ENDOCRINE DISRUPTING APEOs IN ISRAELI/PALESTINIAN WATER RESOURCES: WHAT SHOULD IT TAKE TO PREVENT FUTURE POLLUTION?

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ABSTRACT

The currently most important nonionic surfactants, which play a major role in detergent formulations, are the branched-chain and, therefore, biodegradation-resistant alkylphenol ethoxylates (APEOs), still in use in Israel. They are environmentally persistent pollutants, their metabolites being more toxic to aquatic organisms than the parent homologs, showing estrogenic-endocrine modulating effects in aquatic organisms and, therefore, constitute an issue of major health concern locally and worldwide. The objective of this work was, to assess the APEOs' concentration profile and homologic distribution in Israeli and Palestinian surface- and ground-water resources, targeting at providing the research-based base-line for a shared policy of preventing future pollution. The concentration profiles of the potential endocrine disrupting APEOs in Israel's rivers, groundwaters and coastal water of the Mediterranean Sea, were found to be within the range of 12.5-74.6, trace – 20.2 and 4.2-25.0 μg/l, respectively, with "skewing" towards the more toxic shorter-chain ethoxylates. Egg production of zebra fish exposed to APEOs, decreased, after 20 days, to 89.6 ± 2.1, 84.7±3.9 and 76.9±2.2% of the baseline levels, compared with control, in concentrations of 10, 25 and 75 μg/L, respectively, suggesting that there is a potential health problem associated with the APEOs, which is seasonally-dependent, particularly in semi-arid regions. Consequently, a ban on the use of APEOs should be seriously considered and a research-based management of the region's water resources should be applied.

KEYWORDS: Surfactants; Alkylphenol Ethoxylates (APEOs); Endocrine Disrupting Chemicals (EDCs); Water Pollution Prevention

INTRODUCTION

It appears to be agreed upon, that the current global 'water problem' is not its scarcity in the hydrosphere, not even in arid zones. It is the non-availability of the required quantities of water, in the appropriate quality and health safety for the different uses in the consumption sites, and at an affordable cost, which facilitates water availability for life – to all. This is the result of the ever-increasing gap between the rate of the used water self-renewal process – via the natural hydrological cycle – and the ever increasing rate and quantities of water consumption in modern technological societies locally, regionally and globally. The result: An accelerated process of soil, surface and ground-water pollution by both anthropogenic and naturally-originating chemicals with all the environmental and health consequences involved.

Sustainable development is a key demand in our world of finite resources and endangered ecosystems. Given the environmental imperatives, the potential ecotoxicological risk of both anthropogenic and naturally-originated chemicals and the limited economic feasibility of even the most advanced treatment and remediation technologies, the currently emerging *corrective-to-preventive* paradigm shift in production, development, consumption and disposal is unavoidable. The essence of the research-based claim, here presented, which has been evolved of the longitudinal Israeli experience – serving here as an illustrative, integrated case study – is the following: Water use, reuse, recycling and reclamation, wherever and whenever, should be applied only if the long-term pollution consequences of the local/regional surface- and ground-water resources can be avoided. Any delay in taking the necessary preventive measures will aggravate the situation – until it is irreversible – rather than solve the water shortage problem (Zoller, 2003).

Israel is located in a semi-arid region, thus experiencing an extreme shortage of water supplies. Of about 5×10^8 m^3/y of sewage water, -- containing ca. 330 ppm of chlorides, -- about 27% and 45% are used, following, mainly, secondary (activated sludge) treatment or *directly*, for aquifer recharge (reclamation) and agricultural irrigation (reuse/recycling), respectively.

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 and, therefore, biodegradation-resistant alkylphenol ethoxylates (APEOs) constituting about 7% of the world surfactant consumption. The APEOs [C_nH_{2n+1}-C_6H_4-O-$(CH_2CH_2O)_mH$] are environmentally persistent organic pollutants (POPs) because their biodegradation is very slow and quite often incomplete for a long period of time. Moreover, several of their degradation products and metabolites are more toxic to aquatic organisms than the parent homologs and, therefore, their persistence and showing estrogenic-endocrine modulating effects in aquatic organisms is a "hot" issue of major health- and environment-related concern worldwide. Although there is still not enough evidence to support the hypothesis that exposure to endocrine-disrupting chemicals (EDCs) is a global environmental human health problem, the following relevant facts have been established.

1. Estrogenic activity of domestic sewage treatment work effluents was shown to occur at levels capable of producing biological effects in fish exposed to this water (Routledge et al., 1998).
2. Many of the xenoestrogens, such as the APEOs, and their degradation products, such as the carboxylated metabolites (Ahel et al., 2000; Field & 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 nanogram to mg/L levels (Britton, 1998; Zoller, 1998; Routledge et al., 1998; Naylor et al., 1998).
3. Although no clearcut evidence of endocrine disruption was demonstrated, a recent study with 4-nonylphenol, a persistent metabolite of APEOs, has indicated that this compound and some of its short-chain polyethoxylates may have toxic effects at environmentally realistic concentrations of 0.01-10 ppb (Billingshurst et al., 1998; Jobling et al., 1996). As previously mentioned, our own results (Zoller et al., 2004) corroborate these findings and their implications (see Section IV).

It is now clear that APEOs as well as their homologues and metabolites constitute a potential environmental health hazard. In chronic toxicity tests, no-observable-effect concentrations (NOECs)

are as low as 6 ppb in fish and 3.7 ppb in invertebrates. There is an increase in the toxicity of both NPEO and OPEO (nanylphenol ethoxylates and octylphenol ethoxylates) with decreasing EO chain length. NPEC (nonylphenol ethoxy-carboxylates) and OPEC are less toxic than the corresponding APEOs and have acute toxicities similar to those of APEO, if they have 6-9 EO units (Servos, 1999). Alkylphenols (AP) and APEO, bind to the estrogen receptor, resulting in the expression of several responses, both *in vitro* and *in vivo*, as mentioned earlier. The available literature suggests that the ability of AP and APEO to bioaccumulate in aquatic biota in the environment is low to moderate. Thus, with respect to the latter, bioconcentration factors (BCFs) and bioaccumulation factors (BAFs) in biota, including algae, plants, invertebrates, and fishy, range from 0.9 to 3400 ppb. The potential of OP and OPEOs to bioaccumulate is expected to be similar to that of the corresponding NP and NPEOs (Servos, 1999). Thus, a systemic conceptual approach is needed in order to analyze and assess, quantitatively, the effect and impact of actual environmental concentrations of the APEOs in the aqueous environment.

THE CASE OF THE APEOs IN ISRAEL (Zoller, 2004)

Israel, as a country with, relatively, a high standard of living and, hence, typified by a high consumption of detergents is located in a semi-arid region, thus experiencing an extreme shortage of water supplies. In the 1890s its sewage contained about 9-12 ppm of anionic (mainly LABS) and 1-3 ppm of nonionic (mainly APEO) surfactants (approx. 85:15 ratio). Since, practically speaking, (1) only secondary treatment is available for sewage effluents in the country; (2) APEOs are quite biodegradation resistant due to their geranched-carbon alkyl chain; and (3) about two-thirds of the nonionic surfactants used in Israel until the early 1990s were of the "hard" APEO type, these nonionic surfactants and/or their metabolites reach surface- and ground-water. Thus, for example, until the start of operation of the combined mechanical activated sludge SAT (soil-aquifer treatment) SHAFDAN national sewage treatment project, about 1,700 kg of anionic (mainly LAS) and about 350 kg of nonionic (mainly APEO) surfactants were discharged daily into the coastal Mediterranean Sea water of Tel Aviv.

The Israeli APEO surfactants case may be considered a well-investigated example, typical of other countries confronted with (superficially conceived as) conflicting interests in the socio-techno-environmental context and problems that require sustainable solutions. As will be demonstrated, hard nonionic surfactants and/or their metabolites, the origin of which are either domestic, institutional, industrial, or agricultural wastewater and/or surface streams polluted by municipal sewage, reach both surface water and groundwater. Neither the existing sewage treatment facilities (Zoller, 2004) nor naturally occurring biodegradation processes in the receiving surface water systems, or physical soil adsorption, appear to be capable of avoiding this environmental pollution.

The concentration and homologic profiles of the potential endocrine disrupting nonionic alkylphenol ethoxylate surfactants as well as of these metabolites in Israel's rivers, groundwaters and coastal water of the Mediterranean Sea, has been the focus of this work, targeting at providing the research-based base-line for a shared policy of prevention of future pollution of shared water resources. This publication is an additional contribution to the several recently reported APEOs issue-related studies (Ferrara, 2004; Giger, 2004; Jonkers et al., 2003; Zoller et al., 2004).

METHODS

Seasonal grab sampling of selected "representative" sewage-containing rivers, groundwater wells and the Mediterranean Sea coastal water (see Figure 1 for sampling sites), was followed by determination of the total APEOs concentration (mainly nonyl/octyl phenol ethoxylates) in the samples (Marcomini and Giger, 1987), as well as their local (at the sampling site) homologic distribution (Kubeck and Naylor, 1990) by reverse and normal HPLC, respectively.

GRAPHIC
Figure 1. Sampling sites

The effect of the total concentrations of APEOs on the zebrafish reproduction was determined using 120 specimens of zebrafish (*Danio rerio*), a common model species in toxicological studies (Legler et al., 2000). They were divided into 15 groups of 8 (4 females, 4 males) each held in 20 L aquarium at 28°C under 16:8 L:D photoperiod. The zebrafish eggs produced under these conditions were counted, for each group once every two days for 10 days for establishing baselines. The fish were, then, exposed to the actually found concentrations of 0, 5, 10, 25 and 75 μg/L of APEOs (3 groups in each concentration) **(**Marlophen 810, Hüls) and eggs production was monitored for the next 20 days. The results were analyzed using ANOVA with repeated measurements to detect significant reduction in eggs production ($p<0.05$).

RESULTS AND DISCUSSION

The APEOs loads of the sewage-containing rivers/streams which enter into the Mediterranean Sea at the sites of the coastal seawater sampling (see Fig. 1) in Israel's groundwater wells adjacent to the sewage-containing rivers sampled, and at the estuaries of these coastal rivers are given in Tables 1-3, respectively (Zoller and Hushan, 2000; Zoller, 2004; Zoller et al., 2004). The homologic distributions of the APEOs in Israel rivers, coastal/river estuaries and offshore Mediterranean Sea water of the country are given in Fig. 2.

The bottom line: The APEO nonionic surfactants concentrations of the country's rivers/streams (clearly containing waste water), groundwater and Mediterranean coastal seawater are within the range of 12-75, trace – 20 and 4-25 μg/L, respectively. The homologic profiles of the APEOs in the sampled sites revealed an homologic distribution,

Table 1. Concentrations of nonionic (APEOs) surfactants concentrations in Israeli (sewage-containing) rivers.

River	APEOs concentration (μg/L)
Achziv	17.6
Gaaton	12.5
Naaman	35.0
Kishon	73.5
Taninim	19.6
Hadera	43.2
Alexander	63.0
Poleg	75.0
Yarkon	75.1
Sorek	74.6

Table 2. Concentrations of Nonionic (APEOs) Surfactants in Israel Groundwater (selected representative water wells).

Well location	Adjacent to river (upstream)	APEOs concentration (μg/L)
Metzer K.	Hadera	11.9
Nazlet Issa	"	20.2
MEK Yad Hana	Alexander	0
Tul Karem A.Q.K.	"	7.6
P. Taibe D.N.	Poleg	8.5
P. Kafr Qasem I.	Yarkon	2.7
Nakhshonim	"	8.7
Mek.Rosh Ha'Ayin 2	"	Trace

Table 3. Concentrations of nonionic (APEO) surfactants in the coastal water of the Israeli eastern Mediterranean Sea

Mediterranean river/stream junction –	APEOs concentration (μg/L)
Achziv	5.9
Gaaton	4.2
Naaman	11.7
Kishon	24.5
Taninim	6.5
Hadera	14.4
Alexander	15.2
Poleg	25.0
Yarkon	25.0
Sorek	24.9

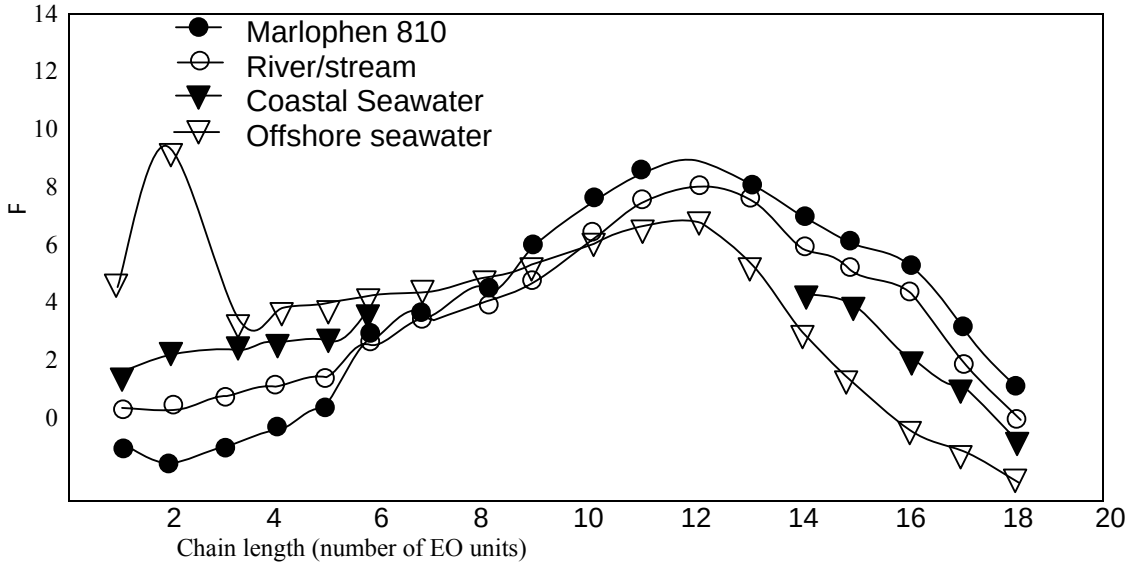

Figure 2. The homologic distribution of APEOs in Israel surface- and ground-water

percentage-wise, within the range of 1-10 with some skewing towards the shorter-chain ethoxylates compared with the original homologic distribution in typical commercial APEOs commonly used in the country, here represented by Marlophen® 810 as a reference (Fig. 2). Thus, for example, 2.8-4.6% (of the total concentration) of the shortest homologs-$APEO_{1-3}$, means survival concentrations of 2.1-3.4 μg/L of this homologs (Zoller et al., 2004) which are known to be more toxic than the longer-chain ones (Lye et al., 1999; Ying et al., 2002) in some of the rivers sampled. Such levels of short-chain APEOs in the aquatic environments of semi-arid Mediterranean region constitute an issue of health-related concern. Indeed, eggs production by exposed zebrafish was significantly reduced after 8, 16 and 18 days in 75, 25 and 10 μg/L of APEOs respectively, and continued to decrease, statistically significantly, until day 20, when APEOs were removed from the water. No significant reduction in egg production was detected after 20 days exposure to 0 (control) and 5 μg/L of APEOs (Zoller et al., 2004). These results suggest, that (a) there is a potential health problem, particularly in countries in which the "hard" environmentally persistent APEOs are still in use; and (b) the related health-risk is seasonally-dependent, particularly in semi-arid regions where the fluctuations in the water quantities in surface- and groundwater are substantial. The levels of the APEOs, particularly of the shorter-chain homologs found in these aquatic environments, constitute, therefore, an issue of major environmental long-term health-risk concern.

CONCLUSIONS

In view of the estrogenic/endocrinic potential of the anthropogenic nonionic APEO surfactants, it appears that there is a health-related risk problem associated with the usage of APEOs in semi-arid regions. Consequently, (a) a ban on the production and use of APEOs in detergent formulation should be seriously considered; (b) effective APEOs removal sewage treatment processes should be applied as long as these POPs are present in or disposed into wastewaters; and (c) an immediate switch to a research-based integrated management of our water resources, groundwater in particular, should be implemented.

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