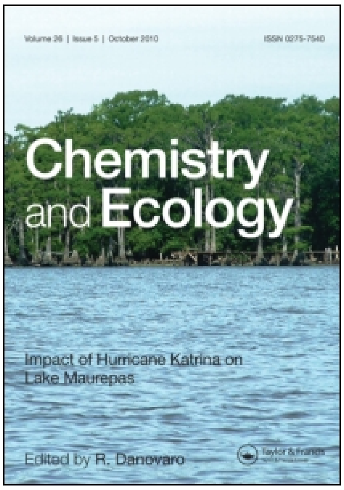

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Particulate organic matter in the Northern and Central Adriatic

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Online publication date: 14 September 2010

To cite this Article Gismondi, M. , Giani, M. , Savelli, F. , Boldrin, A. and Rabitti, S.(2002) 'Particulate organic matter in the Northern and Central Adriatic', Chemistry and Ecology, 18: 1, 27 — 38
To link to this Article: DOI: 10.1080/02757540212692
URL: http://dx.doi.org/10.1080/02757540212692

Chemistry and Ecology, 2002, Vol. 18(1-2), pp. 27–38

PARTICULATE ORGANIC MATTER IN THE NORTHERN AND CENTRAL ADRIATIC

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(Received 1 November 2000)

The particulate organic matter distribution and its elemental composition in the northern and central Adriatic Sea during different seasonal periods are shown, highlighting the principal processes and factors influencing their distribution and characteristics.

In the low salinity waters the concentrations of particulate carbon, nitrogen and phosphorus were higher and more variable than in the dense waters, mainly due to dilution effects which induce an abundant phytoplankton growth.

Generally in summer the particulate organic matter distribution followed the trophic gradient while in winter resuspension events often became more important. Differences between summer and winter were more evident in the diluted waters and were mainly due to the seasonal heat exchanges and to the fresh water inputs.

Marked differences in C/P ratios were observed in the POM: high ratios in the northern diluted waters and low in the more saline waters and in the central Adriatic.

Keywords: Particulate organic matter; POC; PON; Adriatic Sea

INTRODUCTION

The circulation of the western coastal waters of the Adriatic Sea is strongly influenced by the fresh water outflow of the Po River which spreads in the surface layer forming a plume separated from the Adriatic waters by frontal surfaces (Grancini and Cescon, 1973). Generally during the summer, the plume is well developed toward the centre of the basin while in winter, it is confined to the western coast (Orlic, 1989) and a southward transport prevails.

In the northern Adriatic the concentrations of particulate organic carbon (POC) and nitrogen (PN) are related to the effects of the Po River outflow, and the concentrations in the surface waters are directly proportional to the phytoplankton crop (Gilmartin and Revelante, 1991). The presence of a vertical and horizontal density gradient due to

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ISSN 0275-7540 print; ISSN 1029-0370 online
DOI: 10.1080/0275754021000001934

riverine input and seasonal cycle, with development of frontal systems in the northern and central Adriatic (Franco and Michelato, 1992) heavily influence the suspended matter distribution. Concentration gradients of POC, increasing from the Istrian peninsula to the Po River delta, have been observed, particularly in the surface microlayer (Marty *et al.*, 1988). More recent works point out marked POC and PN gradients increasing towards the western coastal waters, where the concentrations referred to water volume can be up to 60–70% higher than in the offshore waters (Giani *et al.*, 2000).

According to the limited information available (Giani *et al*, 2000), the distribution of the total particulate phosphorus (TPP) seems to follow the same trend as POC and PN, with offshore values reaching 10% of coastal concentrations.

The aim of this work is to improve the knowledge of the distribution pattern and the composition of suspended matter in the northern and central Adriatic along the dilution gradients trying to delineate the main processes taking place in these discontinuity zones.

MATERIAL AND METHODS

In the framework of the PRISMA II Project four cruises were carried out in June, 1996, February, 1997, June, 1997 and February, 1998, (identified as BC1, BC2, BC3 and BC4), in two areas of the Adriatic Sea: a northern one, off the Po delta, and a central one, along the coast between Pesaro and Ancona. In each area, samplings and measurements were performed along 2–4 transects (Fig. 1). Conductibility and temperature were measured by a Seabird CTD mod. SB9 and fluorescence by a Seatech fluorometer. Water samples were prefiltered on a 200 μm nylon net and filtered through 25 mm GF/F Whatman filters for particulate organic carbon and nitrogen determinations and through 47 mm GF/F filters for total particulate phosphorus analysis. Organic carbon and nitrogen were determined by a Perkin Elmer 2400 CHN analyser after exposure to hydrochloric acid fumes (Hedges and Stern, 1984) and total phosphorus was determined by a Spectro Modula ICP - AES after combustion at 550°C for 4 h and extraction with 1N hydrochloric acid for 16 h (Aspila, 1976). Total suspended matter (TSM) was determined by gravimetry on preweighted 25 mm GF/F filters, after drying for 4 h at 60°C. The determination of each parameter was carried out on 616 samples: 264 relative to the central area and 352 relative to the northern one. POC, PN and TPP are expressed as concentrations referrred to the water volume (μM or $\mu mol\, dm^{-3}$) and as contents referred to the mass (%). Salinity is expressed according to the Practical Salinity Scale (PPS 78).

In the two investigated areas the water masses have been divided in different classes according to their salinity as shown in Table I.

RESULTS

Northern Adriatic Area

The vertical and horizontal stratification of the water column, with a strong contribution of riverine waters in the superficial layers, was present during the cruises (Fig.

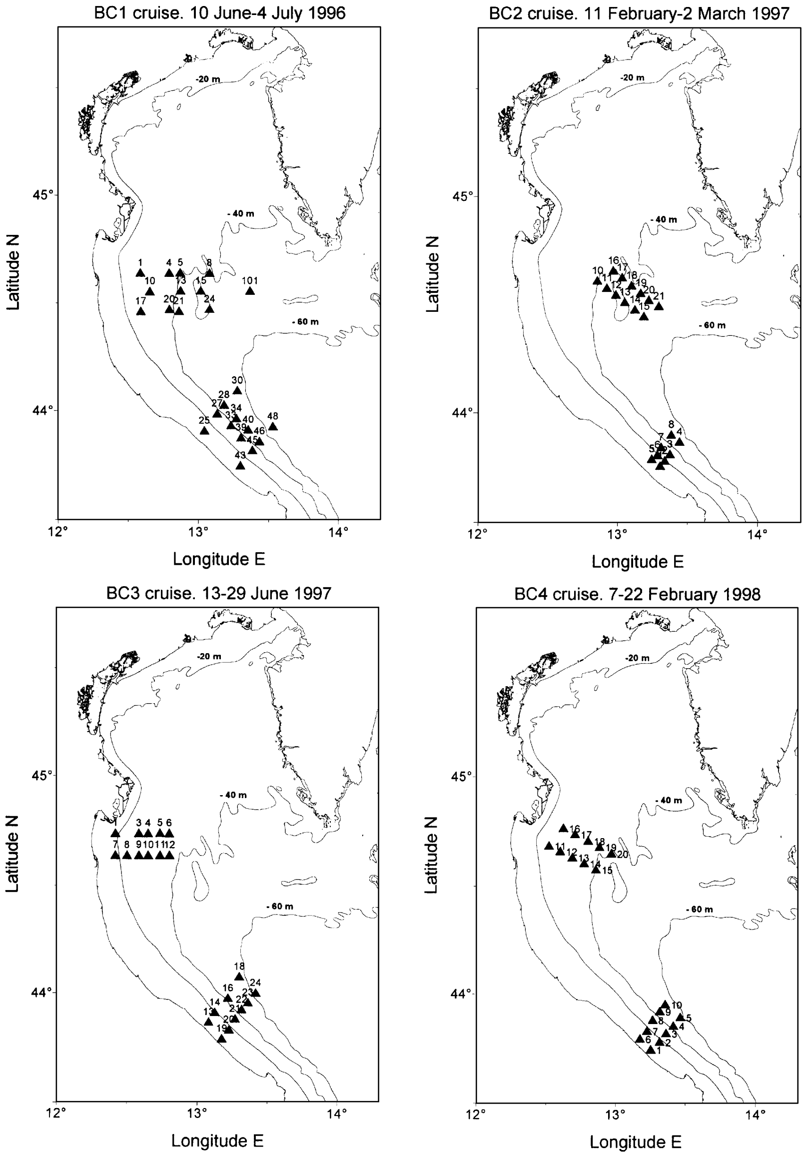

FIGURE 1 Station location and sampling sites.

2) and determined a corresponding gradient in the particulate matter content. The dilution effect influenced the coastal stations and the density structure of the water masses was characterised by a horizontal gradient, determining a surface frontal system well evident in June, 1997 and February, 1998. Generally, in all the four cruises a horizontal gradient of POC, PN and TPP concentrations, decreasing seaward, was observed.

Average concentrations of total suspended matter, particulate organic carbon, nitrogen and phosphorus, relative to the two salinity classes considered, are reported in the Table II. Low/intermediate salinity waters always showed higher concentrations of all the parameters with the exception of TSM. The highest concentrations of POC, PN

TABLE I Mean values and standard deviations of salinity and temperature in the two sampling areas for the different salinity classes

	Low/Intermediate salinity			*High salinity*		
		S	*T (°C)*		*S*	*T (°C)*
			Northern Adriatic area			
June '96	S ≤ 37.50	35.79 ± 1.09	22.54 ± 1.48	S > 37.50	37.85 ± 0.15	15.30 ± 4.56
February '97	S ≤ 37.50	36.28 ± 1.66	10.16 ± 0.42	S > 37.50	37.67 ± 0.16	11.06 ± 0.40
June '97	S ≤ 36.50	34.63 ± 2.62	20.54 ± 3.28	S > 36.50	37.00 ± 0.30	14.57 ± 2.72
February '98	S ≤ 37.50	36.01 ± 1.63	9.04 ± 0.35	S > 37.50	37.94 ± 0.17	10.60 ± 0.51
			Central Adriatic area			
June '96	S ≤ 37.50	36.68 ± 0.72	19.47 ± 1.97	S > 37.50	37.80 ± 0.19	14.54 ± 3.28
February '97	S ≤ 37.50	35.52 ± 1.79	9.62 ± 0.94	S > 37.50	37.84 ± 0.13	11.42 ± 0.33
June '97	S ≤ 37.50	36.64 ± 0.53	20.22 ± 1.87	S > 37.50	37.78 ± 0.14	14.10 ± 2.48
February '98	S ≤ 38.00	35.84 ± 1.64	8.42 ± 1.19	S > 38.00	38.38 ± 0.16	11.51 ± 0.60

and TPP have been observed in June, 1997 (24.8 ± 25.5 μM, 3.3 ± 3.3 μM and 0.098 ± 0.094 μM) when a wide area was involved in superficial dilution, and probably an increase of the phytoplankton biomass took place. The organic carbon content in the particulate matter was highest in June (36.1–41.5%), in the less saline waters, whereas in the high salinity waters of the February cruises, the organic carbon contents were the lowest (6.6–9.2%).

Near the bottom an increase of suspended matter with relatively high values of POC, PN and TPP, was observed in all the examined situations. In February, this high concentrations were presumably due to resuspension events, as fluorescence did not increase, while in June the fluorescence increased at the bottom layer, showing a possible presence of biological activity also in the deeper part of the water column.

Central Adriatic Area

During, the February, 1997, and higher in the February, 1998 cruises, the water mass structure was mainly influenced by the presence of a vertical front (Fig. 3) dividing the coastal waters, less dense and rich in particulate organic matter, from the dense offshore waters characterised by low TSM, POC, PN and TPP concentrations (Tab. II). During these cruises a marked horizontal gradient of concentration was present in the inshore side of the front, while in the offshore side the values ranged in a more restricted interval and the water column was quite homogeneous.

The highest concentrations of POC, PN, TPP and TSM were recorded in February (POC: 25.4–38.4 μM; PN: 3.9–4.8 μM; TPP: 0.106–0.207 μM; TSM: 2.96–9.15 mg/l in the low/intermediate salinity waters), when a southward transport of particles takes place in the coastal belt. The highest organic carbon and nitrogen contents were observed in June, pointing out a relevant contribution of the phytoplankton biomass during the summer period.

In June, 1997 the particulate organic matter distribution reflected mainly that of the phytoplankton biomass; high concentrations of TPP, POC and PN were observed in the more coastal stations and in the bottom waters (Fig. 3), where high values of TSM

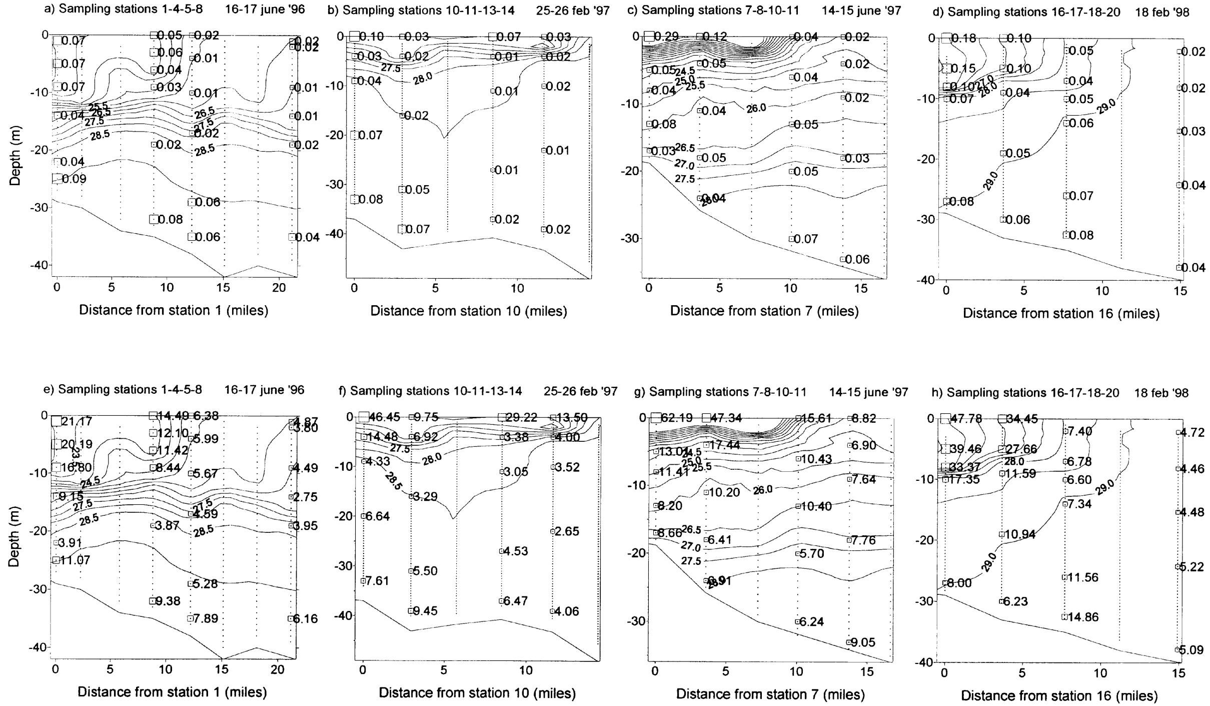

FIGURE 2. Concentrations (μmol dm^{-3}) of total particulate phosphorus (a, b, c, d) and particulate organic carbon (e, f, g, h) in the northern area. Isopleths represent density anomaly (kg m^{-3}).

TABLE II Average concentrations and standard deviations of total suspended matter (TSM), particulate organic carbon (POC), particulate nitrogen (PN) and total particulate phosphorus (TPP) in low/intermediate and in high salinity waters of the northern Adriatic and of the central Adriatic Sea

	TSM (mg/l)	*POC/TSM (%)*	*PN/TSM (%)*	*POC (μM)*	*PN (μM)*	*TPP (μM)*
			Northern Adriatic			
Low and intermediate salinity waters						
June '96	0.34 ± 0.18	41.5 ± 13.8	6.4 ± 2.3	11.2 ± 4.9	1.5 ± 0.7	0.042 ± 0.021
February '97	0.73 ± 0.54	16.3 ± 8.6	2.7 ± 1.3	9.7 ± 9.3	1.4 ± 1.3	0.030 ± 0.020
June '97	1.11 ± 1.28	36.1 ± 22.7	5.7 ± 3.7	24.8 ± 25.5	3.3 ± 3.3	0.098 ± 0.094
February '98	1.73 ± 0.77	16.5 ± 6.6	2.8 ± 1.1	24.2 ± 15.7	1.7 ± 0.8	0.077 ± 0.043
High salinity waters						
June '96	0.47 ± 0.72	34.1 ± 20.6	5.1 ± 3.0	4.7 ± 2.3	0.6 ± 0.3	0.029 ± 0.026
February '97	0.92 ± 0.74	9.2 ± 5.1	1.6 ± 0.9	5.1 ± 2.5	0.8 ± 0.3	0.032 ± 0.021
June '97	1.39 ± 2.1	15.8 ± 14.1	2.5 ± 2.1	9.1 ± 2.3	1.3 ± 0.3	0.065 ± 0.035
February '98	1.81 ± 1.56	6.6 ± 4.2	1.2 ± 0.7	6.1 ± 1.8	0.9 ± 0.3	0.047 ± 0.022
			Central Adriatic			
Low and intermediate salinity waters						
June '96	0.42 ± 0.54	20.8 ± 8.7	3.2 ± 1.5	4.7 ± 2.1	0.6 ± 0.3	0.039 ± 0.025
February '97	2.96 ± 1.21	14.7 ± 8.5	2.2 ± 1.2	38.4 ± 30.4	4.8 ± 3.7	0.106 ± 0.049
June '97	1.41 ± 1.42	17.3 ± 9.8	2.9 ± 1.5	10.1 ± 4.6	1.5 ± 0.8	0.054 ± 0.039
February '98	9.15 ± 4.84	3.5 ± 1.1	0.6 ± 0.2	25.4 ± 10.8	3.9 ± 1.9	0.207 ± 0.078
High salinity waters						
June '96	0.80 ± 0.90	15.6 ± 11.2	2.4 ± 1.7	4.9 ± 3.5	0.7 ± 0.5	0.037 ± 0.031
February '97	3.05 ± 2.43	5.1 ± 4.0	0.7 ± 0.5	9.0 ± 5.8	1.1 ± 0.7	0.055 ± 0.036
June '97	1.08 ± 1.05	11.6 ± 7.8	2.0 ± 1.2	6.1 ± 2.1	0.9 ± 0.4	0.036 ± 0.019
February '98	1.65 ± 1.30	5.1 ± 2.7	0.9 ± 0.5	5.3 ± 2.3	0.8 ± 0.4	0.042 ± 0.028

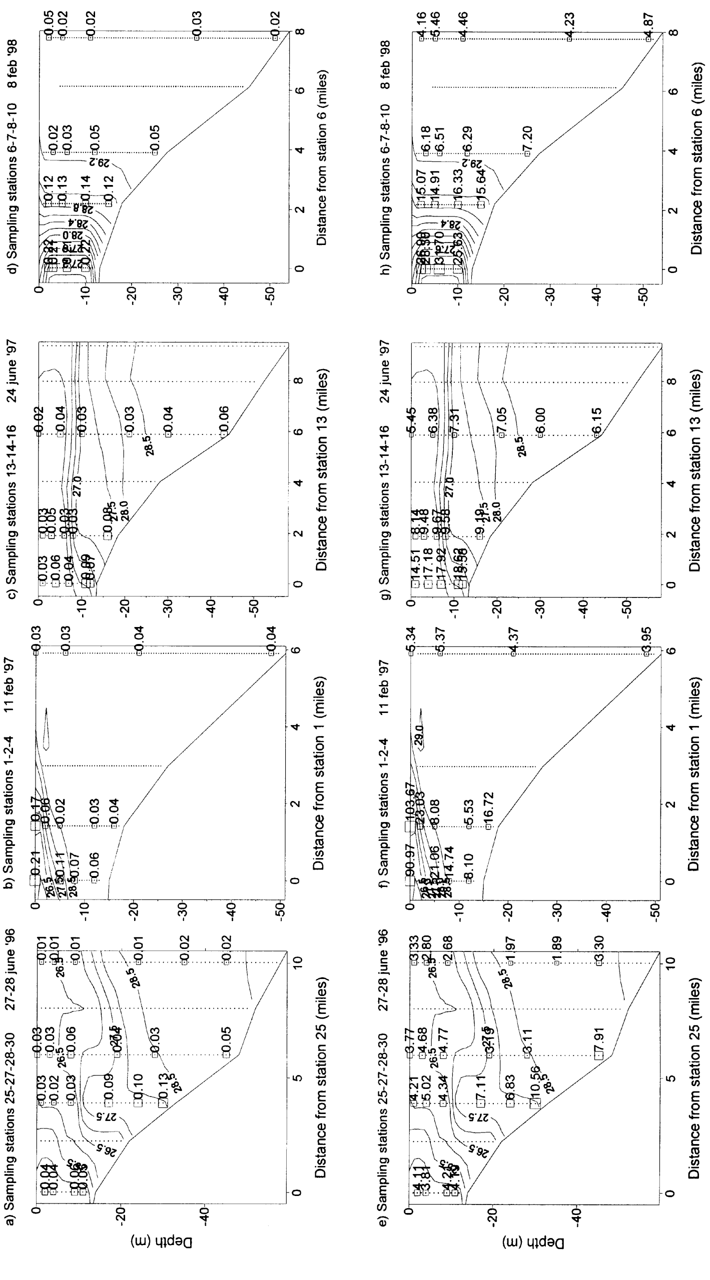

FIGURE 3 Concentrations (μmol dm^{-3}) of total particulate phosphorus (a, b, c, d) and particulate organic carbon (e, f, g, h) in the southern area. Isopleths represent density anomaly (kg m^{-3}).

and fluorescence were recorded. In June, 1996, high concentrations of POC, PN and TPP were observed near the bottom.

DISCUSSION

The variability of hydrological and biological conditions in the Northern Adriatic determines a wide variation in the quantity and quality of the particulate matter. The POC, PN and TPP, expressed with reference to water volume, were low and ranged in a restricted interval in the high salinity waters of both the northern and the central Adriatic, while in the diluted waters the values were higher and more variable. In the low salinity waters of the two areas the TSM distribution was highly influenced by dilution and it showed an inverse correlation with salinity ($p < 0.001$) in both cases. In the high salinity waters of the northern area the TSM distribution showed an inverse correlation with the C/P and N/P ratios probably due to the influence also of re-suspension processes; the high concentrations of POC, PN and TPP recorded in February in these waters, without an increase of the fluorescence, may strengthen this hypothesis. During the June cruises with POC, PN and TPP also fluorescence increased at the bottom showing a possible presence of biological activity also in the deeper part of the water column.

In June, 1997, and February, 1998, diluted waters covered a wide area in the northern Adriatic and the mean concentrations of POC, PN and TPP (POC: 13.1–17.4 μM; PN: 1.9–2.3 μM; TPP: 0.059–0.083 μM) were closer to the values recorded off the Po and the Adige river mouths by Giani *et al.* (2000). Similar concentrations of POC and PN were also reported by Gilmartin and Revelante (1991) for the surface waters of the northern Adriatic. The concentrations of TPP observed during these cruises were higher than those reported by Abdel-Moati (1990) for the southeastern Mediterranean Sea and by Copin-Montegut and Copin-Montegut (1983) for the northwestern Mediterranean Sea. In the other investigated periods (June, 1996 and February, 1997), the area was less interested by dilution and the average concentrations of POC, PN and TPP (7.1–8.3 μM; 0.9–1.2 μM; 0.030–0.034 μM) were in the range of values reported for offshore Adriatic areas (Giani *et al.*, 2000).

In the central Adriatic a difference between the two winter periods was observed: during the February, 1997, the organic carbon content in the diluted waters was high and inversely correlated with the salinity ($r = -0.72$; $p < 0.001$) pointing out a probable contribution of biological activity in determining the TSM distribution and characteristics; in February, 1998, there was no correlation between the two parameters due to a greater influence of resuspension events.

Both in the northern and in the central Adriatic Sea the concentrations of particulate organic carbon, total nitrogen and total phosphorus were significantly correlated with each other (Tab. III). From the elemental ratios of suspended matter the principal processes influencing the origin of suspended matter can be suggested.

In the northern Adriatic the low C/P and N/P ratios in the high salinity bottom waters were probably related to the resuspension of bottom sediments, relatively rich in phosphorus with respect to organic carbon and nitrogen. In the diluted and generally highly productive waters the high C/P ratios could be due to particles depleted in

TABLE III Linear regression equations correlation coefficients and significance levels in the different salinity classes

	Northern Adriatic				Central Adriatic			
Low and intermediate salinity waters								
	POC = 0.62 + 7.16 PN	$r = 0.981$	$p < 0.001$	$n = 26$	POC = 0.23 + 7.32 PN	$r = 0.958$	$p < 0.001$	$n = 42$
June '96	POC = 2.29 + 209.27 TPP	$r = 0.923$	$p < 0.001$	$n = 23$	POC = 2.45 + 58.62 TPP	$r = 0.725$	$p < 0.001$	$n = 42$
	PN = 0.24 + 28.57 TPP	$r = 0.915$	$p < 0.001$	$n = 23$	PN = 0.32 + 7.69 TPP	$r = 0.727$	$p < 0.001$	$n = 42$
	POC = − 0.33 + 7.36 PN	$r = 0.995$	$p < 0.001$	$n = 59$	POC = − 0.67 + 8.11 PN	$r = 0.992$	$p < 0.001$	$n = 22$
February '97	POC = − 0.96 + 361.30 TPP	$r = 0.761$	$p < 0.001$	$n = 59$	POC = − 20.80 + 558.80 TPP	$r = 0.894$	$p < 0.001$	$n = 22$
	PN = − 0.12 + 50.32 TPP	$r = 0.784$	$p < 0.001$	$n = 59$	PN = − 2.68 + 70.79 TPP	$r = 0.925$	$p < 0.001$	$n = 22$
	POC = − 0.81 + 7.77 PN	$r = 0.998$	$p < 0.001$	$n = 43$	POC = 1.26 + 5.70 PN	$r = 0.948$	$p < 0.001$	$n = 50$
June '97	POC = 0.19 + 250.34 TPP	$r = 0.927$	$p < 0.001$	$n = 43$	POC = 5.26 + 89.42 TPP	$r = 0.765$	$p < 0.001$	$n = 50$
	PN = 0.14 + 32.13 TPP	$r = 0.925$	$p < 0.001$	$n = 43$	PN = 0.64 + 16.86 TPP	$r = 0.866$	$p < 0.001$	$n = 50$
	POC = − 0.64 + 7.11 PN	$r = 0.988$	$p < 0.001$	$n = 33$	POC = 6.60 + 4.81 PN	$r = 0.834$	$p < 0.001$	$n = 26$
February '98	POC = 0.38 + 307.71 TPP	$r = 0.854$	$p < 0.001$	$n = 33$	POC = − 0.06 + 122.75 TPP	$r = 0.885$	$p < 0.001$	$n = 26$
	PN = 0.08 + 44.06 TPP	$r = 0.880$	$p < 0.001$	$n = 33$	PN = − 0.57 + 21.96 TPP	$r = 0.898$	$p < 0.001$	$n = 26$
High salinity waters								
	POC = 0.28 + 7.19 PN	$r = 0.958$	$p < 0.001$	$n = 44$	POC = − 0.01 + 7.44 PN	$r = 0.981$	$p < 0.001$	$n = 26$
June '96	POC = 2.47 + 74.95 TPP	$r = 0.876$	$p < 0.001$	$n = 42$	POC = 1.69 + 85.99 TPP	$r = 0.754$	$p < 0.001$	$n = 25$
	PN = 0.30 + 10.42 TPP	$r = 0.904$	$p < 0.001$	$n = 42$	PN = 0.20 + 12.24 TPP	$r = 0.815$	$p < 0.001$	$n = 25$
	POC = − 0.43 + 7.13 PN	$r = 0.988$	$p < 0.001$	$n = 27$	POC = − 0.37 + 8.33 PN	$r = 0.953$	$p < 0.001$	$n = 30$
February '97	POC = 2.67 + 76.78 TPP	$r = 0.662$	$p < 0.001$	$n = 27$	POC = 5.23 + 69.97 TPP	$r = 0.427$	$p = 0.029$	$n = 30$
	PN = 0.42 + 11.27 TPP	$r = 0.701$	$p < 0.001$	$n = 27$	PN = 0.68 + 8.34 TPP	$r = 0.445$	$p = 0.022$	$n = 30$
	POC = − 0.60 + 7.66 PN	$r = 0.945$	$p < 0.001$	$n = 38$	POC = 1.38 + 5.13 PN	$r = 0.949$	$p < 0.001$	$n = 23$
June '97	POC = 6.34 + 42.69 TPP	$r = 0.651$	$p < 0.001$	$n = 38$	POC = 2.94 + 86.06 TPP	$r = 0.753$	$p < 0.001$	$n = 23$
	PN = 0.90 + 5.59 TPP	$r = 0.692$	$p < 0.001$	$n = 38$	PN = 0.31 + 16.65 TPP	$r = 0.787$	$p < 0.001$	$n = 23$
	POC = 0.63 + 5.88 PN	$r = 0.878$	$p < 0.001$	$n = 52$	POC = 1.07 + 5.35 PN	$r = 0.826$	$p < 0.001$	$n = 44$
February '98	POC = 4.12 + 42.84 TPP	$r = 0.518$	$p < 0.001$	$n = 52$	POC = 2.45 + 67.80 TPP	$r = 0.813$	$p < 0.001$	$n = 44$
	PN = 0.66 + 5.86 TPP	$r = 0.475$	$p < 0.001$	$n = 52$	PN = 0.35 + 10.42 TPP	$r = 0.809$	$p < 0.001$	$n = 44$

phosphorus by the bacteria. High phosphatase activities, in comparison to glucosidase and protease activities, were in fact reported for some areas of the northern Adriatic, including the Po mouth, pointing out a more efficient solubilization of phosphorous with respect to carbon and nitrogen (Azam *et al.*, 1999). The contribution of marine aggregates to the total particulate matter is not well known, especially during winter periods, but it may be hypothesised that gel-like degraded substrate can affect the total suspended matter C/P ratio. Another hypothesis is that the organic matter synthesised in a phosphorus depleted environment may have a C/P atomic ratio higher than that proposed by Redfield *et al.* (1963). High C/P and N/P ratios have already been reported for the offshore northern Adriatic waters (Giani *et al.*, 2000).

In the diluted waters of the central Adriatic, the C/P and N/P ratios were very high only in February, 1997, while in the other cruises the C/P values were similar or lower than the Redfield ratios (Redfield *et al.*, 1963). In the high salinity waters the C/P and N/P obtained from the regression equations ranged in restricted intervals (67.8–86.1; 8.3–16.7).

In the two areas, when low C/P ratios were recorded, the residual organic carbon (organic carbon concentration correspondent to the intercept of the POC *vs* TPP regression line) amounted to 34–70% of the mean POC concentration, whereas low residual carbon was associated with high C/P values. These differences may be due to different degradation efficiency of the organic matter by bacteria; high C/P values and low residues were in fact recorded when the aminopeptidase activity was high (Zaccone *et al.*, 1999). Residual organic carbon represents a refractory detritus, probably constituted by carbohydrates, lipids or phosphorus depleted substrates (Copin-Montegut and Copin-Montegut, 1983).

Comparing the C/P and N/P ratios with those reported for the western Mediterranean Sea (Copin Montegut and Copin Montegut, 1983) our ratios are higher in the diluted waters of the northern area, more similar in the diluted waters of the central area, and lower in the high salinity waters. In addition to the values found in the framework of the previous PRISMA 1 Project (Giani *et al.*, 2000), other reported C/P ratios for the Adriatic Sea concern only the Gulf of Trieste (Faganeli *et al.*, 1988). All these ratios fall in the lowest range of our results.

Differences between the winter and the summer periods are pointed out by the discriminant analysis (Fig. 4) and are mainly due to the seasonal heat exchanges and to the fresh water inputs. Differences between the winter and the summer period are much more marked, both in the northern and in the central area, in the low salinity waters than in the high salinity ones.

CONCLUSIONS

In the northern Adriatic the distribution of particulate organic matter is primarily determined by the fresh water input. High organic matter contents are associated to the high phytoplankton biomass production in the diluted waters during summer, whereas in winter the decrease of solar radiation and the enhancement of resuspension processes lead to a decrease of the organic fraction.

In the central Adriatic during winter, the coastal waters, rich in TSM and POM, are separated from the open waters by a frontal system, while in summer, the particulate

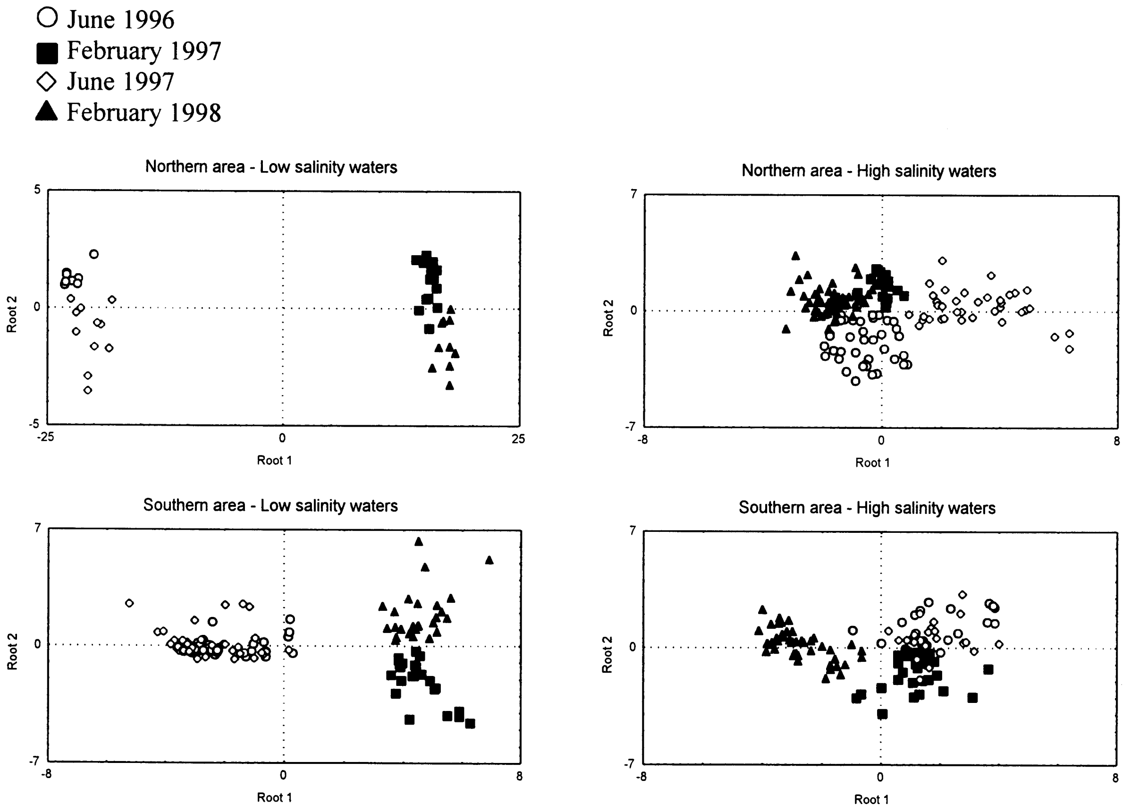

FIGURE 4 Discriminant analysis of the data sets including temperature, salinity, TSM, POC, PN and TPP.

matter distribution is more linked to the fresh water stratification. Generally during winter the storm driven resuspension events decrease the organic carbon content in the particulate matter, but an exception was observed in the diluted waters of February, 1997, when there was a high phytoplankton biomass.

The C/P and N/P ratios point out a contribution of resuspension of bottom sediments above all in the dense waters of both the areas since low values were recorded; high C/P ratios in the diluted waters of the northern area were probably linked to the fraction of POM which has undergone bacterial phosphorus depletion.

Acknowledgements

This work was supported by the Italian Ministry of University and Scientific and Technological Research (MURST) and the National Research Council (CNR) in the framework of the PRISMA II – Biogeochemical Cycles Research Project.

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