



Seasonal variations of some physico-chemical parameters in a lentic system: Kirmir Creek and tributaries, Turkey

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Abstract

The goal in this study was to determine the seasonal variations of nitrogen and phosphorus fractions with silica concentrations in Kirmir Creek and its tributaries (Süveri Creek and İlhan Creek) between January and December 2007. The lowest ammonia-nitrogen value was assessed at 0.044 mg L⁻¹ in April in İlhan Creek, whereas the highest value was 0.568 mg L⁻¹ (August) in Süveri Creek. The minimum nitrite nitrogen concentration was 0.001 mg L⁻¹ (March) in both Kirmir Creek and İlhan Creek, while the maximum value was assessed at 0.024 mg L⁻¹ (August) in İlhan Creek. The minimum value of nitrate nitrogen was 0.26 mg L⁻¹ (January) in Kirmir Creek and the maximum concentration 3.57 mg L⁻¹ (June) in İlhan Creek. The minimum mean values of total phosphorus and total orthophosphate were 0.0004 and 0.0002 mg L⁻¹, respectively (January) in İlhan Creek, whereas the highest values were 0.006 mg L⁻¹ (March) in Kirmir Creek and 0.003 mg L⁻¹ (February) at the same station, respectively. Silica concentrations varied between 14.22 (September) in Kirmir Creek and 58.18 mg L⁻¹ (July) in Süveri Creek. The range of the examined values of pH and dissolved oxygen were 7.03–8.65 and 7.4–11.5 mg L⁻¹, respectively. This study on water quality, conducted in Kirmir Creek and its tributaries, will be used to create databases for future research. It is a well-known fact that there is a number of variables and/or mechanisms affecting water quality; however, in the present situation, there is no risk of the deterioration of the water system in this study.

Key words: Nitrogen, phosphorus, silica, water quality, Kirmir Creek.

Introduction

Aquatic ecosystems are particularly vulnerable to environmental change and many are, at present, severely degraded. Ironically, this vulnerability makes aquatic ecosystems good sentinels and integrators of environmental change at scales ranging from local (e.g. extinctions of endemic species) to global (e.g. climate change)¹.

In recent years, because water is one of the most fundamental and important renewable resources, significant advances have been made to increase our understanding of stream ecology through numerous studies concerning nutrients in lentic systems. The constituents of stream water include suspended inorganic matter, dissolved major ions, suspended and dissolved organic matter, gases, trace metals and especially dissolved nutrients. Freshwater characterization is related to nutrients such as nitrogen, phosphorus and silica; these chemical elements are very important in stream ecosystems.

In order to understand the nitrogen cycle in aquatic systems, the seasonal variations in ammonia nitrogen and nitrite and nitrate nitrogen should be determined through scientific research. Phosphorus in freshwater occurs as organic phosphorus in the biota absorbed and it is a limiting element, restricting the growth of the aquatic plants. In stream water, total phosphorus concentration is generally between 0.01 and 1.0 mg L⁻¹², while concentration of total phosphorus from agricultural runoff water ranges from 0.05 to 1 mg L⁻¹³.

Silica might be expected to become another limiting nutrient in fresh water because the frustles of diatoms are composed of silicious material and diatoms are a major component of the periphyton of cool, shaded streams⁴. Silica accumulates in sediment and/or diffuses into the water column under certain physico-chemical circumstances, and paleolimnologists use silica concentration in order to observe the trophic variations of aquatic systems^{5,6}.

The objective of this study, conducted in Kirmir Creek and its tributaries, was to quantitatively determine nitrogen and phosphorus fractions with silica concentrations in order to see what information could be gained from this data, and to monitor the seasonal changes of these parameters. Moreover, it is thought that in the light of this research, similar studies could be conducted in other river systems. The studied area, which is located near the capital city of Turkey, was chosen due to the fact that the water quality and trophic status of this system have been influenced by human actions ranging from agricultural runoff to untreated domestic pollution sources in the catchment area.

Materials and Methods

Study site: Kirmir Creek is located in the northwestern part of the Central Anatolian region of Turkey at 40-41° N and 32-33° E, and the basin lies within the boundaries of Ankara province. The

depth of the creek is generally shallow (30-50 cm), but reaches 2-3 m at some points. The bottom structure varies between sandy, stony and muddy ⁷. This study was carried out in Kirmir Creek and its tributaries (Süveri Creek and İlhan Creek) in the Sakarya River basin. Three stations situated in the same agricultural area were assigned on Kirmir Creek (130 km long) and its tributaries for taking water samples and measuring water characteristics (Fig. 1).

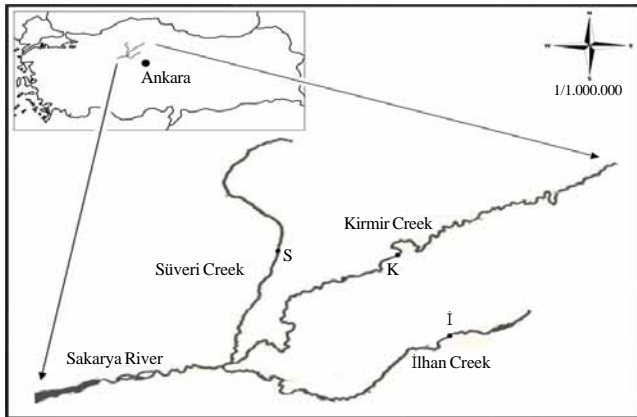


Figure 1. Location map of the study site showing the 3 sampled creeks.

Field work: Water samples were collected at monthly intervals between January 2007 and December 2007 using replicate polyethylene bottles. Sampling locations were deemed representative of the majority of the creeks. Samples were analysed as soon as they were taken to the laboratory. They were preserved at a temperature of 4°C prior to the laboratory analyses. Dissolved oxygen and pH of the water samples were measured on-site by Consort oxygen-pH meter.

Laboratory analyses: The nesslerisation method was applied to the water samples to determine the concentration of ammonia nitrogen ($\text{NH}_3\text{-N}$), calculated colorimetrically using the Nessler reactive reagent at a wavelength of 420 nm. The nitrite nitrogen ($\text{NO}_2\text{-N}$) was determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye; colorimetric measurement was then performed by spectrophotometer at 520 nm. In the nitrate nitrogen ($\text{NO}_3\text{-N}$) analysis, after the reaction between nitrate ions and brucine, the absorbance of the yellow color was determined spectrophotometrically at 420 nm ⁸.

Water samples were analysed for phosphorus fractions; total phosphorus (TP) and total orthophosphate $\text{PO}_4\text{-P}$ (TO) as molybdate-reactive phosphorus. Total phosphorus concentration was analysed first by digestion using the persulphate fragmentation technique, and then both TP and TO analyses were performed, using the ascorbic acid method according to the American Public Health Association ⁸. Total silica (Si) analyses of water samples were done spectrophotometrically using the silicomolybdate method ⁸.

Statistical analyses: Statistical analyses were performed using the Minitab and MSTAT programs for Windows. ANOVA and Duncan's multiple-range test were used to evaluate differences in water samples between months and stations ⁹.

Results and Discussion

The minimum concentration of ammonia nitrogen in İlhan Creek was $0.044 \pm 0.001 \text{ mg L}^{-1}$ in April, and the maximum concentration ($0.568 \pm 0.002 \text{ mg L}^{-1}$) was found in Süveri Creek in August. The minimum concentration of nitrite nitrogen was $0.001 \pm 0.00 \text{ mg L}^{-1}$ in both Kirmir and İlhan Creeks in March, whereas the maximum value ($0.024 \pm 0.00 \text{ mg L}^{-1}$) was measured in İlhan Creek in August. Nitrate nitrogen concentrations varied between 0.26 ± 0.007 (in Kirmir Creek) and $3.57 \pm 0.08 \text{ mg L}^{-1}$ (in İlhan Creek) in January and June, respectively (Tables 1-3).

It is a well-known fact that in polluted stream waters the mean total nitrate concentration is $100 \mu\text{g L}^{-1}$, whereas in this study ammonia and nitrite concentrations were 15 and $1 \mu\text{g L}^{-1}$, respectively ¹⁰. In North American stream waters, nitrate nitrogen concentration was between 0.01 and 0.86 mg L^{-1} ¹¹. In general, stream water nitrate concentrations range between 0.003 and 7.00 mg L^{-1} , while ammonium values vary between 0.005 and 10.00 mg L^{-1} ⁵. In a previous study in Kirmir Creek ¹², samples taken for ammonia, nitrite, nitrate and orthophosphate concentrations were examined in August 1994, October 1994, March 1995 and June 1995. During the study period the highest value of ammonia concentration (4.16 mg L^{-1}) was found in October and the lowest ammonia value (0.52 mg L^{-1}) was in March. The maximum value of nitrite concentration (0.085 mg L^{-1}) was measured in March and the minimum value (0.02 mg L^{-1}) was found in August. The minimum and maximum values of nitrate concentration were identified in June (1.5 mg L^{-1}) and in August (3.83 mg L^{-1}), respectively. To date, several studies have been performed concerning the nitrogen fractions of the rivers in Turkey ¹³⁻¹⁵. In this study, carried out in Kirmir Creek and its tributaries, the nitrogen fractions ($\text{NH}_3\text{-N}$ 0.04- 0.568 mg L^{-1} ; $\text{NO}_2\text{-N}$ 0.001- 0.024 mg L^{-1} ; $\text{NO}_3\text{-N}$ 0.26- 3.57 mg L^{-1}) were generally determined to be lower than the above-mentioned values of other researchers. Generally, nitrogen fractions in different rivers are found to be higher in the spring months and lower in the summer ¹²⁻¹⁵, while in this study, these fractions were high in June and August but low in January, March and April. It can thus easily be understood that our findings are not in keeping with the seasonal changes of the nitrogen fractions for the above researchers' data. In this study, due to decreased rainfall in the spring period, irrigation was needed in the agricultural fields surrounding the sampling stations; therefore, nitrogen concentrations increased in summer (June and August) originating from the drainage of this agricultural area into the stream basin.

In a study in England, the median $\text{NO}_3\text{-N}$ values of the Avon and Wye Rivers were 8.2 and 11.2 mg L^{-1} , respectively ¹⁶. This research identified agricultural land-use practices which posed the highest risk for nutrient loss at the field and farm scale dominated by grassland, and the forms in which the key nutrients (nitrogen, N, and phosphorus, P) were exported. In their research, the authors examined the impacts of agricultural land use and sewage effluent discharges on nutrient concentrations and loads ¹⁶. Our findings regarding $\text{NO}_3\text{-N}$ was lower than the above researchers' data. In this study conducted in Kirmir, İlhan and Süveri Creeks, considering the lower values of nitrate nitrogen, it can easily be concluded that the agricultural source did not have a highly negative effect on this river system at the time of the study.

In general, total phosphorus concentrations in streams range between 0.01 and 1.0 mg L^{-1} ², while the same parameter in water from agricultural fields vary between 0.05 and 1 mg L^{-1} ³. In another

Table 1. Variation of ammonia nitrogen in water samples according to month and station (N = 4).

Stations/Month	NH ₃ -N (mgL ⁻¹)		
	Kirmir	İlhan	Süveri
Jan.	0.057±0.001 ^{A^dB^{***}}	0.054±0.001 ^{Bd}	0.053±0.001 ^{Cd}
Feb.	0.055±0.001 ^{Cd}	0.062±0.001 ^{Ad}	0.060±0.001 ^{Bd}
Mar.	0.045±0.001 ^{Cd}	0.065±0.002 ^{Ac^d}	0.055±0.002 ^{Bd}
Apr.	0.057±0.002 ^{Bd}	0.044±0.002 ^{Ce}	0.061±0.001 ^{Ad}
May.	0.066±0.001 ^{Bd}	0.077±0.002 ^{Ac}	0.078±0.001 ^{Ac}
Jun.	0.067±0.001 ^{Bd}	0.077±0.001 ^{Ac}	0.077±0.001 ^{Ac}
Jul.	0.100±0.002 ^{Bc}	0.103±0.002 ^{Ab}	0.087±0.001 ^{Cc}
Aug.	0.346±0.005 ^{Ca}	0.520±0.001 ^{Ba}	0.568±0.002 ^{Aa}
Sep.	0.124±0.003 ^{Abc}	0.108±0.004 ^{Bb}	0.082±0.003 ^{Cc}
Oct.	0.108±0.005 ^{Ac}	0.098±0.002 ^{Bb}	0.068±0.002 ^{Cd}
Nov.	0.168±0.000 ^{Ab}	0.124±0.001 ^{Bb}	0.092±0.000 ^{Cb}
Dec.	0.064±0.004 ^{Ad}	0.046±0.003 ^{Cc}	0.053±0.004 ^{Bd}

* The different capital letters in the same row show the differences between the stations in the same month (p<0.01). ** The different lower-case letters in the same column show the differences between months in the same station (p<0.01).

Table 2. Variation of nitrite nitrogen in water samples according to month and station (N = 4).

Stations / Month	NO ₂ -N (mgL ⁻¹)		
	Kirmir	İlhan	Süveri
Jan.	0.010±0.000 ^{A^bB^{***}}	0.010±0.000 ^{Ab}	0.002±0.000 ^{Bd}
Feb.	0.002±0.00 ^{Bc}	0.003±0.000 ^{Bd}	0.005±0.000 ^{Ab}
Mar.	0.001±0.000 ^{Bc}	0.001±0.000 ^{Bc}	0.002±0.000 ^{Ad}
Apr.	0.004±0.000 ^{Ad}	0.003±0.000 ^{Bd}	0.004±0.000 ^{Ab}
May.	0.005±0.000 ^{Bc}	0.006±0.000 ^{Ac}	0.005±0.000 ^{Bb}
Jun.	0.005±0.000 ^{Bc}	0.006±0.000 ^{Ac}	0.005±0.000 ^{Bb}
Jul.	0.005±0.000 ^{Ac}	0.004±0.000 ^{Bd}	0.003±0.000 ^{Cc}
Aug.	0.022±0.001 ^{Ba}	0.024±0.001 ^{Aa}	0.017±0.001 ^{Ca}
Sep.	0.004±0.000 ^{Ad}	0.003±0.000 ^{Bd}	0.002±0.000 ^{Cd}
Oct.	0.002±0.000 ^{Ac}	0.002±0.000 ^{Ac}	0.002±0.000 ^{Bd}
Nov.	0.005±0.000 ^{Ac}	0.004±0.000 ^{Ad}	0.002±0.000 ^{Bd}
Dec.	0.006±0.000 ^{Bc}	0.008±0.001 ^{Ab}	0.003±0.001 ^{Cc}

* The different capital letters in the same row show the differences between the stations in the same month (p<0.01).** The different lower-case letters in the same column show the differences between months in the same station (p<0.01).

Table 3. Variation of nitrate nitrogen in water samples according to month and station (N = 4).

Stations / Month	NO ₃ -N (mgL ⁻¹)		
	Kirmir	İlhan	Süveri
Jan.	0.26±0.07 ^{B^{***}}	0.37±0.04 ^{Ad}	0.38±0.08 ^{Ac}
Feb.	0.55±0.04 ^{ABd}	0.68±0.04 ^{Ac}	0.42±0.04 ^{Be}
Mar.	0.33±0.04 ^{Bc}	0.86±0.04 ^{Ac}	0.94±0.08 ^{Ab}
Apr.	0.88±0.07 ^{Ad}	0.44±0.07 ^{Bd}	0.81±0.06 ^{Ac}
May.	3.40±0.08 ^{Aa}	3.51±0.07 ^{Aa}	2.94±0.11 ^{Bd}
Jun.	3.49±0.08 ^{Aa}	3.57±0.08 ^{Aa}	2.83±0.08 ^{Bd}
Jul.	0.92±0.05 ^{Bd}	1.03±0.11 ^{Bb}	1.27±0.05 ^{Ab}
Aug.	2.94±0.09 ^{Ab}	1.36±0.05 ^{Cb}	2.57±0.04 ^{Bd}
Sep.	0.90±0.44 ^{Ad}	0.72±0.04 ^{Bc}	1.01±0.05 ^{Ab}
Oct.	0.66±0.05 ^{Bd}	0.97±0.07 ^{Ab}	0.90±0.04 ^{Ab}
Nov.	1.76±0.00 ^{Ac}	1.44±0.62 ^{Bb}	0.53±0.00 ^{Cd}
Dec.	0.44±0.01 ^{Ac}	0.36±0.01 ^{Ad}	0.53±0.01 ^{Ad}

* The different capital letters in the same row show the differences between the stations in the same month (p<0.01). ** The different lower-case letters in the same column show the differences between months in the same station (p<0.01).

study conducted in the Upper Sakarya River ¹⁷, the highest total phosphorus and total orthophosphate values were 304.50±2.71 mg m⁻³ in July and 60.64±0.41 mg m⁻³ in November, respectively, while the lowest values were determined at 104.68±2.19 mg m⁻³ in October and 22.38±1.05 mg m⁻³ in May, respectively. Another study of Kirmir Creek the minimum and maximum levels of orthophosphate concentration were between 0.48 (June) and 0.80 mg L⁻¹ (March) ¹². In this study, the lowest values of total

phosphorus and total orthophosphate were 0.001±0.00 and 0.0002±0.00 mg L⁻¹ in İlhan Creek in January, while the highest values were 0.01±0.0001 mg L⁻¹ in Kirmir Creek in March and 0.003±0.000 mg L⁻¹ in February at the same station (Figs. 2 and 3). The findings in this study are lower than the values found in other works ^{12, 17}; when compared seasonally to these studies the results were found to differ from each other. This shows that in our study no pollution problem was indicated.

In our study, the silica concentration of the water samples showed temporal variations: the minimum silica concentration was 14.22±0.01 mg L⁻¹ in September in Kirmir Creek, whereas the maximum value 58.178±0.056 mg L⁻¹ in July in Süveri Creek (Fig. 4).

In river systems, mean silica concentration has been determined at 13 mg L⁻¹ ⁵. In this study, the minimum concentration of silica in the Upper Sakarya River was 4.19 mg L⁻¹ in October and the maximum concentration 10.9±0.06 mg L⁻¹ in February ¹³. Some studies reported the minimum silica concentration for the Asi River in October and the maximum value in May ¹⁸, whereas Wall *et al.* ¹⁹ reported an increase in silica concentration in the spring and summer months. In this research, silica concentration values (14.22-58.178 mg L⁻¹) are keeping with findings of Wall *et al.* ¹⁹. Silica is limiting only to diatoms; therefore, seasonal changes of silica concentrations affect the growth of diatoms.

According to the findings of our study; the ammonia, nitrite and nitrate nitrogen, total phosphorus and total orthophosphate concentrations were found to be lower than the values generally specified for river systems. However, the mean silica concentrations were between the values reported for river systems ⁵. Higher concentrations in non-forested watersheds were associated with agricultural land use or point sources of N and P.

Aquatic ecosystems are particularly vulnerable to environmental change and have a vital importance in providing water for drinking, recreation, industrial and agricultural use. Furthermore, there are a number of aims to be moved toward in regard to the protection and improvement of water quality. This research conducted in Kirmir Creek and its tributaries on water quality will be used to create databases for future studies. Although in its present situation there is no risk of deterioration of the water system, there are a number of variables and/or mechanisms affecting water quality. Consequently, in the light of this fact, our results demonstrated that long-term monitoring programs are needed due to the irrigational and recreational use of this river system. Additionally, further research could be conducted on water bio-physico-chemical parameters regarding phytoplankton composition and also the effect of sediment characteristics on water quality.

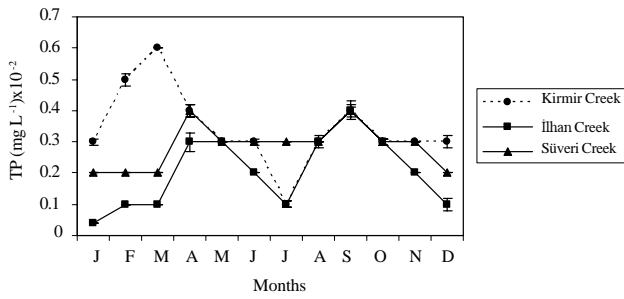


Figure 2. Variations of total phosphorus concentrations in water samples according to month and station.

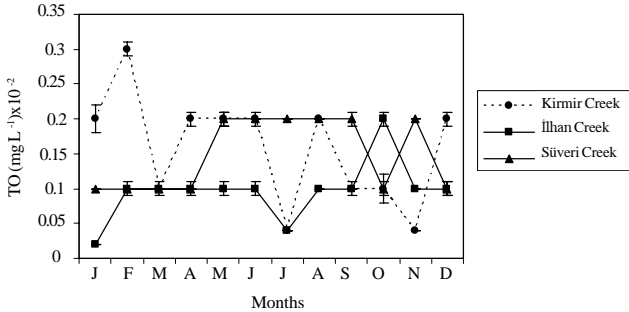


Figure 3. Variations of total orthophosphate concentrations in water samples according to month and station.

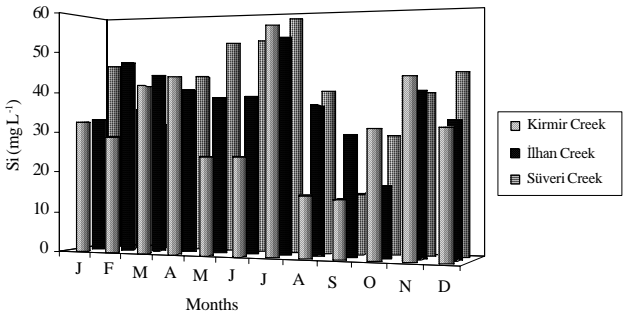


Figure 4. Variation of silica concentrations in water samples according to month and stations.

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