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Distributions of Anionic Surfactant in Sea Water and Total Organic Carbon in Bottom-Surface Sediment along the Turkish Coast of the Black Sea

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Abstract

The aim of this work is to determine the distributions of anionic surfactant (AS) in seawater, total organic carbon (TOC) in bottom-surface sediment and to make an assessment of the organic matter pollution. Seawater samples for AS in the autumn of 2010 and winter of 2011, and bottom-surface sediments for TOC in the autumn of 2010 were collected from the Black Sea coastline of Turkey. According to the results, concentrations of AS in sea water were changed with seasons, regions and distance from the anthropogenic sources including industrial and domestic discharges. Generally, winter values of AS were higher than autumn at the nearshore stations of the eastern and middle Black Sea coasts. Maximum AS values (except Yenice River mouth) were measured in surface seawater of Ordu and in bottom seawater of Şile in the autumn and in surface and bottom seawater of Bafra in the winter. Additionally, the highest amount of AS in both seasons near Yenice River mouth showed the influence of the river. On the other hand, the highest amount of TOC was obtained in the sediment of İğneada (9.73%) and the C/N ratios indicated that organic matters in the sediment samples could be related to both marine and terrestrial sources. Anionic surfactant values were positively correlated (r=0.8-0.9) with total suspended solid negatively correlated with pH (r=0.6-0.4) and dissolved oxygen (r=0.96-0.87) in surface seawaters of the nearshore stations.

Keywords: Detergent, TOC, pollution, anthropogenic, terrestrial.

Karadeniz'in Türkiye Kıyıları Boyunca, Deniz Suyunda Anyonik Yüzey Aktif Madde ve Dip-Yüzey Sedimanında Toplam Organik Karbon Dağılımları

Özet

Bu çalışmanın amacı; deniz suyundaki anyonik yüzey aktif madde (AYM) ve dip yüzey sedimanındaki toplam organik karbon (TOK) dağılımlarını belirleyerek organik maddelerden kaynaklanan kirliliğin değerlendirmesini yapmaktır. Karadeniz'in Türkiye kıyısı boyunca, 2010 sonbaharında toplanan sediman örnekleri TOK, 2010-Sonbahar ve 2011-Kış mevsimlerinde deniz suyu örnekleri AYM için toplanmıştır. Sonuçlara göre, deniz suyundaki AYM derişimleri, mevsime, bölgelere ve antropojenik kaynakların uzaklığına bağlı olarak değişmiştir. Genel olarak, orta ve doğu Karadeniz kıyılarına yakın istasyonlarda, AYM kış değerleri sonbahardan yüksektir. Maksimum AYM değerleri (Yenice nehir ağzı hariç), sonbaharda Ordu yüzey suyunda ve Şile dip suyunda ve kışın Bafra yüzey ve dip suyunda ölçülmüştür. Ayrıca, Yenice nehir ağzında her iki mevsimde ölçülen yüksek AYM değerleri nehrin etkisini göstermiştir. Öte yandan, maksimum TOK değeri İğne ada sedimanında (9,73%) belirlenmiştir ve C/N oranları sediman örneklerindeki organik maddenin hem denizel, hem de karasal kaynaklarla ilgili olabileceğini göstermiştir. Kıyıya yakın istasyonların yüzey sularında, AYM değerleri, toplam askıda yük ile pozitif bağlantılı (r=0,8-0,9), pH (r=0,6-0,4) ve çözünmüş oksijen (r=0,96-0,87) ile negatif bağlantılıdır.

Anahtar Kelimeler: Deterjan, TOK, kirlilik, antropojenik, karasal.

Introduction

All of the autochthonous and allochthonous organic matter (OM) are subjected to various processes in the water column, small fraction settled to the bottom and incorporated into the sediment. OM sources can be natural from overland runoff, shoreline erosion, decomposition of plants and animals, excretions of zooplanktons, animals and primary production by phytoplankton or benthic microalgae, terrestrial inputs via river discharges and also production by macrophyte systems such as seagrasses, macroalgal beds, mangroves and salt marshes. So, types of organic carbon varies from freshly deposited litter such as leaves, twigs, branches to highly decomposed type like humus. Anthropogenic sources contribute the organic carbon content of the wastes such as oil and surfactants. They spill or release into the environment from oil-drilling activities, ship accidents, agricultural applications, food-processing plants, domestic waste, sewage effluents, garbage dumps and different organic carbon bearing particles such as wood fibers from pulp mill wastes (Schumacher, 2002).

Surfactants (surface-active substances) with hydrophilic and hydrophobic parts of the structure make up a very reactive part of the organic matter in the sea. They tend to concentrate at the interfaces between water and other phases like air, oil and particles. They have the cleaning and dispersant effects and above a certain concentration, surfactant molecules are able to form micelles in aqueous solution (Hummel, 2000). Linear alkylbenzene sulfonate (LAS) is the most commonly used anionic surfactant in detergent industry and is the most studied surfactant as being useful tracer of domestic waste inputs. High consumption of surfactants for washing of textiles, dishwashing, laundering, cleaning motor vehicles, etc., is caused to increase their presence in domestic and trade waste effluents and most of these end up in the aquatic environment. Fate and distributions of the anionic surfactants, including LAS, have been studied by many researchers in different environment (e.g. seawater, river, sediment). They observed that LAS accumulated first at the water-atmosphere interface and showed non-conservative behavior because of the biodegradation, sorption and settling of material in suspension (González-Mazo *et al.*, 1998). Additionally, LAS concentration changed as a function of the regional and seasonal variations (Boran *et al.*, 1998; Okbah *et al.*, 2013) and decreased due to decreasing trend in LAS's discharge and increasing biodegradation rate (Miura *et al.*, 2008; Takada *et al.*, 1992). Because of the presence in different environment, ecotoxicity of anionic surfactants to aquatic life has been investigated by many scientists and effective concentrations of LAS detected for the species such as marine copepod *Acardia tonsa*, 1-10 mg/L LAS (Kusk and Peterson, 1997); micro algae *A. ussurensis*, 0.1-1 mg/L (Markina and Aizdaicher, 2007). About environmental impacts of detergents on marine phytoplankton, significant changes on chlorophyll-a content, primary production potential, and adrastic reduction in *P. tricornutum* (diatom) cell density have been observed at concentrations 2.0-5.0 mg MBAS/l (Aidar *et al.*, 1997). In the review studies, fish gills damage, excess mucus secretion, decrease respiration in the common goby and damaged swimming patterns in bluemussel larva are reported between 0.02-1.0 mg/L LAS (Venhuis and Mehrvar (2004) in Mungray and Kumar, 2009) and Ying (2006) is noticed that the aquatic chronic toxicity concentration of surfactants is greater than 0.1 mg/L.

TOC content reflects the accumulation of OM in sediment. When organic matters reached to the seafloor, they provide food supply for benthic ecosystems, but excess OM can be harmfull by causing oxygen depletion in the sediment and overlying water. Therefore, in addition to describe the recent and ancient sediment, TOC is also used to asses the ecological risk and recognized as an indicator of pollution and eutrophication rate (EPA, 2002).

The Black Sea is a nearly enclosed sea and only connected to the Marmara Sea through the Istanbul (Bosphorus) Strait and to the Mediterranean Sea through the Çanakkale (Dardanelles) Strait. The Black Sea has lighter fresh water mostly from river discharges at the surface and saline water from Mediterranean Sea water inputs at the bottom and over the years, a stagnant, anoxic seawater basin occurred in the Black Sea due to the lack of vertical mixing and/or exchange of deep water. According to the vertical stratification, it has an oxic surface layer, an anoxic deep layer and between them, a suboxic layer which contains extremely low oxygen and sulphide together (Murray *et al.*, 2005).

The highlands of the Southern Black Sea coast are covered with forest and scrub, green meadow, some other plants tea and corn. This region takes more precipitation of snow and rain, and heavy rains often caused to flooding in the rainy season (Ceylan *et al.*, 2007). Many rivers and small streams flow through the cities, towns before reaching to the sea, and coastal waters near densely populated cities (Zonguldak, Samsun, Ordu, Giresun, Trabzon, Rize) are exposed to pollution through different sources such as industrial effluents, shipping activities, domestic waste, combined sewage and storm-water overflows, mining activities, landfill sites, irregular garbage disposal and agricultural runoff (Bakan and Büyükgüngör, 2000; Tuncer *et al.*, 1998).

In this paper, latest concentrations of the anionic surfactant in sea water and TOC (with C/N ratios) in bottom-surface sediment are presented along the Turkish coast of the Black Sea, and variations in concentrations from autumn to winter, the influence of river inputs, relations with some physicochemical parameters, and possible affects to the aquatic environment are discussed.

Sampling and Methods

The surface and bottom water samples [1, 3, 5nmi away from the coast (1nmi: 1.852 km)] were collected by using Niskin bottles and surface sediments by a Van Veen type grab sampler in the southern Black Sea. The sampling stations are shown in Figure 1. The colorimetric (methylene blue) method was used to quantify the total concentrations of anionic surfactant as methylene blue active substances (MBAS) (Leithe, 1973). Sea water was shaken with a mixture of phosphate buffer (pH=10),

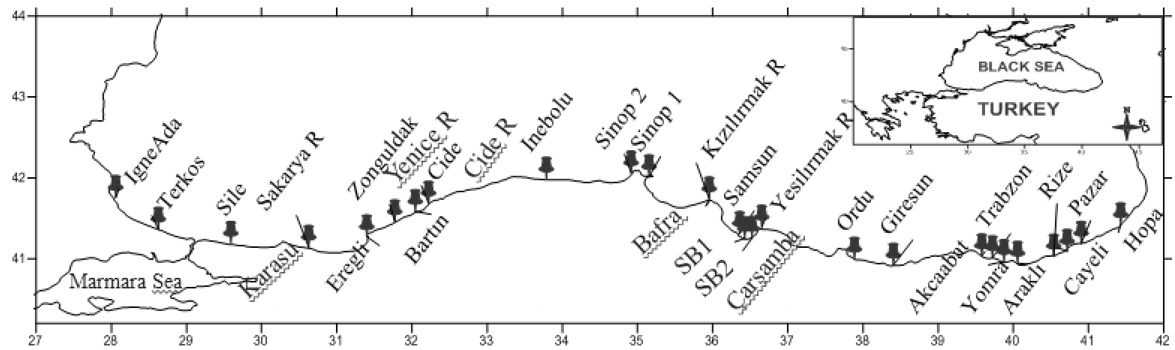

Figure 1. The locations of the sampling stations along the Black Sea coast of Turkey. SB: Samsun Bay

neutral methylene blue and chloroform. Then, the separated chloroform layer was shaken with distilled water and acidic methylene blue solution in a second separatory funnel. The extraction into chloroform from acidic aqueous medium was repeated two more times by adding chloroform. The intensity of the resulting blue color, which was proportional to the concentration of the extracted AS in the organic phase, was measured by spectrophotometer (Shimadzu, UV-1800). AS was calculated in terms of a reference material, commercial linear alkylbenzene sulfonic acid (LABSA: %96, average molecular weight: 322, liquid at room T°C) which is an intermediate compound in the manufacture of linear alkylbenzene sulfonic acid sodium (LAS - solid at room T°C) (CBIC, 2003). The amount of carbon, hydrogen and nitrogen of the sediment sample was determined using a Thermo Finnigan Flash EA 1112 elemental analyzer in the advanced analyses laboratory which is the center laboratory in the Technology Transfer Center of Istanbul University (MERLAB, 2015). The method was based on dry combustion method directly (Schumacher, 2002). The sediment samples (1-2 mg) were combusted in pure oxygen and in the presence of catalysts at high temperature (<900°C) and then the combustion products were passed through a chromatographic column, in which they are converted into simpler components and quantified by a thermal conductivity detector. The pH of the sea water was measured using WTW pH meter (model 5269). Determination of dissolved oxygen in sea water was carried out according to the Winkler method (Grasshoff *et al.*, 1999). The method was based on the quantitative oxidation of iodide ions (I^-) to iodine (I_2) by oxygen in the sample. The standart method 2540D (Clesceri *et al.*, 1998) was used for quantification of the total suspended solid (TSS) which was based on a gravimetric measurement of the sample dried to a constant weight at 103-105°C. Statistically; the relations between AS, pH, DO and TSS were established via Pearson's correlation coefficient (PCC) in MS Excel-2010. PCC measures the strength of the association between the two variables and values constrained between +1 (positive correlation) and -1 (negative correlation), and -0- indicates no correlation (Glantz, 2005).

Results and Discussion

Distributions of Anionic Surfactant (AS)

The regional and seasonal variations of AS concentration in surface and bottom water of the southern Black Sea coasts are shown graphically in Figure 2 and minimum/maximum and mean values are given in Table 1. Considering total number of the surface and bottom samples; 84-86% in autumn and 71–75% in winter (Table1), AS values were found less than the recommended value 0.1 mg/L (Ying, 2006).

Generally, based on the seasonal variations, winter values of AS in surface and bottom waters were higher than autumn values at nearshore stations of the eastern and middle Black Sea coasts (except Ordu station) as shown in Figure 3. No clear differences in the amount of AS between autumn and winter were observed in surface water of İnebolu and Çarşamba (1nmi), Terkos and Ordu (3nmi), İğneada (5nmi) and in bottom water of Karasu and Samsun Bay-SB2 (1nmi), Ereğli (3nmi), Zonguldak (5nmi) (Figure 3). But, max. differences between autumn (A) and winter (W) values of AS were observed in surface water of Ordu (A>W) (1nmi); Bafra (A>W) (3nmi), Şile (A>W) (5nmi) and in bottom water of Bafra (W>A) (1nmi), Bartın (A>W) (3nmi), Şile (A>W) (5nmi). Seasonal variations in precipitation (rain and snow) produce seasonal differences in river discharge volume and flow rate. River discharge can cause to dilution and suspension of sediment particles at high flows. Transportation of more surfactant in nearshore stations during high river runoff could be due to sweeping the settled pollutant in the river bed into the coast (Puig *et al.*, 1999) because sorbed LAS is more persistent after being deposited in the sediment (Tabor and Barber, 1996). Local variations may be attributed to the discharge type (discharges to the upper or deeper layer) and domestic and/or industrial utilization of AS (González-Mazo *et al.*, 1998). Additionally, seasonal change in temperature, and

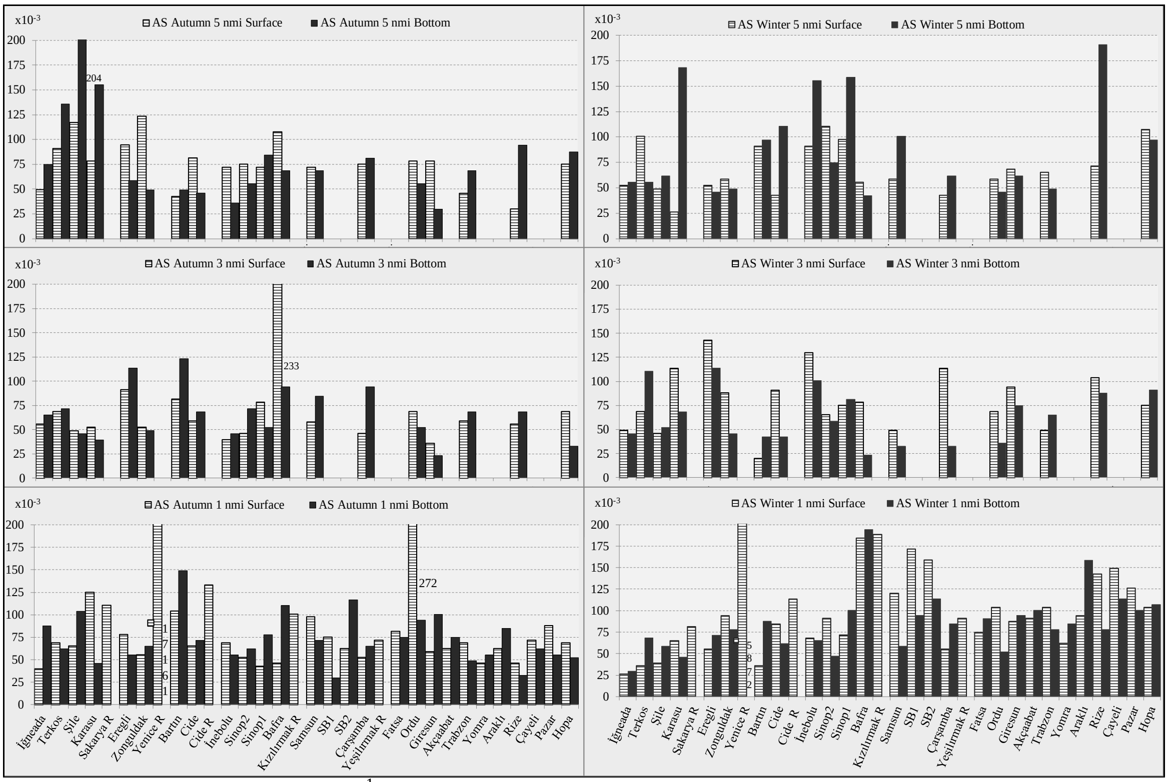

Figure 2. Distributions of AS (mg·l^{-1}) in autumn (left) and winter (right) in surface and bottom sea water along the Turkish coastline of the Black Sea.

light could affect the rate of chemical reactions. For example, Sales *et al.*, (1999) observed that the biodegradation of LAS decreased at lower temperature whereas increased with light. So, decreased temperature (average) at the surface from 16.4°C (autumn) to 10.4°C (winter) may cause to increase the amount of AS as a result of decreasing the biodegradation. Because of same reason, LAS values in the winter months were detected about ten times higher than those in the summer months (Takada *et al.*, 1992) and similar increasing trends in the amount of LAS and MBAS were observed between summer, fall and spring (Tabor and Barber, 1996).

AS in the Western Coasts of the Black Sea (Between İğneada and Zonguldak)

İğneada, Terkos, Şile coasts are not industrialized and the low degree pollution has been reported for these coasts (Sur *et al.*, 2012). AS concentrations were lower than 0.1 mg/L in most of the surface and bottom water (Figure 2) and higher in the offshore water of Terkos (bottom: 0.14 mg/L) and Şile (surface: 0.12 mg/L; bottom: 0.204 mg/L, max. in autumn) (Table 1). Terkos and Şile coasts are exposed to dense ship traffic and high values may be due to illegal or accidental discharges of bilge water including detergents during passages of cruise ships, tanker etc. (EPA, 2008). Additionally, some municipal waste of the Istanbul city discharge into the lower-layer of the Bosphorus and most of the waste reach the Black Sea within 18 hours (Gunnerson and French, 1996, p. 285). High AS concentration possibly caused by this Bosphorous outflow which is mixing with cold intermediate layer (water temperature decreases to 7°C) on the continental shelf just north of the Bosphorus (Tolmazin, 1985b in Murray *et al.*, 2005). Other reasons for Şile station possibly related to summer tourism (Renzi *et al.*, 2012; Okbah *et al.*, 2013) and deep-sea discharge system. Because, Şile is a small resort town and the amount of waste water increases with increasing population density about four-five times during summer (SDG, 2008) and municipal wastewater is dumped to seawater via deep-sea drainage system. Nemirovskii and Kuftarkova (2004) observed the vertical displacement (from 42m to 79 m) of the wastewater from the deep-sea discharged zone and promotion of the vertical transport of organic matter, biogenic compounds and phytoplankton from the photic zone to the deep-sea water.

AS concentration decreased (from autumn to winter) from 0.11 to 0.08 mg/L near Sakarya R mouth (Figure 2) and from 0.13 (1nmi) to 0.03 mg/L in surface and to 0.07 mg/L in bottom water of Karasu station which is affected by Sakarya R discharge. Decreased AS value can be related to dilution effect of river and to sorption by suspended solids because, TSS also decreased from 21 to 10 mg/L (1nmi) in surface waters. In contrast, high values were observed for AS (0.16-0.17 mg/L) and TSS (14 to 18 mg/L) in

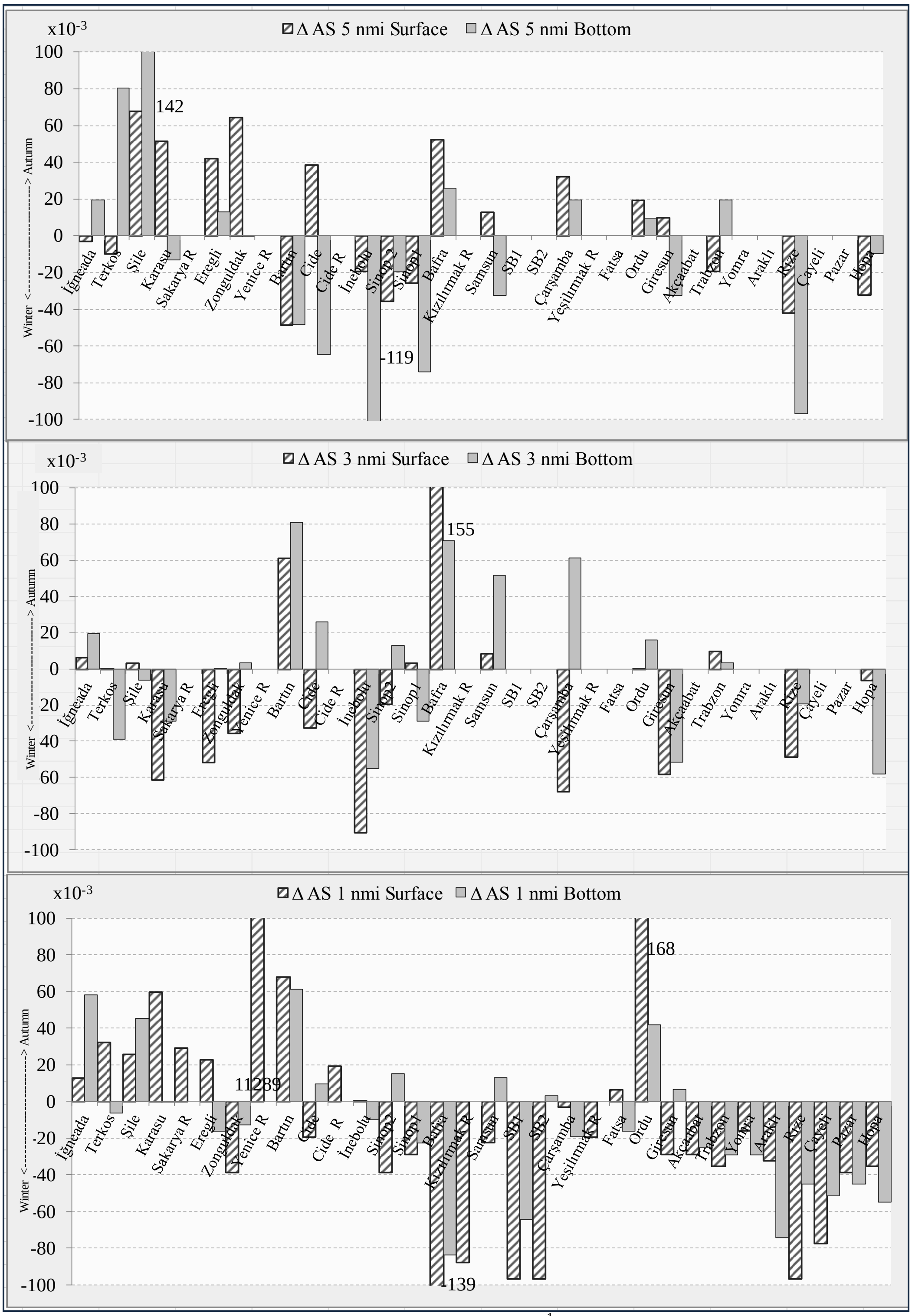

Figure 3. Differences (Δ) between autumn and winter AS levels (mg·l^{-1}) in surface and bottom sea water of the southern coast of the Black Sea.

the offshore bottom water (650 m) of the Karasu. Sampling depth was around 100 m in 5nmi offshore stations (except Karasu and Rize). High AS could be due to sorption on suspended solids because, sorbed LAS is being more stable than in the water column and transported to distant locations before deposited (Tabor and Barber, 1996). Gardner *et al.* (1985) indicated that small amount of organic carbon were found in deeper part as associated with biogenic matter and carried by rapidly falling particles. DO is decreased to 1 mg/L at around 120 m and Murray *et al.* (2005) reported that anoxic decomposition of organic matter is slower than oxic decomposition and oxygen exposure time in the Black Sea is minimal as sinking particles reach anoxic conditions (between 100 m and 2000 m) just below the euphotic zone. So, AS probably sorbed onto suspended solid and transported in an undissolved form to the deeper part of the offshore stations. In addition, study needs more sampling at different depths but, another type of methylene blue active surfactant could be exist in the bottom water such as alkyl sulfate, dioctyl sodium sulfosuccinate (DOSS) (Nyankson *et al.*, 2014) which might be used as an oil spill dispersant to transfer the oil from the surface in the Mediterranean waters (EMSA, 2010). Because, after application of DOSS for deepwater horizon oil spiil, Kujawinski *et al.*, (2011) found that DOSS was sequestered in deepwater hydrocarbon plume and had not been biodegraded in two mouths at distances of nearly 300 km from the well.

Zonguldak region is densely populated and has high ship traffic because of the commercial operations of iron-steel making company on the Ereğli shore and most of the industrial plants such as food, textile, pulp and paper manufacturing, coal mining, iron and steel, have waste water treatment system (DEF-Zonguldak, 2010) and so AS in nearshore surface and bottom seawater was lower than 0.1 mg/L in both seasons. Besides that, low AS might be due to sorption on particles like carbon which is discharged directly into the sea water as a residue from a coal preparation plant (Ergin *et al.*, 1996). High AS values in winter (Figure 2) were measured in surface water of Ereğli (0.143 mg/L, 3nmi) and Zonguldak (0.123 mg/L, 5nmi) because of the shipping activities, and in bottom water (0.114 mg/L, 3nmi) of Ereğli station due to domestic waste water discharge to the sea water via deep- sea discharge system.

Yenice R flows through the Zonguldak province and highest AS concentrations (17.0-5.87 mg/L, Table 1) were detected near Yenice R mouth in both seasons due to the direct discharge of AS and /or adsorption onto particles which were also higher than the other stations TSS (50-56 mg/L). Similar high AS values have been reported for Riva R, which placed about 35 km west of the Şile, flows into the Black Sea and carries high waste water because of the summer activities along the riverside (Yardımcı and Temel, 2007). These extreme AS levels might be related to high load detergent as a function of the directly discharge of municipal and industrial sewage (Bakan and Büyükgüngör, 2000) and also might be related to decreased river runoff at the mouth of the Yenice River in autumn (Sur *et al.*, 1994; DEF-Zonguldak 2010). In addition, because of their amphiphilic structure, AS molecules are able to make micelles via salt bridges (Sammalkorpi *et al*., 2009) and can be associated with dissolved humic substances which reduces the photodegradation of LAS (Hermann *et al.*, 1997).

AS concentration at Yenice R mouth decreased three fold in winter mostly with dilution effect of river but it was still high because of continuous reaching of AS to the sea water and decreasing temperature in winter which might prevent removal of more AS by decreasing both biodegradation and sinking velocities (Bach *et al.*, 2012).

AS in the Middle Coasts of the Black Sea (Between Bartın and Çarşamba)

The influence of Yenice R is appeared on the Bartın coast with high AS level in surface (0.104 mg/L 1nmi) and in bottom water (0.150-0.123 mg/L, 1 and 3nmi). Because, AS was very high in Yenice R mouth and possibly mixed with the water column by wind and waves, and then dispersed via entrainment and subsurface transport (mixing and advection) by turbulent forces. In this region, riverine influence has been observed in the Coastal Zone Color Scanner images that the eastward bending plumes from the perennial runoff sources (Yenice R and Bartın R which flows towards Bartın) extended up to 27nmi (50km) offshore, with a colour signature indicating terrigeneous sediment and organic inputs (Sur *et al.*, 1994).

AS value in autumn near Cide R mouth decreased in winter from 0.132 to 0.110 mg/L due to mostly dilution because of increased fresh water volume as a function of seasonal change in rainfall. Cide (district of Kastamonu province) has no waste water treatment system (DEF–Kastamonu, 2010). Similar to the bottom water of 5nmi away stations Karasu, Terkos, Şile; high AS values were detected in winter at Cide, İnebolu, Sinop and Samsun stations (0.11, 0.16, 0.16, 0.10 mg/L respectively) mostly due to transportation of the dissolved AS or adsorbed AS by the combined effects of horizontal advection, vertical settling, turbulent diffusion and non uniform currents. Presence of AS around 100 m depth indicated that AS might be stable as a function of the decreasing degradation conditions since, temperature was around 8.5°C, DO was low (around 1.45-2.75 mg/L for Cide and Inebolu respectively).

Samsun coasts also receive considerable amount of pollutants (including detergent) from domestic, industrial effluents and agricultural runoff directly and via many streams and rivers Kızılırmak R, Yeşilırmak R and Mert R (reaching to the Black Sea near Samsun Bay) (Bakan and Büyükgüngör, 2000; Bakan and Şenel, 2000). Amount of AS in the Kızılırmak R mouth increased from 0.10 to 0.189 mg/L (Figure 2) in winter because of the high river discharge during/after rainfall and significantly higher than the concentrations measured near the mouth of the Cide R, Sakarya R and Yeşilırmak R. Compared to this work, higher AS values have been recorded in waters of Kızılırmak R (mean: 1.62 mg/L) and Yeşilırmak R (mean: 1.57 mg/L) (Akbal *et al*., 2011). During winter, AS increased from 0.046 to 0.186 mg/L in surface and from 0.11 to 0.194 mg/L in bottom water (1nmi, Figure 2) of Bafra because of the Kızılırmak R runoff as well as the shipping /fishing activities, and reduced concentrations found from 0.233 to 0.078 mg/L for 3nmi and from 0.108 to 0.055 for 5nmi offshore surface water (Table 1 and Figure 2) due to transportation and/or dilution in seawater because of the seasonal change in the action of waves.

Seasonal differences of AS concentration between surface water of Samsun Bay stations; SB1 and SB2 (Figure 3) were very low (ΔAS≈ 0.1 mg/L). In bottom sea water (Figure 2), AS in SB2 was around 0.12 mg/L in both seasons while AS in SB1 increased from 0.03 mg/L in autumn to 0.09 mg/L in winter due to the discharge of more pollutants such as TSS, organic materials including detergent mainly from domestic sources near the discharge basin of Mert R (Bakan and Büyükgüngör, 2000; Bakan and Şenel, 2000). Mean levels of AS (autumn: 0.08 mg/L; winter: 0.15 mg/L, Figure 2) in nearshore station of Samsun coast were much lower than reported values of Akbal *et al.* (2011) that may be due to differences in sampling time and specificity of the sampling site (Akbal *et al.* (2011) samplings were possibly closer to the discharge region). González- Mazo *et al.* (1998) found the highest LAS value near the direct urban effluent which releases into the sea water as a function of the discharged time, and concentration is decreased with distance from the discharged point. Tuncer *et al.* (1998) have sampled the domestic discharges four times in a day, in order to see differences in the composition during 24 hours period.

AS in the Eastern Coasts of the Black Sea (Between Ordu and Hopa)

AS concentrations in the eastern coasts were higher in most of the surface and bottom water in winter (Figure 3) compared to the western coasts. AS concentration decreased (about 3 fold) only in nearshore surface water of Ordu in winter (Figure 2) while AS increased about 2-3 fold in surface water of Rize. These results possibly occurred as a result of the seasonal change in discharge volume of the rivers. There are many fast-flowing rivers with high freshwater and sediment load in the eastern part of the Black Sea. Ordu has higher rainfall in autumn and snowfall is not common; rivers and seawater are polluted with waste waters (domestic and industrial) directly and by dumping garbage near the mouth of the river or seashore (DEUP- Ordu, 2011). So, high amount of AS in nearshore water of Ordu could be transported to the coastal zone by flush during/after rainfall (Takada *et al.*, 1992) and then AS decreased three times mostly by the dilution. On the other hand, Rize province has low rainfall and high snowfall on the highland and because of this, rivers have low flow rate and volume during winter (e.g. Fırtına river flows through Rize and its flow rate is 11.3 m^3/s in January and reaches up to 65.2 m^3/s in June) (DEF-Rize, 2010). Increased amount of AS in winter in surface waters of Rize from 0.05 to 0.143 mg/L (1nmi), from 0.05 to 0.104 mg/L (3nmi) (Figure 2) is attributed to discharge of untreated domestic waste water directly to the sea water or via deep-sea drainage system (DEF-Rize, 2010) and to the lack of the dilution effect of rivers during low river flow period. There were small differences between autumn and winter values of AS in Trabzon seawater (Figure 3) and concentration ranged between 0.046-0.104 mg/L. Similar AS concentrations have been detected at nearshore stations of Trabzon (Boran *et al.*, 1998) and decreased with distance horizontally and vertically because of the dilution and biodegradation.

Distribution of Pearson's Correlation Coefficient

Pearson's Correlation Coefficient measures the linearships between two variables and positive correlation indicates that both variables increase or decrease simultaneously whereas negative correlation indicates that one variable increases, so the other decreases. PCC distributions between AS and pH, DO, TSS in surface seawater are shown in Figure 4. AS showed moderate negative correlation with pH (r= 0.6-0.4) and strong negative correlation with DO (r= 0.96-0.87) during autumn-winter respectively, in nearshore (1nmi) surface water (Figure 4). Many

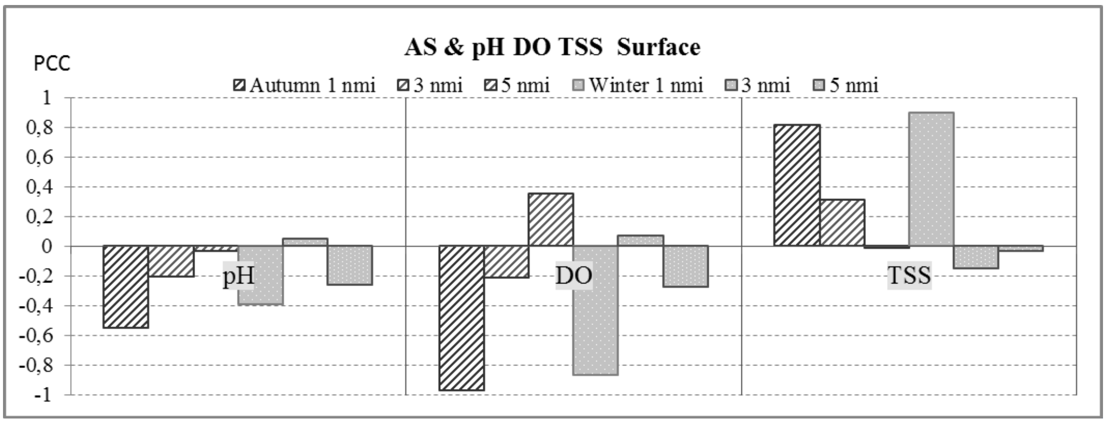

Figure 4. Pearson's Correlation between AS and pH, DO, TSS in autumn and winter in surface sea water.

factors can influence DO and pH in sea water, such as the rate of photosynthesis and respiration, aeration of water (by turbulence or wave action), temperature and some other chemical reactions (e.g. oxidation/reduction) (Stumm and Morgan, 1970). Inverse correlation between AS and pH may be related to sorption of dissolved AS on sediments. Because dissolved AS concentration decreases with increasing sorption as a function of the pH (i.e. increasing H^+activity) which can be attributed to either electrostatic interactions or to specific chemical interactions (surface complexation or ligand exchange) with surface functional groups (Westall *et al.*, 1999). Small variations in pH were observed in this study from 7.65 to 8.35 in autumn and 7.55 to 8.32 in winter, therefore, correlation was not very significant which could be due to presence of some ions such as sodium (Na^+), sulfate (SO_4^{2-}), calcium Ca^{+2}, chloride Cl^- and potassium (K^+) nitrate (NO_3^-) in solution and they tend to limit the mobility of hydrogen ion, thereby decreasing the activity of H^+ (Hach Company, 2010).

Accumulation of AS at the interface of sea water and air could cause to the oxygen depletion by preventing the oxygen diffusion into the sea water. For example; AS was very high near surface water of Yenice R mouth and DO was low 2.9 mg/L in autumn. During winter in surface water of Rize, decreasing trend of AS was observed with distance (from 0.143 mg/L (1nmi) to 0.104 mg/L (3nmi), to 0.072 mg/L (5nmi)) while DO showed increasing trend 8.88, 9.07, 9.18 mg/L, respectively. On the other hand, this trend may be related to also seasonal variations in the action of waves which can cause to both dilution of AS as a function of mixing and to diffusion of more DO from the atmosphere. Similar negative correlation between AS and DO has been observed by Okbah *et al.*, (2013).

Direct relationship was detected between AS and TSS (0.80-0.90). Relations decreased with distance from the shore due to the changing concentrations during transportation. Since, suspended solids settle depending on their particle size i.e. large particles fall rapidly while fine particles settle slowly; during settling through the water column and /or horizontal spreading on the surface, removal processes could cause to decrease in the concentrations of AS. For example, LAS can adsorb on the negatively charged sediment solids after forming a positively charged complex with Ca^{+2} (Westall *et al.*, 1999). González-Mazo *et al.* (1998) observed that the percentage of undissolved LAS increased to 60% at the farthest station, due to association with the particulate matter while dissolved LAS decreased with the distance from the discharged point of the effluent.

Distributions of TOC and C/N Ratios in the Black Sea

Sediment samples taken from the shallow water stations were considered as oxic because the average dissolved oxygen concentration was 8.3 mg/L above the sediment-water interface. TOC varied from 0.18% (Pazar) to 9.73% (İğneada) (Figure 5). Hydrogen and/or nitrogen were found together with organic carbon (except Ereğli sediment) and sulfur was not detected in any sediment samples.

TOC in sediment is considered as an important food or a stress source for the benthic community. The benhtic communities colonize the substrate again as a respond when they exposed to human impacts (e.g. industrial pollution, dredging and deposition mud). TOC in the sediment and the benthic communities are important for ecological quality and so, impaction of benthic communities at different time interval is investigated within the benthic area. TOC in the sediment above 3.5% acts as reducing factor for benthic abundance, biomass and species diversity (Hayland *et al.*, 2005 in Ansari *et al.*, 2014). In the study about the critical points of TOC corresponding to major shifts in the benthic fauna, Ansari *et al.*, (2014) observed that the density and biomass peaked at moderate TOC (<2%) and reduced at TOC (>3%). Albayrak *et al.* (2006) recorded low risks at TOC <0.6%, high risks at TOC >2.2% and intermediate risks between these levels for reduced species' richness and diversity. In typical pelagic sediments, TOC concentrations are less than 1% and according to EMAP-VP four-year assessment analysis (Paul *et al.*, 1999). TOC values between 1 and 3% were associated with impacted benthic communities. EPA (2002) noticed that the thresholds are still under evaluation for TOC in sediments but also recommended the following assessment categories for impaction: Low: $\leq$1% carbon; Intermediate: >1-3% carbon; High: >3% carbon.

So, TOC concentrations in most of the sediments were found in the medium and low organic level, while TOC in four samples were high (Figure 5).

The organic carbon content in bottom-surface sediment depends on sedimentary characteristics, rate of microbial degradation, water column productivity and proportion of terrestrial inputs.

C/N ratio of total organic matter reflects the original proportions of algal and land derived materials and it has been used as a source indicator of organic matter in aquatic sediments. Meyers (1994) observed that most of the organic matters are exposed to destruction and alteration during sinking and sedimentation but C/N ratio and the $\delta^{13}C$ as bulk identifiers of organic matter sources appear to undergo little change. C/N ratio is ranged between 4 and 10 for algae because of the protein content and it was greater than 20 for vascular plant because of the cellulose, lignin and cutin content which are relatively resistant to microbial degradation (Meyers, 1994). Agah *et al.* (2013) reported that TOC ranged from 0.5 to 3.5 % and C/N ranged from 3 to 8 in the bottom-surface sediment due to recent algal bloom. In another study, C/N ratio was $\geq$ 20 for higher plant tissues and

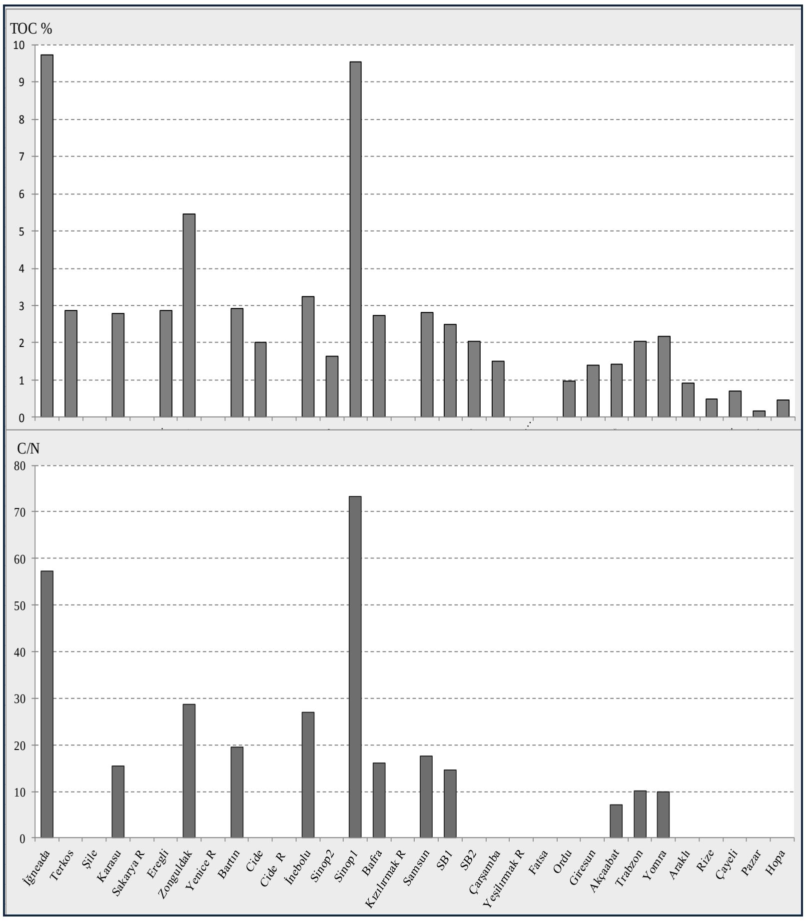

Figure 5. Distribution of TOC (%) (top) in surface sediment and C/N ratios (bottom) along the Turkish coastline of the Black Sea.

about 7, 4, and 10 for plankton, bacteria and fungi respectively (Hedges *et al.*, 1986a in Hedges *et al.*, 1997). The elemental ratio in marine plankton C:N:P is expressed as 106:16:1 by Redfield *et al.* (1963), and Atkinson and Smith, (1983) stated that the C:N ratio of benthic plants is 18 and/or can range from 10 to 70 and pointed out some deviations from the Redfield ratio (6.6) which can be dependent on growth conditions of organisms.

TOC can be formed from decaying natural organic matter (NOM) (e.g. humic acid, fulvic acid, amines, and urea) and from synthetic sources (e.g. detergents, pesticides, fertilizers, herbicides, industrial chemicals, and chlorinated organics). Humic substances (HS) contribute the TOC in the range 40% to 70% in aquatic environment since HS can be derived from terrestrial origin (allochtonous substances) and from biological activities (i.e. degradation of dead organic matter within the water body itself (autochthonous substances) (Frimmel, 2001). So, HS have different C/N ratios due to age and structural differences (hydrophilic- Fulvic acid: FA and hydrophobic- Humic acid: HA) in the original sample: Brown water: FA: 64, HA: 45; Soil seepage: FA: 76, HA: 50; Secondary effluent: FA: 17, HA: 7.4 (Frimmel, 2001).

In this study, C/N ratios were found higher than 15 in the western and middle coasts mostly which could be derived from mixed (allochthonous and autochthonous) sources, while in the eastern part, nitrogen was detected only in the Trabzon samples and the C/N ratios were close to the marine sources.

TOC in the Western Coasts of the Black Sea (Between İğneada and Zonguldak)

In the western part, the highest TOC level was measured at İğneada (9.73%) and C/N ratio was 57. Along the Romanian coast, in the autumn of 2010, TOC levels ranged from undetectable to 14.94% in sediment and higher values were related to the Danube's influence on the Northern coast and to the wastewater treatment plant of Constanta city (Lazar *et al.*, 2012). İğneada is a small district and there is no important wastewater input to the İğneada coast like Constanta city. İğneada has a different ecosystem with rivers, fresh and salt lakes, sand dunes, fresh and salty swamps, different type of trees, endemic plants on the sand-dunes and longos (floodplain) forests (Özyavuz, 2011). The Longos forests are protected by the Erikli and Mert lakes which are typical lagoons and both connected to the sea through the streams during rainy season. Krishna *et al.* (2013) were found the higher C/N ratios in the shelf (range: 9.9-46.6) and indicated that coastal regions receive huge amount of terrestrial OM, detritus of agricultural crops through river discharge from the nearby continents and contribute the sediment content. So, the excess carbon in the İğneada sediment could be related with deposition of degraded plants from forest (allocthonous or terrestrial source) and humic substances (Frimmel, 2001).

The gravel type of sediment obstructed measurement of TOC at Şile station. In Karasu sediment, TOC and C/N ratios were lower than the İğneada station, TOC was not very high for impaction (2.79) but C/N was higher (15.5) than marine plankton which is about 7 (Hedges *et al.*, 1986a in Hedges *et al.*, 1997), indicating the increase of riverine material. This result could be explained by mixing phenomenon as Kennicutt *et al.* (1987) (in Hedges *et al.*, 1997) has observed this relationship in Orinoco delta sediment with C/N ratios for marine samples and a wide range of 15 -30 for terrestrial samples.

Another high TOC (5.5%) and C/N ratio (29) at Zonguldak station is due to high anthropogenic discharges including domestic and industrial waste waters (Tuncer *et al.*, 1998; Bakan and Büyükgüngör, 2000; DEF-Zonguldak, 2010). In addition, high TOC in Zonguldak sediment and the presence of only organic carbon (2.9%) in Ereğli could originate from the deposition of coal dust from the nearby Zonguldak coal basin where bituminous coal is mined and residues are discharged directly into the sea from a coal preparation plant (Ergin *et al.*, 1996). TOC in Ereğli sediment was equal to the TOC of Terkos sediment which had a small amount of hydrogen. Carbon content can be attributed to lignite bed in the Terkos region (MTA, n.d.), because, contribution of coal-derived organic matter to the sedimentary organic matter has been reported as a result of transportation through direct coastal erosion or possibly leaching and/or river run-off from the coal source in the Arctic realm (Svalbard) (Kim *et al.*, 2011).

TOC in the Middle Coasts of the Black Sea (Between Bartın and Çarşamba)

The other highest TOC level (9.54%) (C/N:73) was detected at station Sinop1 (Figure 5) due to the decaying of primary producers and humic matter. Aysel *et al.* (2004) detected highest number of species algae, seagrasses around this region, and contribution of mixture of primary producers such as; phanerogams (e.g. *Z. noltii*, *Z. marina*), benthic macroalgae, microphytobenthos, phytoplankton, to sedimentary organic carbon has been detected as C/N ratio (mean$\pm$SD) 39.6±25.7 for terrestrial plant in watershed and 15.0±2.9 for seagrasses (Dubois *et al.*, 2012). Additionally, Atkinson and Smith (1983) has reported that the C/N ratio could be up to 70. On the other hand, together with decaying of primary producers, humic matter might contribute to the sediment organic carbon content, as a function of transportation through the coastal wave erosion at Sinop peninsula and autochtonously derived matter from biological activities. Because, C/N ratio is reported 76 for FA and 50 for HA in soil seepage (Frimmel, 2001) and HA with high C/N ratios (71.48-87.36) have been detected in the river bottom sediments by Rahman *et al.* (2010). There was no significant difference between TOC values in Sinop and İğneada sediments but higher C/N ratio in the Sinop sediment (Figure 5) could be attributed to preferential nitrogen depletion in N-rich labile compounds (like proteins) during early diagenesis of OM (Krishna *et al.*, 2013).

3.25% TOC was found in Inebolu sediment and C/N ratio (27.1) was similar with the sediment of Zonguldak. TOC value could be related with ore deposits of graphite in the Inebolu region and high flora and forest on the highland (DEF–Kastamonu, 2010). Because of the high vegetation, TOC can be originated from fresh land-drived organic matter which has been reported with C/N ratios 25–35 (Davies and Ghabbor, 1998; Rahman *et al.*, 2010).

TOC concentrations were ranged between 2.5 and 2.9% (Figure 5) in Bartın, Bafra, Samsun and SB1 sediments and C/N ratios were 19.5, 16, 17.6, 14.6 respectively. C/N ratios were not very different but higher C/N ratio in Bartın surface sediment also indicated nitrogen depletion. High C/N ratios in Bartın, Bafra, Samsun and SB1 could be due to terrestrial sources which have been observed with C/N ratios: 17.5-12.1 (Prahl *et al.*, 1994) and could be due to the contribution of the wastewaters (untreated municipal and industrial) which may also contain humic matter (with C/N:17; Frimmel, 2001). High organic matter has been reported (Bakan and Arıman, 2004) and TOC value was similar with this study around the same location in the Samsun Bay. For example, when TOC is calculated from their organic matter content assuming TOM: 1.274 TOC (Schumacher, 2002), TOC content was 2.72 % near fertilizer factory in the Samsun Bay.

TOC in the Eastern Coasts of the Black Sea (Between Ordu and Hopa)

TOC values in the eastern coasts sediments were lower than the other sediment and C/N ratios were obtained in Akçaabat, Trabzon and Yomra sediments as (TOC $\approx$ 2.0 C/N$\leq$ 10) (Figure 5). CN ratio in the sediment of Trabzon may be attributed to the algal blooms, because, high biomass and red tides have been reported as a result of increased nutrient loading along the coast of Trabzon (Feyzioğlu and Öğüt, 2006). Only carbon together with hydrogen detected in the sediment of Yeşilırmak R and eastern part stations of the Black Sea coast (except Trabzon coast) and TOC values varied between 0.18% and 1.5% (Figure 5) at these stations. Carbon and Hydrogen are the main contents of organic material, both plant and animal, and detection of C and H can be related with hydrocarbons which originate from natural (e.g. marine biomass) and anthropogenic sources (spillage of petroleum). Hydrocarbons can be derived from phytoplankton, benthic algae, zooplankton, bacteria and terrestrial plants and have different classes such as aliphatic (alkanes, alkenes), alicyclic, and aromatics (Saliot, 1981). For example, terrestrial n-alkane has been observed from the riverine input in surface sediment (Prahl, 1994). Non-aromatic and aromatic hydrocarbons, aliphatic hydrocarbons (n-alkanes) have been detected in the sediment of the Khniss coast in Tunisia as a result of the petroleum contamination in the region which was attributed to the increased marine activity (Zrafi *et al.*, 2013). Shipping and fishing activities are the common income source in the eastern region; therefore, hydrocarbons might also be originated from petroleum products in this region.

Conclusion

The present study focused on the distribution of AS (LAS) in sea water and TOC in sediment along the Turkish Black Sea coast. Regional and seasonal variations of AS concentrations and river influence were observed significantly at the nearshore stations. AS concentration in sea water mostly changed as a function of the distance from the discharged area, changed by some removal processes and transported by the boundary currents, turbulent mixing and meandering motions. But, AS releases to the environment continuously from anthropogenic sources (domestic, industrial) and not removed exactly because of the structural properties. Most of the measured concentrations of AS were low but in some seawater samples like Yenice R mouth, concentrations were high to be harmful. To prevent the impact to the marine environment, the amount of pollutant discharge containing surfactant must be decreased and wastewater treatment plant must be build. TOC distributions and C/N ratios showed that Southern Black Sea coasts have different sediment structure because of the marine and terrestrial source of organic matter, and anthropogenic sources contributed the organic content of the sediment. TOC results and C/N ratios were not enough to clearly discriminate the dominant sources of organic matter. On the other hand, removal of organic matter from sea water is important for marine environmental risk of AS, therefore, removal from seawater column by precipitation, adsorption, and biodegradation should be further studied. The studies on the effect of surfactants on marine ecosystems are relatively limited along the Turkish coast of the Black Sea. So, the fate and effects assessment of organic matter including surfactants (LAS and others) and source identification for seawater and sediment should be improved with a research program in river and marine environment.

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