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MONITORING OF ANIONIC SURFACTANTS IN ANKARA STREAM

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ABSTRACT

Anionic surfactant levels (mg/ml) and pollution load (MBAS kg/day) of the Ankara stream were determined with the MBAS method during 12 month periods, from 1979 to 1980, 1990 to 1991 and 1994 to 1995. Results indicate that the mean anionic surfactant concentration and pollution load of the water in 1994 gradually decreased compared to the 1979-1980 and 1990-1991 periods. Anionic surfactant levels for the periods are 1.3 ± 1.10, 2.00 ± 0.79 and 0.92 ± 0.35, respectively. These data are discussed considering the 1987 prohibition of tetrapropylene benzen sulfonate (TBS) in Turkey and also by commenting the impact of other pollutants present in the stream.

RESUMEN

Se determinaron los niveles de surfactantes aniónicos (mg/ml) y la carga de contaminantes (MBAS kg/día) en el arroyo Ankara, utilizando el método MBAS, durante períodos de 12 meses de 1979 a 1980, de 1990 a 1991 y de 1994 a 1995. Los resultados indican que la concentración media de los surfactantes aniónicos y la carga de contaminantes en 1994 disminuyó gradualmente al compararla con los periodos de 1979-1980 y 1990-1991. Los niveles de surfactantes para estos períodos son 1.3 ± 1.10, 2.00 ± 0.79 y 0.92 ± 0.35, respectivamente. Estos resultados se discuten considerando la prohibición de 1987 en Turquía sobre el bencensulfonato de tetrapropileno (TBS) asimismo, se comenta el impacto de otros contaminantes que se encuentran en el arroyo.

INTRODUCTION

Anionic surfactants that work as surface active agents, mainly alkylbenzene sulfonates, have been used as basic ingredients of laundry detergents and household cleaning formulations since ca. 1955 in Turkey (Vural and Kumbur 1982). Prior to 1965 predominantly branched alkylbenzene sulfonates (tetrapropylene benzene sulfonates: TBS or ABS) were produced; these compounds were unbiodegradable and caused environmental problems in wastewaters (Maurer *et al.* 1971, Rapaport and Eckhof 1990). During the mid 1960's due to their stability in the environment, TBS's were gradually replaced by the highly biodegradable linear alkylbenzene sulfonates (LAS) in many countries (Palla and Decros 1984, Eganhouse 1986). But in Turkey, gradual replacement of LAS for branched alkylbenzene sulfonates began in 1987 (TSE 1987). Approximately 32 321 tons of LAS were imported in 1987. At present they are produced in Turkey and their total amount raised to 372 x 10^6 tons in 1994 (DIE 1996).

In one of our previous studies, before the replacement of TBS by LAS, we reported the results of anionic surfactant monitored at the Ankara stream where domestic and industrial effluents of Ankara City drain (**Fig. 1**) (Vural and Kumbur 1982). Further, we aimed to compare those high levels of anionic surfactants in Ankara stream after TBS use was banned in Turkey (Vural and Duydu 1992). This study describes the results of extensive monitoring of anionic surfactants from 1979-1995 and indicates the effect of LAS on the concentration of alkylbenzene sulfonates in the stream. Residual anionic surfactant was measured as methylene blue active substance (MBAS) in stream water.

MATERIAL AND METHODS

Water samples from the Ankara stream were collected during 12 month periods, namely November 1979-October 1980, November 1990-October 1991 and November 1994-October 1995, four times a month at the location shown in **Fig. 1**. 90% of domestic and industrial effluents of Ankara City are drained to the stream which is 90 km length and covers 3153 square km. The stream water is used for irrigation.

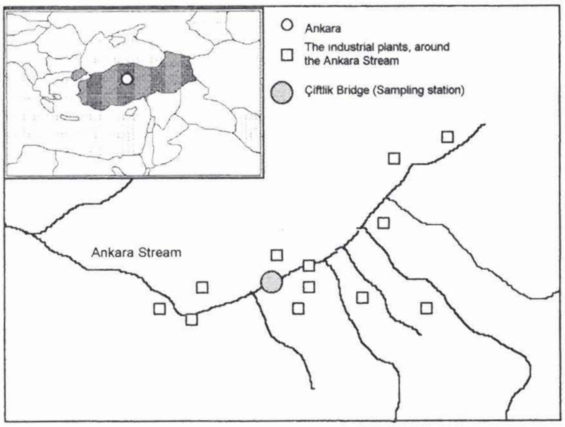

Fig. 1. Location of Ankara stream

Stream water samples were taken following the techniques described in *Standard Methods for the Examination of Waters and Wastewaters* (1980). Water samples were preserved with chloroform. The flow rate of the stream at the sampling site was recorded from the results of the goverment office. Anionic surfactant concentration in the stream was measured by a spectrophotometric method based on the formation of a complex when the anionic surfactant reacts with the colored methylene blue cation (MBAS procedure) (Vural and Kumbur 1982).

Anionic surfactant pollution load was calculated using the following ecuation:

Pollution load (kg/day) = c x f x 3600 x 24 x 10^{-6}

Where c is the surfactant concentration as mg/l and f is the flow rate of stream water as m^3/s.

Statistical evaluation of results was performed by using Student's *t*-test.

RESULTS AND DISCUSSION

The water sampling site as seen in **Fig. 1**, is the junction where all branches of the stream carrying domestic and industrial effluents join. In our previous study, this sampling station was accepted as a reference sampling site for the investigation of the stream pollution (Vural and Kumbur 1982, Vural and Duydu 1992).

There are some factories and industrial plants such as food industry (sugar, beer, wine factories) a cement factory and electronic industry along the stream. In general they discharge their effluents into the stream and only a few of them have sewage treatment systems. The stream then runs into Sakarya river after 50 km travel distance from Ankara (**Fig. 1**). All stream pollutants are carried along by the water from the sampling station. But we have no data on LAS and other pollutants mass balance during discharge of effluents to the stream. Anionic detergent pollution mainly raised from the domestic use.

Monthly distribution and mean values of anionic surfactant concentrations in the Ankara stream for each sampling period are shown in **table I**.

There are significant differences ($p < 0.05$) between means and monthly surfactant levels when the results of 1990-1991 period are compared with the 1979-1980 sampling period. This significant increase in anionic surfactant concentration in the stream can be explained by the increase of the detergent amount consumed by the increasing population too; and secondly, official records confirmed that the use of nonbiodegradable surfactant continued, at least partially, after 1987.

When the monthly distribution of anionic surfactant concentrations of the stream covering the period 1994-1995 were compared with the results of the two previous periods, excluding a few months, a significant decrease ($p < 0.05$) is observed. Altough the mean concentration of the 1994-1995 period is not significantly low ($p > 0.05$), the decrease of the anionic detergent level of the stream after the period 1990-1991 confirms the contribution of biodegradable anionic surfactant detergent formulations to the stream's pollution. These results also confirm our considerations mentioned above.

Monthly distribution of anionic surfactant load, flow rates and the mean results covering the sampling periods are also shown in **table I**. Residual anionic surfactant concentration of the stream showed the highest levels for a few months in the 1979-1980 monitoring period. Those highest concentrations can be due to the lower flow rate of the stream during those months as compared with the 1991-1992 and 1994-1995 sampling periods. Monthly anionic surfactant concentration and load of the stream during the sampling period 1994-1995 indicate a significant increase during the first three months and then a significant decrease as compared with the other two sampling periods. Those higher concentrations in the first months can be explained because detergent formulations still contained the nonbiodegradable surfactant TBS at least in a small percentage.

Monthly distribution of anionic surfactant levels and

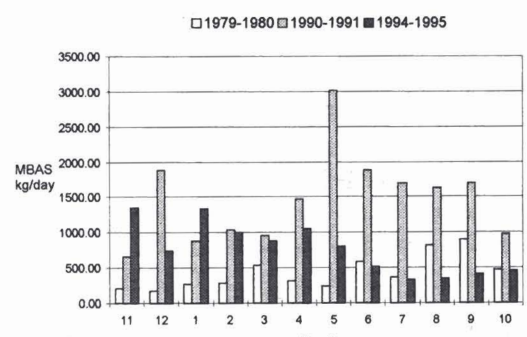

Fig. 2. Monthly distribution of anionic surfactant load during the monitoring periods in the Ankara stream

TABLE I. MONITORING RESULTS OF ANIONIC SURFACTANTS IN THREE PERIODS IN THE ANKARA STREAM

Months	Monitoring periods								
	I 1979-1980			II 1990-1991			III 1994-1995		
	mg/l[a]	kg/day[b]	m^3/s[c]	mg/l	kg/day	m^3/s	mg/l	kg/day	m^3/s
11	0.58±0.02[d]	198.23±6.63	4.04±0.12	0.97±0.02	655.38±27.55	7.82±0.26	1.57±0.05	1345.63±117.03	9.92±0.27
12	0.55±0.05	167.97±15.18	3.61±0.30	2.38±0.15	1883.59±286.08	9.16±0.31	0.94±0.10	737.44±129.33	9.08±0.16
1	0.77±0.06	265.78±81.50	4.08±0.13	0.99±0.08	884.44±178.49	10.34±1.73	1.43±0.11	1329.42±278.29	10.76±0.98
2	0.47±0.09	275.95±81.19	6.94±0.14	1.16±0.09	1028.00±185.68	10.26±0.29	1.27±0.08	1005.11±179.35	9.16±0.22
3	0.44±0.12	530.44±154.35	14.25±0.31	1.64±0.12	959.28±186.10	6.77±0.23	0.86±0.13	878.27±129.19	11.82±0.10
4	0.55±0.08	315.94±68.13	6.79±0.17	1.80±0.08	1477.44±256.01	9.50±0.56	0.95±0.12	1045.70±114.03	12.74±0.57
5	0.42±0.06	230.25±81.49	6.48±0.33	3.00±0.09	3006.72±343.26	11.60±0.48	0.98±0.07	804.38±113.62	9.50±0.44
6	1.83±0.11	580.57±104.11	3.75±0.57	2.79±0.08	1885.06±355.78	7.82±0.65	0.66±0.05	512.65±81.49	8.99±0.74
7	1.14±0.08	368.42±122.79	3.82±0.65	2.92±0.10	1692.85±353.29	6.71±0.17	0.43±0.03	324.71±96.86	8.74±0.17
8	3.25±0.13	808.35±122.79	2.94±0.33	2.67±0.14	1637.88±343.26	7.10±0.18	0.58±0.07	339.26±104.83	6.77±0.41
9	3.26±0.05	901.85±209.81	3.27±0.17	2.51±0.09	1695.88±291.76	7.82±0.49	0.63±0.11	407.15±97.88	7.48±0.33
10	2.36±0.14	473.18±138.67	2.37±0.26	1.19±0.08	976.75±209.81	9.50±0.49	0.69±0.09	461.43±138.65	7.74±0.41
The average value of the three periods									
	1.30±1.10	426.41±239.33	5.20±3.23	2.00±0.79	1481.96±642.28	8.70±1.58	0.92±0.35	765.93±365.10	9.39±1.74

a: detergent concentration; b: detergent load; c: flow rate; d: mean ± S.D.

Statistical evaluations

Months	mg/l			kg/day			m^3/s		
	I-II	II-III	I-III	I-II	II-III	I-III	I-II	I-III	II-III
11	S	S	S	S	S	S	S	S	S
12	S	S	S	S	S	S	S	N	S
1	S	S	S	S	S	S	S	N	S
2	S	S	S	S	N	S	S	S	S
3	S	S	S	S	N	S	S	S	S
4	S	S	S	S	S	S	S	S	S
5	S	S	S	S	S	S	S	S	S
6	S	S	S	S	S	N	S	N	S
7	S	S	S	S	S	N	S	S	S
8	S	S	S	S	S	S	S	S	S
9	S	S	S	S	S	S	S	N	S
10	S	S	S	S	S	N	S	S	S
The average value of the three periods									
	S	S	N	S	S	S	S	N	S

S: significant ($p < 0.05$), N: not significant ($p > 0.05$)

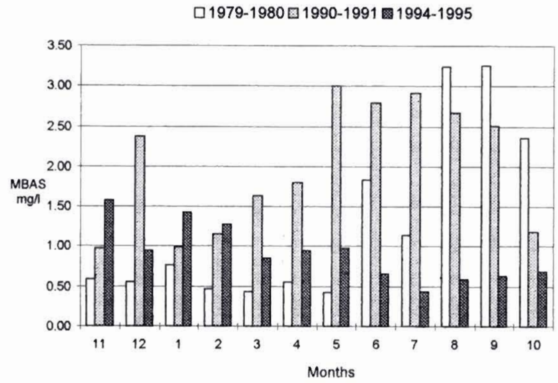

Fig. 3. Monthly distribution of anionic surfactant levels during the monitoring periods in the Ankara stream

pollution load of the stream covering the sampling periods are shown in **Figs. 2** and **3**. The variations can be clearly seen.

As a conclusion, anionic surfactant (detergent) pollution of the Ankara stream showed a significant decrease after the banning of TBS. But anionic surfactant concentration in the water is still above the permissible level, 0.2 mg/L, according to Turkish regulations. Our results are far higher than the data obtained by similar studies in other countries where sewage treatment systems have been established (Rapaport and Eckhof 1990). These high results can be atributed to the other water pollutants such as high metal and phosphorus concentrations and low dissolved oxygen that affects the biodegradability of LAS (Knabel *et al.* 1990). The pollution can only be prevented by establishing water treatment systems before the effluents are drained to the stream; a few of them have been already established by some industrial plants.

We believe that this study must continue by monitoring LAS with specific methods other than MBAS. The reaction of an anionic surfactant with methylene bluee and extraction into chloroform is subject to interferences by non-LAS methylene blue active substances in the water sample. Gas chromatography, microdesulphonatiòn gas chromatography and UV/HPLC methods have been used in the monitoring of LAS in recent years (Kimele and Swicher 1977, De Henan *et al.* 1986, Eganhouse 1986, Rapaport and Eckhof 1990). On the other hand, more research is needed to collect more data such as measurement of LAS in sediment, infïluent sewage, effluent sewage and mass balance for LAS during sewage treatment. Those results can then be evaluated for the LAS toxicity on aquatic organisms and terrestrial systems.

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