# Temporal Variations in Water Quantity and Quality of Orontes River, Turkey

BERKANT ÖDEMİŞİ, MUSTAFA KEMAL SANGÜN\* and DURSUN BÜYÜKTAއ

Department of Chemistry, Faculty of Arts and Sciences Mustafa Kemal University, 31024 Antakya, Hatay, Turkey Fax: (90)(326)2455907, E-mail: ksangun@gmail.com

The aim of this study was to determine variations in physical and chemical water quality parameters of the Turkish part of Orontes River, whose basin is shared by Lebanon, Syria and Turkey, between 1984 and 2002. Due to very low amount of surface water in the region, groundwater is densely used for irrigation. In this case, it causes an increase in the salinity in some regions of Amik Plain, Hatay, Turkey. As a result of extensive usage of the river for irrigation in the region, the flow rate has decreased significantly. The most important impairment in flow rate occurred in 2000. The value of EC and pH were found to be relatively low in the year of 1984 and then found to increase in 2002. OM level showed a decreasing trend between the years of 1984 and 1992. The total boron content showed yearly periodic cycles and generally had a decreasing trend. The river has a notably fluctuating flow rate and the amount of water varies seasonally. According to the long-term data, the flow rate was falling to an average value of 3.66 m<sup>3</sup> s<sup>-1</sup> in August. Organic pollutant parameters (TDS, BOD and COD) fluctuated at rainy, transitional and dry seasons. Between 1999 and 2001, TDS and COD values showed an increasing trend, while BOD levels showed a decreasing trend.

Key Words: Orontes (Asi) River, Water quality, Flow rate, Organic pollution, Boron.

## INTRODUCTION

For developing sustainability both quality and quantity of water resources need to be monitored and preventive and mitigative measures need to be taken<sup>1-4</sup>. Biswas *et al.*<sup>5</sup> reported that the major reasons for a decrease in the quality and quantity of water resources are rapid growth of the world population, depletion of groundwater resources, pollution of water resources and biological invasions

<sup>†</sup>Department of Irrigation and Drainage, Faculty of Agriculture, Mustafa Kemal University, 31024 Antakya, Hatay, Turkey.

<sup>‡</sup>Department of Irrigation and Drainage, Faculty of Agriculture, University of Akdeniz, Antalya, Turkey.

712 Ödemis et al. Asian J. Chem.

of exotic species. In this study, the Orontes river was chosen because of its importance in the region as a 380 km-long transboundary river originating from Lebanon and shared by Syria and Turkey. Subsequent to the irrigational use of its waters for 12000 ha area of the Amik Plain, Hatay, Turkey, the Orontes River concludes in the Mediterranean Sea at the south edge of Samandağ, Hatay, Turkey. The Orontes River is projected to have a potential use for irrigation in about 50000 ha of the Amik plain<sup>6</sup>. Having completed a dam in Syria, the river flow rate in Turkey decreased in the summer and adversely affected agricultural production in the Amik Plain. Due to insufficient surface water, the farmers have to use saline groundwater resources for irrigation. The high salinity of groundwater has led to secondary salinization of some 3073 ha, 2813 ha being slightly saline (2 dS m<sup>-1</sup> < ECe < 4 dS m<sup>-1</sup>) and 260 ha highly saline (ECe > 4 dS m<sup>-1</sup>).

In the region, 61% of the working population depends on agriculture, fishing, stockbreeding and forestry. All these jobs need water to maintain life in the region. Therefore, water availability and quality of Orontes River has very important socio-economic effects on the region. A total of 158417 women and 112491 men were noted to engage in agricultural sector in Hatay despite the fact that males are dominant in the industrial sector<sup>7</sup>. In 1994, totally 1,675,302 tons of cereal crops, vegetables and fruits were produced in the Amik Plain. The crops of Amik Plain are mainly cotton (*Gossypium hirsutum* L.), maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.) with a total production of 604,923 tons in 1994. The vegetables and fruits were produced to the extent of 702,635 and 371,744 tons in 1994, respectively<sup>8</sup>. Mostly African catfish (*Clarias gariepinus*) and other fishes were caught in the delta of the Orontes River. Other fishes such as European eel (*Anguilla anguilla*), some cyprinids and some cobitis were also caught and grown up in Orontes River<sup>9</sup>. Total production capacity of fishes is about 148,000 kg per year<sup>10</sup>.

It is crucial for the future of the region to determine the spatial and temporal analysis of water quality characteristics of the Orontes River. In this study, the temporal and spatial changes in the hydrological and water quality parameters of the river were investigated.

#### EXPERIMENTAL

**Study Area:** Lower Orontes Basin, which occupies 7796 km<sup>2</sup>, is located in southern Anatolia (36°45′ and 38°15′ longitude, 35°50′ and 37°16′ latitude) and surrounded by Euphrates Basin in the east, by Ceyhan Basin in the north, by the Mediterranean Sea in the west and by Syrian borderline in the south (Fig. 1).

Turkish part of the Orontes River Basin has a Mediterranean climate with the remarkable rainy season in the spring and winter (November–April). Climatic data reflecting the characteristics of the valley were obtained from the Antakya Meteorology Station, located in the middle of the valley. Mean annual precipitation and temperature (period 1945–1995) were 1124 mm and 18.1°C, respectively<sup>11</sup>. The statistical analyses of the 'climatic' data (Duncan Test) showed that three seasons could be classified, *i.e.*, dry season (June to September), rainy season (December to March) and transitional season (April, May, October and November).

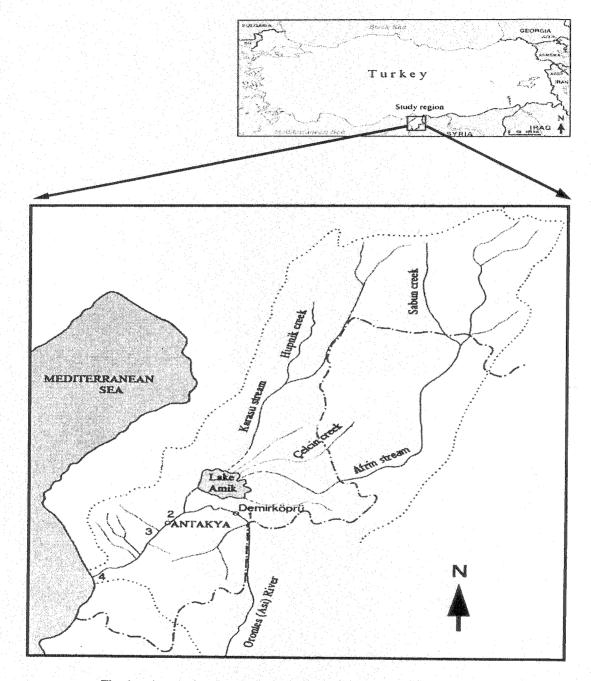


Fig. 1. A map showing the sample sites on the Orontes River (no scale)

The Orontes River Basin is intensively used for agriculture owing to the existence of very fertile soil around the river. However, nearly 200 industrial and hundreds of small size factories were located around or nearby the river and discharge their effluents into the Orontes River at a rate of 500,000 m<sup>3</sup> per year<sup>12</sup>. In this research, the pollution parameters of the river water were investigated between 1999 and 2001. Those parameters were total dissolved solids (TDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The investigation of TDS, COD and BOD was carried out by samples collected in four replicates at four sites along the Orontes River. The four sites were coded as follows: (1) entry from Syria to Turkey, (2) entry to Antakya, (3) exit from Antakya and (4) discharge into the Mediterranean Sea.

714 Ödemis et al. Asian J. Chem.

Water sample collection and analyses: Monthly flow, temperature, pH, EC and Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> + Mg<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, organic matter (OM) and boron concentration data were taken from the General Directorate of Electrical Power Resources Survey and Development Administration (EIE) at Demirköprü (36°12′14″ E–36°15′10″ N, altitude of 85 m, drainage area of 16170 km<sup>2</sup>) and Antakya sites (36°9′40″ E–36°12′11″ N, altitude of 73 m, drainage area of 22624 km<sup>2</sup>)<sup>13–14</sup>. At Demirköprü site, for the period 1984–2002, OM only was measured in 1991 and at Antakya site for the period 1997–2002, OM was not measured.

Additionally, four sites were sampled between 1999 and 2001 three times per year, in January (rainy season), May (transitional season) and August (dry season). The four sites were coded as follows: (1) entry from Syria to Turkey, (2) entry to Antakya, (3) exit from Antakya and (4) final discharge into the Mediterranean Sea. Water samples were taken in glass amber bottles and analyzed for EC, TDS, pH, COD, BOD.

EC-meter (Hanna® Instruments EC214) was used to determine electrical conductivity (EC). Sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) were analyzed by flame photometer, carbonate ( $CO_3^2$ ) and bicarbonate ( $HCO_3^2$ ) by sulfuric acid titration, chloride (Cl<sup>-</sup>) by silver nitrate titration (AgNO<sub>3</sub>) and calcium ( $Ca^{2+}$ ) and magnesium ( $Mg^{2+}$ ) by Versanat titration. Sulphate ( $SO_4^{2-}$ ) was calculated by subtracting the total amount of anions such as  $HCO_3^-$ ,  $CO_3^{2-}$  and Cl<sup>-</sup> from total amount of cations. pH was measured using a glass electrode pH-meter (Hanna® Instruments, pH 211). Boron was analyzed using Carmen solution and method of calorimeter. OM was determined by method of permanganate<sup>15</sup>. COD, TDS and BOD were determined by Merck® spectrophotometer, SQ118 Merck® spectrophotometer and VELP®, respectively. The flow rate was measured by AA price type low-level mulines<sup>16</sup>. Corrosive tendency was calculated using the equation  $K = (Cl^- + SO_4^2)$ /alkalinity ( $HCO_3^-$ , meq  $L^{-1}$ )<sup>17</sup>.

Statistical analyses: The data was analyzed statistically using Statistical Package for the Social Sciences (SPSS) software. For the Antakya and Demirköprü sites, spatial differences and seasonal trends with respect to time were evaluated. The results obtained were checked by t-test in order to see if any spatial and temporal differences exist in the region. Also, Duncan test was performed to find out the temporal classification. The standard deviation (SD) values of the observed parameters were calculated and presented as figures and tables. Also, nonparametric Kendall's tau test was employed and correlations of the parameters were presented in Table-1<sup>18</sup>.

### **RESULTS AND DISCUSSION**

Maximum-minimum values of hydrologic and water quality parameters of the Orontes River are given in Table-2. Most of the investigated parameters varied spatially and temporally. Maximum values of the water quality parameters during the study period were mostly measured at Antakya sampling site. The region between Demirköprü and Antakya sampling sites consisted mostly of agricultural area, where water consumption from the river during spring and summer months when agricultural production rises was rather high. In travelling from Demirköprü to Antakya, the flow rate decreases because of increased agricultural and intensive

RANGES OF SOME HYDROLOGICAL AND WATER QUALITY MEASUREMENTS OF THE ORONTES RIVER DURING THE DRY AND RAINY MONTHS AT THE DEMIRKÖPRÜ AND ANTAKYA SITES TABLE-1

		Demirköprű (min-max ± SD)	SD)		Antakya (min-max ± SD)	()
Parameter	Dry months $(n = 73)$	Rainy months $(n = 72)$	Transitional months $(n = 66)$	Dry months $(n = 14)$	Rainy months $(n = 21)$	Transitional months $(n = 19)$
Flow Rate	0.935-45.80 ± 5.11	2.72-158.56 ± 28.60	2.053-81.67 ± 11.32	0.51-21.63 ± 6.66	$16.21 - 284.17 \pm 62.30 \ 11.80 - 73.2 \pm 14.27$	$11.80 - 73.2 \pm 14.27$
	$15-30\pm3.09$	7-16±2.08	$12-27 \pm 2.40$	$16-31 \pm 3.83$	$8-16\pm1.90$	$13-24 \pm 3.12$
<b>Hd</b>	7.5-8.7 ± 0.20	$7.65 - 8.70 \pm 0.18$	$7.20-8.65 \pm 0.20$	7.75-8.70 ± 0.34	$7.72 - 8.69 \pm 0.20$	$8.01 - 8.74 \pm 0.17$
EC	$342-1860 \pm 455.50$	687-1926 ± 222.5	246-1317 ± 187.43	$641-1020 \pm 106.33$	563-1692 ± 226.6	652-1817 ± 159.06
$N_a^{\dagger}$	0.97-4.10 ± 0.29	$1.17-4.86\pm0.73$	$0.10 - 4.13 \pm 0.52$	$1.23-2.65\pm0.34$	$1.03-5.00\pm0.90$	$1.34-5.69\pm0.78$
K	0.03-0.25 ± 0.56	$0.02-0.25\pm0.12$	$0.04 - 0.17 \pm 0.02$	$0.06-0.25\pm0.07$	$0.06-0.13\pm0.02$	$0.01-0.13 \pm 0.02$
$Ca^{2+} + Mg$	$2.69-16.41 \pm 1.54$	5.10-7.12 ± 2.06	2.40-13.30 ± 1.73	$5.40-8.78\pm0.78$	5.22-14.06 ± 1.80	5.30-14.28 ± 1.13
CO3-	0.00-1.30 ± 0.22	$0.00-1.54\pm0.23$	$0.00-1.20\pm0.21$	$0.00-1.20\pm0.42$	$0.00-0.92 \pm 0.30$	0.10-1.18 ± 0.24
HCO <sub>3</sub>	$0.40 - 5.94 \pm 1.07$	$0.95-5.40 \pm 1.06$	$1.25-5.18 \pm 1.10$	$1.84-5.58 \pm 1.05$	$2.52 - 5.14 \pm 0.57$	$2.31-5.33 \pm 0.81$
ď	$0.36 - 4.30 \pm 0.45$	0.84-4.36 ± 0.62	$0.11-3.75\pm0.49$	$1.07 - 2.20 \pm 0.28$	0.98-4.57 ± 0.75	$1.20 - 5.92 \pm 0.65$
507	$0.95-12.48 \pm 1.00$	$1.56-12.43 \pm 1.89$	$0.79-10.63\pm1.39$	$0.89 - 3.85 \pm 0.34$	$1.41-9.58 \pm 1.97$	$1.76-10.20\pm1.26$
OM	$0.40 - 1.90 \pm 0.33$	$0.80 - 3.00 \pm 0.53$	$0.90-2.20\pm0.29$	l	I	1
Boron	$0.00-1.00\pm0.18$	$0.00-0.50\pm0.13$	$0.00-0.50 \pm 0.12$	$0.03-0.34\pm0.15$	$0.02-0.62 \pm 0.11$	$0.02-0.35\pm0.11$
Hardness	13.50-82.05 ± 7.70	$25.50 - 85.60 \pm 0.28$	$12.00-66.25 \pm 8.63$	$27.00 - 43.90 \pm 3.90$	$26.1 - 70.3 \pm 9.21$	26.50-71.40 ± 5.65
<b>×</b>	$0.73-9.93\pm0.94$	$0.72 - 6.34 \pm 1.13$	$0.56 - 5.28 \pm 0.79$	$0.40-2.25 \pm 0.28$	$0.61 - 4.28 \pm 0.69$	$0.49 - 5.17 \pm 0.69$
	6	The state of the s				

SD: Standard deviation; Flow rate:  $m^3 s^{-1}$ ; T: Temperature, °C; EC: Electrical conductivity, mhos cm<sup>-1</sup>; Anions and cations: meg L<sup>-1</sup>; OM: Organic matter, mg L<sup>-1</sup>; Boron: mg L<sup>-1</sup>; K: Corrosion coefficient.

TABLE-2

	$\times$	1.71	2.22	1.82	2.81	2.73	5.09	2.13	1.90	0	1 48	1.06	1.55	1.00 C	70.07	0.1	0,20	1.20	1.38	1.23	1.29	1.30	0.77	1 20	200	1 43	Cr.
	Hardness	49.22	51.10	50.82	48.00	54.82	8.7	52.82	40.00	38 98	20.50	20.00	31.34	51.55	33.97	28.10	30.10	31.15	38.54†	29.25	35 82+	31 50	34.05	32 10	22.10	25.12	30.23
ITES	Boron	0.12	0.16	0.12	0.16	0.13	0.19	0.14	0.13	0.14	10 C	0.10	0.13	o :	0.14 4.5	0.21	0.16	0.20	<u> </u>	0.13	0.15		21.0	0.17	0.10	0.20	CI.O
KÖPRÜ SI	SO2-	5.11	5.96	5.59	6.48	6.44	4.95	622	437	202	0.0	18.7	2.86	3.13	2.25	2.65	1.01	2.65	3.05+	245	5 6	7.17	71.7	7.0	7.77	2.15	336
D DEMIR	   C	2.70	3.46	3.02	2.51	3.56	2.56	3 10	77.0	17.7	1.//	2.05	tourid 	1.67	1.60	1.88	1.38	173		1.74	1.00	0/.1	1.70 2.0	1.30	1.80	1.35†	1.75
HEN ANTAKWA AND DEMIRKÖPRÜ SITES	HCO3	4.61	4.24	4.70*	3.20	3.92	3 50	) VC V	17.7	0.40 of ,	4.4/*	3.28	4.57‡	3.10	4.75†	3.03	4.89	3.55	J	4.11	74.0	C	5.45	4.53	3.52	4.20	3.57
TEEN A NIT	CO2-	0.45	0.27	0.22	0.28	0.48	2,0	0.37	00	۲.5 د د د	0.42	0.25	0.31	0.25	0.25	0.27	0.46	5.00	47.0	0.737	0.70	0.487	0.35	0.53	0.26	0.58	0.47
IABLE-2	Ca+Me	0 84	10.22	70.01	09.6	10.06	000	0.00	10.30T	3. 3.	7.79	6.16	7.46	6.27	6.79	5.62	600	3000	67.0	7.711	5.85	7.16†	6.30	6.84	6.42	6.62	7.25
A TO A BATTORY	K+	000	. c. c.	200		0.10	5 6	) 5:5	) (0.0	S):	*90.0	0.08	0.00	0.11	0.16	0.13	+000	0.20	71.0	0.09	0.12	0.08+	<u> </u>	0.11	0.13	0.10	0.12
	No+ K+ Ca+Mg	200	2.73	20.7	0.70	326+	0.70	97.7	3.16	2.15	1.84	1.77	1.90	1.97	1.90	103	1.73	1.33	2.01	2.23	1.96	2.19	1.92	1.54	1.84	1.56	<u></u>
		ב ב ב	1104	1323	1150	1240	1340	1033	1240	950	888	753	865	784	820	733		771	789	***	748	856	880	99/	950	758	1000
1	THE COMPARISON OF I	ud ,	8.3J*	8.10 7.10	0 0 0 0	0.10 CI 0	8.29	8.20	8.41+	8.18 8.18	8.36*	8.07	8.26	8.09	8 12	0 17	0.17	8.37	8.14	8.54†	8.17	8.42†	8.21	8.40	8.00	8.45	8.25
			07.71	11.39	12.40	11.83	17.60	13.05	16.20	15.28	18.00	18.84	2000	50.63	77.67	20.00	10.77	25.50	23.21	21.00	21.56	20.00	19.31	15.75	5,3	12.83	12.40
	6	Flow Kate	64.68	33.46	77.53	8.64	94.16	38.28	47.53†	23.87	28.03	15 88	14 M	0.18	4.81	7 C	3.70	0.51	3.66	11.56	5.98	16.02	10.85	18.25	13 34	35.40	24.11
		Month	an.	,	Feb.		Mar.		Apr.		Mav	Ç.	Timo	Amn o		July		Aug.		Sept.		Oct.		No.	:	رو	j

\* and † refer to significant differences between Antakya and Demirköprü sites at p < 0.05 and p < 0.0,1 respectively. First and second values were mean values of Demirköprü and Antakya sites, respectively. Flow rate:  $m^3 s^{-1}$ ; T: Temperature, °C; EC: Electrical conductivity, mhos cm<sup>-1</sup>; Anions and cations: meg L<sup>-1</sup>; Demirköprü and Antakya sites, respectively. OM: Organic matter, mg L<sup>-1</sup>; Boron: mg L<sup>-1</sup>; K: Corrosion coefficient.

industrial consumptions. The average flow rate in Demirköprü site decreased between 1984 and 2002 (r = -0.392, p < 0.05) (Fig. 2).

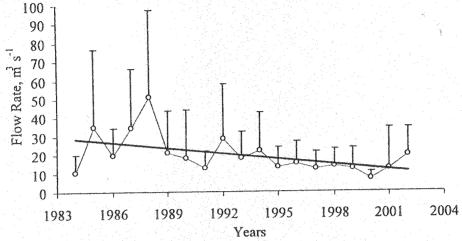


Fig. 2. Annual changes in the flow rate of the Orontes River at Demirköprü site

Based on 212 measurements at Demirköprü site, flow rate values and their percentages were classified as follows:  $0-10 \text{ m}^3 \text{ s}^{-1}$  (48%),  $10-50 \text{ m}^3 \text{ s}^{-1}$  (43%) and over 50 m<sup>3</sup> s<sup>-1</sup> (8%). The lowest flow rates occurred in July (3.70 m<sup>3</sup> s<sup>-1</sup>) and in August (3.65 m<sup>3</sup> s<sup>-1</sup>). Due to rainy season, the maximum flow rates were reported in February (49.00 m<sup>3</sup> s<sup>-1</sup>). Statistical analyses showed that flow rate values changed monthly in Demirköprü site (p < 0.01) (Fig. 3).

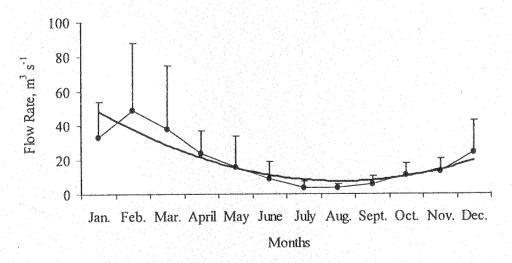


Fig. 3. Monthly changes in thee flow rate of the Orontes Rivers aaat Demirkörü site

Duncan test performed for comparison of the changes on a monthly basis showed that June, July, August and September comprised the dry season; December to March comprised the rainy season and April, May, October and November comprised the transitional season. Annual average water temperature was maximum in 1984 (22°C) and minimum in 1992 (15.55°C).

Between 1984 and 1994 the average of the water temperature showed a decreasing trend; after 1994 it started to increase. Six groups were classified according to monthly water temperatures: (1) December to March, (2) April and November, (3) May and October, (4) June, (5) September, (6) July and August.

Electrical conductivity rose (Fig. 4) from 789.14 μmhos cm<sup>-1</sup> in 1984 to 1200.23% μmhos cm<sup>-1</sup> in 2002. The EC values were high during the rainy season and relatively low during the dry season. The flow rate values in the rainy season

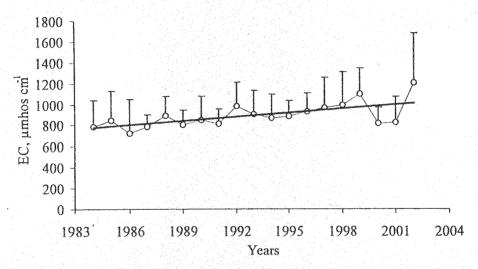


Fig. 4. Annual changes in the electrical conductivity (EC) at Demirköprü site

increased by about 30%, relative to the dry season. In the rainy season, saline materials leach through the soil, thus increasing ion concentration in the river. The conductivity measured at Demirköprü site was 880  $\mu$ mhos cm<sup>-1</sup>. Because of heavy industrial flow rates at Antakya site, the average EC was 978  $\mu$ mhos cm<sup>-1</sup> due to erosion and discharge of industrial waste water<sup>19</sup>.

Fig. 5 shows a gradual increase in pH values. The average values indicated slight alkalinity (pH = 8.03 to 9.02). Low pH values were observed in 1989, 1991 and 1996. The average pH was  $8.15 \pm 0.20$ . pH values between the observation points increased over time (r = 0.58; p < 0.01) with greatest value observed at Antakya. pH values were higher at the rainy seasons, with maximum value (8.25)

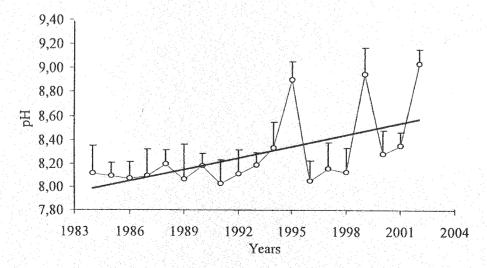


Fig. 5. Annual changes in pH values at Demirköprü site.

in December and minimum value (8.06) in May. The reason for maximum pH observed in December could be attributed to the dissolving effect of the rains on the basic calcareous and limy ground as well as the excessive effluents of olive oil and leather factories. Increasing SO<sub>x</sub> and NO<sub>x</sub> gases in the atmosphere in the dry season and associated acid depositions may be the causes of less alkaline pH. It should be noted that Hatay Province has the second largest truck and TIR fleet in Turkey. Therefore, it is not surprising to see increasing SO<sub>x</sub> and NO<sub>x</sub> gases in the atmosphere during the dry summer months. There was an increase in Na+,  $K^+$ ,  $Ca^{2+} + Mg^{2+}$ ,  $HCO_3^-$  and  $Cl^-$  ion concentrations over time except for  $CO_3^{2-}$ . Increasing rates of Ca<sup>2+</sup> + Mg<sup>2+</sup> concentrations were more than those of the other elements.

The monthly mean values of the ion concentrations showed a decrease during the dry season and then peaked in January and February.

As seen in Table-3, the flow rate values in April and September, the pH values in January, April, May, September and October were found to be different between the Antakya and Demirköprü sampling sites.

The sodium absorption ratio  $(SAR = Na^{+}/[Ca^{2+} + Mg^{2+})/2]^{1/2})$  is a very important parameter for the quality of water used in agricultural sector<sup>20</sup>. SAR was determined to be lower than the harmful level and varied between 0.99 and 1.34.

The lowest value of OM was 1.26 mg L<sup>-1</sup> in 1984, while the highest value was 1.59 mg L<sup>-1</sup> in 1985 and 1988. The monthly average values for the lowest and highest levels were determined as 1.01 mg L<sup>-1</sup> in August and 2.11 mg L<sup>-1</sup> in February. Normally, OM should increase in the dry season and should decrease in rainy season. According to data OM decreased in the dry season and increased in the rainy season. OM may be increased by discharge of municipal wastes into the river in the rainy season and it is the main source of OM accumulation. Another reason of OM increase during rainy season is that the rain could be carrying the fertilizers that were used for agricultural purposes and carrying the plant residues after the harvest. Due to the bad smells around the river in the dry season, municipal wastes were not allowed to be discharged into the river canal.

Boron concentration varied between 0.04 and 0.39 mg L<sup>-1</sup> for the study period. The minimum annual Boron concentration was found to belong to the year of 1991 (0.04 mg L<sup>-1</sup>). The minimum boron concentration monitored monthly was found to belong to October (0.12 mg L<sup>-1</sup>). Statistical analyses showed that mean concentration of boron was not changed monthly or seasonally except 1990's dry and rainy seasons (p < 0.05). Boron is necessary for plant growth and it is a toxic element for plants when it is higher than 0.50 mg/L21. Özdilek22 noted that although boron concentration in river water is close to each other at Demirköprü and Antakya sampling sites, boron flux in the river increases remarkably between these two observation stations, specifically in wet season. The results showed a relative decrease in temperature during the rainy season compared to an increase in the dry season. According to observed months, the water temperature was constituted six different groups: (1) Dec. to Mar., (2) Nov., April, (3) May, Oct., (4) June, (5) Sep., (6) July, Aug. Results also showed that the water temperatures at Demirköprü sampling site and Antakya sampling site were about the same

KENDALL CORRELATION MATRIX OF THE WATER QUALITY PARAMETERS DETERMINED TABLE-3

			20						- the second sec							-
	Year	Flow Rate	[	I	EC	Na+	K <sup>+</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	CO3-	HCO3	Cl	SO <sup>2</sup> -	SAR	OM	Boron	$\bowtie$
Flow rate	-0.392*				-											
	0.041	-0.298														
	0.437†	-0.106	0.165													
EC	0.497†	0.018	-0.135	0.295												
+_/	0.422†	-0.188	0.188	0.373*	0.598‡											
‡∡	0.568†	-0.528†	0.247	0.337	0.301	0.442*										
Ca <sup>2+</sup> + Mg <sup>2+</sup>	0.434†	0.059	-0.129	0.278	0.868‡	0.488†	0.214									
- <u>5</u> 00	-0.036	0.167	-0.203	0.343*	0.084	0.042	-0.150	0.162								
20 <u>3-</u>	0.413	-0.389*	-0.012	0.161	0.413†	0.219	0.418*	0.420†	-0.199							
5	0.465†	0.160	0.100	0.344*	\$89.0	0.844‡	0.437*	0.555‡	0.072	0.261						
SO <sub>4</sub> -	0.176	0.223	-0.080	0.254	0.633‡	0.453†	-0.010	0.665‡	0.210	0.160	0.448†					
A	0.231	-0.270	0.397*	0.322	0.231	0.641‡	0.385*	0.119	0.018	0.060	0.554†	0.202				
OM	-0.180	0.691*	-0.255	0.222	0.327	-0.109	-0.520	0.473	-0.038	-0.070	-0.110	0.546 -0.330	-0.330			
Boron	9	0.251	-0.203	900.0	0.024	900.0	-0.180	0.042	0.1524	-0.140	-0.020	0.018	0.036	0.148		
Hardness	0.214	0.429	0.214	0.214	0.929†	0.786†	0.367	1.000‡	0.222	0.327	0.786†	0.714†	0.445	1	0.470	
	-0.110	0.368*	0.041	0.224	0.228	0.282	-0.170	0.223	0.418	-0.342*	0.312	0.493	0.254	0.255†	0.000	0.357
			***************************************	-			-						100000000000000000000000000000000000000			

\*, † and ‡ values are significant at confidence level of p < 0.05, p < 0.01 and p < 0.001, respectively. Flow rate:  $m^3 s^{-1}$ ; T: Temperature, °C; EC: Electrical conductivity, µmhos cm<sup>-1</sup>; Anions and cations: meg L<sup>-1</sup>; OM: Organic matter, mg L<sup>-1</sup>; Boron: mgL<sup>-1</sup>.

throughout the study period (7-30°C, 8-31°C, respectively). The water temperature was between 13-30°C in the dry season and 7-24°C in the rainy season.

The less alkaline pH range (7-8), with dissolved oxygen ratios equal to or below 0.25, indicates general resistance to corrosion, whereas increasingly higher ratios generally indicate more aggressive waters which damage the water supply systems. The corrosion coefficient K in waters of optimal composition is not higher than 0.25. An increased ratio indicates the corrosive water tendency and these waters are rated as lower quality.

A correlation matrix was constructed to find the relationship and the changes of the water quality parameters over time (Table-1). The temperature showed a negative correlation with most water quality parameters given in Table-1. Depending on the flow rate of the river, some properties were found to be negative (K+ and HCO3) and some of them were positive (OM and K). EC values had a positive correlation at the level of p < 0.001 with anions and cations except K<sup>+</sup> and  $CO_3^{2-}$ .

The average COD results between 1999 and 2001 were 31.11 mg  $\rm L^{-1}$  at the site 1, 54.83 mg  $L^{-1}$  at site 2, 105.56 mg  $L^{-1}$  at site 3 and 68.94 mg  $L^{-1}$  at site 4, respectively. The average BOD results between 1999 and 2001 were 7.46 mg L<sup>-1</sup>,  $13.70 \text{ mg L}^{-1}$ ,  $85.38 \text{ mg L}^{-1}$  and  $52.61 \text{ mg L}^{-1}$  for the sites, respectively. Chemical oxygen demand and biological oxygen demand increased from site 1 to site 3 and then decreased to site 4 (p < 0.05). Because of the sea tide and the creeks, which run to the river, the river water was diluted. Therefore, COD and BOD values varied in sites. The average TDS results between 1999 and 2001 were 14.31 mg  $L^{-1}$  for site 1, 27.12 mg  $L^{-1}$  for site 2, 48.80 mg  $L^{-1}$  for site 3 and 38.51 mg  $L^{-1}$ for site 4. TDS values increased in site 3 because of the municipal untreated wastewater discharges at this site. Another reason for high TDS values could be the streams, mostly urbanized, of the river carrying sediments to the river.

Although TDS and COD values increased between 1999 and 2001 (p < 0.05), BOD values did not show an increasing trend in the same period. The maximum and minimum levels of the TDS values were found to belong to January (54.81) and May (19.31); for BOD values to January (89.59) and to August (11.91); for COD to August (68.48) and to May (62.20). According to results of the Duncan test, TDS and BOD values were in the same group in May and August. The monthly differences in COD values were not determined to be statistically significant. Three different groups were constituted between TDS, BOD and COD for each parameter and site (for TDS and BOD: sites 1, 2-4 and 3; for COD: sites 1-2, 4 and 3; p < 0.05). Comparing the TDS, BOD and COD values in different observation sites, the highest values of 48.80, 85.38, 105.56 mg  $L^{-1}$  for TDS, BOD and COD respectively were obtained in site 3.

#### **Conclusions**

Data showed an increase in the values of pH, EC, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> + Mg<sup>2+</sup>, HCO<sub>3</sub> and Cl<sup>-</sup>concentrations in the Orontes River between 1984 and 2002. The flow rate of the river was significantly decreased in the study period. The river had varying flow rates with 3.66 m<sup>3</sup> s<sup>-1</sup> during the dry season, thus causing serious problems in meeting agricultural water requirements. Increasing EC values of the 722 Ödemis et al. Asian J. Chem.

river over time decreased the potential of agricultural water consumption significantly. In this study period, EC levels increased by almost 52%. If EC increase in water continues and the river water is used for irrigation, the soils and associated biological productivity will most likely be impacted due to salinization and alkalinization. To avoid the adverse effects, efficient irrigation management practices such as surface and subsurface drip irrigation should be implemented in the region. The ion concentrations, with the exception of CO<sub>3</sub><sup>2-</sup>, also showed a similar tendency such that the ion concentrations generally decreased in dry season and increased in rainy season. The maximum increase was found to be in the concentration of Ca<sup>2+</sup> + Mg<sup>2+</sup>. The increase in pH during 18 years was approximately 0.91 (pH increased from 8.11-9.02). pH was found to be high at Antakya region (8.74). Discharging of mostly raw industrial and untreated municipal wastewaters into the river between Demirköprü and Antakya was the major cause of this increase in pH. The temperature values show a quadratic correlation in the study period. There was a high correlation between monthly air temperature and water temperature (r = 0.99; p < 0.01). The lowest and the highest surface water temperatures were 11.39 in January and 23.21°C in August, respectively.

Boron values increased considerably between 1987 and 1991 with the highest value of 0.39 mg L<sup>-1</sup> in 1990 but decreased with respect to the entire study period. Boron concentration in the dry season was slightly higher than that of the rainy season, with standard deviation found to be quite high in all months. OM in the dry season was found to be lower than that of the rainy season, with the lowest value of 1.01 mg L<sup>-1</sup> in August. The major cause of the increased OM in surface water in the early winter was most probably eutrophication caused by fertilizer applications. The corrosion values were found to be very high (1.84) in the water compared to the threshold value of 0.25.

TDS, COD and BOD results varied at the Antakya edge between 1999 and 2001. According to results, average TDS values were found to be 14.31 mg L<sup>-1</sup> in site 1 and increased up to  $27.12 \text{ mg L}^{-1}$  in site 2, then  $48.80 \text{ mg L}^{-1}$  in site 3. Finally, in site 4, TDS value was found to decrease to 38.51 mg L<sup>-1</sup>. Also average COD values were found to be 30.11 mg L<sup>-1</sup> in site 1 and increasing up to 54.83 mg L<sup>-1</sup> in site 2, then 105.56 mg L<sup>-1</sup> in site 3. Finally, in site 4, TDS value was determined to be 68.94 mg L<sup>-1</sup>. Besides average BOD values that were found to be 7.46 mg L<sup>-1</sup> in site 1 and increasing up to 13.70 mg L<sup>-1</sup> in site 2, then 85.38 mg L<sup>-1</sup> in site 3. Finally in site 4, TDS value was found to decrease to 52.61 mg L<sup>-1</sup>. While the river is leaving Antakya and approaching sea at site 4, TDS, COD and BOD results decrease in this segment. The reason could be the dilution of the polluted water by sea water at the estuarine environment. Before site 4, where river water is also used for irrigation, this could be another reason to reduce the TDS, COD and BOD levels due to estuarine characteristics. Pollution parameters were found to be higher in the samples taken in January between 1999 and 2001. The reasons could be fertilizers and pesticides, used for agriculture, dissolved and carried by rain. Additionally, in rainy season, the high flow rate of the wastes of industries and municipal effluents discharging into the river increase the river flow, resulting in eutrophication and a rise in TDS, COD and BOD values.

Turkey and Syria should be in close cooperation to determine sustainable management of the Orontes River. During irrigation season, the decrease in flow rate is a characteristic factor for the planning and the good production of agriculture in the region. Also, the water allocated for agriculture in the region should be reduced and the irrigation systems should be improved in order to save water used in the agrarian sector. Especially, drip irrigation systems should be preferred and be used widely and effectively for the irrigation. Besides water flow rate and amount, water quality should also be taken into consideration. The municipal and industrial wastes should be cleaned in wastewater treatment systems before the wastewater is poured into the river. The river pollution increases in dry season and it causes an unhealthy situation, bad smells and unwanted views in the middle of the city centre of Antakya. For this reason, the public should be informed and should have an active role in the management of the river water.

#### REFERENCES

- 1. N.S. Kulsreshtha, Water Res. Manag., 12, 167 (1998).
- 2. B. Schultz, Irrig. Drain., 50, 261 (2001).
- 3. S. Ravichandran, Environ. Monit. Assess., 87, 293 (2003).
- 4. M.S. Kambole, Phy. Chem. Earth, 28, 1105 (2003).
- 5. A.K. Biswas, Internat. J. Water Res. Dev., 9, 3 (1993).
- 6. E. Altunlu, Potential Water Resources of Hatay, Turkey, p. 86 (2002).
- 7. DPT (State Planning Organization) National Environment Action Plan, Population and Environment (compiled by A. Toros, M. Ulusoy and B. Ergöçmen), Turkey, p. 67 (1997).
- 8. DPT (State Planning Organization) Report of Hatay City, Turkey, p. 54 (1997).
- 9. S. Yalçin, Fishes of Asi River (Orontes)-IX, National Water Products Symposium, Isparta, Turkey, p. 73 (1997).
- 10. N. Munsuz, I. Unver and G. Cayci, Waters of Turkey, Ankara University Agriculture Faculty Publication No. 1505, p. 467 (1999).
- 11. DMI (Turkish State Meteorological Service) Monthly Weather Reports, Department of Meteorology Forecast, Ankara, Turkey (1995).
- 12. Y. Karakilçik and H. Erkul, Management of Asi River, Detay Publications, Ankara, Turkey, p. 356 (2002).
- 13. EIE (General Directorate of Electrical Power Resources Survey and Development Administration), Observations of Water Qualities in Turkey Rivers, Ankara, Turkey, p. 323 (1996).
- EIE (General Directorate of Electrical Power Resources Survey and Development Administration), Observations of Water Qualities in Turkey Rivers, Ankara, Turkey, p. 243 (2002).
- 15. USSL, Diagnosis and Improvement of Saline and Alkali Soils, in: L.A. Richard (Ed.), Agriculture Handbook, No. 60 (1954).
- 16. EIE (General Directorate of Electrical Power Resources Survey and Development Administration), Hydrology Engineering Data Base, EIE/ODTU Report, Ankara, Turkey (1984).
- 17. N.S. Giljanovic, Environ. Monit. Assess., 83, 229 (2003).
- 18. M.G. Kendall, Rank Correlation Methods, 4<sup>th</sup> Edn., Griffin, London, UK (1970).
- 19. L.O. Odokuma and G.C. Okpokwasili, Environ. Monit. Assess., 45, 43 (1997).
- 20. S.R. Ayers and D.W. Westcot, Irrigation and Drainage, Paper No. 29, Rev. 1 (1994).
- 21. F.M. Eaton, J. Agric. Res., 69, 237 (1944).
- 22. H.G. Özdilek, Turkish J. Aquatic Life, 1, 176 (2003).