



# Estuarine and coastal zone marine pollution by the nonionic alkylphenol ethoxylates endocrine disrupters: Is there a potential ecotoxicological problem?

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## Abstract

The nonionic biodegradation-resistant (“hard”) alkylphenol ethoxylate (APEO) surfactants and their degradation products are known endocrine disrupting chemicals (EDCs). We report here the findings concerning the APEOs concentrations and homologous distribution profiles in Israel’s estuarine and coastal zone seawater to serve as a case study. The concentrations in sewage-containing rivers, estuaries and 50–60-m offshore sea (Mediterranean) water were found to be 12.5–75.1, 4.2–25.0 and 0.9–2.6 µg/L, respectively. The corresponding homologous distribution profiles were found to be within the range of 1–10% each, somewhat skewing, as expected, towards the more toxic shorter-chain ethoxylates. Egg production by zebrafish, exposed to 75, 25 and 10 µg/L of a typical industrial APEOs was reduced up to 89.6%, 84.7% and 76.9%, respectively, between the 8th and 28th days of exposure. Apparently, there is a potential APEOs-related ecotoxicological health risk problem.

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## 1. Introduction and background

Although the sea covers more than 70% of the surface of our planet, the continental shelf is the most important portion as far as human activities are concerned since it is the main source of living marine resources used as food for humans and it is most significantly impacted by anthropogenic factors. The shallow part of this zone, along the coast, is the most sensitive due to its smaller volume of water and proximity to point and diffuse sources of wastewater discharge. The output of anthropogenic contaminants as a result of domestic, industrial and agricultural human activities, directly or via rivers, into estuaries and marine environments is consequently, steadily increasing (Zoller and Hushan, 2000). In most cases, the impact and synergistic effects of those contaminants on the marine ecosystem and their potential risk to humans are not known.

Surfactants play a major role in detergent formulations. The surface activity, which depends on their chemical makeup, is the key to their effectiveness and performance in their

numerous applications. The currently most important uncharged nonionic surfactants are the branched-chain; therefore, biodegradation-resistant alkylphenol ethoxylates (APEOs) constitute about 17% of the total output of nonionics in the US (Zoller, 1994) and 7% of the world surfactant consumption, around  $\sim 7 \times 10^6$  tons annually (Hager, 1998).

The APEOs are environmentally persistent pollutants because their biodegradation is very slow and, quite often incomplete for a long period of time (Britton, 1998). Moreover, many of their degradation products are more toxic to aquatic organisms than the parent homologs, whereas both parents and metabolites (e.g., carboxylic acid degradation products and nonylphenol) remain in the affected aquatic environmental compartments for a long time, particularly in sediments (Ahel et al., 1994).

The occurrence and persistence of anthropogenic pollutants in the environment showing estrogenic–endocrine modulating effects in aquatic organisms is a “hot” issue of major health- and environment-related concern worldwide (Legler et al., 2000). A well-known group of potentially endocrine disrupting chemicals (EDCs) are the nonionic APEOs, especially the branched-chain nonylphenol and octylphenol ethoxylates (NPEOs and OPEOs, respectively) (Naylor et al., 1998), which

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Table 1  
APEOs concentrations in Israeli sewage-containing rivers, estuaries and offshore sea water

River/Estuary	APEOs concentration ( $\mu\text{g/L}$ )		Mediterranean Sea	
	River	Estuary	Offshore (m) <sup>a</sup>	Concentration ( $\mu\text{g/L}$ )
Achziv	17.6	5.9	60	1.5
Gaaton	12.5	4.2	60	2.6
Naaman	35.0	11.7	50	0.9
Kishon	73.5	24.5		
Taninim	19.6	6.5		
Hadera	43.2	14.4		
Alexander	63.0	15.2		
Poleg	75.0	25.0		
Yarkon	75.1	25.0		
Sorek	74.6	24.9		
Habonim			150	2.2

<sup>a</sup> Opposite to the indicated river/estuary.

constitute environmentally persistent pollutants (POP). Moreover, many of their degradation metabolites are more toxic to aquatic organisms than the parent molecules, and these metabolites remain in the affected environmental compartments for a long period of time (Thiele et al., 1997). Both, the parents and their metabolites, are known to elicit estrogenic response (i.e., capable of mimicking or antagonizing the action of steroid hormones) in both mammals and fish (Jobling et al., 1996). Indeed, they were found in tissues of mature and juvenile fish (flounder), indicating an environmental/estrogenic exposure (Lye et al., 1999), apparently to wastewater discharges.

Thus, the nature and extent of possible effects of EDCs on human health and wildlife is receiving growing attention from the scientific community, regulatory agencies, and the public at large, particularly with respect to their capability of affecting the endocrine system.

There is still not enough evidence to conclusively support the hypothesis that exposure to endocrine-disrupting/estrogenic chemicals is a global environmental health problem. Yet (a) an estrogenic activity of domestic sewage treatment works effluents was shown to occur at levels capable of producing biological effects in fish exposed to this water (Rutlage et al., 1998); (b) nonylphenol and some of its short chain polyethoxylates may have toxic effects at environmentally realistic concentrations of 0.01–10.0  $\mu\text{g/L}$  (Jobling et al., 1996; Ying et al., 2002); and (c) many of the APEOs (annual world consumption ca. 500,000 tons) and consequently, their degradation products, such as the carboxylated metabolites (Field and Read, 1996), enter the aquatic environment by means of discharge from municipal sewage-treatment works, industrial effluents and untreated sewage, and can occur in effluents and

rivers from ng to mg/L levels (Britton, 1998; Rutlage et al., 1998; Zoller and Hushan, 2000; Zoller et al., in press).

Data on sublethal (chronic) effects of APEOs are scarce and, therefore, more data concerning the chronic effects of the APEOs are needed. Lower concentrations and/or chronic exposure may cause sublethal damages that cannot be detected by LD<sub>50</sub> or short-term tests-based estrogenic effects. Nevertheless, it is now clear, that the homologous mixtures of APEOs, as well as their metabolites, may constitute a potential environmental health hazard. Thus, for example, in chronic toxicity tests, it was found that there is an increase in the toxicity of both NPEOs and OPEOs with decreasing EO chain length. NPECs (nonylphenol-ethoxy-carboxylates) and OPECs are less toxic than the corresponding APEOs and have acute toxicities similar to APEOs if having 6–9 EO units (Servos, 1999).

Recent studies with APEOs have indicated reproductive abnormalities in populations of marine organisms (Billinghurst et al., 1998), thus supporting the contention that exposure of wildlife to environmentally persistent endocrine/estrogenic chemicals can result in deleterious reproductive consequences.

Thus, these environmentally persistent endocrine disrupters have recently caused great concern, due to their ability to directly and indirectly influence vital endocrine functions in humans and wildlife. It is essential, therefore, to study the abundance, concentrations, homologous distribution and effects of this class of anthropogenic pollutants in estuarine coastal zone seawater of heavily populated marine regions. In this paper we report and discuss the results of such studies, aiming at establishing the APEOs' concentration and homologous distribution profile of these potential EDCs in estuarine and coastal zone marine environments, using Israel's Mediterranean Sea estuaries and coastal water as a case study. This is justified since in spite of many years of efforts to prevent pollution of receiving water bodies, studies have indicated that both surface and groundwaters are contaminated by surfactants, the 'hard' APEOs in particular (Zoller, 1997; Zoller and Hushan, 2000; Zoller, 2004). Furthermore, the APEOs are still extensively used in several Mediterranean countries and in accord, the potential estrogenic effects should be taken into consideration in related ecotoxicological studies.

## 2. The case of Israel

Israel, as a country with a high standard of living and, hence, typified by high consumption of detergents, is located in a semi-arid region, thus experiencing an extreme shortage of water

Table 2  
The homologous distribution profile (%) of APEOs in Israeli rivers, estuaries and coastal seawater

Environmental compartments	Number of EO units in APEOs																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Rivers/Streams	2.8	3.0	3.3	3.7	3.9	5.0	5.6	5.8	6.7	7.9	8.8	8.9	8.2	7.2	6.7	5.9	3.8	2.8
Estuaries	3.5	4.4	4.6	4.8	4.9	5.4	5.7	6.0	6.8	7.9	8.2	8.3	8.0	6.2	6.0	4.3	3.0	2.0
Offshore seawater	6.0	10.1	5.1	5.3	5.5	5.7	5.9	6.0	6.8	7.9	8.1	8.3	6.5	4.9	3.8	1.9	1.2	1.0

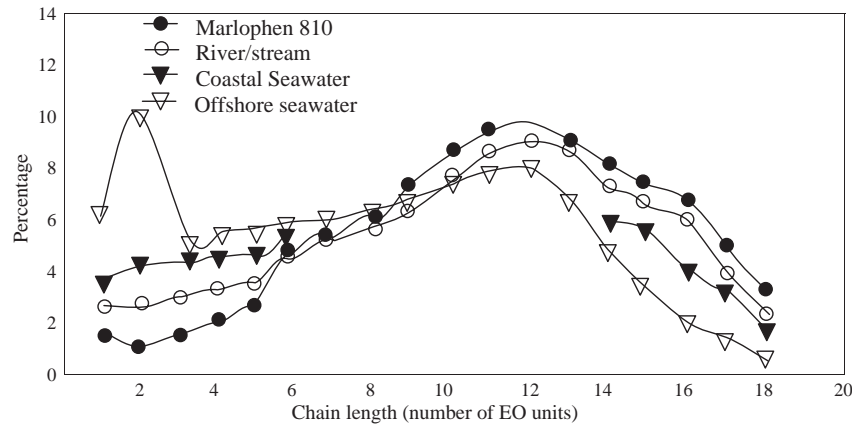


Fig. 1. Homologic distribution of APEOs (% of total distribution) in Israel's rivers, estuaries and Mediterranean sea water.

supplies. Of about  $5 \times 10^8$  m<sup>3</sup> of the annually produced sewage-containing ca. 9–12 mg/L of anionic (mainly LABS) and 1–3 mg/L of nonionic (mainly APEOs) surfactants (approx. 85:15 ratio)—about 27% and 45% of the total quantity are reused, following secondary treatment, or directly—for aquifer recharge and agricultural irrigation, respectively. About 15% of the total amount finds its way to the Mediterranean Sea. Since (i) only secondary treatment is available for sewage effluents in the country, (ii) the “hard” APEOs are barely affected by this treatment, and (iii) about 2/3 of the nonionic surfactants until recently used in Israel, were of the ‘hard’ APEO type, these nonionic surfactants and/or their metabolites reach surface and groundwater. Neither the existing sewage treatment facilities nor naturally occurring biodegradation processes appear to be capable of avoiding this environmental pollution, including that of the eastern Mediterranean estuarine and coastal zone.

### 3. Materials and methods

Grab sampling of selected “representative” sewage-containing rivers (just before their entrance into the sea), their estuaries and the Mediterranean Sea coastal water of the country, was followed by reverse phase HPLC determination of the total APEOs concentration (mainly nonyl/octylphenol

ethoxylates) in the samples (Marcomini and Giger, 1987; Naylor et al., 1998) as well as their local (at the sampling sites) homologic distribution by normal HPLC (Kubeck and Naylor, 1990).

The effect of the total actually found environmental concentrations of APEOs on zebrafish (*Danio rerio*) reproduction was determined via their exposure to these concentrations of APEOs in the Israeli Mediterranean estuaries and the corresponding sewage-containing rivers, followed by the monitoring of the fish's eggs production during 3 weeks of exposure. (Zoller et al., in press). The effect of exposure to APEOs having shorter vs. longer ethoxylate chains on egg production was also studied.

### 4. Results and discussion

The APEOs concentrations in the sewage-containing rivers/streams, just before they enter into their Israeli Mediterranean Sea estuaries, in the coastal seawater and offshore are given in Table 1 (Zoller and Hushan, 2000; Zoller et al., in press). Table 2 provides the homologic distribution profiles of the APEOs in these estuarine and marine environments.

Thus, the concentrations of the APEOs in the country's rivers/streams and the marine coastal seawater were found to be within the range of 12–75, and 4–25 µg/L, respectively. The homologic profiles of the APEOs in the sampled sites revealed an homologic distribution, percentage-wise, within the range of 1–10, somewhat *skewing*, as one could expect, towards the more toxic shorter-chain ethoxylates

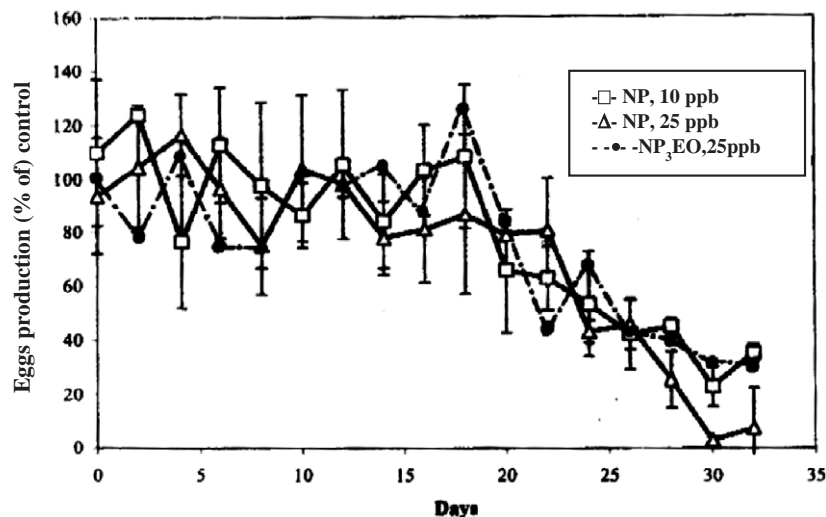


Fig. 2. The effect of 21 days (days 12–32) exposure of zebrafish (*Danio rerio*) to NP and NP<sub>3</sub>EO.

compared with that in the commonly used commercial product — Marlophen 810 (Hüls) here used as the baseline reference (Fig. 1). Such levels of short-chain APEOs in the aquatic estuarine and marine environments, particularly those in semi-arid regions (in which the “dilution effect” is expected to be relatively small) constitute an issue of major health-related concern.

Indeed, egg production by exposed zebrafish was significantly reduced after 8, 16 and 28 days in the actually found concentrations of 75, 25 and 10 µg/L of the APEOs, respectively, and continued to decrease statistically significantly until days 20 to 89.6, 84.7% and 76.9% of the baseline levels, respectively (Zoller et al., in press). No significant reduction in egg production was detected after 20 days exposure to 0 (control) and 5 µg/L of APEOs.

In a follow-up study (Zoller and Plaut, in press), we have found that exposure of zebrafish to concentrations of 10 and 25 µg/L of commercial NP<sub>3</sub>EO and NP<sub>15</sub>EO (both found to be mixtures of homologous APEOs, picking at 3 and 15 EO units, respectively), resulted in significant reduction in egg production in the case of the first (NP<sub>3</sub>EO; 25 µg/L), but not in the second (NP<sub>15</sub>EO), the pattern of the reduction being very similar to that observed in the exposure of zebrafish to nonylphenol (NP) at the same concentration (Fig. 2).

Our overall results suggest, that the APEOs concentrations found in Israel's estuaries and Mediterranean seawater, may be detrimental to the aquatic fauna. In addition, they should be evaluated as potentially environmental/health (endocrine disrupting) risk. Further, the effect of the APEOs is both time and concentration positively related, so that long term exposure to APEOs may affect fish reproduction even in lower concentrations than those here examined. Thus, the draft EPA water quality guidelines for NP [freshwater, 6 µg/L (4 day average) and 26 µg/L (1 h average)] appears to be rather liberal since these potential EDCs were found to affect other stages in fish and invertebrate reproduction processes (Harries et al., 2000).

## 5. Conclusion

The hard nonionic APEO surfactants and their biodegradation/degradation metabolites/products, the origin of which are either domestic, industrial, or agricultural wastewater, reach rivers/streams as well as estuarine and marine environments in Israel and persist there. Consequently, the levels of the APEOs, particularly those of their shorter-chain homologs found in these aquatic environments, constitute an issue of major environmental long-term health risk concern, particularly in such semi-arid countries with limited water resources.

In view of (a) the estrogenic/endocrine potential of the anthropogenic APEOs, (b) the case of the APEOs in Israel's estuaries and marine water here presented, and (c) the direct effect of APEOs on zebrafish eggs production found by us, as well as the results of several relevant ecotoxicological/toxicological studies conducted by others (Pikering and Sumpter, 2003), it appears that there is a potential APEOs-related ecotoxicological health risk problem. Consequently, a total ban on the use of the ‘hard’ APEOs in detergent formulation should be seriously considered and, in parallel, appropriate measures with respect to wastewater treatment and a switch to research-based management of water resources should be implemented accordingly. In the final analysis, the direction to take is *prevention* rather than *correction*. The long-term beneficial tradeoffs of such a voluntary and purposeful

move by all involved, rather than the imposition of delimiting regulation, are apparent.

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