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Nemrut Bay Seawater Quality Assessment at the Planning Stage of Marine Outfall

Deniz Deşarjı Planlaması Aşamasında Nemrut Körfezi Deniz Suyu Kalitesinin Değerlendirilmesi

Esin ESEN [1*]

[1] SRK Consulting Turkey (SRK Danışmanlık ve Müşavirlik A.Ş.) Ankara, Turkey
(formerly Dokuz Eylul University Institute of Marine Sciences and Technology, Izmir, Turkey)

*Sorumlu Yazar / Corresponding Author: Esin ESEN, esinsn@gmail.com

ÖZET

Ege Denizi kıyı bölgesinde evsel ve endüstriyel atıksuların doğrudan deşarjı önemli bir konudur. Herhangi bir kıyı yapısının hayata geçirilmesi öncesinde çevresel durum tesbit programının tasarımı kıyısal dinamiklerin karmaşıklığı nedeniyle fizibilite çalışmalarının en hayati bölümü olmaktadır. Bu çalışmada Nemrut Körfezi su kolonunun biyojeokimyasal durumu olası bir endüstriyel atıksu deşarjının etkilerini değerlendirebilmek amacıyla ortaya konmuştur. Denizsuyu örneklemesi kış (tam karışımlı) ve yaz (tabakalaşmalı) mevsimsel koşullarını yansıtacak şekilde toplanmış ve çözünmüş ağır metal iyonları (Hg, Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe, Mg), çözünmüş ve partikül nutrientler (NO3-, NO2-, PO43-, Si, TOC, TPP, POC, PON), çözünmüş oksijen (DO), ve klorofil-a (Chl-a) içeriği açısından analiz edilmiştir. Mevcut durum tesbiti Türk Çevre Mevzuatı gereklilikleri açısından değerlendirilmiştir. Örneklerin analiz sonuçları kıyı çizgisine yakın istasyonlarda antropojenik kaynaklı etkilere işaret etmiştir. Nemrut Körfezi etrafındaki endüstriyel ve denizcilik aktivitelerine rağmen oldukça düşük seviyelerde kirlilik etkileri göstermiştir.

Anahtar Kelimeler: Çözünmüş Metal İyonları, Nutrientler, Trofik Seviyeler, TRIX, Deniz Kirliliği

ABSTRACT

Direct discharges of domestic and industrial wastewaters to the coastal zone of Aegean Sea are an important concern. Design of an environmental baseline assessment program prior to any coastal development is a crucial part of the feasibility studies due to the complexity of the coastal dynamics. The background biogeochemical status of the Nemrut Bay's water column was set to assess the impact of a proposed industrial discharge. The seawater samples were collected on seasonal bases representing winter (mixed water column) and summer (stratified) conditions, and were analyzed for dissolved heavy metal ions (Hg, Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe, Mg), dissolved and particulate nutrients (NO_3^-, NO_2^-, PO_4^{3-}, Si, TOC, TPP, POC, PON), dissolved oxygen (DO) and chlorophyll-a (Chl-a) contents. The baseline assessment was based on the Turkish regulatory liabilities. The analyses of the samples showed that anthropogenic influence is mostly detected in stations closer to the shoreline. The Nemrut Bay has quite a low level of pollution regarding the impacts of high intensity of industrial and maritime activities in its vicinity are considered.

Keywords: Dissolved Metal Ions, Nutrients, Trophic Levels, TRIX, Marine Pollution

1. INTRODUCTION

Environmental impact predictions depend on understanding cause-effect relationships and the status and trends of environmental characteristics. Baseline studies establish the current state of ecosystems and provide valuable sources of information prior to the development of civil works i.e. disposal of treated or untreated wastewaters into the ocean through marine outfall systems which are preferable by most of the coastal cities due to economic reasons. Environmental measures for permitting the marine discharge have been defined at international, national, regional, and/or local levels for the protection of the marine ecosystem (Andreada, 1997). The criteria of marine disposal of wastewater has to take account the seasonal biogeochemical characteristics of the environmental water (Mossa, 2006). Measurements of baseline biogeochemical parameters of water column and sediment are important components of marine outfall design and discharge monitoring. Many of these parameters determine water column mixing potential and vital for setting the background ecological state in order to assess the impact of discharge (Mossa, 2006; Lattemann and Höpner, 2008).

Semi-enclosed coastal waters, such as bays, have generally been regarded as highly productive aquatic systems in which nutrient supply is an important factor. Coastal areas receive large amounts of material from land, and apart from nutrients trace metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risk (Gavriil and Angelidis, 2005). Particulate organic matter (POM) is of considerable biogeochemical and oceanographic importance, representing a carrier for transport of chemical elements from surface waters to the sediments (Bizsel et al., 2011).

The trophic status of the marine ecosystem is generally defined by TRIX index that was originally developed in the Northern Adriatic Sea for the Italian waters and has been applied in many European seas, such as the Adriatic, Tyrrhenian, Baltic, Black and North seas (Pettine et al., 2007). TRIX has recently become one of the indices used for monitoring the trophic state conditions in coastal waters (Balkıs et al., 2012; Baytut et al., 2010; Dyatlov et al., 2010; Giovanardi and Vollenweider, 2004; Medinets et al., 2010; Moncheva et al., 2002; Vargas-González et al., 2014). It is ecologically relevant, regionally applied and considered internationally (OSPAR Commission, 2012).

The biogeochemical properties of Nemrut Bay as a subsystem within the Candarli Bay, Aegean Sea and as a neighboring marine environment of Aliaga town were investigated in order to assess the possibility of marine discharge from a proposed industrial activity (Figure 1). Aliaga town and its vicinity have been subjected to extensive industrial developments for decades.

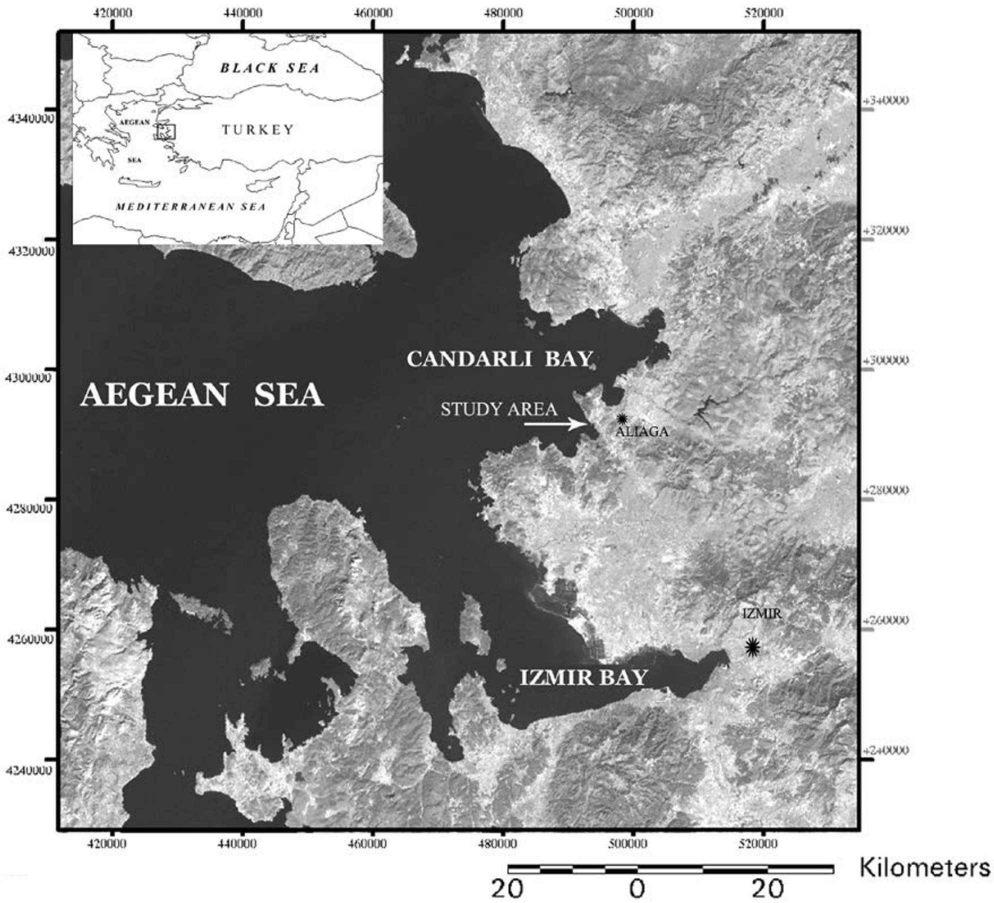

Figure 1. Location of the study area in Mediterranean. Nemrut Bay is the inner part of the Çandarlı Bay along Turkish coast in Aegean Sea.

2. MATERIALS & METHODS

Marine surveys were carried out by Research/Survey Vessel (RV) Koca Piri Reis in three cruises (February 25-28, July 3-5, September 29, 2005). Oceanographic data were collected by Seabird CTD (Conductivity/Temperature/Depth) instrument through water column in each of the fixed 15 stations (Figure 2). The stations - except station 15 - were located in a 1 km^2 surface area whereas station 15 was fixed as a reference point to represent the offshore conditions.

Physical properties were measured at all three cruises. Nutrients and dissolved oxygen were measured at February and July whereas dissolved metal sampling were carried out at February and September campaigns.

The samples were collected by Niskin bottles at three depths (surface, middle, and bottom) and were preserved in suitable conditions for chemical analysis and brought to the laboratory of Institute of Marine Sciences and Technology (IMST). Dissolved Oxygen (DO) was recorded in situ by the Winkler (1988) procedure.

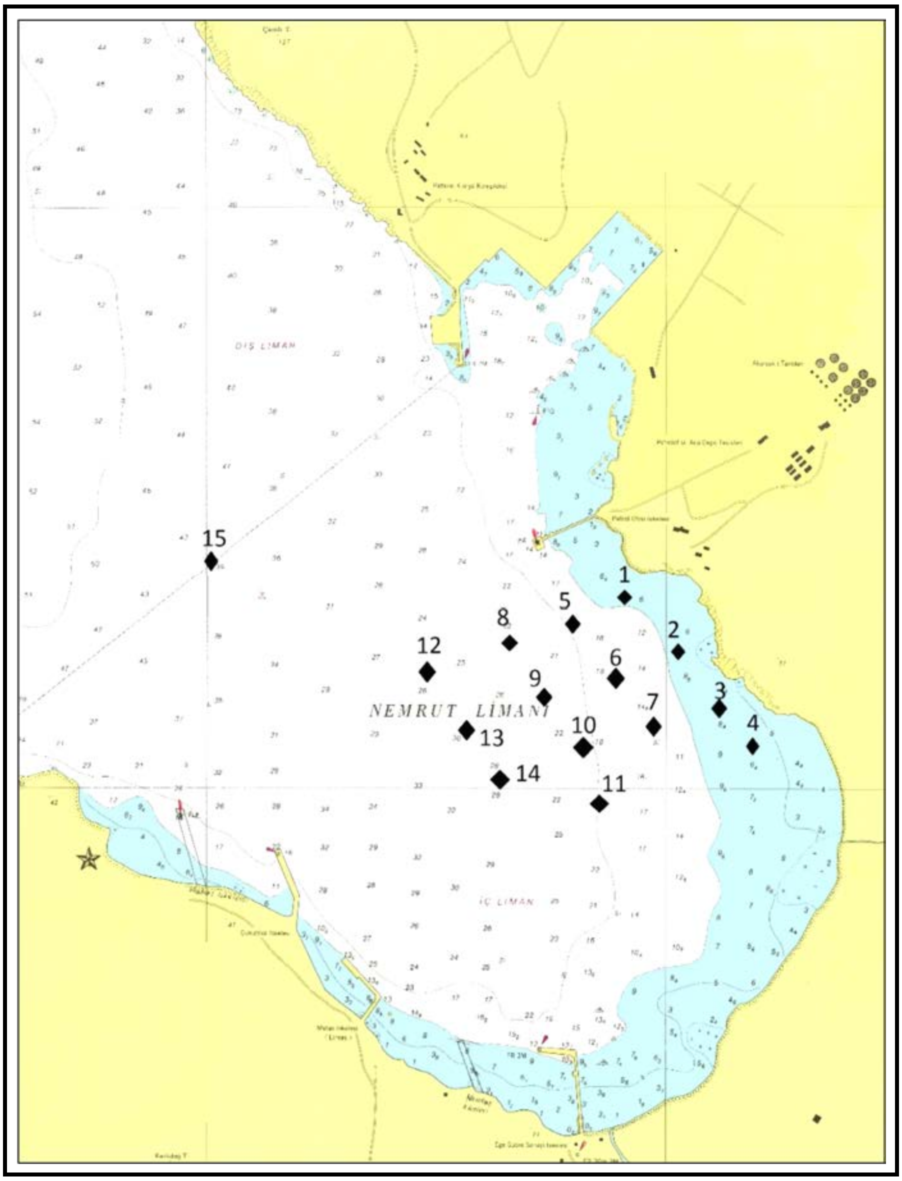

Figure 2. Location of water quality sampling stations in Nemrut Bay which are defined in order to assess the baseline status of the potential discharge area.

Analyses have been carried out according to the methods presented in (APHA, AWWA, WEF, 1980; Grasshoff et al., 1983; Stricland and Parsons, 1972). Dissolved nutrients i.e., nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and phosphate (PO_4^{3-}), measurements were carried out in Spectrophotometer (Philips) and Autoanalyzer (Skalar-5100). The Particulate Phosphorus (TPP) and Total Dissolved Phosphorus (TDP) samples were processed and measured according to the method proposed by (Solórzano and Sharp, 1980); and Total Organic Carbon (TOC) measurements were carried out by "APHA 5310 B Total Organic Carbon, High Combustion Method" (APHA, AWWA, WEF, 1999). Regarding the measurement of dissolved trace metal ions (Hg, Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe, Mg), for enrichment Chelex-100 chelator (Bio-Rad; 200-400 mesh size: 74-37 µm) were used which contained a styrene-divinylbenzene copolymer chelating exchanger having iminodiacetate functional groups. After sampled water passed through the Chelex-100 column, a mixture of 0.6 M UP HCl and 0.2 M UP HNO_3 was added to the columns in 5 ml portions for the elution of metals. The concentration of eluted metals was determined using pyro-coated graphite furnace atomic absorption spectrophotometry (by using Varian AA 300/400, flammable, graphite furnace and cold vapor techniques). Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON) contents were analyzed at CHN analyzer (Karl et al., 1991). Analyses of Chl-a were carried out by the fluorometric methods after filtering of samples on to glass fiber filters (Whatman GF/F) and then extraction in acetone.

The nutrient ratios were obtained by linear regression analysis. Trophic index (TRIX) was used to characterize the trophic state of coastal marine waters of Nemrut Bay. A simple method of coastal water integrated assessment using TRIX has been proposed by (Vollenweider et al., 1998) and is based on measurements of Chl-a, oxygen saturation, total nitrogen and total phosphorus. It provides useful metrics for the assessment of trophic status of coastal waters. TRIX, as a multi-metric index, offers the advantage of utilizing routinely collected and directly measured environmental variables, which make information comparable over a wide range of trophic states. In this study, TRIX was tested by applying to data sets from coastal waters with different water quality status: Eutrophic, Mesotrophic and Oligotrophic on the eastern part of Aegean Sea.

In order to determine spatio-temporal distribution of TRIX values for the study area the equation proposed by Vollenweider et al., (1998) was used:

$$TRIX=(\log_{10} [Chl\text{-}a \times DO\% \times DIN \times TP] + k) / m \quad (1)$$

where;

i) Chl-a (μg/l) and DO% (oxygen as absolute % deviation from saturation), as indicators of direct/real primary productivity.

ii) DIN (μg/l-Dissolved inorganic nitrogen (NO_3+NO_2+NH_4) and TP (μg/l-Total Phosphorus), as indicators of potential primary productivity.

The parameters k=1.5 and m=1.2 are scale coefficients, introduced to fix the lower limit value of the Index and the extension of the related Trophic Scale, from 0 to 10 TRIX units. According to (UNEP, 2007), the reference values for TRIX represent corresponding trophic states and related coastal water quality conditions (Table 1), described by (Mazziotti, 2013).

Table 1. Reference values for TRIX represent corresponding trophic states and related coastal water quality conditions (UNEP, 2007; Mazziotti, 2013).

TRIX	Trophic Status	Water Quality Conditions
<4	**Elevated**	• Scarcely productive waters. • Good water transparency. • Absence of anomalous water colours. • Absence of Oxygen undersaturation in the bottom waters.
4-5	**Good**	• Moderately productive waters. • Occasionally water turbidity. • Occasionally anomalous water colors. • Occasionally bottom waters hypoxia episodes.
5-6	**Mediocre**	• Very productive waters. • Low water transparency. • Frequently anomalous waters colors. • Hypoxia and occasionally anoxia episodes in the bottom layers. • Suffering of the benthic communities.
>6	**Bad**	• Strongly productive waters. • High water turbidity. • Diffuse and persistent anomaly in the water colors. • Diffuse and persistent hypoxia/anoxia episodes in the bottom waters. • High mortality rate of benthic organisms. • Alteration of the benthic communities and strong decrease of the biodiversity

3. RESULTS & DISCUSSION

February sampling represented the typical winter conditions. The water column was well-mixed due to the cold weather and strong winds. In July, sea surface temperature increased, stratification was developed and depth of thermocline was observed at about 20 m. In September, the stratification was fully developed as the thermocline was observed at around 25-30 m. Seasonal stratification results from solar warming of the surface waters of Nemrut Bay as there is no dominant freshwater input.

Dissolved oxygen values for July sampling varied between 6.29-7.20 mg l^{-1} that were found to be lower than the values measured for February sampling (7.50-8.28 mg l^{-1}) as expected. Oxygen depletion occurs primarily during the summer. No anoxic (<0.2 mg/l O_2) or hypoxic (<2.0 mg/l O_2) conditions were determined at any of the stations during the surveys.

The upper limits of the parameters that are used in determination of different trophic states specific to Aegean and Mediterranean seas have been provided in Surface Water Quality Management Directive, 2012 of Turkish Ministry of Environment and Urbanization (TMEU) and presented on Table 2 for evaluation of the Nemrut Bay's biogeochemistry.

Table 2. Eutrophication Criteria for the Transition and Coastal Waters for Aegean and Mediterranean Seas (TMEU, 2012)

	DIN (µM)	**TP (µM)**	**Chl a (µg l^{-1})**
Oligotrophic	<1.42	<0.32	<0.4
Mesotrophic	1.42-7.11	0.32-0.65	0.4-2
Eutrophic	7.11-14.21	0.65-0.97	>2-4
Hypereutrophic	>14.21	>0.97	>4

The NO_3^- , NO_2^- and NH_4^+ concentrations (i.e., DIN) of Nemrut Bay as presented in Table 3, were at eutrophic range in February (0.47-13.09 µM) and at mesotrophic range in July (0.30-2.28 µM) according to criteria provided for Aegean and Mediterranean coastal waters (Balkıs, 2009; Redfield, 1958). PO_4^{3-} concentrations of February samples were measured in the range of 0.01-4.56 µM where they varied from 0.03 µM to 0.09 µM in July samples.

The TRIX values were calculated only for February due to lack of summer TP measurements. The calculated TRIX values representing February varied between 2.66 (Station 7) and 5.14 (Station 2). Three water quality categories (excellent, good and mediocre) were distinguished (Table 1).

Table 3. Maximum and Minimum Concentrations of Nutrients, Dissolved Oxygen and Chlorophyll-a of the seawater samples of Nemrut Bay

Parameter	**Unit**	**February 2005**	**July 2005**
P-PO$_4$	µM	4.56-0.01	0.09-0.03
DOP	µM	2.91-0.03	
PP	µM	0.26-0.04	0.10-0.03
DP	µM	5.41-1.20	
TP	µM	5.55-1.30	
POC	µM	25.56-4.35	8.68-0.09
DOC	µM	255-68	938-43
TOC	µM	267-77	946-42
PON	µM	5.72-1.37	2.72-0.01
N-NO$_3$	µM	2.90-0.10	0.60-0.09
N-NO$_2$	µM	0.29-0.10	0.08-0.01
N-NH$_4$	µM	9.90-0.27	1.60-0.20
Chl-a	µg l^{-1}	0.24-0.07	0.15-0.01
DO	mg l^{-1}	8.28-7.50	7.01-6.29

The relative concentrations of N and P have been used to estimate which of these nutrients is limiting the growth of algae in aquatic systems since the observation of Redfield (1958) that marine phytoplankton contains a molecular C:N:P ratio of 106:16:1 (50:7:1 by weight) (Ekholm, 2008). The nutrient ratios were obtained by linear regression analysis and presented in Table 4. The significant correlations were shown as bold and highlighted as grey. NO_3^-:PO_4^{3-} ratios were calculated as 0.7:1 for February and 3.7:1 for July samplings.

Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON) and Particulate Phosphorus (PP) values decreased in July about 3-5 times compared to February. POC values were below the detection limits in mid-depth and benthic waters in July. POC:PON:PP ratios were calculated as about 3:14:1 for February and about 2:9:1 for July samplings. The percentages of POC over TOC were determined within the range of about 4%-26% for February and 0.05%-18% for July. Carbon to Chlorophyll (C:Chl-a) ratio is calculated as 82 for July that has been decreased approximately 9 times when compared to the ratio of February. Average values of suspended material (TSS) vary from 0.52 mg l^{-1} to 3.50 mg l^{-1} for February and from 0.20 mg l^{-1} to 3.47 mg l^{-1} for July.

Table 4: Nutrient Ratios for Nemrut Bay

February Nutrient Ratios	**Correlation Coefficient, r**	**Significance, p**	**Sample Size, n**
POC = 10.6355 + 0.0529xPON	0.0165	0.9325	29
POC = 11.0374 - 1.7454xPP	-0.0252	0.8967	29
PON = 2.9768 - 3.2115xPP	-0.1490	0.4405	29
NO_3 = 0.1041 + 0.6534x PO_4	0.9355	**0.0000**	27
July Nutrient Ratios	**Correlation Coefficient, r**	**Significance, p**	**Sample Size, n**
POC = -0.8597 + 3.0379xPON	0.9202	**0.0002**	10
POC = -1.6336 + 46.2795xPP	0.4459	0.1965	10
PON = 0.1458 + 8.8769xPP	0.2824	0.4293	10
NO_3 = 0.1744 + 1.4175xPO_4	0.1482	0.6828	10

The heavy metal content of the water column has been determined for February and September (Table 5) samples for: Hg, Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe, Mg. Hg.

The maximum and minimum concentrations of the measured heavy metals were below the critical values given by USEPA (2014) and Turkish Legislation (TMEU, 2004; TMEU, 2005). The concentrations of Hg, Cd, Zn, Fe and Mg with regard to water column were lower than the typical sea water levels while Pb, Cr, Cu, Ni and Mn were higher.

Table 5. Average, Maximum and Minimum Concentrations of Heavy Metals in Water Column of Nemrut Bay

	Hg µg/l	**Cd µg/l**	**Pb µg/l**	**Cr µg/l**	**Cu µg/l**	**Zn mg/l**	**Mn mg/l**	**Ni mg/l**	**Fe mg/l**	**Mg mg/l**
Avg	0.005	0.002	1.502	0.167	0.986	0.003	0.001	0.003	0.003	1475
Max.	0.018	0.003	2.800	0.280	3.100	0.009	0.004	0.005	0.009	1504
Min	0.001	0.001	0.790	0.100	0.260	0.002	0.001	0.002	0.001	1402
Abundance[1]	0.03	0.11	0.03	0.05	3.0	0.010	0.002	0.002	0.01	1350
EPA[2]	0.94-1.8	8.8-40	8.1-210	100	3.1-4.8	0.058-0.19	0.002	0.0082-0.074	-	-
WPCD[3]	0.4	10	100	100	10	0.10	-	0.1	-	-
CPCDSAED[4]	0.3	0.25	100	100	10	0.003	-	0.1	0.7	-

[1] [Horne, 1969]
[2] [USEPA, 2014]
[3] [TMEU, 2004]
[4] [TMEU, 2005]

Classification of the trophic status of seawater is usually based on levels of algal biomass and/or nutrients and other related physical and chemical parameters. There is no permanent freshwater input to the Nemrut Bay's hydrography to support nutrient delivery thus enhance biological productivity. The nutrient loads coming to Nemrut Bay have been dominated by stormwater runoff in the wet season and air emissions. The nutrient levels could be classified as eutrophic along stations closer to the shoreline and oligotrophic for offshore waters with respect to the definitions in (Ignatiades, 2005) where the limits defined for Chl-a indicated that Nemrut Bay's water was oligotrophic for the sampling period (Ignatiades, 2005; TMEU, 2012). C:Chl-a ratio is below the ratio given for eutrophic waters (150-500).

The theoretical residence times of water in Nemrut Bay were provided as a result of a modeling study presented in Esen et al. (2011), revealing that the system flush nutrients very rapidlysuch that phytoplankton might not have the opportunity to bloom extensively in such short residence times (4 - 5 days at maximum).

Among nutrient ratios calculated, only February NO_3^- and PO_4^{3-} data and July POC and PON data were significantly correlated. The others had high variances. The high variation in the ratios indicated that the inputs to the Bay that were due to allochthonous sources (coming to the site from different pathways) have been varying in quite a wide range depending on the meteorological conditions and the coastal uses.

The NO_3^-:PO_4^{3-} ratio (several times smaller than the Redfield ratio, N:P=16:1) suggested that phytoplankton production was potentially nitrate limited. In winter season the decrease in primary production caused less consumption thus high values of nutrients in February were determined as expected. The high concentrations found in the inner stations might be related to anthropogenic organic-rich sources associated with re-mineralization processes as also stated in Lopes et al. (2007). Possible nutrient uptake would explain the lower concentrations of nutrients during summer. In summer season the primary production were again at low level where the nutrients might already depleted after spring bloom period. Maximum concentrations for nitrate occurred in winter, coinciding with the winter rains flushing nitrate from the catchment. Minimum nutrient concentrations occur in summer as land based runoff that transport nutrients is negligible during the hot season.

Particulate matter results showed that the TOC load in Nemrut Bay increases due to degradation of phytoplankton and other microorganisms already available in the system. The relevance of the autotrophic component to the particulate matter pool was defined by POC:Chl-a ratio (Fabiano, et al., 1999). The relatively high POC:Chl-a ratio in February (756:1) indicated that the carbon is associated with the heterotrophic and detrital component. The POC:Chl-a ratio for summer campaign (82:1) showed the enhancement of autotrophic fraction as well as the decrease in the grazing activities.

From the TRIX values it was apparent that the mediocre states occurred mainly in the stations closer to the shoreline which had a potential to exhibit eutrophic states mainly due to urbanization related pressures, e.g., industrial outfalls during spring and summer periods.

Heavy metals such as Zn, Fe and Cu, are essential biological micronutrients required for the growth of many aquatic organisms. These micronutrients can become toxic at high concentrations where other metals, for example Pb and Cd, are not required for growth and are highly toxic in trace amounts (Beltrame et al., 2009). The concentrations of Pb, Cr, Mn and Ni were higher than the abundances given in literature where these metals, especially Ni, have been used in metal plating industry. Copper is an abundant trace element found in the earth's crust and is also a naturally occurring element that is generally present in surface waters where mining, leather products, fabricated metal products, and electric equipment are a few of the industries with copper-bearing discharges that contribute to anthropogenic inputs of Cu to surface waters (USEPA, 2014). The maximum concentration of Cu in Nemrut Bay was measured as 3.1 µg l^{-1} which corresponds to the critical value provided by USEPA (2014) for estimates of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. Trace metals did not show strong seasonal variations. Gavriil and Angelidis (2005) analyzed various dissolved metals in Kalloni Bay, Lesvos (Aegean Sea). Cd concentrations were reported up to 0.02 µg l^{-1}, Cu as 0.55 µg l^{-1}, Ni as 1.5 µg l^{-1}, Pb as 3.1 µg l^{-1} and Zn as 4.0 µg l^{-1}. Ayas et al. (2009) reported minimum and maximum dissolved Cd, Cr and Pb in Mersin Bay as 0.14-0.16 µg l^{-1}, 2.00-3.19 µg l^{-1}, 12.73-15.79 µg l^{-1} respectively. The dissolved heavy metal concentrations of Nemrut Bay were lower than those results except of Cu's.

The heavy metal content of the sediments in Nemrut Bay has been studied by Esen et al. (2008). Contamination factors (CF) and Metal Enrichment Factors (EF) have been calculated. When CF<1, there is no metal enrichment by natural or anthropogenic inputs; 1≤CF<3 for a particular metal means that the sediment is moderately contaminated by the element; 3≤CF<6 means that there is considerable contamination and if CF>6 then there is very high contamination for that metal (Hokanson, 1980; Pekey et al., 2004). 0.5 ≤ EF ≤1.5, it suggests that the trace metals may be entirely from crustal materials or natural weathering processes. EF>1.5, it suggests that a significant portion of trace metals are provided by other sources (Zhang et al., 2007). Pb and As had very high contamination levels where there were considerable Zn contamination in most of the sediment samples [39]. Hg concentrations corresponded to very high contamination and the elevated enrichment levels of Pb (2.03-16.06) and Zn (1.08-8.52) indicated anthropogenic pollution (Esen et al., 2008).

4. CONCLUSIONS

Design of environmental baseline assessment program prior to any coastal development is the crucial part of the feasibility studies. There are no prescriptive approaches fitting to every civil work such as marine outfalls due to the complexity of the coastal dynamics where each case has its unique properties. Environmental measures which are required for the protection of marine ecosystem have also to be met for permitting the marine discharge. The background biogeochemical condition of the Nemrut Bay's water column was set to assess the impact of a proposed industrial discharge. The biogeochemical properties of the water column in Nemrut Bay showed that the anthropogenic influence is mostly detected in stations closer to the shoreline. The Nemrut Bay is of quite a low level of pollution when the impacts of high intensity of industrial and maritime activities in Çandarlı Bay are considered. It is likely that efficient flushing and effect of prevailing northerly winds restricts impacts with sediment structure and composition only along the shallow shoreline band revealing an advantage for a deep sea wastewater disposal due to the high assimilation capacity of the Bay. Meanwhile, any change in these physical conditions, i.e., climatic or meteorological oscillations, can rapidly reduce this assimilation capacity. A risk assessment on this possibility seems necessary for a proper impact assessment studies. Direct discharges of domestic and industrial wastewaters to the coastal zone of Aegean Sea are an important concern thus any new/additional pollutant source have to be monitored cautiously.

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