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Determination of Alkylphenol Polyethoxylates and their Metabolites in Estuarine Waters by High-Performance Liquid Chromatography

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Alcohol polyethoxylates and alkylphenol polyethoxylates (APnEO) represent about 80% of the total manufacture of nonionic surfactants. Their annual consumption figures for Western Europe were in 1987 230 000 and 150 000 tons, respectively. In spite of somewhat lower consumption alkylphenol polyethoxylates are considered ecotoxycologically much more critical compounds than the alcohol polyethoxylates. The reason for that is their higher persistence towards biodegradation as well as the high toxicity of the formed lipophilic metabolites to the aquatic life.

Biogeochemical behaviour of alkylphenol polyethoxylates in the wastewater treatment as well as in various types of freshwaters was recently intensively investigated (1,2) but the reports on APnEO and their metabolites in the marine environment are very scarce.

The results presented in this paper represent the first data on the determination of alkylphenol polyethoxylates and their lipophilic metabolites in the polluted part of the Krka River estuary. The area of investigation is a highly stratified estuary located in the Yugoslav Middle Adriatic region (3).

Grab samples of the surface waters were taken in glass bottles at different distances from the wastewater outlets in the Šibenik Harbour. In addition, samples on the vertical profile of the water column were collected by scuba diving (4).

Table 1. *Concentrations (µg/L) Alkylphenol Plyethoxylates and Their Lipophilic metabolites in the surface Waters (0.5 m) of the Šibenik Harbour*

Location	Distance[a] (m)	NPnEO	NP	NP1EO	NP2EO
SH1	1	72	2.1	26	27
SH2	1	28	2.7	3.4	3.2
SH4	1	19	1.0	2.5	2.7
SH4-A	10	-	0.36	0.64	0.35
SH4-B	100	-	0.064	0.042	0.01
SH4-C	200	-	0.048	0.053	0.020
SH4-D	300	-	0.068	0.057	0.015
SH4-E	400	-	0.058	0.036	<0.01

[a] distance from the sewage outlet

Unfiltered water samples were analysed for APnEO and lipophilic metabolites using highly specific chromatographic methods which were originally developed for the analysis of the freshwater samples (5,6). Briefly, the parent compounds were determined by the reversed-phase HPLC using spectrofluorimetric detection (277/300 nm). Prior HPLC anačysis APnEO were extracted using the standard Wickbold procedure and the extracts were purified on the column of partially deactivated aluminium oxide (5). The lipophilic metabolites (nonylphenol: NP, nonylphenol monoethoxylate: NP1EO, and nonylphenol diethoxylate: NP2EO) were enriched in cyclohexane employing continuous steam-distillation/extraction in a specially designed apparatus and the extracts were directly analysed by the normal-phase HPLC (6).

Table 2. *Vertical Distribution of Lipohphilic Metabolies of Alkylphenol Polyethoxylates in the Water Column of the Šibenik Harbour (µg/L)*

Location/Depth	Salinity (‰)	NP	NP1EO	NP2EO
E4a/0.5 m	13.0	0.054	0.043	0.015
E4a/1.25 m	15.0	0.300	0.036	0.030
E4a/1.5 m	22.0	0.067	0.050	0.013
E4a/6 m	36.5	0.100	0.051	0.017
E4a/20 m	37.5	0.084	0.165	0.031
E4a/40 m	37.5	0.230	<0.010	<0.010

The concentrations of APnEO in the samples taken immediatelly at sewage outlets (Table 1) were very low (7-72 µg/L). The strongly predominant homologues were nonylphenol polyethoxylates while octylphenol polyethoxylates were not detected. The concentrations of the lipophilic metabolites in the same type of samples were, as expected, even lower than the concentrations of parent compounds (1.9-55.1 µg/L) but indicated that they could significantly contribute to the total concentration of the nonylphenol compounds. According to the results presented in the Table 1 it seems that their dispersion and/or elimination in the Šobenik Harbour is very fast. Namely, after 100 m distance from the sewage outlet further decrease of the concentration is not any more significant.

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