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Deposition of organic and inorganic carbons on the Turkish continental margins (1984–1996)

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Abstract: This study reevaluates the published total inorganic carbon (TIC) and total organic carbon (TOC) percentages of 695 seafloor sediment samples collected from the continental margins of the Black Sea, Sea of Marmara, Aegean Sea and Mediterranean Sea between 1984 and 1996. An inverse relationship is observed between the average TIC and TOC percentages in the four seas surrounding Türkiye. The explanation for this phenomenon is closely connected to the terrestrial, marine, climatic, and environmental factors of the continental margins from which the samples were collected.

Key words: Turkish Seas, organic carbon, inorganic carbon, sediments, continental margins

1. Introduction

Organic and inorganic matters are one of the most basic and important components of continental shelf sediments and can provide useful information for reconstructing past environmental changes (e.g., Meyers, 1997). It is important to monitor the temporal and spatial changes in total organic (TOC) and inorganic carbon (TIC) amounts in seafloor sediments to monitor the time-dependent changes of environmental factors. In Berner (1982), it is emphasized that to model the global carbon cycle, it is necessary to first understand the dynamics of the carbon cycle in productive environments. It has been emphasized that approximately 90% of TOC in marine environments is deposited (accumulated or conserved) along continental shelf sediments, while the remaining 10% is stored (accumulated or preserved) on the deep ocean floor. Therefore, it should be known that the most productive environments for TIC and TOC storage areas in marine environments are the continental margins.

The TIC and TOC content of the sediments on continental shelves is of both terrestrial and marine origins. In these areas, coastal riverine inputs and aerosol deposition are the main sources of terrestrial organic and inorganic inputs (Turner and Rabalais, 1991; Redalje et al., 1994; Hedges and Keil, 1995). On the other hand, the TIC content of marine sediments is closely related to the amount of carbonate minerals in biogenic and lithogenic forms in the sediment. The TOC content of marine sediments

depends on primary productivity, sedimentation rate, sediment grain size distribution, sediment composition, oxygen content of the water column, water depth, and input of terrestrial organic matter (Müller and Suess, 1979; Demaison and Moore, 1980; Thunell et al., 1984; Petersen and Calvert, 1990; Calvert et al., 1992). The TIC and TOC concentrations of sea floor sediments are used as reliable data to investigate changes in temperature and precipitation from past to present. An increase in the TIC concentration implies an increase in temperature whereas higher TOC concentrations reflect greater precipitation rates (Xiao et al., 2006).

In this study, the distribution characteristics of TIC and TOC parameters obtained from seafloor sediments sampled from the continental margins of Türkiye between 1984 and 1996 were compiled and processed in order to use them as background values in future studies for determining environmental changes.

2. Material methods

In this study, the published TOC, TIC, and TC data of 695 surficial sediment samples from the continental margin of Turkish Seas (Black Sea, Sea of Marmara, Aegean Sea and Mediterranean Sea) were compiled (Figure 1).

The samples were recovered by grab samplers on board the research vessels (RVs) Bilim, Lamas and Erdemli during various projects of the IMS-METU between 1984 and 1996. The results of the data obtained within the scope

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Figure 1. Map showing the distribution density of seafloor sediment samples along the continental margins of the Turkish Seas and coastal rivers.

of the projects carried out by IMS-METU, which were used in this study (IMS-METU, 1984; IMS-METU, 1985a, 1985b; IMS-METU, 1986), have been published in numerous international journals (Ediger, 1987; Bodur and Ergin, 1988; Alavi et al., 1989; Ergin and Yörük, 1990; Ergin et al., 1990; Ergin et al., 1991; Yücesoy and Ergin, 1992; Ergin et al., 1992; Ergin et al., 1993; Ergin et al., 1994; Bodur and Ergin, 1994; Ergin et al., 1996). The continental margin sediment data were analysed by dividing them into 22 different zones, taking into account their location, coastal geometry, oceanography, and data distribution patterns. The depth of the continental margins, ranging from 0 m to 500 m, was examined by dividing them into 50-m intervals (Figure 1). The TOC and TIC contents of the sediment samples were analysed in the IMS-METU geochemistry laboratory. TIC, represented as total carbonate weigh percentage, was determined using the gasometric method after treating the grounded dry bulk samples with a dilute (10%) HCI acid solution (Müller, 1967). Total inorganic carbon (TIC %) values were calculated based on the atomic weights (weight %) of each element in CaCO₂.

TOC measurements were conducted using the modified Walkley-Black method (Gaudette et al., 1974), which relies on the exothermic heating and oxidation of organic matter with potassium dichromate and sulphuric acid. Total carbon (TC) was calculated by summing the percentages of TIC and TOC values. The absolute precision for total carbonate and total organic carbon determinations was $\pm 0.5\%$ and $\pm 0.2\%$, respectively (Ergin et al., 1996).

2.1. Oceanographic setting of the Turkish Seas

Türkiye is surrounded by four distinct seas, each possessing unique atmospheric, oceanographic, and sedimentological characteristics. These seas are the Black Sea (BS), Sea of Marmara (SM), Aegean Sea (AS), and Mediterranean Sea (MS), from north to south (as depicted in Figure 1).

Located in northern Türkiye, the Black Sea is a semienclosed anoxic inland basin fed by several large rivers that carry significant amounts of nutrients and pollutants (Tugrul et al., 1992). The Black Sea is interconnected with the Sea of Marmara via the Bosphorus (İstanbul Strait) and is also linked to the Aegean Sea and Mediterranean Sea through the Dardanelles (Çanakkale Strait) (Murray et al., 1991). The high salinity seawater (38‰) of Mediterranean origin enters through the İstanbul Strait and partially ventilates the western Black Sea at intermediate and deeper depths (Ovchinnikov, 1984; Murray et al., 1991). The surface water salinity remains at approximately 18‰ due to the constant input of freshwater from coastal rivers. This causes a permanent and strong halocline that inhibits vertical mixing in the sea (Sorokin, 1983; Lyons et al., 1993; Oğuz et al., 2006). This permanent halocline renders the Black Sea a semienclosed marine basin with net estuarine circulation and anoxic, sulphide-rich deep water (Oğuz et al., 2006). The stratification is generated by coastal freshwater input and the Mediterranean inflow of water of a higher salinity. Seasonal fluctuations in sea surface temperature (SST) range from 8 °C to 26 °C, while deep-sea temperature remains stable at approximately 8.5 °C. The upper layer of the Black Sea is dominated by a meandering rim current system cyclonically encircling the basin, creating a cyclonic gyre within the eastern and western parts of the interior, and additional anticyclonic eddies along the rim current (Oğuz et al., 2006).

Over the past two decades, the Black Sea ecosystem has undergone significant changes as a result of increasing nutrient and organic matter input from land via rivers, along with waste discharge.(Mee, 1992; Cociasu et al., 1996, 1997). The Black Sea is a biologically productive and the largest anoxic marine environment. While open waters exhibit relatively modest primary production, coastal regions flourish due to the influence of freshwater inflow (Yunev et al., 2002; Yilmaz et al., 2006).

In addition to pollution originating from coastal cities, the Danube River, which drains substantial parts of central and eastern Europe, serves as a primary pollutant source in the shelf and upper slope regions of the Black Sea. The Danube water is transported along the coastal areas by the cyclonic rim current. Another pollutant source is the Mediterranean inflow that transports domestic and industrial pollutants from the Sea of Marmara (Sarı et al., 2018).

The Sea of Marmara is a restricted depression between the world's largest anoxic basin, (Black Sea) in the northeast and the saline Aegean Sea in the southwest (Beşiktepe et al., 1994). The Sea of Marmara, together with the İstanbul (Bosporus) and Çanakkale (Dardanelles) straits, is called Turkish Straits System (TSS). This system provides the connection between the less salty Black Sea waters and the salty Mediterranean waters (Beşiktepe et al., 1994). A sharp halocline of 15-25 m thick separates the upper and lower waters throughout the basin. The surface layer of the Sea of Marmara is composed of brackish waters (22-26‰) originating from the Black Sea, while the lower layer consists of saline Mediterranean waters (38.5-38.6‰) (Ünlüata et al., 1990). Temperature variations within the Sea of Marmara exhibit seasonal fluctuations, with upper layer temperatures ranging from approximately 7 °C to 26 °C, and lower layer temperatures spanning 14 °C to 16 °C. The coastal areas and semienclosed inlets in the Sea of Marmara are generally exposed to considerable anthropogenic inputs and industrial discharges (Okay et al., 1996; Morkoç et al., 2001; Tolun et al., 2001; Yaşar et

al., 2001; Alpar et al., 2003; Balkıs, 2003; Algan et al., 2004; Ediger et al., 2016; Sarı et al., 2020; Arslan Kaya et al., 2022; Arslan Kaya et al., 2023; Özen et al., 2023).

The Aegean Sea, which is part of the Eastern Mediterranean Sea, is bounded to the east by the Turkish coastline, to the north and west by the Greek mainland and to the south by the island of Crete. Its coastline exhibits significant irregularities, featuring numerous small and large bays, peninsulas, and islands (Soukissian et al., 2017). The surface water circulation pattern of the Aegean Sea is complex, showing temporal and seasonal variations. This sea establishes connections to the Levantine and Ionian Seas to the south through the Cretan Straits, while its northern link lies with the Sea of Marmara-Black Sea via the Canakkale Strait. The sea surface temperature across the Aegean ranges from approximately 8 °C to 26 °C, accompanied by salinity levels varying from 31‰ to 39‰. These parameters exhibit variations influenced by both location and time of year (Poulos et al., 1997).

The Aegean open sea displays oligotrophic properties. However, eutrophication risk has developed in some semienclosed bays of the NE Aegean Sea, which are subject to large loads of domestic and industrial waste waters (Bizsel et al., 2001; Kontas et al., 2004; Kucuksezgin, 2011; Talas et al., 2023). Sarı and Çağatay (2001) documented that the coastal regions of the northeastern Aegean Sea have experienced the influence of both anthropogenic and natural discharges from coastal rivers.

The Mediterranean is a semienclosed sea characterized by high salinities and temperatures. The characteristics water masses within the NE-Mediterranean Sea (Levantine Basin) are the Levantine Surface Water, the Modified Atlantic Water, the Levantine Intermediate Water, and the Levantine Deep Water (Özsoy et al., 1989; 1991; 1993; Brenner et al., 1991). The Levantine Basin is the easternmost part of the Mediterranean. The Eastern Mediterranean basin is connected to the North Atlantic Ocean through the Western Mediterranean and Ionian Basin as well as to the Black Sea through the Turkish Straits System and Aegean Sea. Salinity and temperature levels within this region range approximately from 36‰ to 39‰ and 16 °C to 29 °C, respectively. The prominent features of the general surface circulation are the midbasin jet and the Asia-Minor current along the Turkish coast, together with quasipermanent anticyclonic eddies in the Eastern Mediterranean (Wüst, 1961; Özsoy et al., 1993; Akpınar et al., 2015).

The Eastern Mediterranean is known as one of the oligotrophic seas over the world due to limited nutrient input to its surface waters from external and internal sources (Krom et al., 1991; Ediger and Yılmaz, 1996; Yılmaz and Tuğrul, 1998). Notably, semienclosed shallow coastal zones, which receive wastewater and riverine inflows, represent potential areas susceptible to eutrophication (Tuğrul et al., 2011).

3. Results

Türkiye is surrounded from north to south by the Black Sea (BS), the Sea of Marmara (SM), the Aegean Sea (AS) and the Mediterranean (MS), which have unique atmospheric, oceanographic, sedimentological, and anthropogenic characteristics and are interconnected by the strait systems (Figure 1). Within the scope of this study, the previously published TIC and TOC percentages of the continental margins of the Turkish Seas were grouped in 22 different areas, the average percentage values for each area were calculated and the obtained results were interpreted.

3.1. Black Sea

The average values of 57 different TIC (%) and TOC (%) data collected from the Black Sea continental margin were grouped in four different areas and the results were interpreted in Figures 2 and 3.

It is observed that TIC percentages decrease from BS-1 to BS-2 in the Eastern Black Sea Region and from BS-3 to BS-4 in the Western Black Sea Region. There was a noticeable increase in TOC percentages within the same directions and areas (Figure 3). The reason for the average TOC values exceeding TIC values in BS-2 and BS-4 can be

attributed to the Black Sea's marginal current system and the intensity of terrestrial inputs affecting these regions. Remarkably, the BS-2 and BS-4 areas stand out as rare areas observed in the continental margins of Türkiye. The BS-4 area in the Black Sea is situated within the influence zones of both the Danube River and the subcurrent of the İstanbul Strait.

High total organic carbon (TOC) levels in this region can potentially be attributed to these factors.

Sarı et al. (2018) have reported that the influence of Danube waters, combined with cyclonic rim currents, affects the region. Additionally, they have indicated that the area is impacted by the subcurrent of the Sea of Marmara, carrying waste materials from the city of İstanbul. On the other hand, BS-2, located within the influence zones of the Kızılırmak and Yeşilırmak rivers, may experience increased TOC levels due to the effects of these rivers.

3.2. Sea of Marmara

The average values of 316 different TIC (%) and TOC (%) data collected from the Sea of Marmara continental margin were grouped in nine different areas (Figure 4) and the results were interpreted in Figure 5.



Figure 2. The map illustrates sediment sampling locations along the continental margin of the Black Sea, highlighting four distinct regions, indicating sediment samples per area, and the main coastal river locations.



Figure 3. Average TIC and TOC percentages in the Black Sea.



Figure 4. The map illustrates sediment sampling locations of the Sea of Marmara, highlighting nine distinct regions, indicating sediment samples per area, and main coastal river locations.



Figure 5. Average TIC and TOC percentages in the Sea of Marmara.

The TIC (%) and TOC (%) values of the Sea of Marmara were divided into nine different regions and their average values were calculated and analysed. Notably, the most remarkable observation was that average TOC percentages exceeded TIC percentages only in the Golden Horn and İzmit Bay, among the areas in the entire Sea of Marmara. This is due to the high anthropogenic inputs entering these areas. Industrial and domestic activities in the Marmara Region influence mainly coastal areas and semienclosed inlets of the Sea of Marmara. İzmit Bay (Okay et al., 1996; Morkoç et al., 2001; Tolun et al., 2001; Yaşar et al., 2001) and the Golden Horn (Ergin et al., 1991) are well-defined polluted coastal inlets of the Sea of Marmara.

The regions with the highest average TIC values were found to be the Bosphorus and Bosphorus-Marmara

Junction areas. The erosion effect of the lower layer current system along the Bosphorus, coupled with the geological formations surrounding the terrestrial areas of the Bosphorus, likely plays a significant role. Additionally, the less saline Black Sea waters may have precipitated some of their suspended solids because of flocculation upon encountering the Sea of Marmara waters at the Bosphorus-Marmara Junction. The suspended solids, which were stored due to flocculation, could have subsequently been carried back to the bottom of the Bosphorus by the lower layer current. Lateral offshore transport in surface waters and biological activities in the water column are believed to be important factors that result in the decrease of particulate organic carbon fluxes to the sediments in this sea (Ergin et al., 1994).

3.3. Aegean Sea

The average values of 87 different TIC (%) and TOC (%) data collected from the Aegean Sea continental margin were grouped in three different areas (Figure 6) and the results were interpreted in Figure 7.

Observations reveal that TIC values reach their highest point in the north of the Aegean Sea, while TOC values reach their peak in the central region. This pattern highlights an inverse relationship between the average TIC and TOC percentages within the three Aegean Sea regions.

High TIC levels in the Northern Aegean Margins may result from significant deposition of suspended solids, mainly composed of limestone particles, transported by coastal rivers. The central region of the Aegean Sea exhibits high TOC (%) values compared to the northern and southern regions. This can be attributed to the intensified anthropogenic pressure in the central region, where large cities are situated.

3.4. Mediterranean Sea

The average values of 231 different TIC (%) and TOC (%) data collected from the NE Mediterranean Sea continental margin were grouped in six different areas (Figure 8) and the results were interpreted in Figure 9.

When investigating the TIC (%) and TOC (%) distribution along six different areas along the Mediterranean continental margin from east to west, the highest TIC (%) value was observed in MS-4, whereas the highest TOC (%) value was found in MS-1 (Figure 9).

The high percentage of TIC in the MS-4 region can be attributed to the influence of the Göksu River, which has a significant flow rate. In contrast, the high percentage of TOC in the MS-1 region can be attributed to its geographical location. This region, under the influence of the Rhodes cyclonic circulation, shows high productivity levels. It is observed that the noticeable decrease in TOC (%) values while the TIC (%) values increase from the MS-1 to MS-4 area. Thus, it is clearly observed that there is an inverse relationship in the distribution of the average TIC (%) and TOC (%) values of these areas (MS-1, MS-2, MS-3).

According to Ergin et al. (1996), the total organic carbon contents of the surface sediments in the Mediterranean Sea vary regionally depending on the complex interaction of biogenic, terrigenic, anthropogenic and hydrodynamic factors.



Figure 6. The map illustrates sediment sampling locations along the continental margin of the Aegean Sea, highlighting three distinct regions, indicating sediment samples per area, and the main coastal river locations.



Figure 7. Average TIC and TOC percentages in the Aegean Sea.



Figure 8. The map illustrates sediment sampling locations along the continental margin of the NE Mediterranean Sea, highlighting six distinct regions, indicating sediment samples per area, and the main coastal river locations.



Figure 9. Average TIC and TOC percentages in the NE Mediterranean Sea.

3. Discussion

The continental margin of Türkiye has been analysed comparatively by dividing it into 22 different areas from the SE Black Sea to the NE Mediterranean. Figure 10 shows the variation in average TIC and TOC percentage values across these 22 regions. The mean TIC percentage exhibited a range from 6.30% (AS-1) to 1.04% (BS-4), while the mean TOC values ranged from 4.72% (SM-3) to 0.37% (BS-1) (Figure 10).



Figure 10. TIC and TOC percentage values and bar graph for areas in sequential order from the East of the Black Sea to the East of the Mediterranean.

Despite generally higher TIC percentages than TOC percentages across all areas, TOC values exceed TIC values in specific regions. Notably, this occurs in BS-2 and BS-4 in the Black Sea, SM-3 and SM-4 in the Sea of Marmara, and MS-1 in the Mediterranean Sea (Figure 10). Among the 22 zones, the Golden Horn (SM-3) sediment exhibits the highest TOC percentages. The high TOC content in this area is probably attributed to significant domestic and industrial wastewater input combined with inadequate regeneration processes in the water column in estuarine sediments (Kanat et al., 2018).

The distinct elevation of TOC percentages compared to TIC percentages in these regions arises from variations in sediment sources and diverse oceanographic and environmental conditions. For instance, in SM-3 (Golden Horn) and SM-4 (İzmit Bay), intense anthropogenic inputs play a significant role, while MS-1 (Western Mediterranean), situated in the Mediterranean-Aegean Junction, may experience partial influence from the Rhodes upwelling area known for its high productivity. In the Black Sea (BS-2 and BS-4), high primary production and anaerobic seabed conditions can influence higher percentages of total organic carbon (TOC) levels.

Yemenicioglu and Tunc (2013) noted that the surface sediments' texture in the Cilician Basin is largely shaped by the irregular bottom topography and terrigenic inputs from coastal rivers. The complex wave and current system, encompassing local eddies and coastal filaments, also play a crucial role in governing sediment composition in the NE Mediterranean.

The average TIC percentages calculated for 22 distinct areas along the continental margins of the Turkish Seas

demonstrate that six areas exhibit TIC percentages higher than 5%. Notably, the first two regions, SM-1 and SM-2, correspond to the Bosphorus and the Bosphorus-Marmara Junction. The two-layer current system within the Bosphorus is considered a significant factor contributing to the storage of high TIC percentages in these areas.

The high TIC percentages observed in the Northern Aegean (AS-1) region can be attributed to the flow of the Meriç River and the Çanakkale Strait and the coastal geology affecting the region. Sarı and Çağatay (2001) reported that the main freshwater and sediment sources of the Northeast Aegean Sea are the Meriç River in the northwest and the Kavak Stream in the east.

The high TIC percentage in the MS-3 and MS-4 areas, which are adjacent to each other, is primarily influenced by the coastal zone's geological composition on the foothills of the Taurus Mountains, comprising limestone, and the presence of the Göksu River. Akcay et al. (2022) note that the wide shelf areas of the Cilician Basin are exposed to substantial amounts of suspended matter transported by the regional rivers (Akcay et al., 2022).

Figure 11 presents bar graphs depicting total carbon (TC) percentages, calculated by summing TIC and TOC percentages, for 22 distinct areas from the SE Black Sea to the NE Mediterranean. Excluding areas SM-1 (Bosphorus), SM-2 (Bosphorus-Marmara Junction), SM-3 (Golden Horn), AS-1, AS-3 (North and South Aegean), and MS-6 (Gulf of Iskenderun), the TC percentage values show a clear increasing trend from BS-1 to MS-4, as illustrated in Figure 11.

Upon examination of the 50-m intervals of the continental margins at depths between 0 and 500 m in the



Figure 11. Sequentially ordered, TC percentage values for regions spanning from the southeastern Black Sea to the northeastern Mediterranean and the statistical outcomes. TC data from areas SM-1, SM-2, SM-3, AS-1, AS-3, MS-5, and MS-6 were excluded from the statistical analysis.

seas surrounding Türkiye, significant findings have been observed (Figure 12). The TIC percentages in the depth zones of the continental margins show a range from the lowest value (2.01%) in the 350–400 m depth zone and the highest value (4.11%) in the 250–300 m depth zone. As expected, the variation of TIC percentage along the continental margin decreases consistently with depth, from 0 m to 250 m. However, contrary to the anticipated gradual decrease in TIC (%) values from 0 m to 500 m depth, higher values were observed in the 250–300 m and 400–450 m zones. This occurrence can be attributed to the geological, tectonic, and topographic characteristics of the seas.

The TOC percentages along the 0-500 m depth zone of the continental margin exhibited an expected variation, ranging between 1.6% and 0.8% in the 0–50 m and 250–300 m depth zones, respectively. The TIC (%) and TC (%) values along the continental margin (0–500 m) showed a similar distribution along the depth zones, mainly due to the substantial contribution of TIC (%) values in this context.

Figure 13 presents the distribution of the average TIC and TOC percentages in the bottom sediments of the four seas surrounding Türkiye (Black Sea, Sea of Marmara, Aegean Sea, and Mediterranean). A notable observation from Figure 13 is the evident inverse relationship between TIC (%) and TOC (%) values along the continental margins of these seas, from north to south. This phenomenon can be attributed to the dilution effect of carbonates on the TOC content.

5. Conclusion

The comprehensive model (Figures 14 and 15) outlines crucial parameters influencing the deposition of TIC and TOC on the continental margins of Türkiye. These key factors encompass atmospheric effects, depth of the environment, distance from the shore, water column temperature, current characteristics, primary production, presence of benthic organism, anthropogenic inputs, coastal lithology, lithology of drainage basins, coastal riverine inputs, coastal geometry, seafloor morphology, and the oxic/anoxic characteristics of the environment.

These parameters control the distribution and abundance of TIC and TOC in the marine ecosystem along the Turkish continental margins. It is important to note that these factors exhibit temporal variations dependent on climate and environmental characteristics. TIC and TOC values are among the important parameters measured in sediment to detect the temporal changes of environmental features.

The primary finding of this study is the established inverse relationship between the average TIC and TOC percentages in samples collected from 22 different continental margins of the Turkish seas. This inverse relationship may be attributed to the dilution effect of carbonates on the TOC content. Zhou (2020) reported that the deposition of organic matter in sediments is typically governed by a combination of bioefficiency, preservation of organic matter in the sediment, and the dilution effect of other inorganic substances present in the sediments.

Numerous investigations have focused on TOC; however, research into TIC from the Turkish continental



Figure 12. The mean percentages of TIC, TOC, and TC throughout the depth of the continental margin within the Turkish Seas.



Figure 13. Mean TIC and TOC percentages along the continental margins of the Turkish Seas (from north to south).

margin remains limited. To our current understanding, this study is the first to evaluate both TOC and TIC in the surface sediment of the Turkish continental margin. Organic and inorganic carbon data for Turkish continental margin between 1984 and 1996 have been compiled, processed, and evaluated for the first time in this study. These archival datasets hold notable importance for the Turkish seas, which have experienced diverse environmental pressures over the past three decades. Furthermore, these data can establish fundamental reference points for future investigation in the area.



Figure 14. Schematic cross section model of wave and current dominated oxic and anoxic depositional environments and sources of inorganic carbon (IC) and organic carbon (OC) deposits.



Figure 15. Coastal rivers, karstic regions and continental margin currents of the Turkish Seas and coastal rivers (adapted from Beşiktepe et al., 1994; Nazik, 2004; Stanev, 2005; El-Geziry and Bryden, 2010; and Tartaron, 2013).

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