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Due to the high production figures and unfavourable metabolic behaviour in the sewage treatment characterized by the formation of the lipophilic toxic metabolites (1, 2) alkylphenol polyethoxylates represent an issue of major environmental concern.

Input and distribution of alkylphenol polyethoxylates in the Krka River Estuary were studied during 1990-1991. Grab samples of wastewaters were taken from the sewering system of the town of Sibenik and at all major outlets in the Sibenik Harbour. In addition, samples of estuarine water were collected at different distances from the wastewater outlets and from the vertical profile of the water column.

Quantitative determination of APnEO was performed by high-performance liquid chromatography (HPLC) involving both normal-phase (distribution of oligomers) and reversed-phase (distribution of homologues) systems (3). The dissolved APnEO (filtered through GF/F filters) were extracted using C_{18} cartridges (4) while the particulate APnEO were extracted using an ultrasonic method.

The concentrations of APnEO in the wastewater varied in a rather wide range from 43-2960 /µg/L. The oligomer distribution was relatively uniform in all of the examined wastewater samples and indicated the predominance of the APnEO which are common for laundry detergents (Fig. 1). The most abundant individual oligomers in the dissolved fraction were those having an average number of EO units per molecule of 9-11. The oligomer distribution in the particulate fraction was significantly different showing a shift of the maximum towards lower oligomers (nEO = 6).
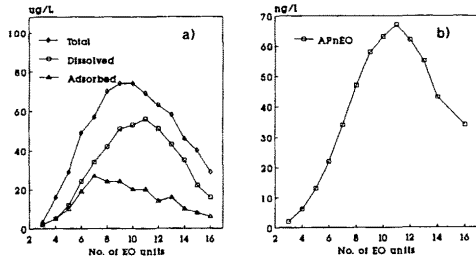

Figure 1. Oligomer distributions of alkylphenol polyethoxylates in a) raw wastewater and b) composite sample of the estuarine water from the vertical profile in the Sibenik Harbour

The study of the horizontal distribution of APnEO suggested that simple dilution was the primary mechanism which caused their rather low concentration levels in the water body of the Sibenik Harbour.

Fast sedimentation with sewage derived particles was indicated as another important mechanism since a significant portion of the total APnEO in the wastewaters (from 11.4 to 61.7 %) was found in the particulate fraction.

The vertical distribution of APnEO in the water column reflected clearly the stratification of the Krka River Estuary. The concentration maxima of APnEO were determined in the surface microlayer (17.1 /µg/L) and at the boundary of the freshwater and salinewater layers (8.6 /µg/L) while the concentration in the underlying salinewater layer was low (< 1 /µg/L). This indicated that the vertical transport of the pollutants was greatly reduced by the freshwater-salinewater boundary.

The oligomer distribution of APnEO in the estuarine water (Fig. Ib) resembled very closely the distribution of the dissolved APnEO in the wastewaters thus suggesting no significant alteration of the original composition by biodegradation. Indeed, the model biodegradation experiments conducted in the laboratory have shown that the biodegradation half-life of APnEO was in the range from 9 to > 25 days depending on the origin of the bacterial culture (freshwater or salinewater layer) and temperature (Fig. 2). The biodegradation was particularly slow in the salinewater layer and under the winter temperature conditions.
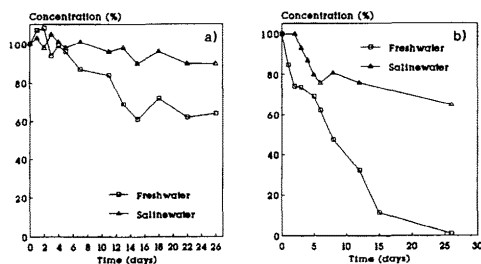

Figure 2. Model biodegradation experiments conducted with two different mixed bacterial cultures from the Krka River Estuary under the a) winter (13 °C) and b) summer (22.5 °C) temperature conditions.
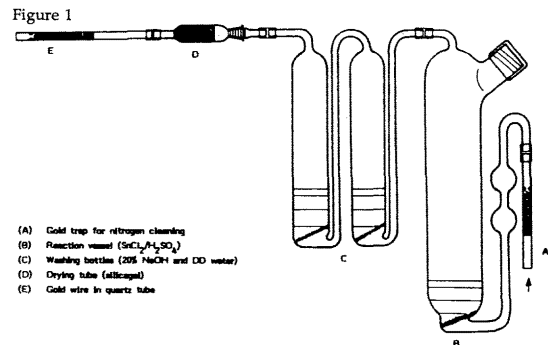
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A single device for the reduction of mercury from the samples and its collection in the elemental form onto gold wire is illustrated in Fig. 1.

Figure 1

(A) Gold trap for nitrogen cleaning
(B) Reaction vessel (SnCl₂/H₂SO₄)
(C) Washing bottles (20% NaOH and DO water)
(D) Drying tube (silicagel)
(E) Gold wire in quartz tube

A method has been applied on the vessel or on-shore within few minutes of sampling, taking into consideration wind direction and lee-side, respectively.

Water samples were taken into a reaction vessel containing a $SnCl_2$ and H_2SO solution where mercury was isolated from the solution after reduction by $SnCl_2$. The mercury was passed over gold wire using extra pure nitrogen as purging gas and sample carrier, and was subsequently amalgamated.

The gold wires with the deposited mercury were stored for several months in a well-protected, closed quartz vessel (Fig. 2), with no significant changes in mercury concentrations (Table 1). Measurements were performed using cold vapour atomic absorption spectrometry (CVAAS).

Figure 2.

(1) Quartz vessel
(2) Quartz tube with gold wire
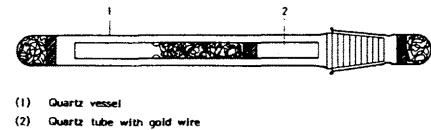
The samples were collected (Sibenik Aquatorium, Adriatic Sea, Croatia) by a diver facing the current direction, thus practically excluding "classical" problems associated with the sampling procedure (1).

In the estuarine water layer of lower salinity the reactive/total mercury ratio was between 0.1 and 0.5, whereas in the estuarine water layer of higher salinity the ratio was between 0.8 and 1.0 as in "clean" coastal seawater (2,3).

Table 1. Reactive mercury concentrations after collection and storage on gold wire

Place of sampling	Date of sampling and collection of reactive Hg onto gold wire	Reactive Hg concentration (direct measurement) ng/l	Date of measurement of reactive Hg collected and storage onto gold wire	Reactive Hg concentration ng/l	
Krka River Estuary (E) S= 19‰	17.09.1990	0.55 (Total Hg 1.1)	19.09.1990 (2 days)	0.5±0.1	n 4
			28.09.1990 (11 days)	0.6±0.2	4
			04.12.1990 (77 days)	0.6±0.2	4
Zlarin Island outer side of coastal zone (C) S=37‰	22.09.1986	0.30 (Total Hg 0.32)	25.09.1986 (3 days)	0.31±0.05	4
			10.10.1986 (18 days)	0.25±0.05	4
			07.11.1986 (46 days)	0.28±0.03	4
			24.11.1986 (63 days)	0.20±0.02	4

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