

Metal Concentrations in Surface Sediments of Beyler Reservoir (Turkey)

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Abstract The accumulation of metals (Iron, Aluminium, Zinc, Copper, Manganese, Boron, Chromium, Nickel, Cadmium, Lead) was seasonally (November 2009 to July 2010) measured in sediment samples taken from different areas of Beyler reservoir which is an important water source for irrigation in West Black Sea region (Turkey). Metals in sediment samples were analyzed by ICP-OES. The difference between the stations except for Zn metal ($p < 0.05$) has not been considered as important and a statistical difference between seasons for Fe, Ni metals ($p < 0.01$) and Cu metal ($p < 0.05$) has been observed. The magnitude of metal concentrations in sediment was determined as Aluminium > Iron > Manganese > Zinc > Chromium > Copper > Boron > Nickel > Lead > Cadmium. Enrichment factor (EF) for all metals has been calculated ($EF < 1$). In the evaluation done by considering the EF values, it is seen that the metal concentrations found in the Beyler Dam Lake sediment stem from the natural composition of the sediment.

Keywords Beyler reservoir · Sediment · Metals

Lake sediment is like a gold mine of information in terms of giving information about the past state of the lake and the surrounding. It is an important source in examining the transformation of toxic metals such as Zn, Pb, Cu, Ni and

Cd. The examining of metals in lake sediment has been used for long years in observing the environmental effects (Salomans et al. 1987; ElBilali et al. 2002; Casas et al. 2003; Feng and Yang 2008).

Human activities (such as industrial wastes, settlement wastes etc.) as well as geological structure constitute the main source of metals in aquatic ecosystems (Karadede and Ünlü 2000; Demirak et al. 2006; Sekabira et al. 2010).

Metals cannot be biologically degraded like organic contaminants and thus they accumulate especially in the sediment by being absorbed in complex structures. Metals which accumulate in the sediment may turn into factors threatening the ecosystem well-being and may constitute a danger and risk factor for the environment (Shrivasta et al. 2003; Wildi et al. 2004; DelValls et al. 1998).

Beyler Dam Lake is a reservoir (240 km²) on İncesu stream in north Anatolia, Turkey. Reservoir located between 41°68′–41°69′N and 33°79′E. *Chalcalburnus* sp. *Leuciscus cephalus*, *Cyprinus carpio* and *Salmo trutta* are the main commercial fishes in the dam lake (DSİ 2007). The dam has got a great potential for fresh-water fishing. Apart from closed season, it is an important area which the locals use as hunting ground for sportive aims, rest area and recreation spot.

In this research it has been aimed to determine the availability rate and the concentrations of some of the metals (Fe, Al, Zn, Cr, Cu, Mn, Ni, B, Cd ve Pb) found in the reservoir of Beyler which is used for the irrigation of a 5,178 ha land.

Materials and Methods

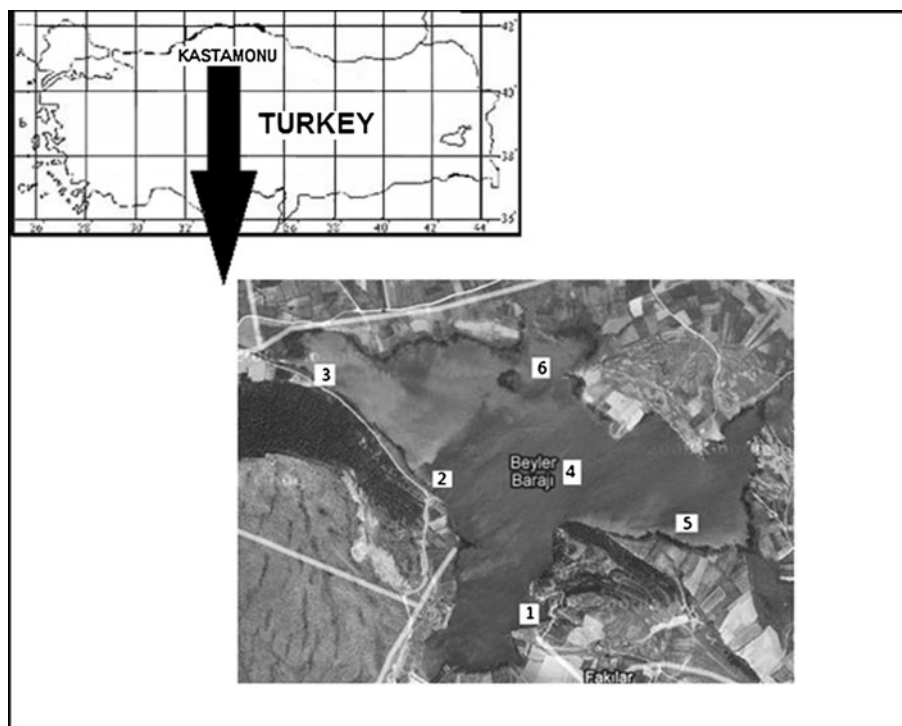
Sediment samples were taken seasonally (November, January, March, and July) in 2009–2010 at six sampling

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Fig. 1 Sampling area

stations shown in Fig. 1 from Beyler reservoir. Ekman grab sampler was used to collect the reservoir bottom sediments. To avoid contamination, sediment was transferred into pre-cleaned polythene bags and then frozen.

The sediments were dried at room temperature, crushed to a powdered form and passed through a 63 μm sieve. Approximately 1 g samples of sediment digested with concentrated HNO_3 (65%) and HCl (37%) (3:1, v/v) in a microwave digestion system (Berghof-MWS-2) to prepare the samples for analysis. The operating conditions for sediment are given in Table 1. All samples were diluted with deionized water and filtered through a 0.45 μm nitrocellulose membrane filter. Some blanks were prepared in the laboratory in a similar manner to the field samples (ElBilali et al. 2002; Buccolieri et al. 2006).

All metals were determined by Perkin Elmer 2100 DV models ICP-OES. The following absorption wavelength were used; Fe 259.9 nm, Zn 213.9 nm, Cu 324.8 nm, Mn 257.6 nm, B 249.8 nm, Cr 367.7 nm, Ni 221.6 nm, Cd 228.8 nm, Pb 220,4 nm and Al 396.2 nm. The metal

concentration in sediment was recorded as mg kg^{-1} wet weight. All working standard solutions were made from stock solutions ($1,000 \text{ mg L}^{-1}$) of all elements, which were supplied by Inorganic Ventures crop, USA. High quality water, obtained using a Human UP 900 system, was used exclusively. Each sample was analyzed in triplicate. Detection limits of elements are Cd 0.0012 mg g^{-1} , Cr 0.0027 mg g^{-1} , Cu 0.0069 mg g^{-1} , Fe 0.0381 mg g^{-1} , Mn 0.001 mg g^{-1} , Pb 0.0078 mg g^{-1} , Zn 0.0015 mg g^{-1} , Al 0.0057 mg g^{-1} and Ni 0.0048 mg g^{-1} .

The accuracy of analytical procedure was checked by analyzing the standard reference materials. Recovery rates ranged from 99% to 100% for all investigated elements.

The averages and standard deviations of the metal concentrations have been calculated in accordance with both stations and seasons. Student *t* test ($p < 0.05$) has been used in order to find whether there is a change between the stations or the seasons. Statistical analysis of data was carried out using SPSS 19.0 statistical package programs for Windows (Serial number: 10241512).

Table 1 Operating conditions to digestion the sediment samples with microwave (Berghof-MWS-2)

Stage	1	2	3
T ($^{\circ}\text{C}$)	180	100	100
Power (%)	99	99	40
Time (min)	25	10	5

Results and Discussion

The metal concentration dispersions as for the stations have been shown in Table 2. It has been found out that the dispersions among the stations apart from Zn is not statistically important ($p < 0.05$). None the less the highest metal concentration values have been found in the third

Table 2 Concentrations of metal in sediment from six sampling stations by mean value \pm standard error and range (mg kg⁻¹)

S	Fe	Al	Zn	Cu	Mn	B	Cr	Ni	Cd	Pb
1	20406.375 \pm 758 (27115–13117.5)	21014.125 \pm 9807 (31058.5–11698.5)	38.800 \pm 14.69 (51.95–24.55)	16.200 \pm 7.006 (22.85–9.10)	372.525 \pm 126.033 (508.00–228.55)	16.150 \pm 9.351 (27.20–7.55)	17.237 \pm 19.16 (45.40–3.15)	11.312 \pm 9.902 (25.75–3.70)	0.200 \pm 0.108 (0.35–0.10)	5.875 \pm 2.577 (9.65–3.90)
2	17311.250 \pm 749 (25646.5–10340)	13389.750 \pm 6870 (7782.5–23353)	31.475 \pm 11.70 (48.00–21.65)	13.275 \pm 8.387 (25.35–7.20)	262.862 \pm 136.182 (394.80–134.05)	8.687 \pm 5.071 (13.85–1.70)	17.912 \pm 16.87 (42.80–7.25)	11.925 \pm 9.942 (26.80–6.05)	0.212 \pm 0.095 (0.35–0.15)	5.225 \pm 4.105 (11.25–2.05)
3	24752.750 \pm 226 (27516.5–22132)	27747.500 \pm 5933 (33869–19932)	48.562 \pm 2.005 (51.40–46.70)	23.862 \pm 1.986 (25.55–21.70)	418.362 \pm 65.500 (514.50–373.50)	23.487 \pm 8.043 (33.95–22.45)	24.100 \pm 14.31 (43.25–9.30)	15.450 \pm 7.629 (25.90–7.60)	0.212 \pm 0.063 (0.30–0.15)	6.812 \pm 2.921 (10.75–3.70)
4	18874.625 \pm 752 (26251.5–12166)	16630.625 \pm 8537 (7832–25146)	36.600 \pm 15.57 (51.15–21.75)	14.925 \pm 6.683 (22.40–8.75)	332.775 \pm 135.228 (496.50–205.70)	9.487 \pm 5.978 (16.00–2.65)	21.512 \pm 12.322 (35.00–9.60)	14.962 \pm 6.533 (20.70–8.35)	0.250 \pm 0.058 (0.30–0.20)	7.000 \pm 2.074 (9.10–4.80)
5	18537.750 \pm 952 (27247–9108)	22276.375 \pm 12849 (34831.5–11060.5)	37.400 \pm 14.55 (52.05–21.55)	14.125 \pm 7.988 (23.15–6.70)	310.812 \pm 186.928 (524.00–132.45)	19.587 \pm 10.51 (29.90–9.60)	15.837 \pm 7.997 (27.80–11.25)	10.762 \pm 4.158 (16.25–6.35)	0.150 \pm 0.091 (0.25–0.05)	3.300 \pm 2.733 (6.40–0.45)
6	22929.500 \pm 608 (29711–15493.5)	25275.250 \pm 7088 (35612.5–19519.5)	45.262 \pm 8.686 (53.25–32.90)	22.425 \pm 5.088 (25.35–14.90)	379.525 \pm 111.370 (518.50–246.75)	21.237 \pm 6.844 (29.90–13.85)	19.837 \pm 10.515 (34.70–11.15)	14.850 \pm 9.466 (27.35–6.95)	0.212 \pm 0.111 (0.35–0.10)	5.500 \pm 3.658 (9.70–1.85)
F	1.684	2.431	6.408*	2.472	0.477	1.371	1.264	0.001	0.100	1.685

Table 3 Concentrations of metal in sediment according to seasons by mean value \pm standard error and range (mg kg⁻¹)

SEASON	Fe	Al	Zn	Cu	Mn	B	Cr	Ni	Cd	Pb
November	16206.67 \pm 2949.31 (25410–9108)	15926.17 \pm 2857.24 (26917–10912)	31.23 \pm 5.18 (47.90–21.55)	13.96 \pm 3.66 (25.55–6.70)	246.72 \pm 43.99 (380.45–132.45)	11.92 \pm 2.36 (22.45–6.65)	10.87 \pm 1.86 (19.60–7.25)	7.14 \pm 0.41 (8.35–6.05)	0.15 \pm 0.013 (0.20–0.15)	3.24 \pm 0.50 (4.80–1.65)
January	15642.92 \pm 2296.43 (24051.5–10340)	16669.58 \pm 4079.05 (33869–7832)	32.96 \pm 4.62 (47.75–21.75)	14.58 \pm 3.53 (25.70–8.00)	268.80 \pm 41.50 (387.55–157.30)	14.68 \pm 4.69 (33.95–2.65)	15.14 \pm 1.99 (25.05–12.60)	10.04 \pm 1.11 (14.60–6.95)	0.15 \pm 0.03 (0.20–0.05)	3.86 \pm 0.97 (6.60–0.45)
March	23452.92 \pm 1728.25 (26790.5–15493.5)	25221.17 \pm 2563.26 (34831.5–19932)	46.417 \pm 2.78 (51.15–48.25)	20.12 \pm 1.46 (25.35–14.90)	376.34 \pm 27.88 (442.1–246.75)	19.38 \pm 3.02 (29.90–12.65)	38.16 \pm 2.76 (45.40–27.80)	22.07 \pm 1.93 (26.80–17.00)	0.30 \pm 0.02 (0.35–0.25)	8.97 \pm 0.78 (11.25–6.40)
July	26572.333 \pm 1101.35 (29711–21593)	26405.5 \pm 3999.39 (35612.5–7782.5)	48.125 \pm 3.43 (53.25–31.20)	21.225 \pm 1.74 (23.75–12.55)	492.716 \pm 19.96 (524–394.8)	19.783 \pm 4.13 (29.90–1.70)	13.458 \pm 3.71 (28.80–3.15)	13.591 \pm 3.63 (27.35–3.70)	0.225 \pm 0.035 (0.35–0.10)	6.408 \pm 0.99 (9.70–4.05)
F	10.223**	.063	3.135	7.414*	3.749	1.140	2.409	9.981**	4.865	4.077

Table 4 Comparative metal concentrations in the sediment of Beyler Reservoir in previous studies (mg kg⁻¹)

	Al	Fe	Mn	Zn	Cr	Cu	B	Ni	Pb	Cd
Beyler Baraj Gölü	21055.60	20468.71	346.14	39.68	19.41	17.47	16.44	13.21	5.62	0.21
Seyhan Baraj Gölü ^a	–	39350	803.63	39.09	118.95	19.80	–	–	–	2.15
Atatürk Baraj Gölü ^b	–	12587	73.6	60.79	–	14.57	–	–	–	–
Kovada Gölü ^c	9990	7345	165.96	23.14	17.59	13.77	–	25.93	4.42	0.27
Avşar Baraj Gölü ^d	–	25268	–	–	14.48	29.98	–	29.99	2.44	0.76
Tokat Gölleri ^e	–	2138	232	38.9	10.7	8.2	–	55.40	7.00	–
Ortalama Skala	80000 ^f	46700 ^f	850 ^f	95 ^f	90 ^f	45 ^f	–	68 ^f	20 ^f	0.3 ^g
EF Değerleri	Referans	0.600	0.0182	0.002	0.4913	0.8857	–	0.430	0.0004	0.000006

^a Çevik et al. (2009)

^b Karadede and Ünlü (2000)

^c Kır et al. (2007)

^d Öztürk et al. (2009)

^e Mendil and Uluözlü (2009)

^f Buccolieri et al. (2006)

^g Shrivasta et al. (2003)

station. The third station is located in the access point of Incesu Stream and has a higher concentration than the other station because of the metal load the stream brings.

The metal concentration dispersions as for the seasons have been shown in Table 3. Statistically difference has not been observed for the Fe, Ni metals ($p < 0.01$) and Cu metal ($p < 0.05$) in inter seasonal dispersion. Fe, Al, Zn, Cu, Mn and B have been in a higher concentration in July compared to other seasons, and Cr, Ni, Cd and Pb metals have been in a higher concentration in March compared to other season. According to Kır et al. (2007) the increase of metal concentrations in sediments in summer is because of the fact that the increasing concentration in water has passed to the sediment easily and more because of evaporation and because of the fact water circulation has decreased.

Some samples of the metal studies carried out in the lake sediment have been shown in Table 4. It has been observed that the values determined in the study are lower than the average scala values that Buccolieri et al. (2006) and Mwamburi had reported. The Fe, Mn, Cr and Cd concentrations values are lower than the values in Seyhan Dam Lake (Çevik et al. 2009), the Pb and Ni values are lower than the values in Tokat Lakes (Mendil and Uluözlü 2009), the Zn metal values are lower than the values in Atatürk Dam Lake (Karadede and Ünlü 2000), Cu heavy metal concentration is lower than the values in Avşar Dam Lake (Öztürk et al. 2009). The other metal concentrations except Ni metal are higher than the concentrations in Kovada Lake (Kır et al. 2007).

One of the factors used to estimate the human related effects in the sediment is the factor of enrichment (Covelli and Fontolan 1997). The average scala values have been

taken from Buccolieri et al. (2006) for Fe, Cr, Cu, Mn, Zn, Al, Ni and Pb metals, and the average scala values for Cd metal have been taken from Mwamburi (2003). EF value has not been calculated for metal B. The calculated EF value for all the metals has been found below 1 (Table 4). As a result, by considering the EF values it can be said that there has not been a human related contamination in the sediment.

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