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Impacts of recent eutrophication and deoxygenation on the sediment biogeochemistry in the Sea of Marmara

İsmail Akçay[1,2], Süleyman Tuğrul[1], Hasan Örek[1], Devrim Tezcan[1], Koray Özhan[1], Barış Salihoğlu[1], Mustafa Yücel[1]

[1]Middle East Technical University, Institute of Marine Sciences, P.O. Box 28, 33731 Erdemli-Mersin, Türkiye
[2]Mersin University-Faculty of Fisheries, Yenişehir-Mersin, Türkiye

Correspondence to: İsmail Akçay (iakcay@mersin.edu.tr)

Abstract. The biogeochemistry of seafloor sediments can be significantly altered in response to deoxygenation and eutrophication-driven organic carbon production, resulting in increased benthic fluxes of dissolved nutrients (such as ammonia and phosphate) and metals. The Sea of Marmara, which also have faced large-scale mucilage outbreaks in recent years, is undergoing severe eutrophication and deoxygenation but the consequences on sediment biogeochemistry and benthic feedback have not been studied so far. This study aims to understand the impacts of deoxygenation and coastal eutrophication on sedimentary biogeochemical processes in the Marmara Sea, which experiences varying degrees of anthropogenic pressure along with natural inputs from the adjacent Black Sea via Bosphorus surface inflows. Multicore-obtained undisturbed sediment core samples indicate that oxic respiration no longer plays a significant role in Marmara sediments but denitrification, metal reduction and sulfate respiration are prevalent. The deep-water sediments become more reducing in the Eastern Marmara, for instance cores from İzmit Bay reveal important biogeochemical processes such as anaerobic oxidation of methane (AOM), carbonate precipitation, iron reduction, and low-temperature silicate diagenesis. Furthermore, sediment total organic carbon concentrations in core samples were observed to be nearly twice those in less productive sites with oxic bottom waters, indicating a refractive particulate organic matter fraction in the buried sediments. Calculated diffusive benthic nutrient fluxes show markedly high phosphate and ammonium fluxes into the near-bottom waters of highly eutrophic areas of the Eastern Marmara, which are expected to enhance primary production in the upper halocline during the dry season. On the other hand, these sediments are a sink for nitrate, indicating denitrification and removal of fixed nitrogen. This trend contributes to the accumulation of organic matter as well as shifting N/P ratios and the development of a steep hypoxic zone at halocline boundary depths. As a result, we show that sediments are already influenced by the widespread hypoxia in the Sea of Marmara and benthic-pelagic coupling have started exacerbated the existing eutrophication problem, analogous to the benthic ‘vicious cycle’ observed in the shallower Baltic Sea. We conclude that the Sea of Marmara Sea is now on a clear path towards being included within the list of famous ‘dead zones’ of the Earth oceans, such as the Baltic Sea, Gulf of Mexico or Chesapeake Bay. In order to reverse the ecosystem degradation complex predictive models and decision support tools are needed to guide decision-makers, but they should take into account hypoxia-induced benthic biogeochemical processes and benthic-pelagic coupled cycling of nutrients in the Sea of Marmara.

1. Introduction

The Sea of Marmara is a key connecting basin between the Black Sea and the Mediterranean, but it is in a state of ecosystem decline. Increasing eutrophication and decreasing deep-water oxygen levels, exacerbated by recent large-scale mucilage outbreaks (Yücel et al. 2021, Savun-Hekimoglu and Gazioglu 2021) have the common cause of excessive nutrient levels in the system. Despite this trend, only few studies were performed to understand seawater nutrient cycling and organic matter dynamics (Tuğrul and Morkoç, 1989; Tugrul and Polat, 1995; Polat and Tugrul, 1995; Polat et al., 1998; Tuğrul et al., 2002; Ediger et al., 2016; Yalçın et al., 2017). The connection between benthic fluxes and eutrophication has received little attention, with most studies on sedimentary biogeochemical processes focused on the effect of the tectonics (Le Pichon et al. 2001; Géli et al., 2008), and gas-induced porewater geochemistry (Evans et al., 1989; Halbach et al., 2002; Çağatay et al., 2004; Sarı and Çağatay, 2010; Tryon et al., 2010; Ruffine et al., 2018; Yang et al., 2018). Here, we present the first process-based study performed in the Sea of Marmara to understand the impacts of eutrophication and the rapid deoxygenation on the sediment porewater nutrient dynamics and solid state geochemistry in the context of the coupled biogeochemical cycling of key nutrients (N, P) coupled to oxygen and metal (Fe, Mn) cycles (Williams, 1987; Jørgensen, 1996).

The Sea of Marmara, a two-layer enclosed sea, connects the Black Sea to the Mediterranean via the two shallow and narrow straits, called Istanbul (Bosporus) and Çanakkale (Dardanelles) Straits (Ünlüata et al. 1990; Beşiktepe et al. 1994; Ediger et al., 2016 and references therein). Marmara's two-layer ecosystem has distinct biogeochemical properties due to water exchanges between the Black Sea and the Mediterranean Sea (Polat, and Tugrul, 1995; Tugrul and Polat, 1995, Tugrul et al., 2002). Marmara Sea ecosystem has been highly influenced by the Black Sea inflow and municipal wastewater discharges in recent decades (Tuğrul and Morkoç, 1989; Tugrul and Polat, 1995; Ediger et al., 2016; Yalçın et al., 2017; Tan and Aslan, 2020). During 1970s, intensive development of eutrophication in the Northwestern Black Sea collapsed Black Sea ecosystem and fisheries (Mee, 1992; Tuğrul et al., 2014), leading to similar changes in the Sea of Marmara during 1980’s (Polat and Tugrul, 1995; Ediger et al., 2016; Yalçın et al., 2017). Marmara’s two-layer density gradient, established permanently between 10-30m depths, limits physical mixing (Beşiktepe et al. 1994), leading to limited exchange of dissolved nutrients and oxygen through the steep pycnocline (Tugrul et al., 2002; Ediger et al., 2016; Yalçın et al., 2017). As a result, dissolved oxygen (DO) concentrations, at near-saturation in the highly productive upper layer of Black Sea origin, decrease rapidly in the permanent steep pycnocline (15-20 m) coinciding with nutricline, allowing limited influx of oxygen to upper depths of sub-halocline waters. Thus, major oxygen source for the Sea of Marmara lower layer is the oxygen-rich Aegean inflow via Dardanelles undercurrent. This leads to a west-to-east decrease of the dissolved oxygen of the deep Marmara waters (Tugrul and Polat, 1995; Tugrul et al., 2002; Ediger et al., 2016; Yalçın et al., 2017). This oxygen deficiency has reached hypoxic (<2 mg/L, or <65 µM) to near anoxic (<0.5 mg/L, <10µM) levels in the deep basin (1200 m) of the eastern Marmara (Yücel et al., 2021; ÇŞİDB, ODTÜ-DBE, 2022; Yücel, M.-Tezcan, E. K. et al., 2023) and central part of the İzmit Bay (depth <150 m) due to increasing inputs of nutrients of different origin from Marmara basin, leading to development of eutrophication in the bays, coastal and open waters of Marmara Sea (Fig.1). Enhanced particulate organic matter (POM) export to the oxygen deficient

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lower layer waters has steadily consumed limited oxygen in the salt deep waters of the euthropic bays and the eastern Marmara basin as experienced in İzmit Bay and the vertical profiles of DO in the Çınarcık depressions since the late 1980's (Yücel, M.-Tezcan, E. K. et al., 2023). Long-term changes in biochemical properties of the two-layer Marmara Sea ecosystem are very likely to influence redox-dependent processes in the oxygen deficient deep waters and muddy sediments with the associated chemical properties (Ediger et al., 2016; Yalçın et al., 2017; Tan and Aslan, 2020).

As a result, Marmara is now a strong candidate to be included on the list of Earth's well-known hypoxic/dead zones such as Gulf of Mexico, Chesapeake Bay or the Baltic Sea; but the consequences of this phenomenon on various levels of ecosystem including sedimentary system, has been poorly tackled so far. Here, we aim to fill a significant gap via investigating the consequences of recent eutrophication and deoxygenation on the sediment biogeochemistry of the Sea of Marmara. The specific aims of this study are (i) to determine the impacts of eutrophication and development of hypoxic and anoxic conditions (deoxygenation) in the near bottom water on the porewater nutrient dynamics, (ii) to understand solid state organic matter (C, N) geochemistry and carbon burial, (iii) to describe early diagenetic processes in the porewaters and sediments and (iv) to determine the porewater diffusive nutrient (Si, N, P) fluxes in the three different regions of the Marmara Sea: İzmit Bay, Çınarcık Basin and the southern Marmara Sea.

2. Methodology

2.1. Study Area

Main physical and biogeochemical parameters were measured at 97 stations in the Marmara Sea (Fig. 1) in the winter and summer of 2019 by R/V Bilim-2 of METU-IMS. Sediment core samples were obtained with a multicorer (Octopus, Kiel) from 13 selected stations in the İzmit Bay, Çınarcık Basin and southern Marmara Sea. Core slices were used to measure porewater nutrients (PO_4, Si, NO_3+NO_2, NH_4), major ions (Cl, SO_4, Br, Li, Na, K, Mg, Ca), hydrogen sulfide (H_2S), dissolved iron (dFe), solid-state total carbon/organic carbon (TC/TOC) and nitrogen (TN) concentrations.

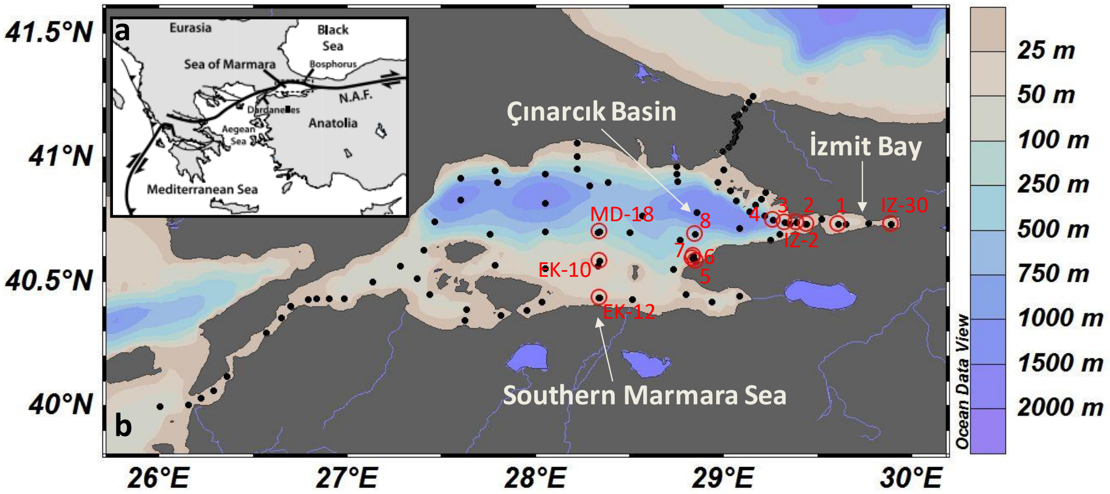

Figure 1: Marmara Sea with (a) the inset, showing the tectonic framework leading to the formation of three deep-basins (a; Tryon et al., 2010) and (b) main panel, outlining the water column sampling locations in winter and summer of 2019. Red circles represent sediment core stations.

2.2. Sampling and Analysis

The temperature and salinity of the water column were measured *in situ* by a SEABIRD 9plus CTD probe that is coupled to a 12-Niskin bottle Rosette System. The Secchi Disk Depth (SDD), an estimation of water transparency, was collected from each water column station (Fig. 1). In addition to the CTD sensor-derived measurements, dissolved oxygen measurements were also carried out by the Winkler titration method (UNEP/MAP, 2005). Total phosphorus concentrations were determined by the wet digestion methods and using the conventional colorimetric detection at 880 nm wavelength (Strickland and Parsons, 1972; Grasshoff et al., 1983) after persulfate oxidation of seawater samples (Menzel and Corwin, 1965). Water column and porewater dissolved inorganic nutrients (nitrate+nitrate, ammonium, phosphate and silicate) were measured using a Bran+Luebbe Model four-channel Autoanalyzer by standardized methods (Grasshoff et al., 1983). The detection limits of dissolved nutrients were 0.05 µM, 0.04 µM, 0.01 µM, 0.04 µM and 0.03 µM for nitrate+nitrite, ammonium, phosphate, silicate and total phosphorus, respectively. Chlorophyll-*a* (Chl-*a*) measurements were carried out by the conventional spectrofluorometric method after digestion of filtered samples by 90% (v/v) acetone solution using a HITACHI model F-2500 fluorescence spectrophotometer (Strickland and Parsons, 1972; UNEP/MAP, 2005). Hydrogen sulfide (H_2S/HS^-) concentrations in seawater and porewater samples were measured on board by the spectrophotometric methylene blue method at 670 nm wavelength (Cline, 1969). Porewater dissolved iron (sum of Fe^{2+} and Fe^{3+}) concentrations were measured on board by the spectrophotometry, after reducing all Fe(III) to Fe(II) by dithionite followed by ferrozine-based assay and detection of the color-producing Fe complex at 562 nm wavelength (Stookey, 1970; Jeitner, 2014).

Sediment core samples were obtained by a multiple-corer (Oktopus, Kiel). Each sediment core was sliced on board under anoxic conditions using N_2 or Ar gas. After obtaining sliced sediments, each sample was put in a 50 mL falcon tube and centrifuged at 6000 rpm for 20 minutes. Then, the porewater samples were extracted using syringe-coupled GF/F filters through 0.45 µm. Dissolved iron and hydrogen sulfide concentrations of porewater sub-samples were immediately determined on board by the methods mentioned above and the remained sub-samples were placed in 15 mL falcon tubes and stored at -20 ºC for the analysis of dissolved nutrients and major ions. Analyses of porewater nutrients were carried out by the same method as water column samples. Analysis of major ions (Cl, SO_4, Li, Na, K, Mg, Ca) in porewater samples were conducted by ion chromatography.

Solid phase sediment samples were also stored for the determination of TC, TOC and TN concentrations and surface sediment porosity measurements. Sediment samples for the TC, TOC and TN measurements were initially freeze-dried. Dry sediments were then powdered and sieved on 63 µm pore size for the homogenization of the samples. For TOC analysis, about 30 mg of dry and homogeneous sediment samples were put into the silver cups which had been pre-combusted at 400 ºC for 6 hours. Then, 10 µL of distilled water was added into each silver cup to wet the samples. After the addition of distilled water, 10 µL of 20 % HCl (v/v) was added to remove inorganic carbon from the sediment samples. The HCl additions were continued until all weak-acid soluble carbonates were removed. Then, the samples were dried at 60-70 ºC for 24 hours. After drying the sediment samples, silver cups were compacted and put into autosampler of the CHN analyzer. TC and TN analyses in sediments were performed by the same method as for the TOC analysis, but without acid addition. TN concentrations were also determined on HCl-added sediment samples and there was no significant difference between HCl-treated and untreated samples indicating significant fraction of TN pool was in the organic nitrogen form. Therefore, TN concentrations of HCl-untreated sediment samples were reported in this study. Total carbon (TC), organic carbon (TOC) and nitrogen (TN) concentrations were determined by dry oxidation method using the Vario El Cube Elementar Model CHN Analyzer (UNEP/MAP, 2006). Porosity of wet sediments was determined by the displacement method as described by Mu et al. (2017).

2.3. Calculation of Diffusive Nutrients (Si, N, P) Fluxes

We have calculated the diffusive nutrient fluxes based on Fick's first law of diffusion (Cheng et al., 2014; Mu et al., 2017):

$$F = \phi D_s (dC/dz)$$

Where F corresponds to the diffusive flux across sediment-water interface, dC/dz to the concentration gradient of nutrients across sediment-water interface, ϕ to the porosity of sediment, D_s to the actual molecular diffusion coefficient corrected for the sediment tortuosity.

Ullman and Aller (1982) proposed an empirical formula related to the actual diffusion coefficient, D_s, and porosity, ϕ:

$$D_s = \phi D_0 \qquad (\phi < 0.7)$$

$$D_s = \phi^2 D_0 \qquad (\phi > 0.7)$$

where D_0 is the self-diffusion coefficient of ions at infinite dilution corrected by *in situ* temperature. For phosphate, nitrate, nitrite and ammonium, D_0 values were taken from Li and Gregory (1974) and for silicate, D_0 values were taken from Rebreanu et al. (2008) as 7.34x10^{-6} cm^2 s^{-1} for PO_4, 19.0x10^{-6} cm^2 s^{-1} for NO_3, 19.1x10^{-6} cm^2 s^{-1} for NO_2, 19.8x10^{-6} cm^2 s^{-1} for NH_4 and 11.7x10^{-6} cm^2 s^{-1} for Si at 25 ˚C, respectively.

3. Results and Discussion

3.1. General Oceanographic State of the Marmara Sea in 2019

We describe the general oceanography of the system based on the two expeditions performed in the Marmara Sea (including the Bosporus and Dardanelles straits) in the summer and winter periods of 2019 by R/V Bilim-2. Physical and chemical oceanographic properties of the two-layer Marmara Sea ecosystem are principally dominated by the brackish (S:17.0-17.5) Black Sea and the salty Aegean inflow (S:35-38) through the Dardanelles (Ünlüata et al., 1990; Beşiktepe et al., 1994; Polat and Tuğrul, 1995; Tuğrul and Polat, 1995; Polat et al., 1998; Tuğrul et al., 2002). Driven by the physical properties of the exchange flows, temperatures of the upper layer waters varied seasonally from 6.93-10.98 ˚C in winter to 19.06-26.17 ˚C in summer. The surface water salinity values increased from 17.29 in the Bosphorus exit to 29.40 in the entry to Dardanelles in winter (Table 1, Fig. 2). Water transparency increased from the East Marmara (SDD 4-5 m) towards Dardanelles (SDD 17-18m) in the summer months. The winter SDDs displayed less pronounced spatial variations, ranging between 4 and 11 m (Table 1). Lowest values were recorded in the Eastern Marmara, notably in the Çınarcık Basin and the İzmit Bay. The lower SDD values measured in the eastern Marmara Sea indicated the increasing effect of eutrophication eastwards in the sea (Fig. 2).

Altogether, our observations on the state of the Sea of Marmara as of 2019 is in line with the previous reports, and pointing out to the combined effect of brackish Black Sea inflow and land-based sources (Tuğrul and Morkoç, 1989; Polat and Tuğrul, 1995; Tuğrul and Polat, 1995; Polat et al., 1998; Ediger et al., 2016; Yalçın et al., 2017; Tan and Aslan, 2020). We have found that the brackish surface waters of Black Sea origin were relatively rich in NO_x (NO_x: NO_2+NO_3) and PO_4 concentrations in winter due to enhanced inputs of nutrients from lower layer by vertical mixing processes (Tuğrul et al., 2002; Ediger et al., 2016; Yalçın et al., 2017). Similar seasonal and regional variations were also recorded in the concentrations of NH_4 and reactive Si with the maximum values recorded at the Bosporus southern exit and eastern Marmara Sea; İzmit Bay and Çınarcık Basin (Fig. 2). The surface water chlorophyll-*a* (Chl-*a*) concentrations increased from western to eastern basin (Fig. 1) and from summer (0.01-1.81 µg/L) to winter (0.26-3.77 µg/L) due to enhanced inputs of inorganic nutrients from lower layer and Black Sea in winter (Tugrul and Polat, 1995). According to eutrophication assessment based on the Chl-*a* values (Simboura et al., 2005), trophic status of the eastern Marmara upper layer and bays were classified to have from “mesotrophic/moderate” to “dystrophic/bad” levels of ecological status in the Izmit Bay having hypoxic to anoxic waters in the halocline and bottom waters during summer months. Enhanced primary productivity (in terms of Chl-*a*) in the upper layer have led to development of eutrophication and hypoxia in the lower layer over the basin and development of anoxic conditions in deep waters of the eastern Marmara Sea and Izmit Bay (Fig. 2). In the Çınarcık Basin of eastern Marmara Sea (max depth 1270m), DO was entirely depleted and anoxia developed in the deep waters particularly below 750 m. Development of similar anoxic conditions were consistently observed in the central deep waters of the Izmit Bay in the last two decades due to enhanced nutrient inputs from terrestrial sources, leading to intense eutrophication and increased particulate organic matter inputs from the eutrophic surface waters. Limited DO inputs from the oxygen-depleted eastern Marmara deep waters remained insufficient for aerobic oxidation of POM, leading to denitrification and sulfate reduction processes and thus hydrogen sulfide accumulation in the bottom waters of the bay during summer months (Yücel et al., 2023).

Table 1: Summary of surface water physical and biogeochemical parameters in the Sea of Marmara in the winter and summer of 2019

Winter	Temperature (˚C)	Salinity	TP (µM)	PO_4 (µM)	NO_x (µM)	NH_4 (µM)	Si (µM)	DO (µM)	Chl-*a* (µg/L)	SDD (m)
Mean	8.80	24.15	0.48	0.19	2.19	1.11	5.56	296.3	1.24	8.2
Std. Dev.	1.28	4.39	0.23	0.18	2.55	1.46	4.10	31.6	0.79	1.8
Min.	6.93	17.96	0.16	0.02	0.09	0.15	0.85	195.3	0.26	4.0
Max.	10.98	28.83	1.11	0.72	9.97	8.84	16.19	344.4	3.77	11.0
N	39	39	39	39	39	39	39	39	39	12

Summer	Temperature (˚C)	Salinity	TP (µM)	PO_4 (µM)	NO_x (µM)	NH_4 (µM)	Si (µM)	DO (µM)	Chl-*a* (µg/L)	SDD (m)
Mean	24.27	23.00	0.53	0.14	0.92	0.30	1.54	235.0	0.23	11.9
Std. Dev.	1.37	2.73	0.46	0.40	2.16	0.10	1.26	9.7	0.24	2.9
Min.	19.06	17.29	0.14	0.02	0.05	0.02	0.20	188.1	0.01	4.5
Max.	26.17	29.40	3.45	3.27	9.28	0.64	7.08	254.1	1.81	17.5
N	84	84	84	84	84	84	84	84	84	45

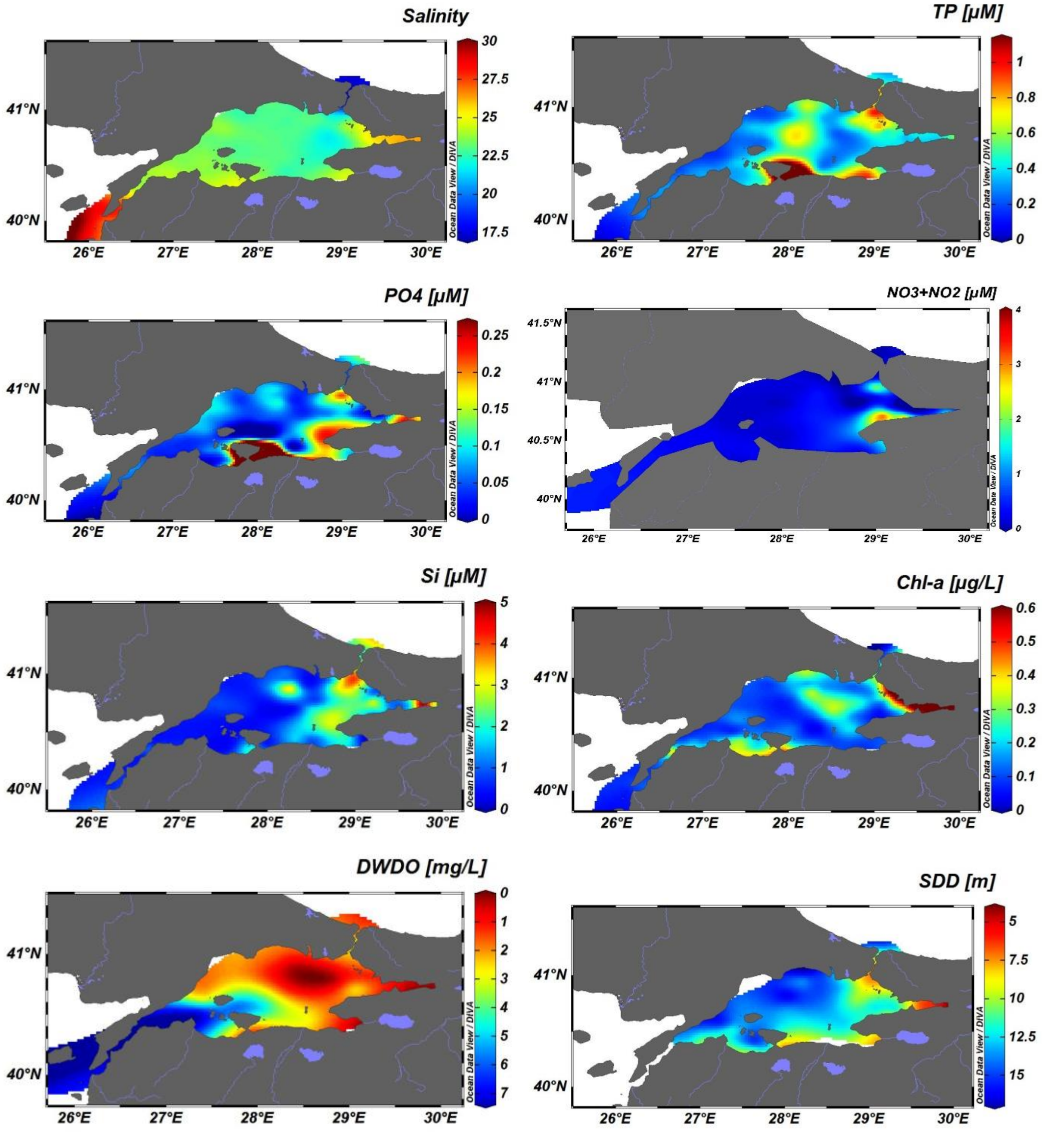

Figure 2: Distributions of surface water salinity, dissolved nutrients, secchi disk depth (SDD) and deep (near-bottom) water dissolved oxygen content (DWDO) in the Sea of Marmara in the summer of 2019.

3.2. Nutrient Trends in the Deep Water Column and Sediment Porewaters.

A comparison of averages of data from >1000m water depth in the Çınarcık Basin indicated an accumulation of reactive Si and PO_4 but consumption of NO_x (via denitrification) in the oxygen-depleted deep waters of Marmara (Fig. 3, more comprehensive analysis of historical trends is in progress, Yücel et al. in prep.). These findings clearly indicate enhanced inputs of POM from the highly productive layer to the lower layer during at least the last three decades, indicating more POM of planktonic origin buried in sediment phase.

Considering the apparent long-term changes in the nutrient and organic matter cycles in the oxygen-depleted deep-waters (Fig. 3), in this study, sediment core samples were obtained from the selected stations to determine the impacts of eutrophication and deoxygenation on the porewater nutrient dynamics and on the sediment organic matter (C, N) geochemistry of the Marmara Sea. Sediment core samples were obtained from three key regions in the Marmara: the highly eutrophic İzmit Bay, eutrophic Çınarcık Basin displaying permanently anoxic properties in the deep waters, and from the mesotrophic/eutrophic southern Marmara Sea shelf with still-oxygen rich bottom waters. The bottom water physical and biogeochemical variables of the core stations presented in Table 2 and also surface water spatial variability of the parameters (Fig. 2) indicated that the selected regions displayed significantly different physico-chemical and biogeochemical properties, allowing the discerning of redox- and organic matter-driven effects on sediment biogeochemistry.

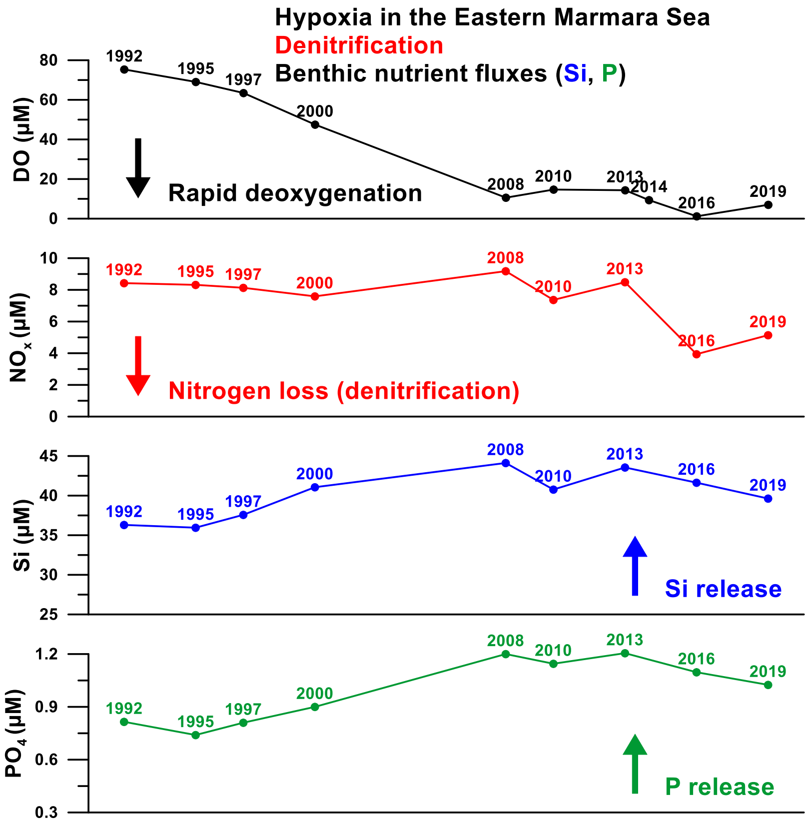

Figure 3: Summary of the deep water (>1000 m, averages) biogeochemical shift in the Çınarcık Basin, eastern Marmara Sea (Yücel et al., 2021; ÇŞİDB, ODTÜ-DBE, 2022; Yücel, M.-Tezcan, E. K. et al., 2023).

Table 2: Bottom water physico-chemical properties of the sediment core stations

Region	Station	Date	Depth (m)	Temperature (˚C)	Salinity	TP (µM)	PO$_4$ (µM)	NO$_x$ (µM)	Si (µM)	NH$_4$ (µM)	DO (µM)
İzmit Bay	IZ-30	05.01.2019	29	15.88	38.63	0.99	0.96	8.44	20.35	0.78	54.1
	1	24.07.2019	63	15.41	38.72	1.15	1.06	9.45	21.39	0.54	45.6
	2	24.07.2019	111	15.27	38.77	1.76	1.03	10.32	23.08	0.43	35.9
	IZ-2	05.01.2019	157	15.63	38.76	1.34	1.13	8.34	26.75	1.18	30.3
	3	24.07.2019	238	14.56	38.71	1.52	1.04	7.66	33.34	0.40	7.8
	4	24.07.2019	425	14.46	38.70	1.28	0.85	5.42	26.12	0.28	10.3
Çınarcık Basin	5	25.07.2019	98	15.32	38.80	0.95	0.85	9.06	20.79	0.22	57.5
	6	25.07.2019	190	14.73	38.73		0.97	9.62	31.02	0.36	17.2
	7	25.07.2019	288	14.51	38.70		1.06	8.32	35.69	0.17	7.2
	8	25.07.2019	407	14.47	38.70		1.29	7.00	40.02	0.24	6.3
Southern Marmara	EK-12	06.01.2019	45	16.22	38.68	0.53	0.40	4.31	8.65	0.47	164.1
	EK-10	06.01.2019	56	15.80	38.84	0.78	0.66	6.49	15.69	0.56	118.4
	MD-18	06.01.2019	145	15.24	38.80	1.09	0.69	6.49	17.21	0.19	51.6

Porewater nutrient concentrations throughout the obtained sediment core samples ranged between 0.47 and 58.2 µM for PO$_4$, 0.34 and 91.5 µM for NO$_3$, 0.17 to 666 µM for NH$_4$ and 9.02 to 335 µM for Si, respectively (Fig. 4). Biogeochemical cycling of key nutrients (N, P) is highly linked to dissolved oxygen concentrations and metal (Mn, Fe) cycles due to rapid degradation of labile organic matter by the redox-processes as denitrification, manganese and iron reduction as well as sulfate reduction and methanogenesis in the uppermost centimeters of sediment column resulting in nutrient releases from the sediments (Williams, 1987; Christensen et al., 1988; Jørgensen, 1996; Ignatieva, 1999; Rasheed, 2004; Al-Rousan et al., 2004; Hille et al., 2005; Rasheed et al., 2006; Rydin et al., 2011; Cheng et al., 2014; Mu et al., 2017). Expectedly, maximum porewater PO$_4$, NH$_4$ and Si concentrations were measured in the highly eutrophic (dystrophic) İzmit Bay (Fig. 4) with the vertical profiles of nutrients displaying an increasing trend with depth throughout the POM-enriched muddy sediment. Porewater NO$_3$ concentrations were highest in the porewaters of core samples (0-5 cm) from the southern Marmara Sea having oxic conditions in the deep waters and lower surface water primary productivity (in terms of Chl-*a*) (Fig. 2). Vertical profiles of porewater NO$_3$ concentrations in the studied sites suggested that denitrification process dominates the uppermost millimeters of oxygen-consumed sediment core samples obtained from the İzmit Bay and Çınarcık Basin whilst oxic respiration was the major process for the organic matter remineralization in the upper 15-20 cm of sediment cores obtained in southern Marmara Sea.

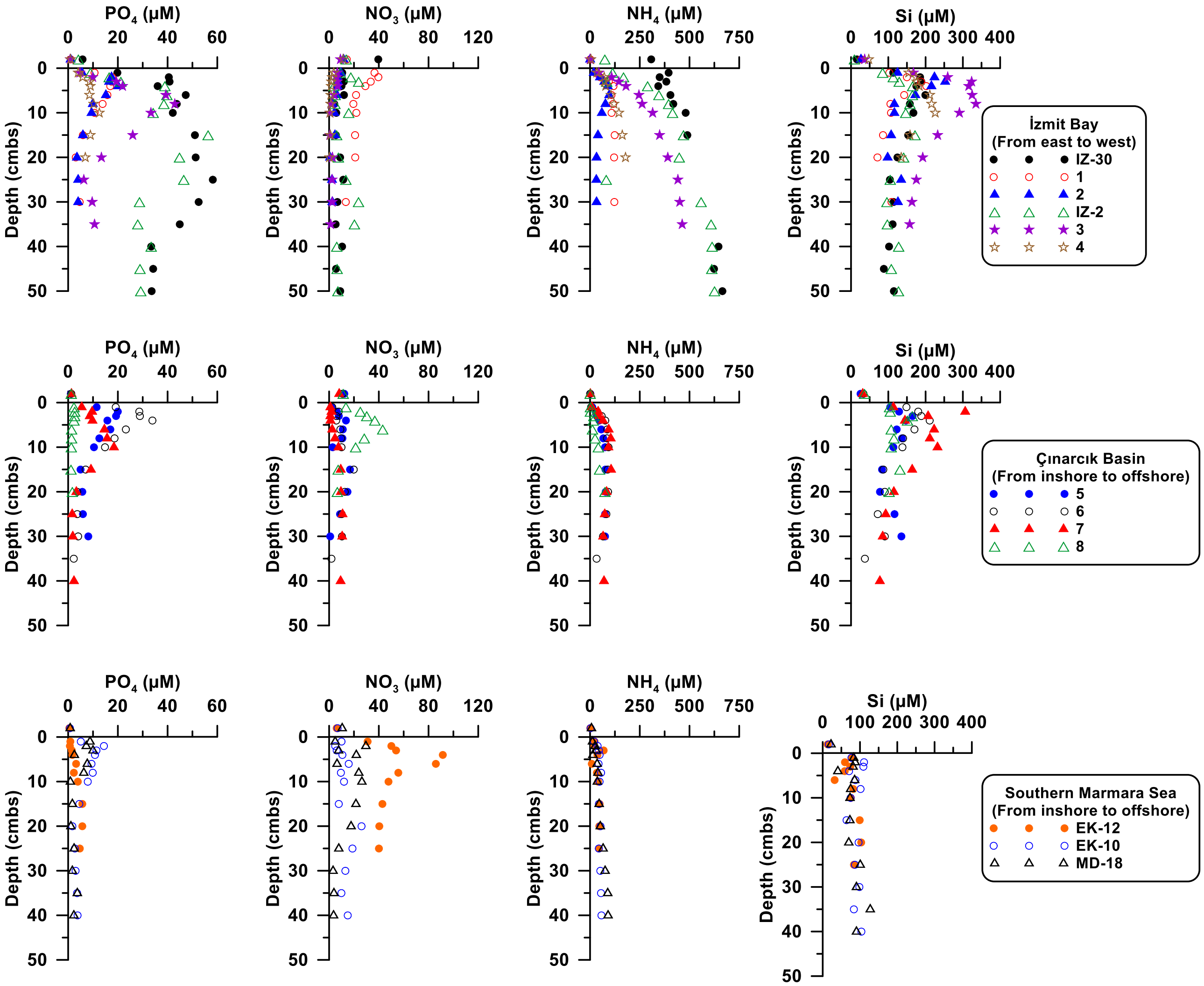

Figure 4: Porewater nutrient concentrations in the sediment cores from the Marmara Sea.

In order to understand the impacts of eutrophication and rapid deoxygenation on the porewater nutrient fluxes from the sediment of Marmara Sea, diffusive nutrient fluxes across the sediment-water interface were calculated based on Fick's first law of diffusion for the southern Marmara Sea, Çınarcık Basin and İzmit Bay having different deep water redox states from oxic to anoxic/sulfidic (Table 3). Calculated porewater diffusive fluxes showed spatial variability in the Sea of Marmara. In the all sites, sediments act as a source for PO$_4$, NH$_4$ and Si, whilst sediments in the highly eutrophic and anoxic/sulfidic sites of the İzmit Bay act as a sink for NO$_x$ (referred to NO$_3$+NO$_2$) due to rapid utilization of NO$_3$ ion as a terminal electron acceptor by denitrification process. Porewater diffusive PO$_4$, NH$_4$ and Si fluxes were highest in the İzmit Bay having eutrophic to dystrophic status with the anoxic bottom waters whereas the lowest diffusive NO$_x$ fluxes were calculated for the oxygen-deficient inner bay sediments due to NO$_x$ loss by denitrification. Porewater diffusive PO$_4$, NH$_4$ and Si fluxes decreased in the

Çınarcık basin, with the the lowest fluxes calculated for the oxic shelf sediments of the southern Marmara Sea, where the highest porewater diffusive NO_x fluxes to the bottom water were obtained (Table 3). The increase in diffusive fluxes of dissolved inorganic nutrients (PO_4, NH_4, Si), reactive iron and manganese in the organic-rich muddy shelf sediments of in the eutrophic and suboxic/anoxic/sulfidic shelf sediments are likely to lead to nutrient accumulation in bottom waters (Konovalov et al., 2007; Noffke et al., 2012; Mu et al., 2017) and contribute to the upper layer chemical fluxes through vertical mixing in across the basin, intensifying in winter period.

The correlation between calculated diffusive nutrient fluxes and the deep water dissolved oxygen concentrations clearly indicated the redox-dependent benthic nutrient dynamics in the Marmara Sea (Fig. 5); the lower deep water dissolved oxygen concentrations resulted the higher porewater diffusive PO_4, NH_4 and Si fluxes in the POM–rich muddy sediments. The apparent denitrification in sediment pore waters must have contributed to the apparent deep-water nitrate loss signal in the Çınarcık Basin during the last decades (Fig. 3). Furthermore, the annual regional diffusive nutrient fluxes also in the anoxic benthic interface of the highly productive NE shelf region of the Marmara Sea and eutrophic inner Izmit bay might further enhance eutrophication in the NE Marmara shelf and bays by vertical mixing processes increasing markedly in winter (Table 3). The Si/N and N/P molar ratios of the measured nutrients in the shelf and deep basin waters of Marmara Sea ranged between 1.8 and 5.5 for Si/N and 5.6-12 for N/P, respectively. The Si/N molar ratios of the diffusive nutrient fluxes (Si/N: 1.0-5.5) were similar to the ratios in deep waters of the studied sites whereas the N/P molar ratios of diffusive nutrient fluxes (8.4-31) were greater than deep water nutrient (N/P) molar composition; but comparable with the N/P molar ratios calculated in the diffusive nutrient fluxes in the Baltic Sea (N/P: 20-30) (Ignatieva, 1999; Van Helmond et al., 2020).

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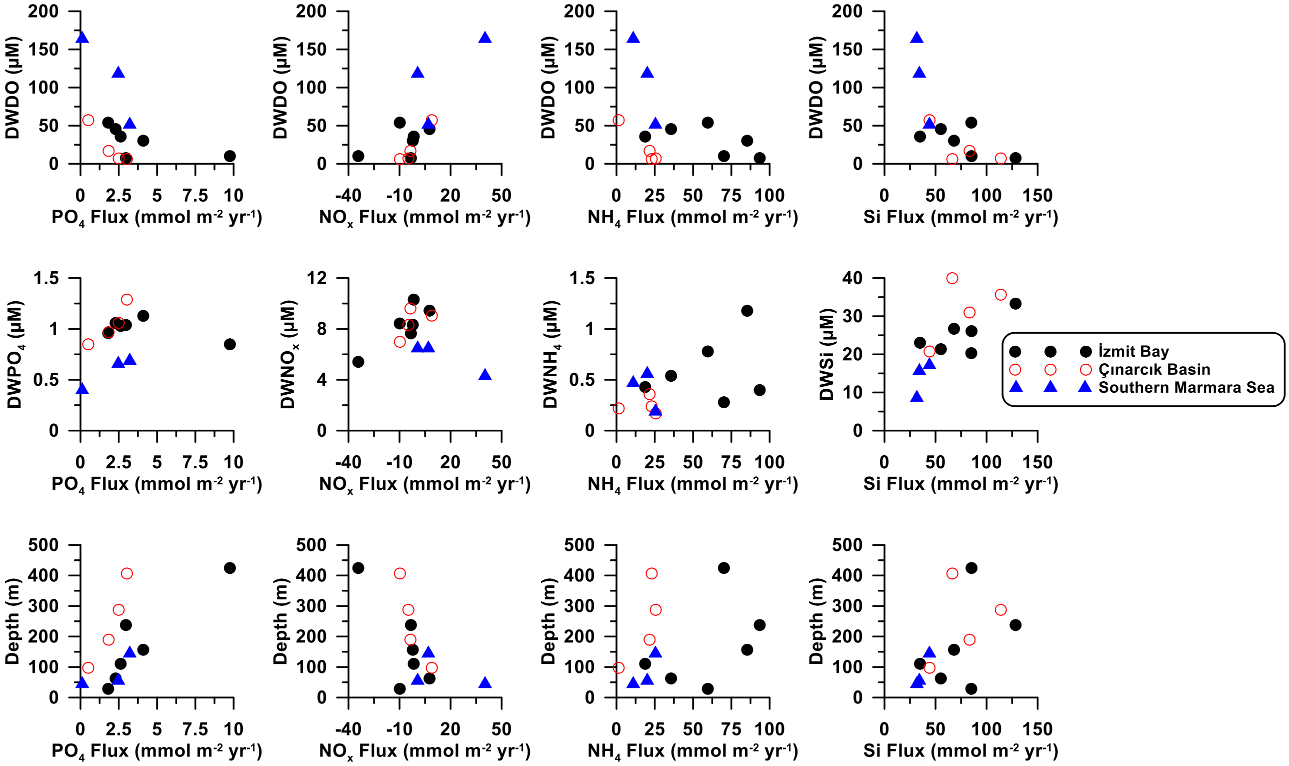

Figure 5: Relationship between calculated diffusive nutrient fluxes and deep-water concentrations of dissolved oxygen and nutrients in the Marmara Sea. A flux with a positive sign indicated that sediment acts a source of that particular constituent whereas a negative sign indicated that sediment acts as a sink.

Table 3: Diffusive nutrient fluxes estimated from the porewater profiles of different regions having distinct trophic and redox states

Region	Trophic Status	Deep Water Redox State	PO4 (mmol m^{-2} yr^{-1})	NOx (mmol m^{-2} yr^{-1})	NH4 (mmol m^{-2} yr^{-1})	Si (mmol m^{-2} yr^{-1})
İzmit Bay[1]	Eutrophic to Dystrophic	Suboxic/Anoxic/Sulfidic	1.81-9.76	-34.2-7.65	18.7-93.5	34.8-128.4
Çınarcık Basin[1]	Eutrophic	Suboxic/Anoxic	0.51-3.03	-9.78-8.98	1.45-25.6	44.1-114
Southern Marmara[1]	Mesotrophic to Eutrophic	Oxic	0.11-3.22	0.65-40.2	10.93-25.4	31.7-44.0
Eastern Mediterranean[2]	Oligotrophic	Oxic	0.60	4.14	6.79	34.51
Red Sea[3]	Oligotrophic	Oxic	1.28	6.32	2.08	20.04
Peruvian OMZ[4]	Eutrophic to Dystrophic	Suboxic/Anoxic	2.3-227.6			
Baltic Sea[5]	Eutrophic to Dystrophic	Suboxic/Anoxic/Sulfidic	0.47-67.82		15.64-1441.23	
Çınarcık Basin[6]	Mesotrophic to Eutrophic	Suboxic	0.60		2.04	

[1]This study; [2]Christensen et al., 1988; [3]Rasheed et al., 2006; [4]Noffke et al., 2012; [5]Ignatieva, 1999; [6]Çağatay et al., 2004

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3.3. Sediment Organic Matter Geochemistry

Close examination of the core samples clearly showed undisturbed accumulations of particulates in the upper 40-50 cm of sediment as experienced in the previous lithological studies performed in the Çınarcık Basin and southern Marmara Sea (Çağatay et al., 2004), and in the İzmit Bay (Sarı and Çağatay, 2010). Solid-state total carbon (TC), total organic carbon (TOC) and total nitrogen (TN) concentrations in sediment cores from different regions of the Marmara Sea displayed spatial variability (Fig. 6). TC concentrations ranged regionally between 1.97 and 4.12 mmol/g dw (dry weight) in the upper 3 cm of the obtained core samples decreased to 0.92-3.25 mmol/g dw levels below 30 cmbs (Fig. 6). Maximum concentrations of TOC and TN were determined in the surface sediments from the İzmit Bay where anoxic/sulfidic conditions have developed in the deep waters (Fig. 6). TOC values were in the range of 0.47 - 2.70 mmol/g dw whilst TN values varied between 0.04 and 0.23 mmol/g dw. The apparent decrease in the TOC and TN concentrations with the increasing depth throughout the sediment column indicated organic matter deposition exceeding the decomposition in the top 8-20 cm of the sediment column. Below this depth, TOC and TN concentrations were relatively constant and did not change noticeably, suggesting the dominancy of refractory organic matter below 20 cmbs buried in the anoxic sediments. The Çınarcık and İzmit bey bottom sediments had higher TOC levels, in line with their more reducing deep-water conditions, also in agreement with the previous studies (Evans et al., 1989; Çağatay et al., 2004; Sarı and Çağatay, 2010; Ruffine et al., 2018; Yang et al., 2018; Tan and Aslan, 2020). Maximum TOC and TN concentrations were detected in the surface sediments of the İzmit Bay with highly eutrophic conditions due to excess anthropogenic inputs from point and diffusive sources as reported previously (Tuğrul and Morkoç, 1989; Yalçın et al., 2017; Tan and Aslan, 2020). Our results further shows that the development of anoxic conditions in the bottom waters has led to increase in the accumulation rates of the organic matter sedimented in the İzmit Bay, leading to organic matter degradation mainly by denitrification and sulfate reduction in bottom water and underlying sediments. Our results also reports for the first time the accumulation of H_2S (0.52 µM at 29 m) in the bottom waters of the inner bay (depth>150 m) in summer months, showing that the bottom waters have shifted to reducing conditions as a result of the general environmental degradation in the Sea of Marmara.

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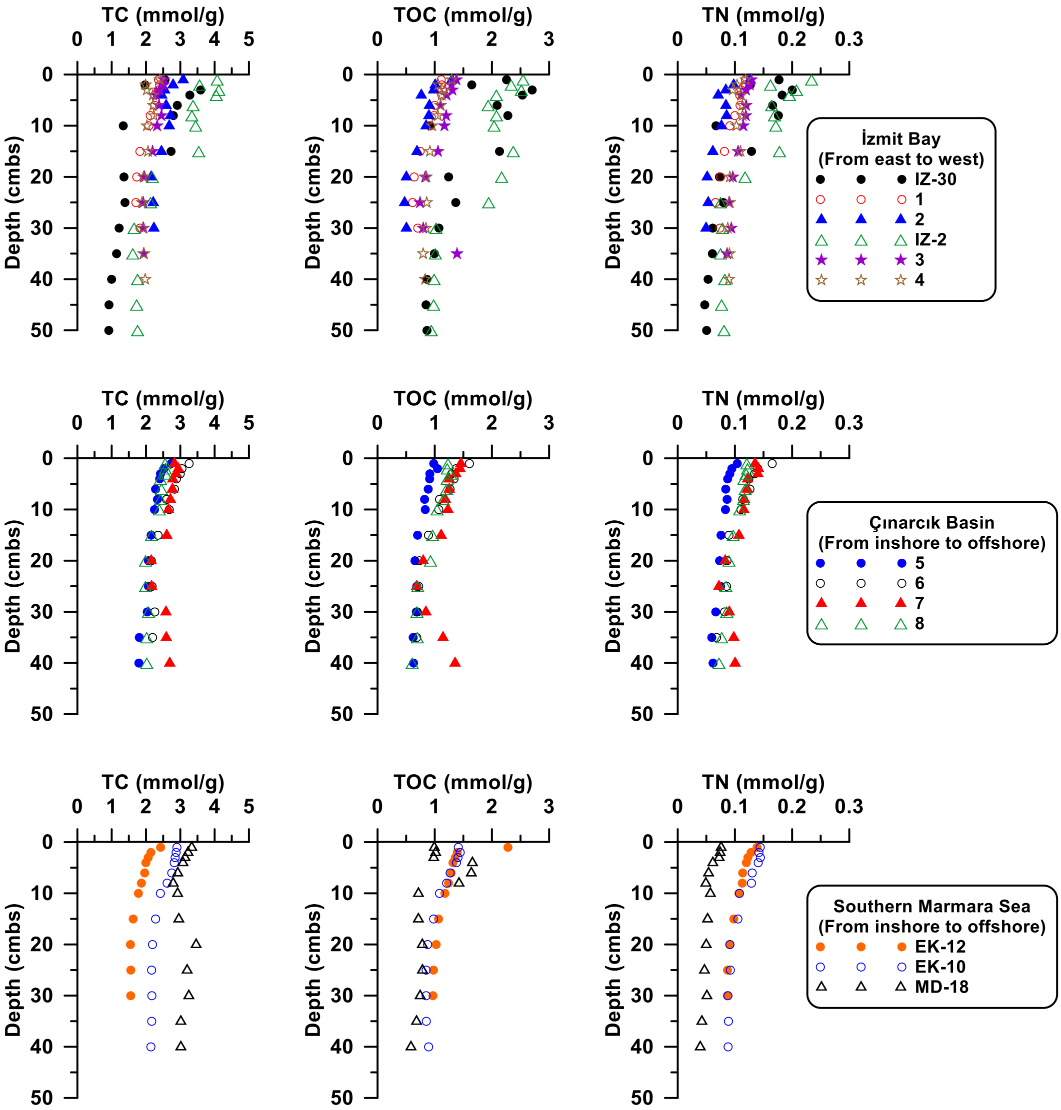

Figure 6: Vertical profiles of TC, TOC and TN in the sediment cores from the Marmara Sea.

The porewater and solid-state results altogether shows that maximum sediment TOC and TN concentrations (Fig. 6) in the İzmit Bay might further enhance eutrophication in the Marmara Sea, analogous to benthic 'vicious cycle' in the much shallower Baltic Sea due to release of increased amount of dissolved nutrients, biologically available for the phytoplankton. In the Çınarcık Basin, relatively lower concentrations of TC, TOC and TN were measured compared to eastern İzmit Bay, but comparable to those measured in the western İzmit Bay having similar deep-water physical and biogeochemical properties (Table 2), indicating redox-dependency on the benthic organic matter dynamics. In the southern Marmara Sea, however, lowest levels of TOC and TN were measured though TC concentrations were comparable with the İzmit Bay and Çınarcık Basin. The lower primary productivity (in terms of Chl-*a*) and also lower sedimentation rate (Çağatay et al., 2004) in the southern Marmara Sea resulted in low organic matter accumulation at the sediment and the higher deep water DO concentrations (Fig. 2, Table 2) prevented the release of reactive phosphate, silicate and ammonium fluxes from the surface sediments. Therefore, development of eutrophication and deep-water hypoxia/anoxia in the Çınarcık Basin and İzmit Bay caused to accumulation of excess amount of organic matter in the upper sediment column highly enhancing the release of dissolved nutrients whereas in the oxic southern Marmara Sea, lower sediment organic matter (C, N) concentrations resulted in lower porewater nutrients concentrations and their diffusive fluxes due to high concentrations of deep water dissolved oxygen.

3.4. Sedimentary Early Diagenetic Processes in the Marmara Sea

In order to complement the above-described solid state and porewater parameters, we further describe and discuss in this section additional parameters that enables us to present a fuller picture of the early diagenetic processes in the Marmara Sea. Concentrations of Cl, SO_4, H_2S, Li, Na, K, Mg, Ca and dFe in porewaters of the collected core samples were determined. Although the measured concentrations of the selected ions exhibited minimal spatial variability within the study region, they demonstrated significant variations with depth (Fig. 7). The ranges of the measured concentrations throughout the sediment column were 326-747 mM for Cl, 0.84-32.6 mM for SO_4, 1.6-3204 µM for H_2S, 8.64-31.7 µM for Li, 313-614 mM for Na, 9.2-15.2 mM for K, 43.9-77 mM for Mg, 3.3-15.8 mM for Ca and 0.2-31.8 µM for dFe, respectively (Fig. 7), similar to previous studies (Çağatay et al., 2004; Tryon et al., 2010; Ruffine et al., 2018). The variations in the porewater concentrations of dissolved nutrients (Fig. 4) and major ions (Fig. 7) throughout the sediment column were affected by a series of microbially mediated diagenetic reactions modifying geochemical composition of the porewaters in the studied sites. It was shown that there is a freshening gradient of major ions (specifically Cl and Na) in the Marmara Sea sediment porewaters due to mixing with the buried brackish water from the ancient 'Marmara Lake' which was observed at all sites in the Marmara Sea with the exception of Western High. This freshening was more pronounced below 250-300 cmbs in the Marmara Sea (Tryon et al., 2010). Relatively low concentrations of major ions, specifically Cl and Na, measured in the porewaters of the obtained core samples in this study and vertical profiles of these ions throughout the sediment column also indicated a downcore freshening in the Sea of Marmara (Fig. 7).

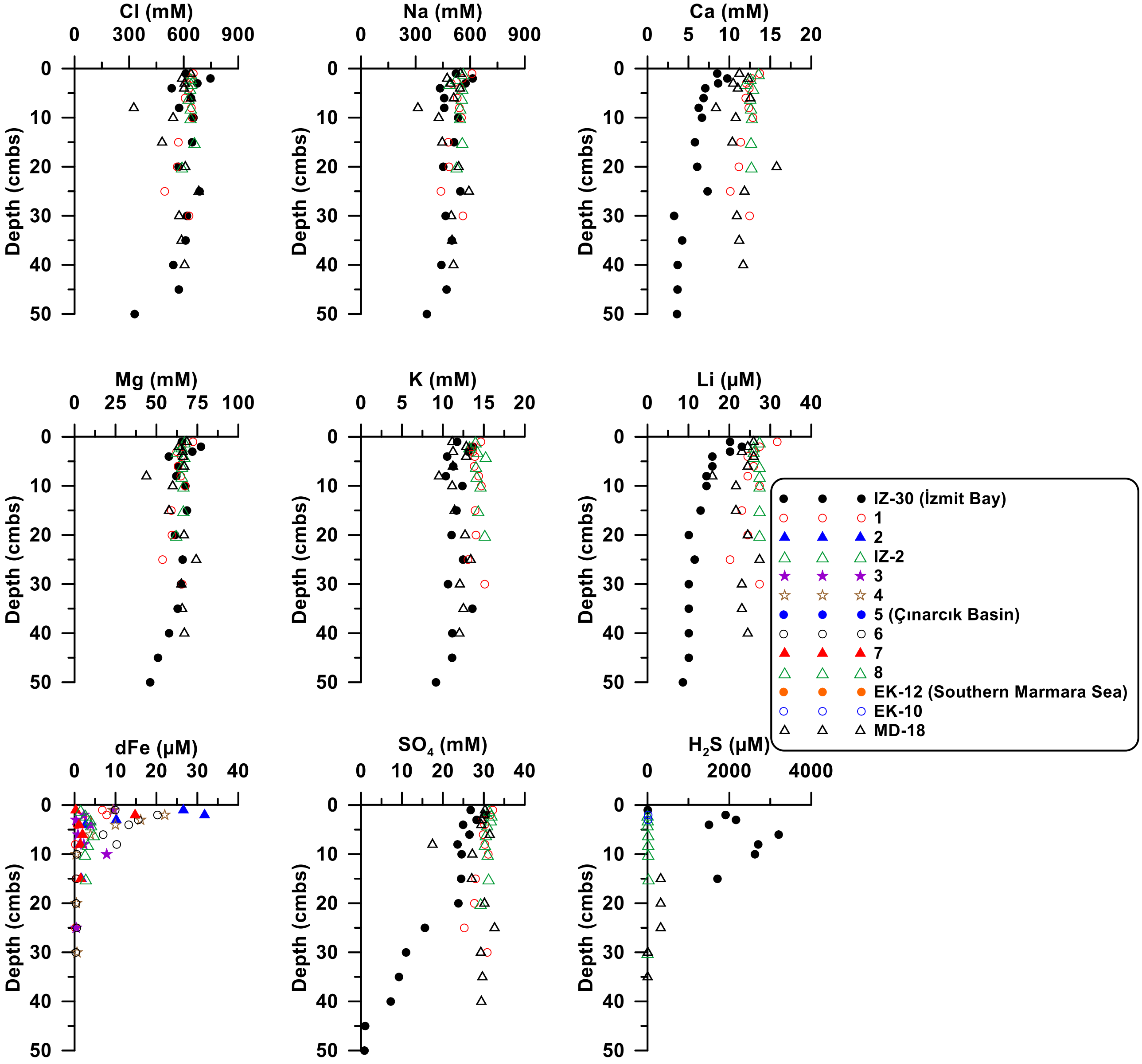

Figure 7: Vertical profiles of Cl, Na, Ca, Mg, K, Li, dFe, SO_4 and H_2S in the sediment porewaters from the obtained core samples in the Marmara Sea.

The series of microbially mediated diagenetic reactions were mainly from the result of organic matter degradation by NO_3 (denitrification), Fe/Mn oxides and SO_4, as well as the processes of the SO_4 depletion by anaerobic oxidation of methane (AOM). Carbonate precipitation and the silicate diagenesis also shaped porewater profiles. Vertical profiles of porewater nutrients (Fig. 4) and solid-state TOC/TN (Fig. 6) concentrations indicated that organic matter degradation processes take place in the upper 10-20 cmbs, introducing high concentrations of porewater reactive Si, PO_4 and NH_4 and removing oxidized nitrogen (NO_3) called denitrification. The decrease in SO_4 concentrations with depth in the sediments was due to sulfate reduction as well as the AOM, releasing H_2S, Mg and Ca in the eastern İzmit Bay. The release of Mg and Ca, then, resulted in carbonate precipitation reactions reducing the porewater concentrations of these ions with depth throughout the sediment column in the eastern İzmit Bay (Fig. 7). Similar chemical composition and diagenetic reactions in the porewaters in different regions of the Marmara Sea have been observed by the studies performed by Halbach et al. (2002), Çağatay et al. (2004), Tryon et al. (2010), Ruffine et al. (2018) and the strong correlation between gas emissions and fast depletion of sulfate in the upper sedimentary column of the Marmara Sea suggested the important role of AOM for preventing complete releases of methane originating from the N.A.F. and associated faults (Géli et al. 2008, Ruffine et al., 2018). The porewater geochemistry of the obtained core samples from this study and previous studies in different regions of the Sea of Marmara (mainly Çınarcık, Central and Tekirdağ Basins, southern Marmara Sea, İzmit Bay) revealed that the sulfate-depletion zone, corresponding to the sulfate-methane transition zone (SMTZ), shifted from a few meters in 1999 to less than 15 centimeters below seafloor in 2014. The observed SMTZ was recorded a few meters below seafloor in the Marmara Sea by the studies in which scientific expeditions were performed before 2010 (Halbach et al., 2004; Çağatay et al., 2004; Tryon et al., 2010), the shallower SMTZ, from less than 15 to 40 centimeters below seafloor, were reported in a recent study carried by Ruffine et al. (2018) when the core samples were collected in 2014. The findings of this study also showed a shallower SMTZ, less than 50 cm, in the eastern İzmit Bay (Fig. 7) due to increase in AOM reaction rates by intense emissions of methane resulting in fast depletion of sulfate in the upper sedimentary column (Ruffine et al., 2018). It should be also noted that the techniques and equipments to obtain core samples were distinct for each study performed in the Marmara Sea. Gravity core samples were used in the studies of Halbach et al. (2002) and Çağatay et al. (2004), piston core samples were obtained by Tryon et al. (2010), ROV-assisted push core samples were obtained by the study of Ruffine et al. (2018) and the core samples were taken in this study using by multiple corer (Oktopus, Kiel), respectively. All these discrepancies of sampling operations might also cause different profiles of porewater geochemistry in the Marmara Sea, but the porewater geochemistry from the results of this study and previous studies showed that there was an apparent upward shift in the SMTZ.

Organic matter degradation by the Fe/Mn oxides released the reduced forms of these metals into the sediment porewaters (Jørgensen, 1996). Though the dissolved manganese was not measured in this study, previous studies performed in the oxic, suboxic and anoxic regions showed that anoxic conditions support accumulation of dissolved manganese whereas oxic sediments become depleted in manganese (Jørgensen, 1996). In the oxic region of the Black Sea, for example, redox transformations and physical processes caused to redistribution of manganese from its initial sources across the bottom waters and leading to accumulation of manganese in oxidized form in the upper sedimentary column (Konovalov et al., 2007). A similar process was observed with the relative depletion of reduced iron in sediments in the Southern Marmara Sea having oxic deep waters and its accumulation in the sediments under hypoxic conditions in the Çınarcık and İzmit Bay as also experienced in the oxic, suboxic and anoxic marine environments (Jørgensen, 1996; Konovalov et al., 2007; Yücel et al., 2010) (Fig. 7). According to a study performed in the sediment cores obtained from oxic, suboxic, anoxic/sulfidic parts of the Black Sea (Konovalov et al., 2007), FeS production is faster than pyrite reacting with zerovalent sulfur or H_2S to form FeS_2. If the

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Fe(III) is available in the sulfidic sediments, Fe(III) reacts with the H_2S to form Fe(II) which in turn reacts with H_2S to form FeS phases. In the Marmara Sea, the obtained geochemical profiles indicated that the H_2S produced by AOM formed iron-sulfide precipitates in the presence of reduced iron (Halbach et al., 2002). In this study, dFe (referred to sum of Fe(II)+Fe(III)) concentrations ranged from 0.2 to 31.8 µM in the porewaters of the obtained sediment core samples displaying a maximum in the upper sedimentary column decreasing to undetectable values below 10-15 cmbs indicating iron-sulfur precipitation reactions as also experienced in the anoxic/sulfidic sediments of the Marmara Sea (Halbach et al., 2002) and Black Sea (Konovalov et al., 2007). The decrease in SO_4 concentrations with depth in the sediments was due to sulfate reduction as well as the AOM, releasing H_2S, Mg and Ca, specifically in the eastern İzmit Bay as discussed above. The release of Mg and Ca, then, results in carbonate precipitation reactions reducing the porewater concentrations of these ions with depth throughout the sediment column (Fig. 7). However, the release of Ca might also be the result of low-temperature silicate diagenetic processes as also shown in a recent study performed in the Marmara Sea (Tryon et al., 2010) since low-temperature silicate diagenetic processes depend not only on the availability of the silicate minerals but also available cations such as K, B, Li, Mg and Na. The end products of these diagenetic reactions, Ca and Sr, are released to the porewaters in the Marmara Sea (Tryon et al., 2010 and references therein). The downcore decreases in the concentrations of Mg, K, Na and Li obtained from this study were also associated with the low-temperature silicate diagenetic processes in the Marmara Sea.

4. Conclusions

Our results showed that the dynamics of porewater nutrients, redox-sensitive elements, major ions involved in the diagenetic processes and also solid-state geochemistry in the Marmara Sea have been influenced by eutrophication and bottom water hypoxia/anoxia. High concentrations of nutrients enhanced surface water primary productivity and hence increased the organic matter (C, N) concentrations accumulated at the sediment. Maximum porewater nutrients (Si, PO_4, NH_4) and sediment TOC and TN concentrations were measured in the anoxic and sulfidic İzmit Bay and Çınarcık Basin of the Marmara Sea having sedimentation rates ranging between 70 and 190 cm/1000 y (Ergin and Yörük, 1990; Ergin et al., 1994; Çağatay et al., 2004). In the southern Marmara Sea with the lower Chl-*a* concentrations in the surface waters and more oxygenated deep waters, relatively low concentrations of porewater nutrients and sediment organic matter were measured with moderately low sedimentation rate of 45 cm/1000 y (Çağatay et al., 2004). It should be also noted that the sediment organic matter degradation processes differed in the three distinct regions where denitrification and sulfate reduction were observed in the Çınarcık Basin and İzmit Bay whilst oxic respiration was the major process for the organic matter remineralization in the uppermost sedimentary column of the southern Marmara Sea characterizing the sediment of the corresponding regions as sink and source for nitrate/nitrite, respectively. Moreover, the distribution of porewater sulfate, hydrogen sulfide, and major elements throughout the sediment column obtained specifically from the İzmit Bay, suggested principal biogeochemical and early diagenetic processes such as anaerobic oxidation of methane (AOM), carbonate precipitation, Fe-reduction, Fe-S precipitation and low-temperature silicate diagenesis.

The dynamics of porewater nutrients, redox-sensitive elements, major ions involved in the diagenetic processes and also solid-state geochemistry in the Marmara Sea were found to be clearly influenced by eutrophication and the subsequent bottom water hypoxia/anoxia. Development of eutrophication and deep water suboxia/anoxia has been experienced in the Çınarcık Basin and İzmit Bay due to enhanced terrestrial pressures during the last several decades. Porewater nutrients (Si, N, P) results indicated that maximum concentrations of porewater reactive silicate, phosphate and ammonium were measured in the eutrophic and suboxic/anoxic İzmit Bay and Çınarcık Basin having higher primary production (in terms of chlorophyll-*a*) resulted in higher diffusive fluxes of nutrients to the deep waters. Lower porewater nutrients concentrations were recorded in the Southern Marmara Sea having lower primary production and more oxygenated deep waters. Porewater nitrate, sulfate and hydrogen sulfide concentrations showed that organic matter degradation processes in the upper 20-30 cmbs have occurred by denitrification and sulfate reduction whilst organic matter decomposition was limited by oxic respiration in the upper centimeters of sedimentary column in the southern Marmara Sea. The depth distributions of porewater measurements obtained specifically from the İzmit Bay core samples strongly suggested principal biogeochemical and early diagenetic processes such as anaerobic oxidation of methane (AOM), carbonate precipitation, Fe-reduction, Fe-S precipitation and low-temperature silicate diagenesis. The depth distribution of TOC concentrations in the sediment core samples and the calculated redox dependent benthic nutrient fluxes in the Marmara Sea indicate high rates of organic matter decomposition and limited trapping of nutrients in the benthic interface. The increased diffusive nutrient inputs especially in the shelf zone of the eastern basin in recent decades is expected to have further enhanced eutrophication in the Marmara Sea, analogous to benthic 'vicious cycle' in the much shallower Baltic Sea. The increased nitrate loss in the lower layer of deep basins and the higher rates of diffusive fluxes of phosphate, ammonium and reactive silicate in the shelf zones may affect the water column nutrients concentrations and thus their molar ratios. These changes naturally altered the ratios of nutrients reaching the upper layer by physical mixing in the Bosphorus junction and over the basin, leading to further ecological problems such as enhanced eutrophication, deep water anoxia, changes in phytoplankton abundance and composition, and mucilage formation recently observed in the Marmara Sea.

We conclude that if sufficient measures are not implemented the Sea of Marmara Sea is now on a clear path towards being included within the list of famous ‘dead zones’ of the Earth, such as the Baltic Sea, Gulf of Mexico or Chesapeake Bay. Predictive models and decision support tools are needed to guide decision-makers, but they should take into account the hypoxia-induced benthic biogeochemical processes as well as redox-dependent processes.

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