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Determination of Linear Alkylbenzene Sulphonates in the Krka River Estuary

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Coastal waters in some densely populated areas receive significant quantities of various detergent derived chemicals, including linear alkylbenzene sulphonates (LAS). Reports on these surfactants in marine and estuarine waters are relatively scarce (Hon-Nami and Hanya 1980; Ishiwatari et al. 1983) compared to the rather numerous studies on the occurrence and behaviour of LAS in the wastewater treatment and in natural waters (Painter and Zabel 1988; Fell, 1989).

The marine environment seems to be particularly sensitive to pollution with synthetic surfactants. The presence of enhanced LAS concentrations could have a significant effect on marine fauna, especially in the first stages of development (Lewis 1991). Moreover, it was shown that biodegradation of LAS in the marine part of an estuary was significantly slower than in its freshwater part (Terzić et al. 1992). Monitoring these pollutants using reliable analytical methods is, therefore, of great importance in preventing deleterious effects in estuarine and coastal environments. The HPLC based methods for the determination of LAS in environmental samples are well established (Nakao et al. 1981; Kikuchi et al. 1986; Marcomini et al. 1987; Marcomini et al. 1989) but the details of the enrichment and HPLC protocols proposed by different authors are sometimes conflicting.

MATERIALS AND METHODS

Clean seawater (salinity = 38 g/L) for the model recovery experiments was collected in eastern coastal waters of the Adriatic Sea, 5 miles off Šibenik (Fig. 1). For the experiments conducted at the lowest concentration level of LAS examined (1 µg/L) the seawater was additionally precleaned by percolation through Sep-pak C_{18} cartridges. In order to determine input and distribution of aromatic surfactants in the Šibenik Harbour (Fig. 1), grab samples of wastewater and estuarine water were taken at different distances from the wastewater outlets during 1990. In addition, samples on a vertical water column profile were collected by scuba diving (Kniewald et al. 1987).

The recovery studies were performed by spiking either Milli-Q water (Millipore, USA) or clean seawater with LAS at concentrations of 1, 10,

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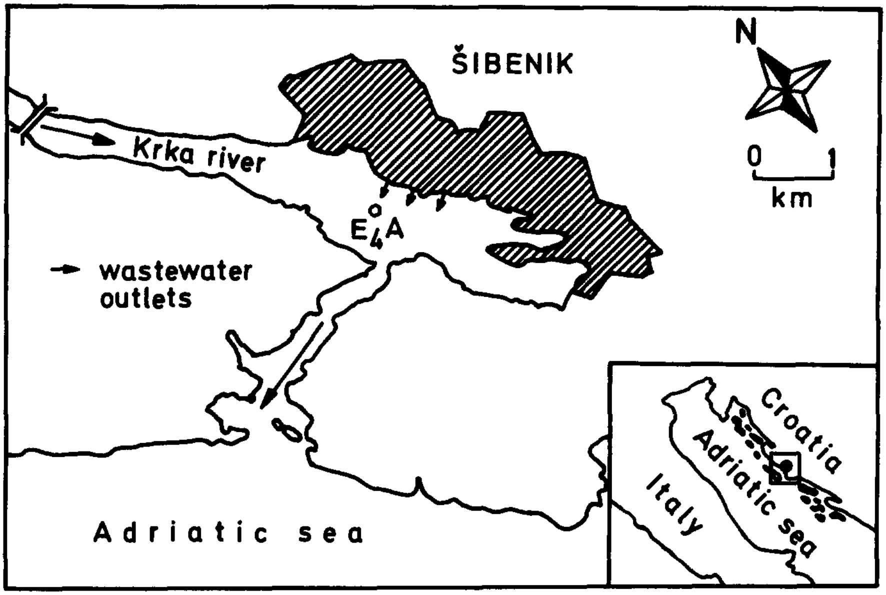

Figure 1. Map of the Šibenik Harbour with indicated sampling stations.

100 and 1000 µg/L. The analyte was enriched from water samples (0.5-2L) using either of the following techniques: a) gaseous stripping into ethyl acetate from the acidified sample ($pH < 2$) after Wickbold (1971) and b) solid-phase extraction using the C_{18} Sep-pak cartridges (Waters Associates, Milford, USA) after Kikuchi et al. (1986). The ethyl acetate extracts resulting from procedure a) were dried over sodium sulphate, evaporated to the dryness, redissolved in 1 mL of methanol/water (1:1) and transferred into a 2.5 mL vial equipped with a Teflon-lined screw cap. In addition this extract was purified by shaking with 1 mL of cyclohexane to remove nonpolar impurities. According to procedure b) the C_{18} Sep-pak cartridges were eluted with methanol, evaporated to a small volume and transferred into a vial equipped with a Teflon-lined screw cap.

Quantitative determination of LAS in the prepared extracts was performed using reversed-phase high-performance liquid chromatography (HPLC) with spectrophotometric detection at 225 nm (LKB-Bromma, 2151 variable Wavelength Monitor) or spectrofluorimetric detection applying an excitation wavelength of 230 and emission wavelength of 295 nm (Perkin Elmer LS-3B). The chromatographic apparatus consisted of a high-pressure pump (LKB-Bromma, Sweden, Model 2150), a system for the control of gradient elution (LKB-Bromma, Model 2152) with low pressure solvent mixing (LKB-Bromma, Model 2040-203), and a Rheodyne injector (Model 7152). Concentrations of individual homologues (C_{10}-C_{13}) were determined under isocratic conditions using a column (100 x 4 mm) packed with irregularly shaped octylsilica particles of 7 µm (Lichrosorb RP-8, Dr Knauer, Berlin) and fitted with a 11 mm long precolumn containing the same packing material. The mobile phase (1.2 mL/min) consisted of a mixture of acetonitrile and water (45/55) which contained 10 g/L of $NaClO_4$.

Peak areas were determined using a Hewlett Packard integrator, Model 3390A. The concentrations were calculated using external calibration with a commercial mixture of LAS (Saponia, Osijek, Croatia) and octylbenzene sulphonate (97%; Aldrich Chem. Co., USA).

RESULTS AND DISCUSSION

Recoveries and reproducibilities of the LAS determination from spiked distilled water and seawater samples using two different enrichment techniques are presented in Table 1.

Table 1. Accuracy and precision of the determination of linear alkylbenzene sulphonates (LAS)

	Sep-pak C_{18}		Gaseous stripping	
	seawater	freshwater	seawater	freshwater
1 μg/L				
Recovery (%)	92	-	-	-
RSD (%)[a]	5.5	-	-	-
10 μg/L				
Recovery (%)	92	93	75	83
RSD (%)[a]	2.8	5.4	3.1	1.8
100 μg/L				
Recovery (%)	97	95	96	-
RSD (%)[a]	1.3	4.7	7.9	-
1000 μg/L				
Recovery (%)	-	-	92	97
RSD (%)[a]	-	-	5.8	1.0

[a] relative standard deviation of the triplicate determination

\- not determined

Both techniques proved accurate for the LAS determinations over wide concentration ranges with a precision usually better than 6 %. As can be seen, the recoveries of LAS using solid-phase extraction are very high (>90%) regardless of the analyte concentration and sample salinity. Thus, an excessive addition of salt (up to 8 %) in order to increase recovery as suggested by Marcomini et al. (1987) was not necessary and can be avoided. Somewhat lower recoveries (75 and 83 %) were obtained using the gaseous stripping technique at 10 μg/L. Reliable determinations at the lowest concentration level (1 μg/L) were possible only by solid-phase extraction since the use of gaseous stripping was prevented by a high blank value (1-2 μg/L) despite the use of an additional purification step. This high blank was thought to be caused primarily by phthalates from the relatively large quantities (100 mL) of ethyl acetate used for the extraction.

All the individual LAS homologues were extracted with similar efficiencies and their original distribution was not significantly altered by either of the applied enrichment techniques.

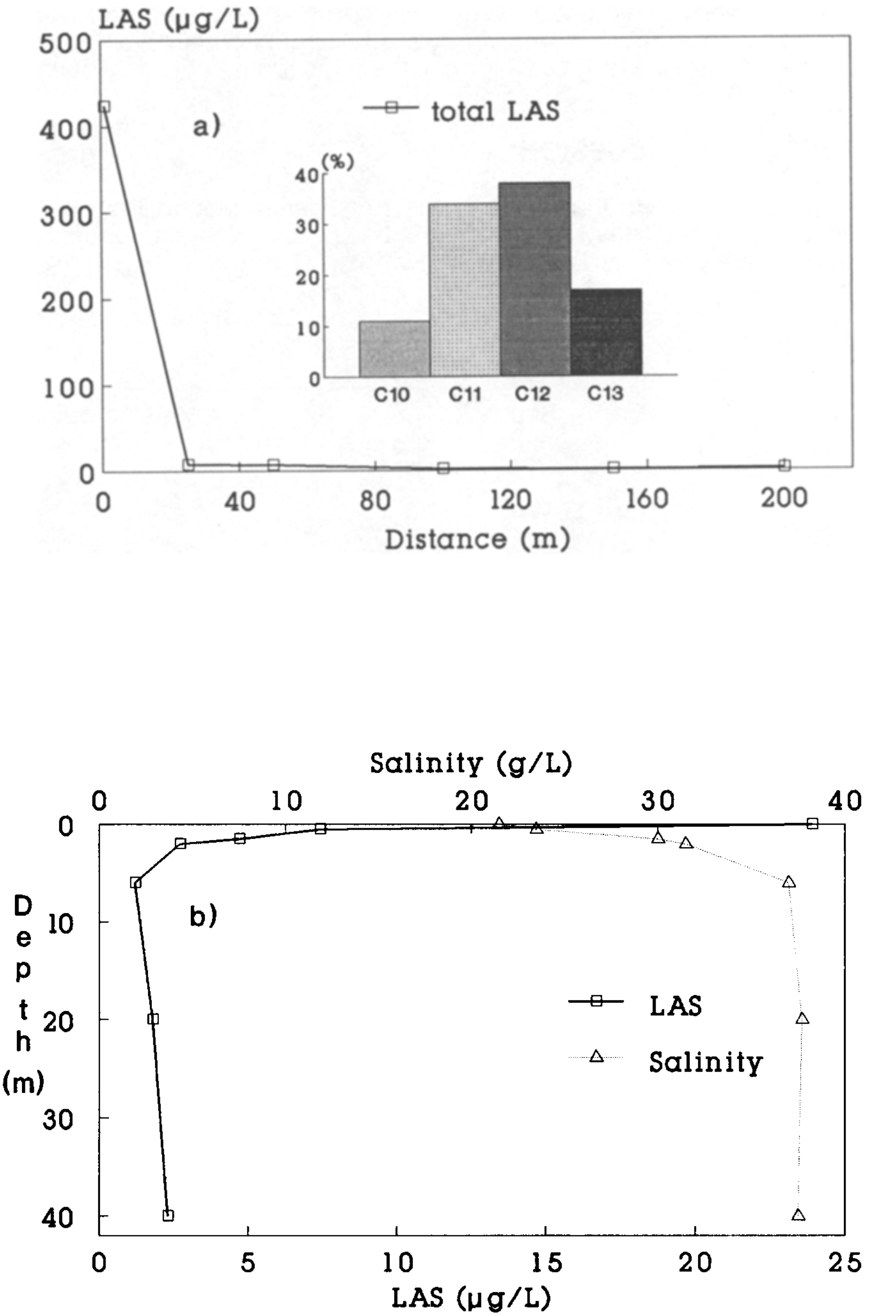

Figure 2. Distribution of LAS in the Krka River Estuary: a) spatial distribution in the freshwater layer of the Šibenik Harbour correlated with the distance from the major wastewater outlet. The symbol inside the figure represents LAS homologue distribution at the outlet; b) vertical concentration profile at the station E_4A.

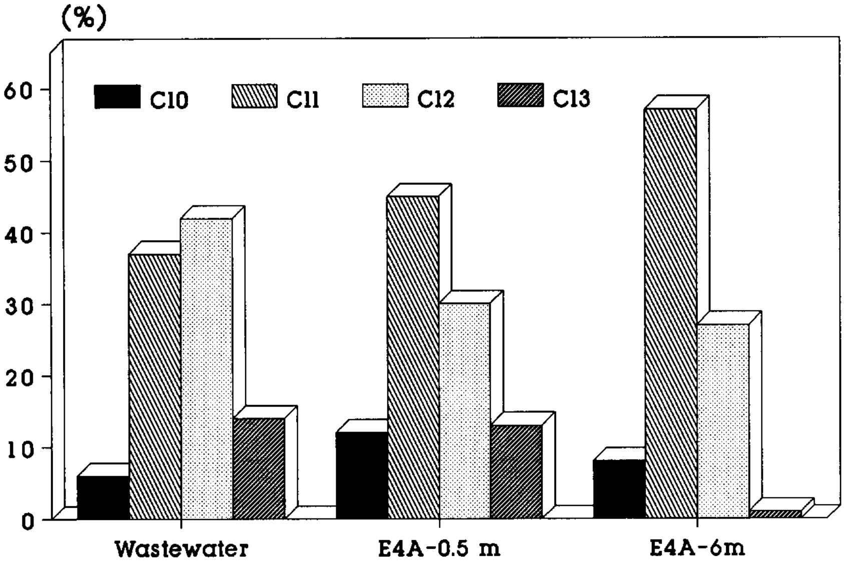

Figure 3. Composition of the individual LAS homologues in wastewater and estuarine water in the Šibenik Harbour (0.5 m = freshwater layer; 6 m = saline water layer).

Solid-phase extraction which proved clearly the more reliable enrichment technique was applied in a study of LAS distribution in the highly stratified Krka River Estuary (Fig. 1). Dispersion of LAS from sewage into the lower part of the estuary (Šibenik Harbour) is very efficient, particularly under favourable wind conditions (Fig. 2a). High LAS concentrations were found only in the immediate region of municipal wastewater outlets (from 420 to 780 μg/L). After a distance of only 50 m from the sewage outlet the concentrations dropped to only 7.2 μg/L and 3.2 μg/L, at depths of 0.5 m and 6 m, respectively. Further decrease in concentration was very slow reaching levels of 1-2 μg/L at the distances greater than 100 m. During longer periods of calm weather the wastewater plume can reach further parts of the Šibenik Harbour. In such situations the concentration of LAS increases significantly in the freshwater layer but not in the saline water layer (Fig. 2b). The vertical distribution of LAS presented in Fig. 2b is characteristic for a highly stratified estuary. The concentrations are negatively correlated with salinity and the maximum was found in the surface microlayer (24.0 μg/L). Obviously, the vertical transport of the pollutants is greatly reduced by the freshwater-saline water boundary (Žutić and Legović 1987).

The distribution of individual LAS homologues in the water column of Šibenik Harbour was rather different from their original composition in the wastewaters (Fig. 3). The increase of the relative abundance of lower (C_{10} and C_{11}) LAS homologues in the estuarine water is indicative of comparatively faster depletion of the higher homologues. The most probable processes responsible for such behaviour could be biodegradation, and/or fast settling with sewage derived particles (Hon-Nami and Hanya 1980; Terzić et al. 1992).

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REFERENCES

Fell B (ed.) (1989) Proceedings of the International Status Seminar "Alkylbenzene Sulphonate (LAS)", Aachen, Nov 9th-10th, 1988. Tenside Surfact Deterg **26**:69-179

Hon-Nami H, Hanya T (1980) Linear alkylbenzene sulphonates in river, estuary and bay water. Wat Res **14**:1251-1256.

Ishiwatari R, Takada H, Yun S-J, Matsumoto E (1983) Alkylbenzene pollution of Tokyo Bay sediments. Nature **301**:599-600

Kikuchi M, Tokai A, Yoshida T (1986) Determination of trace levels of linear alkylbenzene sulphonates in the marine environment by high-performance liquid chromatography. Wat Res **20**:643-650

Kniewald G, Kwokal Ž, Branica M (1987) Marine sampling by scuba diving. 3. Sampling procedures for measurement of mercury concentrations in estuarine waters and sea water. Mar Chem **22**:343-352

Lewis MA (1991) Chronic and sublethal toxicities of surfactants to aquatic animals: a review and risk assessment. Wat Res **25**:101-113

Marcomini A, Capri S, Giger W (1987) Determination of alkylbenzenesulphonates and alkylphenol polyethoxylates and nonylphenol in waste water by high-performance liquid chromatography after enrichment on octadecylsilica. J Chromatogr **403**:243-252

Marcomini A, Stelluto S, Pavoni B (1989) Determination of linear alkylbenzenesulphonates and alkylphenol polyethoxylates in commercial products and marine waters by reversed- and normal-phase HPLC. Intern J Environ Anal Chem **35**:207-218

Nakao A, Tsuji K, Yamanaka M (1981) Determination of alkyl chain distribution of alkylbenzenesulphonates by liquid chromatography. Anal Chem **53**:1818-1821

Painter HA, Zabel TH (1988) Review of the Environmental Safety of LAS. Water Research Centre Medmenham, Marlow Bucks, United Kingdom

Terzić S, Hršak D, Ahel M (1992) Primary biodegradation kinetics of linear alkylbenzene sulphonates in estuarine waters. Wat Res **26**:585-591

Wickbold R (1971) Enrichment and separation of surfactants from surface waters by transport at the gas/water interface. Tenside Deterg **8**:61-63

Žutić V, Legović T (1987) A film of organic matter at the fresh-water/sea-water interface of an estuary. Nature **328**:612-614

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