

Investigation of Water Quality and Heavy Metal Levels in Sediment in Kucuk Menderes River Deltaic Zone (Selcuk, Izmir, Turkey)

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Abstract: Kucuk Menderes river deltaic zone is the most important wetland in the Western part of Turkey. Water and sediment quality parameters were collected monthly from May 2003 through April 2004 at six stations. pH, conductivity, temperature, dissolved oxygen, nutrients (Nitrate-nitrogen, ammonium-nitrogen, phosphate-phosphorus) and chlorophyll a were measured in water column. Cu, Zn, Mn, Cd, Cr, Ni and Pb were investigated in sediment samples. A large spatial and temporal variability in dissolved oxygen was identified which can probably be related seasonal effects, specification of river and anthropogenic impacts. Kucuk Menderes river deltaic zone was found first quality in terms of nitrate concentrations but third quality for ammonium and dissolved oxygen levels according to Turkish regulation of quality criteria for the freshwater resources. The major factors influencing the nutrients are suggested to be agricultural runoff and domestic sewage. Metal concentrations found in this study were compared with the sediment quality guidelines for freshwater ecosystem. The concentrations of Cr, Ni, Zn, Cu and Mn were above the threshold effects levels especially in station 4 (Belevi bridge) because of industrial and agricultural activities.

Key words: Water quality, Kucuk Menders deltaic zone, nutrients, heavy metals, chlorophyll a

INTRODUCTION

Coastal areas such as estuarines, deltaic zones, lagoons and bays are ecosystems which have an indispensable function in sustainability of natural equilibrium and produce highest biologic output all over the world. Particularly, coastal wetlands are habitats which are under the pressure/risk of toxic and anthropogenic waste waters discharged by domestic and industrial processes as well as agricultural activities.

The major functions of wetlands to hold and recycle nutrients, provide wildlife habitats, stabilize shorelands, control and buffer natural floods, recharge groundwater, provide treatment for pollutants in water and so on (Jing *et al.*, 2001). For all these reasons, water analysis of coastal wetlands or deltaic zones and build up of metals in sediments play a very important role in environmental implications for local communities. Waters of coastal deltaic zones are important locations for nutrient pollution and as such should be included in routine environmental monitoring although, they do not provide quantative data on the absolute degree of pollution.

Kucuk Menderes (K. Menderes) deltaic zone is an important nature reserve and has recently been designed as a Ramsar (The convention wetlands of international importance especially as waterfowl habitat). Because K. Menderes has been contaminated with fertilizes and drugs from agricultural areas, domestic and industrial wastes dumped into the river in and around settlements through

which it flows with being hardly or never treated, water pollution has dramatically increased in recent years. Although, there are research and studies into fauna and flora of K. Menderes river and deltaic zone (Ustaoglu and Balik, 1990; Ustaoglu *et al.*, 2000; Aysel *et al.*, 2002; Yildiz *et al.*, 2010) the very few published data are available on water quality and heavy metal concentrations (Turgut, 2003; Gundogdu and Ozkan, 2006; Boyacioglu, 2010).

The aim of this study was to determine water quality and the heavy metal concentrations on sediment and assess pollution status of the Kucuk Menderes deltaic zone, an important wetland of Aegean region.

Description of the site: Kucuk Menderes, is one of important rivers such as Gediz and Buyuk Menderes in Aegean region. Covering about 3500 km², K. Menderes river basin area extends westward to Aegean sea coast in Western Turkey, being morphologically divided into four subbasins from East to West namely Kiraz, Odemiş-Tire, Bayindir-Torbali and Selcuk (Pusatli *et al.*, 2009).

Approximately 175 km long the river, forms an alluvial plain of 11×5 km in area and flows into Aegean sea. Data of 1975-2000 years was used to determine climatic characteristics of K. Menderes deltaic zone according to which Selcuk was found to be of Mediterranean Thermic Regime, a type of climate having hot summer and mild winter with annual rainfall of 673.3 mm (Sutgibi, 2009). Approximately one thirds of the watershed is used for

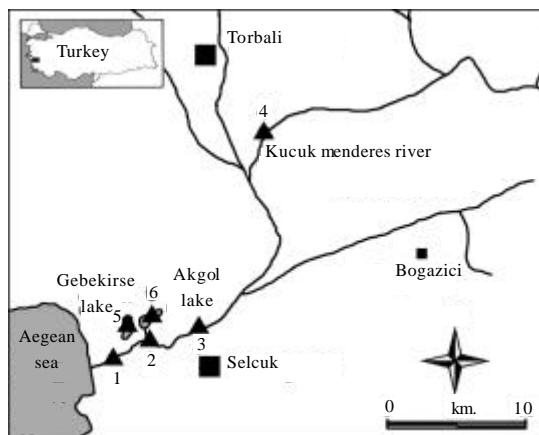


Fig. 1: Map of the study area and sampling stations

agricultural activities. Main crops grown in area are olive, cotton, cereals, potatoes and tobacco. Other uses are for forests, meadows, urban settlements, roads and industries (Gundogdu and Ozkan, 2006).

Whole of the K. Menderes river deltaic zone covers 1500 ha area and is under the protection of Department of National Park and Wild Life of Forest and Environmental Ministry of Turkey. According to Ramsar classification this wetland is Marine/Coastal, Saline water Wetland (Somay *et al.*, 2008).

Lake Gebekirse with 75 ha in area and 5 m dept, the nearest lake to the Aegean sea is protected due to its ornithological and vegetation values as Lake Gebekirse Wild Life Protection Area. Separated from lake Gebekirse by hill, Akgol has 74 ha in area and 4 m depth. The deltaic zone covers Akgol and Gebekirse lakes as well as a large area of swamp called Elaman with the latter being under protection as wetland.

K. Menderes river flows through counties of Beydag, Odemis, Tire, Bayindir and Selçuk, carrying domestic and industrial wastes as well as pollution caused by agricultural fertilizers and drugs into Aegean sea.

This study sampled two lake (Gebekirse ve Akgol) and 3 river station in K. Menderes deltaic zone. Samples were collected from the station under the bridge between Selçuk and Ozdere (Station 1), junction of Akgol with K. Menderes river (Station 2), Zeytinkoy bridge (Station 3), Belevi bridge (station 4), Gebekirse lake (Station 5), Akgol (Station 6) (Fig. 1).

MATERIALS AND METHODS

To determine water and sediment quality of K. Menderes river deltaic zone, samplings were made on a monthly basis at four sampling points in the river (Station

1-4) and at two (Station 5, 6) in the lake from May 2003 to April 2004. During the sampling, water temperature (T) and electrical conductivity were measured by YSI 30 conductivity meter whereas Dissolved Oxygen (DO) determined by WTW Oxi 330i oxygen meter and pH determined using a WTW 330i model pH meter at all the stations. Collected water samples were transferred to the laboratory in a cool box for further analyses. Samples were kept in the refrigerator until analyses on the following day. Nutrients (Nitrate-nitrogen, ammonium-nitrogen, phosphate-phosphorus) were determined spectrophotometrically (APHA/AWWA/WPCF, 1995). Chlorophyll a (chl a) values were measured *in vivo* by Turner design 10 AU Fluorometer.

The sediment samples were collected with Van-veen grap from the surface sediment. Having been air dried, sediment samples were passed through a sieve of 2 mm prepared for analysis (Jackson, 1967). Metal contents in the sediment samples (Zn, Mn, Cu, Cd, Cr, Ni and Pb) were extracted by HNO_3 +HCl extraction method to measure the related values by means of Atomic Absorption Spectroscopy (Varian SpectrAA.220) (Kick *et al.*, 1980; Slawin, 1955). Standard solutions (ICP Multi Element Standart Solution IV CertiPUR 1.11355.0100) were used for calibration.

Normal distribution of the data was tested using Kolmogorov-Simirmov and homogeneity of the variances tested by Levene Statistical Analyses. It was found that some of the data was not normally distributed, based on which non-parametric Kruskal-Wallis and Mann Whitney U-tests were performed to determine whether differences among sampling stations and seasons were significant or not. SPSS 16.0 for Windows was used to perform all statistical analyses.

RESULTS AND DISCUSSION

Surface water temperatures in K. Menderes deltaic zone ranged from 9.2-28.7°C (Table 1). Because there are no endustrial processes in Selçuk located in K. Menderes deltaic zone, any sudden temperatural increases or decreases are not observed.

pH varied between 6.4 and 8.9 (Table I). pH during summer months differed from that of winter and spring months, with those in spring and autumn also being different from each other ($p < 0.05$). Differences of pH between the stations were of no significance ($p > 0.05$). According to the Regulations of Water Pollution and Control (RWPC) issued by the Ministry of Environment and Forestry, K. Menderes deltaic zone was found to be first class in pH values. Those between 6.5 and 9.5 in natural values are also considered to be of first class. Somay *et al.* (2008) found that pH changed from 7.0 and

Table 1: Pysico-chemical parameters at sampling stations in K. Menderes river deltaic zone (Minimum, maximum and mean±standart error)

Parameters	Temperature (°C)	Dissolved oxygen (mg L ⁻¹)	Conductivite (μS cm ⁻¹)	pH
Station1	9.2-28.2 18.3±2.00	0.0-7.90 4.3±0.70	1385.5-11600 3222.9±1060.9	6.5-8.6 7.6±0.1
Station 2	9.5-28.7 18.9±2.10	0.8-9.30 5.5±0.80	341-5910 2498.6±537.5	6.4-8.9 7.8±0.2
Station 3	9.9-27.1 18.9±2.00	0.0-12.7 5.8±1.00	317-4100 2023.1±439.7	6.8-8.7 7.8±0.1
Station 4	10.6-28.1 18.4±1.80	0.0-7.80 3.4±0.80	328-4937 2076.3±484.8	6.7-8.7 7.8±0.1
Station 5	10.0-27.5 19.1±1.90	5.3-10.2 7.5±0.40	518-11800 6205±1179.7	7.1-8.6 7.7±0.1
Station 6	8.9-26.3 18.6±1.50	2.4-11.0 6.4±0.80	737-6960 3119.8±659.5	7.0-8.3 7.7±0.1

9.45 in the section including Selcuk plain and coastal wetland of K. Menderes river which is consistent with the values of pH that we established.

Considering mean values of dissolved oxygen, the lowest concentration was observed in Station 4. Those of dissolved oxygen tend to significantly oscillate in the river stations (Table 1). Critical values were seen due to industrial and domestic wastewaters from Torbali and its adjacent area (<5 mg L⁻¹) particularly in station 4 because of which fish were found to have been killed in the station of Belevi bridge in September 2003. In addition according to criteria of classification of intra-continental water sources in regulation for water pollution, assesment of annual means shows that station 1, 2, 3 and 4 were of third class while stations on lakes with secondary class waters (Anonymous, 2004). Lakes of Gebekirse and Akgöl showed more stable in dissolved oxygen. Station 5 was different from station 1 and 4 ($p<0.05$).

Conductivity values were observed to have significantly ranged from 385.5-11600 μS cm⁻¹ especially in station 1 which was accounted for by flow of seawater into river which was also seen in Lake Gebekirse (Table 1). Station 5 was statistically different from stations 2, 3, 4 and 6 in conductivity ($p<0.05$). Somay *et al.* (2008) reported that seawater has penetrated lake owing to its carstic structure. Salinity in the lake has been caused by the fact that groundwater has been pumped away for irrigation and occasional areas of K. Menderes delta are lower than sea level and its associated seawater into the lake (Somay *et al.*, 2008). Conductivity varied seasonally. Values of conductivity were found to increase especially in summer when evaporation is highest with summer conductivity being different from that of winter and spring months.

Ammonium nitrogen concentrations ranged from nd (non detected) to 3.8 mg L⁻¹ with highest annual means in stations 4 and 3 (1.92 ve 1.63 mg L⁻¹) (Fig. 2). Because annual means of stations 1, 2, 3 and 4 are above 1 mg L⁻¹,

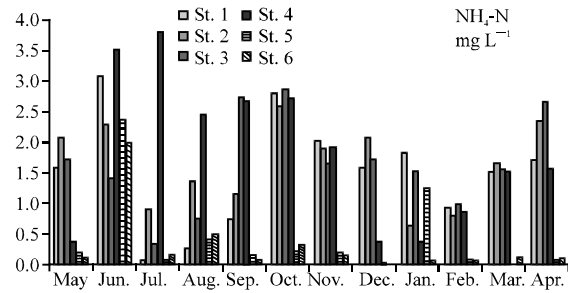


Fig. 2: Temporal and spatial distribution of NH₄-N in K. Menderes deltaic zone

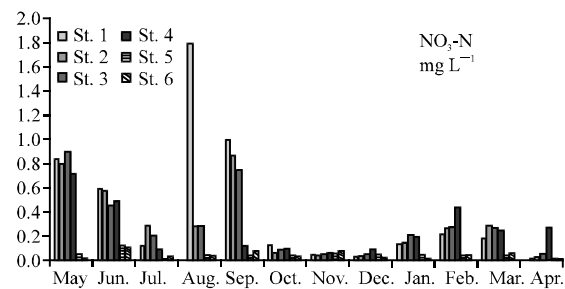


Fig. 3: Temporal and spatial distribution of NO₃-N in K. Menderes deltaic zone

they have third class water quality (Anonymous, 2004). Ammonium is generally dominant nutrient in the Kucuk Menderes river deltaic zone compared with nitrate nitrogen and phosphorus. Turkoglu *et al.* (2007) found similar conclusions in the study on Goksu, Seyhan, Ceyhan, Lamas and Berdan rivers in Mediterranean region with all their ammonium concentrations exceeding limit values. Station 5 and 6 on the lake showed minimal concentrations of ammonium nitrogen, differing from those of other stations ($p<0.05$).

Highest nitrate value was determined in station 2 in K. Menderes river in August (1.78 mg L⁻¹). Nitrate nitrogen values ranged from 0.1-0.12 mg L⁻¹ for Gebekirse and Akgol lakes (Fig. 3). Statistically significance in nitrate was found between stations 2, 5, 6 ($p<0.05$). Highest annual mean nitrate concentrations were established in station 2 (0.42 mg L⁻¹) which was particularly chosen in the junction between K. Menderes River and Akgol lake where there are stabilizing ponds of the treatment plant of Selcuk in which occasional problems could emerge. Therefore, this situation can change nitrate values in the river concerned. According to Turkish regulation of quality criteria, assesment of annual means shows that nitrate values in all the stations are of first quality because annual nitrate means is >5 mg L⁻¹. Another study made in K. Menderes river

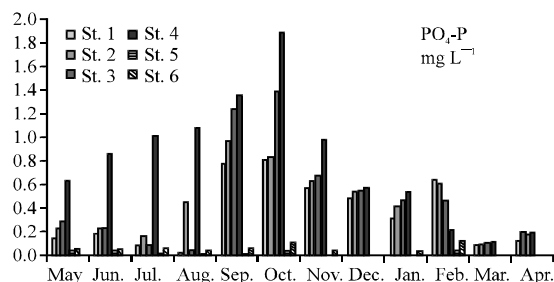


Fig. 4: Temporal and spatial distribution of $\text{PO}_4\text{-P}$ in K. Menderes deltaic zone

indicated that nitrate values have first quality which is consistent with those of our study (Boyacioglu, 2010). On the other hand mean values of nitrates at all sampling sites were higher than those of $100 \mu\text{g L}^{-1}$ reported by Meybeck as mean nitrate concentrations found in unpolluted rivers (Meybeck 1982).

Phosphate concentrations varied between 0.03 and 1.88 mg L^{-1} at the river stations with the highest of all being at station 4 in October (Fig. 4). The other river stations showed highest phosphate concentrations in September and October, when primary production was low and rainfall extremely absent. Similar observations were reported from the River Pinios in Greece as well (Bellos *et al.*, 2004). The lake stations however, showed significantly low concentrations with a maximum of 0.1 mg L^{-1} . Phosphate concentration in clean water typically ranges from 0.01 - 0.1 mg L^{-1} (Wetzel, 1983) which is why Gebekirse and Akgol lakes are included in the category of clean water. The statistical analysis found significant differences between stations 5 and 6 and 1-3 ($p < 0.05$). There were no seasonal variations in ammonium and nitrate ($p > 0.05$) with only statistically significant changes in phosphate in spring and autumn ($p < 0.05$).

Examination of total inorganic nitrogen (TIN)/ PO_4 ratios showed them to range between 4 and 8 in K. Menderes deltaic zone. Phosphate is a production limiting element in fresh water ecosystems (Mallin *et al.*, 1999; Vilicic *et al.*, 2001; Voutsas *et al.*, 2001). However, there are some exceptions to these generalizations usually associated with anthropogenic processes such as agricultural drainage and discharge of domestic wastewaters into the lake and river where (TIN)/ PO_4 values were therefore found to be low (< 16). Effects of domestic and agricultural waste waters were quite evident at station 4 in particular in Kucuk Menderes. According to Jarvie *et al.* (1998), ratio values < 16 were described to be polluted in rivers.

Chlorophyll a (chl a) values was found to have ranged from nd to 13.8 mg L^{-1} in which K. Menderes delta

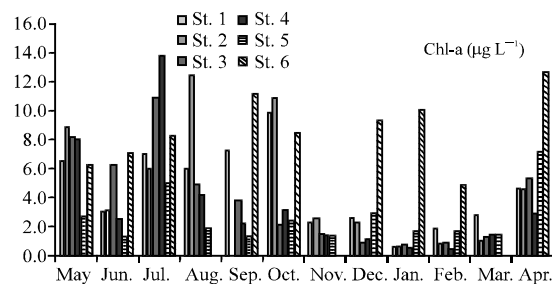


Fig. 5: Annual mean and SE (Standart Error) values of Chlorophyll a (chl a) at the sampling stations

lies. Highest values at lake stations were $7.2 \mu\text{g L}^{-1}$ and $12.8 \mu\text{g L}^{-1}$ in Gebekirse and Akgol lakes in spring, respectively (Fig. 5). The station on Akgol showed a maximum means of chl a ($8.74 \mu\text{g L}^{-1}$) which was slightly higher than threshold values ($8.0 \mu\text{g L}^{-1}$) used to control eutrophication of the lakes and reservoirs (Anonymous, 2004). Morkoc *et al.* (2009) reported chl a values ($41 \mu\text{g L}^{-1}$) in Omerli reservoir and explained by the fact that phytoplankton flourishes in the surface layer where light and nutrient inflow are abundant. Chlorophyll a concentrations maintained an expected seasonal variation and higher values were observed at times of intense solar radiation and increased temperatures which are the factors to affect photosynthesis (Chau and Jin, 2002). K. Menderes rivers showed lowest chl a values of $0.6 \mu\text{g L}^{-1}$ at stations 2 and 4. A study made in Gediz, one of the major rivers flowing into Aegean sea exhibited higher chl a concentration than that of K. Menderes river systems which is accounted for by the fact that a dense nutrient discharge dumped into the river, Gediz with great fluctuations (1.05 - $29.2 \mu\text{g L}^{-1}$) in phytoplankton life cycle stimulated by high nutrient concentrations (Growth phase, death phase) (Sunlu *et al.*, 2002). Conclusion from the statistical analysis found considerable differences in chl a levels between station 6 and stations 3, 4 and 5 ($p < 0.05$).

To determine the trophic state of the Gebekirse lake (Station 5) and Akgol (Station 6), Carlson method was applied to chlorophyll a values (Carlson, 1977). The Carlson's Trophic State Index (TSI) are calculated according to the following equations:

$$\text{TSI}_{\text{chl a}} = 9.81 \ln(\text{chl a}) + 30.6$$

where, chl a concentrations are expressed in $\mu\text{g L}^{-1}$. TSI values < 40 reflect oligotrophic between 40 and 50 mesotrophic, between 50 and 60 eutrophic and > 70 hypereutrophic conditions. TSI values calculated according to chl a ranged from 33-50 in Gebekirse lake

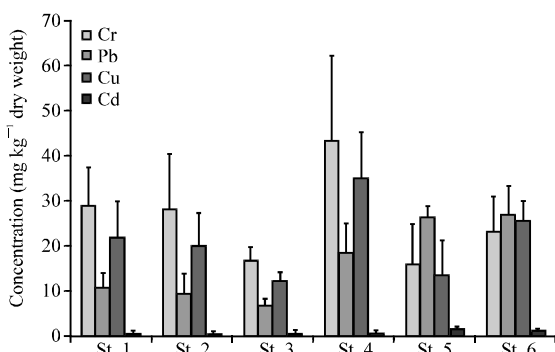


Fig. 6: Annual mean and SE (Standart Error) values of Cr, Pb, Cu, Cd at the sampling stations

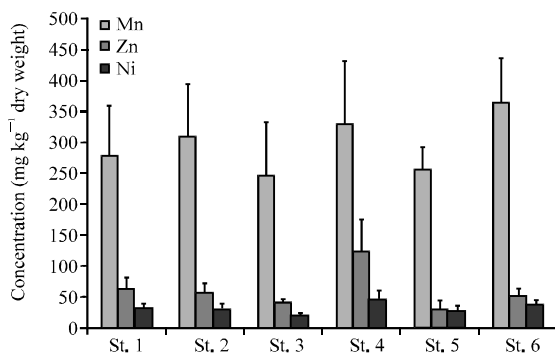


Fig. 7: Annual mean and SE (Standart Error) values of Mn, Zn, Ni at the sampling stations

with an annual means of 39 while they varied between 31 and 56 with a yearly means of 46. According to Carlson's Trophic state indice, Gebekirse was of oligotrophic whereas Akgol of mesotrophic characters. Similarly Tahtali reservoir remained in the oligotrophic category according to TSI values of chl a and secchi disk (Aksu *et al.*, 2011).

It followed from annual means changes of chrome and zinc in sediments in K. Menderes deltaic zone that maximum values were from station 4 (Fig. 6 and 7). Chrome concentrations ranged from 5.04-69.25 mg kg⁻¹ dry weight (d.w.) while zinc concentrations varied between 16.2 and 227.4 mg kg⁻¹ d.w. with lowest annual means of zinc and chrome at station 5 on Gebekirse lake. Station 4 proved different from all the other stations in Cr and Zn variations ($p < 0.05$). In addition, Zn concentrations were different between stations 1 and 5 ($p < 0.05$). Because standards have not been established concerning heavy metals in sediments of freshwater ecosystems in Turkey, the study compared them with Threshold Effect Concentrations (TEC) by MacDonald *et al.* (2000). The TEC's were aimed at identifying contaminant concentrations below which harmful effects on sediment inhabiting organisms were

not expected. Industrial and domestic waste waters from Torbali and Tire in the K. Menderes river basin where station 4 exists on Belevi bridge include, textile, leather and olive oil by products thus station 4 has higher annual Cr and Zn means than given standard values (43.4 and 121 mg kg⁻¹ d.w) for chrome and zinc as 43.6±18.9 and 124.24±52.1 mg kg⁻¹ d.w, respectively. Akcay *et al.* (2003) conducted a study in Buyuk Menderes and Gediz rivers into Aegean sea to discover that chrome values of 170 and 220 mg kg⁻¹ for Gediz and of 160 and 195 mg kg⁻¹ for Buyuk Menderes both of which were remarkably higher than those for Kucuk Menderes. Oner and Celik (2011) found higher zinc values in sediment (60.7 and 279.7 mg kg⁻¹) in Gediz river than K. Menderes.

Annual means of nickel and copper in sediment showed similar variations with highest means for them at station 4 and lowest at station 3 (Fig. 6 and 7). Nickel and copper concentrations ranged from 13.39-68.25 mg kg⁻¹ d.w and 6.9-58.35 mg kg⁻¹ d.w, respectively. From examination of annual nickel concentrations it follows that all those but station 3 had more than the standard value of 22.7 mg kg⁻¹ d.w. As with annual copper variation however, none but station 4 was <31.6 mg kg⁻¹ d.w which is the threshold value for copper. Following the statistical assesment, Nickel concentration at station 4 differed from those at stations 1, 2, 3 and 5 ($p < 0.05$). On the other hand, copper concentration at station 4 varied from those at other stations ($p < 0.05$). In addition, station 3 was different from stations 1 and 6 in copper and nickel ($p < 0.05$). Nickel and copper concentrations in Gediz river varied between 44.2 and 69.4 and 53.7 and 96.5 mg kg⁻¹ d.w, respectively both of which were remarkably higher than those in Kucuk Menderes (Oner and Celik, 2011).

Annual manganese concentration was highest at stations 6 and 4 and ranged from 152.1-439.2 ppm at all stations with lowest concentration at station 3 (Fig. 7). Statistical analysis showed that concentration at station 6 was considerably different from those at station 3 and 5 ($p < 0.05$).

Annual lead and cadmium concentrations at the lake stations were much higher than those of the river stations (Fig. 6). These metals may be in lake sediments through indirect discharge (Industrial and agricultural activities) or from atmospheric deposition (released from car exhaust and burning coal or oil). Highest means values of lead were 26.99±6.5 and 26.44±2.5 mg kg⁻¹ d.w. at station 6 on Akgol and station 5 on Gebekirse lakes whereas those were 1.34±0.45 mg kg⁻¹ d.w. and 1.78±0.46 mg kg⁻¹ d.w. for cadmium at the same stations, respectively. The values measured for lead in K. Menderes deltaic zone were less than that of 35.8 mg kg⁻¹ d.w., the threshold value while

those for cadmium were $>0.99 \text{ mg kg}^{-1} \text{ d.w.}$, the threshold value. Lead values at stations 1, 2 and 3 were significantly different from those at 4, 5 and 6 ($p<0.05$). Cadmium concentrations at station 5 were different from all the stations. On the other hand station 6 values varied from those of 1, 2, 3 and 4 stations ($p<0.05$).

The study made in Buyuk Menderes river found that concentrations of copper, nickel, manganese and of lead ranged between 130 and 150, 168 and 418, 380 and 420, 35 and 75 mg kg^{-1} , respectively. The same study found the range of values from 108-152, 101-129, 480-550 and $105\text{-}140 \text{ mg kg}^{-1}$ for copper, nickel, manganese and lead, respectively in Gediz river which were all much higher than those found in K. Menderes (Akcaý *et al.*, 2003).

In addition, there were no seasonal differences for Pb, Cd, Zn, Ni and Cu values ($p>0.05$). Manganese values varied in autumn and winter and those for Cr showed considerable variations in autumn and spring ($p<0.05$).

CONCLUSION

Kucuk Menderes river deltaic zone was found first quality in terms of nitrate concentrations but third quality for ammonium and dissolved oxygen levels according to Turkish regulation of quality criteria for the freshwater resources due to the agricultural activities and industrial wastewater discharges. In addition, the results of the present study revealed that the trophic state of the Gebekirse was of oligotrophic whereas Akgol of mesotrophic characters according to Carlson's Trophic Index of chl a. Due to the fact that agricultural activities are still taking place around the lakes, nitrogen and phosphorus are unalterable discharged into the lakes. Although Akgol is mesotrophic the lake has the potential to be come eutrophic the situation continuing.

Untreated or insufficiently treated industrial wastewaters from Torbali and Tire in the K. Menderes river basin where station 4 exists on Belevi bridge include, textile, leather and olive oil by products, thus station 4 has higher Cr, Zn, Ni, Cu and Mn concentrations than sediment quality guidelines for freshwater ecosystems.

It is believed that these apportionment results could be very useful to the local authorities for the pollution control of the K. Menderes deltaic zone.

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