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Anionic detergent LAS pollution and discharged amount from Turkish coasts to the Black Sea during 2004-2007

Aniyonik deterjan LAS'ın 2004-2007 yıllarında Türkiye sahillerindeki kirliliği ve Karadenize verilen miktarı

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Abstract

In this work LAS pollution was investigated at 82 stations of Turkish Black Sea coast and discharged LAS amount given to the Black Sea from undercurrent (Mediterranean Sea water) of Bosphorus and rivers of Turkey flow to the Black Sea during 2004-2007.

The maximum LAS levels were measured during the years in the examined area are (μg/l): in 2006 as 82.91, at st.4 (Terkos, west part 1), 136.56 at st.13A (Zonguldak, west part 2) and 86.88 at st.47 (Giresun, east part) and in 2007 as 398.78 at st.13A (Zonguldak). Among the Turkish cities located in the Black Sea coast, the highest level LAS has been found in Zonguldak harbour (st.37A) in 2005, 2006 and 2007. LAS level in the east part (Sinop-Hopa) was found generally lower than west part (Şile-Ayancık) of Turkish coast of the Black Sea.

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The maximum level was found (µg/l) in the cities Giresun (st.47), 86.88, Ordu (st.44) 68.43, Samsun (st.35) 69.49, Hopa (st.62) 71.56 in 2006.

LAS level was found not uniform in investigated area of the Black Sea. Its distribution strongly affected by sea current. There are two currents in the Turkish straits; Bosphorus, Sea of Marmara and the Dardanelles. Upper current carries the Black Sea water directed to the Sea of Marmara then the Aegean Sea/Mediterranean Sea. The sewage of Istanbul city is dumped from various plants into undercurrent of Mediterranean Sea flow to the Black Sea via Bosphorus. The quantity of undercurrent water is an average 193 km^3 per year. The maximum amount of LAS found in undercurrent Bosphorus was (µg/l): 63.56 in 2004, 36.5 in 2005, 118.77 in 2006 and 101.92 in 2007.

Discharged LAS amount was estimated to the Black Sea from the undercurrent of Bosphorus as: 12352 t/y in 2004, 7044 t/y in 2005, 22774 t/y in 2006 and 19686 t/y in 2007. From the Turkish rivers as: Sakarya 225 t/y, Bartın 148 t/y, Kızılırmak 122 t/y and Yeşilırmak 168 t/y. Total LAS amount was estimated to be 20349 t/y from Turkish part to the Black Sea in 2007.

When the pollution level between the monitoring years is compared and the year 2006 (except as st.13 in 2007) is found highest in all examined stations.

In this investigation, the loss of LAS was also studied during sampling and analysis date and found that the loss reached after 5 days of sampling up to 60% and after 10 days 80%. These findings showed that the determination of LAS must be done immediately just after the sampling.

This study is a first record for the detergent pollution in Turkish Black Sea coast and LAS amount given from Turkey to the Black Sea.

Keywords: LAS level, Turkish Black Sea coast, undercurrent of Bosphorus and rivers.

Introduction

The term of detergent came from de-tergeo, pp.-tersus to wipe off. Detergents are composed of mainly surface active agents (surfactants) and other additives as inorganic builders, water softener, whitening agents, optical bleaches etc. Inorganics contain soda, sodium metasilicate, condensed phosphates (trisodium phosphate, sodium pyrophosphate, glassy phosphates, metaphosphates), sodium

carboxymethylcellulose, ethylenediaminetatracetic acid (EDTA) salts etc.

The surfactants were divided into four groups: 1-Anionic, 2-Cationic, 3-Nonionic, 4-Amphoteric.

1-Anionic detergents: In this group linear alkylarylsulfonates are dominant. Especially LAS is degraded easily.

2-Cationic detergents: They are quaternerammonium salts (alkylbenzyl dimethylammonium chloride) used as tallow textile softener. They are stable compounds.

3-Nonionic detergents: 4-nonylphenol polyethoxylate (mixture of 4-nonylphenol mono, di, triethoxylate). Their alkyl chain was degraded but not aromatic ether band (Scott and Jones 2000). It used in liquid detergent products and softeners in a concentration of 5-15%.

4- Amphoteric detergents: This group compounds contain anionic and cationic group in the same formula and degrade well under aerobic conditions.

Surfactants are biologically active substances. They are also toxic compounds and cause hemolysis, skin and eye irritation, enzyme inhibition. Cationic detergents show herbicidal activity and highly toxic for anabaena, mollusks, ascarides and bacteria. The degradation products of surfactants can also be toxic. As an example Nonylphenol (NP) is a degradation product of nonionic detergent which is very toxic.

The detergent affects on marine life. Its film covers on surface water and prevent entrance penetration of oxygen to sea from air. On the other hand, the content of phosphate ions causes eutrophication.

The characteristic of surfactant is surface tension depression. It forms a mono molecular layer over surface and alters the relationship between surface tension and area. Thus, LAS in water rises to the surface from the depth and accumulate on the surface and disperses by environmental conditions as wind and current of water (Gonzales-Mazo and Gomez-Para 1996).

LAS is widely used as anionic surfactant. Commercial LAS (linear alkylbenzene sulfonate) is not a unique compound. It is a complex mixture containing approximately 26 isomers and homologues with the general structure of $R^1.C_6H_4SO_3Na$ (R^1 Alkyl chain). The exact composition of commercial LAS is not clearly known.

LAS was characterized by a lipophilic moiety and hydrophilic sulfonic acid group. It is not stable in marine environment (Swisher 1963, Visoottiviseth et al. 1988, Wakabayashi et al. 1989, Okpokwasili and Olisa 1991, DeFerrer et al. 1991, Terzic et al. 1992, Han and Yang 1992, Guckert et al. 1996, Perales et al. 1999) and is degraded approximately in 20 days (Hon-Nami and Hanya 1980, Koç et al. 2002, Güven et al. 2008).

The many inconvenient, the determinations of surfactants are important. The determination of surface active agents are generally made on the measurement of anionic surfactant (LAS) and rarely for nonionic detergent as degradation products of nonyl phenol, but not cationic or other surface active agents.

Various methods were proposed to determine anionic detergent, LAS concentrations in town water, rivers and seawater. LAS determination is based on generally spectrophotometric methods (MBAS) (Standard Methods 1995) using commercial LAS reference material.

In MBAS (Methylene Blue Active Substances) method, the complex formed between methylene blue (MB) with LAS has blue color and it is soluble in chloroform thus its concentration can be determined by measuring the absorbance at λ_{max} 652 nm. Another spectrophotometric method is proposed by Güven et al. (1994). It is based on metachromasy (Akıncı and Güven 1997, Bektaş and Güven 2004). In this method similarly to MBAS method a complex is formed between a metachromatic dye and LAS. It is soluble in chloroform and the absorbance can be measured at metachromatic β band (590-600 nm) and also λ_{max} of dye α band (637-652 nm) as MBAS method. Both methods gave the similar results. The other methods used in this subject are: IR (Hellman 1979); GC/MS (Hon-Nami and Hanya 1978, 1980, Raymundo and Preston 1992, HPLC (Terzic et al. 1992, Terzic and Ahel 1993,

Marcomimi and Giger 1997, Koç et al. 2001) and AAS (Crips et al. 1978).

MBAS method is relatively simple but some substances such as organic sulphonates, sulfates, carboxylates and phenols and inorganic substances as thiocyanates, cyanates, nitrates, chloride and sulfate may transfer more or less methylene blue into the chloroform phase (Srivastava et al. 1977). They called positive and negative interferences with the organic and inorganic substances. The aqueous back wash step removes these positive interferences. The negative interference was due to the presence of cationic surfactants, other cationic materials and particular matter. The latter was eliminated by filtration. The presence of sulfides in wastewater may react with methylene blue to form a colorless reduction product. The salinity of the water is also a major factor the measurement of LAS by MBAS method in marine environment (Standard Methods 1995, Marcomimi et al. 1987, Hon-Nami and Hanya 1980, Gonzales-Mazo and Gomez-Para 1996, Scott et al. 2000, Çetintürk and Güven 2003, published in 2009, Güven and Cumalı 2007). Thus the determination of anionic detergents with methylene blue depends on the pollutant of seawater and results vary depending on the pollution of sampling regions.

The determination made also on C_{11}, C_{12} content of LAS but it does not correspond to the total LAS pollution level in examined area while its alkyl chain length and the position of the benzene ring were not the same in all LAS products.

The surfactants in seawater are not distributed uniformly. Its distribution is strongly affected by wind conditions, sea current and surface activity properties. This problem is also important for the Turkish Black Sea side.

The first oceanographic observation of the current in Bosphorus was done by Marsilli (1681) and later Makarov in 1881-1882 (cited by Vyazilov and Mikhailov 1999) owing to which the existence of the two layers current was established. A comprehensive study in this area was made in 1917-1918 by Merz (1919, 1922) and calculated upper and undercurrent of Bosphorus sea water amount as 313 km^3/y for upper

current towards Sea of Marmara and 193 km^3/y for under current in opposite direction. The level of LAS was also affected by water circulation between these currents.

The rivers flow into the Black Sea also contains detergent from sewage of the cities. The flow rates of Turkish rivers flow to the Black Sea are: Sakarya 5.6 km^3/y, Kızılırmak 5.90 km^3/y, Yeşilırmak 5.30 km^3/y (Jaoshvili 2007); Bartın River 25 m^3/sec. Istanbul city sewage (762000000 m^3/y) is discharged into undercurrent of Bosphorus (Mediterranean Sea water) via Bosphorus and Sea of Marmara.

There are not found a new literature on the detergent pollution of the Black Sea. Earlier reports are summarized as: 48000 t/y of detergent flow from the rivers (Zaitsev 1992), from the Danube River in 1995, 20000 t/y (Fashchuk and Shaporenko 1995) and in 1983-1987, 3.6 thousand t/y (Mandych and Shaporenko 1992); from the Dnieper in 1983-1987, 13.9 thousand t/y (Mandych and Shaporenko 1992). Detergent in flow to the Black Sea from Crimea coast as 5.2 t/y in 1989, Anapa-Sochi 24.4 t/y in 1999 (Fashchuk and Shaporenko 1995).

Surfactant concentrations were also determined by various authors as: in Dnieper 25 mg/l (Fashchuk and Shaporenko 1995), Yalta region 1991 up to 100 µg/l area 50-450 µg/l, sea shore and open and Alusta 30 µg/l cited by Polikarpov (1991), in Danube River > 100 µg/l, and in the Danube River adjacent area > 1200 µg/l (Mikhailov 1992), Odessa 520 µg/l, Anapa 25 µg/l, Novorossiysk 25 µg/l, Sochi 26 µg/l, Batumi 220 µg/l (Fashchuk and Shaporenko 1995).

In this paper, the level of LAS in the Turkish Black Sea coast and discharged of LAS amount from Turkish side of the Black Sea is reported.

Materials and Methods

Sea water samples are taken from the Black Sea coasts of Turkey during 2004-2007 by R/V Arar, Istanbul University.

LAS (98%) was supplied by Lever, Izmit, Turkey. Solvent and chemicals were Merck (Darmstadt) product.

The sampling stations in Turkish Black Sea coasts are shown in Figure 1 and its coordinates in Table 1.

Table 1. The coordinates of sampling stations

Station	Latitude	Longitude	Station	Latitude	Longitude
1	41,87042	28,05885	**34**	41,301567	36,34658
2	41,86417	28,11385	**35**	41,34692	36,38852
3	41,8259	28,6058	**36**	41,37652	36,41212
4	41,36845	28,62488	**37**	41,39357	36,65402
5	41,389	28,64668	**38**	41,42038	36,65197
6	41,58638	28,84902	**39**	41,42038	36,65197
7	41,19253	29,5939	**40**	41,0357	37,50253
8	41,23718	29,60333	**41**	41,06695	37,52507
9	41,34232	29,64693	**42**	41,06768	37,52805
10	41,14495	30,62908	**43**	40,99665	37,88333
11	41,1679	30,64085	**44**	41,0196	37,90825
12	41,17763	30,64368	**45**	41,07037	37,99925
13	41,46018	31,77185	**46**	40,9228	38,4019
14	41,46813	31,77563	**47**	40,93335	38,41165
15	41,50182	31,77263	**48**	40,94437	38,4116
16	41,58753	32,04418	**49**	41,08595	39,37027
17	41,59063	32,05052	**50**	41,08872	39,3675
18	41,6064	32,03577	**51**	41,09693	39,36122
19	41,68965	32,21883	**52**	41,00585	39,74318
20	41,69222	32,21877	**53**	41,01577	39,73447
21	41,69592	32,21653	**54**	41,03047	39,72583
22	41,98807	33,7814	**55**	41,0345	40,54113
23	41,99847	33,786	**56**	41,0469	40,53477
24	42,08255	33,78638	**57**	41,05687	40,53258
25	42,06513	34,91758	**58**	41,19387	40,90417
26	42,08277	34,90598	**59**	41,20152	40,90402
27	42,13868	34,86482	**60**	41,21063	40,90573
28	42,01722	35,15623	**61**	41,42323	41,4292
29	42,00542	35,16623	**62**	41,42403	41,42177
30	41,99848	35,3152	**63**	41,424033	41,42177
31	41,74632	35,95893	**E1**	41,27385	31,39905
32	41,74323	35,95595	**E2**	41,28752	31,37367
33	41,75322	35,94557	**E3**	41,31438	31,32677

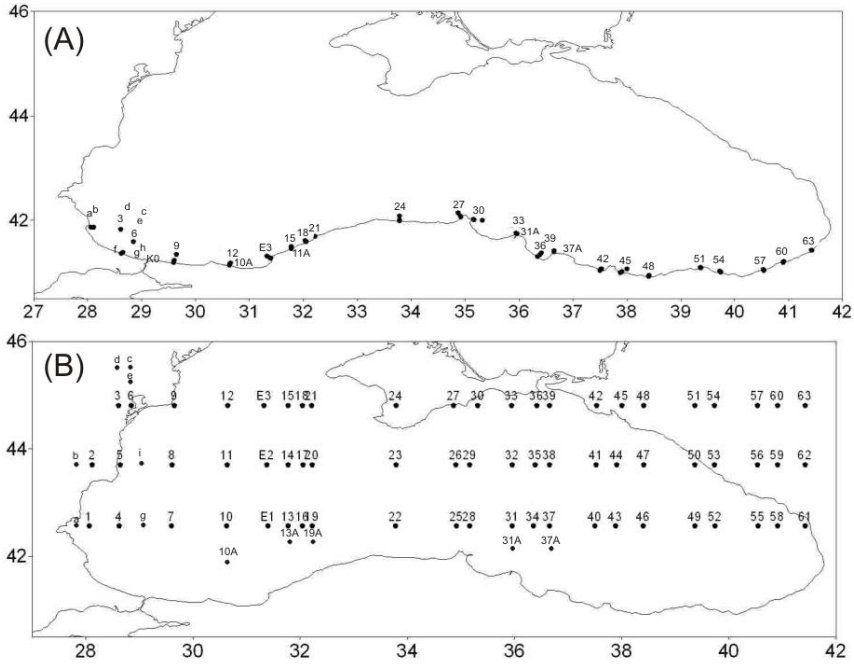

Figure 1. The sampling stations in Turkish Black Sea coasts. The stations are chosen on the lines following depth contours of 10, 50 and 100 meters. The real locations with the original coordinates are shown in Figure 1a and Figure 1b shows the extended illustration of the station distribution.

Sampling dates in 2004-2006 are: September 2004, April and October 2005, April 2006, and September 2006. The sampling dates in 19-26 September 2007 are for st.1-12, and E1-E3, in 20-30 September 2007 for st.13-33 and 1-4 October for st.34-63 (st: station, E: Ereğli).

Calibration curve of LAS (Standard Method 1995)

The calibration curve of LAS was plotted in a concentration of 20-150 µg/l in distilled water. 800 ml sample was taken and alkalinized with 0.1N NaOH (Reagent 5 drops of phenolphthalein solution) then acidified by 0.1 N H_2SO_4. After addition of 25 ml methylene blue solution (1/1000) it was extracted 3 times with 30 ml of chloroform. The organic phases were combined and shaken with 50 ml wash solution (6.8 ml conc. H_2SO_4, 50 g NaH_2PO_4 in 1000 ml distilled water) then filtered. The volume of filtrate was adjusted to 100 ml with chloroform. The calibration curve was plotted in a spectrophotometer (Shimadzu UV 1601) at 652 nm against pure chloroform. The correlation equation was calculated from three calibration curve equations.

Measurement of LAS in sea water

3 l seawater sample was taken and divided to three portions and applied on each 800 ml sample the method described in calibration curve. The amount of LAS in the samples was calculated using three correlation curve equations.

Results and Discussion

The correlation equation is: $y= 0.038x+0.011$ $r^2= 0.991$

The Black Sea coast of Turkey was investigated in three parts:

1. West part 1 European side of Turkish Black Sea coast
1.1. st.1-6 (1a)
1.2. st.a-k (1b)
1.3. st.K_1-K_3 (1c)
2. West part 2 Anatolian side Şile–Ayancık
3. East part (Sinop–Hopa)

1. *The results of LAS level in the west part 1 of the Turkish Black Sea coast at the st.1-6 (1a), st. a-k (1b) and st.K_1-K_2-K_3 (1c) are shown in Table 1a.*

1.1. The results of LAS pollution in the st.1-6 are shown in Table 1a.

Table 1a. LAS concentration as station no.1-6 (µg/l).

st. / year	1	2	3	4	5	6
2004	14.80 (S)	10.73 (S)	9.260 (S)	8.380 (S)	13.26 (S)	15.18 (S)
2005	19.66 (A)	18.39 (S)	21.29 (A)	19.21 (A)	17.38 (A)	15.14 (A)
2006	42.51 (S)	43.26 (S)	52.60 (S)	82.91 (S)	33.40 (S)	63.43 (S)
2007	32.70 (O)	26.44 (O)	26.87 (O)	35.29 (O)	37.63 (O)	28.21 (O)

st.: stations, A: April, S: September, O: October

The LAS concentration was varied as (µg/l): at st.1-6 in 2004: 9.26-15.18, in 2005: 15.14-21.29, in 2006: 33.40-82.91, in 2007: 26.44-37.63.

As can be seen in the Table 1a, the pollution of LAS is the highest in 2006.

1.2. LAS pollution level in st. a-k are shown in Table 1b.

These stations were only monitored in 2004.

Table 1b. LAS concentration in the station (a-k) of west part 1 of the Black Sea in 2004, June.

st.a	st. b	st. c	st. D	st.e	st. f	st.g	st.h	st.i	st. j	st.k
37.22 (D)	42.98 (D)	30.4 (50m)	19.48 (T)	29.45 (T)	36.06 (S)	31.85 (D)	52.0 (D)	42.0 (10m)	25.92 (D)	54.14 (40m)

st: stations, S:Surface, T: Thermocline, D: Deep

The concentration of LAS in 2004 is high at st.k as 54.14 µg/l at 40 m at deep. This station was not monitored in 2005 and 2006.

1.3. The concentration of LAS at the station of K_1, K_2, K_3 (near the Bosphorus) during 2004-2007 are shown in Table 1c.

These stations are important while they situated approximately 15 km far from the northern entrance of Bosphorus. Istanbul city sewage

discharged in undercurrent water (Mediterranean Sea) flow to the Black Sea from the northern entrance of the Bosphorus (st.K_0)

There are 7 physical and 5 biological treatment plants in Istanbul city. Two of them outfalls directly into the Black Sea and the others discharge to undercurrent (deep water, Mediterranean Sea in the Sea of Marmara and Bosphorus).

Table 1c. The range of pollution level at west part 1 st. K_1, K_2, K_3 stations in the Black Sea during 2004-2007 (μg/l).

Station / Year	K_1		K_2		K_3	
	D	T	D	T	D	T
2004	25.50-46.02	27.70-47.60	13.22-71.50	-	15.18-22.95	-
2005	28.43-46.16	-	21.80-56.40	-	14.90-25.89	-
2006	12.38-119.79	27.70-91.73	23.64-147.50	22.43-60.78	24.75-66.98	-
2007	34.94-73.17	36.54-83.53	24.24-133.49	22.05-90.65	22.69-62.69	-

D: Deep, T: Thermocline

These stations (K_{1-3}) were monitored in all months of years. In the Table 1c only the minimum and maximum pollution results are shown.

The highest level of LAS at deep water was found in these stations in 2006 as (μg/l): at K_1 119.759; at K_2 147.50, at K_3 66.98.

In the Table 2 shows LAS pollution is the highest in 2004. Interestingly the amount of LAS is similar at thermo cline in all experimented years.

4. *The concentration of LAS at surface water of the west part 1 of Turkish Black Sea coast (Anatolian sides) in 2004-2007 at st.7-30 (between Şile-Ayancık) are shown in Table 2.*

Table 2. LAS amount at surface water of the st.7-30 (between Şile-Ayancık) during 2004-2007 (µg/l).

Year / Stations	Sept.04	April 05	Oct.05	April 06	Sept.06	Oct.07
1	14.81	19.66	18.41	26.86	42.51	32.70
2	10.73	16.18	18.39	15.79	43.26	26.44
3	9.26	21.29	18.76	9.39	52.60	26.87
4	8.38	19.21	15.93	14.10	82.91	35.29
5	13.26	17.38	11.65	16.14	33.30	37.63
6	15.18	15.14	11.21	8.60	63.43	28.91
7	11.76	9.86	10.63	18.21	68.86	30.04
8	19.81	19.66	13.24	16.55	39.13	38.06
9	6.40	23.54	10.31	21.18	42.38	39.09
10	15.48	17.73	12.65	10.21	34.94	24.29
10A	-	4.24	-	-	40.21	31.53
11	21.89	17.35	9.43	15.20	36.61	33.21
12	10.42	15.31	10.96	15.31	40.63	29.38
13	12.16	24.93	22.15	21.84	103.50	36.40
13A	-	-	70.20	14.73	136.36	398.78
14	9.11	11.55	11.24	18.59	69.92	30.34
15	14.75	9.31	7.98	10.35	60.11	35.32
16	8.68	9.08	9.80	7.98	51.29	26.29
17	7.31	9.70	7.98	9.89	44.20	27.50
18	10.36	9.90	9.70	17.33	91.13	41.23
19	14.81	15.00	7.09	13.01	63.64	31.18
19A	-	-	43.81	21.21	26.42	44.13
20	8.89	10.31	9.59	20.48	79.97	23.16
21	10.64	12.55	7.05	21.76	42.13	35.28
22	8.59	21.88	7.43	5.60	37.59	36.26
23	10.18	38.29	6.68	9.98	32.82	29.02
24	10.45	14.63	5.81	19.10	35.81	35.39
25	20.70	17.59	9.21	13.08	49.50	31.25
26	13.32	18.63	16.35	16.45	36.37	30.62
27	9.78	13.28	10.53	18.90	57.21	40.49

The highest LAS amount in surface water (except of river mouth and st. 37A) was found as (µg/l): 20.70 in 2004 September at st.25, 38.29 in 2005 April at st.23, 103.50 µg/l in 2006 September at st.13 and 91.13 µg/l in 2007 at st.18, 41.23 µg/l in 2007 at st.18.

5. *LAS concentration in east part of the Black Sea Turkish coast in surface water during 2004-2007 at st. 31-63 (Sinop-Hopa) are shown in Table 3.*

Table 3. LAS concentration in surface water of the Black Sea stations no. 31-63 (between Sinop-Hopa) during 2004-2007 (µg/l).

year / st	Sept.04	April 05	Oct.05	April 06	Sept.06	Oct.07
28	7.40	10.63	15.49	11.90	37.14	29.10
29	12.31	17.63	15.51	16.65	31.46	28.32
30	5.82	9.90	13.90	8.33	42.38	25.39
31A	-	-	4.89	3.00	20.76	15.76
32	10.64	8.21	20.29	3.00	21.19	23.39
33	9.72	11.65	20.43	6.46	26.80	33.21
34	12.92	14.90	20.66	11.45	51.15	30.94
35	13.99	14.59	25.48	3.24	65.49	27.27
36	7.34	11.45	35.66	10.96	52.91	28.95
37	5.57	7.98	17.18	8.33	31.67	52.19
37A	-	-	5.40	-	31.70	42.92
38	19.51	11.90	22.74	11.31	39.34	44.32
39	10.51	5.81	22.95	0.34	31.32	24.25
40	5.73	16.38	19.66	8.01	28.79	30.71
41	9.17	7.66	25.69	13.73	24.41	32.12
42	12.13	6.71	31.04	10.28	28.70	30.51
43	13.04	12.08	14.83	22.25	31.53	37.75
44	7.65	13.90	23.05	12.18	68.43	37.87
45	8.01	12.10	24.93	13.45	45.11	34.27
46	8.90	29.13	26.00	14.83	74.69	27.81
47	11.40	8.66	18.76	13.69	86.88	34.50
48	18.81	12.51	32.46	13.10	38.50	29.93
49	12.80	12.69	22.15	9.45	36.44	32.24
50	19.39	10.96	17.79	13.86	22.54	33.49
51	18.35	15.55	20.39	9.18	25.27	37.16
52	21.21	32.39	19.00	14.83	22.75	27.15
53	14.66	11.51	13.28	12.93	33.90	27.11
54	11.76	10.49	16.21	11.08	50.55	35.17
55	9.69	28.60	17.86	16.83	30.52	31.75
56	9.51	12.96	12.86	19.14	27.81	29.77
57	9.78	8.01	16.41	17.21	22.30	30.94
58	7.01	7.05	13.28	15.51	23.30	36.50
59	9.57	7.29	21.08	15.83	31.16	33.29
60	15.27	9.66	22.70	16.73	29.99	38.61
61	13.14	7.84	15.49	14.93	66.87	19.48
62	12.40	10.28	13.73	16.76	71.56	24.84
63	28.84	8.43	16.94	16.10	69.32	22.30
E1	-	-	-	-	-	20.54
E2	-	-	-	-	-	27.85
E3	-	-	-	-	-	32.78

St.:Stations, E: Ereğli, Sept: September, Oct. October.

The highest LAS concentrations were found in these stations are as follows: at st3: 28.34 µg/l in September 2004, at st.36: 32.46 µg/l in October 2005, at st.47: 86.88 in September 2006, at st.36: 52.19 µg/l in October 2007.

6- LAS amount at mouth of Turkish rivers flow to the Black Sea.

The level of LAS concentration in rivers as:

Sakarya River (10A) 4.24 µg/l in 2005 April 40.21 µg/l in 2006 September 31.53 µg/l in 2007 September.

Bartın River (19A) 45.51 µg/l in 2005, 26.42 in Sept 2006, 44.13 µg/l in 2007.

Kızılırmak (31A) 4.89 µg/l in 2005 October, 20.76 µg/l in 2006 September, 20.58 µg/l in 2007 September.

Yeşilırmak (37A) 5.40 µg/l in 2005 October, 31.70 µg/l in 2006 September, 42.92 µg/l in 2007 September.

When compared the results of LAS amount in the rivers of Turkey, the pollution level was increased in the years to 2007.

7- The highest of LAS concentration in the cities of Turkish Black Sea coast are:

Zonguldak (13 A), 70.20 µg/l in 2005, 136.36 µg/l in 2006, 15.76 µg/l in 2007.

Cide, 43.81 µg/l in 2005, 26.42 µg/l in 2006, 44.13 µg/l in 2007.

The highest pollution of LAS was found in Zonguldak city.

The range of pollution level at K_0 station in 2004-2007 as (µg/l): in 2004, at deep water 14.11- 63.56, in thermocline 16.22- 45.80, in 2005 at deep water 15.59- 36.57, in thermocline 14.28- 39.44, in 2006 at deep water 18.14- 118.27, in thermocline 29.72- 133.64, in 2007 at deep water 30.77-101.92, in thermocline 19.50-96.92 µg/l.

8. The discharged LAS amount to the Black Sea from Turkey.

8.1- LAS amount discharged into undercurrent of Bosphorus (at st K_0, deep water, Mediterranean Sea) via Dardanelles, Sea of Marmara.

The LAS concentrations at deep water of K_0 station (Northern entrance of the Bosphorus) flow to the Black Sea were calculated: in 2004, 63.56 µg/l /l, in 2005 36.57 µg/l, in 2006 118.00 µg/l, in 2007 102.00 µg/l.

Outflow from the under current, Mediterranean Sea water via Bosphorus to the Black Sea in the rate of 193 km^3/y.

It was estimated that LAS amount discharged to the Black Sea via under current (including LAS content of Aegean Sea/Mediterranean Sea, Dardanelles, Sea of Marmara and Bosphorus) is: 12352 t/y in 2004, 7044 t/y in 2005, 22774 t/y in 2006 and 19686 t/y in 2007 and from the rivers Sakarya 225 t/y, Bartın 148.54 t/y, Kızılırmak 122 t/y and Yeşilırmak 168 t/y.

Thus total LAS amount was estimated as 20349 t/y from Turkish side to the Black Sea.

Conclusion

The highest detergent pollution levels were found:

1. In west part of Black Sea coast of Turkey st.1 at surface water 36.06 µg/l in June 2004. 54.14 µg/l at 40m, in 2006 at st.4 (Terkos) 82.91 µg/l and at st.7 (Şile) 68.86 µg/l.
2. In the stations at K_1, K_2, K_3 detergent pollution was found 80.29 µg/l at surface water and 47.76 µg/l at deep water.
3. Between Şile-Ayancık the amount of LAS at surface water as 398.78 µg/L in 2007 at Zonguldak, 57.21 µg/l in 2006 at Ayancık.
4. In the east part (Sinop-Hopa) of the Turkish Black Sea coast the LAS pollution was in September 2006 at st.36 (Samsun) 65.49 µg/l, at st.45 (Ordu) 68.43 µg/l, at st.48 (Giresun) 86.88 µg/l, at st.54 (Trabzon) 50.55 µg/l, at st.55 (Rize) 30.52 µg/L, at st.61 (Hopa) 71.56 µg/l.
5. The LAS concentration was varied in the surface water of Turkish rivers flow into the Black Sea as: Sakarya (10A) 40.21 µg/l in 2005, 31.53 µg/l in 2007, Bartın (19A) 43.81 µg/l in

2005, 44.13 µg/l in 2007, Kızılırmak (31A) 20.76 µg/l in 2006, 20.58 µg/l in 2007, Yeşilırmak (37A) 31.70 µg/l in 2006, 42.92 µg/l in 2007. Pollution level in rivers were increased during the years.

6. When the west and east part of Turkish coast cities are compared Zonguldak was found to be the most polluted.
7. Calculation of LAS amount discharged to the Black Sea from Turkish coast is in 2007, 20349 t/y.
8. Finally, the LAS concentration in the Black Sea stations was increased in 2004 to 2006 and then decreased in 2007.
9. The loss of LAS during the transportation of the samples is important and analysis must be made immediately after the sampling.

Özet

Bu çalışmada Karadeniz'in Türkiye sahillerinde 82 istasyonda anyonik deterjan, LAS kirliliği miktarları incelenmiştir. Türkiye geçitlerinde, İstanbul Boğazı, Marmara Deniz'ine ve oradan Çanakkale Boğazında iki ayrı deniz suyu akıntısı vardır. Bunlardan biri üst su olup Karadeniz'den, İstanbul Boğazı üzerinden, Marmara Denizi ve Çanakkale Boğazından Ege ve Akdeniz'e akar. Alt su ise Çanakkale Boğazı, Marmara Denizi'ne İstanbul Boğazından Karadeniz'e geçen Akdeniz suyudur. Bu araştırmada Karadeniz'e giden Akdeniz suyunda (İstanbul, Çanakkale ve Marmara Denizi şehirlerinden ve Akdeniz'den gelen sudaki dahil) LAS miktarı 2004 yılında 12352 t/y, 2005 yılında 7044 t/y, 2006 yılında 22774 t/y, 2007 yılında 20349 t/y hesaplanmıştır.

Karadeniz Türkiye şehirleri arasında en yüksek LAS miktarı Zonguldak limanında bulunmuştur. İncelenen yıllar arasında en kirli yıl da 2006'dır.

Kirlilik açısından Batı ve Doğu Karadeniz mukayesesinde kesin bir hükme varılamamıştır. Karadeniz'de LAS miktarı 2004'den 2006'ya yükselmiş, 2007'de ise biraz düşmüştür.

Diğer bir bulguda LAS tayininin bekletmeden yapılması ile ilgilidir. Örneklemeden 5 gün sonra yapılan tayinde LAS kaybının % 56, 10 gün sonra

ise %80 olduğu saptanmıştır. Bu sonuçlara göre LAS tayininin örneğin alınmasından hemen sonra yapılması gerekliliği saptanmıştır.

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