* Neutral monosaccharide composition (wt %) of macroaggregates in the southeastern part of the Gulf of Trieste in July 1991.

| | |
|---|---|
| Fuc | 0.5 |
| Rib | 1.5 |
| Ara | 2.3 |
| Xyl | 1.1 |
| Man | 14.5 |
| Gal | 6.3 |
| Glu | 60.2 |
| Fru | 12.7 |
| Tot. CHO | 78.9 % |
| CHO-C | 39.6 % |

### *Composition of macroaggregates*

Chemical analysis (Table 1) showed that the principal constituents were carbohydrates. The high C/N ratio (12; atomic) was due to the low protein content (2.5%). This was shown to be a cell constituent, since the amino acid composition of macroaggregates from 1989 was similar to that observed in summer POM in the Gulf of Trieste not affected by macroaggregate formation (Posedel & Faganeli 1991). The $^{13}C$ composition of the macroaggregates was $-19.0$ ‰ and thus similar to those of naturally blooming and batch-cultured (in the stationary phase of growth) diatoms, flagellates and dinoflagellates from the Gulf of Trieste (Faganeli et al. 1989), suggesting the prevalently phytoplanktonic origin of these macroaggregates.

The analysis of the neutral monosaccharide composition of the macroaggregates (Table 1) revealed glucose as the major component, followed in decreasing order by mannose, fructose, galactose, arabinose, ribose, xylose and fucose. This composition suggests that the monosaccharides were mostly combined in structural heteropolysaccharides of the phytoplanktonic cell wall (Hama & Handa 1992), composed prevalently of xylose, mannose, galactose, fucose and rhamnose (Haug & Myklestad 1976). According to Ittekkot et al. (1982) the composition of structural monosaccharides is similar to that of mucous. Part of the high glucose content could also be bonded to water-soluble reserve glucans (Handa 1969; Handa & Yanagi 1969), since in macroaggregates from 1989 it was found that up to 35% of total carbohydrates were water soluble (Posedel & Faganeli 1991). In contrast to reserve polysaccharides the structural heteropolysaccharides are less water soluble, more resistant towards acid hydrolysis and probably highly branched (Percival 1970). Fructose probably originates from fructans present in some diatoms and green algae (Ittekkot et al. 1982), and thus could be considered of phytoplanktonic origin.

### *Sedimentation of POM*

The temporal variations of carbohydrate sedimentation rates (Fig. 4) showed the highest rates at a depth of 10 m in the whole summertime during the presence of macroaggregates and especially at the end of August 1991. This indicated the highest accumulation rate of macroaggregates at that depth in the decaying (or mature) stage of this phenomenon about 6–7 weeks after its first appearance.

The above observation is supported by temporal variations of $\delta^{13}C$ values of sedimented POC. The highest values, identical to that of macroaggregates collected by hand in the surface waters (−19.0‰), were found at a depth of 10 m in the whole summertime during the presence of macroaggregates and especially at the end of August 1991. The macroaggregate imprint was also seen from higher C/N ratio (9–11, atomic) of the summer sedimented POM observed at a depth of 10 m.

The variation of particulate protein sedimentation rates, on the other hand, more directly reflected the growth and sedimentation rates of phytoplankton (see the similarities between particulate protein and Chl a concentration variations).

The highest particulate protein sedimentation rate observed at the end of August 1991 was due to the sedimentation of phytoplankton bloom occurring within macroaggregates in mid August 1991 (Fig. 3). This also coincided with the highest $\delta^{13}C$ value and lower C/N ratio of sedimented POM at a depth of 10 m (Fig. 4).

The neutral monosaccharide composition of sedimented POM collected at the depths of 10 and 20 m (Fig. 5) in early September 1991 contained up to 3-fold lower contents of glucose than in summer macroaggregates. This would suggest that the majority of glucose bonded in the phytoplanktonic reserve, probably 1,3-$\beta$-glucans, is degraded in the water column and dissolved in surrounding water (Ittekkot et al. 1982; Tanoue & Handa 1987; Cowie et al. 1992). High $\beta$-glucosidase activity observed in the northern Adriatic macroaggregates (Herndl 1992) could be the consequence of rather high content of this reserve glucan. The composition of other monosaccharides, probably bonded in the structural heteropolysaccharides, was retained. Glucose was one of most abundant monosaccharide in sedimented POM in other periods while the differences in the monosaccharide composition (Fig. 5) should be attributed to variations in plankton community and their growth

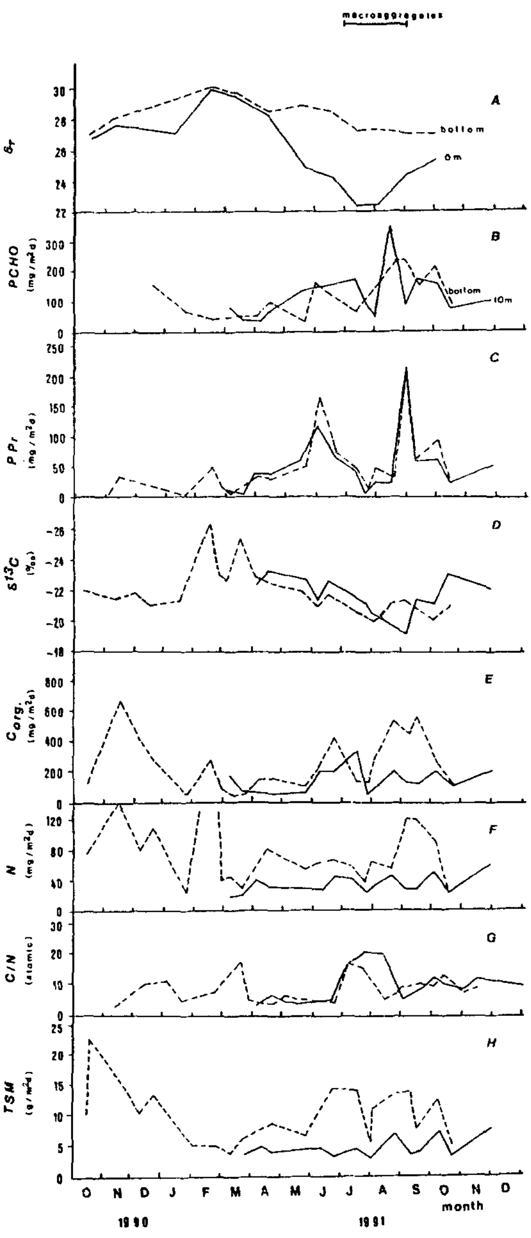

*Fig. 4.* Variations of density (A) in surface (0 m; solid line) and bottom (20 m; dashed line) layers and sedimentation rates of particulate carbohydrates (B) and particulate proteins (C), $\delta^{13}C$ values of sedimented particulate organic carbon (D) and sedimentation rates of particulate organic carbon (E), total particulate nitrogen (F), their C/N ratis (G) and sedimentation ratios of total suspended matter (H) at a depth of 10 m (solid line) and 20 m (dashed line) at the station F. Horizontal line at the top indicates the occurrence of macroaggregates.

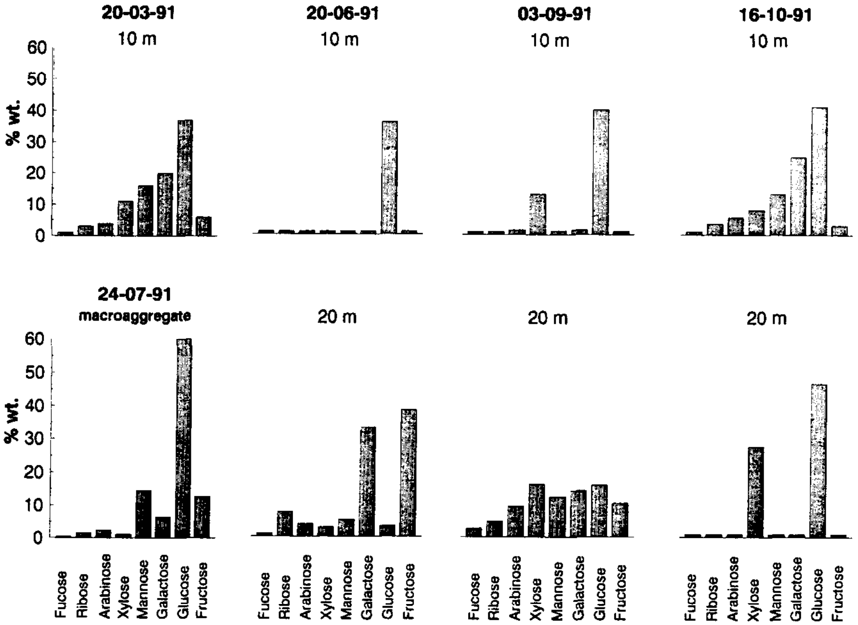

*Fig. 5.* Neutral monosaccharide composition (wt %) of hydrolysates of sedimented matter at the station F.

rates (Haug & Myklestad 1976). It is interesting to note the rather high percentage of fructose in the bottom sedimented POM, suggesting either that fructose is more resistant towards water column degradation or that it is not entirely of phytoplantkonic origin (Mopper et al. 1980).

The particulate protein sedimentation rates from 1991 were similar to those described in the Gulf of Trieste in the period of macroaggregate appearance in summer of 1989, but the total particulate carbohydrate sedimentation rates were about 2-fold higher than the water soluble particulate carbohydrates measured in 1989 (Posedel & Faganeli 1991). Comparison of these particulate protein sedimentation rates with those of particulate amino acids (Faganeli 1989) showed very similar rates, suggesting that the majority of sedimented amino acids was bonded to proteins. Analyzing the relationship between particulate nitrogen (PN) and particulate protein (PPr) sedimentation rates in the present study at the depth of 10 m we found a correlation line in the form PN = 0.276 PPr + 24.25 ($R^2 = 0.79$; $n = 16$) and hence the sedimentation rate of non-protein N of about 24 mg $m^{-2}d^{-1}$. This N could be bonded in humics since a significant correlation ($r^2 = 0.44$; $n = 15$) between PN and particulate humic sedimentation rates was also found. The lack of both correlations at the depth of 20 m was probably due to the resuspension of surficial sediment.

The annual deposition of total suspended matter (TSM), POC and PN at the station F at a depth 20 m amounted to 4033 g $m^{-2}$, 194.4 g $m^{-2}$ and 29.0 g $m^{-2}$, respectively, and was similar to the rates observed in the period 1986–87 at the inner sampling point in the same area apparently not affected by the occurrence of any summer bloom (Faganeli 1989). This would suggest that episodic events have little impact on the yearly budget of C and N in this coastal area. The annual deposition rates at a depth of 10 m were about 43%, 66% and 53% lower, respectively, and amounted to 1727 g $m^{-2}$, 125.0 g $m^{-2}$ and 14.0 g $m^{-2}$.

A comparison of the above annual gross sedimentation rate measured by sediment traps and those estimated from accumulation rate of 1.2 mm $yr^{-1}$, using $Pb^{210}$ geochronology (Faganeli et al. 1991), a dry density of 2.8 g $cm^{-3}$ and an average porosity of 0.8 (Ranke 1976) at the station F revealed up to 30-fold differences at a depths of 20 and 10 m, which are attributed to bottom sediment resuspension. Similar large differences were observed in the comparison of gross sedimentation of organic C and total N with that of the average fluxes determined by the above derived accumulation rate and surficial sediment properties and the organic C and total N contents in surficial sediment (Faganeli et al. 1991). This is due to surficial sediment resuspension and degradation of the sedimented biogenic debris in the water column and at the sediment-water interface.

It is also instructive to compare the annual utilization of C and N in phytoplankton production, using the values of primary production in the Gulf of Trieste of about 50 g $m^{-2}$ $yr^{-1}$ (Faganeli et al. 1982) and the C/N Redfield ratio, to that measured by sediment traps. This comparison revealed about 2-fold higher C and N sedimentation rates measured by traps at a depth of 10, and about 3-fold higher rates at a depth of 20 m. Again, these differences should be attributed to bottom sediment resuspension, but of some extent to the impact of allochtonous POM.

The fraction of sedimented POM of allochtonous (terrigenous) origin varied between 0–75% throughout the study period. Low values of terrigenous fraction (0–4%) were observed at both depths in the summer period. This fraction was calculated using the mixing equation of $\delta^{13}C$ values of terrigenous ($C_t$) and marine ($C_m$) organic matter in the Gulf in the form (Fontugne 1983):

$$\delta^{13}C = F_t\delta^{13}C_t + F_m\delta^{13}C_m \text{ and } F_t + F_m = 1.$$

$F_t$ and $F_m$ are the percentages of terrigenous and marine organic matter. For $\delta^{13}C_t$ and $\delta^{13}C_m$ the mean values of terrigenous (−28.0‰) and marine (−21.0‰) POM in the gulf were used (Faganeli et al. 1988).

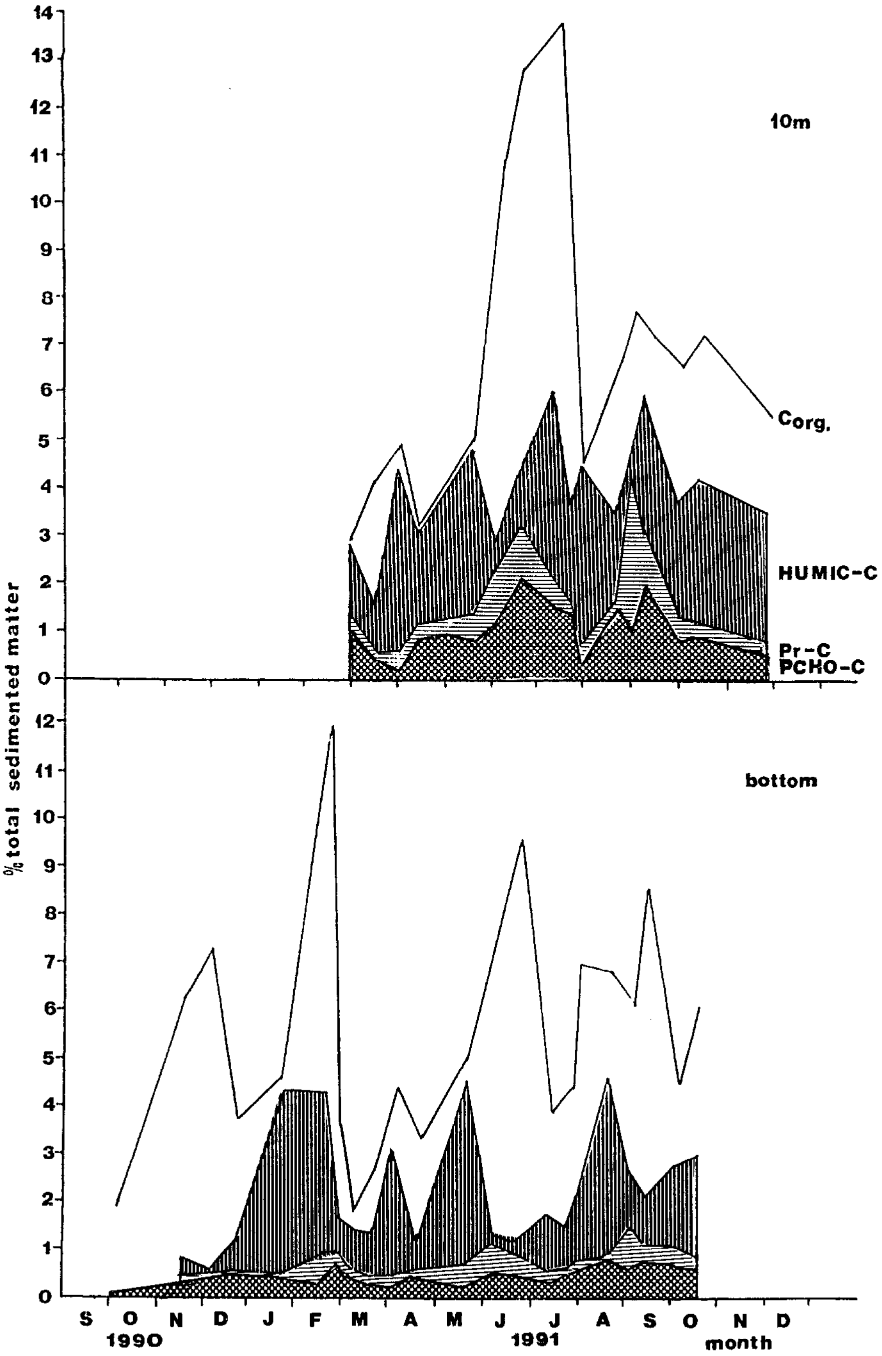

*Fig. 6.* Variations of composition of sedimented matter in terms of organic carbon ($C_{org.}$), humic-C, protein-C (Pr-C) and carbohydrate-C (PCHO-C) at a depth of 10 m and 20 m at the station F.

### *Gross biochemical inventory*

The highest percentages of carbohydrates (3–5%) and proteins (2.2–7%) in total sedimented matter at a depth of 10 m were found in the summertime during the presence of macroaggregates (Fig. 6). The percentage of both constituents in the bottom layer (20 m) were lower, represented respectively between 1.6–2% and 1.1–1.4% of sedimented matter due to the slow sedimentation and degradation of macroaggregates in the summer stratified water column. The presence of macroaggregates was also reflected in the high organic C content (12–14%) and high C/N ratio of total sedimented matter at 10 m in the summer period.

The percentages of total sedimented matter from the sediment trap data represented by organic C and total N at the depth of 10 m averaged 6.6 and 0.77%, respectively, over the year. The percentages at a depth of 20 m averaged 5.2 and 0.76%, respectively. Humics were the major measured form of total sedimented matter and decreased from 4.9 at a depth of 10 m to 2.4% at a depth of 20 m. Polysaccharides represented 2.5% and 1.2%, and proteins 1.3% and 0.6%, respectively. These combined biochemical components at the depth of 10 m represented on average 8.7% and at a depth of 20 m 4.2% of the total sedimented matter. The percentages of total sedimented organic C represented by humics, polysaccharides and proteins were calculated using the approach based on the percentages of C in standards: glucose for carbohydrates (40%), casein for proteins (48%) and humics (55%) isolated from coastal marine sediment. The sum of all three determined constituents comprised on average 6.6% at a depth of 10 m and 4.1% at a depth of 20 m of the sedimented organic C. 38% of carbohydrate-C, 46% of protein-C and 36% of humic-C were lost during sedimentation to the sediment-water interface. These decreasing percentages suggest the utilization of these compounds in degradation processes in the water column, as well as the export of a certain percentages from the Gulf. The latter could be seen from the decrease of humic content between the depths of 10 m and 20 m since the humics are known to be more resistant towards degradation. However, the bottom sediment resuspension should be also taken into consideration since in the summer period of 1989 up to 2/3 of the sedimented particulate matter in the bottom layer was assigned to resuspended particulates in this area (Posedel & Faganeli 1991).

## Conclusions

1. Suspended and sedimented POM was a minor fraction of the total particulate matter in the SE part of the Gulf of Trieste. POM was mostly

composed of humics followed by carbohydrates and proteins and was prevalently of marine origin.

2. Seasonal variations of particulate protein and carbohydrate concentrations were correlated with variations in phytoplankton biomass (from chlorophyll a concentrations). 'New' production occurring in late spring as a consequence of massive riverine inputs of $NO_3$, Si and $PO_4$ in surface layer produced high particulate protein and carbohydrate concentrations. Subsequent depletion of the 'new' nutrients caused the decrease of the particulate protein but not of particulate carbohydrate concentrations. The prolonged plankton biosynthesis of carbohydrates successively produced marine snow and later macroaggregates, representing thus a transition between dissolved and particulate organic matter in the water column.

3. Macroaggregates were characterised by rather high C/N ratio (12, atomic) and $\delta^{13}C$ values of $-19.0‰$, typical for phytoplankton in the Gulf of Trieste, and were mostly composed of low water soluble and acid hydrolysis resistant heteropolysaccharides. The polysaccharides were mostly composed of glucose (approx. 60 wt. %), followed in decreasing order by mannose, fructose, galactose, arabinose, ribose, xylose and fucose, suggesting their prevalent origin from phytoplanktonic cell wall (structural polysaccharides) which are thought to be similar to that of phytoplanktonic mucous.

4. Sedimentation of particulate organic constituents in the summertime, characterised by the presence of macroaggregates above the pycnocline, was the highest at a depth of 10 m at the end of this phenomenon (about six weeks after the first appearance). These downward fluxes were clearly traced by characteristic $\delta^{13}C$ value and carbohydrate content. The monosaccharide composition was influenced by selective degradation in the water column. The sedimentation near the sea bottom was more affected by surficial sediment resuspension.

5. The yearly 40–50% decrease of protein-C and carbohydrate-C between 10 and 20 m indicates the utilization of these constituents in the water column while the decrease of humic-C is probably more the indication of the POM exported from the Gulf. However, the dilution of POM by sediment resuspension especially in the bottom layer should be also taken into consideration.

6. These episodic events appear to have little impact on the annual budget of C and N in such coastal areas.

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