Seasonal and Spatial Distributions of the Metals in the Water from the River Asi in Southern East Mediterranean Area of Turkey

Mustafa TÜRKMEN[*], Evren ÇALIŞKAN[**]

* Giresun University, Faculty of Science and Arts, Department of Biology, Giresun, TURKEY

** Mustafa Kemal University, Faculty of Fisheries and Aquaculture, İskenderun, Hatay, TURKEY

Corresponding author: mturkmen65@hotmail.com

Abstract

Seasonal and spatial variations of cadmium, iron, lead, zinc, copper, manganese, nickel, chrome, and cobalt were determined in water from River Asi in northern east Mediterranean area. Concentrations of the analyzed metals in water were significantly affected by sampling sites and seasons. Metal levels in water were compared with national and international water quality criteria, background concentrations and permissible limits. Concentrations of the metals such as Cu, Fe and Zn in water were generally found higher than background and legal concentrations.

***Keywords*:** Metals, Seasonal variations, River Asi, Water

Introduction

Metals such as iron, copper, zinc and manganese, are essential metals since they play an important role in biological systems, whereas mercury, lead and cadmium are non-essential metals, as they are toxic, even in traces. The essential metals can also produce toxic effects when the metal intake is excessively elevated. Heavy metal discharges to the aquatic environment are of great concern all over the world, and have a great ecological significance due to their toxicity and accumulative behavior. Thus, it can both damage aquatic species diversity and ecosystems (Matta et al., 1999). Heavy metals in aquatic environment can remain in solution or in suspension and precipitate on the bottom or be taken up by organisms.

River Asi rises near the city of Baalbek in Lebanon, and flows in a northerly direction between the Lebanon and anti-Lebanon mountains into Syria. It runs through the Syria and enters Turkey, in the province of Hatay. It flows north to the city of Antakya, bends westward, and then empties into the sea near Samandağ, in the northern east of Mediterranean Sea, through a total course of about 380 km. The damming of the River Asi in Syria provides irrigation water for the rich river valley. In ancient times the valley of the river formed a corridor between Asia Minor and Egypt. Like all other rivers in the world, this river has also an important role in the irrigation of the fields surrounding it, especially in Syria and Turkey. The river includes a number of the economically important fish species such as African catfish, *Clarias gariepinus* (most consumed species by local people), common carp, *Cyprinus carpio*, chub, *Liza aurata,* eel, *Anguilla anguilla* and *Carasobarbus luteus*. Mainly untreated agricultural, municipal and industrial wastes affect the river direct or indirectly. This study has been undertaken to determine the seasonal and spatial variations of cadmium, iron, copper, chrome, cobalt, zinc, lead, nickel and manganese in the water from the River Asi.

Materials and methods

Water samples were collected from selected four stations along a length of 88 km in the part of Turkey of River Asi. These stations are the Border Area (BA), Güzelburç Area (GA), Sümerler Area (SA) and Samandağ Area (SAM) (Figure 1). The samples were collected from a depth of 0.5 m with 1 liter polyethylene bottles, which had previously had

been washed with detergent, deionized water, 2 M concentrated nitric acid, deionized water again and finally medium water, in October 2003 and January, April and July 2004. Samples were acidified with 0.5 ml high-purity concentrated HNO_3 (Merck), brought to laboratory by placing on ice, filtered through a 0.45 μm filter. Standard solutions were prepared from stock solutions (Merck, multi element standard). Samples were analyzed three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by ICP-AES Varian Liberty Series-2. The absorption wavelengths for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were 228.8, 238.9, 267.7, 324.8, 259.9, 257.6, 231.6, 220.4, and 213.9 in nm, respectively. Metal contents were expressed as $\mu g\ l^{-1}$.

To determine the differences between months at same site and stations in total for the water samples, and one way ANOVA were performed. Post hoc test (Duncan) was tested to determine statistically significant differences following ANOVA. Possibilities less than 0.05 were considered statistically significant ($p<0.05$). All statistical calculations were performed with SPSS 13.0 for Windows.

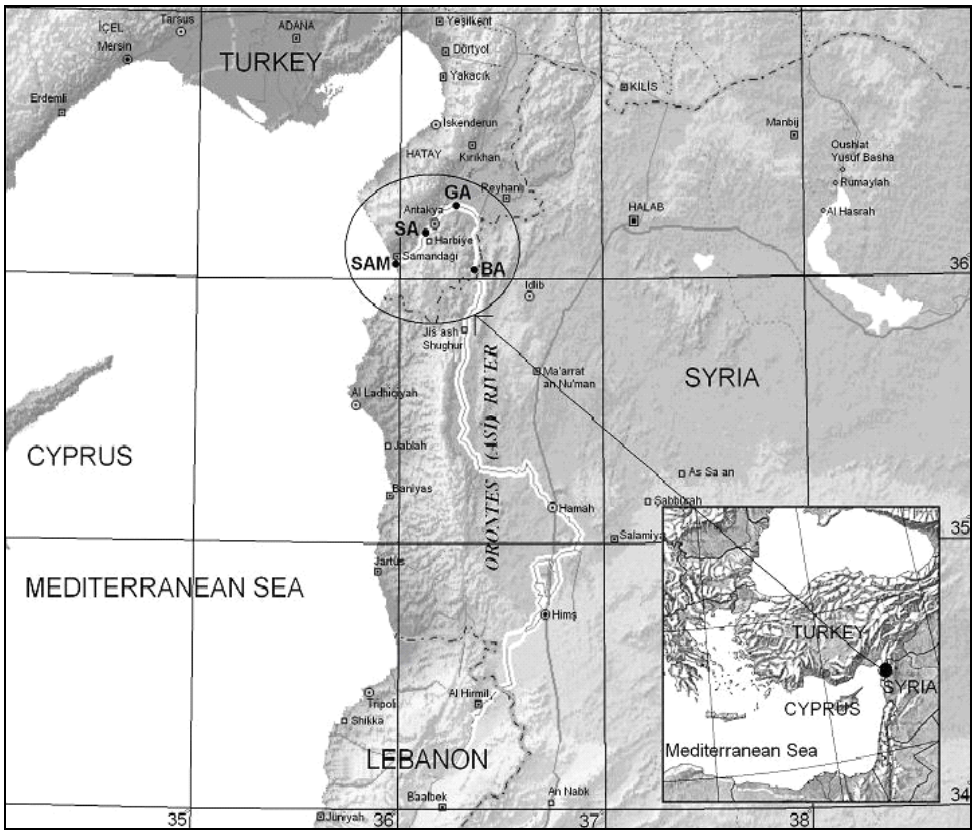

Figure 1. Location map of sampling stations in River Asi

Results and discussion

This study examined the seasonal and spatial variations of the concentrations of Cd, Fe, Cu, Zn, Cr, Co, Mn, Ni and Pb in water from River Asi in Northern East Mediterranean Area of Turkey.

Table 1. The seasonal and spatial variations of the mean metal concentrations in the water from the River Asi (five water samples in each month for each station)

Stations/ months	Metal concentrations, in μg l^{-1*}								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
BA									
October-2003	1.5^{a}	11.7^{b}	5.4^{a}	30.4^{a}	27.9^{a}	1.1^{a}	33.2^{a}	12.0^{a}	39.2^{a}
January-2004	$---^{nd}$	0.8^{a}	4.6^{a}	23.8^{b}	408^{b}	69.3^{b}	13.6^{b}	2.4^{b}	91.4^{b}
April-2004	---	0.4^{a}	5.5^{a}	23.6^{b}	683^{c}	21.1^{c}	17.4^{ab}	2.1^{b}	244^{c}
July-2004	0.1^{b}	2.3^{a}	31.1^{b}	23.7^{b}	5474^{d}	246^{d}	54.2^{c}	2.6^{b}	103^{d}
Total	0.80^{x}	3.8^{x}	11.6^{x}	25.4^{x}	1643^{x}	84.4^{x}	29.6^{x}	4.8^{x}	119^{x}
GA									
October-2003	1.0	10.2^{b}	7.8^{a}	29.0^{a}	170^{a}	6.9^{a}	22.6^{a}	9.1^{a}	137^{a}
January-2004	---	9.7^{b}	10.1^{ab}	23.3^{b}	2250^{b}	124^{b}	7.3^{b}	0.8^{b}	103^{b}
April-2004	---	0.3^{a}	11.4^{b}	23.9^{b}	641^{c}	30.5^{c}	9.3^{b}	4.0^{b}	526^{c}
July-2004	---	25.9^{c}	253^{c}	49.6^{c}	9734^{d}	760^{d}	653^{c}	17.4^{c}	155^{d}
Total	1.0^{x}	11.5^{y}	70.5^{y}	31.4^{y}	3199^{y}	230^{y}	173^{y}	7.8^{x}	230^{y}
SA									
October-2003	1.1^{a}	10.9^{b}	7.9^{a}	30.7^{a}	55^{a}	1.6^{a}	24.9^{a}	8.6^{a}	71.9^{a}
January-2004	---	10.9^{b}	5.2^{a}	23.0^{b}	901^{b}	116^{b}	5.4^{b}	---	103^{b}
April-2004	---	1.4^{a}	61.4^{b}	22.8^{b}	956^{c}	37.6^{c}	26.1^{a}	2.7^{b}	292^{c}
July-2004	0.8^{a}	1.1^{a}	34.9^{c}	24.2^{b}	3339^{d}	202^{d}	44.8^{c}	10.0^{a}	144^{d}
Total	0.95^{x}	6.1^{z}	27.4^{z}	25.1^{x}	1313^{z}	89.2^{z}	25.3^{x}	7.1^{x}	153^{z}
SAM									
October-2003	1.2	13.2^{a}	5.3^{a}	29.9^{a}	159^{a}	14.1^{a}	12.5^{a}	8.4^{a}	48.4^{a}
January-2004	---	10.6^{a}	6.4^{ab}	21.7^{b}	1050^{b}	103^{b}	4.0^{a}	0.6^{a}	7.2^{b}
April-2004	---	0.8^{b}	7.6^{ab}	23.5^{c}	272^{c}	25.1^{c}	20.1^{a}	2.3^{a}	233^{c}
July-2004	---	0.5^{b}	9.9^{b}	23.0^{bc}	1315^{d}	75.2^{d}	16.7^{a}	9.4^{a}	172^{d}
Total	1.2^{x}	6.3^{z}	7.3^{w}	24.5^{x}	699^{w}	54.2^{w}	13.3^{z}	5.2^{x}	115^{w}

[*] Vertically, letters a, b, c and d show differences among different months at same stations; x, y, z and w between stations. Within columns, means with the same letter are not statistically significant, $p>0.05$

[nd] not detected

In water samples, iron was found in the highest concentrations ranging from 27.9 to 9734 μg l^{-1}, and its concentrations were also higher than those of other metals in all stations and months, except Cu, Ni and Zn in October 2003 in station BA and Zn in October 2003 in station SA (Table 1). Following Fe; Zn showed the second highest levels in all months for all stations except Mn level in July in station SA. In October, although Cd, Co, Cr, Cu and Pb levels were generally similar in all stations, Fe, Mn and Zn in station BA, and Ni in station SAM were minimum levels. Fe and Zn in station GA, Mn in station SAM, and Ni in station BA were maximum levels. In January, Cu, Ni and Pb levels in station BA, Cr, Fe, Mn and Zn levels in station GA, and Co and Zn levels in SA were higher than those in other stations. In April, Cu and Zn levels in station GA, and Co, Cr, Fe, Mn, Ni and Pb levels in station SA were higher than those in other stations. In July, Co, Cr, Cu, Fe, Mn, Ni and Pb levels in station GA, Cd in station SA, and Zn in station SAM were higher than those other stations. In general, there are statistically differences between the metal levels in different stations ($p<0.05$). In addition, there are differences between the metal levels in different months from the same stations ($p<0.05$).

The concentrations of metals in the water of River Asi were compared with other studies, world average and water quality criteria in Table 2. When compared with Turkish water quality criteria, the river is acceptable as polluted water for Fe and Ni, as less polluted water for Cr, Cu and Mn, and as clean water for Cd, Co, Pb and Zn (TEG, 1988). Although the concentrations of Cu, Fe and Zn measured in this were higher than Turkish permissible concentrations, others were lower than those (TKB, 2002). As seen in Table 2, when compared with US EPA recommended water quality criteria, the metal concentrations measured in this study were higher than it except Cd (for CMC and CCC), Ni and Pb for CMCs (US EPA, 1999). On the other hand, if compared with world average back ground concentrations, the concentrations of all metals measured in this river were higher (Klavins et al., 2000). When other studies are considered (Table 2), Cr, Cu, Fe, Mn, Ni and Zn levels in River Asi were generally higher than those in Lake Texoma, Gomti River and Küçük Menderes River waters (except Zn for Küçük Menderes River), were lower than Dil Stream (except Cd). Copper, Fe, Mn and Zn levels in River Asi lower than those in Beyşehir Lake, Fe, Mn and Ni levels were higher than those in Atatürk Dam Lake. Cadmium levels were lower than those in Lake Texoma and Dil Stream, and were higher than those in Küçük Menderes River.

Table 2. Comparison of the overall metal concentrations in the water of River Asi with other studies and water quality criteria (μg l^{-1}).

Studies and guidelines	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study[a]	0.99	6.90	29.2	26.6	1714	114.5	60.3	6.23	154.4
TKB (2002)[b]	10	1000	100	10	700	1000	300	100	3.0
TEG (1988)[c]									
Class I	3.0	10	20	20	300	100	20	10	200
Class II	5.0	20	50	50	1000	500	50	20	500
Class III	10	200	200	200	5000	3000	200	50	2000
Class IV	>10	>200	>200	>200	>5000	>3000	>200	>50	>2000
US EPA (1999)[d]									
CMC[*]	4.3	-	16	13	-	-	470	65	120
CCC[*]	2.2	-	11	9.0	-	-	52	2.5	120
An & Kampbell (2003)[e]	20	<2.0	4.0	24	119	7.0	5.0	15	59
Singh et al. (2005)[f]	-	-	1.3-5.7	-	34-117	1.3-5.3	9-17	19-39	11-32
Turgut (2003)[g]	0.81	-	0.093	13.1	-	-	2.27	0.59	249
Pekey et all. (2004)[h]	8.0	21	42	37	4030	-	-	120	700
Klavins et all. (2000)[I]	0.02	0.08	-	1.0	-	6.0	0.3	0.2	10
Tekin-Özan (2008)[j]	-	-	-	100	100-2740	20-520	-	-	20-420
Karadede & Ünlü (2000)[k]	-	-	-	25-220	62	3.9-4.1	11-15.4	-	64-197

[a] Mean, the number of analyzed samples= 40 for Cd, 75 for Pb, 80 for others.
[b] Turkish Permissible Concentrations.
[c] Turkish Water Quality Criteria (Class I: clean water, Class II: less polluted water, Class III: polluted water, Class IV: heavily polluted water).
[d] US EPA Recommended Water Quality Criteria.
[e] Lake Texoma, border of Oklahoma and Texas.
[f] Gomti River, India.
[g] Küçük Menderes River, Turkey.
[h] Dil Stream, Turkey.
[I] Background concentrations, world average.
[j] Beyşehir Lake, Turkey.
[k] Atatürk Dam Lake, Turkey.
[*] CMC and CCC: Criteria Maximum Concentration and Criterion Continuous Concentration.

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