Behaviour of Linear Alkylbenzene Sulphonates in the Krka River Estuary

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Despite the numerous investigations of the occurrence, behaviour and fate of linear alkylbenzene sulphonates (LAS) in the wastewater treatment and natural waters (1), reports on these surfactants in marine and estuarine environments are relatively scarce (2, 3).

In order to determine input and distribution of aromatic surfactants in the Krka River Estuary, grab samples of wastewater and estuarine water were taken in the Sibenik Harbour at different distances from the wastewater outlets during 1990-1991. In addition, samples on the vertical profile of the water column were collected by scuba diving.

Quantitative determination of LAS was performed using reversed-phase high-performance liquid chromatography (HPLC) with spectrofluorimetric detection (230/290 nm). Prior HPLC analysis the samples were filtered through glass fiber (GF/F) filters. Dissolved LAS from the filtrate was extracted on C_{18} cartridges (3) while LAS adsorbed on the particles was extracted in methanol using an ultrasonic method.

The concentrations of LAS determined in the wastewater were in the range from 285-1039 μg/L. Dispersion of LAS into the Sibenik Harbour after the wastewater discharge was very fast (Fig. 1). Apparently, after a distance of only 100 m from the sewage outlet further concentration decrease was very slow. Two concurrent physico-chemical processes were thought to be responsible for such behaviour: dilution and fast sedimentation with sewage derived particles. This supposition was well supported by rather high percentage of the adsorbed LAS in the examined wastewaters (from 11 to 59 %). Moreover, selective partitioning of the individual LAS homologues between liquid and solid phase was noticed with the higher homologues (C_{12}, C_{13}) being significantly enriched in the particulate phase.

Distribution of the LAS obtained on the vertical profile of the water column (Fig. 1) can be interpreted as a consequence of strongly pronounced stratification in the Krka River Estuary. The wastewater plume spreads into the Sibenik Harbour almost exclusively in the freshwater layer while the saline layer remains hardly affected. Maximal concentration of LAS was determined in the surface microlayer (24.0 μg/L) but a smaller maximum was also observed at the boundary of the freshwater and salinewater layers. The concentrations of LAS in the underlying salinewater layer were very low (<2 μg/L) indicating that its vertical transport was greatly reduced by the freshwater-salinewater boundary.

An assessment of the LAS input via wastewaters and its quantity present in the water column of the Sibenik Harbour indicated significant losses due to the elimination processes, most probably by biodegradation and/or fast settling of sewage derived particles containing high concentrations of LAS (up to 2245 mg/kg). It was shown by the laboratory simulated biodegradation experiments that the biodegradation half-life of LAS was in the range from 2.8 to >38 days depending on the origin of the bacterial culture (freshwater or salinewater layer) and temperature (4). Significantly slower biodegradation was observed in the salinewater layer compared to the freshwater layer, especially under the winter temperature conditions (Tab. 1).

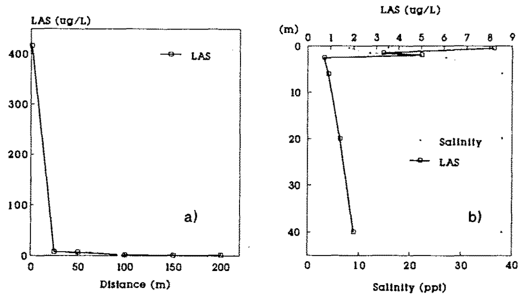

Figure 1. Distribution of LAS in the Krka River Estuary:
a) spatial distribution in the freshwater layer of the Sibenik Harbour correlated with the distance from the major wastewater outlet;
b) vertical concentration profile at the station E4A.

Table 1. The main kinetic parameters of primary biodegradation of linear alkylbenzenesulphonates (LAS) by two mixed bacterial culturesa from the Krka River Estuary.

culture origin	T (°C)	lag-phase (days)	k (days^{-1})	$t_{1/2}$ (days)
E_4A-0.5 m	14	2	0.161	4.3
E_4A-6 m	14	>38	-	>38
E_4A-0.5 m	23	0	0.247	2.8
E_4A-6 m	23	0	0.156	4.4

[a] E_4A-0.5 m = freshwater layer of the estuary
E_4A-6 m = salinewater layer of the estuary

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Distribution of nutrients in the Eastern Adriatic coastal sea - Post Algal Bloom -

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This paper describes the distribution of nutrients (phosphate, nitrate, nitrite, ammonium and silicate) in water samples from 20 sampling stations on the eastern Adriatic coast (Figure 1) collected during August 1989 (post non-seasonal algal bloom).

During summer 1989, like in 1988, large quantities of organic substances and mucouse aggregations were recorded along the coast of northern and middle Adriatic. Vertical stratification of sea water was nominated as a principal cause of bloom. The low horizontal movement retained nutrients in the area that extends from the Po Delta, and the nutrients could not be exported and remained to be biologically used and recycled (DEGOBBIS, 1989).

Due to basic hydrographic parameters during the summer 1989, pronounced stratification of water column occurred in the study area along with the minimum horizontal current. Less saline water in the surface layer was flowing out of the Adriatic and intermediate water of the Mediterranean origin was flowing in to replace that surface water (BULJAN *et al.*).

During this period (August 1989) values of salinity exceeded 38.50 in the bottom layer of the northern Adriatic. Changes of ecological conditions such as migration of some marine organisms from the middle Adriatic (net zooplankton and copepods) were found in the northern Adriatic in this period.

Values of nutrients, except nitrate, were very poor (Table 1) throughout the area in this period due to prevailing processes of assimilation with consumption of nutrients by phytoplankton.

Considerable quantities of nitrate were recorded throughout the area even an order of magnitude higher than the "normal" values. This nitrate enrichment could be attributed to process of regeneration of these salts from organic matter and degradation of large quantities of organic matter mucouse aggregations by bacterial activity. This effect can be confirmed by very high bacterial biomass throughout the investigated area.

Cycles of nutrients in the eastern Adriatic Sea are defined not only by oceanographic and meteorological factors but to a considerable extent, by biological cycles of the organic matter in the sea.

Table 1. Means concentration of nutrients in mmol m^{-3} on investigated area

PARAMETER / STATIONS	NO_3 - N	NO_2 - N	NH_3 - N	PO_4 - P	SiO_3 - Si	O_2	pH
S - 1	3.98	0.118	1.58	0.068	2.74	5.20	8.14
S - 3	3.89	0.096	1.31	0.067	0.47	5.64	8.14
S - 4	5.62	0.162	0.75	0.048	1.70	4.84	8.17
S - 6	5.80	0.155	1.30	0.051	2.58	4.66	8.15
S - 10	3.12	0.158	0.73	0.055	0.98	4.86	8.19
S - 12	3.26	0.105	0.94	0.044	0.17	5.21	8.20
S - 14	4.37	0.085	0.95	0.051	0.59	5.00	8.20
S - 16	5.37	0.105	1.30	0.060	0.69	5.26	8.19
S - 19	7.90	0.098	1.09	0.046	1.50	4.98	8.19
S - 22	8.11	0.092	0.88	0.046	0.56	4.82	8.19
S - 23	9.17	0.094	0.93	0.061	0.71	4.88	8.21
S - 26	8.20	0.080	0.42	0.036	0.46	4.66	8.22
S - 27	9.53	0.113	0.60	0.049	0.89	4.94	8.21
S - 31	5.30	0.142	0.48	0.070	0.64	5.75	8.23
S - 32	3.51	0.112	0.79	0.063	1.43	5.19	8.23
S - 37	1.29	0.100	0.49	0.074	0.46	5.45	8.23
S - 40	1.98	0.080	0.50	0.059	1.02	5.11	8.23
S - 42	3.05	0.085	0.66	0.057	1.24	5.09	8.23
S - 43	2.66	0.087	0.57	0.052	0.87	5.05	8.24
S - 46	1.27	0.105	1.65	0.055	0.69	5.24	8.23

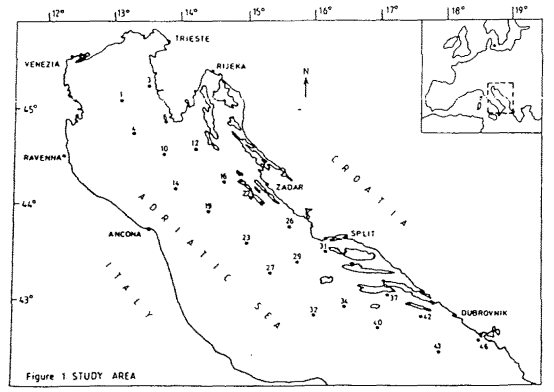

Figure 1 STUDY AREA

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