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Dissolved and particulate trace elements' configuration: Case study from a shallow lake

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Trace element distribution was monitored for Uluabat lake water polluted with point and non-point sources in Bursa. An examination of Zn, Cr, Ni, Cu, Pb, As, B concentrations during the study period indicated that the particulate phase at the bottom of the water column were high in regard to dissolved phase. The source of trace elements in the deeper parts of the water column was derived from the higher concentrations of suspended solids present. Storm conditions and resuspension process in the lake was targeted as the source of trace elements' configuration in the dissolved and particulate phases. Significant correlations were found among temperature, pH, organic matter percentage, suspended solids, chlorophyll-a and particulate trace elements parameters. Factorial Anova Analysis was performed to help to understand the effects of parameters on adsorption of trace elements. Decrease in water level, increase of pH, organic matter percentage and suspended matter were appeared responsible for the increase of dissolved and particulate trace elements concentrations in summer season. Especially Cr, Zn, Pb and Cd concentrations were detected higher than the standards of EPA and WHO. The concentrations of trace elements in water column have to be monitored and the external loading with heavy metals coming from point and non-point sources has to be reduced for the conservation of ecological values.

Key words: Trace elements, dissolved phase, suspended particulate matter, Lake Uluabat.

INTRODUCTION

Certain heavy metals and trace elements in the form of dissolved and suspended particulate matter can introduce easily into the sediment layer (Stumm and Morgan, 1996; Sigg et al., 1987). Dissipation of trace elements from the water column is originated by the cycles of major elements in lake as photosynthetic production, $CaCO_3$ formation, iron and manganese oxides, aluminium and silicates (Stumm and Morgan, 1996). The pH interval in natural waters is between 7 to 8.5 which is the most acceptable range for adsorption of trace element ions to hydroxides and organic particulates. The heavy metal cations are completely

released under circumstances of extreme acidic conditions (Shukla et al., 2002). Temperature, pH, redox potential, organic matter, ion exchange processes and microbiological activity affect some characteristics of trace elements such as mobility and bioaccumulation properties (Filgueiras et al., 2004). International standard values are used for determination of the evaluation of heavy metal's toxicity. Values of WHO and EPA guidelines can be given as an example for the standards (Anonymous, 2006a, b). The study site is shallow Lake Uluabat. It is subject to the "Convention on Wetlands of International Importance, especially as Waterfowl Habitat" (the RAMSAR Convention), which was approved in Ramsar, Iran in 1971. It was selected as the study area due to the international importance of this lake. The surface area of the lake is 161 km^2 at maximum water level and 138 km^2 at minimum water level and its average depth is 3 m (Dalkıran et al., 2006). Lake Uluabat has been contaminated by domestic and industrial waste waters and polluted runoff waters resulting from rainwater for many years. Particular problems of the Lake are eutrophication (Akdeniz et al., 2011) and heavy metal pollution. There are 67 residential areas, factories, workplaces, agricultural operations and mines in the basin of the Mustafakemalpaşa (MKP) creek which feeds the lake (Dalkıran et al., 2006). Furthermore, the MKP creek carries a significant amount of suspended solids, which is linked to a 12% reduction in the surface area and the volume of the lake, recorded between 1984, 1993 and 1998 (Aksoy and Özsoy, 2002). One of the most important centers in the MKP Basin, Tavşanlı has a sewage system without any treatment facility and the wastewater of Tunçbilek Thermal Power Plant and lignite plant are discharged to Orhaneli creek after being physically treated. The sewage water of MKP creek, wastewater of the leather organized industrial zone with physical treatment, wastewater of 27 dairy and butchery plants are discharged to the MKP creek without any treatment. In addition, there are 16 residential areas along the creek. The domestic and industrial wastewater of Akçalar is discharged to Akçalar creek, and then finally to Uluabat Lake (Dalkıran et al., 2006). Uluabat, Atabay and Karaoğlan pumping stations is that some of the neighbouring residential areas and factories discharge their wastewaters into the drainage canals of State Hydraulic Works (SHW). Reverse current occurs in the Kocasu creek draining the lake, because of flow rate is increased by rainfall during winter. The Kocasu creek formed by the merging of the Nilüfer and Simav creeks carry pollutants into the lake.

The objective of this study is to examine the concentration of selected trace elements in dissolved and particulate phase at 8 stations in Lake Uluabat annually between May 2008 and 2009. In addition, it is aimed to evaluate the effects of pH, temperature, organic matter percentage, suspended solids, chlorophyll-a and electrical conductivity parameters against trace element adsorption.

MATERIALS AND METHODS

Study area and sampling

The water and sediment samples were taken once in a month for annually, between May 2008 and 2009 in order to observe seasonal differences. The samples were taken on the same day from 8 stations, which were selected according to their distances from the contaminant sources in the lake and their hydrodynamic characteristics. The sampling stations presented different degrees of pollution around the lake. The first station is located in the outflow of Lake Uluabat. The second station is located near to the Atabay pumping station. Whereas the third station represented the north part of the lake, the fourth station is located in the entrance of the Mustafakemalpaşa creek. The fifth station represented the southwestern part of Island Mutlu which is located in nearby of Eskikaraağaç village. The sixth station is situated between Island Mutlu and Gölyazı village. The seventh station is presented at the near of Eskikaraağaç village. The new planned highway would pass close to these villages and finally the eighth station is located at the near of Akçalar village. The coordinates of sampling stations were determined with GPS and are shown in the map (Figure 1) and in Table 1. Determination of coordinates was based on European 1950 UTM coordinate system by the help of Magellan XL handheld GPS.

Samples were taken from all the sampling stations at two heights within the water column. The water samples at 0.5 m below the surface were taken by using the precleaned dark polyethylene bottles (Nguyen et al., 2005; An and Kampbell, 2003; Katip, 2010; İleri, 2010) and the others were taken from the lake bottom (just above the layer of the sediment) by using a precleaned standard sampling device (Hydro-Bios brand), which can take samples along the depth. Samples were transferred into dark-colored polyethylene (PE) bottles that had been washed with HNO$_3$ and deionized water. During sampling in situ, Temperature (T), pH and Electrical conductivity (EC) were measured using a HACH brand Sension 156 device (Burton and Pitt, 2002; Katip et al., 2012a, b). Sediment samples were taken from the top 5 cm of the sediment with an Ekman sediment sampler (Hydro-Bios brand) and transferred to the laboratory in plastic bags (Burton and Pitt, 2002). Arm-length gloves were used during sampling (Nguyen et al., 2005). A 1-liter water sample was taken along the water column in order to determine the chlorophyll-a concentrations, which is known to be linked to suspended solid concentration. In summer, as the algae increases, the SS concentrations also increase (Stumm and Morgan, 1996). The samples were transferred into the laboratory in dark-coloured PE bottles (Parsons and Strickland, 1963).

Sample handling and analysis

Suspended solids were determined gravimetrically by filtering 100 ml sample through a pre-weighed Milipore filter paper (pore size of 0.45 μm) (APHA, 1998). After the 1 L of sampled water was filtered through a GF/C filter paper, chlorophyll-a concentrations were measured by extracting the filtered water in 90% acetone and then reading the results on a spectrophotometer at 665, 645 and 630 nm wavelengths (Parsons and Strickland, 1963). Percentage of organic matter of sediment was measured by incineration method. pH and conductivity parameters of sediment were measured by 1 : 10 sediment-water mixture (Radojevic and Bashkin, 1999).

For trace element analyses, the following procedures were implemented. Water samples were filtered through a Milipore filter paper with preweighed 0.45 μm pore-size. The filter papers were then put into precleaned petri dishes and stored in a freezer. The filtered water samples were acidified with 0.2% (v/v) concentrated nitric acid and kept in glass bottles cleaned with detergent, water,
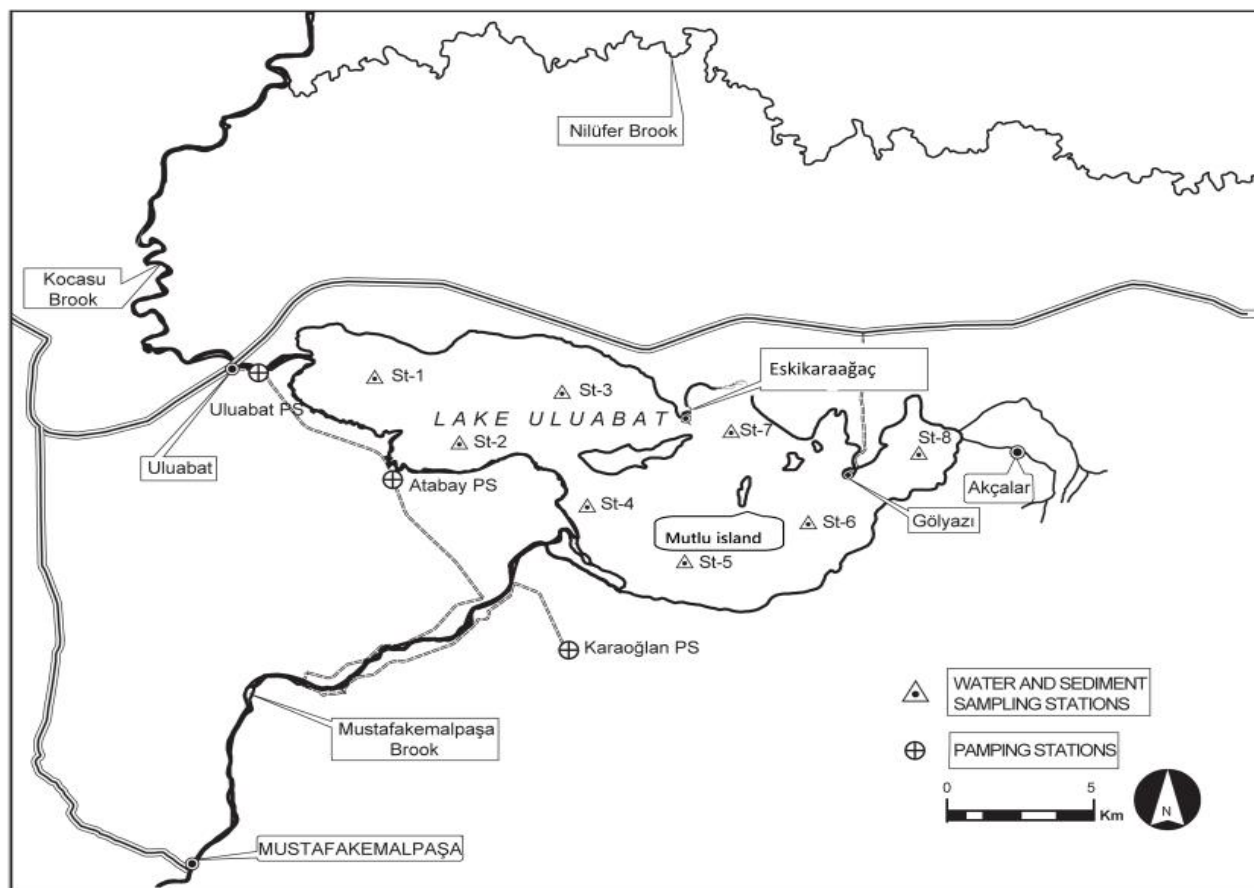
Figure 1. Sampling Stations in Lake Uluabat.

Table 1. The coordinates of sampling stations in Uluabat Lake.

Station No	X (East) (1950 UTM m)	Y (West) (1950 UTM m)
1	626865	4451240
2	629634	4448777
3	633217	4450699
4	633953	4446460
5	637299	4444284
6	641498	4445781
7	638853	4449214
8	645313	4448410

nitric acid and Mili-Q water respectively (An and Kampbell, 2003). The filter papers containing the suspended solids were air dried and reweighed again. They were digested with 4/1 (v/v) HNO_3/HCl mixture using a microwave device. After cooling, digestions were diluted to 30 ml with Mili-Q water. Samples were placed in Teflon cups and digestion operations were performed in a CEM brand Mars 5 model microwave device. Microwave decomposition operations were programmed as a 3-phase process. The device operated at 34.45 kPa for 1 min in the 1st stage, at 172.25 kPa for 5min in the 2nd stage and at 826.8 kPa for 60 min in the 3rd stage (Nguyen et. al., 2005). Trace elements were determined using the VISTA-MPX model of the VARIAN brand ICP-OES device. The operating conditions of the device, the wavelengths used in the detection of the elements and detection limits for analytical methods are shown in Tables 2 and 3 respectively (Anonymous, 2007a).

Three different groups were formed while preparing the standards in order to prevent elements from interfering with each other during detection. The grouping is as follows: 1st Group, Fe, Zn, Cr, Mn, Ni, Cu; 2nd Group, B, Cd, Pb; 3rd Group, As. The element As, in the 3rd group, was analyzed using a hybrid system. A standard stock solution of 1000 µg ml^{-1} (5% HNO_3) was used in the preparation of standards. As the concentrations of trace elements

Table 2. Operating conditions of the ICP-OES.

Parameter	
Power (kW)	1.2
Plasma flow (L min^{-1})	15
Auxiliary flow (L min^{-1})	1.5
Nebulizer flow (L min^{-1})	0.9
Replicate read time (s)	5
Instry stabilization delay (s)	30
Sample uptake rate (s)	40
Pump rate (rpm)	15
Rinse time (s)	10
Replicates	3
Display mode	Axial
Gas	Argon

Table 3. Wavelengths used in the detection of the elements.

Elements	Wavelength (nm)	Detection limit (µg L^{-1})
As	188.98	3
B	249.772	0.1
Cd	214.439	0.2
Cr	267.716	0.5
Cu	327.395	0.9
Fe	238.204	0.3
Mn	257.61	0.1
Ni	231. 604	0.7
Pb	220.353	1.5
Zn	213.857	0.2

dissolved and particulate in water are very different concentrations according to the each other, three different standard series (low, mid and high) were prepared at ppb level. The device was calibrated using a solution of 5 mg l^{-1} prepared from a Merck Mn solution of 500 mg L^{-1}. The ambient temperature was kept at 25°C to prevent possible expansion during the calibration (Anonymous, 2007a).

Statistical analysis of dissolved and particulate forms of trace elements in water was done. Correlation coefficients (r values) determine the correlations between parameters and p values show the significance levels. Factorial ANOVA Analysis was carried out by using General Linear Model method to be able to understand whether the differences of the trace element concentrations in the dissolved and particulate forms among stations, months and depth were significant. Study sample size is 192. All analyses were done in duplicate. The significance level was detected as p=0.05. All statistical calculations were done with Minitab 15.0 Program (Anonymous, 2007b).

RESULTS AND DISCUSSION

Dissolved trace elements

The concentrations of dissolved trace elements in the samples from Lake Uluabat varied between 0.0653 and 15.7298 mg L^{-1} (Fe), 0 and 0.1732 mg L^{-1} (Mn), 0.0011 and 1.3471 mg L^{-1} (Zn), 0 and 0.3508 mg L^{-1} (Ni), 0.0016 and 1.9597 (Cr), 0 and 0.3846 (Cd), 0 and 0.116 (Cu), 0.0012 and 0.0933 (As), 0.2253 and 5.5038 (B), 0 and 0.5028 mg L^{-1} (Pb), respectively. A comparison between the dissolved trace element concentrations found in Lake Uluabat and other fresh waters is presented in Table 4. It is seen that Fe, Zn, Cr, Ni, B and Pb concentrations in Lake Uluabat are higher than those of other water resources and other elements are within the similar ranges.

The degree of toxicity of dissolved metals according to their annual mean concentrations was evaluated with the help of international standards. Accordingly, As, Ni and B concentrations were found to be high according to standard values for potable water published by the World Health Organization (WHO) (Anonymous, 2006a) and low (except B) according to EPA guidelines (Anonymous, 2006b). Pb concentrations were found to be high according to WHO values and chronic effect values published by the EPA, and low according to the level of acute effect (Anonymous, 2006b). It was determined that mean Mn and Fe concentrations were below the standards. It was determined that Cd concentrations were higher than the standards of both WHO and EPA; Cu concentrations exceeded the chronic toxicity level and were very close to the acute level; Cr concentrations were higher than the chronic toxicity level; and Zn concentrations were higher than both the chronic and acute toxic limit values (Anonymous, 2006b). Table 5 shows the mean dissolved trace element concentrations in Lake Uluabat in comparison with international standard values.

Factorial ANOVA analysis of dissolved trace elements

Differences in the annual mean concentrations of dissolved trace element according to stations, depths and months; and differences in depths according to stations (interaction between station and depths) were examined using analysis of variance. The Factorial ANOVA results for dissolved trace elements are shown in Table 6. Analysis of variance showed significant differences between sampling stations in terms of Cr, Cd, Cu, Ni, B and Pb levels, and non-significant in differences between levels of As, Fe, Mn and Zn. The concentrations of Cr, Cu, Ni, B and Pb were highest at the 1st station, which is close to the outlet of the lake. The Kocasu creek which provides the outflow of the lake and reverse currents occasionally occur in it and Uluabat and Atabay Pumping Stations which are point sources of pollution are close to the 1st station. As the current in the stations 6, 3, 4 and 8 are faster than the other sampling locations, trace elements have a higher chance of being adsorbed to suspended solids and they are far from the pollution source. Trace elements concentrations were determined

Table 4. Dissolved trace element concentrations in Lake Uluabat and other fresh waters.

Elements	References	Mean ± SD
As (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	<0.033
	(Lake Uluabat)	0.023 ± 0.0179
B (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	0.225 ± 0.049
	(Lake Uluabat)	2.1668 ± 0.9964
Cd (mg L^{-1})	Lake Balaton (Nguyen et al., 2005)	0.000002
	River Vistula (Gue´guen and Dominik, 2003)	0.00056 ± 0.000018
	Lake Texoma (An and Kampbell, 2003)	0.020 ± 0.061
	(Lake Uluabat)	0.0116 ± 0.0427
Cr (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	0.004 ± 0.002
	River Vistula (Gue´guen and Dominik, 2003)	0.0013 ± 0.00005
	(Lake Uluabat)	0.0992 ± 0.2347
Cu (mg L^{-1})	Lake Balaton (Nguyen et al., 2005)	0.000475
	Lake Texoma (An and Kampbell, 2003)	0.024 - 0.020
	River Vistula (Gue´guen and Dominik, 2003)	0.03085 ± 0.0008
	(Lake Uluabat)	0.0115 ± 0.0142
Fe (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	0.119±0.093
	(Lake Uluabat)	0.5344 ± 1.3989
Mn (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	0.007 ± 0.018
	River Vistula (Gue´guen and Dominik, 2003)	0.35813 ± 0.00491
	(Lake Uluabat)	0.0116 ± 0.02
Ni (mg L^{-1})	Lake Texoma (An and Kampbell, 2003)	0.005 ± 0.003
	Lake Balaton (Nguyen et al., 2005)	0.0006
	(Lake Uluabat)	0.0304 ± 0.0448
Pb (mg L^{-1})	Lake Balaton (Nguyen et al., 2005)	0.00009
	Lake Texoma (An and Kampbell, 2003)	<0.015
	River Vistula (Gue´guen and Dominik, 2003)	0.00023 ± 0.00001
	(Lake Uluabat)	0.0355 ± 0.0567
Zn (mg L^{-1})	Lake Balaton (Nguyen et. al., 2005)	0.00085
	Lake Texoma (An and Kampbell, 2003)	0.059 ± 0.036
	River Vistula (Gue´guen and Dominik, 2003)	0.09225 ± 0.000966
	(Lake Uluabat)	0.1955 ± 0.2384

as minimum at these sampling stations. It was determined that while elements like Cu, Pb, Hg and Zn are affected by organic ligands, Cd formed a complex with inorganic ligands especially in muddy and summer conditions (Bradl, 2005). Highest Cd levels were found in the 2nd and 1st stations. The relation between the suspended solid substances and the trace elements was presented in Suspended particulate trace elements section.

The molar ratios of B:Fe:Zn:Mn:Cr:Ni:As:Cu:Cd:Pb are 200425:9160:2439:2238:1631:517:240:201:86:171 respectively and their order of size according to their concentrations was B>Fe>Zn>Cr>Pb>Ni>As>Cu>Mn>Cd, which were determined using their annual mean concentrations. Figure 2 shows the changes in the dissolved forms of Cr, Cd, Cu, Ni, B and Pb according to sampling stations. The concentration levels were observed to be low during

Table 5. Mean values of dissolved trace element concentrations in Lake Uluabat and international standard values (Anonymous, 2006 a, b).

Trace elements (mg L^{-1})	WHO	EPA, water quality criteria		Lake Uluabat
	Drinking water	CMC	CCC	
As	0,01 ^{P}	0.34 A,D,K	0.15 A,D,K	0.0182 ±0.0176
B	0,5 ^{T}			2.1668 ± 0.9964
Cd	0,003	0.002 D,E,K	0.00025 D,E,K	0.0097 ± 0.0371
Cr		0.57 D,E,K	0.074 D,E,K	0.0848 ± 0.2092
Cu	2	0.013	0.009 D,E,K	0.0128 ± 0.0141
Fe			1	0.5116 ± 1.2313
Mn	0,4 ^{C}			0.0123 ± 0.0217
Ni	0,02^P	0.47 D,E,K	0.052 D,E,K	0.0304 ± 0.0416
Pb	0,01	0.065 D,E	0.0025 D,E	0.0355 ± 0.0567
Zn		0.12 D,E,K	0.12 D,E,K	0.1595 ± 0.2169

CMC, Acute; CCC, Chronic; P, Provisional value. It is known to be hazardous but there is limited data about its effects on health; T, Provisional data; The measured values are below the refinable level; A, Recommended criterion derived for As (III). Adopted for total As because it shows similar effects with As (V); D, Recommended water quality criterion, based on the criteria for aquatic organisms by use of a conversion factor (CF); E, Standard values measured as a function of the hardness in the water column; K, Adapted from the criteria developed for aquatic organisms in 1995.

Table 6. Factorial ANOVA results of dissolved trace elements.

| Elements	Stations	Depths	Months	Stations*Depths
As	0.411	0.123	0 *	0.959
B	0 *	184	0 *	0.613
Cd	0.002 *	0.545	0.010 *	0.983
Cr	0.008 *	0.763	0.057	0.6
Cu	0.007 *	0.081	0 *	0.632
Fe	0.767	0.621	0.394	0.376
Mn	0.330	0.600	0.516	0.651
Ni	0.004 *	0.175	0.003 *	0.987
Pb	0 *	0.202	0.001 *	0.384
Zn	0.439	0.513	0 *	0.563

* $p < 0.05$.

rainy season with respect to arid season. The monthly variations were statistically significant for As, Cd, Cu, Ni, Zn, B and Pb, and non-significant for Cr, Fe and Mn.

The trace elements with significant variations in monthly concentrations had high concentrations in summer and at the beginning of autumn in September, when there is no rain, and low concentrations in spring, in mid autumn and in winter, when concentrations were diluted by the increased rainfall. While the highest value of Cu was observed in summer, its lowest value was observed in October. This may be because of rainfall increase during this month, transporting more suspended solids to the lake by surface flows. Because if the lake is shallow compared to the winter months it mixes more easily, thereby increasing adsorption. In contrast to other metals, B levels were highest in November. It is thought that this was due to the increase in the flow rate and runoff in this month because of the pollution sources and rainfall. The monthly variations in the levels of dissolved As, Cd, Cu, Ni, Zn, B and Pb are presented in Figure 3.

Stronger winds cause vertical mixing of bottom sediment within the water column. This promotes to bonding between dissolved trace elements and particulates. The annual mean concentrations of suspended solids at the surface and the bottom of the water column were 37.15 and 60.70 mg L^{-1}, respectively. According to Table 6, concentrations showed non-significant differences depending on regions and significant differences depending on sampling stations. Factorial ANOVA analysis showed non-significant variation between the concentrations of dissolved trace elements at the surface and the bottom layers of the
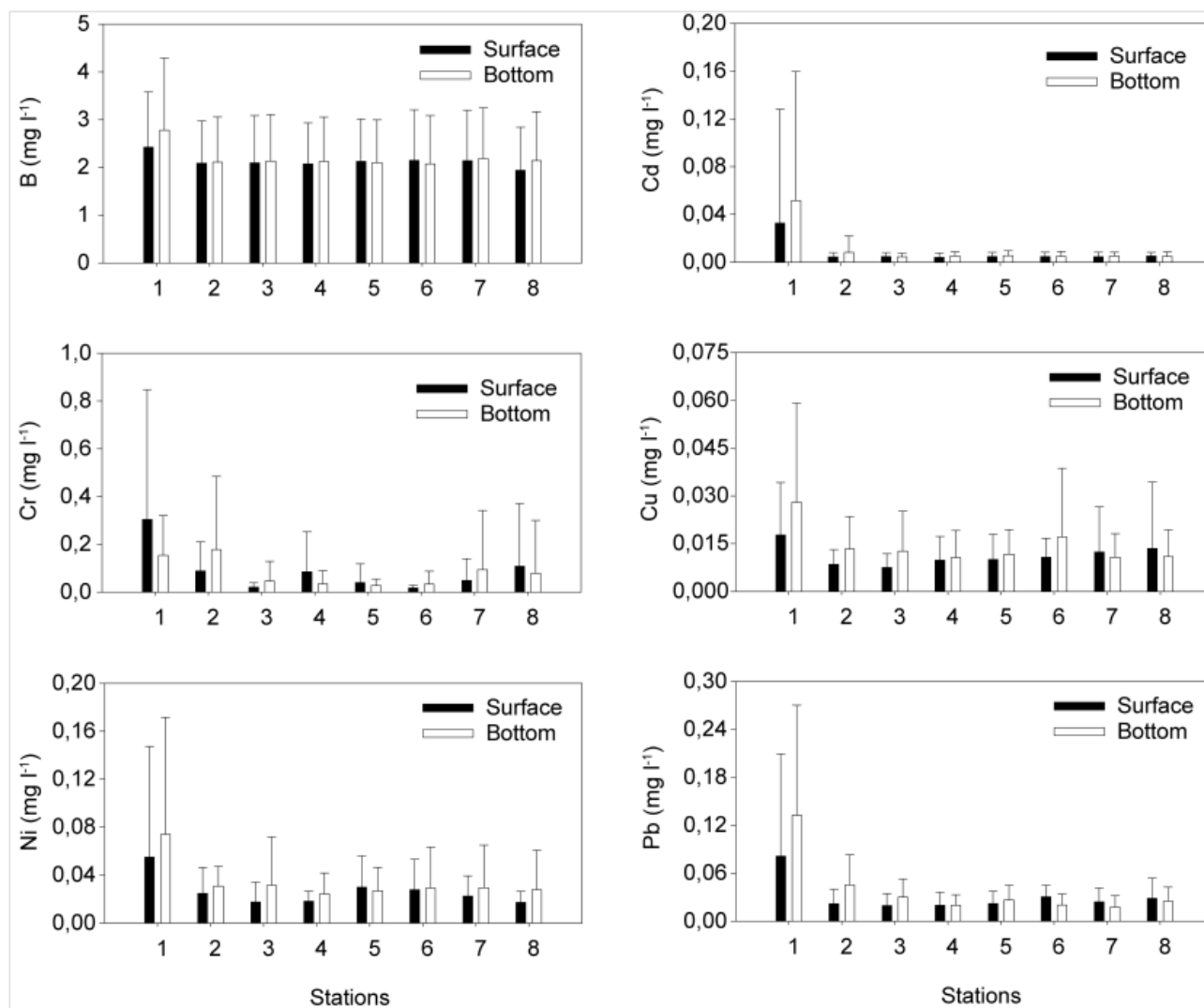
Figure 2. Variations in the concentrations of dissolved Cr, Cd, Cu, Ni, B and Pb according to sampling stations.

water column.

Suspended particulate trace elements

Factorial ANOVA analyses of suspended particulate trace elements

Table 7 shows annual means, standard deviations and concentration intervals of the particulate trace elements. In general concentration intervals are wide range. Adsorption-desorption mechanisms affected the particulate trace element concentrations within the suspended solids in the lake.

Factorial ANOVA was used to examine variations in the annual mean concentrations of particulate trace elements according to stations, surface and bottom distinction and season. Variations in Cr, Zn and B according to stations

were found to be significant, and variations in the other trace elements were found to be non-significant. The maximum concentrations of Cr, Zn and B were observed at the 2nd, 3rd and 1st stations respectively. This may be because of those regions are exposed to a lot of wind and are also affected by the nearby SHW pumping stations, both of which cause water turbulence and increase the suspended solids concentration. The highest level of suspended solids (94.04 mg L^{-1}) was recorded at the 2nd station and the second-highest level of suspended solids (45 mg L^{-1}) was recorded at the 3rd station. Variations in the concentrations of particulate Cr, Zn and B according to sampling stations are shown in Figure 4. The statistical analysis showed that the variations in monthly means were significant for all of the elements. Therefore, the monthly variations in particulate trace elements are presented graphically in Figure 5. The annual mean of organic matter percentage in sediment
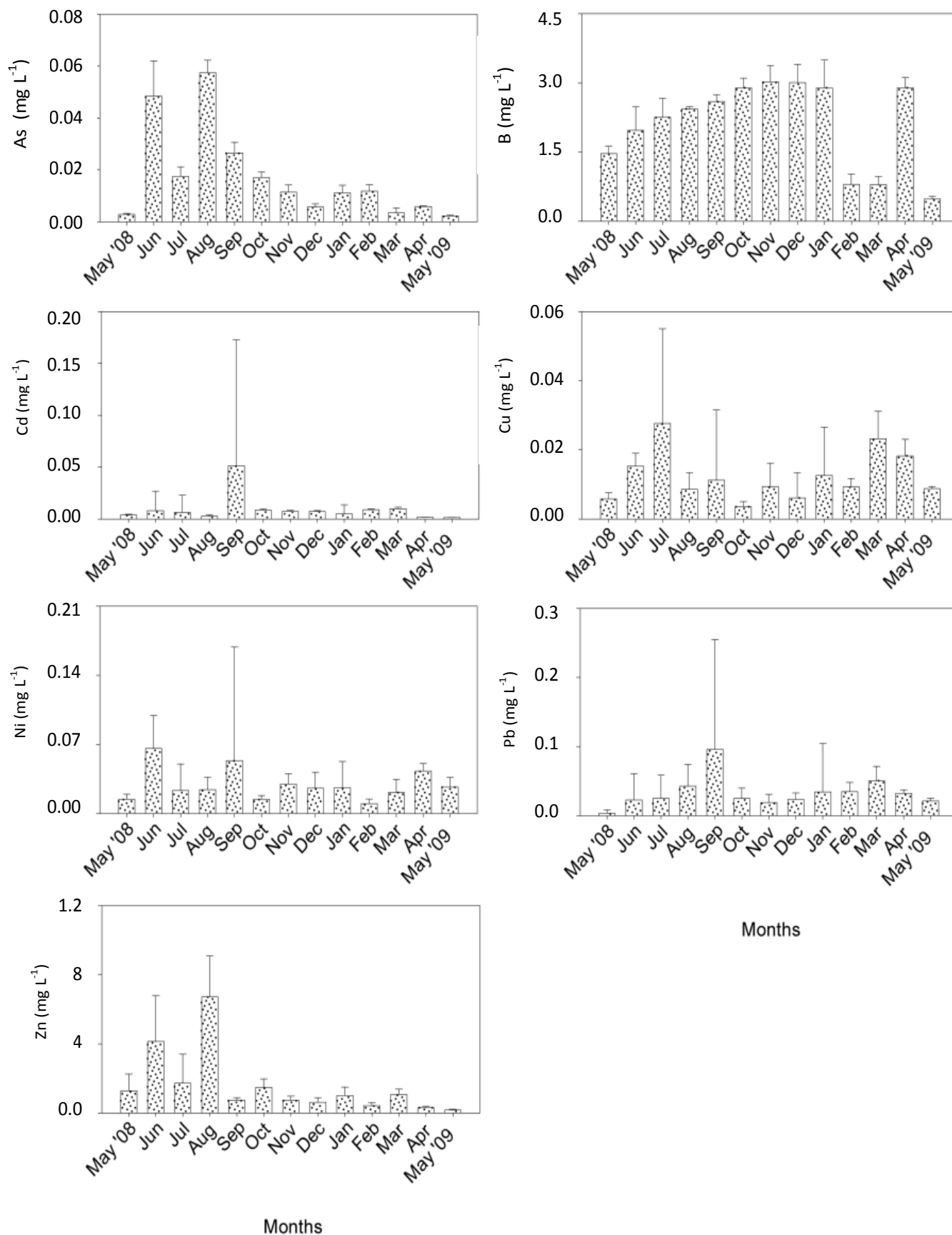
Figure 3. Monthly variations in dissolved As, Cd, Cu, Ni, Zn, B and Pb.

Table 7. Particulate trace element concentrations in Lake Uluabat and other fresh waters.

Elements	References	Min. - Max.	Mean ± SD
Cd (mg kg^{-1})	Changjiang and Hangzhou Bay (Che et. al., 2003)	0.04 - 8.39	0.565 ± 0.82
	Lake Balaton (Nguyen et al., 2005)	0.11 - 1.25	0.385
	River Danube (Yiğiterhan and Murray, 2008)		1.14
	Lake Uluabat	0 - 6.1877	1.1667 ± 0.5874
Cr (mg kg^{-1})	Lake Balaton (Nguyen et al., 2005)		19
	Lake Uluabat	0.0140 - 168.1396	13.4087 ± 20.2079
Cu (mg kg^{-1})	Changjiang and Hangzhou Bay (Che et al., 2003)	0.5 - 157.5	46.05 ± 25.6
	Lake Balaton (Nguyen et al., 2005)		16.5
	River Danube (Yiğiterhan and Murray, 2008)		115
	Lake Uluabat	0 - 49.9319	5.3701 ± 5.2744
Fe (mg kg^{-1})	Lake Balaton (Nguyen et al., 2005)	3700 - 27300	9950
	River Danube (Yiğiterhan and Murray, 2008)		36000
	Lake Uluabat	33.1149 - 26509.08	2039.2269 ± 2949.51
Mn (mg kg^{-1})	Lake Balaton (Nguyen et al., 2005)	199 – 12500	1300
	River Danube (Yiğiterhan and Murray, 2008)		1700
	Lake Uluabat	3.9596 - 565.8088	50.9093 ± 66.6561
Ni (mg kg^{-1})	Lake Balaton (Nguyen et al., 2005)		25
	Lake Uluabat	0.0161 - 123.9227	18.6455 ± 26.0972
Pb (mg kg^{-1})	Changjiang and Hangzhou Bay (Che et al., 2003)	2 – 175	32.5 ± 18.3
	Lake Balaton (Nguyen et al., 2005)		29.5
	River Danube (Yiğiterhan and Murray, 2008)		84
	Lake Uluabat	0 - 105.247	7.61223 ± 9.4288
Zn (mg kg^{-1})	Lake Balaton (Nguyen et al., 2005)	18-147	71.5
	River Danube (Yiğiterhan and Murray, 2008)		248
	Lake Uluabat	0.2246 - 162.4596	26.8742 ± 27.4318

was found to be 3.81% for the lake; this increased to 3.99% in summer and decreased to 3.55% in winter. The highest organic matter content for an individual sampling station was 4.2%, recorded at the 8th station. This station had the lowest values of Cr, Zn and B. Moreover, it was determined (Table 8) that the level of Zn is related to the percentage of organic substances in the sediment. When monthly variations of trace elements were examined, it was found that concentrations tended to increase in summer and in September while to decrease from the mid autumn to the end of spring in general.

This increase in summer was thought to occur as a result of elements transferred from the sediment to the water column, as a result of wind induced mixing (Bailey and Hamilton, 1997) and the decrease in dilution and the reduced water level. The transfer of elements from the sediment to the water showed a particular increase as a result of the increase in the solubility of metals as temperature increases, and elements bounded to the

suspended solids again. Cd, Cu, Zn, As and B were found in high concentrations during rainy seasons. This may be resulted by the adsorption of those elements to solid substances which are increased with surface flows and then carried into the lake and by the amount of phytoplankton increases especially in spring (Straškraba et al., 1993).

The molar ratios of B:Fe:Mn:Zn:Ni:Cr:Cu:As:Cd:Pb, were 37002:365145:9266:4110:3175:2606:845:127:103:367, respectively, which were determined by taking the annual mean of the particulate trace elements in the lake. Their order of size according to their concentrations was Fe>Mn>B>Zn>Ni>Cr>Pb>Cu>Cd>As. This differed from the size order of dissolved trace elements. A comparison of the concentrations of the particulate trace elements with the other fresh waters sources is presented in Table 7. According to this comparison, except for Cd, the concentrations of the other metals examined were at low levels. The reason is that Cd can form a complexation
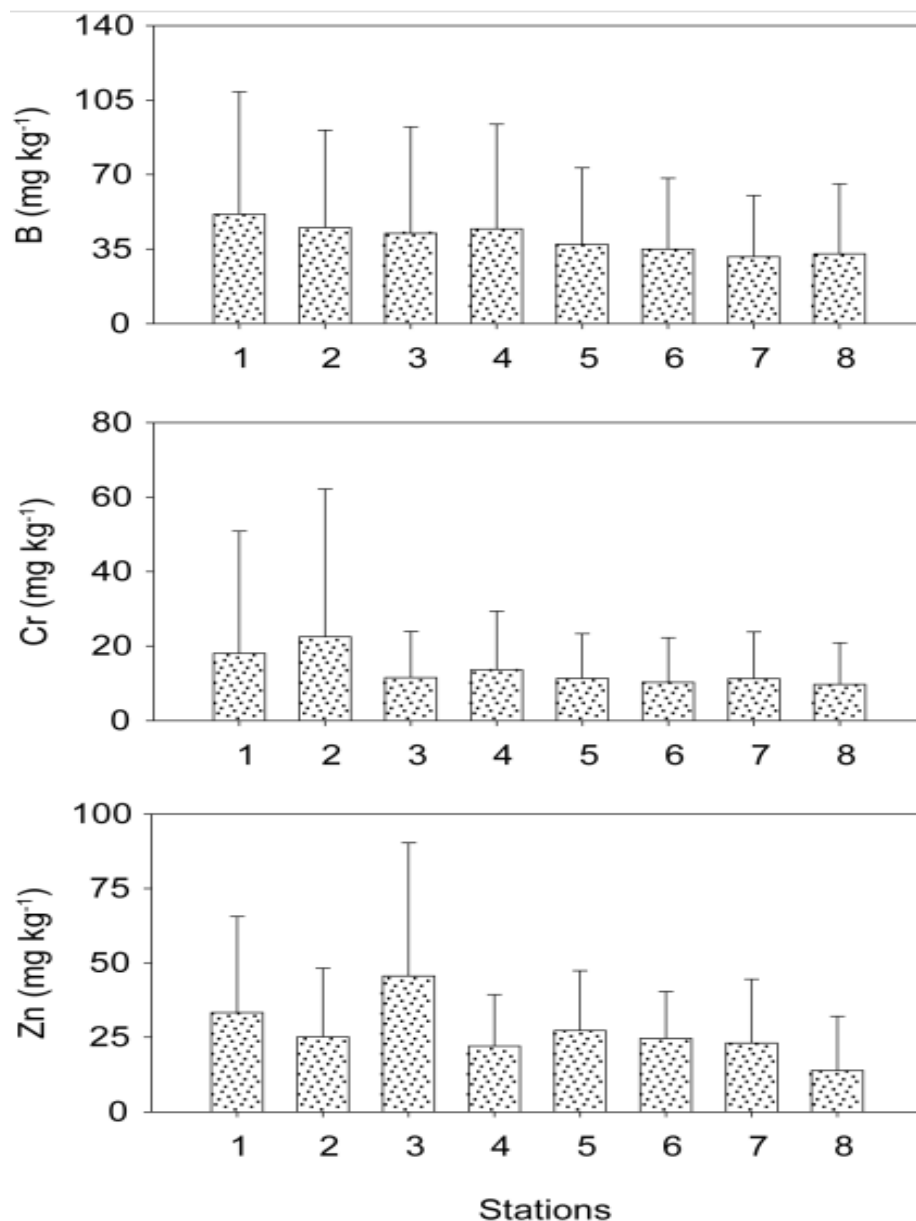
Figure 4. Variations in the concentrations of particulate Cr, Zn and B according to sampling stations.

with inorganic ligants in mudier and arable soils (Bradl, 2005). Therefore, Cd was accumulated in the mudier sediment layer of Uluabat lake. Concentration of particulate form of Cd was increased by flows in water and resuspension process. Some dissolved trace elements like Fe, Zn, Cr, Ni, B, Pb concentrations are higher than the water sources. Another reason is that heavy metals coming from point sources such as creeks and pump stations located around the lake are in dissolved form.

Factorial ANOVA analysis showed higher concentrations of particulate Cu, Ni, Fe and Mn within

samples at the bottom of the water column compared to surface samples. The other elements showed non-significant variations between surface and bottom samples. This was resulted from the greater amount of suspended solids at the bottom of the water column and the relationship between chlorophyll-a and suspended solid concentrations. Due to these differences between surface and bottom concentrations, variation graphs of the particulate trace element concentrations were produced by calculating the surface-bottom means of each station. Figure 6 showed examples of concentration difference for particulate Cu and Fe at the surface and
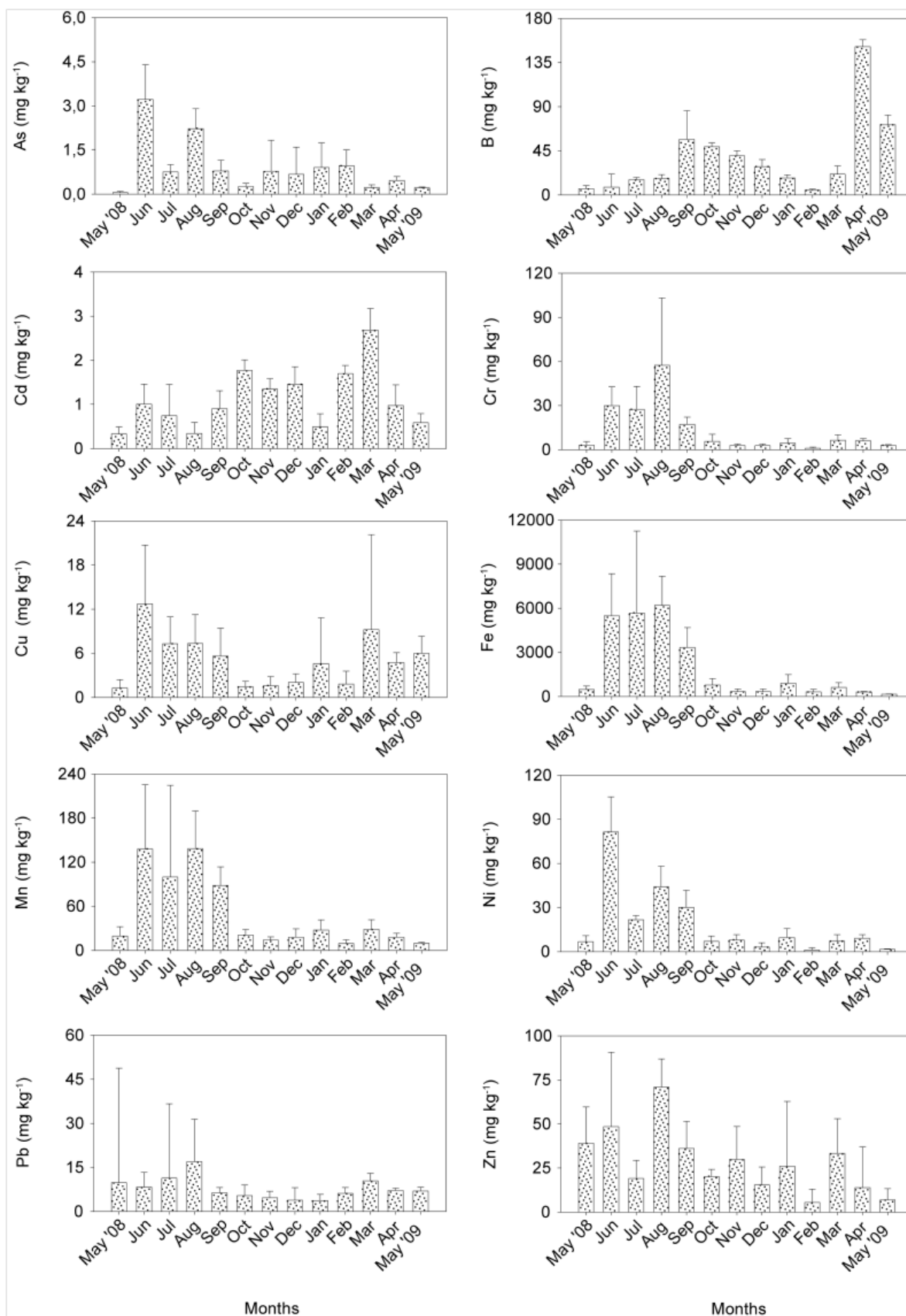
Figure 5. Monthly variations in particulate trace elements.

Table 8. The matrix of correlation coefficients (r-values) among particulate trace elements with water and sediment quality parameters.

|	As	Cr	Cd	Cu	Ni	Fe	Mn	Zn	B	Pb	pH	T	EC	Chl-a	Organic Matter
Cr	0.414 *														
Cd	-0.21 *	-0.12													
Cu	0.203 *	0.288 *	0.012												
Ni	0.709 *	0.578 *	-0.196	0.428 *											
Fe	0.4 *	0.747*	-0.061	0.292 *	0.614 *										
Mn	0.445 *	0.731 *	-0.029	0.327 *	0.677 *	0.961 *									
Zn	0.359 *	0.436 *	-0.076	0.294*	0.447 *	0.363 *	0.37 *								
B	-0.33 *	-0.2	-0.136	-0.12	-0.23 *	-0.23 *	-0.226 *	-0.14							
Pb	0.272 *	0.318 *	-0.102	0.224 *	0.356 *	0.29 *	0.295 *	0.284 *							
pH	0.35 *	0.062	-0.039	-0.14	0.134	0.071	0.08	-0.07	-0.284 *	-0.142					
T	0.288 *	0.525 *	-0.3 *	0.385 *	0.589 *	0.524 *	0.505 *	0.287 *	0.083	0.382 *	-0.101				
EC	0.231 *	-0.01	-0.027	0.011	0.225 *	0.079	0.117	0.036	-0.096	-0.064	-0.099	0.099			
Chl-a	0.326 *	0.295 *	-0.112	0.278 *	0.509 *	0.398 *	0.445 *	0.047	-0.145	0.015	0.209 *	0.549 *	0.331 *		
Organic Matter	0.326 *	0.153	-0.067	0.192	0.361 *	0.158	0.191	0.362 *	-0.047	0.293	-0.014	0.335 *	0.303*	0.241 *	
SS	0.228 *	0.445 *	-0.033	0.21 *	0.614 *	0.519 *	0.607 *	0.237 *	-0.051	0.16	0.006	0.332 *	-0.008	0.445 *	0.116

*$p < 0.05$.

the bottom.

Relationship between the particulate trace elements and the water-sediment quality parameters

Relationship between the particulate trace elements and the Chlorophyll-a concentrations (Stumm and Morgan, 1996) were studied. The effects of temperature, conductivity and pH on trace elements are emphasised (Ikem et al., 2003). Dissipation of trace elements from the water column is realised with absorption to algae and precipitation. The decrease in pH and the increase in temperature affect the disssolution of metals (Fernández et al., 2000). Therefore, the relationships among organic matter percentage, temperature, pH and conductivity parameters in the sediment layer were analysed. Also, suspended solids, particulate trace elements and chlorophyll-a parameters in lake water were evaluated statistically. The results showed a significant relationship between all of the elements, except for Cd, which only showed a significant relationship with As. Particularly the correlation between Fe with Mn, Cr and Ni, and the relation of Mn with Cr and Ni, were found to be higher compared to the other correlations. This findings reflected that the movements of elements can be similar to each other. Significant relation-ships were found between temperature and all of the elements except B; between suspended solids and all the elements other than Cd, B and Pb; and between chlorophyll-a and all the elements other than Cd, Zn, B and Pb. The positive correlations were found between suspended solids and chlorophyll-a showing that elements can be adsorbed to solid substances. It was determined that the amount of organic matter percentage in the sediment was related with As, Ni, Zn and Pb; conductivity was related with As and Ni; and pH was related with As and B. It was thought that there may be transfer from the sediment to the water as a result of decomposition of organic matter and an anaerobic condition resulting from the increase in temperature, the percentage of organic matter and therefore the conductivity. The matrix of correlation coefficients (r - values) among particulate trace elements with water and sediment quality parameters are presented in Table 8 and the correlation graphs between particulate Cr, Ni, Fe Mn and suspended solids are presented in Figure 7.
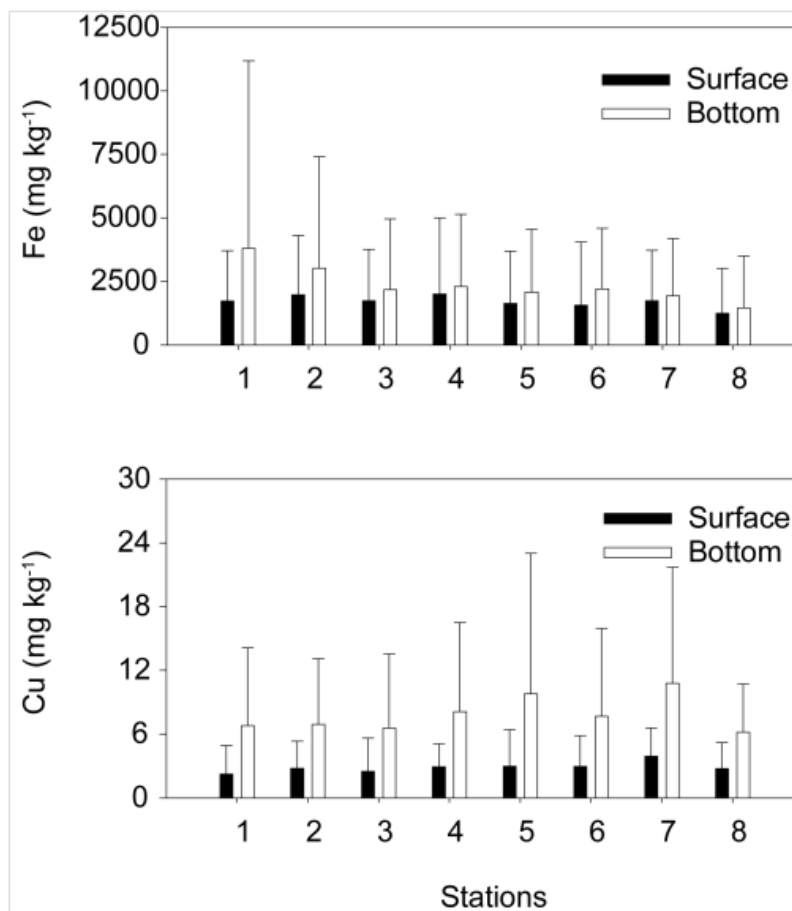
Figure 6. Surface and bottom concentrations of particulate Cu and Fe.

Conclusion

Dissolved and particulate trace elements concentrations were examined in lake water and sediment for 8 sampling stations representing the different regions of Lake Uluabat in Turkey. The dissolved and particulate trace elements concentrations were determined at the surface and the bottom layers within the water column. In general the highest concentrations of trace elements were observed in the particulate form. Lower organic content in water indicated that the suspended solids were transferred from the sediment. Concentrations of particulate Cr, Zn and B were detected lowest at the 8th sampling station where organic matter percentage in the sediment was highest.

The size of the trace elements according to the concentrations of the elements were B>Fe>Zn>Cr>Pb>Ni>As>Cu>Mn>Cd for the dissolved trace elements; and Fe>Mn>B>Zn>Ni>Cr>Pb>Cu>Cd>As according to particulate trace elements.

The differences between the surface and the bottom layers of the water column were non-significant in terms

of dissolved trace elements, but significant in terms of some of the particulate trace elements (Fe, Mn, Cu and Ni). The concentrations of dissolved trace elements at the bottom of the water column were observed to be higher than those of surface samples. This difference was resulted from the higher concentrations of suspended solids present in the deeper parts of the water column.

Mostly, the dissolved and particulate trace elements were detected high in summer season. The main reason was the increase of concentrations of dissolved trace elements depending on solubility, decrease in water level and increase in air temperature. Furthermore, increase in photosynthetic production by implication of pH, concentration of $CaCO_3$ and adsorption capacity of iron and manganese oxides have caused this situation. In addition increasing wind velocity in summer season induced the mixing of sediment layer into the water column bringing about suspended trace elements. Significant correlations were found between suspended solids and particulate Fe, Mn, Zn, Cr, Cu, As, Ni elements; between Chl-a and particulate Fe, Mn, Cr, Cu, As, Ni elements. Same correlation was observed for particulate trace elements (except B) and temperature;
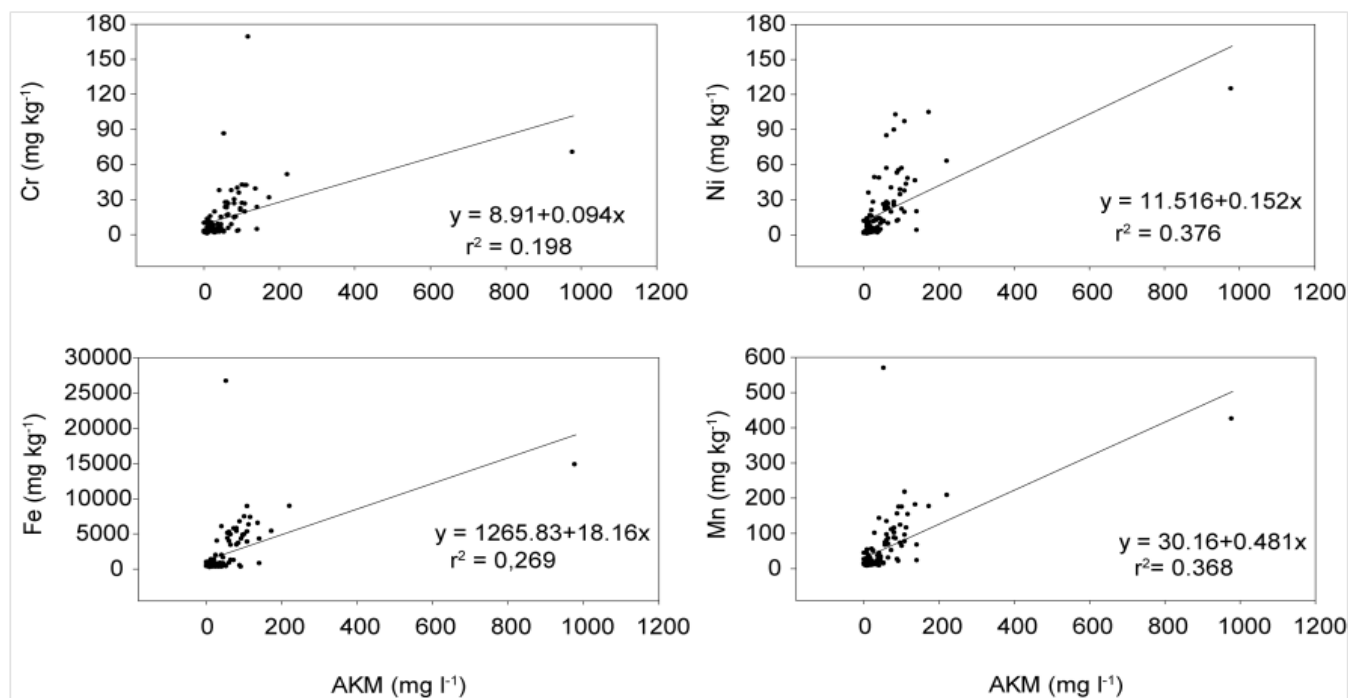
Figure 7. Correlation graphs between particulate Cr, Ni, Fe Mn and suspended solids.

pH and As, B and organic matter percentage with As, Ni, Zn elements. Annual means of dissolved trace elements were compared with WHO and EPA international standards. In lakes which have eutrophic status like Uluabat, trace elements absorbed to algae can pass to food web by release easily. Consequently, the lake will become more toxic when the probable decrease of pH. As a result, the long term monitoring and control of domestic and industrial wastewaters, restricted uses of agricultural pesticides are the important factors have to be taken into consideration in lake management. It is necessary to produce and apply new management strategies or plans in controlling point and non-point sources.

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