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A study of ionic composition and inorganic nutrient fluxes from rivers discharging into the Cilician Basin, Eastern Mediterranean

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Abstract Present water quality of the perennial rivers; Göksu, Lamas, Efrenk, Tarsus and Seyhan discharging into the Cilician Basin have been investigated. Monthly surface samples collected from three stations downstream of the rivers during the period of October 2004–May 2005 were analyzed to determine ionic composition (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+ and K^+), in addition to measurements of pH, electrical conductivity, alkalinity and total hardness. The results have been compared with recommended water quality standards. Excluding Göksu, Seyhan and Efrenk river mouths, values for almost all measured parameters, except NH_4^+, were found to be lower than the desirable limits. In particular, inorganic ammonium, phosphate and nitrate concentrations for Göksu and Seyhan Deltas were 10^1 or 10^2 orders of magnitude higher than the concentrations of the rest of the samples. Temporal variation in levels, primarily observed in PO_4^{3-}, suggest the impact of agricultural fertilizers intensively used around Göksu and Seyhan Rivers. According to Turkish National Water Pollution Control Regulations, all rivers were found to be unpolluted with respect to their nitrate, chloride, sulfate and sodium ion contents, while they all could be considered as slightly polluted with respect to their phosphate contents. In contrast to nitrate and phosphate, ammonium exceeded the maximum permissible limits of water quality criteria in almost all samples. Among the sampled rivers, Tarsus River was better in water quality, with the lowest electrical conductivity, alkalinity, total hardness and nutrient concentration values. Calculated values of elemental inorganic N and P fluxes suggest a substantial increase in nitrogen loads within the last decade, compared to a significant decrease in phosphorus loads of the rivers during the same period.

Keywords Cilician Basin · Eastern Mediterranean · Göksu Delta · Inorganic nutrients · Macro-nutrient flux · Water quality assessment

Introduction

Land use is one of the most important factors controlling water quality of inland waters (Allan and Flecker 1993). Growth in population causes changes in land use patterns and consequently creates adverse effects on the water quality of aquatic resources. During the last few decades, the Mediterranean Coast of Turkey has been subjected to urbanization due to rapid population and industrial growth, agricultural and touristic activities, marine transport linked to the harbours of Mersin, İskenderun and Taşucu, oil storage and pipeline terminals

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at Yumurtalık, Ceyhan and Dörtyol (including the recently completed Bakü–Tblisi–Ceyhan pipeline transporting oil and gas from the Caspian Sea), leading to significant environmental stresses, with adverse effects on river waters, currently used for drinking and irrigation. In general, river water quality assessments have been lacking, excluding the regular river mouth measurements carried out by the Institute of Marine Sciences, METU during the years 1983–1991 (Yılmaz et al. 1992) and 2003–2006 (Tuğrul et al. 2007) to monitor coastal pollution from land-based sources. Seasonal measurements conducted at Göksu, Lamas, Tarsus, Seyhan and Ceyhan River Mouths revealed large coastal inputs of dissolved inorganic nitrogen in comparison to dissolved inorganic phosphorus, particularly from the Göksu, Seyhan and Ceyhan Rivers, leading to very high naturally occurring N/P ratios (Tuğrul et al. 2007).

The monitored rivers, Göksu, Lamas, Efrenk, Tarsus and Seyhan, are all perennial rivers discharging to the Cilician Basin of the NE Mediterranean. These sources including Ceyhan and some other smaller rivers supply a total fresh water flux of 27 km^3/year (870 m^3/s), accounting for about half the river discharge along the Turkish Mediterranean–Aegean coasts. This flux is much greater than the present discharge of Nile in the Eastern Mediterranean which is estimated to be 540 m^3/s (Pinardi et al. 2005). Particularly, following almost 90% reduction in the discharge of the River Nile in the 1960s Cilician Rivers have become one of the main fresh water and nutrient sources for the entire Levantine Basin of the "oligotrophic" Eastern Mediterranean (Özsoy and Sözer 2006). Phosphate is known to be the limiting nutrient for phytoplankton production in the Mediterranean, as a result of which the Eastern Mediterranean surface and deep waters are characterized with high N:P ratio (>20:1) (Krom et al. 1991; Krom et al. 1993). The extensive nutrient budget calculations by Krom et al (2004) have revealed that the high N:P ratio is primarily a result of the high biologically available N:P ratios of all sources, particularly that of the atmosphere (117:1). Since there is a general lack of data on river sources, except those for the Po and Nile, the Vollenweider et al (1996) model has been widely used to calculate riverine N and P fluxes, according to which the atmosphere was reported as the main source of nutrients for the Eastern Mediterranean Marine Environment (Krom et al. 2004).

Surface water samples collected from Göksu, Lamas, Efrenk, Tarsus and Seyhan Rivers were analyzed to determine concentrations of major ions (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+) in addition to the measurements of pH, electrical conductivity, alkalinity and total hardness. The data have been evaluated from two different perspectives:

The present water quality of the rivers was determined through comparison of the measured values with recommended drinking water quality standards of several organizations e.g. World Health Organization (WHO); Environmental Protection Agency (EPA); Turkish Standards Institute (TSI).

Soluble macro-nutrient contents of the studied rivers were quantified and their elemental flux contributions of $PO_4^{3-} - P$ and $NH_4^+ + NO_3^- - N$ into the Cilician Basin were calculated. The trend in river supply of macro-nutrients was evaluated for the last decade.

Materials and methods

Site description and sampling procedure

The Cilician Basin, located in the northeastern part of the Levantine Basin of the Eastern Mediterranean Sea covers the area between Turkey and the island of Cyprus. Mersin and Iskenderun Bays adjoining wide continental shelves and river deltas of the Göksu, Seyhan, Tarsus and Ceyhan are located along the Turkish coast (Fig. 1). Taurus and Amanos mountain ranges bound the Cilician Basin in the north and east, respectively, lined with the narrow coastal plains in those regions excluding the vast delta plains of Seyhan and Ceyhan Rivers. The climate is typical of the Eastern Mediterranean, with hot, dry (no rain) and humid summers, mild and rainy winters and short transitional seasons. Northerly winds dominate the winter (November to March) while southwesterly winds dominate the summer (April to October). Weather steered by steep mountain ranges but intercepted by valleys along the northern shore, such as the Göksu River Valley and the Gulf of İskenderun. (Reiter 1979; Özsoy 1981; Özsoy and Sözer 2006). Mean annual precipitation and the number of rainy days calculated for a period of 30 years (1963–1994) were found to be 580 mm and 67.2, respectively (Özsoy and Saydam 2001). In general, Cilician Basin consists of mainly terrigenous carbonates, derived from limestone, dolomite and calcretes (Yetiş et al. 1995). Rivers originate from calcareous-karstic Taurus mountains, mostly of Paleozoic and Mesozoic formation, reaching heights of 600–1,500 m in the north (Kapur et al. 2000) and flow through highly calcareous soils before converging to the Mediterranean. More than 72% of the soils in the region is reported to be extremely calcareous, the rest being moderately calcareous (ÇDR 2006). The total lengths of the main stem of Göksu, Lamas, Efrenk, Tarsus and Seyhan Rivers are 268, 130, 100, 150 and 560 km, with monthly mean flow rates of 45, 4, 2, 42 and 168 m^3/s, respectively (DSİ 2007). The lower reaches of these rivers, are sensitive natural preserves. For instance, the Göksu River Delta is one of the five wetland areas in Turkey under the protection of Ramsar convention, covering 14,500 ha of salt marsh subjected to anthropogenic and natural stresses arising agricultural and fishery activities, fluvial inputs and coastal currents.

Three sets sampling locations were chosen along the main courses of the selected rivers which are signed as black circles in Fig. 1. The first set consists of "delta stations" selected close to the mouths of the rivers. The second set consists of "central stations," near big settlements with important sources of municipal wastewater. The third set of samples were collected at "source stations" upstream of the rivers and remote from the direct influence of any big

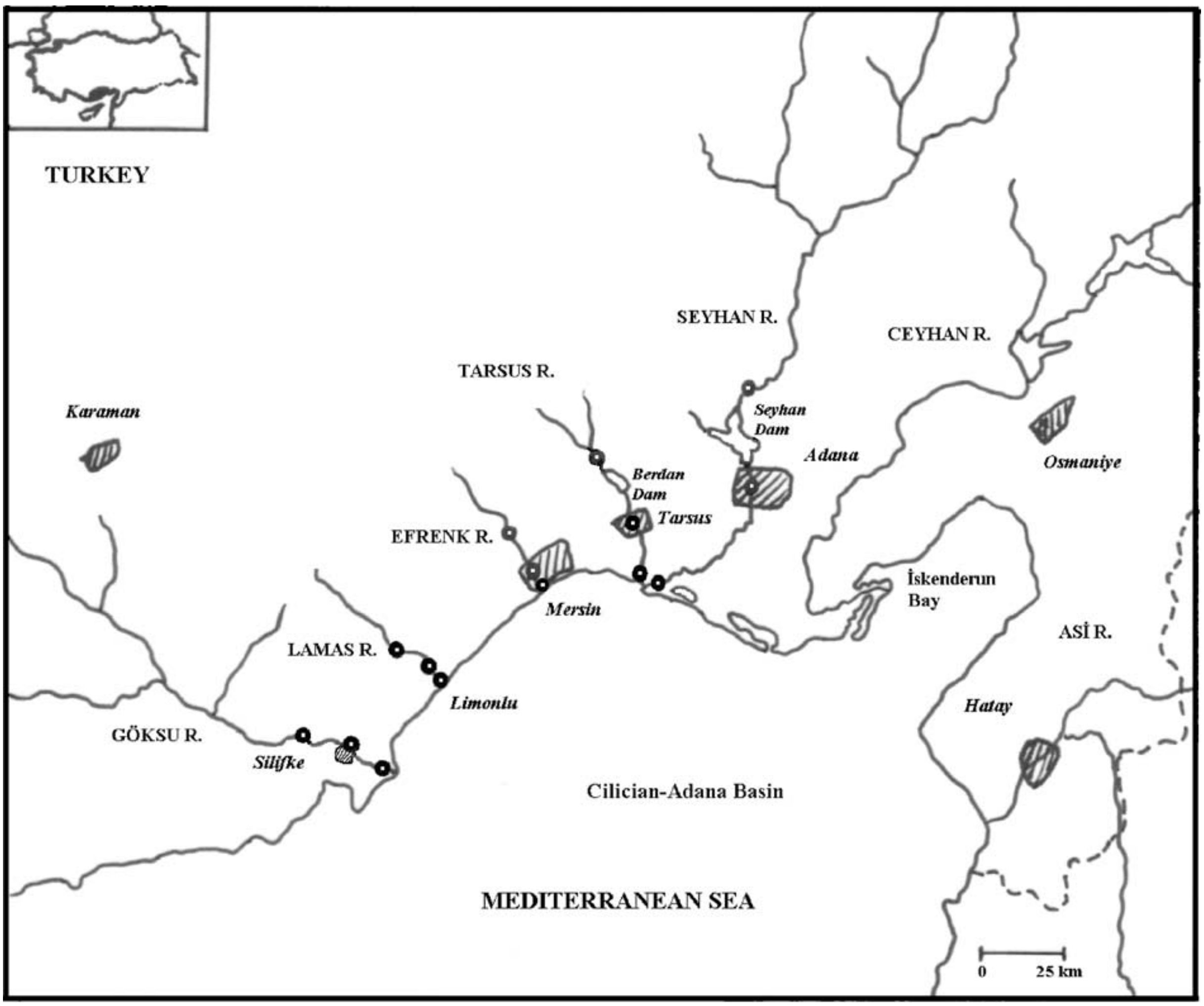

Fig. 1 Cilician Basin Coastal System showing delta, central and source sampling stations

settlements. The distance between the central and source stations is at least 10 km for Göksu, Lamas and Efrenk Rivers. Suitable source stations were selected on the Tarsus and Seyhan Rivers upstream of the Berdan and Seyhan dam reservoirs, approximately 16 km and 22 km from the towns of Tarsus and Adana, respectively. The Berdan dam has been constructed on this river (upstream of Tarsus) in 1984 to supply drinking water to the cities of Mersin and Tarsus and irrigation water for agriculture. A hydroelectric power generation facility, Seyhan dam has been constructed on Seyhan River in 1956, 15 km upstream of Adana, with the retained waters utilized for irrigation of the Çukurova plain. The exact location of central and source sampling stations, with the distances to the respective river mouths are summarized in Table 1.

All sampling stations were selected at least 200 m away from any industrial or municipal wastewater discharge points. River water samples were collected on five occasions: 22 October 2004; 27 November 2004, 19 December 2004; 26 February 2005 and 1 May 2005 from the above set of stations, mainly during the rainy season. Unfortunately, no sample could be collected during the dry season (except 1 May 2005) due to insufficient technical personnel and facilities. River water samples were collected manually from the surface of the river (upper 50 cm) using 2.0 dm^3 capacity PE bottles pre-cleaned according to the procedures in APHA (1992).

Analytical methods

The pH and electrical conductivity were measured at the sampling site, using a Mettler Toledo MP120 pH-meter and a DIST H198300/3 (mS) and /4 (μS) Conductivity/TDS-Meters with automatic temperature compensation, respectively. Water samples were then immediately transferred to the laboratory at Mersin University, Çiftlikköy Campus. Alkalinity and total hardness were determined according to standard methods (APHA 1992). The water samples were filtered through 0.45 μm pore size membrane filters (MFS, cellulose acetate, 47 mm diameter) for the analysis of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). Samples reserved for major anion (Cl^{-}, SO_4^{2-}, NO_3^{-}, PO_4^{3-}) analyses were filtered through a 0.22 μm pore size membrane filter (Sartorius, celulose acetate, 47 mm diameter) in order to protect anion exchange column used for the major anion analysis. Subsamples of river waters were transferred in rigorously cleansed PE (polyethylene) bottles and preserved at 4°C; Subsamples reserved for PO_4^{3-} analysis were transferred in PE bottles and preserved in a deep-freeze at −18°C until analysis time. Aliquots for major cation analysis were preserved by acidification with 0.1 M HNO_3 before storage.

NH_4^{+}analyses have been performed as soon as possible, since it is unstable with respect to oxidation, Spectrophotometric Nessler method was applied using a Shimadzu UV-1601, UV–VIS Spectrophotometer. Analytical data are summarized in Table 2. The detection limit defined as three times the standard deviation of the blank value and reproducibility (CV %) defined as the standard deviation of seven replicate analysis of subsamples. A Varian Liberty II Model ICP-AES, at the Central Research Laboratory of Mustafa Kemal University in Antakya, was used for the analysis of Na^{+}, K^{+}, $Ca^{2+}$and Mg^{2+} cations. The ICP-AES with axial torch was controlled by a personal computer. Plasma power was 1.0 kW and integration time was 1.5 s with three replicates. A DIONEX 3000 model IC coupled with a VYDAC 302 IC anion exchange column was used for the analysis of Cl^{-}, NO_3^{-} and SO_4^{2-} at the Test and Analysis Laboratory of The Scientific and Technological Research Council of Turkey (TÜBİTAK) in Ankara. PO_4^{3-} analyses were performed using a Shimadzu UV-1601, UV–VIS Spectrophotometer with the application of ascorbic acid method (Murphy and Riley 1962). The samples having very low phosphate content were concentrated according to the magnesium-induced coprecipitation (MAGIC) procedure which can reliably detect 1 nmol soluble reactive P in 1 L of seawater or freshwater samples (Karl and Tien 1992). The solutions of all reagents

Table 1 The basic characteristics of central and source sampling stations with the distances (km) to the river mouths

River	Settlement (population)	Central station	Source station	Constructed dam
Göksu	Silifke (65,000)	18	28	–
Lamas	Limonlu (5,000)	0.7	11	–
Efrenk	Mersin (800,000)	2	12	–
Tarsus	Tarsus (350,000)	19	35	Berdan dam
Seyhan	Adana (2,000,000)	45	67	Seyhan dam

Table 2 Analytical details of the measured parameters in river water samples

Parameter	Method	Detection limit	Precision CV %	Accuracy (% relative error)
pH	pH-Meter	0.01 pH unit	–	<3.7
Conductivity	Conductivity/TDS Meter	1 μS cm^{-1}	–	<3.7
NH_4^+	NESSLER	0.005 mg/L	9.0	15
Ca^{2+}	ICP-AES	0.010 mg/L	0.3	4.9
Mg^{2+}	ICP-AES	0.003 mg/L	1.3	6.4
Na^+	ICP-AES	0.004 mg/L	0.9	6.4
K^+	ICP-AES	0.005 mg/L	4.1	<5.0
Cl^-	IC	0.075 mg/L	7.2	<3.7
NO_3^-	IC	0.070 mg/L	3.8	<3.7
SO_4^{2-}	IC	0.090 mg/L	4.1	<3.7
PO_4^{3-}	MAGIC	0.035 μM	9.9	–

CV: Coefficient of variation.

were prepared using ultra-pure water (18.2 μS cm^{-1}, Milli-Q System, Millipore, Bedford, MA, USA). The data for total concentrations of each parameters were obtained from triplicates (*n*: 3) with mean±standard deviation. The same procedures have also been applied to the field blanks collected twice within the sampling period. The concentration of field and laboratory blanks measured throughout the study were all below the detection limit of the measured species. The accuracy of the data are cross-checked by analysing the simulated rainwater samples of WMO/GAW (World Meteorological Organisation/ Global Atmosphere Watch).

Results and discussion

Water quality of the rivers

Due to possible intrusion of sea water to the sampling points at delta stations it was considered that the water samples collected from the river estuaries might not be representative to the fresh river water alone. Therefore, the data obtained from delta stations have been evaluated separately. Statistical results, arithmetic means with standard deviations and the range of the measured ionic concentrations, pH, electrical conductivity, alkalinity and total hardness of the fresh river water samples (collected from central and source stations) for the sampling period (from October 2004 to May 2005) are depicted in Table 3, while the statistical results of delta station samples are presented in Table 4. Total number of samples are given in parentheses.

Almost all values measured at delta stations of Göksu, Efrenk and Seyhan Rivers are higher than the rest of the data. Additionally, concentrations show larger variations with standard deviations typically larger than the arithmetic means of the measured parameters than the statistical results of freshwater data. For instance, Electrical conductivity, nitrate and sulfate concentrations of Göksu and Seyhan Delta station samples are 10^1 order of magnitude higher than the respective freshwater samples of these rivers. Due to possible seawater intrusion to the sampling points, major cation (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and chloride concentrations of Göksu and Seyhan delta station samples (Table 4) are found to be 10^2 or even 10^4 orders of magnitude higher than the respective freshwater values (Table 3). In order to determine the present water quality of the rivers discharging into the Cilician Basin, the data (Table 3) are compared to the recommended water quality criteria of several organizations, presented in Table 5. There are no specific rules that can easily be applied to calculate guideline values for chemical parameters in fresh waters. Therefore, WHO Guidelines for Drinking Water Quality (WHO 1998); EPA (1989) and Turkish National Drinking Water Quality Standards (TSI 1997) are used for this comparison.

Due to certain geomorphological characteristics of the region all rivers were found to be alkaline in nature, having high pH values and total hardness. Though it has no direct effect on human health, the pH values of most of the water samples fell within the permissible limits of WHO (1998) and TSI (1997). Hardness of water depends mainly upon the contents of calcium and/or magnesium salts. The limits of total

Table 3 Statistical results of the measured parameters in fresh river waters, collected from central and source stations for the sampling period (from October 2004 to May 2005)

Parameter	Göksu (10)	Lamas (8)	Efrenk (10)	Tarsus (10)	Seyhan (10)
pH	8.06–8.28	7.96–8.21	8.26–8.98	8.19–8.41	8.11–8.45
	8.16±0.07	8.12±0.08	8.58±0.24	8.27±0.07	8.29±0.10
E. conductivity	240–464	280–392	340–629	260–384	260–399
μS cm^{-1}	359±82	333±43	433±111	313±40	346±50
Alkalinity	176–282	247–372	204–393	168–351	155–334
mg $CaCO_3$ L^{-1}	234±35	290±48	298±59	230±65	218±48
Total hardness	250–314	240–300	249–397	193–272	207–299
mg $CaCO_3$ L^{-1}	278±20	278±21	327±55	238±28	253±22
NH_4^+	0.52–3.30	0.97–1.79	0.20–2.29	0.33–0.86	0.01–0.68
mg L^{-1}	1.46±1.01	1.39±0.30	1.32±0.68	0.58±0.16	0.36±0.18
Ca^{2+}	51.0–63.1	83.4–85.8	49.0–66.3	46.0–63.9	38.7–49.4
mg L^{-1}	57.8±4.8	84.9±1.0	58.9±7.2	56.8±7.9	44.2±4.5
Mg^{2+}	12.4–20.6	6.6–7.1	34.9–41.2	9.6–12.7	17.5–20.0
mg L^{-1}	16.3±3.2	6.8±0.2	37.4±3.0	11.3±1.2	18.7±1.0
Na^+	BDL–2.78	0.17–0.56	2.49–4.45	BDL–2.52	BDL–3.12
mg L^{-1}	1.89±0.70	0.39±0.17	3.20±0.86	1.41±1.13	2.29±1.30
K^+	0.81–1.60	0.43–0.72	1.09–3.76	0.49–1.23	0.98–1.87
mg L^{-1}	1.10±0.36	0.58±0.16	2.19±1.07	0.75±0.33	1.60±0.38
Cl^-	3.14–42.76	2.41–8.62	6.06–16.45	4.62–12.29	5.48–15.25
mg L^{-1}	10.38±11.80	4.50±1.95	10.23±3.33	8.69±3.09	12.21±3.25
NO_3^-	2.15–19.43	2.92–11.77	2.27–11.85	1.40–13.78	1.08–18.71
mg L^{-1}	6.11±5.52	5.69±2.68	5.62±2.79	5.30±4.01	3.42±3.38
SO_4^{2-}	4.27–31.3	3.68–10.09	10.39–40.55	5.52–12.95	10.81–31.44
mg L^{-1}	16.83±8.34	7.19±2.25	22.20±10.13	10.18±2.96	23.93±7.04
PO_4^{3-}	3.23–781.7	5.79–249.0	3.61–369.2	3.61–94.97	4.37–374.8
μg L^{-1}	164.0±299.3	81.0±103.9	100.6±140.7	31.7±33.2	86.0±130.3

Total number of samples are given in parentheses.

BDL: Below detection limit.

hardness in potable water range from 100 to 500 mg $CaCO_3$ L^{-1} (EPA 1989). Total hardness for all the central and source station samples varied from 193 to 397 mg $CaCO_3$ L^{-1}, not exceeding the maximum permissible limit. The same situation is also valid Ca^{2+} and Mg^{2+} ions. Mean concentrations of these ions are all within the recommended limits of both EPA (1989) and TSI (1997).

The electrical conductivity (EC) is an indicator of the amount of dissolved material in water; and it ranged from 240 to 629 μS cm^{-1} for all the central and source station samples. Mean EC values are all below the desirable limit value (750 μS cm^{-1}) of WHO (1998).

Sodium and chloride ions in river waters are usually originated from the dissolution of halite minerals in river beds or from the municipal wastewater discharges. According to Versari et al. (2002) chloride concentrations higher than 200 mg L^{-1} are considered to be of 'risk' for human health and may cause unpleasant taste of water. The desirable concentrations of Na^+ for public water supplies are 50 mg L^{-1} (WHO 1998) and 20 mg L^{-1} (TSI 1997). Mean Na^+ concentrations of almost all samples from central and source stations were significantly lower than these limit values. Similarly, Cl^- concentrations of the same samples were all lower than the desirable limits of WHO (1998) (250 mg L^{-1}) and TSI (1997) (25 mg L^{-1}). These results are consistent with the low salt (halite mineral) content of regional soils. It is reported that more than 96% of the soils in the region are devoid of salt (ÇDR 2006).

Sulfate can be originated from the dissolution of gypsum ($CaSO_4$ $2H_2O$) which is common in the Cilician Basin. Particularly, around Mersin–Tarsus region tertiary sedimentary rocks consist of a succes-

Table 4 Statistical results of the measured parameters in samples collected from delta stations for the sampling period (from October 2004 to May 2005)

Parameter	Göksu (5)	Lamas (4)	Efrenk (5)	Tarsus (5)	Seyhan (5)
pH	7.69–8.06	7.98–8.22	8.14–9.03	8.22–8.42	7.89–8.41
	7.88±0.15	8.08±0.10	8.52±0.34	8.33±0.07	8.22±0.18
E. conductivity	2,030–5,580	290–410	355–2,060	260–356	280–18,810
$\mu S\ cm^{-1}$	5,530±5,730	348±49	834±713	312±42	3,426±7,536
Alkalinity	262–372	257–448	232–396	165–354	165–260
mg $CaCO_3\ L^{-1}$	325±40	315±90	316±59	228±74	221±33
Total hardness	650–862	259–342	268–477	203–272	207–3,900
mg $CaCO_3\ L^{-1}$	719±89	293±36	373±95	232±29	858±1,490
NH_4^+	1.83–6.48	0.30–1.77	0.22–2.46	0.33–0.90	0.31–7.13
mg L^{-1}	3.41±1.84	1.22±0.64	1.58±1.01	0.56±0.23	1.61±2.71
Ca^{2+}	122.6–11,549	85.0–86.5	63.4–70.8	46.5–63.3	38.1–104,590
mg L^{-1}	3,934±6,595	85.9±0.8	66.3±4.0	56.5±8.9	26,181±52,273
Mg^{2+}	61.1–92.9	6.9–7.3	37.4–64.4	10.8–12.7	17.8–309,420
mg L^{-1}	79.3±16.4	7.1±0.2	50.0±13.6	11.7±0.9	77,369±154,700
Na^+	130–2,420	0.93–1.73	4.98–65.6	BDL–2.78	BDL–949,450
mg L^{-1}	918±1301	1.33±0.32	34.4±30.4	1.63±1.44	247,364±494,724
K^+	4.0–3,358	0.53–0.76	3.16–97.3	0.55–1.21	1.35–104,120
mg L^{-1}	1129±1,930	0.65±0.11	35.6±53.4	0.80±0.36	26,031±52,059
Cl^-	379–1,280	4.90–7.32	10.3–308.7	5.73–11.9	7.59–8,175
mg L^{-1}	835±334	6.20±1.00	74.3±131.1	8.72±2.86	1,373±3,332
NO_3^-	12.7–132.2	2.77–5.25	1.60–32.3	1.91–8.70	1.64–948
mg L^{-1}	74.1±51.3	4.48±1.16	14.5±14.9	3.89±2.78	162.7±385
SO_4^{2-}	58.7–1,490	4.68–10.14	6.72–78.6	2.30–11.59	11.95–1,069
mg L^{-1}	397.3±612.5	7.52±2.25	27.2±29.3	6.58±3.51	198.6±426.3
PO_4^{3-}	15.0–342.8	4.56–265.9	7.22–384.6	5.03–95.0	5.03–803.2
$\mu g\ L^{-1}$	110.8±136.0	83.6±123.9	102.8±158.2	33.2±37.0	208.8±313.0

Total number of samples are given in parentheses.

BDL: Below detection limit.

sion of marine, lacustrine and fluvial deposits that are rich in evaporates e.g., gypsum and sodium sulfate (Demirel and Külege 2005). Adverse health effects of sulfate ion are catharsis, dehydration and gastrointestinal irritation (Saleh et al. 2001). Sulfate concentrations in freshwater samples ranged from 3.68 to 40.55 mg L^{-1} (Table 3). According to TSI (1997) and WHO Guidelines, sulfate concentration in drinking water may not exceed 250 mg L^{-1} (Table 5). Therefore, it is verified that there is no health risk due to sulfate ion to the consumers.

Nutrient concentrations

Among the analyzed parameters ammonium, nitrate and phosphate are not essential elements and can be considered as pollutants from the water quality point of view. On the other hand, these constituents can also be evaluated as nutrients for the aquatic life and may cause eutrophication in excess amounts. It is generally thought that P is limiting in freshwater systems (Schindler 1974) while N is limiting in marine systems (Hecky and Kilham 1988). Nitrate is often used as an index of water quality. It is highly mobile and regulated by a variety of biological controls (Swank 1988). Nitrate concentrations measured at central and source stations of the rivers (1.08–19.43 mg L^{-1}) are all below the desirable limit of 25 mg L^{-1} (TSI 1997), however standard deviations of the mean NO_3^- concentrations for all the rivers are quite high suggesting a seasonal variation in this parameter. Similar situation is also valid for PO_4^{3-} concentrations. Monthly mean values of nitrate, ammonium and phosphate concentrations of the rivers are presented against the climatological mean precipitation based on the long term (1990–2003) measure-

Table 5 Water quality criteria for fresh waters intended for human consumption

Parameter	Desirable limit	Maximum permissible limit	Organization
pH range	7.0–8.5	6.5–9.2	WHO
	6.5–8.5	6.5–9.2	TSI
E. conductivity ($\mu S\ cm^{-1}$)	750	2,500	WHO
	400	2,000	TSI
Total hardness ($mg\ CaCO_3\ L^{-1}$)	100	500	EPA
NH_4^+ ($mg\ L^{-1}$)	10	–	WHO
	0.05	0.5	TSI
Ca^{2+} ($mg\ L^{-1}$)	75	200	EPA
	100	200	TSI
Mg^{2+} ($mg\ L^{-1}$)	30	50	TSI
Na^+ ($mg\ L^{-1}$)	50	175	WHO
	20	175	TSI
K^+ ($mg\ L^{-1}$)	10	12	TSI
Cl^- ($mg\ L^{-1}$)	250	600	WHO
	25	600	TSI
NO_3^- ($mg\ L^{-1}$)	25	50	TSI
	–	50	WHO
SO_4^{2-} ($mg\ L^{-1}$)	25	250	TSI
		250	WHO
PO_4^{3-} ($\mu g\ L^{-1}$)	1,000	–	WHO
	535	6700	TSI

WHO (1998), TSI (1997), EPA (1989).

ments of the Turkish Meteorological Service, Mersin station in Figs. 2, 3 and 4, respectively.

Monthly mean nitrate (Fig. 2) ammonium (Fig. 3) and phosphate (Fig. 4) concentrations exhibit different patterns of variation for each one of the monitored rivers. The main sources for these constituents are most probably leaching into the river of artificial fertilizers extensively used in the region, and domestic wastewater discharges containing detergents, particularly in the case of phosphate (Maki et al. 1984). It was reported that 40,850 tons of nitrogen and 9,974 tons of phosphorus fertilizers have been applied to the agricultural soils around Mersin region in 2005 (ÇDR 2006). Following application of these fertilizers during March–June period an abrupt increase has been observed in phosphate concentrations of all rivers (Fig. 4). Mean phosphate concentrations during May 2005 survey were 10^1 (for Lamas, Efrenk and Tarsus) or even 10^2 (for Göksu and Seyhan) orders of magnitude higher than the mean phosphate concentrations of the December 2004 survey. Even though very high phosphate concentrations have been measured in all samples during the May 2005 survey, none of the phosphate concentrations have exceeded the maximum permissible limit of 6,700 $\mu g\ L^{-1}$ (TSI 1997) (Table 5). Only central (675 $\mu g\ L^{-1}$) and source (782 $\mu g\ L^{-1}$) station samples of Göksu River during May 2005 survey have exceeded the desirable phosphate limit of 535 $\mu g\ L^{-1}$ (TSI 1997) (Table 5).

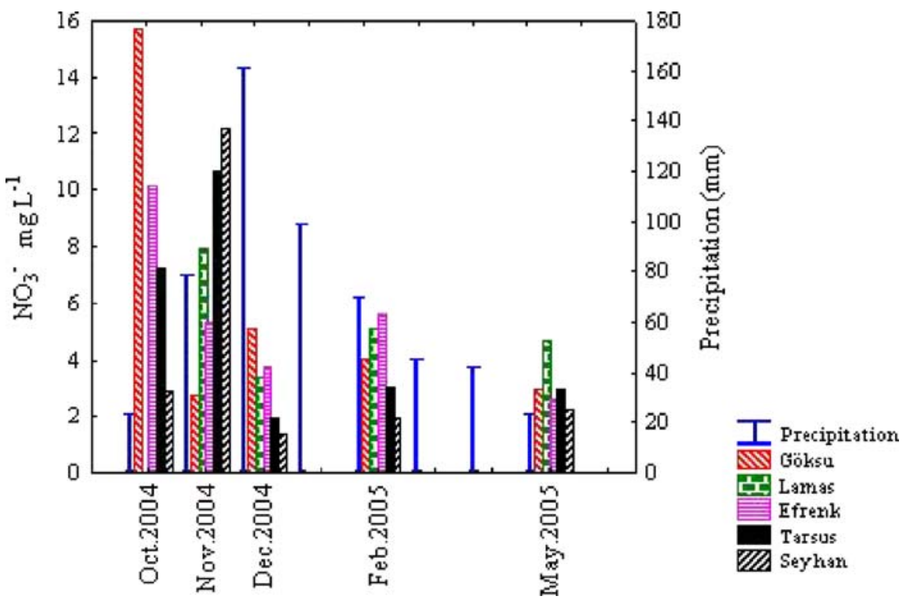

Fig. 2 Monthly mean nitrate concentrations of the rivers against the climatological mean precipitation based on the long term measurements of the Turkish Meteorological Service, Mersin station

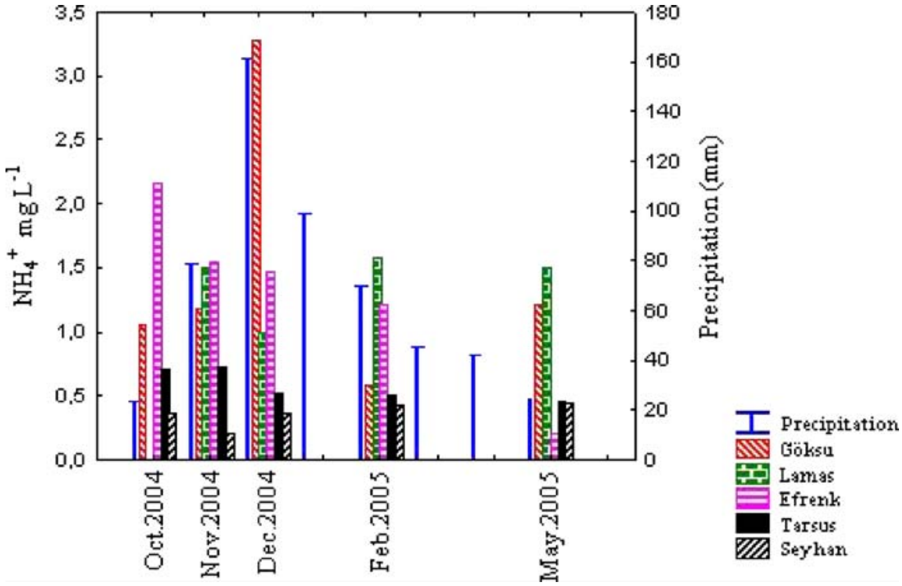

Fig. 3 Monthly mean ammonium concentrations of the rivers against the climatological mean precipitation based on the long term measurements of the Turkish Meteorological Service, Mersin station

In addition to the lack of fertilizer application during winter months, another reason for the measured low phosphate levels during October, November and December 2004 surveys could be the regional precipitation regime. Rain waters possibly could have caused dilution of river waters which are naturally devoid of phosphate due to the low solubility of this constituent from the crust. Presence of ammonia shows that the water has recently been polluted. No definite seasonal variation pattern of ammonium (Fig. 3) observed for almost all rivers suggest that the main source of this constituent is continuous discharge of domestic waste waters rather than application of fertilizers during certain times, as in phosphate. In contrast to nitrate and phosphate levels almost all ammonium concentrations measured in all of the rivers exceeded the maximum permissible limit (0.5 mg L^{-1}) of TSI. Among the rivers, Göksu has relatively higher ammonium values varying in the range of 0.52–3.30 mg L^{-1} for the central and source stations. Exceedence of the critical values is even more extreme for the delta stations. Maximum ammonium concentrations of 6.48 mg L^{-1}, 2.46 mg L^{-1} and 7.13 mg L^{-1} were measured in the delta

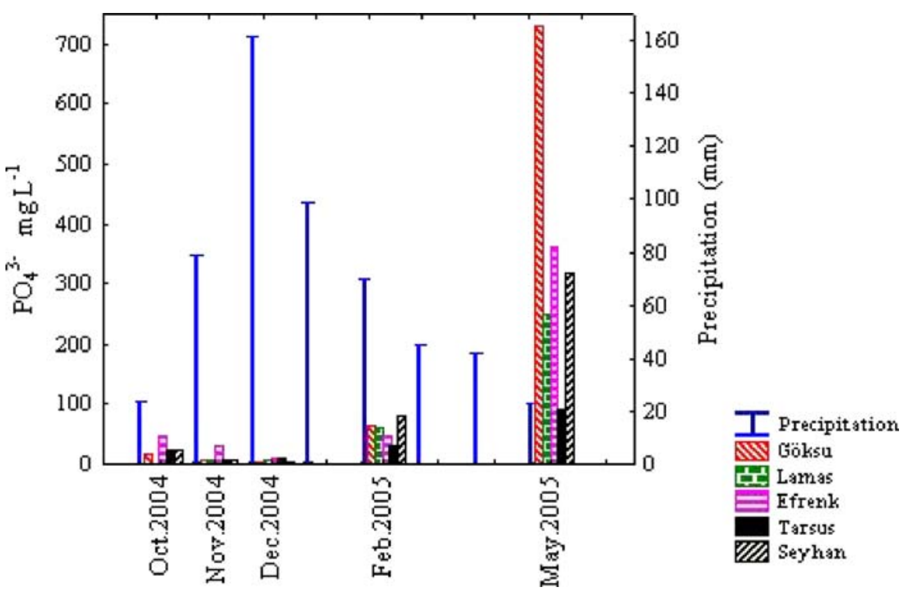

Fig. 4 Monthly mean phosphate concentrations of the rivers against the climatological mean precipitation based on the long term measurements of the Turkish Meteorological Service, Mersin station

stations of Göksu, Efrenk and Seyhan Rivers, respectively (Table 4).

Pollution level of the rivers is evaluated according to the comparison of the mean concentrations of certain parameters with the Turkish quality criteria of the surface waters (SKKY 2004) which is presented in Table 6. All rivers appear unpolluted with respect to their nitrate, chloride, sulfate and sodium ion contents while they all can be considered as slightly polluted with respect to their phosphate contents. It has already been stated that high levels of ammonium concentrations were observed in most of the samples and it was found that Lamas, Efrenk, Tarsus and Seyhan Rivers have slightly polluted while Göksu River has moderately polluted waters with respect to ammonium. To test for significant differences among nutrient concentrations of the rivers, Student's *t*-test was applied to the data. The results of this statistical test ($P<0.05$) indicated that there were no significant differences between the nitrate and phosphate contents of the rivers, due to the high seasonal variation and hence the high standard deviation observed in these parameters. Mean ammonium concentrations of Göksu, Lamas, Efrenk and Seyhan Rivers were not significantly different from each other while mean ammonium concentration of Tarsus River was significantly lower than the others. It can be concluded that among the rivers Tarsus has the highest quality of waters with lowest electrical conductivity, alkalinity, total hardness and nutrient concentrations.

Nutrient fluxes

In order to calculate elemental nutrient fluxes from rivers of the Cilician Basin region into the NE Mediterranean coastal waters, monthly mean concentrations of nutrients measured at freshwater samples of central and source stations were multiplied by monthly mean flow rates (m^3/s) of the rivers. Based on these monthly fluxes, total annual fluxes of NH_4^+-N, NO_3^--N and $PO_4^{3-}-P$ were calculated and presented in Table 7 as flux1. These annual fluxes might not be representative of the real values, since this study comprises only half a year of sampling duration, particularly the rainy season. With due caution, the results obtained from this study can be viewed as a first order estimation.

Elemental nutrient fluxes appear proportional to the mean flow of the rivers. Among the studied rivers, Seyhan contributes the highest amount of nutrients into the Cilician Basin while Göksu comes as the second in rank. Even though the nutrient concentrations of the Tarsus River are relatively lower compared to all others, due to its higher flow, the magnitude of the elemental N and P fluxes from this river are found to be third in rank, after Seyhan and Göksu. Annually, freshwaters of the studied rivers supply 10,045 tons of N (62% in nitrate, 38% in ammonium form) and 356 tons of P to the NE Mediterranean coastal waters (Table 7). The actual inorganic N input is most probably higher than the calculated value which excludes NO_2^- that was not analyzed in this study. These results, based on freshwater data, are the very first estimates of riverine nutrient fluxes into Eastern Mediterranean, as the previous studies were all based on data obtained from delta stations (DeGobbis et al. 2000; Yılmaz and Tuğrul 1995; Yılmaz et al. 1997). In order to compare our results with the previous studies, similar flux calculations based on delta concentrations were also carried out for comparison: monthly mean nutrients measured at delta stations were multiplied by monthly mean flow rates (m^3/s) of the rivers and presented in Table 7 as flux2 values. According to these results, the rivers annually supply 73,000 tons of N and 355 tons of P to the NE Mediterranean coastal waters. It is interesting that flux1 and flux2 values of total P are the same, while flux2 of total N is seven times higher than flux1. These results suggest that the lower reaches of Göksu and Seyhan Rivers are under the stress of excessive nitrogen loadings compared to phosphorus, most likely due to the extreme application of nitrogen fertilizers in the region. This result is consistent with Tuğrul et al. (2007).

Table 6 Turkish quality criteria of the surface waters (SKKY 2004)

Parameter	Unpolluted	Slightly polluted	Moderately polluted	Seriously polluted
pH	6.5–8.5	6.5–8.5	6.0–9.0	6.0<–>9.0
NH_4^+ (mg l^{-1})	0.26	1.3	2.6	>2.6
NO_3^- (mg l^{-1})	22	44	88	>88
PO_4^{3-} (µg l^{-1})	60	500	2,000	>2,000
Cl^- (mg l^{-1})	25	200	400	>400
SO_4^{2-} (mg l^{-1})	200	200	400	>400
Na^+(mg l^{-1})	125	125	250	>250

Table 7 Annual $NH_4^+ - N$, $NO_3^- - N$ and $PO_4^{3-} - P$ fluxes (ton year^{-1}) based on freshwater (flux1) and delta (flux2) concentrations of the Cilician Basin Rivers

River	Meanflow	$NH_4^+ - N$		$NO_3^- - N$		$PO_4^{3-} - P$	
	(m^3/s)	flux1	flux2	flux1	flux2	Flux1	flux2
Göksu	45.1	1,592	4,350	1,466	18,228	125.5	72.0
Lamas	4.2	133	117	146	123	5.0	5.2
Efrenk	1.7	76	87	92	172	2.2	2.2
Tarsus	42.8	564	538	1,350	1,130	19.4	20.3
Seyhan	167.9	1,461	3,015	3,165	45,262	203.3	255.3
Total		3,826	8,107	6,219	64,915	356.0	355.0
		ΣN				ΣP	
		flux1: 10,045		flux2: 73,022		Flux1 = flux2	

The average annual total nitrogen and phosphorus (organic + inorganic fractions) loads from land-based sources has been calculated respectively as 57,200 and 9,600 tons for the NE Mediterranean coasts (Yılmaz and Tuğrul 1995). The inorganic parts of these inputs, as in $NO_3^- + NO_2^- - N$ and $PO_4^{3-} - P$ forms have been reported respectively as 11,300 and 2,700 tons (or as 20% and 30% of the total input) on an annual basis (Yılmaz et al. 1997). Elemental inorganic N flux calculated in this study is more than six times higher than the value reported by Yılmaz et al. (1997), while elemental inorganic P flux is considerably lower (1/8) than the value reported within the same reference. Even though this comparison does not depend on the same basis (the number of the monitored rivers and the analyzed inorganic nitrogen species are different) it gives partial credence to the idea that possibly there has been an increase in the elemental inorganic nitrogen load while there has been a decrease in the elemental inorganic phosphorus load of the rivers within last decade. The present results support the earlier observation of high N/P ratios in the coastal environment, and reinforce 7the existing arguments for a P-limited marine ecosystem in the NE Mediterranean Basin, possibly also leading to further increases in the N/P molar ratio in parallel to the trend in pollution.

Conclusions

1. Present water quality of the perennial rivers; Göksu, Lamas, Efrenk, Tarsus and Seyhan discharging into the Cilician Basin have been investigated. According to Turkish National Water Pollution Control Regulations, all rivers were found to be unpolluted with respect to their nitrate, chloride, sulfate and sodium ion contents, while they all could be considered as slightly polluted with respect to their phosphate contents. In contrast to nitrate and phosphate, ammonium exceeded the maximum permissible limits of water quality criteria in almost all samples.
2. Since having high N/P ratio is one of their general characteristics, this ratio is used as an indicator of pollution level of the rivers relative to each other. Molar N/P ratios based on freshwater data of Seyhan, Göksu, Lamas, Efrenk and Tarsus Rivers were found in an ascending order of 50, 54, 125, 168 and 219, respectively. According to this result, Seyhan can be evaluated as the most polluted while Tarsus is the least polluted one among the rivers.
3. Based on delta concentrations, the studied rivers totally supply 73,000 tons of N (89% of this amount is in the nitrate form while 11% is in the ammonium form) and 355 tons of P to the NE Mediterranean coastal waters, per annum. The comparison of these elemental fluxes with the previous data reveals an ascending trend in the already high N/P ratios of the discharges of the studied rivers within the last decade. Since these rivers are one of the major suppliers of nutrients for coastal waters, this trend is reinforcing the P-limited nature of the NE Mediterranean Basin.

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