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RESEARCH ARTICLE

Impact of nutrient load coming from Göksu River on the northeastern Mediterranean

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ABSTRACT

Even though North-Eastern Mediterranean (NE Med) is classified as oligotrophic, inshore areas are highly eutrophic due to the discharge of silicate and nitrate-rich surface waters. Aim of this study was to investigate the nutrient load coming from the Göksu River and to estimate its impact on the river domain using satellite images. Monthly, average nitrite (NO_2), nitrate (NO_3), ammonium (NH_4) and phosphate (PO_4) load found to be varying between 0.07-31.2 ton/month, 15-1226 ton/month, 0.5-539 ton/month, 1-267 ton/month, respectively. Satellite images showed that surface chlorophyll–*a* (chl-*a*) in the river downstream had an increase in both winter and spring seasons as a result of intense precipitation; while, primary production at the offshore regions was mainly impacted by winter mixing and summer stratification. The highest chl-*a* concentration was observed at the river impacted zone and decreased by more than two folds at the offshore regions. Increased NO_3 load observed during winter and spring leads to phytoplankton blooms in the river downstream. The high P content of Göksu River surface waters has increased the productivity at all seasons. As a consequence, correlation analysis showed significant relationship between surface chl-*a* concentration and PO_4-NO_3 load.

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Introduction

Human-induced activities cause variations in the land use patterns that lead to the alteration in both quality and quantity of surface runoff reaching the surface waters. Surface waters become vulnerable for several types of polluters including high nitrogen and phosphorus concentrations (Song, 2009). Incoming pollutant and nutrient load cause an alteration in the bio-physicochemical balance of receiving environments (Kangur & Möls, 2008) such as decrease in dissolved oxygen concentration, light penetration. This phenomena is called as eutrophication (Nixon, 1995).

The inshore area of Northeastern Mediterranean (NE Med) is classified as eutrophic due to the discharge of silicate and nitrate-rich surface waters (Tugrul et al., 2016); whereas, the offshore area is classified as oligotrophic (Krom et al., 1991).

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Göksu River; among other surface waters; is mainly suffered from domestic and agricultural discharges that increase the organic content of the surface flow. These nutrient-rich waters could not diffuse offshore due to the blockage of Asian Minor Current (AMC) which increases the eutrophication risk of the receiving environment (Akpınar et al., 2016).

Knowledge of nutrient load coming from surface waters to open sea is crucial; since it directly affects the chemical and biological loop in the surrounding environment. This study was conducted to (i) determine the nutrient load coming from Göksu River (NH_4, PO_4, NO_2, and NO_3), (ii) to evaluate the seasonal variations in the nutrient load, (iii) to determine the impact of Göksu River on the primary production using satellite images.

Material and Methods

Göksu River descends from the Taurus Mountains and discharges its waters to NE Med from Silifke. As a result of the Mediterranean climate, its flowrate starts to increase during winter, and reach its maximum level in spring due to the rainy season, and decrease in the hot summer as a consequence of the powerful evaporation (DSİ, 2019). Almost 95% of the Göksu Basin is forest, semi-natural areas, and agricultural lands (Figure 1). So, the Göksu River carries a significant amount of nutrient load to the NE Med (Ayaz et al., 2013).

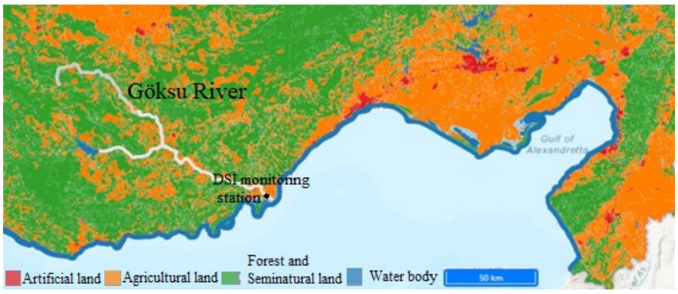

Figure 1. Land use map of Göksu River surrounding

Monitoring study results that belong to the downstream of Göksu River station were taken from the State of Hydraulic of Turkey including seasonal flow rate (Q), nitrite (NO_2), nitrate (NO_3), ammonium (NH_4), and phosphate (PO_4) concentrations from 1992 to 2016. Dataset was used to calculate nutrient load using an interpolation-based average estimator model (Quilbé et al., 2006) (Eq. 1).

$$Load = K(\sum_{i=1}^{n})\left(\frac{C_i Q_i}{n}\right) \quad (1)$$

where;

K = conversion factor to take account of the period of record

C_i = instantaneous concentration associated with individual samples (mg/L)

Q_i = instantaneous discharge at the time of sampling (m^3/L)

n = number of samples

Satellite images were used to evaluate the impact of Göksu River on NE Med by evaluating the surface chlorophyll-*a* distribution. Satellite images were obtained from NASA's 3rd level browser belonging to the Ocean Color Web application (https://oceancolor.gsfc.nasa.gov/). NASA emerges in-situ chl-*a* measurements with remote sensing to predict the surface chl-*a* concentration. Current implementation, algorithm description and constraints of the model was described in Morel & Maritorena (2001), Hu et al. (2012) and can be obtained from official webpage (https://oceancolor.gsfc.nasa.gov/atbd/chlor_a/). The monthly chl-*a* images were downloaded from the MODIS-Aqua sensor with a resolution of 4 km (NASA Goddard Space Flight Center, 2014) and processed using the SeaDAS program (Baith et al., 2001). Surface chl-*a* imaging was coherently conducted to the nutrient sampling time.

Pearson correlation analysis was used to test the existence of a linear relationship between the surface chl-*a* concentration obtained from satellite images and nutrient load.

Results and Discussion

Properties of Göksu River Surface Waters

Coastal area of NE Med is fed by nutrients coming from surface waters (Tugrul et al., 2016) which could not be penetrate to the offshore due to the blockage of AMC (Akpınar et al., 2016). For that reason, eutrophic conditions prevail in coastal areas, which make monitoring of upcoming nutrient load from surface waters an issue. As a result of these concerns, several studies were undertaken in the Göksu River basin. Demirel et al. (2011) reported that the NO_2, NO_3 and PO_4 concentration in different parts of the Göksu basin as 0.03-1.31 mg/L, 3.6-17.3 mg/L, and 0.03-0.88 mg/L, respectively. Yıldırım et al. (2018) reported that the NO_2 concentration in the Göksu River ranged between 0.001-0.091 mg/L in October, reaching to 0.107-1.46 mg/L in May. They also reported the NO_3 concentration variation as 2.69-7.95 mg/L and 1.77-5.9 mg/L in October and May, respectively. Similar to the previous studies, in this study, NO_2, NO_3, NH_4 and PO_4 concentration were varied from 0.001 mg/L to 0.114 mg/L, from 0.18 mg/L to 4.8 mg/L, 0.008 mg/L to 2.8 mg/L and from 0.01 mg/L to 0.92 mg/L, respectively (Table 1).

Marine Science and Technology Bulletin

Table 1. Nutrient concentration in the downstream of Göksu River and estimated nutrient load

Year	Concentration (mg/L)				Load (ton/year)			
	NO_2	NO_3	NH_4	PO_4	NO_2	NO_3	NH_4	PO_4
1992	0.002	0.84	0.33	0.03	17	4 264	850	260
1993	0.003	0.71	0.26	0.08	17	2 720	1 831	215
1994	0.006	0.62	0.27	0.10	8	1 147	314	107
1995	0.003	0.89	0.47	0.06	3	1 150	593	66
1996	0.003	0.59	0.22	0.11	13	2 225	948	444
1997	0.005	0.79	0.24	0.11	19	2 476	956	368
1998	0.007	0.83	0.19	0.24	19	2 502	403	863
1999	0.006	0.86	0.15	0.11	17	2 875	399	252
2000	0.009	0.95	0.43	0.12	36	3 418	747	418
2001	0.009	0.81	0.57	0.09	44	3 071	2 472	362
2002	0.013	0.77	0.62	0.12	28	2 293	1 393	300
2003	0.005	0.66	0.53	0.10	12	1 646	1 256	268
2004	0.008	0.80	0.46	0.15	17	1 912	1 032	436
2005	0.010	0.87	1.06	0.15	15	1 431	1 756	264
2006	0.014	0.85	0.64	0.13	18	1 526	1 021	219
2007	0.010	0.97	1.54	0.09	9	1 046	1 578	94
2008	0.004	1.02	0.36	0.08	4	1 172	490	90
2009	0.004	0.59	0.09	0.06	13	1 665	236	123
2010	0.016	0.85	0.25	0.41	15	1 209	246	955
2011	0.018	1.15	0.31	0.28	22	1 645	525	546
2012	0.039	1.36	0.42	0.38	66	2 466	1 060	479
2013	0.056	2.15	0.38	0.14	196	7 304	1 338	486
2014	0.058	1.25	0.25	0.11	105	1 819	547	167
2015*	0.033	1.20	0.25	0.01				
2016	0.017	1.45	0.06	0.23	48	2 585	158	649
2017	0.041	0.81	0.02	0.06	74	1 789	37	110
Mean	0.015	0.95	0.40	0.14	33	2 294	887	342

Note: *load calculation could not be carried out due to missing instantaneous flowrate data.

According to the quality standards of Surface Water Quality Management Regulation (Ministry of Forestry and Water Management, 2015) which determines the procedures and principles required to protect the water quality of surface waters in Turkey, Göksu River was suffered from nitrite, ammonium, and phosphate pollution (Figure 2). Depending on this high nutrient load, Göksu River and its downstream were categorized as sensitive area (Ayaz et al., 2013; Ministry of Forestry and Water Management, 2016).

Nitrite and nitrate salts are chemically active in water (Birkinshaw & Ewen, 2000; Shamrukh et al., 2001; Demirel et al., 2011), and their presence in water usually associated with agricultural activities (Ledoux et al., 2007; Ogwueleka, 2015). Similarly, the presence of dissolved phosphate in water is usually linked with fertilizer usage in agricultural activities (Sing et al., 2005; Ogwueleka, 2015), as well as, natural causes like soil and rock erosion (Koçak et al., 2010; Beusen et al., 2016). In addition to diffuse pollution, the presence of nitrate and phosphate pollution indicates the existence of point pollution sources.

Similar to findings in this study, Beusen et al. (2016) reported that agricultural surface runoff is the primary source of N and P inputs to the ocean globally. Also, NE Med received a significant amount of mineral dust coming from Sahra, Middle East, and Arabian deserts (Guerzoni et al., 1999; Kubilay et al., 2000; Koçak et al., 2004). 90% of dissolved nitrogen and 40% of dissolved phosphate were obtained from atmospheric sources in NE Med (Koçak et al., 2010).

Nutrient Load Estimation

Similar to the nutrient concentrations, the monthly average nutrient load reaching the NE Med varied in time. Monthly average of NO_2, NO_3, NH_4 and PO_4 load varied between 0.07-31.2 ton/month, 15-1226 ton/month, 0.5-539 ton/month, 1-267 ton/month, respectively (Table 1).

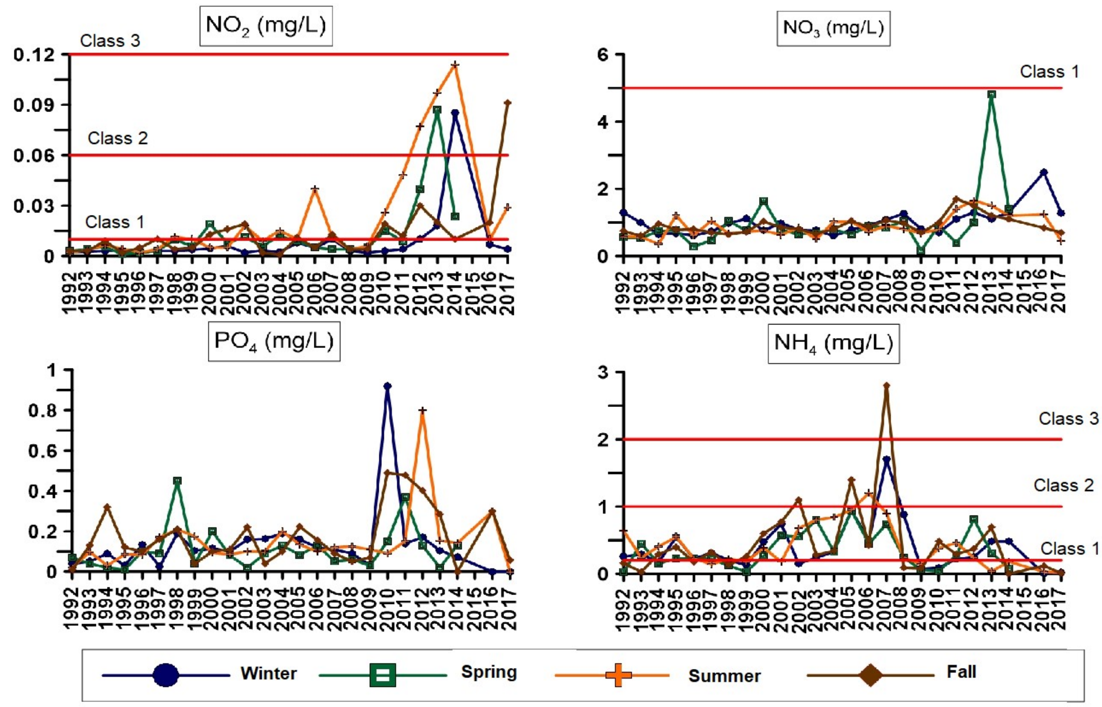

Figure 2. Comparison of nutrient concentration of Göksu River with surface water quality management regulation

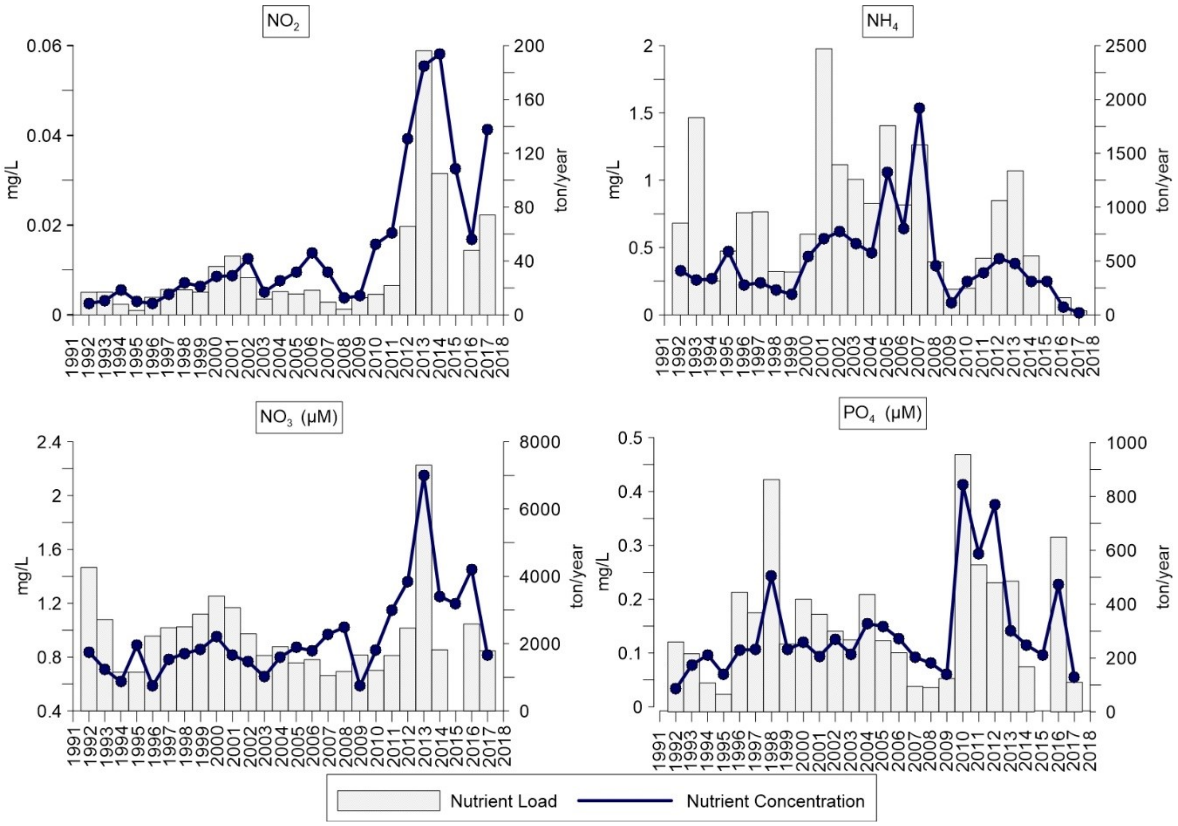

Figure 3. Annual nutrient load reaching to NE Med

Akçay & Tuğrul (2018) estimated the annual average NO_2, NO_3, NH_4, PO_4 load coming from Seyhan, Ceyhan, Berdan, Lamas, and Göksu Rivers as 966, 19 420, 2 796, 10 214 ton/year, respectively. In this study, the nutrient load coming from the Göksu River was estimated as 33 ton NO_2/year, 2.294 ton NO_3/year, 887 ton NH_4/year, and 342 ton PO_4/year (Table 1). As compared with the data from Akçay & Tuğrul (2018), the amount of NO_2, NO_3, NH_4, PO_4 coming from the Göksu River constitutes 3 %, 11 %, 32 %, and 33 % of the collected food load reaching the NE Med, respectively.

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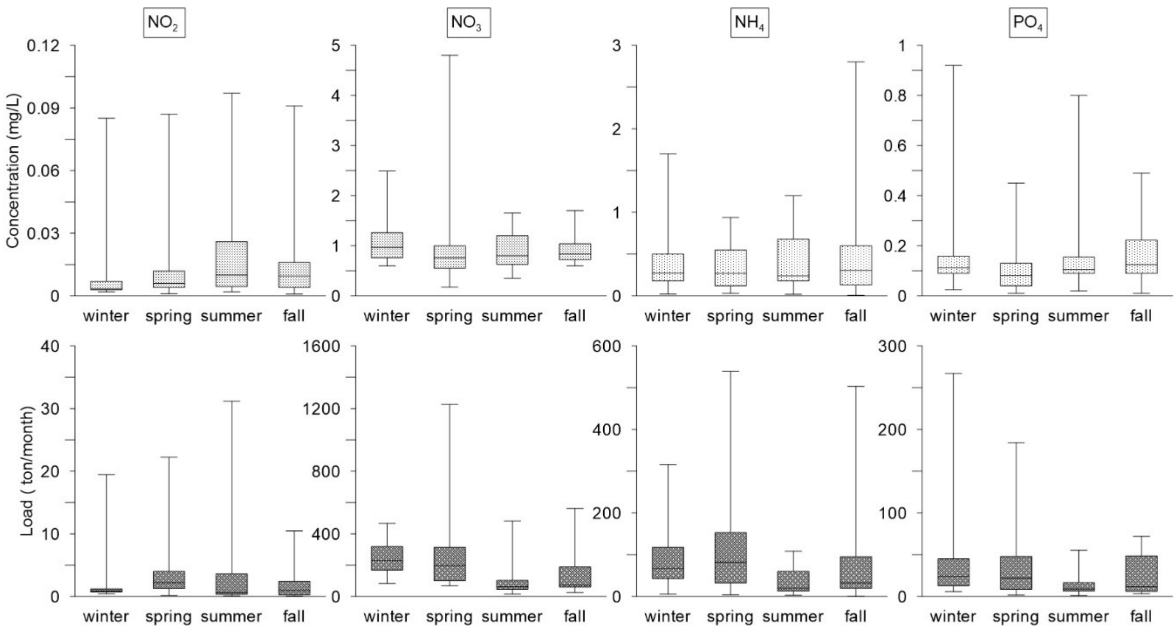

Figure. 4. Seasonal variation in nutrient load and nutrient concentration

Riverine nutrient load was estimated to be highest between 2012 and 2014. According to Eastern Mediterranean Climate Center database, precipitation observed in February and May of 2010-2013 was significantly greater than annual precipitation average of 1970-2010 (EMCC, 2020). This intense precipitation could increase the phosphate and nitragen load in the surface runoff considering the intense agricultural activity in the downstream of Göksu River (Figure 1).

Results revealed that nutrient load was increased with increasing nutrient concentration (Figure 3) throughout the sampling period as expected; since, both quality and quantity of surface runoff affect the nutrient load carried by rivers (Ackerman & Schiff, 2003). Also, both annual average load and concentration of NO_2, NO_3, and PO_4 were seen to be increasing between 2010 and 2015 which is coherent with the previous studies conducted in Cilician Basin (Akçay & Tuğrul, 2018; Kılıç et al., 2018).

Even though there was no statistically significant seasonal variation observed in both nutrient load and nutrient concentration ($p>0.05$), a high standard deviation was observed depending on seasons (Figure 4). In general, the highest nutrient concentrations observed in summer seasons due to significant evaporation, and the highest nutrient load observed in winter-spring when precipitation is dominant.

Satellite Images

The chemical composition of phytoplankton in the ocean is known as the Redfield ratio which is 106 C:16 N:1 P (Goldman, 1979).

Parameters which cause deflection from this ratio are referred to as limiting nutrient for growth (Redden et al., 2009). Göksu River contains a large amount of phosphate to sustain the growth; whereas, suffers from a lack of nitrogen (Figure 5). Therefore, high phosphate-containing waters of the Göksu River cause an increase in the primary productivity of NE Med where growth is mainly nitrogen-limited as a result of high N/P ratio (Krom et al., 1991; Koçak et al., 2010).

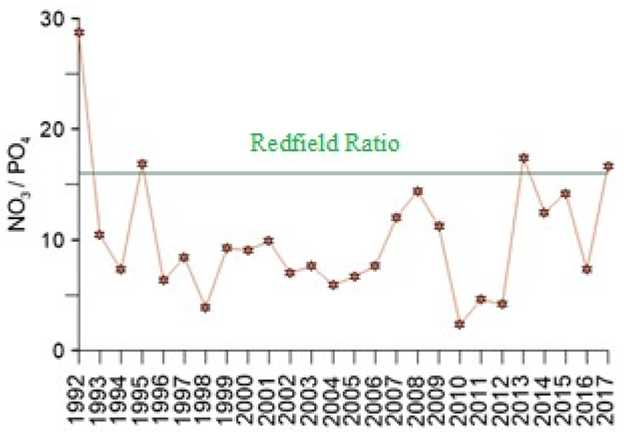

Figure 5. Redfield ratio of Göksu River

Satellite images representing the impact of the Göksu River on NE Med were also confirmed the relationship between river effluents and coastal waters (Figure 6). It is found that nutrient-rich waters of Göksu River transported along the coastline toward the west and southwest via Asian Minor current that results in the enrichment in the surface chl-*a* concentration of coastal zone. Also, chl-*a* concentration in the inshore area is increasing depending on nutrient load coming from the Göksu River.

Satellite images showed unique oceanology features of the NE Med which occupy a very important place in primary production in the region (Figure 6). During winter when nutrient-rich waters of deep waters were brought to the surface

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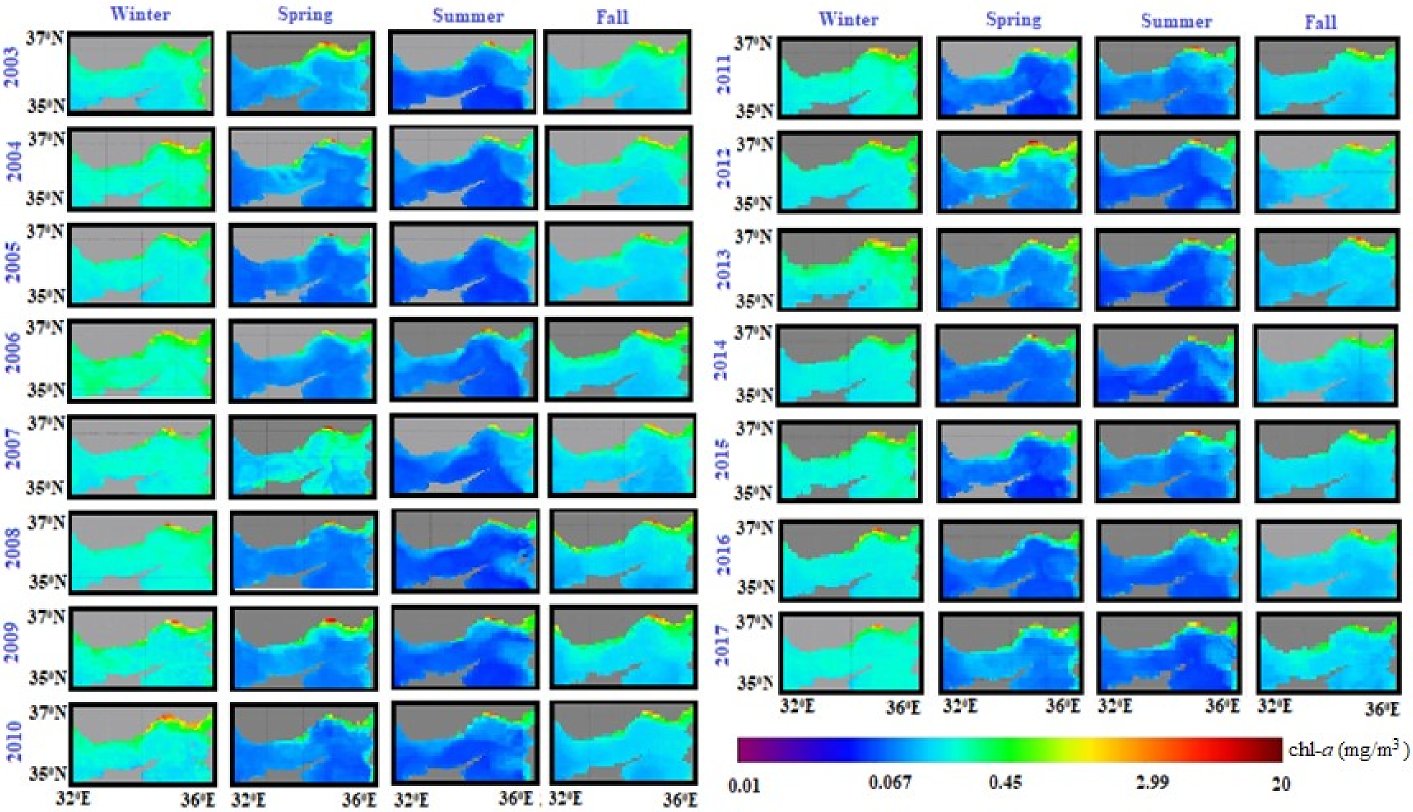

Figure 6. Seasonal surface chlorophyll-*a* concentration between 2003 and 2017

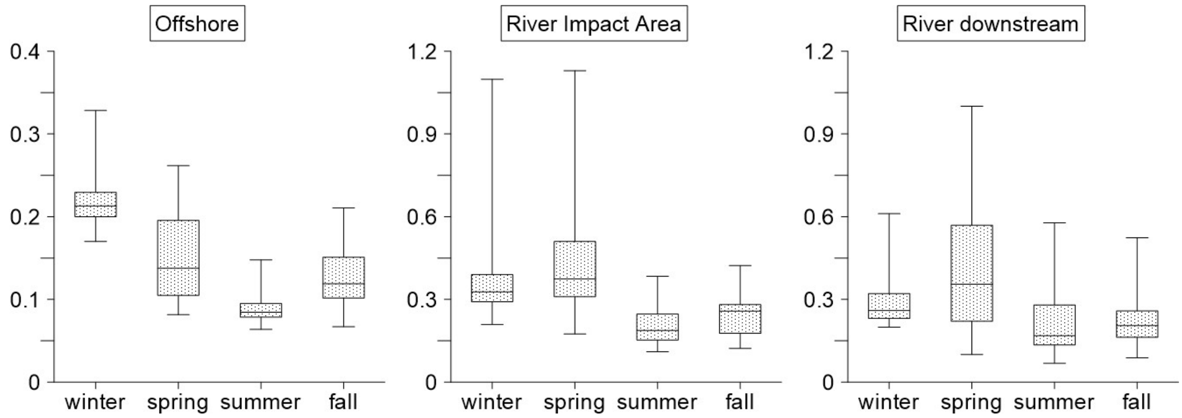

Figure 7. Seasonal variation in surface chlorophyll-*a* concentration

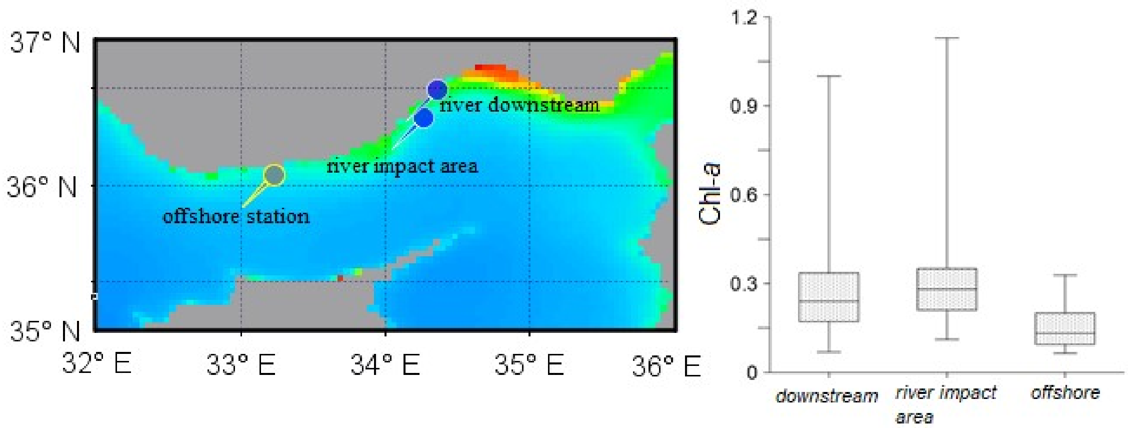

Figure 8. Variation of surface chl-*a* concentration (mg/m^3) depending on station type

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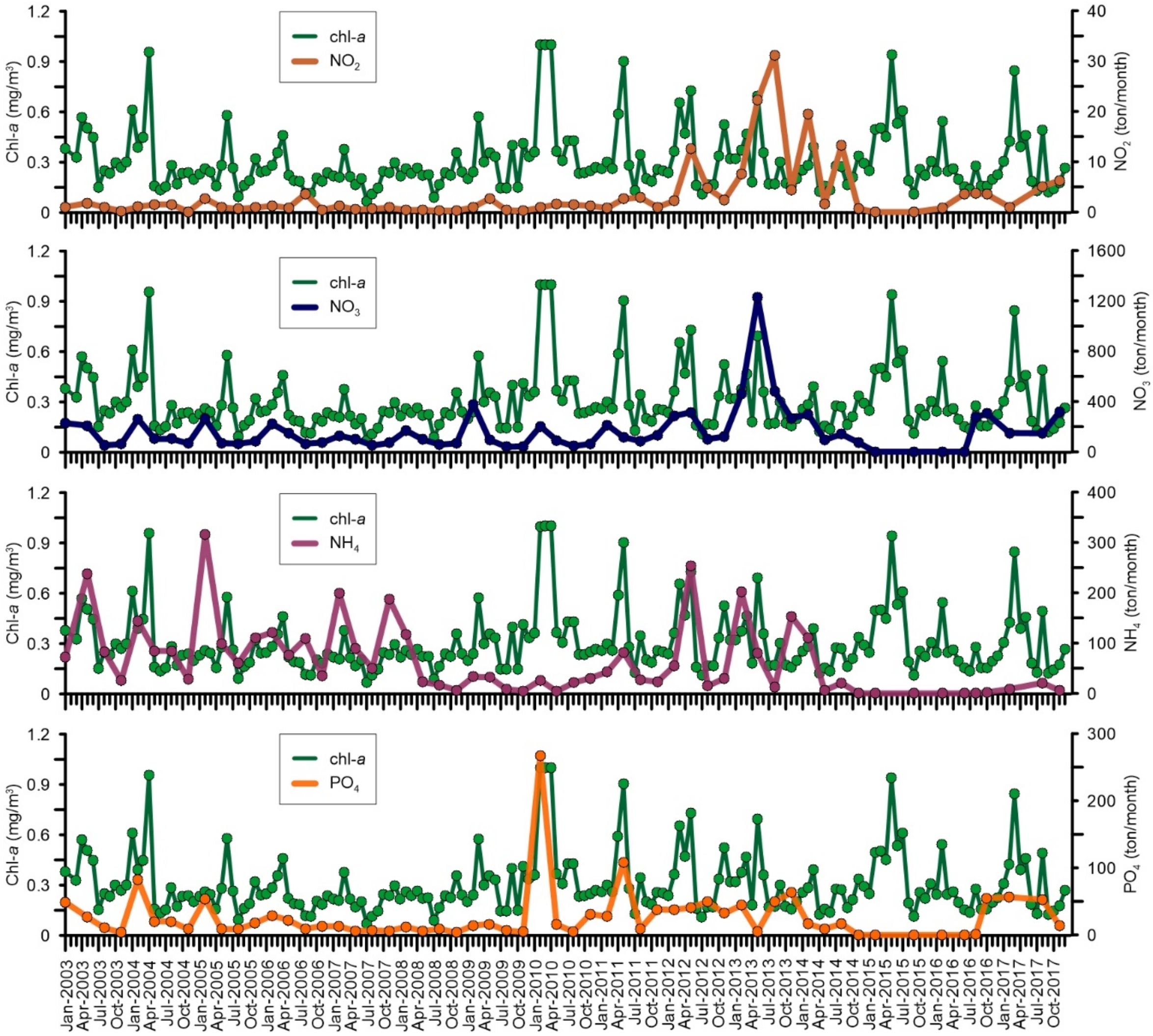

Figure 9. Relationship between nutrient salts and surface chl-*a* concentration

with mixing (Doğan Sağlamtimur & Tuğrul, 2008), surface chl-*a* concentrations were reached to the peak levels in the offshore station (Figure 6, Figure 7). On the contrary, strong summer stratification observed in the NE Med caused a strong decrease curve in the nutrient concentration in the euphotic zone (Latasa et al., 2017; Mena et al., 2019), which leads to the decrease in chl-*a* concentration in summer (Figure 6, Figure 7). Even though, these conditions were also valid for the river discharge area, increasing nutrient load as a result of increased precipitation alter the primary production dynamics. Nutrient rich-low salinity waters of Göksu River could not diffuse offshore due to blockage of Asian Minor current (Akpınar et al., 2016). As a result, chl-*a* concentration was increased in the river discharge area; whereas; it was still low in the offshore region (Figure 6). Therefore, as a consequence of physicochemical dynamics of NE Med, surface chl-*a* concentration was sorted from lowest to highest as winter>spring>fall>summer.

To understand the impact of Göksu River on the productivity of receiving environment, surface chl-*a* concentration in 3 different stations representing the river downstream (34.14 N, 36.43 E), river impact area (34.05 N, 36.25 E), and open waters (33.01 N, 35.85 E) were examined from satellite images (Figure 8).

The average surface chl-*a* concentration in the Göksu River downstream, impact area, and offshore area were determined as 0.29 mg/m^3, 0.31 mg/m^3, and 0.15 mg/m^3, respectively (Figure 8). In the river downstream phytoplankton have to adapt to the changing environmental conditions such as low salinity; while, in the river impact area phytoplankton grow under more stable physical conditions (Uysal et al., 2019). For that reason, the highest surface chl-*a* concentration was observed at the river impacted area. On the other hand, the lowest surface chl-*a* concentration was observed at the offshore station where chl-*a* concentration was decreased by more than 2 folds (Figure 8).

Besides, surface chl-*a* concentration at the Göksu River downstream and river impact area have a higher variation range than offshore waters (Figure 8). This indicates that surface chl-*a* concentration in the coastal zone was more sensitive to anthropogenic activities; whereas, variations in the offshore

Marine Science and Technology Bulletin

Table 2. Results of Pearson correlation analysis

		Chl-*a* (mg/m³)	NO_2 (mg/L)	NO_2 (ton/month)	NO_3 (mg/L)	NO_3 (ton/month)	NH_4 (mg/L)	NH_4 (ton/month)	PO_4 (mg/L)	PO_4 (ton/month)
Chl-*a* (mg/m³)	r	1								
	s									
NO_2 (mg/L)	r	-0.06	1							
	s	0.659								
NO_2 (ton/month)	r	0.117	0.783(**)	1						
	s	0.387	0							
NO_3 (mg/L)	r	0.056	0.484(**)	0.510(**)	1					
	s	0.68	0	0						
NO_3 (ton/month)	r	0.273(*)	0.419(**)	0.675(**)	0.719(**)	1				
	s	0.04	0.001	0	0					
NH_4 (mg/L)	r	-0.199	-0.132	-0.115	-0.088	-0.125	1			
	s	0.137	0.329	0.395	0.514	0.355				
NH_4 (ton/month)	r	0.107	-0.111	0.09	-0.11	0.239	0.649(**)	1		
	s	0.426	0.413	0.506	0.417	0.073	0			
PO_4 (mg/L)	r	0.322(*)	0.042	-0.054	-0.029	-0.046	-0.105	-0.086	1	
	s	0.015	0.76	0.691	0.832	0.738	0.441	0.528		
PO_4 (ton/month)	r	0.592(**)	-0.071	0.044	-0.144	0.148	-0.159	0.106	0.760(**)	1
	s	0	0.602	0.747	0.29	0.277	0.241	0.436	0	

Note: (*) Correlation is significant at 0.05 level. (**) Correlation is significant at 0.01 level. Where *r*: Pearson correlation coefficient, *s*: significance.

zone mainly driven by climatic variations like winter mixing and summer stratification.

To evaluate the relationship between nutrient load coming from Göksu River and surface chl-*a* concentration in the downstream of Göksu River, Pearson correlation analysis was used. The results revealed a linear relationship between PO4 concentration from the river and surface chl-*a* concentration ($p<0.01$) and a statistically significant correlation between NO_3 concentration and surface chl-*a* concentration. On the other hand, there was no significant relationship detected between chl-*a* and NO_2 and NH_4 salts (Table 2, Figure 9).

The amount of NO_3 and NH_4 reaching the NE Med by wet or dry deposition is reported to be significantly higher than PO_4 (Koçak et al., 2010). Therefore, in P-limited NE Med, phytoplankton meets the PO_4 amount essential for growth from riverine inputs. In other words, a combination of P-rich waters of Göksu River with N-rich NE Med increases the primary productivity in the Göksu River impact area sharply. The linear relationship observed between chl-*a* and PO_4 load also confirm this relationship (Figure 9).

NE Med coasts are known with the large size phytoplankton (mainly diatom) blooms observed during rainy seasons when nutrient load coming from surface waters was significant (Siokou-Frangou et al., 2010; Yücel et al., 2017). It was reported that NO_3 uptake affinity of diatoms and pico-eukaryotes were comparatively higher than other phytoplankton groups (Painter et al., 2014; Moschonas et al., 2017). As a result, a significant relationship between NO_3 salt and surface chl-*a* concentration was observed during bloom seasons ($p<0.05$) (Table 2; Figure 9).

Interpolation-based average estimator model was reported as a sufficient tool in nutrient load calculations (Laznik et al., 1999; Stalnacke et al., 1999; Bettiol et al., 2005; Johnes, 2007; Buhvestova et al., 2011; Kılıç et al., 2018). Such models are particularly satisfactory in monitoring long-term seasonal trends and time-dependent changes (Johnes, 2007). However, underestimation and overestimation could be also possible due to many reasons. Firstly, it is possible to observe different nutrient concentrations depending on the river section (Johnes, 2007) or flow rate variation depending on season. Secondly, mass transport and transformation kinetics were related to the many environmental constraints which are usually hard to interpret (Kılıç et al., 2018). Lastly, some uncertainties were also possible in using seasonal data to estimate annual nutrient load since it also may cause deflection from the actual load. In order to overcome these existing uncertainties, it is necessary to ensure the accuracy, effectiveness of the monitoring program, and the accuracy of the statistical method in which the nutrient load is calculated (Stalnacke et al., 1999). Long-term (1992-2017) monitoring results from the national monitoring program were used to ensure the accuracy of the data obtained in this study.

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Conclusion

This study is conducted to evaluate the impact of the nutrient load of the Göksu River on the NE Med. Monthly average NO_2, NO_3, NH_4 and PO_4 load varied between 0.07-31.2 ton/month, 15-1226 ton/month, 0.5-539 ton/month, 1-267 ton/month, respectively. Even though, there was no statistically significant seasonal variation observed in both nutrient load and nutrient concentration ($p>0.05$), a high standard deviation was observed depending on season. The greatest nutrient load observed in the winter-spring season lead to an increase in primary productivity the downstream of Göksu River. Surface chl-*a* concentration showed more than a two-fold decrease from inshore to an offshore area that proves the positive impact of the Göksu River. The linear relationship between discharged PO_4 load and surface chl-*a* concentration was detected which represents the positive impact of the combination of P-rich waters of Göksu River with N-rich NE Med ($p<0.01$). Also, a significant relationship observed between discharged NO_3 load and surface chl-*a* concentration ($p<0.05$) was represent the impact the phytoplankton blooms observed during the winter-spring season.

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Compliance With Ethical Standards

Authors' Contributions:

EK and NY designed the study. EK conducted the necessary calculations, data processing and statistical applications. NY advises the processing of study and contributes to discussion of obtained data. Both authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

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