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Original Article

The Asi River's Estimated Nutrient Load and Effects on the Eastern Mediterranean

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ABSTRACT

Rivers are primary receiving environments for agricultural runoff and for domestic and industrial discharges. Rivers assimilate and treat incoming pollution load until self-purification capacity is reached. The remaining pollution load and natural nutrients are carried to and discharged into the sea causing variations in the receiving area's nutrient concentration. This study evaluated nutrient loads and effects of the Asi River on the northeastern Mediterranean Sea. Monitoring data from 2006 to 2014 from the State of Hydraulic Works of Turkey were analyzed with an interpolation-based average-estimator model for nutrient load calculation. The nutrient load's impact on the receiving area was determined using satellite images. Annual nitrite (NO_2), nitrate (NO_3), ammonium (NH_4), and phosphate (o-PO_4) loads were found to be 234 102 tones/year, 2 402 066 tones/year, 1 123 714 tones/year, and 603 669 tones/year, respectively, with all nutrients showing distinct seasonality. The Asi River's load increases during winter and reaches its maximum in spring. High stream flow due to increased precipitation during spring months could explain this situation. Similar results were obtained from satellite images. Chlorophyll-a concentrations in the receiving area increase during winter due to high nutrient load. In other words, nutrient load increases the receiving area's primary productivity.

Keywords: Orontes River, Riverine input, chlorophyll, İskenderun Bay, Eastern Mediterranean

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INTRODUCTION

With the impact of industrialization and urbanization, human-induced activities cause variations in land's surface. As a consequence of transformation of land use around rivers, natural habitat has been changed (Vitousek et al., 1997). In addition, microbiological communities around rivers have been altered by harvesting activities, excess fertilizer usage in agriculture and introduction of non-native species which result in the variation in hydrological cycle (Chapin et al., 1997). These activities have an impact on the composition of surface runoff and altered the composition of water carried to the river. Also, as a result of urbanization, rivers were started to be used as a treatment agent of domestic and industrial discharges (Zhou et al., 2007).

As a result of all these human-driven activities, there has been a significant increase in the nutrient concentrations of surface waters. Nutrient enrichment of rivers cause an increase in the primary productivity of the discharge area (Yücel, 2013). This phenomenon, defined as eutrophication, shifts the phytoplankton composition of the receiving environment toward those that are bloom forming, toxic or cannot be consumed by the grazers (Smith, 1999). As a result, water column transparency decreases, dissolved oxygen content of deep water decreases, fish and shellfish yields reduces and massive fish deaths may occur (Smith, 2003). In order to prevent eutrophication at the receiving environments, usually seas, it is vital to know nutrient load coming from rivers and estuaries.

Even though, the eastern Mediterranean Sea is one of the most oligotrophic sea in the world (Krom et al., 2004), İskenderun Bay is known with its high productivity because of the river discharges and limited interaction with offshore waters (Uysal et al., 2008). The most important of these are the Ceyhan River, which primarily affects the western part of İskenderun Bay, and the Asi River discharged from Samandağ. These rivers suffer from diffuse pollution which contains high organic pollutants and dissolved nutrient in addition to domestic wastewater discharges (Polat, 2002; Kılıç, 2017). Therefore, it is important to know the nutrient load coming from rivers in order to prevent eutrophication problem that may arise in future. Although river-based nutrient load coming from Ceyhan River to the İskenderun Bay is known (Koçak et al., 2010), Asi River nutrient load and its impact on the eastern Mediterranean Sea is unknown. The aims of this study are (i) to determine nutrient load coming from Asi River and (ii) to evaluate the effect created by the Asi River on the eastern Mediterranean Sea.

Table 1. Mean concentrations of water quality parameters with their standard deviation between 2006-2014.

	NH_4 (mg/L)	NO_2 (mg/L)	NO_3 (mg/L)	o-PO_4 (mg/L)	Q (m^3/s)
Minimum	0.19	0.01	0.10	0.08	0.34
Maximum	3.60	8.52	12.80	4.05	798.45
Mean	1.07	0.55	2.42	0.65	235.10
Standard deviation	1.00	1.53	2.21	0.70	221.83

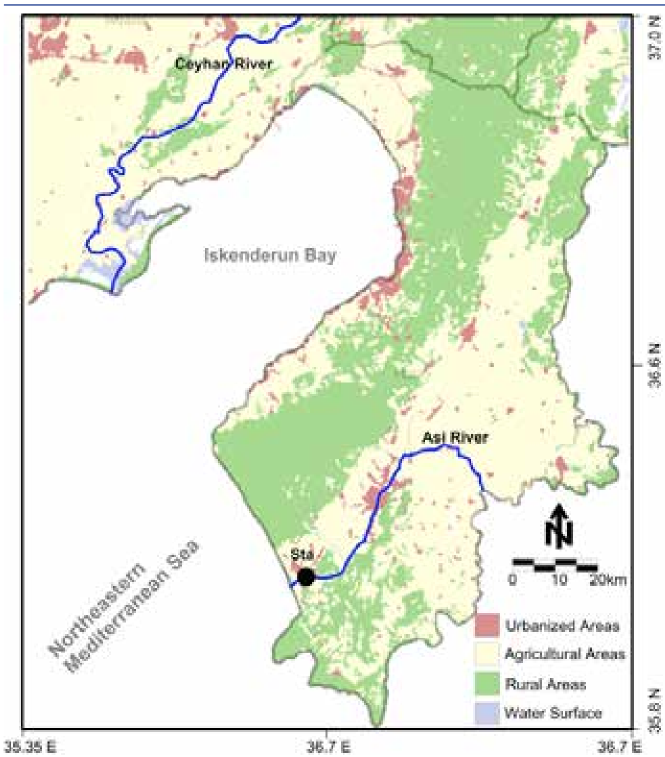

Figure 1. Location of sampling station (Samandağ station)

MATERIAL AND METHOD

Asi River is a transboundary river that is shared by Lebanon (8%), Syria (69%) and Turkey (23%) and long as 453 km (UNESCO-IHE, 2002). Main anthropogenic activities at the Asi basin include agriculture, agricultural industry, animal husbandry, small scale iron-steel industry (Yılmaz and Doğan, 2007; TÜBİTAK MAM, 2013). As a result of these activities, Asi River is exposed to industrial and domestic wastewater discharge from many different locations (Taşdemir and Göksu, 2001). Asi River is suffer from diffuse pollution which contains high amount of phosphate, nitrate and mineral salts (Kılıç, 2017).

Therefore, to analyze the natural and anthropogenic nutrient load carried through Asi River, data taken from State of Hydraulic of Turkey was investigated for Samandağ station, which is at the proximity of Asi River. Seasonal concentrations of NO_2, NO_3, NH_4 and o-PO_4 for 2006-2014 were evaluated (Figure 1). Nutrient load was calculated using interpolation based average estimator model (Quilbé et al., 2006) [Eqn. 1]. Calculations were carried out using Microsoft Excell 2011.

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

where;

K=conversion factor to take account of period of record

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

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

n=number of samples

Additionally, satellite images showing chlorophyll-*a* concentration were used as a proxy to describe the effect of the pollution load reaching eastern Mediterranean. Sea surface chlorophyll-*a* concentration from multi satellite observations were generated using E.U. Copernicus Marine Service Information (Simoncelli et al., 2014). The product used in this study is prepared by combining data from SeaWiFS, Modis-AQUA, VIIRS and MERIS sensors using specific algorithms for the offshore (Case-1) and coastal (Case-2) waters of the Mediterranean. Case-1 algorithm is an update of the empirical Mediterranean algorithm (MedOC4, Volpe et al., 2007) and for the Case-2 waters, it is the AD4 algorithm (D'Alimonte and Zibordi, 2003). Merging of the two algorithms are done following (D'Alimonte et al., 2003).

RESULT AND DISCUSSION

Nutrient Load Calculation

Mean NO_2, NO_3, NH_4 and o-PO_4 concentration are found as 0.55 mg/L, 2.42 mg/L, 1.07 mg/L and 0.65 mg/L, respectively (Table 1). Wide range and high standard deviation indicate seasonal dependence of water quality in the study area. When the mean concentrations of parameters were examined within the scope of Water Pollution Control Regulation of Turkey (Ministry of Environment, 2004) (Table 2), it is found that water quality is second class in terms of NH_4, fourth class for NO_2 and first class for NO_3. However, it is important to note that water quality near the Samandağ stations change from first

Table 2. Environmental standards according to Water Pollution control Regulation

	Class-1	Class-2	Class-3	Class-4
NH_4 (mg/L)	0.20	1.00	2.00	>2
NO_2 (mg/L)	0.002	0.01	0.05	>0.05
NO_3 (mg/L)	5.00	10.00	20.00	>20

Table 3. Nutrient load reaching to the Mediterranean Sea from Asi River between 2006-2014

	Nutrient Salt Load (tones/year)			
Year	NO_2	NO_3	NH_4	o-PO_4
2006	121087	973 315	2 695 040	251 948
2007	33 863	1 228 792	906 140	117 766
2008	9 552	905 063	212 276	81 952
2009	113 804	1 284 363	774 191	268 973
2010	65 838	895 511	114 475	501 471
2011	171 637	2 308 495	2 247 995	1 059 816
2012	138 424	3 245 501	343 832	1 087 348
2013	581 067	11 556 587	1 973 580	771 831
2014	281 877	3 756 590	564 969	1 141 000
Annual mean	234 102	2 881 722	1 123 713	603 669

class to fourth class depending on seasons for all parameters. Nitrogenous compounds and phosphate concentration in surface water are usually related to the excess usage of fertilizers and linked to the agricultural activities (Singh et al., 2005; Ogwueleka 2015).Residuals of fertilizers carried to the river with surface runoff during rainy seasons cause a reduction in water quality.

Mean nutrient loads carried to the eastern Mediterranean Sea through Asi River were calculated as 234102 ton/year for NO_2, 2402066 ton/year for NO_3, 1123714 ton/year for NH_4 and 603669 ton/year for o-PO_4 (Table 3). The ranking order of nutrient concentrations is as follows NO_3>NH_4>o-PO_4>NO_2. Higher load of nitrate and ammonium is related with the higher concentration in surface flow and may be related with more frequent usage of ammonium nitrate containing fertilizers.

When nutrient load change through monitoring period was examined, it is found that nutrient load is maximum at 2013 (Figure 2). Highest flow rate observed in 2013 may be the result of this phenomena. High flow rate conditions change the laminar flow conditions into tubular flow conditions. This condition accelerates the mass transport kinetics in both sediment and water leading to high nutrient load. In addition, it is found that NO_3, NO_2 load reaching to the Mediterranean Sea was increased with time. On the other hand, there has not been any regular relationship between NH_4 load and time. The highest and the lowest NH_4 load was observed at 2006 and 2010, respectively. Additionally, o-PO_4 concentration was decreased till 2008 and increased sharply until 2014.

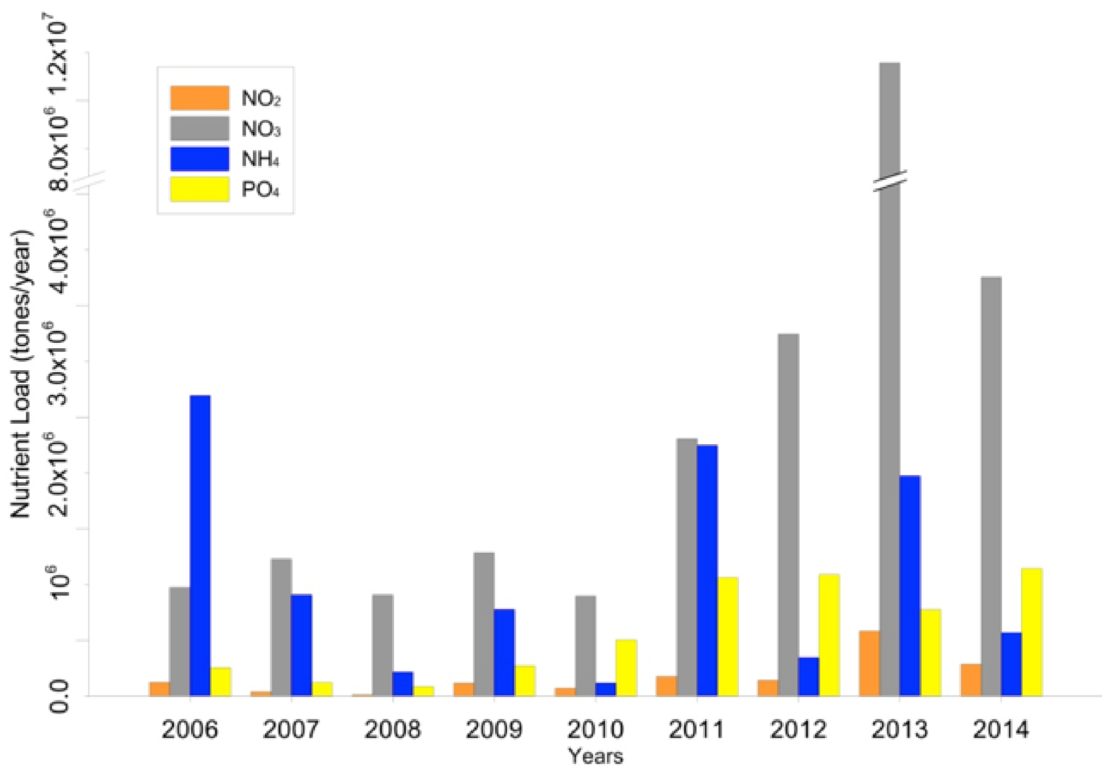

Figure 2. Nutrient load reaching to the northeastern Mediterranean Sea from Asi River between 2006-2014

The relationship between mean nutrient load and seasons can be summarized as winter>spring>fall>summer (Figure 3). This situation is expected since Mediterranean climate is effective at the region. Seyhan, Ceyhan Rivers were also located at the same climate zone and similar seasonal variation in the riverine nutrient load is reported (Koçak et al., 2010). During rainy seasons, precipitation carries the nutrients from land with surface runoff to the river. On the other hand, during summer months, high evaporation reduces the flowrate of the river which adversely affects sediment transport. On the contrary to other seasons, o-PO_4 concentration variation is greater in spring season (Figure 3). This condition may represent the impact of phosphate based fertilizer usage since monitoring station is near the agricultural area. Similar outcome was obtained by Morkoç et al. (2009). They found that highest pollution load to the Omerli reservoir was obtained during spring and summer; whereas, slowest concentrations of pollutions were measured in summer and autumn. This flow dominated nutrient load increase is observed in several countries depending on their climate. For example, Laznik et al. (1999), found a significant increase in the nutrient load reaching the Riga gulf during spring months, especially in April, as a result of predominant peak observed in hydrological regime.

Koçak et al. (2010), investigate the riverine nutrient inputs of Seyhan, Ceyhan and Göksu rivers to the northeastern Mediterranean Sea. Results showed that nutrient input coming from Asi River is lower than other rivers. Seyhan, Ceyhan Rivers passes through highly populated city centers, several organized industrial zones and treated wastewater from domestic and industrial wastewater treatment facilities directly discharged to those rivers. In addition, Çukurova plain is one of most fertile agricultural areas of Turkey and dense agricultural activities are carried out at the plain. All of these anthropogenic activities increase the nutrient concentration in Seyhan and Ceyhan rivers resulting in higher riverine load than Asi River.

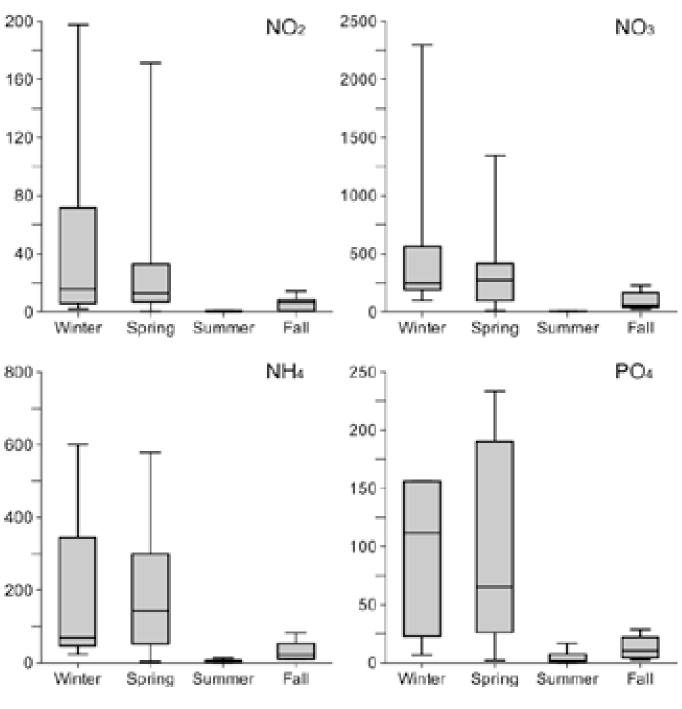

Figure 3. Nutrient load variation depending on seasons

It is also important to note that atmospheric nutrient inputs also affect the nutrient composition of seas by wet and dry deposition (Koçak et al., 2010). Koçak et al. (2010), found that atmospheric inputs are as effective as riverine inputs in the northeastern Mediterranean. On the other hand, Bettiol et al. (2005), found that riverine nutrient inputs are greater than atmospheric nutrient inputs in the lagoon of Venice. This difference may be related with difference in land uses, point and diffuse pollution sources and evaluated parameters.

Even though interpolation based average estimator model is practical and effective tool for riverine nutrient input determination, misestimation is possible due to many reasons. Firstly, nutrient load coming from sediments were not included to the calculations due to lack of data and this condition could cause underestimation. Secondly, mass transport and transformation kinetics, mainly; advection, dispersion and absorbance depended on many environmental factors and they are interrelated with each other. Nutrient load estimation based on these kinetics become more comprehensive and time-consuming process and require variety of input data which are unknown. For that reason, deviations from actual load are possible. Lastly, it is possible to obtain more accurate outcome using more frequent monitoring results. Therefore, the uncertainty while trying to reflect natural ecosystems arises from (i) accuracy of monitoring data, (ii) efficiency of monitoring program and (iii) statistical methods used to calculate nutrient loads (Stalnacke et al., 1999). In this study, results of long time monitoring data obtained from national monitoring programs to ensure the quality of dataset. To conclude, it is found that interpolation based average estimator model is a handy tool to compare nutrient load change depending on year and season regardless of deviations.

Evaluation of Satellite Images

In this study, satellite images showing chlorophyll-*a* concentration were used as a proxy to describe the effect of nutrient load coming from Asi River on the northeastern Mediterranean (Figure 4). Images showed that primary productivity near the discharge of Asi River increasing during winter when river flow was high. This condition is expected due to two main reasons. Firstly, surface flow cause an erosion and carry the nutrients into river which lead to greater nutrient concentration in the surface runoff. Second reason is strongly related with mass transport phenomena. Increased surface flow cause an increase in the advection and dispersion process which lead to the greater amount of mass transportation through river leading to greater nutrient discharge into sea. On the other hand, there were no significant change observed at the river discharge during spring, summer and autumn.

Images also indicate the importance of currents on the productivity of the area. Dispersion and direction of discharged nutrient load are directly related with northbound current. Examining satellite images of February 2006, 2010 and 2013, it

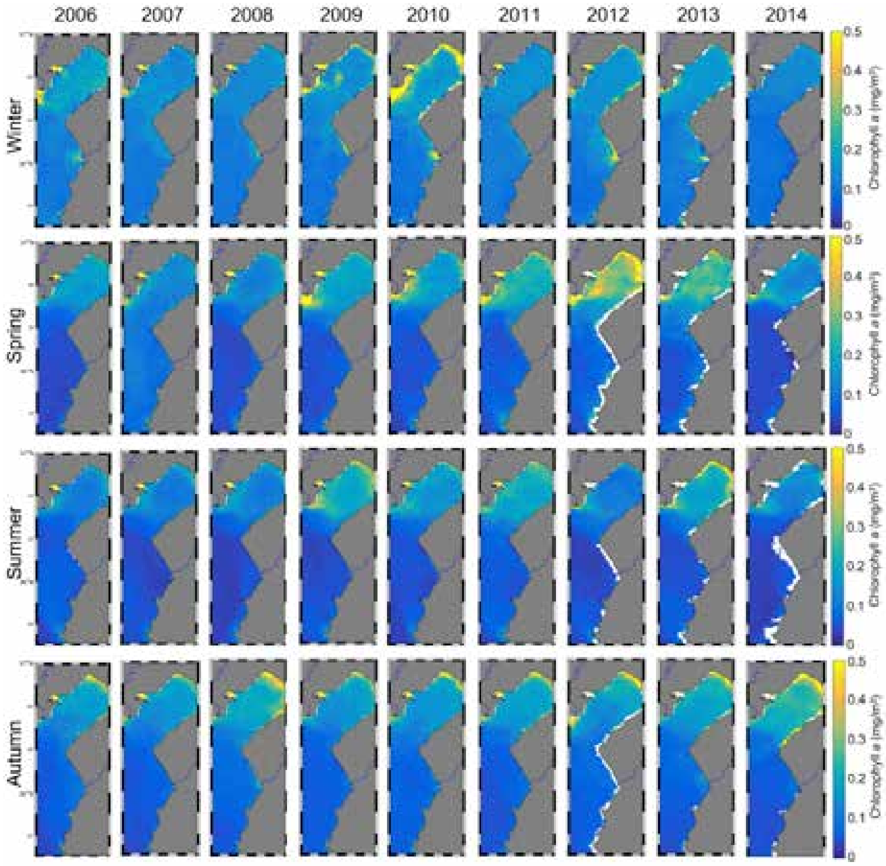

Figure 4. Satellite images showing chlorophyll-a concentration in north eastern Mediterranean including İskenderun Bay

can be seen that nutrient load coming from Asi River tends to disperse through Mediterranean Sea. On the contrary, nutrient load tends to go through İskenderun Bay on February 2009 and February 2012. The difference between these dates could be the impact of Asia Minor current. In this way, Asi River increase the productivity in southern western part of the İskenderun Bay; even though, it did not directly discharge its waters.

Satellite images also showed that impact of Asi River on the İskenderun Bay is not as effective as Ceyhan River which has higher flow rate. Primary productivity in Iskenderun Bay is mainly controlled by Ceyhan River discharge which is transported to the inner zone by the surface current (İyiduvar, 1986). Surface chlorophyll-*a* concentrations in Ceyhan River discharge area exceeded 0.5 mg m^{-3} and coverage area of higher chlorophyll (greater than 0.3 mg m^{-3}) reached to maximum in spring, 2012 in İskenderun Bay (Figure 4). Ceyhan River passes through Çukurova Plain where agricultural activities are dominant and suffer from many industrial and domestic wastewater discharges resulting in high nutrient load. Therefore, it is concluded that even though Asi River impacts the productivity at the discharge area; even though its affect is negligible compared to Ceyhan River.

Lastly, Strobl et al. (2009) investigated the riverine nutrient load of Mediterranean Sea. They found that Turkey is responsible for the highest percentage of phosphate load (43%) among other countries. Similarly, 17% of TN load reaching to the Mediterranean Sea is coming from Turkey's inland waters. Therefore, water quality of inland waters is a important concern. Even though the standards used to describe water quality is national, causes on the environment is international issue.

CONCLUSIONS

This study was conducted to determine nutrient load coming from Asi River and to understand its effect on the eastern Mediterranean Sea. Recently, increased human induced activities, mainly industries, agricultural activities and wastewater discharges, adversely affect the ecosystem in the coastal regions. Water quality carries a primary importance for aquatic livings and worsening of water quality impacts all living being. According to the results of this long term data analysis study, eastern Mediterranean Sea which known with its oligotrophic features, coastal areas are exposed to eutrophication risk. Impact of Asi River on the coastal area was increased during rainy seasons, spring and winter, as a result of increase in river flow. In addition, it is found that impact of Asi River was reaching to inner part of İskenderun Bay with the dominant currents. For this reason, it is recommended that priority should be given to taking necessary measures to reduce nutrient salt loads (especially phosphorus) transported to coastal areas in order to protect the natural ecological features and decrease the risk of eutrophication, especially in semi-enclosed water such as Iskenderun Bay, where the exchange is limited.

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