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Dissolved Nutrient Behaviour along the Estuarine Salinity Gradient at the Gediz River Mouth (Aegean Sea, Turkey)

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Abstract

The Gediz River is the largest fresh water source for İzmir Bay. Several studies have been carried out on the river's physical and biogeochemical dynamics. However, there has not been a particular geographical focus on the mouth of the river. In this study, along the salinity gradient towards the bay in 2004 and 2005, the dissolved inorganic nutrients were seasonally measured at the river mouth. During the sampling period, the concentration of the constituents showed variability in the range of 0.04-156 μ M for NO₃⁻, 0.02-12 μ M for NO₂⁻, 0-237 μ M for NH₄⁺, 0.02-26 μ M for PO₄³⁻, and 1-293 μ M for SiO₂, while the river discharge fluctuated between 5.2 and 123 m³/s. Resulting highly contrasted salinity gradients between 0.29 and 39.62 psu significantly influenced the concentrations of dissolved inorganic nutrients. Furthermore, simultaneous sampling carried out over the entire bay area provided an opportunity to study the effects of the river on the bay during periods of maximum and minimum discharge.

Key words: Nutrients, Salinity gradient, PCA, Gediz River, Izmir Bay

Introduction

The areas where the river current meets the sea, termed estuaries, are ecologically specific environments. The quite unique biophysicochemical properties of these areas drive biogeochemical processes that may have positive or negative consequences for the seas as "*receivers*".

Rivers are collectors and as such they collect sediments from erosion, dissolved material from decaying plants and animals, and substances of anthropogenic origin. They are one of the main sources of nutrients for the ocean. Environmental threats are becoming more prominent in parallel with increasing populations. These threats affect freshwater sources and thereby coastal ecosystems, which are more productive regions than the offshore regions. At the coast, where the rivers end, the fate of the discharge determines how the collected material will be distributed. During the last decade, studies have reported that the nutrient levels are 4 times higher in the western European rivers than those flowing into the Mediterranean (MED POL, 2002).

Rivers, with their dynamism, help flush terrestrial pollution. However, concentrations of the dissolved material are important factors affecting the properties of the river water (Froelich et al., 1982). Rivers are the main sources of phosphorus (Froelich et al., 1982), silica (Treguer et al., 1995), and nitrogen (Schlesinger, 1997). Phosphorus in rivers is usually absorbed by soil materials (Meybeck, 1982; Froelich, 1988) and, in the plume area (i.e. the river mouth), desorption renders phosphorus available for phytoplankton uptake (Fox et al., 1986; Froelich, 1988). In the process of particle transportation by rivers, clay minerals have an important role for carrying silica to the oceans (Mackenzie and Garrels, 1965; Mackenzie et al., 1967; Milliman and Boyle, 1975). Silica is also important for phytoplankton, particularly for those that form siliceous shells. According to recent reports, nitrate levels have dramatically increased in the Mediterranean rivers (EEA/UNEP, 1999). This is in contrast to the decline in silica levels, mainly due to the reduction in material loads of 2 major sources (e.g., the Danube and Nile). Therefore, phytoplankton in the Mediterranean lacks essential nutrients to grow (Turley, 1999).

A wide variety of inter-connected geochemical and biological processes operate in the estuarine environment to alter the concentration and speciation of biologically important nutrient materials, metals, and pollutants. Individual elements (e.g., sodium and chloride) may be non-reactive within the estuary. Their concentrations reflect the relative dilution of the freshwater or saltwater end members (Kaul and Froelich, 1984). Humborg (1997) reported that the inorganic nutrients are the most reactive substances in estuaries and they frequently demonstrate non-conservative behaviour. Other materials are also actively taken up or released into the solution (Figure 1 in Furnas, 1995). The transition from freshwater (a medium with low ionic strength) to saltwater (a medium with high ionic strength) directly affects the concentration and speciation of many elements and ions carried in river waters. For these reasons, the plume zones have dynamic characteristics.

The aforementioned reports and findings on the biogeochemical dynamics at river mouths are the main motivation for the present study. In the Turkish context, there is a lack of research focusing on producing data and information on the evolving status of Turkish estuaries. The selected site, the Gediz River, is the largest freshwater source for Izmir Bay and also the third largest for the Aegean Sea. Although there are several studies being carried out on the river's physical and biogeochemical dynamics, none of them includes the dynamics at the mouth of the river. In this research, the dissolved inorganic nutrients were seasonally measured at the mouth of the river and along the salinity gradient towards the bay in 2004 and 2005. The following section provides a description of the study area and details of the sampling and analysis methods. We also present the results and discuss their significance together with some suggestions for future studies.



Figure 1. Monthly discharge from Gediz River during 1980 - 2005.

Materials and Methods

Study area

The Gediz River basin collects water from more than 400 industrial locations, 4 cities (Kütahya, Uak, Manisa, and Izmir), 17 towns, and 106 villages. Most importantly, it is the largest freshwater source for İzmir Bay, with its 17,500 km² watershed, the second largest river flowing into the Aegean Sea from Anatolia, and the third largest for the whole Aegean basin. It reaches the sea at the north-eastern section of Izmir Bay, between Foça and Izmir, after flowing a distance of 401 km. Since 1960, the river's regime has been controlled via the Demirköpru Dam, which has a reservation capacity of $1,125,00 \text{ m}^3$. The water is usually collected during winter and spring, and is used for irrigation during summer and early autumn (DSI, 2007). It is reported that the crossing point of Karacay Creek and Gediz River, the final crossing before the river reaches the bay, is the most polluted segment (Sunar and Ersan, 1989; Bayar and Oğuz, 1990; Okur et al., 1997). These studies agree that the Gediz River is heavily polluted due to agricultural drainage and industrial wastewater, as well as domestic wastewater from the entire provincial area. Hence, it is a pollution source for Izmir Bay (Uslu, 1994; Aksu et al., 1998; Murathan, 1999; Batk, 2002; Gündoğdu and Turhan, 2004).

In general, the Gediz River has higher flow rates from December to March (Figure 1). Since 1990, the flow rate has decreased. The data from the last measurement station preceding the river mouth showed that annual mean flow rates were $45.31 \text{ m}^3/\text{s}$ in the 1970s, $47.40 \text{ m}^3/\text{s}$ in the 1980s, $16.70 \text{ m}^3/\text{s}$ in the 1990s, and $20.27 \text{ m}^3/\text{s}$ in the 2000s.

The prevailing wind directions on the western part of the Gediz Basin are east-south-east (ESE) in the winter and north-north-west (NNW) in spring, summer, and autumn (Uslu, 1994; Batk, 2002; DMIGM, 2007). Karahanli (2002) and Sayn (2003) reported that an anti-cyclonic current system forms near the mouth of river when the wind blows from the NW with a velocity higher than 5 m/s.

Sampling and analyses

In order to be able to reflect the patterns formed by the salinity gradients, the study area is divided into 4 zones (Figure 2): the Fresh Water Zone (river mouth), the Plume 1 Zone (Stations 11D, 11E, 11F), the Plume 2 Zone (Stations 11A, 11B, 11C), and the Reference Zone (Stations 11, 11X). The locations of the stations in the plume zones were determined by the salinity profiles. However, the shallowness and site-specific rapid spatio-temporal alterations in the bathymetric patterns of the area make the locations of the stations variable.

Sampling was carried out seasonally by a small boat shuttled from and to the main research vessel R/V K. Piri Reis, in August 2004, November 2004, February 2005, April 2005, and August 2005. The observations and measurements demonstrate that the freshwater dispersed into the plume area through a very thin surface layer in the order of tens of centimetres. The locations of stations in the plume areas were determined by the salinity profiles obtained via the YSI 556 multi-probe system during the sampling operation. Water samples collected were stored in 10-1 pre-cleaned plastic jars and were filtered through Whatman GF/F filters pre-exposed to $450 \circ C$ in the oven. The filtered water samples were kept frozen for analysis in the laboratory. SiO_2 and NO_2^- were analysed using the method described by Grasshoff et al. (1983), and $(NO_2^- + NO_3^-)$, $NH_4^+ PO_4^{3-}$ following Strickland and Parsons (1972).

In addition to the data gathered for this study, an identical and complementary data set obtained in a simultaneous monitoring study for İzmir Bay was also used in order to take the impacts of the Gediz River on the bay's nutrient regime into consideration.

Results and Discussion

The vertical profiles at the stations showed that the river had a salt wedge property throughout all sampling periods. This property was particularly more prominent during the period of maximum flow (i.e. February 2005), when there was a freshwater layer with a thickness of <50 cm overlying all plume zones.

Table 1 lists the means and the variation ranges of each parameter measured. Discussion of the results is presented under separate sections for each constituent group.



Figure 2. Location of the sampling area in Izmir Bay (top left). Stations in the sampling area at each sampling period. P1 and P2 are the transects over the plume area.

Dissolved inorganic nitrogen forms (NO_2^-, NO_3^-, NH_4^+)

The maximum value of the total dissolved inorganic nitrogen (TIN) was observed in February 2005 (mean 190 μ M) when the flow was at its maximum (Figure 3). Nevertheless, the TIN values were also quite high in April 2005 (mean 130 μ M) and even in November 2004 (mean 116 μ M) when the flow was at its minimum. During these 3 months, water was not released from the dam and the river flow depended only on the precipitation over the lower section of the catchment basin between the dam and the bay. However, water was released from the dam in August for irrigation, and hence the river flow was directly determined by the volume released, since there was practically no precipitation during that month. In this period, the dam water was first transported to

the regulation area and then distributed via channels to the agricultural area for irrigation. Along this path, it is assumed that the pollution load of the river water was reduced by enhanced sedimentation since there are several reservoirs, particularly at the junction points of the network of the irrigation channels, in which the water flow declines temporarily. Quite high TIN levels were reported along this path in the winter period (e.g., 626 μ M in January 1996, 251 μ M in February 1996, and 60 μ M in February 1999) (Okur et al., 1997; Batk, 2000). During the study period, the TIN forms, particularly NH_4^+ and NO_3^- , were remarkably high at the mouth of the river, except in August 2004 and 2005, and these relatively high levels were sustained towards the reference station (Figure 3). NH_4^+ and NO_3^- were the dominant forms in the river mouth and plume zones. NH_4^+ was obviously the dominant form in November

| Date | Zone | Salinity psu | Temperature $\circ C$ | DO mg/l | $PO_4^{3-}\mu M$ | $NO_2^-\mu M$ | $NO_3^-\mu M$ | $NH_4^+ \mu M$ | $Si_2O \mu M$ |
|---------------|-------|--------------|-----------------------|-------------|-------------------------|---------------|-------------------------|----------------|---------------|
| | Ref | 39.45 | 24.47 | 5.31 | 0.13 | 0.02 | 0.58 | 0.67 | 2.10 |
| | Do | 39.2 - 39.5 | 24.33 - 24.4 | 3.34 - 6.19 | 0.08-0.1 | 0.12 - 0.2 | 0.22 - 0.6 | 1.1 - 14.4 | 2.1 - 2.8 |
| Aug-04 | P2 | (39.3) | (24.4) | (4.38) | (0.1) | (0.1) | (0.4) | (5.6) | (2.3) |
| | D1 | 1.83-40 | 26.5-29 | 7.46-9.02 | 0.29-5 | 0.02-2 | 0.6-37 | 0.83-22 | 4.7-111 |
| | PI | (25.2) | (27.7) | (8.1) | (2.3) | (0.6) | (10.0) | (6.8) | (38.2) |
| | Ref | 39.31 | 20.16 | 6.72 | 0.12 | 0.17 | 0.38 | 0.25 | 3.40 |
| - | Do | 12.8-13 | 19.04-19.12 | 6.85 - 7 | 1.8-6.8 | 1.0-4.4 | 3.0 - 8.6 | 39-75 | 20-98 |
| | P2 | (12.9) | (19.1) | (6.90) | (4.10) | (2.43) | (5.23) | (56.33) | (52.00) |
| Nov-04 | Ρ1 | 10.6-13 | 17.3-18 | 5.34-7 | 0.53 - 19 | 0.13-10 | 0.63-43 | 1.4-219 | 12-188 |
| - | | (11.6) | (17.7) | (5.99) | (11.18) | (6.04) | (21.88) | (134.47) | (125.00) |
| | Gediz | 5.0 | 12.8 | 8.8 | 26.0 | 4.7 | 10.3 | 237.0 | 220.0 |
| | D.f | 30.3-36.7 | 13-13.4 | 7.79 - 7.9 | 0.11 - 0.3 | 0.02 - 0.3 | 0.33 - 5.4 | 0.1 - 2.3 | 1-13.0 |
| - Feb-05 _ | Rei | (33.5) | (13.2) | (7.85) | (0.19) | (0.14) | (2.84) | (1.18) | (7.00) |
| | DЭ | 1.5 - 4.1 | 12.4 - 13.6 | 1.52 - 2.9 | 1.1 - 1.6 | 4.9 - 11.6 | 59.1 - 86.4 | 134 - 158 | 225 - 238 |
| | Γ2 | (2.7) | (13.0) | (2.21) | (1.30) | (8.81) | (75.52) | (149.33) | (232.00) |
| | P1 | 2.7 - 3.02 | 11.14 - 12.5 | 2.22 - 3.4 | 1.3 - 2.2 | 4.9 - 6.3 | 70.3 - 86.7 | 143 - 174 | 226-293 |
| | L T | (2.85) | (11.68) | (2.99) | (1.70) | (5.63) | (80.03) | (159.00) | (266.00) |
| | Gediz | 0.29 | 9.95 | 3.31 | 1.50 | 7.30 | 95.20 | 161 | 249 |
| | Pof | 38.8 - 38.9 | 15.6 - 15.9 | 6.95 - 7.6 | 0.02 - 0.1 | 0.1 - 0.3 | 0.26 - 1.4 | 0.17 - 2.2 | 2.6 - 3.9 |
| | ner | (38.80) | (15.73) | (7.25) | (0.07) | (0.20) | (0.84) | (1.19) | (3.25) |
| | P2 | 15 - 34.2 | 16.97 - 19.2 | 5.17-8 | 3.3-4 | 2.3-8 | 25.7-70 | 44-119 | 38-61 |
| Apr-05 | | (23.38) | (17.78) | (6.78) | (3.50) | (5.70) | (52.63) | (89.00) | (50.00) |
| 1 | Ρ1 | 14.4 - 18.2 | 16.7 - 18.2 | 6.65 - 8.4 | 3.2 - 3.8 | 7 - 12.0 | 71 - 156 | 55 - 97 | 31-41 |
| | | (16.70) | (17.70) | (7.46) | (3.60) | (8.77) | (99.90) | (80.00) | (36.67) |
| | Gediz | (2.1) | 17.5 | 9.6 | 1.3 | 8.2 | 116.8 | 33.0 | 10.0 |
| | Rof | 39.4 - 39.41 | 24.7-25 | - | 0.56 - 0.9 | 0.12 - 0.2 | 0.04 - 0.7 | - | 2.7 - 7.0 |
| | nei | (39.40) | (25.14) | - | (0.75) | (0.14) | (0.39) | - | (4.82) |
| | D0 | 23.2 - 37.7 | 26.6-27.2 | 6.35 - 8.3 | 1.56 - 11.4 | 0.14 - 0.8 | 0.09 - 13.1 | 0-3.6 | 5.1 - 80.4 |
| Aug-05 | 1 2 | (32.44) | (26.89) | (7.53) | (5.52) | (0.39) | (4.77) | (1.74) | (32.01) |
| 0 - | P1 | 18.4 - 25.3 | 27.5-27.9 | 7.65 - 9.1 | $1\overline{6.4}$ -18.4 | 0.82 - 1.1 | $1\overline{3.7}$ -16.5 | 1.46-4 | 81-96.2 |
| | 11 | (20.85) | (27.66) | (8.17) | (17.19) | (0.99) | (15.05) | (3.10) | (91.07) |
| | Gediz | 8.54 | 28.74 | 8.75 | 22.17 | 1.29 | 38.45 | 4.03 | 134.51 |

Table 1. Physical parameters and dissolved inorganic nutrient ranges, with means in parentheses.



Figure 3. Time series of spatial distribution of TIN and its forms during the study period. The percentages refers NH_4^+ values in the TIN. Distributions are given for P1 and P2 transects, Gediz and the reference stations.



Figure 4. Time series of dissolved oxygen (DO) concentrations at the surface layer.



Figure 5. The distributions of TIN $(NO_3^- + NO_2^- + NH_4^+)$ in the Izmir Bay and at the mouth of Gediz River during the parallel sampling surveys.

2004, while NO_3^- was the dominant form in April and August 2005, even though its level was not as high as that of NH_4^+ . The availability of DO might be the controlling factor (Figure 4). When the data obtained from the simultaneous monitoring survey in the bay were analysed (Figure 5), it was found that NO_3^- and NH_4^+ were the dominant forms over the entire bay. On the other hand, the comparison of the TIN levels measured at the river mouth to those measured in the upper segments of the river in previous studies revealed that the TIN levels were usually lower at the river mouth (Bizsel et al., 2008).

In February 2005, while NH_4^+ concentration was high, DO levels were very low at the river mouth and in plume zones. The NO_2^- levels declined gradually from the river mouth towards the reference station (Figure 6) with consistent and expectedly very low percentages among TIN forms. This may be interpreted as an indicator of the efficiency of nitrification and/or denitrification processes in the study area. The higher values at the river mouth and in plume zones can be attributed to the deficiency in DO supply during nitrification, or conversely to the release of DO during denitrification. The maximum NO_2^- (12) μ M) was observed in the P1 Zone in April 2005 and in the P2 Zone (11.6 μ M) in February 2005. As salinity increased, the removal processes (i.e. conservative behaviour) within the Gediz Estuary were usually observed for TIN forms (Figure 7). As displayed in the figure, NH_4^+ may have had a non-conservative character (i.e. higher solubility) within the estuary (e.g., in April and August 2005), while it usually showed conservative behaviour. Table 2 shows that the water quality criteria in terms of NH_4^+ and $NO_2^$ were clearly exceeded.



Figure 6. Temporal (top) and spatial (bottom) distributions of NO_2^- concentration.



Figure 7. Variations in the concentrations of TIN forms along the salinity gradients existed at each sampling period.

Table 2. Water Quality Standards (WQS) for coastal waters and the study zones (WQS was announced in the Gazette number 19919 on September 4, 1998).

| (μM) | Ι | II | III | IV | Gediz | P1 | P2 | Ref |
|-----------|-------|-------|--------|---------|-------|-----|-----|-----|
| NH_4^+ | 14.3 | 71.4 | 142.8 | >142.8 | III | III | II | Ι |
| NO_2^- | 1.43 | 0.71 | 3.55 | >3.55 | IV | IV | III | Ι |
| NO_3^- | 356.9 | 713.8 | 1427.6 | >1427.6 | Ι | Ι | Ι | Ι |

Dissolved inorganic phosphate (PO_4^{3-})

The mean values of PO_4^{3-} were higher in November 2004 (8.99 μ M) and August 2005 (10.2 μ M) compared to other months. In regard to the occurrence of the lowest flow rate $(5.2 \text{ m}^3/\text{s})$ in November 2004 and an average flow rate $(30.6 \text{ m}^3/\text{s})$ in August 2005, it seemed that the flow rate did not have a determining effect on the PO_4^{3-} concentration. Consequently, the dynamical properties of the interaction between the river and sea at the mouth of the river (i.e. in the plume zone) were likely to be the determining factors. In that case, the sediment re-suspension from the shallow bottom of the plume zone may be the

actual source of PO_4^{3-} . In general, PO_4^{3-} concentration decreased along the track from the river mouth (mean 12.7 μ M) to the reference station (mean 0.28 μ M) (Figure 8). Measurements carried out in the upper segments of the river in previous studies demonstrated that the total phosphate concentration (i.e. dissolved and particulate forms) decreased as waters approach the sea, which is in complete contrast with the properties of TIN forms (Okur et al., 1997; Batk, 2000). The data obtained from the simultaneous monitoring surveys (Figure 9) revealed that the dissolved forms of phosphate, both organic and inorganic, are abundant in the bay (Bizsel et al., 2008).



Figure 8. Temporal (top) and spatial (bottom) distributions of PO_4^{3-} concentration.



Figure 9. The distributions of TPO_4^{3-} (o-P₄4, DOP, PP) in Izmir Bay and at the mouth of Gediz River during the parallel sampling surveys.

In the literature, a number of studies report that PO_4^{3-} is transported by clay minerals of approximately 2 μ m in size. The distributions of PO₄³⁻ and the counts of the suspended particulate matter between 2 and 5 μ m in size along the salinity gradient (Figure 10) did not display a significant negative correlation. Instead, 2 threshold values of salinity were apparent at 2.7 and 17.5 psu, which may imply an acceleration in desorption of PO_4^{3-} at these particular salinity levels. However, the only concrete outcome from this case was the dependence of PO_4^{3-} concentrations on the occurrence of re-suspension, as stated at the beginning of this section. Thus, both the conservative and non-conservative behaviour of PO_4^{3-} observed during the study could be explained (Figure 11). The comparison of PO_4^{3-} values with those of other rivers revealed that the level in the Gediz River was quite high (Table 3).

Silica (SiO_2)

The importance of the role of silica in primary production is well known. Diatoms, which comprise 60% of all phytoplankton, use silica dissolved in seawater for building their cell wall (i.e. frustule) (Hamm et al., 2003). The molar ratio for diatoms reflecting the growth of living cells (i.e. Redfield ratio) is C:Si:N:P = 106:16:16:1. This also represents the equivalent amount of substances released to the seawater when cells die (Redfield et al., 1963; Brzezinski, 1985). Therefore, diatoms are the main consumers of dissolved silica, and hence play an active role in the determination of the silica levels in aquatic environments.

In April 2005, the silica level expectedly dropped to $10 \ \mu M$ because of increasing phytoplankton

biomass (i.e. an average of 7,540,609 cells/l) (Bizsel et al., 2008). The sharpness of this decline relative to the value measured in February 2005 (195 μ M) was attributed particularly to the occurrence of a monospecific diatom bloom of *Melosira* sp. at the level of 1,092,679 cells/l. The bloom was more appar-

ent at the mouth of the river. The maximum value observed was in February 2005 at 249 μ M. The spatial and temporal variations in the mean values are given in Figure 12. It was observed that the higher concentration at the river mouth gradually decreased through P1 and P2 towards the reference station.



Figure 10. The distributions of PO_4^{3-} and Silicate concentrations together with the counts of 2-5 μ m particles along the salinity gradient in the surface water.



Figure 11. Variations in the concentrations of $o-PO_4$ along the salinity gradients existed at each sampling period.

| | NH_4^+ $(\mu\mathrm{M})$ | NO_3^- (μM) | NO_2^- (μM) | $NO_{3}^{-}+NO_{2}^{-}$ (μM) | PO_4^{3-} (μM) | $Si_2O(\mu M)$ | Source |
|--------------------------|-------------------------------------|----------------------|----------------------|-------------------------------------|-------------------------|----------------|---------------------------|
| Wonokromo Estuary | 0.1-0.2 | 0.2 - 118.5 | 0.1 - 5.4 | | 0.2-3 | 38-180 | Jennerjahn et al., 2004 |
| Porong Estuary | 0.1 - 0.2 | 0.3 - 104.9 | 0.1 - 2.6 | | 0.1 - 2.4 | 49.2 - 182.4 | Jennerjahn et al., 2004 |
| Harvey Estuary | | I | | · | 0.5(0-3.23) | ı | Gerritsea et al., 1998 |
| Rhine River | 140 | 175 | ı | ı | 2 | I | Bennekom et al., 1975 |
| The Mississippi River | | I | ı | 78.5 | | ı | Briggs and Ficke, 1977 |
| Murray River | | I | | ı | 3.2(0.32 - 12.9) | I | Gerritsea et al., 1998 |
| Serpentine River | | ı | | · | 4.5(0-12.9) | ı | Gerritsea et al., 1998 |
| Serpentine River | | ı | | · | 3.9(1.6-6.5) | ı | Gerritsea et al., 1998 |
| Mkurumuji River | 0.54 - 2.11 | ı | | 0.52 - 6.47 | 0.82 - 2.47 | | Ohowa et al., 1997 |
| Kidogoweni River | 0.62 - 1.90 | ı | | 0.26 - 3.48 | 0.72 - 1.44 | | Ohowa et al., 1997 |
| Gediz River | $58.2 \ (0-237)$ | 32 (0-156) | 3.3 (0.02 - 12) | 55.3 (0-168) | 4.8(0.02-26) | 80.5(1-293) | This study |
| Meric River (Uzun Köpru) | 799.4 | 1 | 471.1 | . 1 | 3.6 | . 1 | Altınayar, 2003 |
| Büyük Menderes River | | 163.5 (374.7) | ı | · | | ı | Boyacioglu, 2004 |
| Asi River | 46.4 | 172.0 | 2.9 | | 7.7 | 223.9 | Tademir and Göksu, 2001 |
| Bakırçay Stream | | 128.5 | 96.4 | ı | | I | Gündouğdu and Turhan 2004 |
| Solak Stream | 21.4 | 78.5 | 0.27 | | | ı | Boran and Sivri, 2001 |
| Surmene Stream | 17.8 | 71.4 | 0.27 | | | ı | Boran and Sivri, 2001 |
| Ankara Stream | (356.9-749.5) | I | (0.07-17.8) | ı | ı | I | Atici and Ahiska, 2005 |

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Figure 12. Temporal (top) and spatial (bottom) distributions of SiO₂ concentration.

Since the clay minerals are potential carriers for silica as they are for PO_4^{3-} , the fluctuations in the concentration of silica may be related to their abundance in the environment. On the basis of this relationship, the fluctuations along the salinity gradient did not indicate any significant correlation between silica and the suspended particulate matters in the 2-5 μ m size range (Figure 10). Similar to the findings for PO_4^{3-} , the only finding was the determining effect of re-suspending bottom sediments in shallow plume zones. Thus, the silica values measured, which were higher in the upper segments of the river (Batk, 2002) than those at the lower segments, i.e. towards the river's mouth, during the study period could also be explained. As shown in Figure 13, the silica displayed conservative behaviour via biological uptake or precipitation during the study period. According

to the results obtained in the simultaneous monitoring survey, the silica values did not exceed 25 μ M, whereas those obtained in this study were higher. It was particularly interesting that the highest values were higher than 150 μ M in both the lowest and highest flow periods, i.e. November 2004 and February 2005, respectively.

Principal Component Analysis (PCA)

Prior to performing the PCA, a correlation matrix was formed for dissolved oxygen, dissolved inorganic nutrients, and physical parameters. The correlation calculations were prepared using the STATISTICA 6.0 package (Table 4). Except for DO and PO_4^{3-} , all parameters have significant correlations among each other. PCA was prepared using the Premier 5.0 package.



Figure 13. Variations in the concentrations of Silicate along the salinity gradients existed at each sampling period.

Table 4. Correlation matrix for dissolved inorganic nutrients, dissolved oxygen, and physical parameters.

| | Salinity | Temp. | DO | PO_4^{3-} | NO_2^- | NO_3^- | NH_4^+ | SiO_2 |
|------------------|----------|-------|-------|-------------|----------|----------|-------------------|------------------|
| Salinity | 1.00 | | | | | | | |
| Temp. | 0.47 | 1.00 | | | | | | |
| DO | 0.26 | 0.48 | 1.00 | | | | | |
| PO_4^{3-} | -0.29 | 0.25 | 0.34 | 1.00 | | | | |
| NO_2^- | -0.69 | -0.57 | -0.33 | 0.09 | 1.00 | | | |
| NO_3^- | -0.66 | -0.50 | -0.26 | -0.07 | 0.84 | 1.00 | | |
| NH_4^+ | -0.71 | -0.68 | -0.48 | 0.25 | 0.80 | 0.57 | 1.00 | |
| SiO_2 | -0.78 | -0.51 | -0.57 | 0.32 | 0.58 | 0.51 | 0.82 | 1.00 |

There is no prominent variance source among the parameters used in the analysis since the variance distribution among them is quite even along the primary axis, which corresponded to 70% of total variance (Table 5). Nevertheless, the plot of the results (Figure 14) shows significant similarities and differences among the sampling periods. The similarity is particularly remarkable between August 2004 and 2005, in which the river flow has quite same pattern. In November 2004, there is a partial similarity with the periods of August through some stations such as B, C, and D. February 2005 and April 2005 are apparently different from each other and all other periods. Consequently, the main determinant of the

variance should be the salinity and temperature, and thereby the intensity of river flow, which influences the area of the river plume, the quantity of the loads carried by the river, and the rates of biogeochemical processes.

Dissolved Inorganic Material (DIM) Loads

The DIM loads mainly depend on the river flow and concentrations in the water. In addition to the magnitude of the loads, their distribution in the marine environment is controlled primarily by the speed and the direction of prevailing winds, the magnitude of tidal movements, and by the river discharge.



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Figure 14. Schematic explanation of PCA for dissolved inorganic nutrients and physical parameters. The sampling period is represented by the number codes given in legend while the letters refers the stations. The distinctive periods are remarked by circles.

| Table 5. | Eigenvalues | and | eigenvectors | for | dissolved | inorganic | nutrients | and | physical | parameters | s. |
|----------|-------------|-----|--------------|-----|-----------|-----------|-----------|-----|----------|------------|----|
| | | | | | | | | | | | |

| \mathbf{PC} | Eigenvalues | %Variati | on Cu | m.%Varia | tion | |
|---------------|-------------------|-----------|--------|----------|------|--|
| 1 | 4.21 | 70.2 | | 70.2 | | |
| 2 | 0.67 | 11.2 | | 81.4 | | |
| 3 | 0.62 | 10.3 | | 91.7 | | |
| | _ | | | | | |
| | I | Eigenvect | ors | | | |
| | Variable | PC1 | PC2 | PC3 | | |
| | Salinity | 0.416 | -0.101 | -0.459 | | |
| | Temperature | 0.351 | -0.161 | 0.823 | | |
| | NO_2^- | -0.434 | -0.423 | -0.027 | | |
| | NO_3^- | -0.393 | -0.652 | 0.085 | | |
| | NH_4^+ | -0.443 | 0.287 | -0.107 | | |
| | SiO_2 | -0.405 | 0.528 | 0.305 | | |

The DIM loads were calculated using river flow measurements (DSI, 2004-2005). The highest DIM load was observed in February 2005 (Table 6). During the winter, the peak season for DIMs, waste ma-

terials accumulated and relatively higher bacterial growth utilized DO at and around the river mouth (Figure 4). It should be emphasised that the sampling day in February 2005 was the day when the highest annual flow $(123 \text{ m}^3/\text{s})$ was recorded. The highest DIM values measured in the simultaneous monitoring survey in the bay also were recorded on the same day in February 2005 (Bizsel et al., 2008). Since highly variable characteristics of the river and plume zones were obvious, the daily loads were calculated only for the periods when the dam was closed (i.e. the 2 periods sampled in August 2004 and 2005) were excluded, since the applied irrigation regime was unpredictable). Excluding that on the PO_4^{3-} , the profound effect of the magnitude of the river flow on these calculated loads became apparent (Table 6). Low concentration during high flow period and high concentration during low flow period was the main factor that mitigated the difference between PO_4^{3-} loads during these opposing periods. For the others, the rule that "the higher the flow, the higher the load" was valid, even in the case when the concentrations were almost equal.

To be able to infer concrete conclusions based on all the results and discussion presented in the above paragraphs, the physical properties of the study area and the river should be reviewed more comprehensively. An anti-cyclonic current system close to the plume zones and reference station has been reported by Sayn (2003) and Karahanli (2002). The main driving force of this system is the NW winds. When triggered, the system first moves the water masses in the study area southward towards Homa Lagoon and then circulates them back through a westward curve to the mouth of the river and plume zones. When the wind blows SE with a sufficient velocity, the system becomes cyclonic and the water masses from Homa Lagoon move towards the river mouth and then circle back again through a westward curve. In August 2004 and 2005, the wind blew from the NW with an average velocity of >9.7 m/s and the anti-cyclonic current system was active in the study area. While the wind blew from the SSE with an average velocity of 11 m/s the cyclonic current system was active in April 2005. During other periods, the wind velocity was below the level (< 5 m/s) that may trigger the current system in both possible directions.

Conclusions

The physical properties of the water masses in the study area are clear evidence that prove the impact potential of the Gediz River on Homa Lagoon. Furthermore, the very same properties restrict the impact potential of the Gediz River on Izmir Bay during extremely high flow periods. In regard to the river's properties, the most important events to be considered are the initial floods of the season, particularly those following prolonged dry periods. These floods frequently contain high concentrations of nutrient materials, dissolved or particulate, which have accumulated within the watershed or are stored in sediments in the upper reaches of individual streams. In this study, this was the case observed in terms of phosphate and silica. Nutrient level comparisons among rivers and/or estuaries in Turkey and elsewhere are given in Table 3. As seen in the table, all DIMs have quite high levels in the Gediz River.

Another significant point to be considered is the strong variability caused by the episodic factors affecting the river's regimes. The results obtained in this study showed highly variable and sitespecific/time-specific interactions in biogeochemical processes occurring between freshwater, seawater, and sediment. Moreover, there were anthropogenic factors (i.e. the dam, irrigation networks, wastes, etc.) and meteorological factors (i.e. precipitation, evaporation, etc.) that interfered in these processes. To be able to resolve, or at least predict, such variability, the rivers and estuaries must be monitored with much finer spatio-temporal resolution at least once or perhaps several times per day during periods of high flow variability. Without attaining such a volume of data, any effort on any scale for mitigating river or coastal pollution, sustaining, protecting or recovering the coastal ecosystems, and enhancing agricultural and fisheries production on and around these environments will at best be admirable, but insufficient and thus expensive attempts.

| Date | Discharge | NO_2^- | NO_3^- | NH_4^+ | PO_4^{3-} | SiO_2 |
|--------|-----------|-----------|-----------|-------------------|-------------|-----------|
| | (m^3/s) | (ton/day) | (ton/day) | (ton/day) | (ton/day) | (Ton/day) |
| Nov-05 | 5.2 | 0.03 | 0.06 | 1.48 | 0.36 | 2.75 |
| Feb-05 | 123.0 | 1.09 | 14.17 | 23.97 | 0.49 | 74.33 |
| Apr-05 | 18.7 | 0.19 | 2.64 | 0.75 | 0.07 | 0.45 |

Table 6. Dissolved inorganic nutrient loads when the Gediz River is flowing at its capacity.

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