JAES
Journal of Anatolian Environmental and Animal Sciences
(*Anadolu Çevre ve Hayvancılık Bilimleri Dergisi*)
DOI: https://doi.org/10.35229/jaes.1325674
Year: 8, No: 4, 2023 (590-594)
AÇEH
Yıl: 8, Sayı: 4, 2023 (590-594)
ARAŞTIRMA MAKALESİ RESEARCH PAPER

Limit Values of Dissolved Nutrients for the Assessment of Eutrophication in the Northeastern Mediterranean Rivers

İsmail AKÇAY * **Özgür ÖZBAY**
Mersin University, Faculty of Fisheries, Yenişehir-Mersin, Türkiye

Geliş/Received: *11.07.2023* ***Kabul/Accepted:*** *19.09.2023* ***Yayın/Puplished:*** *31.12.2023*

How to cite: **Akçay, İ. & Özbay, Ö. (2023).** Limit Values of Dissolved Nutrients for the Assessment of Eutrophication in the Northeastern Mediterranean Rivers. *J. Anatolian Env. and Anim. Sciences,* ***8***(4), 590-594. https://doi.org/10.35229/jaes.1325674
Atıf yapmak için: **Akçay, İ. & Özbay, Ö. (2023).** Kuzeydoğu Akdeniz Nehirlerinde Ötrofikasyonun Değerlendirilmesi için Çözünmüş Besin Tuzları Sınır Değerleri. *Anadolu Çev. ve Hay. Dergisi*, ***8***(4), 590-594. https://doi.org/10.35229/jaes.1325674

*: https://orcid.org/0000-0001-8738-8359
: https://orcid.org/0000-0001-7837-350X

***Corresponding author's:**
İsmail AKÇAY
Mersin University, Faculty of Fisheries,
Yenişehir-Mersin, Türkiye
: iakcay@mersin.edu.tr

Abstract: This study attempted to determine the limit values of dissolved nutrients for assessing trophic status and water quality of Northeastern Mediterranean Rivers from the previously published nutrient data sets. Study findings indicated that the oligotrophic river waters should have concentrations of total phosphorus, orthophosphate, ammonium and total nitrogen less than 0.13 mg/L, 0.07 mg/L, 0.11 mg/L and 0.90 mg/L, respectively. The proposed limit values defining oligotrophy, mesotrophy and eutrophy differed from those reported by the Surface Water Quality Regulation and the commonly used reference values. These discrepancies were probably due to the rivers' distinct physical and biochemical characteristics. New approaches, such as modeling studies, are needed to define threshold and reference values of dissolved nutrients to produce more sensitive assessment tools for sustainable management of NE Mediterranean Rivers.

Keywords: Dissolved nutrients, eutrophication, limit values, northeastern mediterranean rivers.

Kuzeydoğu Akdeniz Nehirlerinde Ötrofikasyonun Değerlendirilmesi için Çözünmüş Besin Tuzları Sınır Değerleri

***Sorumlu yazar:**
İsmail AKÇAY
Mersin Üniversitesi Su Ürünleri Fakültesi,
Yenişehir-Mersin, Türkiye
: iakcay@mersin.edu.tr

Öz: Bu çalışmada, daha önce yayınlanan besin tuzu veri setlerinden Kuzeydoğu Akdeniz Nehirlerinin trofik durumunu ve su kalitesini değerlendirmek için sınır değerler belirlenmeye çalışılmıştır. Çalışma sonuçları, oligotrofik özellikte nehir sularının toplam fosfor, ortofosfat, amonyum ve toplam azot için konsantrasyon değerlerinin 0,13 mg/L, 0,07 mg/L, 0,11 mg/L ve 0,90 mg/L'den az olması gerektiğini göstermiştir. Oligotrofi, mezotrofi ve ötrofiyi tanımlayan önerilen sınır değerler, Yerüstü Kalitesi Yönetmeliği tarafından bildirilen değerlerden ve yaygın olarak kullanılan referans değerlerden farklı bulunmuştur. Bu farklılıklar, muhtemelen nehirlerin farklı fiziksel ve biyokimyasal özelliklere sahip olmasından kaynaklıdır. Kuzeydoğu Akdeniz Nehirlerinin sürdürülebilir yönetimi için çözünmüş besin maddelerinin sınır ve referans değerlerini tanımlamak üzere daha hassas değerlendirme araçları üretmek amacıyla modelleme çalışmaları gibi yeni yaklaşımlara ihtiyaç vardır.

Anahtar kelimeler: Çözünmüş besin tuzları, kuzeydoğu akdeniz nehirleri, ötrofikasyon, sınır değerler.

INTRODUCTION

Safe and healthy freshwater systems provide many goods and services for the society (Richter et al., 2003). Rivers, a significant source of freshwater supply, have been used for many purposes though wastewater discharges have highly polluted them originated from human-induced activities (Akçay et al., 2021; Mouri et al., 2011; Mustapha et al., 2013). The assessment of eutrophication in river and stream waters is, therefore, a major issue for these freshwater ecosystems that serve for the society's human health and economic development (Carlson, 1977; Mamun et al., 2021).

Aquatic ecosystems are affected by the enrichment of nutrients by changing molar nutrient ratios, along a continuum from fresh water through estuarine, coastal, and marine ecosystems. There are positive relationships between the fluxes of nutrients (N, P) and the primary production, and fisheries yield. However, there are thresholds where the fluxes of nutrients into the estuarine, coastal and marine ecosystems when exceeding the assimilation capacity of nutrient-enhanced production (Rabalais, 2002). Eutrophication classification tools are generally related to the intercorrelation of state variables which are direct (nutrient concentrations, surface DO, biomass, turbidity values) and indirect (oxygen deficiency in deep waters and biodiversity changes) indicators of eutrophication (Ferreira et al., 2011; Ignatiades et al., 1992; Primpas et al., 2010; Tavakoly Sany et al., 2014). Many studies have been performed to determine trophic status of river and stream waters using various eutrophication classification tools (Carlson, 1977; Dodds et al., 1998; Karr & Chu, 2000; Paula Filho et al., 2020; Ülker et al., 2020). However, the classification scales and limit values of these classification tools may vary regionally due to distinct physical and biochemical characteristics of the studied river and stream waters.

The Mediterranean Sea, a typical example of semi-enclosed seas, is characterized by high values of salinity, temperature and density. Since the net evaporation exceeds the precipitation, an anti-estuarine circulation through the Strait of Gibraltar is observed that contributes to very low nutrient concentrations in the surface waters (Tanhua et al., 2013). Though offshore waters of Northeastern (NE) Mediterranean Sea displays oligotrophic properties with low nutrient concentrations and primary productivity , its coastal region has been fed by many regional rivers and creeks (Akcay et al., 2022; Akçay, 2023; Tugrul et al., 2019). For the NE Mediterranean shelf waters, a comparison of riverine nutrient fluxes with the atmospheric, wastewater and sediment-diffusive nutrient fluxes clearly showed that NE Mediterranean coastal region is principally fueled by riverine nutrient inputs, leading to coastal eutrophication (Akçay et al., 2021).

In order to attain good environmental status of regional rivers and NE Mediterranean Sea, sustainable management of eutrophication is of critical importance. In this study, therefore, an attempt was made to determine the limit values of dissolved nutrients for assessing the trophic status and water quality of NE Mediterranean Rivers. The proposed limit values for nutrients were also compared to those reported by Surface Water Quality Regulation and the study of Dodds et al., (1998).

MATERIAL AND METHOD

The NE Mediterranean regional rivers are Asi, Ceyhan, Seyhan, Berdan, Göksu, Lamas, Manavgat, Aksu, Eşen and Dalaman Rivers (Akçay, 2023). In this study, the examined nutrients were orthophosphate (PO_4), total phosphorus (TP), ammonium (NH_4) and total nitrogen (TN). The nutrients data were obtained from the studies of Demirel et al. (2011), Özbay et al. (2012); Kılıç et al. (2018), Akçay & Tuğrul (2018) and Türkeri et al. (2023) (Table 1). The studied rivers were shown on the map presented in Figure 1.

Table 1. The Northeastern Mediterranean Rivers studied between 2006 and 2022.

River	Study Period	Sampling Frequency	# of stations	Parameters	Reference
Göksu R.	2006-2008	Seasonal	6	NH_4, PO_4, TP	Demirel et al. (2011)
Berdan R.	2008-2008	Monthly	6	TN, PO_4, TP	Özbay et al. (2012)
Asi R.	2006-2014	Seasonal	1	NH_4, PO_4	Kılıç et al. (2018)
Ceyhan R.	2008-2015	Seasonal	1	NH_4, PO_4, TP	Akçay & Tuğrul (2018)
Seyhan R.		Seasonal	1	NH_4, PO_4, TP	
Berdan R.		Seasonal	1	NH_4, PO_4, TP	
Göksu R.		Seasonal	1	NH_4, PO_4, TP	
Lamas R.		Seasonal	1	NH_4, PO_4, TP	
Bedan R.	2021-2022	Monthly	3	TN, PO_4, TP	Türkeri et al. (2023)
Göksu R.		Monthly	5	TN, PO_4, TP	

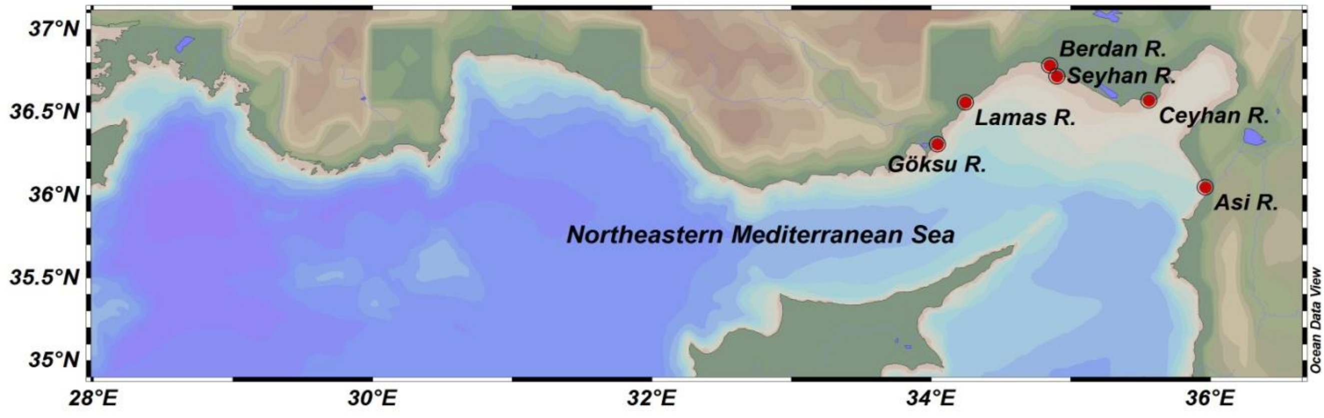

Figure 1. The studied rivers flowing into the Northeastern Mediterranean Sea between 2006 and 2022 (Sampling strategies were presented in Table 1).

The limit values of nutrients were proposed by the method presented in the study of Ignatiades et al., (1992). Firstly, all data sets were evaluated after removing outliers according to the method described by Crawley (2007). Since the log transformation is the most common method for the normal distribution of environmental parameters, log transformation of the data sets was applied. Then, all the reported data sets and the log-transformed values were examined for normality. Kolmogorov-Smirnov statistics was applied by using IBM SPSS Statistics 26. Finally, the limit values of nutrients for the eutrophication assessment were determined from the mean values of log-transformed data and the standard deviation of the data after removing outliers (Ignatiades et al., 1992).

RESULTS AND DISCUSSION

Though there are positive relationships between the fluxes of nutrients (N, P) and the primary production, and fisheries yield, excess amount of nutrient inputs into the estuarine, coastal and marine ecosystems has led to degradation of water qulity (Rabalais, 2002). Northeastern (NE) Mediterranean Sea offshore waters displays oligotrophic properties. However, its coastal region has been affected by many regional rivers and creeks, leading to development of coastal eutrophication (Akcay et al., 2022; Akçay, 2023; Tugrul et al., 2019). For the management of eutrophication in the regional rivers and NE Mediterranean sea shelf waters, determination of nutrients concentrations, their fluxes and defining the target values of riverine nutrients are critically important. In this study, the limit values of dissolved nutrients for the assessment of trophic status and water quality of Northeastern Mediterranean Rivers were determined. In this study, simple statistics of the obtained data sets were presented in Table 2. All the reported values indicated that the studied NE Mediterranean Rivers showed marked spatial and temporal variability. The maximum values were generally reported in wet winter-spring periods in Seyhan and Ceyhan Rivers while minimum values were recorded in the least contaminated Lamas River (Akçay & Tuğrul, 2018). The frequency distributions and normality tests showed that log-transformed data approached normality (Figure 2-3, Table 3).

Table 2. Simple statistics of the obtained data sets ((a): Raw data before removing outliers, (b): Data after removing outliers.

(a)	TP (mg/L)	PO_4 (mg/L)	NH_4 (mg/L)	TN (mg/L)
Mean	0.36	0.26	0.96	2.17
Std. Dev.	0.65	0.58	2.93	2.44
Min.	0.02	0.002	0.01	0.18
Max.	3.89	4.05	15.68	9.00
N	124	57	30	96
(b)	TP (mg/L)	PO_4 (mg/L)	NH_4 (mg/L)	TN (mg/L)
Mean	0.19	0.12	0.18	1.16
Std. Dev.	0.17	0.10	0.15	0.90
Min.	0.02	0.002	0.01	0.18
Max.	0.70	0.39	0.56	4.29
N	112	50	26	80

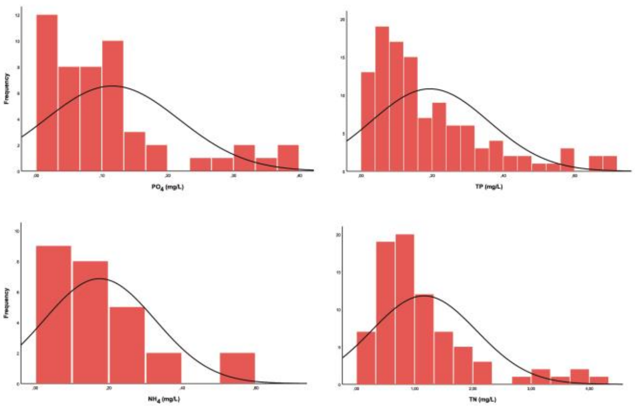

Figure 2. Frequency distribution of nutrients after removing outliers.

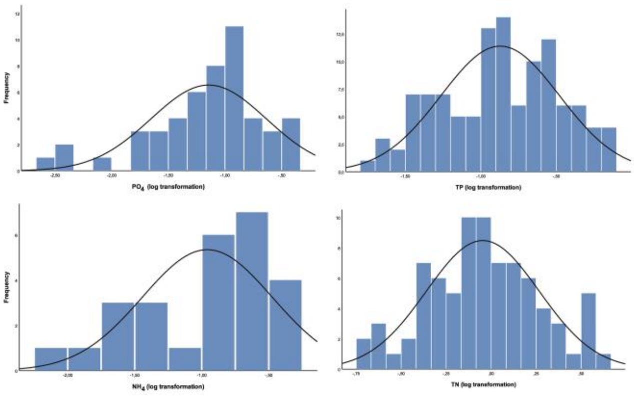

Figure 3. Frequency distribution of nutrients after log transformation.

Table 3. Kolmogorov-Smirnov statistics for normality of the nutrients data and log transformed nutrients data.

	Kolmogorov-Smirnov[a]		
Parameters	Statistic	df	Sig.
TP (mg/L)	0.158	112	0.000
PO_4 (mg/L)	0.211	50	0.000
NH_4 (mg/L)	0.137	26	0.200*
TN (mg/L)	0.158	80	0.000
TP (log transformation)	0.064	112	0.200*
PO_4 (log transformation)	0.125	50	0.050
NH_4 (log transformation)	0.158	26	0.095
TN (log transformation)	0.050	80	0.200*

*This is a lower bound of the true significance.
[a]Lilliefors Significance Correction

Assessment of trophic status can be determined by using concentrations of nutrients obtained by systematic data sets. Ignatiades et al. (1992) performed a statistical analysis of nutrients for scaling aquatic environments into oligotrophic, mesotrophic and eutrophic water quality. Furthermore, in a recent study performed by Nikolaidis et al. (2022), the boundary concentrations between good and moderate status for the nutrient concentrations of Rivers in Europe to achieve good environmental status and deliver ecosystem services. They reported that the nutrient targets established for rivers ranged from 0.5 to 3.5 mg/L TN and from 11 to 105 μg/L TP, respectively (Nikolaidis et al., 2022). In this study, limit values of dissolved nutrients for assessing the trophic status and water quality of NE Mediterranean Rivers were determined from the mean values of log-transformed data and the standard deviation of the data after removing outliers (Table 4). According to limit values, the oligotrophic river waters should have concentrations of TP, PO_4, NH_4 and TN less than 0.13

mg/L, 0.07 mg/L, 0.11 mg/L and 0.90 mg/L, respectively (Table 4). A close examination of the proposed limit values for oligotrophy and eutrophy indicated that our proposed limit values for the PO_4 and TP were much greater than the values reported in Surface Water Quality Regulation and the values reported by Dodds et al., (1998) (Table 5-6). Though our proposed limit values for oligotrophy were similar to those reported by Dodds et al. (1998), our TN limit values were much lower than those according to Surface Water Quality Regulation.

Table 4. The proposed limit values for the assessment of eutrophication in the Northeastern Mediterranean Rivers.

Trophic Status	TP (mg/L)	PO_4 (mg/L)	NH_4 (mg/L)	TN (mg/L)
Oligotrophic	<0.13	<0.07	<0.11	<0.90
Mesotrophic	0.13-0.43	0.07-0.25	0.11-0.37	0.90-2.70
Eutrophic	>0.43	>0.25	>0.37	>2.70

Table 5. Water quality classes according to Surface Water Quality Regulation.

Water Quality Classes	TP (mg/L)	PO_4-P (mg/L)	NH_4-N (mg/L)	TN (mg/L)
Class 1	<0.08	<0.05	<0.20	<3.5
Class 2	0.20	0.16	1.00	11.5
Class 3	>0.20	>0.16	>1.00	>11.5

Table 6. Limit values for the assessment of eutrophication proposed by Dodds et al. (1998).

Trophic Status	TP (mg/L)	TN(mg/L)
Oligotrophic	<0.025	<0.70
Mesotrophic	0.025-0.075	0.70-1.50
Eutrophic	>0.075	>1.50

In Türkiye, nutrient (N, P, Si) concentrations and trophic status assessment of the regional rivers flowing into the NE Mediterranean shelf region were reported in many studies (Akçay & Tuğrul, 2018; Akçay et al., 2021; Demirel et al., 2011; Kılıç et al., 2018; Kılıç, 2020; Koçak et al., 2010; Özbay et al., 2012; Tuğrul et al., 2009; Türkeri et al., 2023). Trophic status assessment of these regional rivers was determined by commonly used classification tools reported by the study of Ülker et al. (2020), as well as water quality assessment by using the limit values presented in Surface Water Quality Regulation published in the official gazette of Türkiye. Defining site-specific reference conditions for the water masses is necessary to assess eutrophication (Tuğrul et al., 2019). The limit values for the river waters ranging from oligotrophic to eutrophic conditions may vary spatially since these waters displayed distinct physical and biochemical variability (Table 2). Regional rivers flowing into the coastal waters of NE Mediterranean Sea were highly contaminated by anthropogenic pressures (Akçay & Tuğrul, 2018; Özbay et al., 2012). Defining limit values from the obtained data sets may be an excellent way to determine eutrophication status of these rivers. However, for a better assessment of eutrophication, it is necessary to determine physical and eutrophication-related parameters over specific periods (Tavakoly Sany et al., 2014). Therefore, monitoring studies are critically important for the sustainable management of regional rivers flowing into the NE Mediterranean shelf waters.

CONCLUSION

In this study, a first attempt was made to determine limit values of dissolved nutrients for assessing trophic status and water quality of NE Mediterranean Rivers. Study findings indicated that our limit values defining oligotrophy, mesotrophy and eutrophy were different than those reported by the Surface Water Quality Regulation and the study of Dodds et al. (1998). These discrepancies were probably due to the rivers' distinct physical and biochemical characteristics. Study findings also showed the importance of systematic monitoring studies for eutrophication assessment in the regional rivers flowing into the NE Mediterranean shelf region. For defining threshold and reference values of dissolved nutrients, new approaches, such as modeling studies, are needed to assess trophic status and water quality to produce more sensitive assessment tools for sustainable management of NE Mediterranean Rivers.

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