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Particulate Organic Matter Contribution of Gediz River to the Aegean Sea

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Abstract

Seasonal behaviour of Gediz River, as a source of particulate matter have been evaluated, by tracing the concentration of suspended solids and ultimate loads across salinity gradients in Izmir Bay. Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON), Total Particulate Phosphate (TPP), phytoplankton abundance, Suspended Particulate Matter (SPM), Particle Sizes (PS), and salinity were measured in and around the river mouth. Sorptive fractionation of nitrogen rich organic material into particles occured in the river mouth during maximum flushing period where POC:PON ratio was <1. Principal Component Analysis (PCA) indicated that the first component was PON, SPM and PS of 2-5 µm, 5-10 µm, 10-20 µm related to 59% of variance, the second component was density, POC and TPP related to 17% of variance and finally 13% of variance was related to DO as the third component. PCA demonstrated that the density, among all other parameters, played the most prominent role in their variations. As a conclusion, the river mouth usually seems to be acting as a trap rather than a source for the particles carried by the river with exceptions occurring during extreme levels of flux when the river acts as a hot spot.

Keywords: Estuarine dynamic, suspended particulate matter, particulate organic carbon, particulate organic nitrogen, Gediz River, Aegean Sea.

Gediz Nehri'nin Ege Denizi'ne olan Partikül Organik Madde Katkısı

Özet

Gediz Nehri'nin partikül madde kaynağı olarak mevsimsel davranışı, İzmir Körfezi'nde yarattığı tuzluluk gradientleri içerisindeki askıda katı madde konsantrasyonlarındaki ve azami yükler değerlerindeki değişimler izlenerek değerlendirilmiştir. Partikül Organik Karbon (POC), Partikül Organik Azot (PON), Toplam Partikül Fosfat (TPP), fitoplankton bolluğu, Askıda Katı Madde (SPM), Partikül Boyutu (PS), Çözünmüş Oksijen (DO) ve tuzluluk nehir ağzının içinde ve dışında ölçülmüştür. Partikül içeriğinde azotça zengin organik materyalin sorptiv fraksiyonlarının oluşumu, POC:PON<1 düzeyiyle, nehir ağzında maksimum kabarma zamanında gözlenmiştir. Temel Bileşenler Analizi (PCA) sonucu, birinci bileşen varyansın %59'unu temsil ederken, bu varyansın PON, SPM ile 2-5 µm, 5-10 µm, ve 10-20 µm boyut sınıflarına ait PS ile ilişkili olduğunu, ikinci bileşenin varyansın %17'sini temsil eder. Bu varyansında POC ve TPP ile ilişkili olduğunu ve nihayet üçüncü bileşenin varyansın %13'ünü temsil ederken, bu varyansında sadece DO ile ilişkili olduğunu göstermiştir. PCA tüm parametreler arasında, yoğunluk değerlerinin varyasyon oluşumunda en belirleyici rolü oynadığını da ayrıca göstermiştir. Sonuç olarak, nehir ağzının, aşırı debi düzeyine ulaştığı ve sıcak nokta rolü oynadığı özel şartlar dışında, nehir tarafından taşınan partiküller için bir kaynak rolü oynamaktan çok, genelde kapan rolü oynadığı görülmektedir.

Anahtar Kelimeler: Nehir dinamiği, askıda partikül madde, partikül organik karbon, partikül organik nitrojen, Gediz Nehri, Ege Denizi.

Introduction

One of the least understood phenomena in river plumes is how the freshwater discharge mixes with ambient coastal waters with respect to biogeochemical processes (Boicourt *et al*., 1998). Nutrients, as well as the species composition and detention time of phytoplankton and zooplankton entrained into the plume zone, depend on the state of coastal processes at the time of entrainment. Suspended particles (SPM), either they are allochthonous or autochthonous, comprise sediment and seston which are suspended in the water column, either permanently or temporarily in a state of exchange with the bed sediment reservoir (Turner and Millward, 2002). In general, SPM affect coastal environments adversely playing a critical role in some of the long-term coastal problems like shoaling and increasing oxygen demand due to the decomposition of organic content. Hydrophobic organic micropollutants and heavy metals adsorb onto surfaces of fine-grained sediment particles and move with the sediments so that they are transferred from land to marine environments (Hong *et al*., 1999; Turner and Millward, 2002; Suzumura *et al*., 2004). The major components of estuarine SPM are particulate organic (POM) and inorganic matters (PIM). PIM includes clay minerals and insoluble salts, whereas POM is likely composed of complex matrix of terrigenous organic matter, living cells of planktonic microorganisms and autochthonous organic debris including nonliving microorganisms (Suzumura *et al*., 2004). The flux of sediment through estuaries, in suspension or as bed load, varies greatly (Eisma and Cadee, 1991), although the bed load in most rivers does not reach the estuary but is deposited in the lower reaches of the river. Therefore, understanding the nature and behavior of SPM in the mouth of the river, in other words in the plume zone, can reveal whether this zone acts as a "*source*" or a "*trap*" for these particles.

The plume zones have very dynamic properties both physicochemically and biologically. Active processes occur between dissolved and particulate matters, as well as among organisms through site and/or time specific salinity gradients. Changes in salinity affect the organic carbon distribution via processes altering the forms such as the dissolved organic carbon by coagulation and adsorption/ desorption properties of particles (Fox, 1983; Ogura *et al*., 1983). Particularly, sorption reactions between dissolved and particulate matters may regulate the nutrient availability and associated biological productivity in an estuarine environment.

Gediz River Basin is located in western Anatolia, the Aegean region of Turkey, extending from 38°56′ N-29°42′ E to 38°30′ N-26°55′ E and Gediz River, has a length of about 275 km, drains an area of 17,700 km^2 and discharges to the Izmir Bay (Figure 1). The River is heavily polluted due to agricultural drainage waters, industrial and domestic wastewaters coming from the catchment area, that mass fish mortalities have been reported since 1989. The impact level of the pollution caused by the River can be perceived with some mass fish mortalities which were expressed by tonnes of mass in the records (Erdur, 1990) as well as with the area about 12 km^2 covered by fish carcasses at the river mouth (reported in local press: Yeni Asir, 5 Dec 2004). The qualitative diversification and quantitative fluctuations of agricultural pollutants carried by the River have also increased due to intense agricultural activities (Esen and Uslu, 2008).

It is well documented that the loads originated from Izmir metropolitan area and Gediz River are the two major pollution sources for Izmir Bay (Aksu *et al*., 1998; Murathan, 1999; Uslu, 2001; Batki, 2002; Gundogdu *et al*., 2005). Izmir Metropolitan Waste Water Treatment Plant has been started up in 2000 and the contribution of the Gediz River as a pollution source for the Bay is expected to become more prominent. On the basis of the recent scientific findings (Batki, 2002; Gundogdu *et al*., 2005), the freshwater and sediment transfer by the River has a potential to constitute an important physical forcing in the Bay, which may radically modify the levels of nutrients (P, N, Si and Organic Carbon) and some heavy metals (Cd, Co, Mn, Ni, Cu, Zn, Fe, etc.), phytoplankton composition and light transmission conditions of the Bay's marine environment. In the previous studies, the measurements were only carried out in the Gediz River's water and all focused on some certain pollutants (Sunar and Ersan, 1989; Bayar and Oguz, 1990; Erdur, 1990; Balık and Ustaoğlu, 1991; Okur *et al*., 1997; Batki, 2002). Thus, the changes in the particulate matters along the salinity gradient were taken into consideration for the first time within this study.

The aim of this study, is to investigate the transportation of particles from the river mouth with

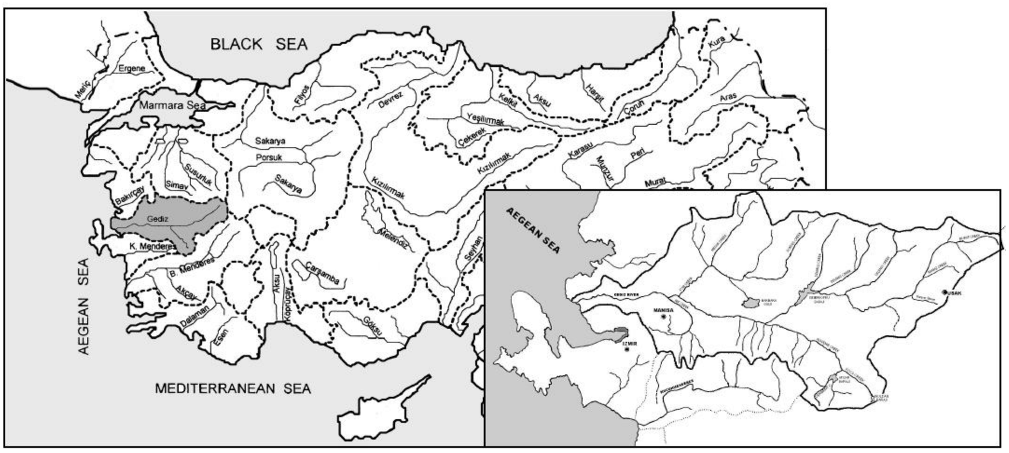

Figure 1. Location of the Gediz Basin (Usul, 2001).

respect to the particle size distribution and the biogeochemical mechanisms determining the composition of particulate matters in the interaction zone, *i.e.* river plume, between Gediz River and Izmir Bay, through the salinity gradient in order to be able to put forth in consideration whether this zone acts as a source or a trap and to discuss on the possible explanatory patterns of any of these two actions.

Materials and Methods

Study Area

The study area covered the Gediz River's mouth and its surroundings bordered by the end of the surface salinity gradient. There were 9 stations, of which one is in the river, *i.e.*, 50 m inward from the river mouth, six over the river plume and two at the adjacent offshore as the reference stations. The study area were divided into four zones (Figure 2); The Freshwater Zone (FZ; river mouth, also referred as Gediz Zone), the Plume Zone 1 (PZ1; Stations 11D, 11E and 11F), the Plume Zone 2 (PZ2; Stations 11 A, 11B and 11C) and the Reference Zone (RZ; Stations 11 and 11X).

The station locations were determined via YSI 556 Multiprobe system by tracing the salinity gradients. However, the station locations within the range of the zones were shifted as an obligation due to the shallowness (1 m or less) and site-specific rapid spatio-temporal alterations in the bathymetric patterns of the area, as illustrated in Figure 2. The distances between stations were kept as constant as possible within the tracks of observed salinity gradients; i.e. approximately 0.40 km for the PZ1 and 0.2 km for the PZ2 along the transects between stations that define each zone. The distance between the reference stations and the river mouth was about 5.5 km.

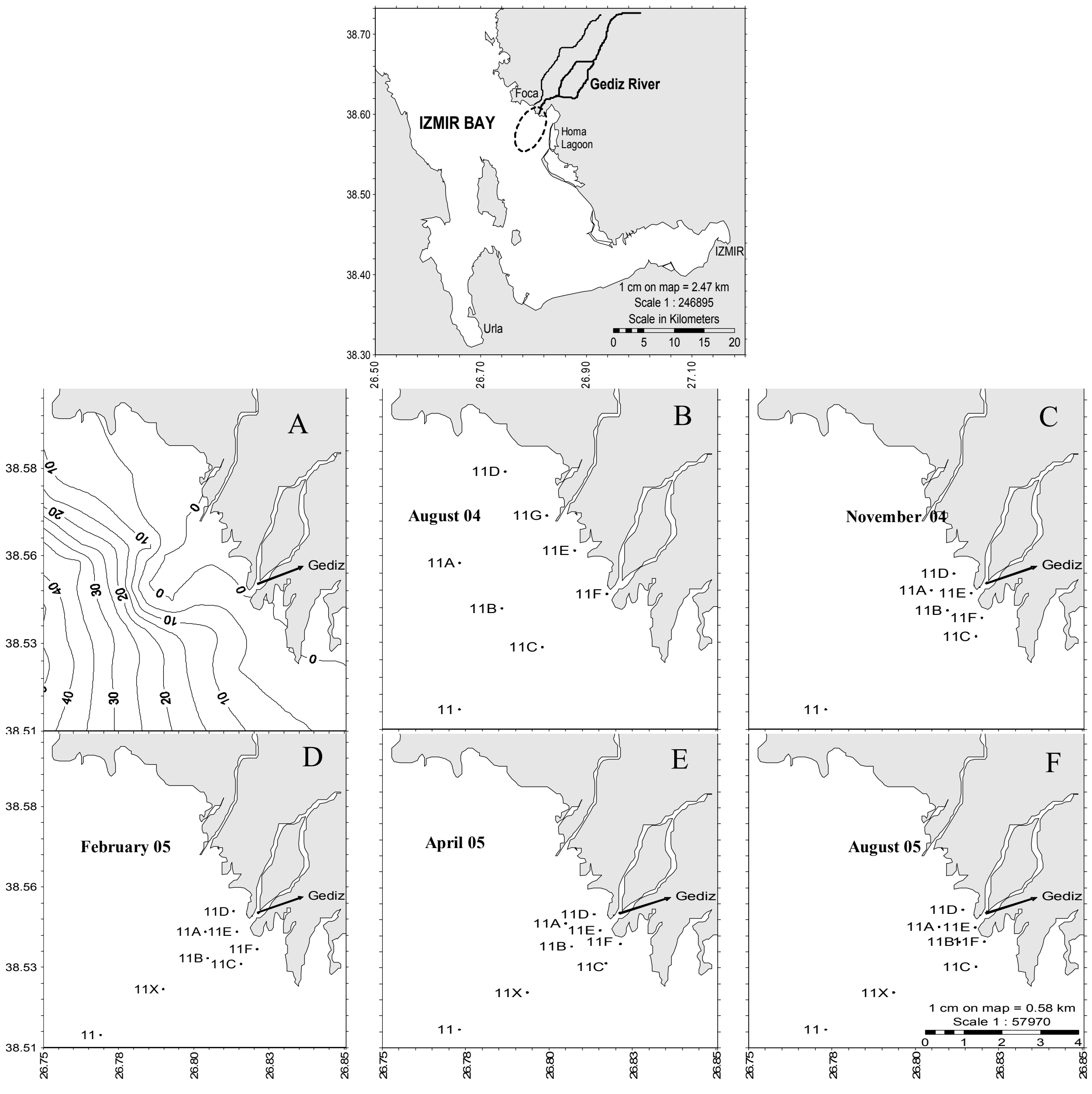

Figure 2. Maps of sampling stations in the study area for each sampling period.

Analyses

The sampling were carried out seasonally by the research vessel R/V K. Piri Reis and a small shuttle boat, in August 2004, November 2004, February 2005, April 2005 and August 2005. The physical parameters such as temperature, salinity and density were measured by YSI 556 probe at the shallow stations while SBE-SeaCAT Profiler was used at the deeper ones. The density values of the shallow stations were computed according to the methods proposed by Fofonoff and Millard (1983) by using temperature, salinity and depth data. The water samples were stored into 10 L pre-cleaned plastic jars. The possible macro planktonic contamination was eliminated by filtering the water samples through 200 µm mesh size plankton net prior to the POC and PON measurements. The residual water filtered through the Whatman GF/F filters which had been pre-exposed to 450°C in the oven.

The POC and PON measurements were carried out by using CHN Carlo ERBA NC2500 Elemental Analyzer. The Total Particle Phosphate (TPP) samples were processed and measured according to the method proposed by Solórzano and Sharp (1980). The SPM measurements were carried out gravimetrically by using pre-weighed Millipore filters with 0.45 µm pore size. The DO was measured by using Winkler methods. The counts of the particles in size categories of 2-5 µm, 5-10 µm, 10-20 µm, 20-40 µm and 40-100 µm were determined by using Coulter Counter (Z series). Phytoplankton was sampled with 5 L Nansen bottle only from the surface. The samples were fixed with lugol solution and identified according to Tomas (1997), Paulmier (1997) and Drebes (1974) and counted under an inverted light microscope with phase contrast attachment (Olympus IX 70).

The dispersion patterns of the River's plume have been traced by the surface variables due to the saltwedge characteristics of the study area. This approach had been considered in the data processing and evaluation methodologies.

All statistical calculations were carried out by using STATISTICA (v.6). The POC:PON:TPP and DOC:POC ratios were obtained by linear regression analysis. The significant correlations were investigated among all variables prior to the Principal Component Analysis (PCA) in order to visualize any possible spatial and/or temporal patterns in terms of overall variations of the parameters considered. The first principal component accounts for the highest possible variance in the data, and each succeeding component explains as much of the remaining variability as possible. In a cross plot of principal components, the samples with similar analyte compositions will be located near each other (Sokal and Rohlf, 1981; Manly, 1986).

Results

The historical data of daily and montly river runoff (1962-2004), precipitation (1938-2004) and SPM concentrations (1984-2004) that have been archived by General Directorate of State Water Works (DSI), General Directorate of Electrical Power Resources Surveying Works (EIEI) and General Directorate of State Meteorological Works (DMI) were reviewed and some periodical fluctuations were distinguished (Figure 3). Similarly, the direct relationships among precipitation, runoff and SPM were also revealed by the significant correlations (Table 1). The annual average precipitation data were analyzed to find out whether any possible periodicity longer than a year exists or not, and further, to estimate the variation range of the precipitation. As displayed in Figure 3a, a periodicity varying roughly between 8 and 13 years seemed to onset and offset high or low precipitation periods. The range of variation for the period was 339-1116 kg m^{-2}, with a mean value of 687±168 kg m^{-2} (avg coef. of variation within a year = 74%±19).

The main factor determining the particle load of the river is runoff. The recorded minimum and maximum runoff values within the period from 1962 to 2005, were 0.08 m^3 s^{-1} and 460 m^3 s^{-1}, respectively according to the archived data. The mean value for this period was 33±51 m^3 s^{-1}.

The minimum runoff was recorded as 5.2 m^3 s^{-1} in November 2004 and the maximum was recorded as 123 m^3 s^{-1} in February 2005 for the sampling periods (Figure 4). The SPM concentration was measured as 526 mg L^{-1} during maximum runoff and the impact was observed as turbidity even at the reference stations in the Bay. The range of the SPM was 1-5176 mg L^{-1} with a mean of 295±571 mg·L^{-1}, and the corresponding values of runoff were 7-105 m^3 s^{-1}, with a mean of 26±34 m^3 s^{-1}.

The velocities and directions of the prevailing winds, which play active roles on the particle transportation as well as on the surface currents, revealed that the prevailing wind directions were NNW for spring, summer and fall whilst ESE for winter. During the study period, the maximum average wind velocity was recorded as 11 km h^{-1} in April 2005 and it blew from west. Instantaneous maximum wind velocity of 24 km h^{-1} from east-southeast direction was recorded in August 2004.

The overall distribution patterns of the parameters representing the composition of particle matters, *i.e.*, POC, PON, TPP, SPM, and phytoplankton abundance for the study period were displayed in Figure 5 as means, standard errors, maxima and minima for each zone representing the salinity gradients. Mean values of all variables decreased from the River's mouth towards the reference stations. The maximum values of SPM and phytoplankton abundance were obtained at the PZ1 zone. The remarkably low mean values with quite

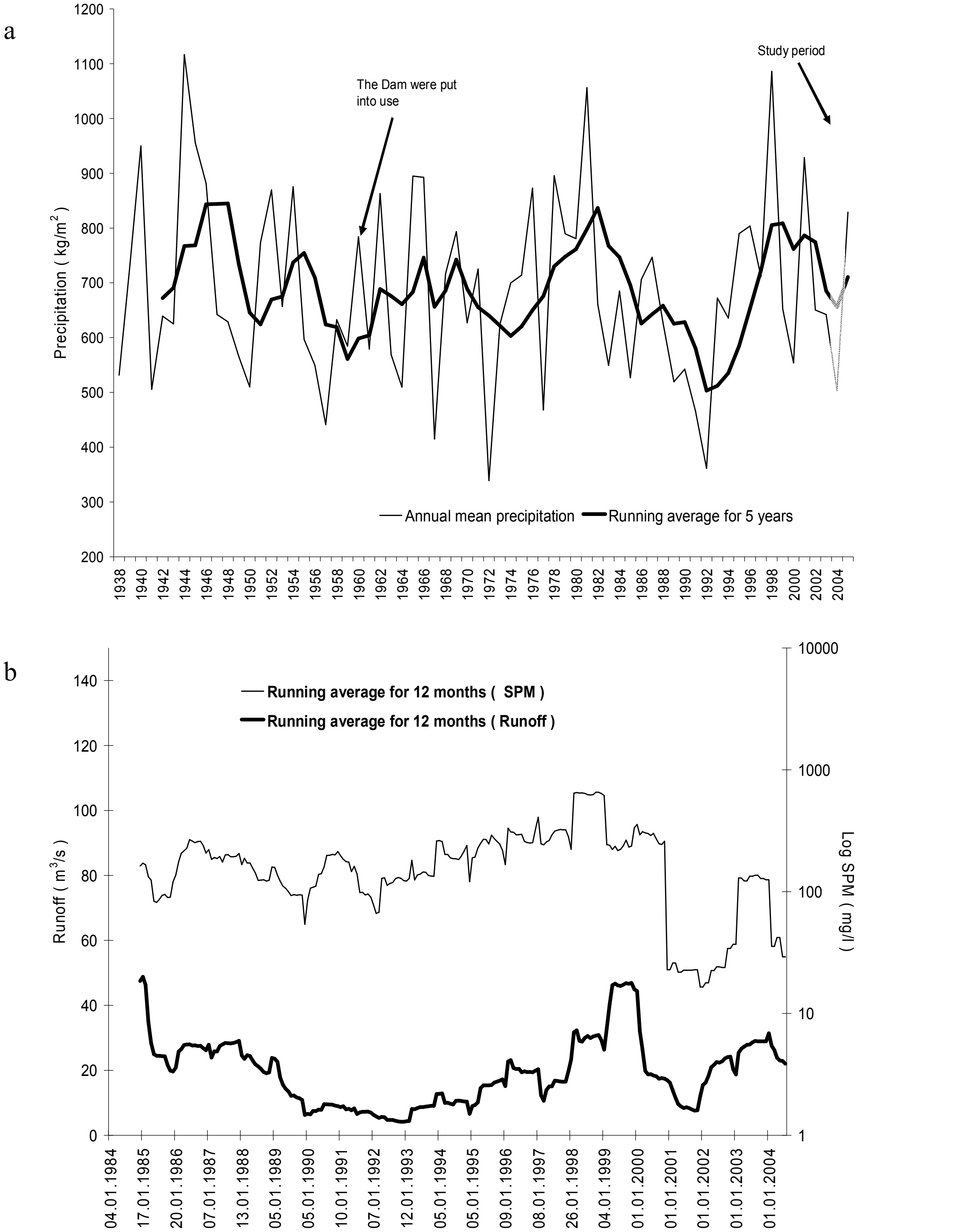

Figure 3. (a): Variation of precipation (1938-2005) and running average for 5 years; (b): Runoff and concentrations of SPM (1984-2005).

Table 1. The correlation matrix of monthly precipitation, river's runoff and SPM data from 1984 to 2005 ($P<0.05$; $n=245$)

	Runoff ($m^3 s^{-1}$)	SPM ($mg L^{-1}$)	Precipitation ($kg m^{-2}$)
Runoff ($m^3 s^{-1}$)			
SPM ($mg L^{-1}$)	0.41		
Precipitation ($kg m^{-2}$)	0.32	0.17	

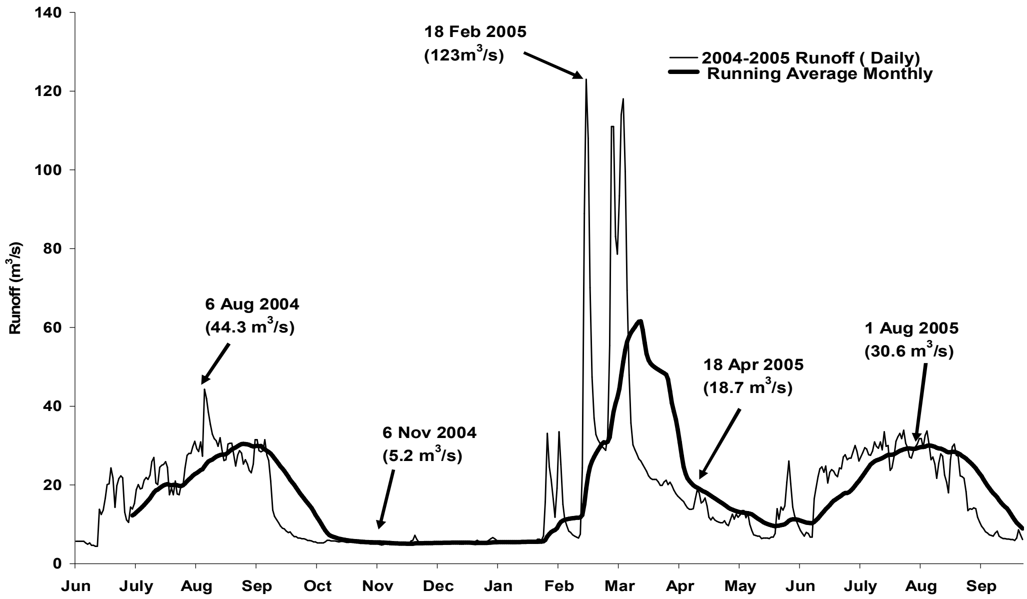

Figure 4. Daily and monthly runoff for Gediz River during 2004-2005 corresponding to the sampling dates.

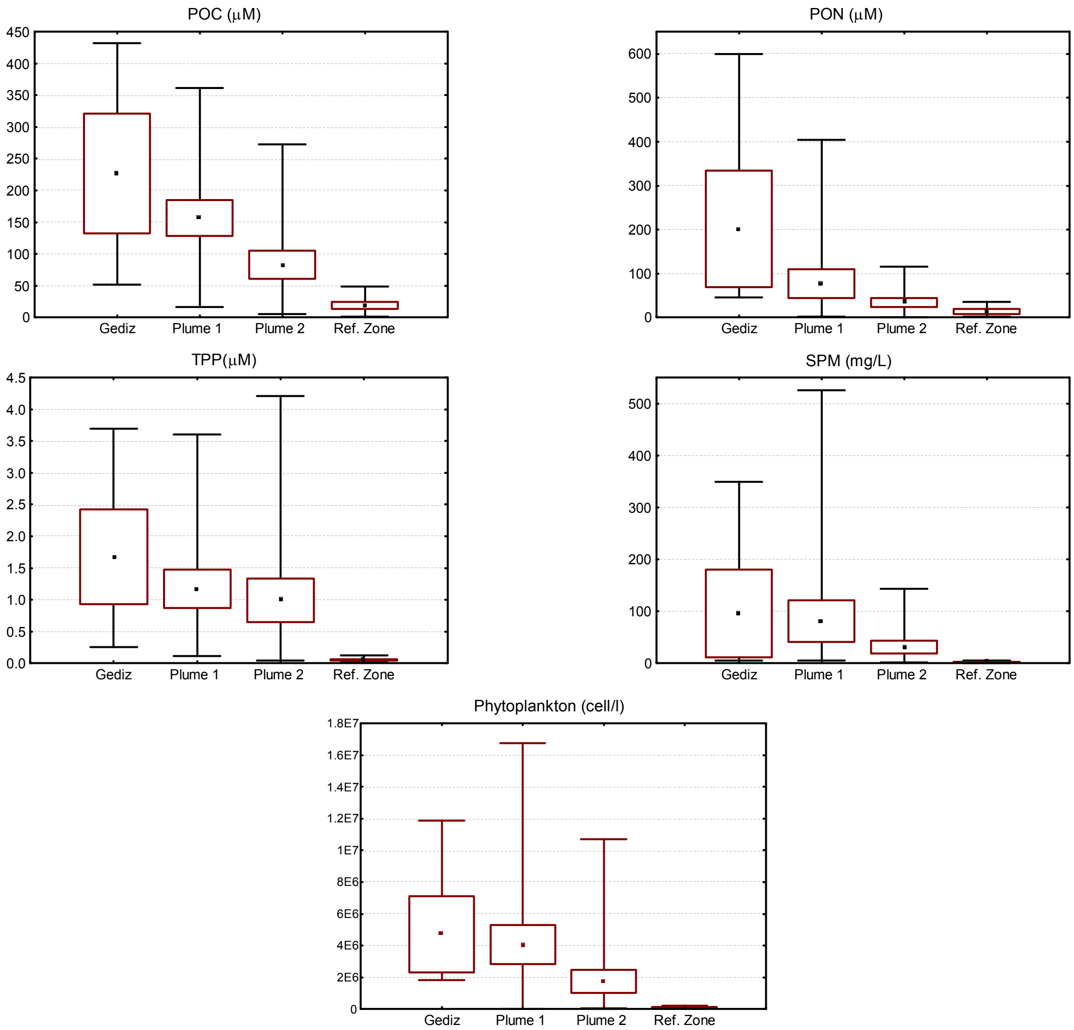

Figure 5. Average and maximum -minimum range of particulate matters for Gediz.

high precision at the RZ were the evidences of their reliability for comparisons. The FZ and the PZs had higher means and variability as expected.

The particle size spectra and their counts were revealed that, the particles smaller than 40 µm constituted more than 85% of the total (Figure 6). As shown in Figure 6, the larger particles (40-100 µm) were absent at some salinity ranges and they could only be observed as a trace amount in the reference stations in February 2005 when the run off was exceptionally high.

The comparison of phytoplankton abundances between the FZ (low salinity sample) and the RZ (high salinity sample) pointed out that the species belonging to taxa Bacillariophyceae and Chlorophyceae were dominant in FZ (Table 2), whereas, there were no Chlorophyceae at all in RZ. Bacillariophyceae were observed only in November

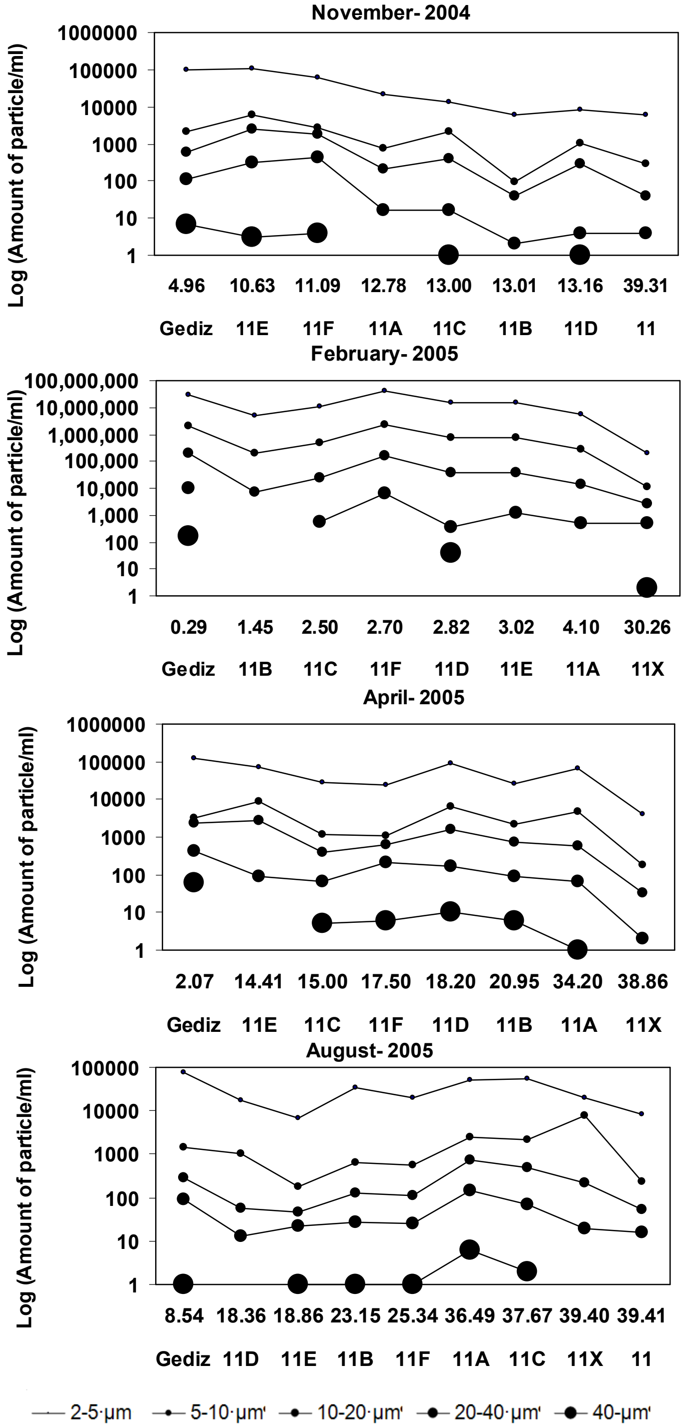

Figure 6. Particle size distribution on the surface water in the sampling dates.

Table 2. High and low salinity dominant species distiribution in the Gediz River Estuary

	High salinity sample			Abundance	Low salinity sample			Abundance
Date	Station	Major Taxa	Species	(ind/L)	Station	Major Taxa	Species	(ind/L)
Aug '04	11	Total Phytoplankton		38,443	11f	Total Phytoplankton		3,493,829
		Nanoplankton		36,203		Nanoplankton		2,171,689
		Dinoflagellata		1,799		Bacillariophyceae		303,497
							Cyclotella sp.	52,083
							Nitzschia sp.	77,282
							Pennate	68,840
						Chlorophyceae		
							Pediastrum sp.	600,021
							Scenedesmus sp.	179,170
							Staurastrum sp.	45,442
Nov '04	11	Total Phytoplankton		39,483	Gediz	Total Phytoplankton		1,992,771
		Nanoplankton		27,073		Nanoplankton		1,311,055
		Bacillariophyceae		8,579		Bacillariophyceae		504,894
			Pleurosigma sp.	2,964		Chlorophyceae		137,243
		Dinoflagellata		1,629			Scenedesmus sp.	94,477
Feb '05	11	Total Phytoplankton		233,835	Gediz	Total Phytoplankton		3,194,174
		Nanoplankton		182,646		Nanoplankton		980,450
		Bacillariophyceae		39,885		Bacillariophyceae		2,172,086
			Chaetoceros decipiens	7,136			Melosira sp.	1,092,679
			Chaetoceros sp.	8,625		Cyanobacteria		165,974
			Rhizosolenia stolterfothii	8,644				
		Cryptophyceae		7,736				
Apr '05	11	Total Phytoplankton		151,071	Gediz	Total Phytoplankton		11,888,740
		Nanoplankton		78,718		Nanoplankton		6,498,026
		Dinoflagellata		20,431		Bacillariophyceae		4,686,298
						Chlorophyceae		
		Cryptophyceae		43,248			Scenedesmus sp.	589,463
Aug'‘05	11	Total Phytoplankton		121,534	Gediz	Total Phytoplankton		1,838,159
		Nanoplankton		101,326		Nanoplankton		1,371,484
		Dinoflagellata		5,525		Bacillariophyceae		243,227
			Gymnodiniacea	1,842			Melosira sp.	60,587
		Cryptophyceae		5,255		Chlorophyceae		
							Pediastrum sp.	79,051

2004 and February 2005. The abundance of Chlorophyceae was 10 times higher in August 2004 than that in August 2005 (Table 2), eventhough the prevailing conditions were quite similar. There were not any significant correlation between the phytoplankton abundance and the total counts of each particle size categories (Table 3).

Regarding the stations, the highest phytoplankton abundance in river mouth was 11,888,740 cells L^{-1} in April 2005 (Table 2) and 3,194,174 cells L^{-1}, in February 2005 when runoff had the highest value. The highest abundance along the PZ1 was 16,740,449 cells L^{-1} (Figure 5). This abundance decreased down to 520,000 cells·L^{-1} in the PZ2. Same trend existed and the abundance reached to the lowest values at the reference stations with 105,402 cells L^{-1} at Station 11X and and 233,835 cells L^{-1} at Station 11. Nevertheless the values obtained during the highest runoff period were actually the highest values observed at all these stations and the particle counts were significantly correlated with SPM, TPP, POC and PON (Table 3). Moreover, the coefficient of determination between PON and the counts of the particles smaller than <40 µm and >40 µm were remarkably high, *i.e.*, R^2=0.90 and R^2= 0.70, respectively. In general, the particle loads during the study period were quite low except that in February 2005 when the runoff was exceptionally high (Table 4). PCA indicated that PC1 and PC2 were respectively corresponded to 59% and 17% of the total variance to which all parameters were contributed almost evenly. In addition, 13% of the variance was explained by PC3 in which DO had a high contribution. Consequently, PCA demonstrated that 90% of the total variance could be explained within three components, where the particles, their sizes and PON played the most prominent role in their variations among all other parameters (Table 5).

Discussion

The spatial variations of particulate matter had been studied in terms of ecological properties and water quality characteristics, and the results revealed their rapid variations in Gediz and the Plume zones. When the C, N and P contents of the SPM were sorted into different salinity ranges, some significant correlations were found (Table 6). The only significant correlation among particule forms within the salinity range of 0-8 psu (fresh water) was achieved between POC and TPP. All particulate forms were significantly correlated for salinity ranges

Table 3. The correlation coefficients. The significant correlations are represented in bold (P<0.05 for n=22)

	Salinity	Temp	Density	pH	DO	TPP	POC	PON	SPM	2-5 µ	5-10 µ	10-20 µ	20-40 µ	40-100 µ
Salinity	1.00													
Temp.	0.69	1.00												
Density	0.99	0.60	1.00											
pH	0.69	0.60	0.67	1.00										
DO	0.45	0.64	0.40	0.60	1.00									
PP	-0.78	-0.82	-0.74	-0.74	-0.84	1.00								
POC	-0.71	-0.66	-0.68	-0.59	-0.44	0.75	1.00							
PON	-0.53	-0.56	-0.51	-0.66	-0.54	0.68	0.54	1.00						
SPM	-0.55	-0.62	-0.52	-0.61	-0.69	0.78	0.62	0.87	1.00					
2-5 µ	-0.53	-0.59	-0.50	-0.60	-0.63	0.74	0.55	0.91	0.94	1.00				
5-10 µ	-0.50	-0.56	-0.47	-0.59	-0.58	0.70	0.53	0.94	0.92	0.99	1.00			
10-20 µ	-0.44	-0.51	-0.42	-0.55	-0.48	0.62	0.49	0.96	0.84	0.95	0.98	1.00		
20-40 µ	-0.38	-0.45	-0.36	-0.51	-0.38	0.53	0.45	0.94	0.74	0.86	0.91	0.98	1.00	
40-100 µ	-0.35	-0.34	-0.34	-0.48	-0.14	0.37	0.50	0.69	0.33	0.46	0.53	0.66	0.75	1.00
Phyto.	-0.11	-0.07	-0.10	0.27	0.43	-0.15	0.33	-0,20	-0.23	-0.22	-0.19	-0.14	-0.08	0.09

Table 4. Daily runoff and particle material loads for Gediz River

Date	Runoff (m^3 s^{-1})	SPM load (t day^{-1})	POC load (t day^{-1})	PON load (t day^{-1})	TPP load (t day^{-1})
Nov-04	5.2	3	0.28	0.69	0.01
Feb-05	123.0	3 709	43.38	89.15	1.22
Apr-05	18.7	37	8.38	1.17	0.09
Aug-05	30.6	15	2.62	1.71	0.02

Table 5. The eigenvalues (a) and eigen vectors (b) of the correlation matrix for the significantly correlated variables during the study period

(a)

PCs	Eigenvalue	% Total Variance	Cumulative Eigenvalue	Cumulative (%)
1	5.923	59.2	5.92	59.2
2	1.725	17.2	7.65	76.5
3	1,274	12.7	8.92	89.2
4	0.392	3.9	9.31	93.1
5	0.297	3.0	9.61	96.1
6	0.136	1.4	9.75	97.5
7	0.111	1.1	9.86	98.6
8	0.079	0.8	9.94	99.4
9	0.038	0.4	9.97	99.7
10	0.025	0.3	10.00	100.0

(b)

Variables	PC1	PC2	PC3
Density	0.234	-0.573	0.415
DO	0.259	-0.174	-0.831
PP	-0.344	0.365	0.185
POC	-0.29	0.438	-0.202
PON	-0.364	-0.228	-0.136
SPM	-0.373	-0.093	0.069
2-5 µ	-0.376	-0.228	-0.019
5-10 µ	-0.372	-0.28	-0.076
10-20 µ	-0.353	-0.353	-0.181

of 8-20 (brakish water), and 20-38 (saline waters). Remarkably, no correlation between the particule forms was achieved for the salinity over 38.

POC:PON ratio in the brakish waters, being the transition zone between river and the sea, reached to the equivalent of the Redfield ratio, *i.e.*, POC:PON≈7 that might be due to the relatively higher phytoplankton abundance ($5x10^6$ cells L^{-1} as an average) and/or, resuspension of POC rich bottom sediments because of the shallowness of this zone. The latter was more likely as the overall maximum value of SPM were observed in this zone as displayed

Table 6. Spatial and temporal POC:PON:TPP and POC:Chl-a ratios. Bold R^2 values refer to the significant relationships

Salinity Range		R^2	n	POC:PON:TPP
	POC=0.3 × PON +179	0.46	6	
0-8 psu	PON=150 × TPP - 222	0.50	7	70:150:1
	POC=70 × TPP + 9	0.69	7	
	POC=8 × PON - 6	0.99	10	
8-20 psu	PON=24 × TPP + 0.1	0.86	10	170:24:1
	POC=170 × TPP + 1	0.79	12	
	POC=PON + 43	0.74	10	
20-38 psu	PON=110 × TPP - 18	0.90	10	78:110:1
	POC=78 × TPP + 21	0.89	11	
	POC=0.3 × PON+12	0.53	7	
>38 psu	PON=1302× TPP - 37	0.43	6	586:1302:1
	POC=586 × TPP - 7.5	0.53	6	
Season		R^2	n	POC:PON:TPP
	POC = 172 × TPP - 1.4	0.96	7	
	PON = 115 × TPP - 19	0.81	8	172:115:1
Autumn	POC = 7 × PON - 2	0.98	7	
	POC = 76 × TPP + 8	0.77	9	
	PON = 99 × TPP - 40	0.51	8	76:99:1
Winter	POC = PON + 121	0.51	9	
	POC = 211 × TPP - 29	0.82	9	
	PON = 25 × TPP - 0.4	0.78	8	211:25:1
Spring	POC = 9 × PON - 35	0.96	8	
	POC =93 × TPP + 19	0.49	13	
	PON = 13 × TPP + 2	0.84	5	93:13:1
Summer	POC = 7 × PON - 9	0.91	6	

in Figure 5. In the salinity range of 20-38 (saline water), there were also significant correlations, similar to those in brakish water among the particulate forms. However, the POC:PON ratio was very low, *i.e.* <1, within this range. In February 2005, the similar low ratios, *i.e.* ~1, were also obtained in a monitoring survey simultaneously carried out in the outer section of Izmir Bay, as was in the study area for the salinity >38. Apparently, such a low ratio was due to the PON values remained almost constant and did not decrease equivalently to those of POC values. For all that, the POC:PON ratios for Gediz River were found to be within the range of 7 to 9 similar to that found in most world rivers (8.1–12.9) (Ittekkott and Zhang, 1989).

When temporal variations considered, the low POC:PON ratios (≤1) were observed in the extremely high and low runoff periods, *i.e.* February 2005 and November 2004, due to the radical alterations in the composition of the transported particles. The ratios were respectively 8 and 7 in spring and summer months when the runoff was around its annual average level (Table 6). The lower POC values in comparison to PON in February 2005 and November 2004 attributed to the restricted efficiency in the biodegradation process of fresh PON rich material supply. The Gediz Basin is an agricultural zone and there are also several industrial sites whose treatment plants discharges their effluents to the River. These conditions created a rich terrestrial source of PON but restricted the bacterial activity (See and Bronk, 2005). The total amount of commercial fertilizers used in the basin was 30,281 t $year^{-1}$ (Anonymous, 2004). For pure nitrogenous fertilizers, the amount in 2004 was 7929 t $year^{-1}$. It has been also reported that the 65% of the total fertilizers used in the basin has been nitrogen-based products (Anonymous, 2007). The structure and chemical composition of humic compounds change significantly during formation, and they are likely be more N-rich than previously thought, in the environment as described in See and Bronk (2005). In this study the humic substances have not been measured. Another explanation could be based on montmorillonites which are quite abundant in the Basin's sediment (Aksu and Piper, 1983). Montmorillonites are known to sorb certain basic aminoacids like arginine, histidine, ornithine and lysine with POC:PON ratios<3 (Muller, 1977) so that they may be the cause of low POC:PON ratio during flooding period. The low C:N ratios might be also caused from ammonia and urea which were likely to be found in high concentrations due to the presence of towns which were dumping sewage into river (Balakrishna and Probst, 2005). As a matter of fact, the ammonia concentration was 3360 µg L^{-1} during the low POC:PON<1 ratio in the mouth of Gediz River.

As the temperature gradually raised and the precipitation continued in the spring period, *i.e.* April 2005, the planktonic activities accelerated and their contribution to POC values increased. Consequently, the POC:PON ratio recovered to a level a bit higher than Redfield ratio, *i.e.*, POC:PON=8, (Table 6). Some activities such as fisheries, mussel collection by dredging, nomadic behaviours of the migratory birds that begin in this period and continue throughout summer, also accelarated the carbon dynamics in the sea bottom with the synergistic impact of physical driving forces such as the shallowness in the estuarine zone and the prevailing stronger winds during this period.

While most of the POC present in the estuary appeared to be composed of allochthonous organic carbon flushed out of the floodplains of the Gediz River in winter, much of the POC was composed of autochtonous organic carbon in spring. This was also supported by POC:PON ratio (~9) which indicated high phytoplankton production (16.10^6 cells L^{-1}).

In general, the overall particle size distribution patterns were determined by the particles smaller than 40 µm (Figure 6), since the larger particles could not be carried far from the river mouth where they were accumulated instead. The only remarkable transversal pattern were observed in August 2005 when almost all particles with size between 2-5 µm were seaborne, which recalled the study of Muller (1977) stating that the C:N ratios primarily determined by the effect of inorganic ammonium and organic nitrogen compounds sorbed by clays.

In Figure 7, the variations in the percentages of the POC and the PON in the SPM throughout the salinity gradient were shown. The percentage of the POC and PON could reach to a maximum level around 20% where the average was 6.7% for POC and 3.4% for PON, except for station 11X in August 2005. The average proportions of the POC and PON in the SPM values less than 23 mg L^{-1} were respectively 7.9% and 3.8%, except for August 2005 in station 11X. There was significant correlation between river runoff and the SPM (Table 1). Moreover, the significant increases in the percentage of POC and PON were observed at the SPM concentrations lower than 25 mg L^{-1} (Figure 7). A similar relationship has been demonstrated in a small river at the same concentration of SPM (20-30 mg L^{-1}) (Blanchi *et al*., 1997) and some large river systems with higher concentrations of SPM (<50 mg·L^{-1}) (Meybeck 1982; Milliman *et al*., 1984; Trefry *et al*., 1994). Such a general pattern can be attributed to a dilution effect of sediment load. These percentage values can elucidate the source of organic carbon. In the present study, the plots in Figure 7 delineated the impacts of both phytoplankton with the samples having lower SPM and higher POC% and allochthonous (=terragenic) organic matter with the samples higher SPM and lower POC%. The curve tended to flatten out at about 1% levels of POC and PON, and the corresponding SPM (65 mg·L^{-1} for POC, 130 mg L^{-1} for PON) indicated the limit of the allochthonous organic matter.

Most of the DOC derived from freshwater is composed of humic and fulvic acids (Frimmel and Christman, 1988; Wetzel, 1992) The DOC:POC ratio in the surface water of the study area ranged between 1 and 6 with a mean of 3.5. This pattern is quite similar to those found in the Bang Nara River, Thailand which has a mean of 2.8 (Yoshioka *et al*., 2002). The lower DOC:POC ratio showed neither the

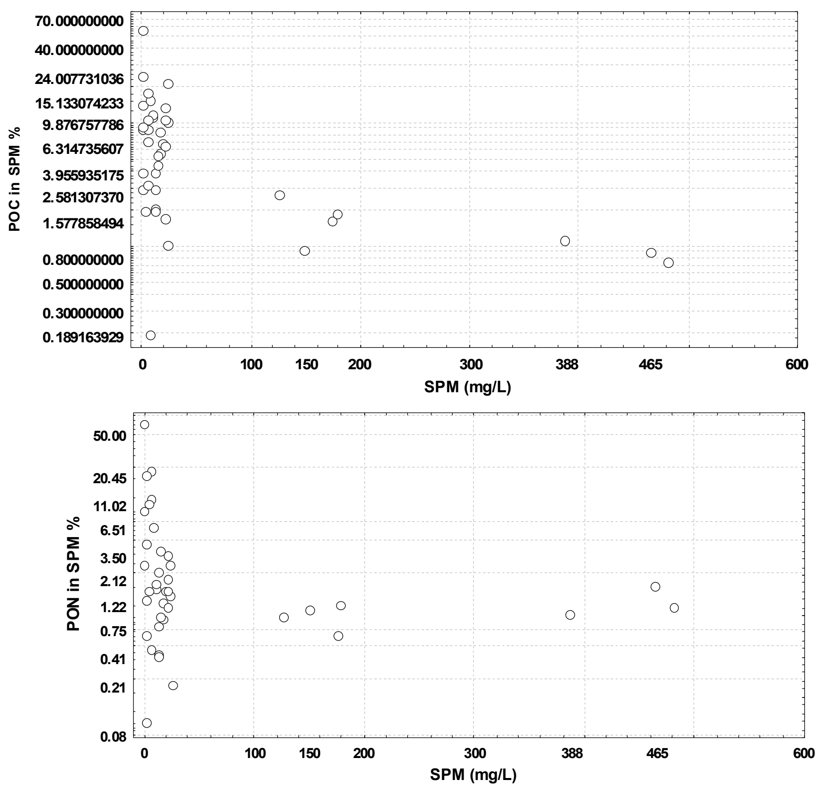

Figure 7. POC% and PON% in SPM at different SPM concentrations.

study region was heterotrophic nor the residence time of particulate matters was short. In the study area, the DOC and POC were flushed through the Gediz River plain and were dispersed into the plume and outer bay as the DOC:POC ratio increased upto 6. The characterization of terrestrial organic carbon transport therefore is essential to elucidate the land–sea linkage.

PCA indicated that PC1 and PC2 were respectively corresponded to 59% and 17% of the total variance to which all parameters were contributed almost evenly. In addition, the 13% of the variance was explained within PC3 related to DO. Consequently, PCA demonstrated that the 90% of total variance could be explained within three components, and the density, among all other parameters, played the most prominent role in their variations (Table 5). As shown in Figure 8, there were not any significant differences among the stations regardless their position in a given salinity gradient as the River's runoff was around 30-50 $m^3 \cdot sec^{-1}$. However, there were substantial differences among stations from the high run off levels, *e.g.* 100 $m^3 \cdot sec^{-1}$ or more.

As a conclusion, the river mouth usually seems to be acting as a *trap* rather than a *source* for the particles carried by the river with exceptions occurring during extreme levels of flux when acting as hot spots. In order to understand these dynamics more satisfactorily, it is essential to carry out a monitoring survey with finer spatio-temporal resolution. Within the frame of the data collected during the present study, the remarkably high alterations occurred in a distance of 5-6 km the study area where the water of Gediz River mixed with the Izmir Bay's water, did not indicate any potential threat for the outer Bay as was thought so in the previous studies.

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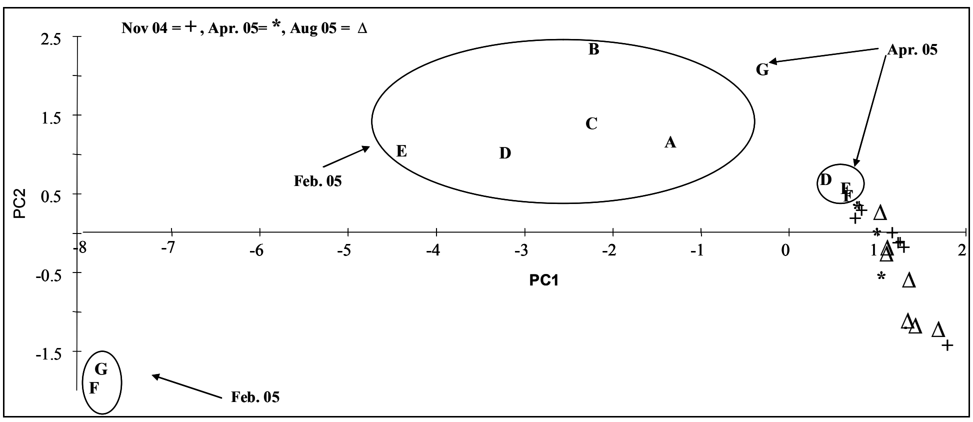

Figure 8. Plots of samples taken during the survey against values for first two principal components: PC1 and PC2 for ecological variables.

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