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Linear Alkylbenzene Sulfonates in the Groundwater and Surface Waters: Ergene Basin Case Study

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Abstract: Ergene Basin is one of the most important industrial centers due to the geographical location in Turkey. Uncontrolled and rapidly increasing industrialization brings together a large number of environmental problems in the basin. In this study, pollution was investigated in the water samples taken at time intervals and different parts of groundwater and surface water resources located within Ergene Basin by methylene blue anionic surfactants (MBAS) analysis method. Turbidity, temperature, pH, electrical conductivity (EC), concentrations of total P and linear alkylbenzene sulfonates (LAS) were simultaneously determined in the investigated water resources. The results were compared with the Turkish Water Pollution Control Regulation specified in the Quality Criteria of the Inland Water Resources according to their class. The total P and LAS concentrations of surface waters are generally higher than groundwater. In terms of LAS concentrations, the groundwater is I-II class and the surface water is II-IV class.

Key words: Surface water, groundwater, surfactant pollution, linear alkylbenzene sulfonates, methylene blue anionic surfactants.

1. Introduction

Recently, the contamination of aquatic environments with organic compounds (e.g., pharmaceuticals, surfactants, endocrine disruptors and polymers) has become the focus of increasing regulation and public concern due to their potential, but still unknown, negative effects on the wildlife that inhabit these ecosystems [1].

Many aquatic systems are subjected to the influence of both urban and industrial wastewater discharges, which are among the main sources of organic contaminants in the environment. Among many other chemicals, synthetic surfactants can be found at relatively high concentrations in wastewater due to their extensive use in a wide variety of applications: paints, pesticide formulations, wetting agents, personal care products and especially, active ingredients of detergents in cleaning products [2].

Anionic surfactants are widely used in both domestic and industrial applications, particularly in laundry detergents. Since, by the nature of their uses, they are destined to be discharged to wastewater, the major surfactants have been extensively studied in term of their environmental properties, including biodegradation characteristics and toxicity to aquatic organisms [3].

Urban wastewater discharges and industrial activities were identified as the main sources for these compounds. Once used, surfactants are discharged via wastewater treatment plants (WWTPs) into aquatic environments [4]. They may enter the aquatic environment when raw or partially treated sewage is discharged [5]. In urban areas of the developing world, poor provision of wastewater treatment means that municipal and household wastewater is discharged directly to receiving waters. The largest group of anionic surfactants is linear alkylbenzene sulfonates (LAS) [6].

LAS are commonly contained in detergent waste. As an anionic surfactant, LAS consists of hydrophobic and hydrophilic group bearing negative charge [7]. Likewise, LAS is one of the most common organic chemicals used in personal care products. Due to its

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widespread use, it has been detected at 5 μg/L [8] in groundwater, 14-155 μg/L [9], 11-342 μg/L [6], 2.3-2,406.8 μg/L [10] in river water and 124 mg/kg [1] in sediment.

As the fast industrial development in the Ergene Basin, the organic chemicals pollution is common. There are mainly textile factories, white goods, glass, oil, food and chemical factories [11]. These factories in the basin discharge their waste into the Ergene River and its branches. These activities, as well as population growth, have substantially increased the burden of contamination. Therefore, the environmental quality in aquatic system of the Ergene River has direct and significant effects on drinking water safety of the city, stability and biodiversity of the aquatic ecosystem and so on.

No studies have been reported on the Ergene Basin on the subject of surfactants pollution. Surface water and groundwater in the basin are constantly subject to pollution caused by the rapid increase in population and the intensity of agricultural and industrial activities. Monitoring of surface waters and groundwater is necessary to establish the levels of contamination in terms of surfactants. Further study of the surfactant pollution is needed to uncover contamination profile in the basin.

The present study aimed to investigate the seasonal changes in some physical-chemical properties of surface waters and groundwater in the Ergene Basin, and determine the concentration and distribution of LAS in surface waters and groundwater in the Ergene Basin.

2. Materials and Methods

2.1 Study Area

Ergene River basin is located on the Northwest of Turkey at the Thrace Region. Three provinces are located in the basin. Being the largest industrial settlement in the south section of the Ergene River basin, Tekirdağ plays a key role not only in storing water, agricultural irrigation, water supply and climatic regulation, but also in producing a good deal of marketable grain and fishing. One of the main activities in the city is agriculture. Agricultural products, such as cereals and sunflower, are the most frequently cultivated [11]. In addition, uncontrolled industrial development, population growth and migrations in the basin have enriched water resources in terms of organic chemicals.

2.2 Sampling and Sample Preparation

Seasonal water samples were taken at three sampling sites and six samples were taken from each site. March, April and May samples were taken in 2014. October, November and December samples were taken in 2015. Samples of the stream-surface microlayer and groundwater were collected along the Çerkezköy (C), Muratlı (M) and Uzunköprü (U), which are richer with anthropogenic activities than the north of Ergene River basin (stations C, M and U), as shown in Fig. 1.

Samples which were put in the acid-rinsed polyethylene containers were immediately taken to the laboratory. Field water sampling and measurements followed standard methods [12]. All chemicals were used of the highest purity available (Merck), and all glassware and laboratory equipment were carefully cleaned before using with HCl to minimize potential contamination.

Water samples were collected by using sample bottles of 1,000 mL for surfactants and 500 mL for physical-chemical parameters. The samples were stored at +4 °C until they were analyzed. Samples were analyzed for five physicochemical parameters: temperature, pH, electrical conductivity (EC), turbidity, total P and surfactant (LAS).

The samples were collected in plastic bottles and brought to the laboratory where filtered. Temperature, pH and EC were measured directly after collection. They were also monitored in the samples using a multi-parameter measurement instrument (WTW 3430) after appropriate calibrations with standard buffer solutions. Values of turbidity were measured using

Fig. 1 Map showing samples taken from groundwater and surface waters.

turbid meter (VELP SCIENTIFICA-TB1). Physical-chemical properties and total P were determined by standard methods [12].

2.3 Methylene Blue Active Substances (MBAS) for Analysis of the Samples

The samples were filtered using 0.45 µm Whatman GF/C glass microfiber filters. Total P and surfactants LAS were measured using UV Spektrofotometre (HACK-DR5000) in Laboratory of Yeşil Beyaz Quality and Environment in Tekirdağ [13].

The determination of low levels (typically 0-20 mg/L) of anionic surface active materials by MBAS as described by ISO 7875-1 [14] is used in the analysis of a wide range of samples including surface and potable waters. Higher concentrations can be diluted for analysis.

Methylene blue dyes were used to determine LAS. 20 mL of the sample solution was put into a 40 mL vial (vial A) equipped with a screw-cap and Teflon liner. Then 2 mL alkaline buffer and 1 mL natural methylene blue solution, followed by 5 mL of chloroform, were added to vial A in that order. The vial was subsequently sealed using a holed screw-cap and Teflon liner, before being vigorously shaken using a vortex mixer for 2 min. After shaking, the vial was left to await phase separation. The screw-cap was loosened to release the pressure inside. Once the two phases were separated, a Pasteur pipette was used to transfer the chloroform layer into a new vial (vial B) containing 22 mL ultra-pure water and 1 mL acid methylene blue solution. Vial B was then shaken using a vortex mixer for 2 min. The cap was loosened for a few seconds and then re-tightened. After the chloroform had completely separated from the water (after about 2 min), the chloroform layer was collected using a Pasteur pipette and put into a 10 mm quartz cell. The absorbance of the chloroform phase was measured with ultra-violet spectrophotometer at a wavelength of 650 nm.

3. Results and Discussion

3.1 Groundwater

Physical-chemical properties, total P and LAS determined in the samples of groundwater are presented in Table 1. The temperature values range from 17.5 °C to 22.8 °C and the pH values are in range of 7.1-8.9. The pH values of Muratlı groundwater are generally higher than other groundwater samples. The turbidity and EC values range from 0.1 NTU to 3.75 NTU and 310 µS/cm to 729 µS/cm, respectively. The EC and temperature values of Çerkezköy groundwater are generally higher than other groundwater samples. In this study, the values of pH, temperature, turbidity and EC are within an acceptable range for irrigation and drinking water according to Turkish Standard Regulation of Water Pollution Control [15] and EC Drinking Water Directive [16]. The total P and LAS concentrations are generally low in groundwater. The highest concentration of total P and LAS were measured as 0.65 mg/L and 0.37 mg/L in Muratlı groundwater (M2-sites) in April, 2014, respectively.

In a similar research, the total concentrations of LAS is > 1,000 mg/L at the groundwater in Spain. Groundwater may suffer pollution from many sources, including water leakage from sewer and septic systems, seepage from rivers and application of fertilizers and agrochemicals, among others. As a result, a wide range of organic pollutants can be found in aquifers posing a risk to groundwater quality [17].

The values of turbidity and EC in groundwater are lower than the surface waters (Figs. 2 and 3). The highest value of turbidity was measured in Uzunköprü surface water (U4) as 43.6 NTU. The highest EC value was measured in Çerkezköy surface water (C4) as 5,080 µS/cm. The wastewater and sludge discharge in both sites are very high. For this reason, they may be higher than other sites.

3.2 Surface Waters

Physical-chemical properties, total P and LAS determined in the surface waters are presented in Table 2. The temperature and pH values are in ranges of 12-24 °C and 7.2-8.2, respectively. The temperature and pH values of Uzunköprü surface waters are generally higher than other surface waters. The turbidity and EC values range from 13.4 NTU to 43.6 NTU and 430 µS/cm to 5,080 µS/cm. The EC values of Muratlı surface waters are generally higher than other surface waters. Because the surface waters of Muratlı have collected domestic and industrial wastewater. Textile and oil factories are located intensively in the site of Muratlı. The values of turbidity are very high in Uzunköprü surface waters.

Table 1 Some physico-chemical properties, concentrations of total P and LAS in groundwater.

Sample code	Name of sample	Date	T (°C)	pH	Turbidity (NTU)	EC (µS/cm)	Total P (mg/L)	LAS (mg/L)
C1	Çerkezköy	March-2014	18.7	7.3	0.22	589	< 0.01	< 0.01
C2		April-2014	18.3	7.3	1.21	729	< 0.01	< 0.01
C3		May-2014	20.7	7.3	0.20	705	0.05	< 0.01
C4		October-2015	22.8	7.1	0.10	680	0.06	< 0.01
C5		November-2015	20.9	7.2	0.21	658	< 0.01	0.19
C6		December-2015	18.3	7.2	0.39	310	< 0.01	< 0.01
M1	Muratlı	March-2014	18.2	7.5	0.40	420	< 0.01	< 0.01
M2		April-2014	17.5	8.0	2.51	540	0.65	0.37
M3		May-2014	19.0	7.8	0.35	580	< 0.01	< 0.01
M4		October-2015	25.0	8.9	3.75	516	< 0.01	< 0.01
M5		November-2015	17.6	8.9	0.07	496	0.1	0.16
M6		December-2015	19.4	7.2	0.14	499	< 0.01	< 0.01
U1	Uzunköprü	March-2014	18.3	7.2	0.81	680	< 0.01	< 0.01
U2		April-2014	20.7	7.5	0.30	653	< 0.01	< 0.01
U3		May-2014	21.0	7.2	0.60	640	< 0.01	< 0.01
U4		October-2015	21.3	7.4	0.27	593	0.11	< 0.01
U5		November-2015	20.3	7.2	0.03	310	< 0.01	< 0.01
U6		December-2015	19.9	7.2	0.21	513	< 0.01	< 0.01

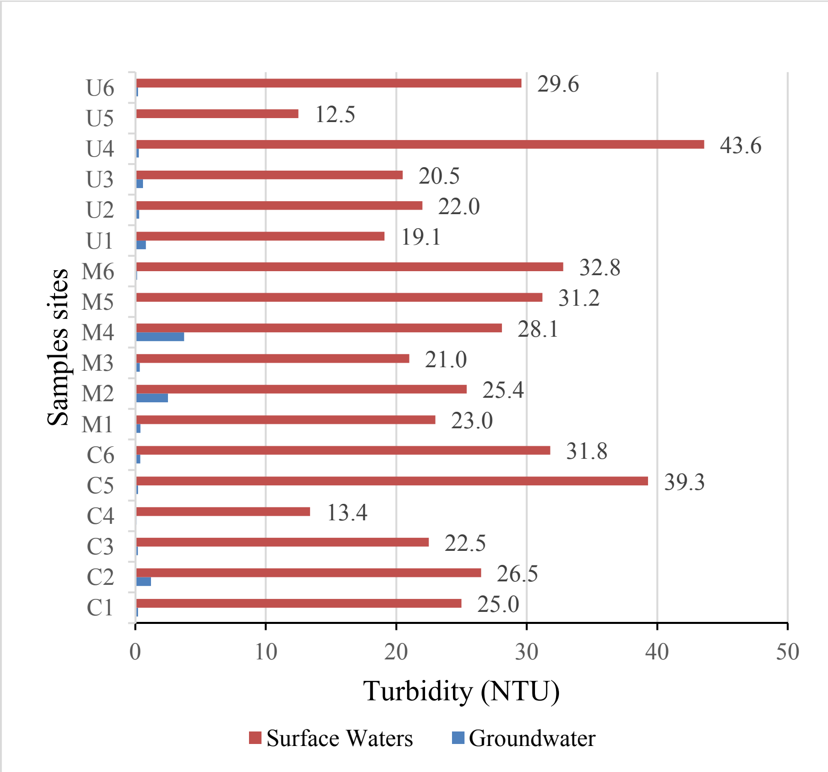

Fig. 2 The values of turbidity in groundwater and surface waters.

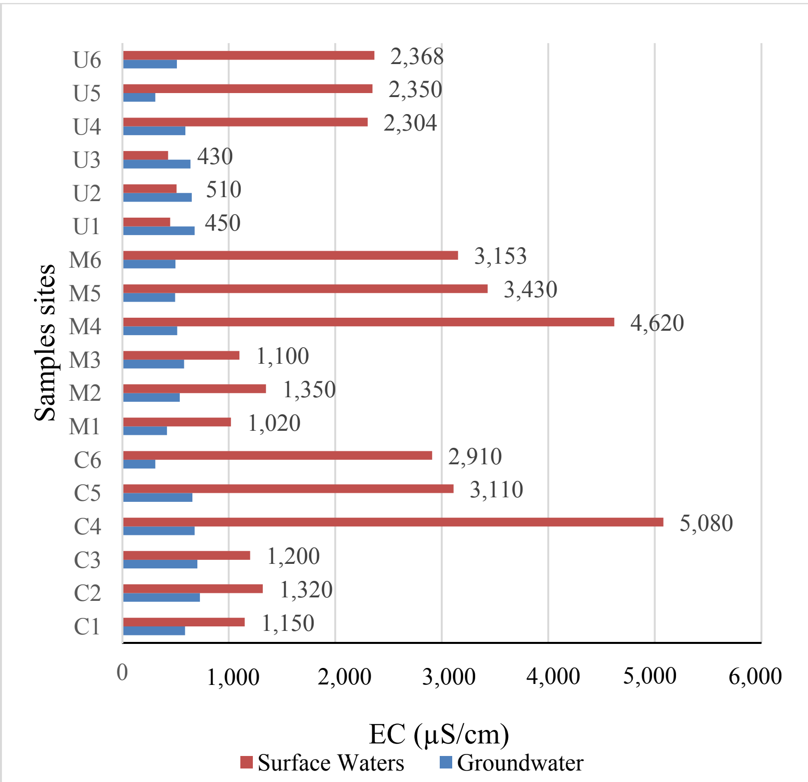

Fig. 3 The values of EC in groundwater and surface waters.

Table 2 Some physico-chemical properties, concentrations of total P and LAS in surface waters.

Sample code	Name of sample	Date	T (°C)	pH	Turbidity (NTU)	EC (μS/cm)	Total P (mg/L)	LAS (mg/L)
C1	Çerkezköy	March-2014	19.5	7.3	25.0	1,150	0.84	0.65
C2		April-2014	19.4	7.3	26.5	1,320	0.80	0.62
C3		May-2014	19.7	7.3	22.5	1,200	0.79	0.50
C4		October-2015	20.8	7.7	13.4	5,080	2.74	0.59
C5		November-2015	18.3	7.8	39.3	3,110	2.36	2.38
C6		December-2015	19.3	7.8	31.8	2,910	3.09	1.98
M1	Muratlı	March-2014	19.0	7.3	23.0	1,020	0.90	0.45
M2		April-2014	12.0	7.5	25.4	1,350	0.92	0.57
M3		May-2014	20.0	7.4	21.0	1,100	0.82	0.50
M4		October-2015	24.0	7.9	28.1	4,620	3.51	0.014
M5		November-2015	17.1	7.9	31.2	3,430	2.81	3.09
M6		December-2015	19.2	7.9	32.8	3,153	2.11	1.78
U1	Uzunköprü	March-2014	18.5	7.4	19.1	450	0.79	0.25
U2		April-2014	19.5	7.2	22.0	510	0.81	0.30
U3		May-2014	20.1	7.4	20.5	430	0.72	0.10
U4		October-2015	20.9	7.9	43.6	2,304	2.56	0.022
U5		November-2015	20.2	7.9	12.5	2,350	1.20	0.30
U6		December-2015	19.3	8.2	29.6	2,368	1.81	2.35

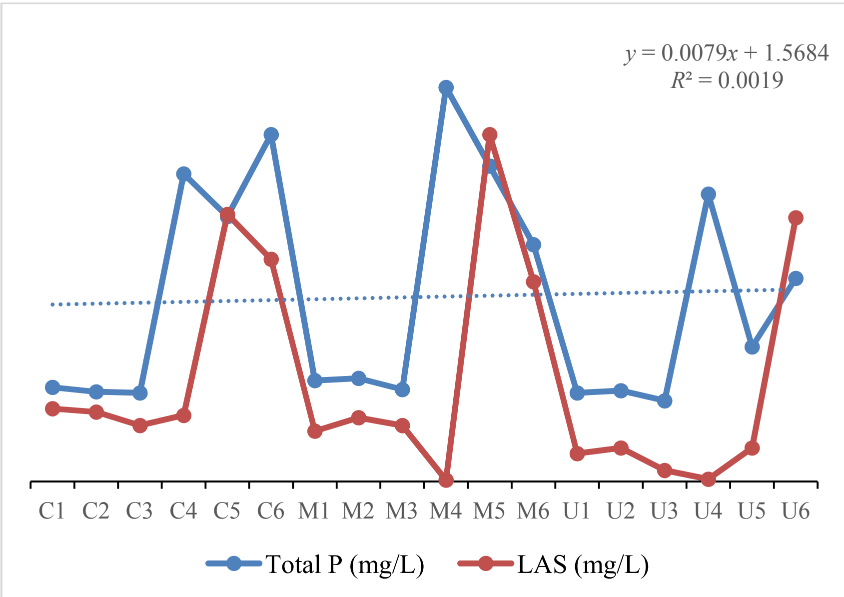

Fig. 4 The relationship between total P and LAS concentration in surface water samples.

Uzunköprü is the site where all the surface waters are collected in Ergene Basin.

The total P and LAS concentrations of surface waters are generally higher than groundwater. The relationship between concentrations of total P and LAS is presented in Fig. 4. The total P concentrations are higher than the LAS concentrations in all surface waters. The highest total P and LAS concentrations were measured in Muratlı surface waters (M4 and M5) as 3.51 mg/L and 3.09 mg/L, respectively. It has been observed that the values determined in this study are less than the values of surfactant (0.084-5.592 mg/L) in Gediz River reported by Minareci [18] and they are higher than the values of surfactant (0.003-1.122 mg/L) in Sapanca Lake reported by Macit [19]. In a similar research, the total concentrations of LAS ranged from

Table 3 Some physical-chemical properties, concentrations of total P and LAS in this study, and comparison with guidelines.

Contents	T (°C)	pH	EC (μS/cm)	Turbidity (NTU)	Total P (mg/L)	LAS (mg/L)
This study						
Groundwater	17.5-22.8	7.1-8.9	310-729	0.1-3.75	0.01-0.65	0.01-0.37
Surface water	12.0-24.0	7.2-8.2	430-5,080	13.4-43.6	0.72-3.51	0.014-2.38
Turkish environmental guidelines						
Class I	≤ 25	6.5-8.5	< 400	-	< 0.03	< 2
Class II	≤ 25	6.5-8.5	400-1,000	-	0.03-0.16	-
Class III	≤ 30	6.0-9.0	1,001-3,000	-	0.16-0.65	-
Class IV	> 30	> 9.0	> 3,000	-	> 0.65	-
Water quality criteria for drinking water						
EC (1998)	-	6.5-9.5	< 2,500	< 1	-	-

240 mg/L to 9,706 mg/L at the Wilmington and Bryan streams [20].

The comparison of this study results with guidelines is presented in Table 3. When the results are compared with the values stated in the limit of the Turkish Water Pollution Control Regulations, the turbidity values are generally < 1 in groundwater and they are very high in surface waters; in terms of temperature values, all waters are in I class; in terms of pH values, the groundwater is in I-III class and the surface water in I class; in terms of EC values, the groundwater is in I-II class and the surface waters in II-IV class; in terms of total P concentrations, the groundwater is in I-III class and the surface waters in IV class; in terms of LAS concentrations, the groundwater is in I-II class and the surface waters in II-IV class.

4. Conclusions

Surfactants are often very potent and also designed to be resistant to biodegradation. This, however, contributes to their environmental pollution. Various approaches have been discussed and applied, including the control of surfactants at source, segregation of sources.

In Ergene Basin, advanced treatment technologies should be applied which also remove surfactants. There is a need to expand on-going scientific research to assess the impact of surfactants, and their metabolites and transformation products on the aquatic environment. The effluent organic matter of treated wastewater needs to be characterized to a greater extent, especially when wastewater is reused for irrigation.

According to the European policy framework, the precautionary principle may be provided in the environment where scientific data do not enable to complete evaluation of the risk because of the possibility of danger to human, animal and plant health.

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