Chapter 43
The Chronic POEDCs Ecotoxicological Impact: An Aquatic Environmental Indicator of Surface and Groundwater

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Abstract 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. The population growth and the increasing scarcity of water in many regions of the world have led to a comprehensive reuse of treated wastewater that, ultimately, may cause a long-term concentration buildup of many toxic persistent organic pollutants (POPs) in the closed cycle of water supply and wastewater treatment and reuse. The endocrinic/mutagenic potencies of the EDCs-branched chain alkylphenol ethoxylates (APEOs), polycyclic aromatic hydrocarbons (PAHs) and their metabolites are well-documented. From ~5.5×10^8 m^3/year of sewage produced in Israel, ~70 % are reused, following a conventional, or advanced, activated sludge or sand aquifer treatment (SAT). A major related question is: Does this practice conform to sustainability? Our studies reveal that (a) the concentrations of APEOs and PAHs in Israel rivers and sediments do pose a potential health risk problem; and (b) the *synergistic* ecotoxicological impact of environmentally relevant mixtures of these POPs, in WWTP effluents, constitutes an inconsistency, health-wise, with sustainability practice.

Keywords Anthropogenic pollutants • Polycyclic aromatic hydrocarbons (PAHs) • Persistent Organic Endocrine Disrupting Compounds (POEDCs) • Persistent organic pollutants (POPs) • Toxicity • Water • Health

43.1 Introduction and Background

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 (Sumpter and

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POEDCs: Persistent Organic Endocrine Disrupting Compounds

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Johnson 2005). The population growth and the increasing scarcity of water in many regions of the world have led to a comprehensive reuse of treated wastewater that ultimately may cause a long-term concentration buildup of many toxic chemicals in ecosystems and closed cycles of water supply and wastewater treatment and reuse (Caldas et al. 2013). Endocrine disrupting chemicals (EDCs) refer to chemicals affecting the endocrine system. Such an effect may be at the level of receptor-mediated hormone action, binding and activating, or not activating the estrogen receptor (estrogenic or antiestrogenic, respectively), hormone synthesis, or clearance. In the aquatic environment there are many well documented examples of EDC-s/persistent organic endocrine disrupting chemicals (POEDC-s) impact on wild life. As such, the EDCs-ecosystems-environmental condition-environmental indicators-sustainability connection is apparent.

Sustainability is a key demand in our world of finite resources and endangered ecosystems. Given the environmental imperatives, the potential ecotoxicological risk of anthropogenic chemicals, and the limited economic feasibility of large scale treatment and remediation technologies, the currently emerging corrective-to-preventive paradigms shift in production, development, consumption, and disposal is unavoidable. Following their use and disposal – into either sewage systems or natural receiving aquatic sinks – and/or the large scale reuse of wastewater for agricultural irrigation, persistent (nonbiodegradable) EDCs/POEDCs ultimately enter aquatic and terrestrial compartments of the environment and persist there as such, or as their (bio-) degradation/metabolites.

43.2 Potential Hazard and Fate of Endocrine Disrupting Chemicals in Wastewater

The occurrence and persistence of anthropogenic POEDCs in the aquatic environment that were found to affect aquatic organisms initiated both health and environment concerns worldwide (Pickering and Sumpter 2003; Sumpter 2008; Ternes et al. 1999; Lee et al. 2013). EDCs refer to those chemicals with a primary effect on the endocrine system. Such an effect may be at the level of receptor-mediated hormone action, binding and activating, or not activating the estrogen receptor (estrogenic or antiestrogenic, respectively), hormone synthesis or clearance. In the aquatic environment there are several well documented examples of EDCs that have been demonstrated to have an impact, such as male feminization and reduced productivity in fish and other wild life (Pickering and Sumpter 2003). The three classes of anthropogenic POEDCs that, ultimately, reach surface and ground water resources, largely via the reuse or disposal of municipal wastewater, are the nonionic alkylphenol ethoxylates (APEOs) (Naylor et al. 1992; Sarmah et al. 2006), polycyclic aromatic hydrocarbons (PAHs) (Mahler et al. 2005), pharmaceuticals (Ternes et al. 1999, 2004) personal care products (PPCPs), and hormones (Esperanza et al. 2004; Huang and Sedlak 2001; Kolpin et al. 2002a, b)

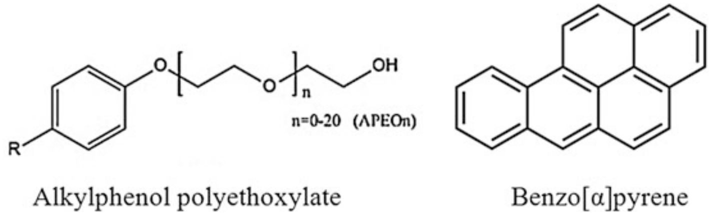

Fig. 43.1 APEOs and PAH representatives

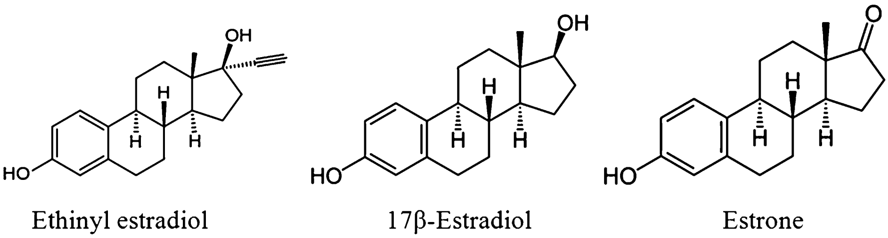

Fig. 43.2 Anthropogenic and natural hormones in Israel's WWTP influents and effluents

(Figs. 43.1 and 43.2). Although the extent of the threat of human exposure to these EDCs still remains to be elucidated, they are naturally biodegradation-resistant and, therefore, environmentally persistent organic pollutants (POPs), creating a major ecotoxicological issue of concern. Since (a) these EDCs and other structurally-related compounds as well as/or their metabolites and/or degradation products do reach surface- and groundwater (Ashton et al. 2004; Bergman et al. 2013; Ying et al. 2002), and (b) they were found to affect the endocrine system of the susceptible animals, triggering a rather wide range of biological effects even at extremely low concentrations (ng-μg/L level), their persistent/survival in the aquatic environment, particularly in public water supply and treatment [activated sludge (AS), river bank (RB), wetland (WL) and soil aquifer treatment (SAT)] systems, constitutes an issue of importance with respect to public health (Heberer and Adam 2004; Zoller et al. 2004; Kidd et al. 2007). Indeed, there is a POEDCs-related environmental health risk problem (McCann 2004; Zoller 2004; Sumpter 2008).

Two major anthropogenic EDCs that, ultimately, reach surface and ground water resources via runoff and reuse or disposal of municipal wastewater (Berryman et al. 2004; Ying et al. 2002) are the persistent organic pollutants (POPs) PAHs and APEOs. The extent of the threat to humans being exposed to these mutagenic/carcinogenic (and also teratogenic) still remains to be elucidated. Thus, the fact that PAHs are structurally biodegradation-resistant and, therefore, environmentally persistent (Nagy et al. 2007) renders an environmental ecotoxicological issue of concern. These EDCs and their metabolites/degradation products, oxidatively or reductively, were found to affect the endocrine systems of the susceptible animals, hence triggering rather large biological effects even at low concentrations. APEO surfactants on their part, especially the branched congeners nonyl-and octylphenol ethoxylates and their metabolites, are known to elicit estrogenic response, i.e., they are capable of mimicking or antagonizing the action of steroid hormones, in both mammals and fish (Jobling et al. 1996). They were found in tissue of mature and juvenile fish (flounder), indicating an environmental /estrogenic exposure to wastewater discharges (Lye et al. 1999). Data on the chronic effects of actual environmental and/or sublethal concentrations of APEOs are available (Zoller 2008). The persistence of these POEDCs in the aquatic environment, particularly in public water supply systems and in reclaimed water where reuse for agricultural irrigation is extensively practiced, constitutes a major environmental health risk problem (Pickering and Sumpter 2003; Zoller 2006). Data concerning the synergistic effects of these two groups, *per se*, in the presence or absence of other EDCs, particularly as far as their synergistic ecotoxicological and health risk potential are concerned, are just starting to emerge (Zoller 2006; Zoller and Hushan 2010). Clearly, the increased solubility of the hydrophobic PAHs in the presence of the hydrophilic APEOs increases the bioavailability of the former, with all the ultimate chronic ecotoxicological impacts involved. The scope of the POEDCs problem is huge, since in addition to the APEOs and PAHs, PPCPs and natural steroidal estrogen hormones (Kolpin et al. 2002a, b; Ternes et al. 2002) are released to the environment after passing through conventional wastewater treatment plants (WWTPs), which, as such, are not designed to remove these compounds from the effluents (Kolpin et al. 2002a, b).

43.2.1 Wastewater Treatment

The continuing rise of the human population, accompanied by the increasing demand on the limited water reservoirs worldwide necessitates seeking alternative water resources. Domestic urban, industrial, and agricultural wastewater is considered to be one of the most important water resources and has gained much interest during the last years. Treated wastewater in WWTPs can be readily reused in agriculture or industry. Various conventional, e.g., active sludge-based, and advanced oxidation processes (AOPs) have been developed and are currently being used for wastewater treatment. However, the majority of conventional treatment processes have been designed, primarily, for reduction of organic and inorganic components in the WWTPs influents to a level permitting their safe discharge into the environment. However, the potential additive and/or synergistic chronic ecotoxicological impact (SCEI) of the POEDCs, such as pharmaceuticals, hormones, antibiotics, and personal care products (PCPs), persists in the effluents to be reused. Awareness of the environmental health hazard posed by such contaminants has resulted in increasing the related public concern and stimulated exploration of the EDCs' occurrence and fate in sewage influents and effluents of WWTPs. Conventional activated sludge (AS) and river bank (RB) systems are, at present, the most common for treatment of domestic wastewater in large cities. In rural areas, wetland systems are also used for wastewater treatment. Anaerobic lagoons are used to treat animal waste, such as that of swine. Since it is highly unrealistic to expect a reduction in the consumption of, e.g., pharmaceuticals (hormones and antibiotics), novel technologies for improving wastewater treatment are continuously being developed that significantly diminish the release of these endocrinic compounds into the environment.

The scope of the problem is huge (Khanal et al. 2006; Lohmann et al. 2007), since the anthropogenic POEDCs, APEOs, PAHs, PPCPs, natural steroidal estrogen hormones (Hanselman et al. 2003; Koplin et al. 2002a, b), and inorganic EDCs are released directly to the environment after passing through conventional WWTPs that are not designed to remove these compounds from the effluents (Halling-Sorensen et al. 1998; Kolpin et al. 2002a, b), and ultimately, reach surface- and groundwater. In fact, concentrations of (10–100 ng/L) of PPCPs and structurally related compounds were already found in wastewaters and surface water, e.g., propranolol and ibuprofen, more than a decade ago (Kolpin et al. 2002a, b; Hanselman et al. 2003; Ternes et al. 2004). Such concentrations of these EDCs, and >10 μg/L of APEOs have the potential to affect adversely the reproductive biology of aquatic wildlife (Tyler et al. 1998; Hanselman et al. 2003; Pikering and Sumpter 2003; Zoller et al. 2004). Thus, the importance of establishing these EDCs' environmental concentration profiles and their synergistic chronic ecotoxicological impact (SCEI) in soil and surface- and groundwater, is apparent.

43.2.2 Treatment Methods

43.2.2.1 Chemically Enhanced Primary Sedimentation (CEPS)

The removal rate of organic carbon load toward secondary treatment can be increased by chemically aided sedimentation, considering that a quite large amount of the organic load (up to 40–50 %) present in sewage is in the colloidal form. The expected increase in the removal efficiency of organic micro-pollutants can have a strong impact on further treatment stages and the ultimate effluent reuse. There have not been many data regarding the removal of POEDCs in CEPS. Some indication could be obtained based on the study of Sharp et al. (2005), who found that coagulation of natural organic matter (NOM) depends on the latter's polarity balance and the charge density. In accordance, a reduction in the CSEI of POEDs in WWTPs' effluents is to be expected.

43.2.2.2 Biological Treatment

It has been reported that various organic micro-pollutants have been removed in activated sludge (AS) systems by two main mechanisms: biodegradation and sorption to the biomass. Nevertheless, the data gathered are somehow controversial. Joss et al. (2006) reported, based on the degradation of a heterogeneous group of

35 compounds, that state-of-the-art biological treatment schemes for municipal wastewater are not efficient in terms of degrading pharmaceuticals. Several distinct categories of PPCs were surveyed along different units of a municipal WWTP, in Spain (Carballa et al. 2004). The overall removal efficiencies within the WWTP ranged between 70 and 90 % for the fragrances, 40–65 % for the anti-inflammatories, ~ 65 % for 17β-estradiol, and 60 % for sulfamethoxazole. However, the concentration of estrone increased along the treatment due to the partial oxidation of 17β-estradiol in the aeration tank. Conventional wastewater treatment has been found efficient in the removal of the potent 17α-estradiol (85–99 %), whereas estrone removal was relatively poor (25–80 %) (Khanal et al. 2006). A study in eight WWTPs in Germany found that the removal efficiency of the hormone ethnylestradiol (birth control pill) reached 90 % (Coors et al. 2004). Several reports depict hydrophobic interaction between aliphatic and aromatic EDCs and the lipophilic moieties of biomass-cell membranes (Thomas et al. 2006), indicating a significant hazard related to sludge application in agriculture.

43.2.2.3 Advanced Oxidation Processes (AOPs)

New emerging technologies utilizing combinations of UV, Ozone, and H_2O_2 are currently being applied for the removal of various contaminants in water and wastewater (Vieno et al. 2007). Ozone was reported to exhibit high removal efficiency of various pharmaceuticals and steroids (Ternes et al. 2004). The effectiveness of Ozone and UV/H_2O_2 for the removal of six medicines was found to be high for all six medicines tested, except clofibric acid. These processes, while being highly efficient, are relatively costly and may result in the formation of toxic intermediates (Thomas et al. 2006). Clearly, application of AOPs following the process in the biological treatment stage in AS-based WWTPs significantly reduces the "endocrinal potential" of the POEDCs SCEI in the discharged effluents.

43.2.2.4 Sorption

Activated carbon has been traditionally used for the removal of many toxic compounds in water works. In a related study, it was found that granular activated carbon could be used successfully for the removal of PPCPs and estrogenic flame retardants in surface waters and WWTPs effluents (Kim et al. 2007). The effect of the nature of the sorbents (i.e., surface charge), PPCPs (i.e., pKa, ionization, hydrophobicity) and aqueous solution (i.e., pH) impacted the sorption of pharmaceuticals (Lorphensri et al. 2006). A strong association was found between increased organic carbon content and increased sorption, or decreased mobility of, e.g., estradiol and testosterone, indicating that hydrophobic interactions are responsible for the sorption process (Casey et al. 2004; Das et al. 2004). As far as the pharmaceuticals are concerned, the more of them that are sorbed on the activated carbon, the less "endocrinic" the WWTPs effluents are expected to be.

43.2.2.5 Membrane Separation Processes

Pressure-driven membrane separation processes comprise microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All these are considered to be emerging technologies for the potential removal of EDCs from WWTPs effluents. Membrane bioreactors (MBR) showed a limited removal of target compounds, but were shown to be effective for eliminating some PPCPs, e.g., acetaminophen, ibuprofen and caffeine; RO and NF showed a >95 % removal of all target substances studied (Kim et al. 2007). However, it was demonstrated that high molecular weight POEDCs, such as 17β-estradiol (MW: 279 g/mol), were still detected in the RO permeate, albeit at very low concentrations (Kimura et al. 2004). Negatively charged compounds are expected to be significantly rejected by NF/RO membranes due to electrostatic repulsion between the compounds and membranes. A high level of rejection (>90 %) associated with negative charge was observed even for low molecular weight compounds (e.g., 110) in NF. For neutral, uncharged compounds, rejection will depend on their physical/chemical properties. The relationship between the physical/chemical properties of compounds and the latter reactions of NF/RO membranes' systems affects the end results and, accordingly, the endocrinal impact of the effluents.

43.3 Synergistic Chronic Ecotoxicological Impact (SCEI) of Persistent Organic Endocrine Disrupting Chemicals (POEDCs)

Regardless of "climate change," the population growth, and the increasing scarcity of water in many regions of the world, arid and semi-arid, in particular, water reuse, mainly of municipal wastewater treatment plants effluents, has increased dramatically (Sumpter and Johnston 2005; Ternes et al. 2004). Consequently, the pollutants, mainly the POEDCs that survive the various treatments – physical, biological, chemical and/or natural environment systems-based (e.g., bank filtration, soil-aquifer treatment-SAT) – constitute an ever-increasing major environmental ecology- and health-related concern. This is due to the estrogenic-endocrine modulating effects of these POPs-EDCs, even in their surviving ng/L concentrations in the WWTPs' effluents, which, ultimately, reach surface- and groundwater resources. The main issue is not the LD_{50} of the separated EDCs in effluents mixtures, but rather the actual combined chronic ecotoxicological impact (SCEI) of this endocrinic mixture, which, in turn, also point at a potential toxic health risk (Fig. 43.3).

Although the extent of the threat to humans being exposed to POEDCs still remains to be elucidated (Zoller and Hushan 2010), their nature, namely their naturally biodegradation-resistance and environmental persistence, turn them into a major ecotoxicological environmental issue of health concern. These EDCs and their metabolites/degradation products were found to affect the endocrine system of exposed animals, triggering rather large biological effects even at extremely low

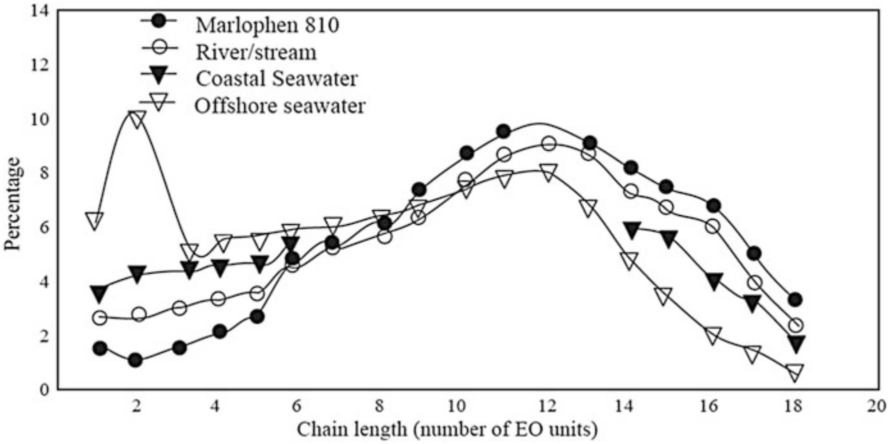

Fig. 43.3 The homologic distribution of APEOs (% of total distribution) in Israel's rivers, estuaries and Mediterranean seawater (Zoller et al. 2004)

concentrations (ng-μg level). The persistence of the POEDCs in aquatic environments, particularly WWTPs effluents reused for irrigation and public water supply systems in semi-arid regions (where reclaimed water reuse, mainly for agriculture irrigation is extensively practiced), constitutes an environmental health problem (Pickering and Sumpter 2003; Zoller 2004). Recently, the focus of the EDCs-related environmental research has been extended to PPCPs (Ternes et al. 2004; Zeng et al. 2005; Bayen et al. 2013; Lee et al. 2013) with respect to their and as well as their recalcitrant metabolites' persistence and estrogenic effects in aquatic environments, particularly whenever wastewater effluents are either being reused or discharged into surface waters (Huang and Sedlak 2001; Kolpin et al. 2002a, b; Yang et al. 2013; Esteban et al. 2004). Consequently, the health-related aspects, have become a major issue of concern, in particular the related SCEI-human health risk potential relationship (Zoller and Hushan 2010).

Many anthropogenic, e.g., APEO surfactants, especially the branched congeners nonyl- and octylphenol ethoxylates and their metabolites, are known to elicit estrogenic responses, i.e., they are capable of mimicking or antagonizing the action of steroid hormones in both mammals and fish (Gabriel et al. 2008; Lye et al. 1999). They were found in tissue of mature and juvenile fish (flounder), indicating environmental estrogenic exposure to wastewater discharges. Similarly, long term chronic exposure of Zebra fish to a mixture of PAHs resulted in substantial reduction in their fertility (eggs' production) (Zoller and Hushan 2010).

43.3.1 The Synergistic Chronic Ecotoxicological Impact (SCEI) of Selected POEDCs

Data on chronic effects of actual environmental and/or sublethal concentrations of POEDCs, the most relevant with respect to the potential public health risk, are

Table 43.1 AEPOs and PAHs concentrations in WWTP influents and effluents

STP	Influent (μg/L)		Effluents (μg/L)		Removal (%)	
	AEPOs	PAHs	AEPOs	PAHs	AEOPs	PAHs
Haifa	48.9	0.38	34.0	0.25	**30.5**	**34.2**
Netanya (Sharon)	49.9	0.38	35.0	0.24	**30.0**	**36.8**
Neve Shaanan Technion	42.1	0.36	27.4	0.23	**34.9**	**36.1**
Sakhnin	48.0	0.23	34.8	0.23	**27.5**	**30.4**

scarce. Clearly, more data concerning the quantitative chronic effects of each environmentally underestimated relevant POEDC and more so the synergistic chronic ecotoxicological impact (SCEI) of environmentally POEDCs' particularly are needed, targeted at the assessment of their ecotoxicological and health risk potential.

The SCEI of real POEDCs mixtures in WWTPs' effluents, surface- and ground-water via appropriate tests, e.g., the ZFEPT (Zoller et al. 2004), fill all the criteria of "environmental indicators" and can be used as "equivalents" to the latter. The related representative results of our research study recently conducted in Israel, based on our (experimentally) developed ZFEPT (Zebra fish Egg Production Test) and to be published shortly, are presented in the next Sect. 43.3.2 of this chapter (Table 43.1).

43.3.2 The SCEI of POEDCs: The Israeli Research-Based Case Study

Israel, a country in the eastern Mediterranean basin, is located in a semi-arid region. The country is experiencing an extreme shortage of water supplies. From the approximately 5×10^8 m^3 of annually produced sewage containing ca. 9–122 mg/L of anionic (mainly LABS) and 1–3 mg/L of nonionic (mainly APEO) surfactants, ~ 90 % is treated in (mainly) activated sludge (AS)-based WWTPs, and about 70 % is reused, mainly in agricultural irrigation. Given this, almost exclusively, secondary activated sludge treatment (AST) practice, the importance of establishing these EDCs' environmental profiles and synergistic ecotoxicological environmental impact in river sediments and water is apparent (Fig. 43.4).

43.3.3 APEOs-PAHs in Israel (Representative) Rivers

Given that about 70 % of Israel's ~550×10^6 m^3/Y of wastewater is being reused, following its treatment in AS-based WWTP or SAT, the remaining concentrations

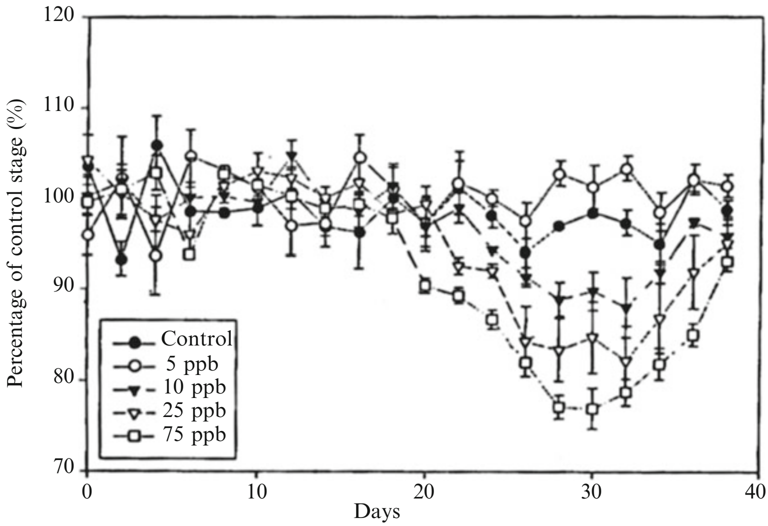

Fig. 43.4 Effect of APEOs mixtures (Marlophen 810) on zebrafish (*Danio rerio*) reproduction (Zoller 2004)

of the APEOS and PAHs in the effluents that ultimately reach surface and groundwaters, mainly via agricultural irrigation, are of particular relevance (Table 43.2).

It is worth noting that (1) the APEOs and PAHs loads in the two urbanic wastewater plants (Haifa and Netanya) were essentially the same, and (2) the percentage of removal of these two POEDCs in the activated sludge (AS)-based treatment was quite similar.

Based on our representative results presented here, the experimentally derived research does respond to the question concerning the potential synergistic ecotoxicological impact of APEO-PAH mixtures and their potential health risk. Similar conclusions have already been reached in many studies focusing on mixtures of hormones (natural and anthropogenic) and selected "representative" PPCPs in wastewater effluents that are actually being reused. Thus, the contemporary wastewater reuse practice constitutes a potential endocrine health risk. This, in turn, requires the application of advanced treatment technologies in WWTPs to ensure the sustainability of their effluents' reuse. In view of recent studies that demonstrated the potential deleterious effects of extreme abiotic factors on chemically-based toxicities/56/, toxicokinetics and toxicodynamics modeling studies may be needed in the future to understand the toxicologic-ecotoxicologic pathways that are involved in environmentally-relevant mixtures of POEDCs and relevant stressors. This would enable the usage of the related SCEI as a solid environmental indicator.

Table 43.2 The impact of APEOs + PAHs + hormones + Pharmaceuticals on zebra fish (*Danio rerio*) egg production

Chemical group	Average concentration in WWTP effluents	Average concentration in WWTP influents	Smaller concentrations which had impact
APEOs	32.6 µg/L	47.8 µg/L	10 µg/L
PAHs	0.23 µg/L	0.35 µg/L	50 µg/L
Hormones			
E1	28.8	73.4	75
E2	7.8	22.4	50
E3	5.8	11.0	1
Pharmaceuticals Sulfa	74.6	154.3	120
Carba	135.7	449.5	120
Diketo	93.6	1,143.6	150
Impact after Exposure (days)	4	4	8
Recovery after Cleaning (days)	Return to 25 % (of eggs) compared to start	Return to 22 %	Return to 40 %
Maximum reduction in egg production	12 %	8 %	16 %

References

Ashton D, Hilton M, Thomas KV (2004) Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. Sci Total Environ 333(1–3):167–184

Bayen S, Zhang H, Desai MM, Ooi SK, Kelly BC (2013) Occurrence and distribution of pharmaceutically active and endocrine disrupting compounds in Singapore's marine environment: influence of hydrodynamics and physical-chemical properties. Environ Pollut 182:1–8

Bergman Å, Heindel JJ, Jobling S, Kidd KA, Zoeller RT (2013) Executive summary. In: State of the science of endocrine disrupting chemicals - 2012: an assessment of the state of the science of endocrine disruptors prepared by a group of experts for the United Nations Environment Programme and World Health Organization. WHO Press. ISBN 978-92-4-150503-1

Berryman BD, Houde F, DeBlois C, O'Shea M (2004) Nonylphenolic compounds in drinking and surface waters downstream of treated textile and pulp paper effluents: a survey and preliminary assessment of their potential effects on public health and aquatic life. Chemosphere 56(3):247–255

Caldas SS, Bolzan CM, Guilherme JR, Silveira M et al (2013) Determination of pharmaceuticals, personal care products, and pesticides in surface and treated waters: method development and survey. Environ Sci Pollut Res 20(8):5855–5863

Carballa M, Omil F, Lema JM et al (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Res 38(12):2918–2926

Casey FXM, Hakk H, Simunek J, Larsen GL (2004) Fate and transport of testosterone in agricultural soils. Environ Sci Technol 38(3):790–798

Coors A, Jones PD, Giesy JP, Ratte HT (2004) Assessing the elimination of estrogenic activity in advanced wastewater treatment with a reporter gene-based bioassay. Water Sci Technol 50 (5, Assessment and Control of Hazardous Substances in Water):181–188

Das BS, Lee LS, Rao PSC, Hultgren RP (2004) Sorption and degradation of steroid hormones in soils during transport: column studies and model evaluation. Environ Sci Technol 38(5):1460–1470

Esperanza M, Suidan MT, Nishimura F, Wang Z-M (2004) Determination of sex hormones and nonylphenol ethoxylates in the aqueous matrixes of two pilot-scale municipal wastewater treatment plants. Environ Sci Technol 38(11):3028–3035

Esteban S, Gorga M, González-Alonso S, Petrovic M, Barceló D, Valcárcel Y (2014) Monitoring endocrine disrupting compounds and estrogenic activity in tap water from Central Spain. Environ Sci Pollut Res 21(15):9297–9310

Gabriel FLP, Routledge EJ, Heidiberger A, Hentsch D, Guenther K, Giger W, Sumpter JP, Kohler H-PE (2008) Isomer-specific degradation and endocrine disrupting activity of nonylphenols. Environ Sci Technol 42:6399–6408

Halling-Sørensen B, Nors Nielsen S, Lanzky PF, Ingerslev F, HoltenLützhøft HC, Jørgensen SE (1998) Occurrence, fate and effects of pharmaceutical substances in the environment- a review. Chemosphere 36(2):357–393

Hanselman TA, Graetz DA, Wilkie AC (2003) Manure-borne estrogens as potential environmental contaminants: a review. Environ Sci Technol 37(24):5471–5478

Heberer T, Adam M (2004) Transport and attenuation of pharmaceutical residues during artificial groundwater replenishment. Environ Chem 1:22–25

Huang C-H, Sedlak DL (2001) Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry. Environ Toxicol Chem 20(1):133–139

Jobling S, Sheahan D, Osborne A, Mathiessen P, Sumpter JP (1996) Inhibition of testicular growth in rainbow trout (Oncorhynchusrnykiss) exposed to estrogenic alkylphenolic chemicals. Environ Toxicol Chem 15:194–202

Joss A, Zabczynski S, Goebel A, Hoffmann B et al (2006) Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme. Water Res 40(8):1686–1696

Khanal SK, Xie B, Thompson ML, Sung S et al (2006) Fate, transport, and biodegradation of natural estrogens in the environment and engineered systems. Environ Sci Technol 40(21):6537–6546

Kidd KA et al (2007) Collapse of fish population after exposure to a synthetic estrogen. PNAS 101:8897–8901

Kim SD, Cho J, Kim IS, Vanderford BJ et al (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res 41(5):1013–1021

Kimura K, Hane Y, Watanabe Y, Amy G, Ohkuma N (2004) Irreversible membrane fouling during ultrafiltration of surface water. Water Res 38(14–15):3431–3441

Kolpin DW, Furlong ET, Meyer MT, Thurman EM et al (2002a) Response to comment on “pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance.”. Environ Sci Technol 36(18):4007–4008

Kolpin DW, Furlong ET, Meyer MT, Thurman EM et al (2002b) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. Environ Sci Technol 36:1202–1211

Lee E, Lee S, Park J, Kim Y et al (2013) Removal and transformation of pharmaceuticals in wastewater treatment plants and constructed wetlands. Drink Water Eng Sci 6:89–98

Lohmann R, Breivik K, Dachs J, Muir D (2007) Global fate of POPs: current and future research directions. Environ Pollut (Amsterdam, Netherlands) 150(1):150–165

Lorphensri O, Intravijit J, Sabatini DA, Kibbey TCG et al (2006) Sorption of acetaminophen, 17α-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium. Water Res 40(7):1481–1491

Lye CM, Frid End CLJ, Gill ME, Cooper DW, Jones DM (1999) Estrogenic alkylphenol in fish tissues, sediments and waters from the U.K. Tyne and Tees estuaries. Environ Sci Technol 33(7):1009–1014

Mahler BJ, Van Metre PC, Bashara TJ, Wilson JT (2005) Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. Environ Sci Technol 39(15):5560–5566

McCann B (2004) Disruptive influences. Water 21:20–22

Nagy P, Fekete J, Sharma VK (2007) Polycyclic aromatic hydrocarbons (PAHs) in surface waters of Rackevei-Soroksari Danube Branch, Hungary. J Environ Sci Health A Tox Hazard Subst Environ Eng 42(3):231–240

Naylor CG, Mieure JP, Adams WJ, Weeks JA, Castaldi FJ, Ogle LD, Romano RR (1992) Alkylphenol ethoxylates in the environment. J Am Oil Chem Soc JAOCS 69(7):695–703

Pickering AD, Sumpter JP (2003) Comprehending endocrine disrupters in aquatic environments. Environ Sci Technol 37(17):331A–336A

Sarmah AK, Northcott GL, Leusch FDL, Tremblay LA (2006) A survey of endocrine disrupting chemicals (EDCs) in municipal sewage and animal waste effluents in the Waikato region of New Zealand. Sci Total Environ 355(1–3):135–144

Sharp EL, Parson SA, Jefferson B (2005) Coagulation of NOM: linking character to treatment. Water Sci Technol 53(7, Particle Separation 2005: Waste Water Treatment):67–76

Sumpter JP (2008) The ecotoxicology of hormonally active micropollutants. Water Sci Technol 57(1):129

Sumpter JP, Johnson AC (2005) Lessons from endocrine disrupting and their application to other issues concerning trace organics in the aquatic environment. Environ Sci Technol 39(12):4321–4332

Ternes TA, Stumpf M, Mueller J, Haberer K et al (1999) Behavior and occurrence of estrogens in municipal sewage treatment plants–I. Investigations in Germany, Canada and Brazil. Sci Total Environ 225(1–2):81–90

Ternes TA, Andersen H, Gilberg D, Bonerz M (2002) Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. Anal Chem 74(14):3498–3504

Ternes TA, Joss A, Siegrist H (2004) Peer reviewed: scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environ Sci Technol 38(20):392A–399A

Thomas P, Rahman MS, Kummer JA, Lawson S (2006) Reproductive endocrine dysfunction in Atlantic croaker exposed to hypoxia. Mar Environ Res 62:S249–S252

Tyler CR, Jobling S, Sumpter JP (1998) Endocrine disruption in wildlife: a critical review of the evidence. Crit Rev Toxicol 28(4):319–361

Vieno NM, Haerkki H, Tuhkanen T, Kronberg L (2007) Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. Environ Sci Technol 41(14):5077–5084

Yang L, Mei K, Liu X, Wu L, Zhang M, Xu J, Wang F (2013) Spatial distribution and source apportionment of water pollution in different administrative zones of Wen-Rui-Tang (WRT) river watershed, China. Environ Sci Pollut Res 20(8):5341–5352

Ying GG, Williams B, Kookana R (2002) Environmental fate of alkylphenols and alkyphenolethoxylates. Environ Int 28(3):215–216

Zeng ZQ, Shan T, Tong Y, Lam SH, Gong ZY (2005) Development of estrogen-responsive transgenic medaka for environmental monitoring of endocrine disrupters. Environ Sci Technol 39(22):9001–9008

Zoller U (2004) The survival and distribution of alkyl ethoxylate surfactants in surface water and groundwater. The case of Israel: is there an environmental problem? In: Handbook of detergents, Part B: environmental impact. Marcel Dekker, New York, pp 467–486

Zoller U (2006) Estuarine and coastal zone marine pollution by the nonionic alkylphenolethoxylates endocrine disrupters: is there a potential ecotoxicological problem? Environ Int 32(2):269–272

Zoller U (2008) Distribution profilers of endocrine disrupting PAHs/APEOs in river sediments: is there a potential ecotoxicological problem? Water Sci Technol 57(2):237–242

Zoller U, Hushan M (2010) Synergistic ecotoxicity of APEOs-PAHs in rivers and sediments: is there a potential health risk? Rev Environ Health 25(4):351–357

Zoller U, Plaut I, Hushan M (2004) The case of the nonionic alkylphenol ethoxylates in the Mediterranean Sea region: is there a problem? Water Sci Technol 50(5, Assessment and Control of Hazardous Substances in Water):79–84