Review

Distribution, exposure pathways, sources and toxicity of nonylphenol and nonylphenol ethoxylates in the environment

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ABSTRACT

Alkylphenols (APs) are ultimate breakdown products of alkylphenol polyethoxylate (APEs) that are used in cleaning and industrial processes. The most commonly used APEs in the market are the nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs). As a result of their widespread use and their lipophilic nature, these compounds are ubiquitous in the environment and are currently of concern because of their toxicity, oestrogenic properties and widespread contamination. This review summarizes the concentrations of NPE and NP in different environmental media. The sources of NPE in the environment and toxicity are reviewed. Their distribution patterns in the environment as well as exposure pathways are discussed with a view to provide better understanding of these emerging environmental contaminants. It is envisaged that this review will heighten the importance of identifying emerging issues and data gaps, and generate a future research agenda on APEs.

Keywords: nonylphenols, nonylphenol ethoxylates, concentrations, exposure pathway, sources, toxicity

INTRODUCTION

Surfactants are a diverse group of chemicals that are designed to have cleaning or solubilization properties (Ying, 2006). They generally consist of a polar group which is well solvated in water and a nonpolar hydrocarbon group which is not easily dissolved in water. Hence, surfactants combine both hydrophobic and hydrophilic properties in one molecule (Ying, 2006; Olkowska et al., 2014). Based on the hydrophobic part of their molecules, surfactants may be classified as cationic, nonionic and/ or anionic compounds (Olkowska et al., 2014). Nonionic surfactants, such as alkylphenol ethoxylates (APEs), are one of the most widely used classes of surfactants. They have been used as detergents and emulsifiers in domestic, industrial and institutional applications, including paper production, leather and textile processing, and cleaning detergents. Also, some examples of this type of surfactant have been used in pesticide formulation (Datta et al., 2002; Ying et al., 2002; Kannan et al., 2003; Siemering et al., 2008; Xie and Ebinghaus, 2008; Bjorkland et al., 2009). The most important members of APEs are nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs), which account for approximately 80% and 20% of total APEs production, respectively (Keith et al., 2001; Diaz et al., 2002; Chiu et al., 2010). The chemical structures of these compounds are illustrated in Fig. 1.

Concern has increased about relatively stable degradation products of APEs, alkylphenols (APs) such as nonylphenol (NP) and octylphenol (OP) (Zhang et al., 2009). APs have been classified together with lower ethoxylates (mono- tri), as endocrine-disrupting compounds (EDCs), because of their effects on the hormonal system of numerous organisms by competing with oestrogen for binding receptors (Gibble and Baer, 2003; Bonefeld-Jorgensen et al., 2007). Exposure to the aquatic ecosystem is of particular concern, since aquatic organisms are exposed to continual introduction of discharged effluents from wastewater treatment works (WWTWs) (Olujimi et al., 2010). Moreover, the polar and non-volatile nature of these compounds prevents their escape from the aquatic realm (Xu et al., 2006). For this reason, NPs and OPs have been phased out in most developed countries and have been designated as priority substances in the Water Framework Directive (Directive 2000/60/EC 2000), and most of their uses are currently regulated (Directive 2003/53/EC 2003). However, in many developing countries, such as those in Africa and Asia, uncontrolled domestic and industrial discharge to waterways contributes to the high levels of EDCs in the aquatic environment (Falconer et al., 2006; Peng et al., 2006), and no schedule has been designed to reduce the use of NP, and use of APEs is these countries may be increasing. For example, the production of NP in 2001 reached approximately 16 000 t in China (Jin et al., 2004) increasing to 31 434 t in 2011 (Gao et

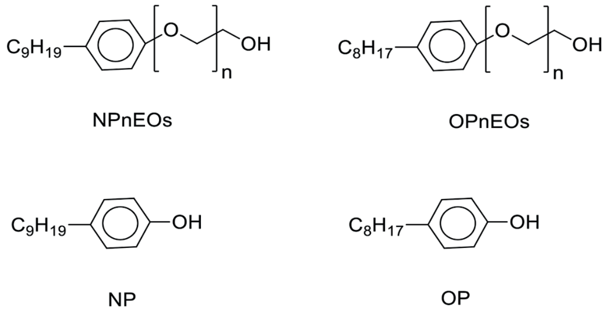

Figure 1
Structures of nonyl- and octylphenol ethoxylates (top left and right) and their metabolites nonylphenol (NP) and octylphenol (OP) (bottom left and right)

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al., 2014). This increase accounted for 10% of total world NP production, according to the records of the China Petroleum and Chemical Industry (Gao et al., 2014). Thus, monitoring of NP in the environment becomes of particular concern because (i) both the NP and its parent compound, NPE, are ubiquitous in the environment, (ii) these compounds indicate a long-term environmental contamination, and (iii) they have shown to be toxic to aquatic organisms. The strong evidence of increasing contamination of the environment by these compounds heightens the importance of identifying emerging issues and data gaps. This review, therefore, focuses on sources, distribution in the environment, exposure pathways, and toxicity of APEs.

SOURCES OF APES IN THE ENVIRONMENT

Environmental release of APEs may occur during their initial synthesis, incorporation into related finished products for use, or as a result of their ultimate disposal or recycling. Nonylphenol and other alkylphenols are synthesized from intermediates in the refinement of petroleum and coal-tar (Núñez et al., 2007). Technical preparation of nonylphenol is a complex mixture of several branched alkyl isomers (Vazquez-Duhalt et al., 2005). The process for the manufacture of alkylphenols is presented in Fig. 2.

Similarly, the synthesis of alkylphenol ethoxylates involves ethoxylation of branched octyl- or nonyl- phenols using ethylene oxide, resulting in isomers (with different alkyl moieties) and oligomers with different numbers of ethoxylate units (De Voogt et al., 1997).

Discharges from wastewater treatment works (WWTW) has been identified as another major source of APEs and their degradation products to aquatic environments (Fujita et al, 2000; Farre et al., 2002; Rice et al., 2003; Esperanza et al., 2004; Jensen and Jepsen, 2005; Johnson et al., 2005; Gatidou et al., 2007; Ying et al., 2008, 2009; Diehl et al., 2012; Chokwe et al., 2015a). Reported removal efficiency of APEs in sewage treatment works varies between 9 and 94%, depending on the region and type of unit treatment process (Jensen and Jepsen, 2005; Johnson et al., 2005). These results are of concern as they indicate that sewage treatment works are only partially efficient in removing such compounds. Primary degradation of APEs in sewage treatment works or in the environment generates more persistent shorter-chain APEs and alkylphenols (APs), such as NP, OP and AP mono- to triethoxylates (NPE1, NPE2, NPE3) (Giger et al., 1984; Ying et al., 2002; Langford et al., 2005). Short-chain APEs, such as NP1E and NP2E, have been analysed in a few studies and are often present in effluents at concentrations higher than their respective alkylphenols (i.e. NP) due to their higher water solubility (Glassmeyer et al., 2005; Loyo-Rosales et al., 2007). Further transformation proceeds via oxidation of the EO chain, producing mainly alkylphenoxy ethoxy acetic acid and alkylphenoxy acetic acid. The general degradation pathway of these compounds is presented in Fig. 3.

Biodegradation of longer-chain NPEs is readily achievable, but ultimate biodegradation of NP1EO, NP2EO, carboxylate derivatives and NP is considerably slower (Health Canada, 2001). The lower rate of biodegradation indicates that these pollutants have the capacity to accumulate in organisms and be transferred between trophic levels, thus leading to a stepwise increase in contamination.

ANALYSIS OF ALKYLPHENOL ETHOXYLATES IN THE ENVIRONMENT

In terms of sample preparations, several techniques have been reported for the isolation of APEs from matrices. For liquid samples, liquid-liquid extraction (Tsuda et al., 2000; Espejo et al., 2002), and solid phase extraction (Chen et al., 2006; Koh et al., 2008; Chokwe et al., 2012), as well as solid-phase microextraction (Pan and Tsai, 2008), have been used. The use of large amounts of generally toxic solvents, and formation of emulsion as well as loss during chromatographic clean-up of extracts derived from liquid-liquid extraction has made the techniques less popular for isolation of APEs in liquid samples. The use of solid-phase extraction (SPE) has received much attention as it is used as a pre-concentration and purification step at the same time. Selection of SPE cartridges with a particular sorbent material such as porous silica bonded with C18 or other hydrophobic alkyl groups such as styrene-divinylbenzene, plays an important role in the achievement of reproducible recoveries of analytes in liquid samples (Gilart et al., 2014).

For solid samples, extraction methods such as microwave-assisted extraction (Fountoulakis et al., 2005), Soxhlet extraction (Sibali et al., 2010), pressurized liquid extraction (Fiedler et al., 2007), and ultrasonic-assisted extraction (Núñez et al., 2007) have been employed for the isolation of NP, NPE1, NPE2 and NPPE. Due to the fact that some of these techniques are too sophisticated or expensive, Soxhlet extraction has been the method of choice for the isolation of APEs in environmental solid matrix (Sibali et al., 2010), though the use of ultrasonic-assisted extraction is becoming more popular (Núñez et al., 2007; Chokwe et al., 2015a, 2016). Prior to extraction, solid samples are dried and homogenized

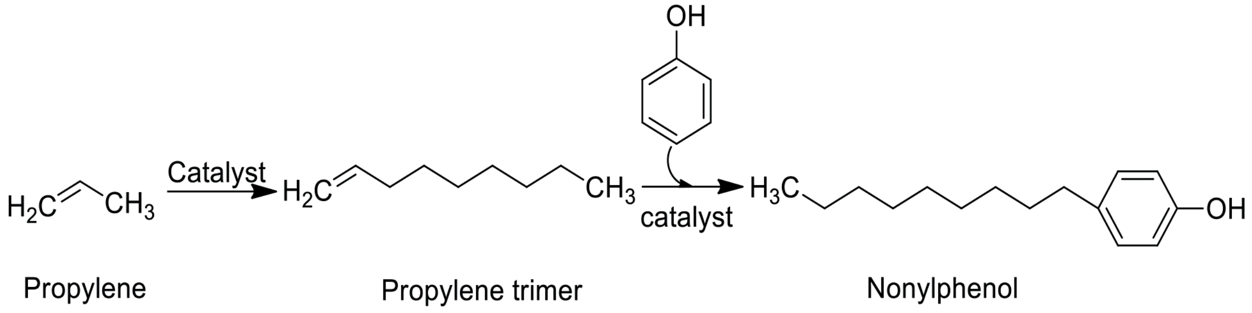

Figure 2
Chemical synthesis of nonylphenol

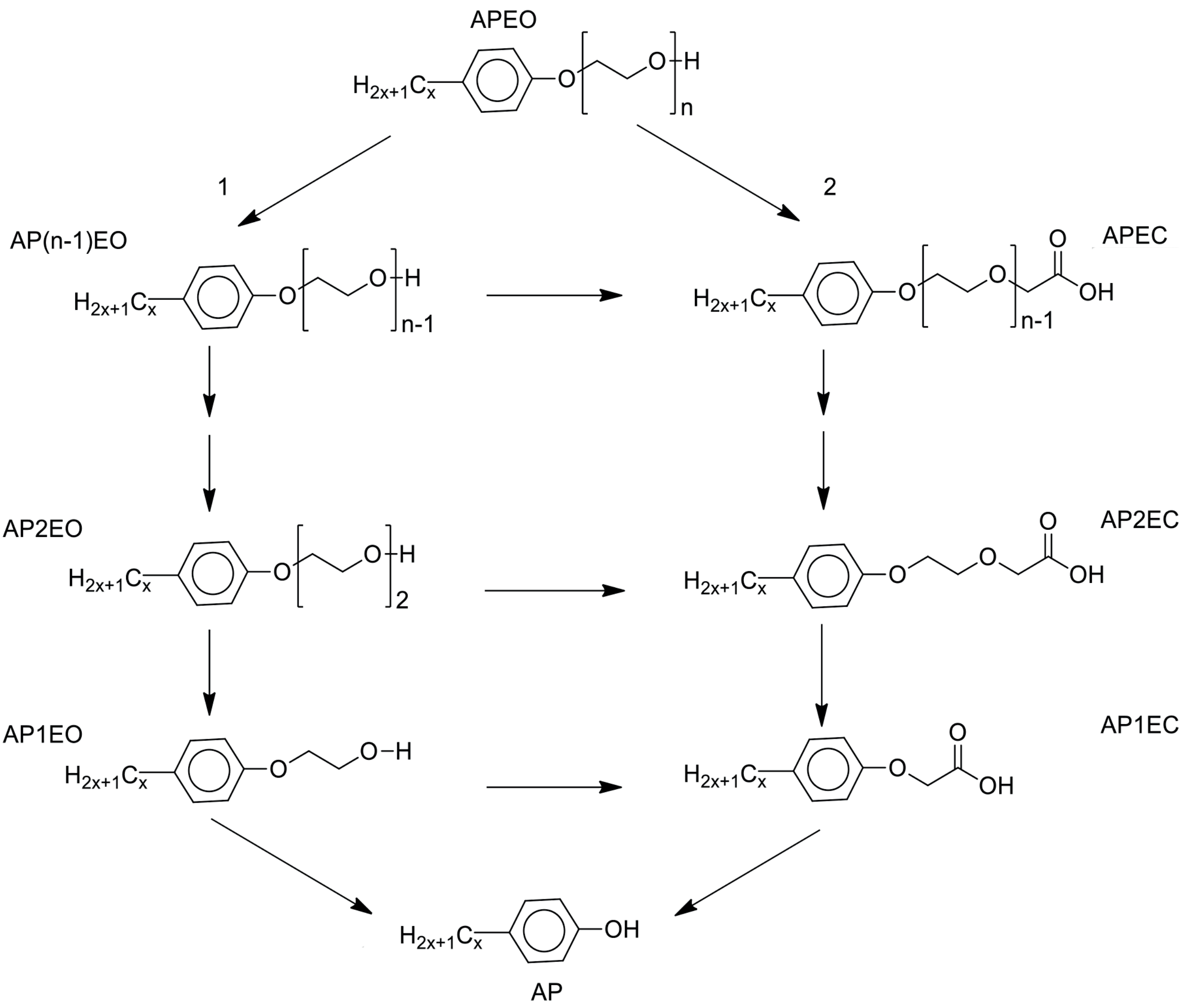

Figure 3
Degradation pathway of APEs (Renner, 1997)

by air-drying or freeze drying, or by mixing with anhydrous sodium sulphate until free flow is obtained. The extracts obtained are purified further by column chromatography or SPE before instrumental analysis.

Separation and identification of APEs in environmental media has been achieved by either high-performance liquid chromatography (HPLC) or gas chromatography (GC) (Lu and Gan, 2014). With both instruments, a mass spectrometer detector (MSD) was the most commonly used detector for quantifying the APEs (Wu et al., 2010; Chokwe et al., 2012). A flame ionization detector (FID) has been used in some instances for the quantification of APEs in the environment (Güenther et al, 2006; Sibali et al., 2010; Guruge et al, 2011). Tandem mass spectrometry (MS/MS) has been used to detect trace amounts of these pollutants in the environment (Schmitz-Alfonso et al., 2003; Shao et al., 2005, 2007; Moeder et al., 2006). The polarity of phenols affects their chromatographic resolution and usually results in broad or tailored peaks (Olujimi et al., 2010). A widely used instrumentation for the analysis of APEs in the environment has been GC after the derivatization of the hydroxyl group (Cathum & Sabik, 2001; Gatidou et al., 2007; Fiedler et al., 2007). Several derivatization methods such as acetylation, alkylation and silylation have been used for GC analysis of phenolic compounds. For example, HFBA was used as a derivatizing agent for the determination of APE and BFR analytes in environmental samples (Chokwe et al., 2012, 2014). In another study, NP and BPA were derivatized within 30 min at 60°C using TFAA (Stehmann and Schröder, 2004). Derivatization of NPEO with *n*-propanol-acetyl chloride at 80°C for 1 h has also been reported (Ding and Tzing, 1998). Cathum and Sabik (2001) described a derivatization procedure for APEO using pentafluorobenzoyl bromide (PFB-Br) as derivatizing agent, aided with K_2CO_3 by sonication. The derivatization took 2 h and was conducted in the dark. Gatidou et al. (2007) reported derivatization of NP, NP2EO, BPA and triclosan with bistrimethylsilylfluoroacetamide (BSTFA) at 65°C for 20 min while Fiedler et al. (2007) derivatized APs with the same reagent at room temperature for 2 h. Furthermore, NPEO was derivatized with BSTFA in the presence of trimethylchlorosilane (TMCS) at 70°C for 4 h (Esperanza et al., 2004). In a separate study, Hoai et al. (2003) reported derivatized NPEOs and NPECs with bistrimethylsilylacetamide (BSA) at 25°C for 1 h.

DISTRIBUTION OF APES IN THE ENVIRONMENT

APEs make up the world's third-largest group of surfactants in terms of production, and have been used widely in the industry for over 50 years (Ying et al., 2002; Koniecko et al., 2014). Their behaviour in the environment is influenced by their physicochemical properties (Ying et al., 2002). The solubility of an APE surfactant depends on the number of polar groups forming the hydrophilic part of the molecule. Lower APE oligomers ($EO < 5$) are usually described as 'water-insoluble' or lipophilic, whereas the higher oligomers are described as 'water-soluble' or hydrophilic (Ahel and Giger, 1993). The solubility of OP1EO- OP4EO ranged from 8 000–24 500 µg/L in water, while solubility of OP was 12 600 µg/L (Ahel and Giger, 1993). NP has a water solubility of 5 430 µg/L while the NP1EO-NP4EO have solubility ranging from 3 020–9 480 µg/L. From these solubility values, the partition coefficients in the octanol/ water system and other logarithmic ($\log K_{ow}$) values were calculated for OP, NP and NP1EO-3EO. The $\log K_{ow}$ for these metabolites ranged from 3.90–4.48 suggesting that these substances are associated with the organic matter in sediments. These solubility and $\log K_{ow}$ results indicate that OP, NP, NP1EO- 3EO have large soil or sediment adsorption coefficients and a large bioaccumulation factor for aquatic life (Ying et al., 2002; Zhu and Zuo, 2013). The environmental fate assessment of OP and NP by Fugacity modelling showed that these pollutants occur at high levels in soil or sediments; lower levels occur in water and the lowest in air (Klosterhaus et al., 2012; Mao et al., 2012; Zhu & Zuo, 2013; Chen et al., 2014; Chokwe et al., 2015a).

APEs presence in the environment is as a consequence of anthropogenic activities. The level of APs and APEs in the environment has been documented in many studies around the globe. NP, OP, octylphenol ethoxylates (OPEs) and NPEs have been detected in air, wastewater, surface water, sediment, sludge and biota samples (Rudel et al., 2003; Petrovic et al., 2003; Esperanza et al., 2004; Micic & Hofmann, 2009; Zhang et al., 2009; Grund et al., 2011; Wang et al., 2012; Chokwe et al., 2015b). A schematic diagram showing the emission, distribution and exposure pathway is given in Fig. 4.

Air

Air concentrations of alkylphenols are rarely reported in the literature. Existing studies show that nonylphenol has been found in indoor environments in air and dust at concentrations higher than outdoor values (air – 100 ng/m^3, and dust – 2 580 ng/g) (Rudel et al., 2003; Saito et al., 2004). Van Ry et al. (2000) reported gas-phase concentrations of nonylphenol and *tert*-octylphenol (tOP) at two sites in the lower Hudson River Estuary. NP concentrations ranged from ND to 56.3 and 0.13 to 81 ng/m^3 for Sandy Hook and New Brunswick sites, respectively. The concentration range of tOP ranged from not detected (ND) to 1.0 and 0.01 to 2.5 ng/m^3 for Sandy Hook and New Brunswick, respectively. NPs and tOP exhibited seasonal trends with higher gas phase concentrations during summer than during autumn and early winter. The results for NP were similar to the results reported by Dachs et al. (1999) from the same sampling points. Xie et al. (2006) reported a concentration range of 14 to 50 pg/m^3 for NP1EO in atmospheric samples from the North Sea. Rudel et al. (2010) investigated the concentration of NP and NPE in indoor and outdoor air samples from California. The indoor NP concentration ranged from < LOQ to 89 ng/m^3 and was

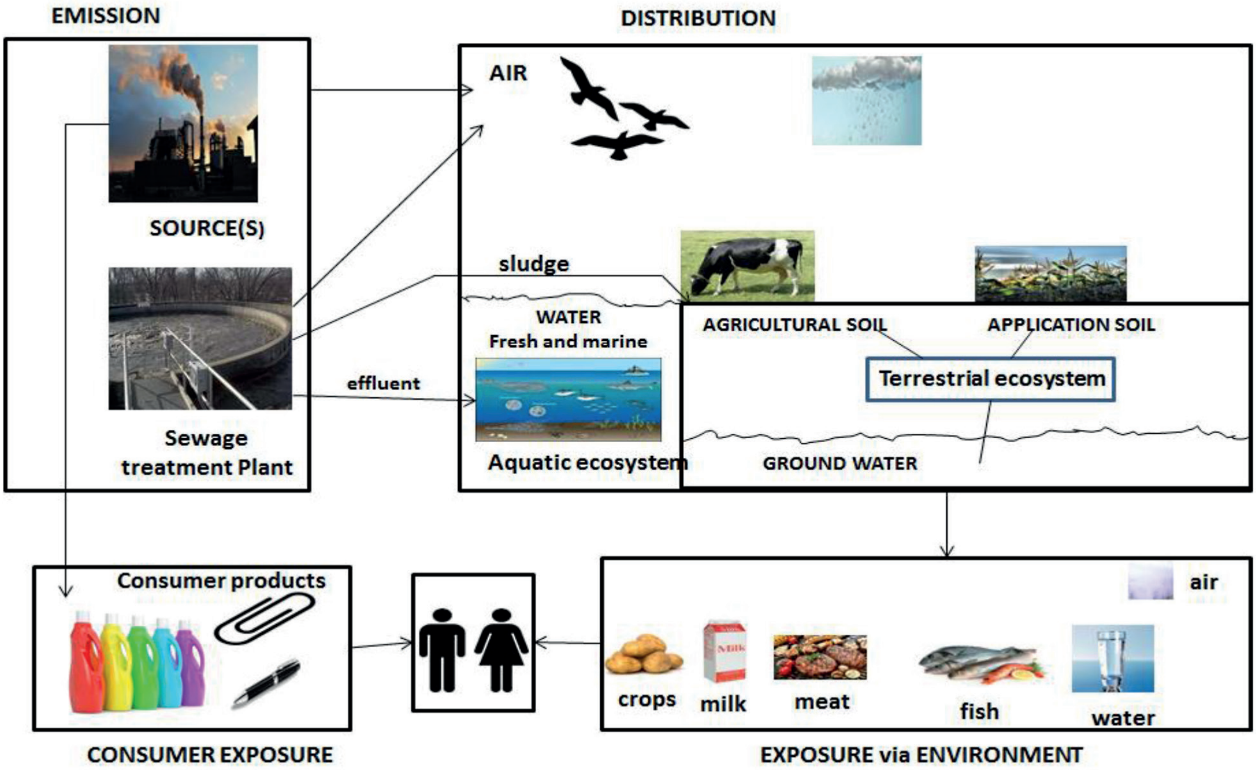

Figure 4
Schematic diagram showing the emission, distribution and exposure pathway of APEs (WHO, 2004)

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higher than that outdoors (< LOQ to 40 ng/m^3); while indoor NPE1 concentration ranged from < LOQ–72 ng/m^3 and was not detected in outdoor samples. Salapasidou et al. (2011) reported a concentration range of 1.6–16.5 and 0.3–12.8 ng/m^3 for NP and NP1EO in the atmosphere of an urban area of Thessaloniki, Greece.

Wastewater

Although they are highly treatable in well-functioning sewage treatment works, APEs and their degradation products (NP, OP, and NPE1–3) have been detected in effluents of many municipal wastewater treatment plants (WWTPs). Table 1 present some of the reported data on the levels of APs and APEs in WWTPs around the world.

The reported concentrations of APs and APEs in sewage effluents varied widely among various WWTPs, from ND–15.3 µg/L. The highest concentration of NP (9.83 µg/L) was detected in effluent samples collected in Cape Town, South Africa (Olujimi et al., 2013) while the lowest concentration (0.028 µg/L) was detected in the UK (Koh et al., 2008). NP was not detected from effluent samples collected in Vereeniging, South Africa (Chokwe et al., 2012), but in the same study quantifiable concentrations of nonylphenol ethoxylates (NPE1, NPE2 and NPPE) were reported. In one of the few studies that determined NPE1 and nonylphenol di-ethoxylates (NPE2), samples from Taiwan (Ding and Tzing, 1998) exhibited the highest concentration (9.6 µg/L and 15.3 µg/L; respectively) with South Africa (Chokwe et al., 2012) reporting the lowest concentrations (2.09 µg/L and 0.55 µg/L; respectively). Both the nonylphenol penta-ethoxylates (NPPE) and octylphenol penta-ethoxylates (OPPE) were detected in effluents from South Africa (Chokwe et al., 2012).

Surface water

Investigations of nonylphenol in surface waters are in agreement that its occurrence is mainly correlated with anthropogenic activities, especially for urban river sediments. The main source of NP appears to be closely related to effluent discharges from WWTPs, proximity of industrial/urban areas and other related activities such as stormwater discharge and runoff (Hale et al., 2000; Petrovic et al., 2002; Corsi et al., 2003; Micic and Hofmann, 2009). The results for NP in surface waters are presented in Table 2.

Nonylphenol concentrations in surface water ranged from ND–30 µg/L. The highest concentration (30 µg/L) was reported by Azevedo et al. (2001) from Portugal followed by 9.35 µg/L reported by Sibali et al. (2010) from South Africa. For nonylphenol mono-ethoxylates, the highest concentration (5.1 µg/L) was reported from Cuyahoga River, USA (Rice et al., 2003). Concentrations ranging between 0.1 and 7.01 µg/L were reported for nonylphenol penta-ethoxylates (NPPE) from the Vaal River, South Africa (Chokwe, 2015). For the octylphenol ethoxylates, a study by Sibali et al. (2010) reported a concentration range from 0.31–6.01 µg/L for OPPE (1–3) from the Jukskei River, South Africa. Freshwater invertebrates and fish are sensitive to this category of chemicals and have demonstrated toxicity to it in varying degrees. A chronic water quality criteria concentration for NP on freshwater species of 6.6 µg/L has been derived by the USEPA's Office of Water (USEPA, 2005) while a no-observable-effects concentration (NOEC) of 0.33 µg/L was derived in the EU risk assessment report (WHO, 2004). Some of the measured surface water concentrations exceeded both the water quality criteria for freshwater species living in the water column as well as the NOEC limit.

Sediments

Sediments are the ultimate sink or reservoir for environmentally persistent and hydrophobic organic pollutants in the aquatic environment derived from various human activities. Thus, globally, nonylphenol was found in higher concentrations in river or lake sediments than dissolved in the aqueous phase (Soares et al., 2008; Brix et al., 2010). The distribution of contaminants in the sediment of a river is also related to sediment properties such as organic carbon and particle size distribution (Baker et al., 1991; Lai et al., 2000). Nonylphenol was found to be resistant to biodegradation

TABLE 1
Concentration of APs and APEs in effluents of WWTPs

Location	Concentration (µg/L)					Reference
	NP	NPE1	NPE2	NPPE	OPPE	
Taiwan	1.6	9.6	15.3			Ding and Tzing, 1998
Switzerland	1–6.8					Espejo et al., 2002
Spain	0.085					Petrovic et al., 2003
USA	1.93	2.95	13.24	11.99[a]		Esperanza et al., 2004
Norway	0.05–1.31					Johnson et al., 2005
Japan	0.5–1.1					Nakada et al., 2006
UK	0.028					Koh et al., 2008
Greece	0.03–0.90	0.34–6.89	0.41–17.4			Stasinakis et al., 2008
Australia	1.627	2.212				Ying et al., 2008
South Africa	ND	2.092	0.55	0.972[b]	1.46	Chokwe et al., 2012
South Africa	0.52–9.83					Olujimi et al., 2013
Hong Kong	0.44–1.56					Xu et al., 2014

[a] *NPE3*
[b] *NPE5*

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in lake water/sediment systems, showing only a slight (9%) loss (after 56 days) and 4.2% loss (after 28 days) (Lalah et al., 2003). The degradation half-life of nonylphenolic compounds was estimated to be greater than 60 years once they enter the sediments (Shang et al., 1999). The levels of NP, OP, OPPEs and NPEs in sediments are presented in Table 3.

Adsorption processes controlling the partition of nonylphenol ethoxylates to sediments demonstrated that the organic content of the sediments was one of the most important determinants of the adsorption process, especially for short-chain nonylphenol ethoxylates (John et al., 2000). Higher concentrations of nonylphenol and its ethoxylates were detected in samples from developed countries as compared to samples from developing countries. Nonylphenol concentrations of up to 1 364 ng/g were reported in sediments collected in Germany (Grund et al., 2011). A study by Verslycke et al. (2005) reported a total concentration of up 1 151 ng/g for longer chain length NPEs (NPE3–16) from The Netherlands. Another study in the USA detected higher concentrations (1 800–11 000 ng/g) for NPE0–14 (Loyo-Rosales et al., 2007). The presence of long-chain NPEs in sediment corroborates findings by Shang et al. (1999) that little degradation of NPEs occurs once these compounds enter the sediment. Sibali et al. (2010) reported a concentration range of 1.94–941 ng/g for OPPE (1-3) in sediments from the Jukskei River, South Africa. Recently, concentration ranges of ND–46; 6.4–51; 13–82 and 24–38 ng/g for OPPE, NPE1, NPE2 and NPPE, respectively, were reported for Vaal River sediments (Chokwe et al., 2016). These results indicate that APs and APEs are ubiquitous in the environment. An NP predicted-no-effect concentration (PNEC) for sediment of 39 ng/g was derived in the EU risk assessment report using the portioning methods (WHO, 2004).

TABLE 2
Concentrations of APs and APEs in surface waters

Location	Concentration (µg/L)						Reference
	NP	NPE1	NPE2	NPPE	OP	OPPE	
Canada	ND				0.048		Cathum and Sabik, 2001
Portugal	0.3–30						Azevedo et al., 2001
USA	1.1	2.01					Kannan et al., 2003
USA		0.13–5.1				0.0053–0.19	Rice et al., 2003
Japan	1.6	0.48	0.56				Hoai et al., 2003
Korea	0.023–0.19						Li et al., 2004
Hong Kong	0.029–2.59				0.011–0.35		Li et al., 2007
China	0.075–1.52				0.021–0.063		Zhang et al., 2009
South Africa	0.38–9.35					0.31–6.01[a]	Sibali et al., 2010
Nigeria	0.044–0.079				0.06–0.07		Oketola and Fagbemigun, 2013
China	0.036–3.105				0.0028–0.542		Chen et al., 2014
South Africa	0.06–0.11	ND–0.73	ND–0.74	0.1–7.01		ND–1.93[b]	Chokwe, 2015

[a] *Sum of OPE1, OPE2, OPE3*

[b] *OPE5*

TABLE 3
APs and APEs levels in sediment samples

Location	Concentration (ng/g)						Reference
	NP	NPE1	NPE2	NPPE	OP	OPPE	
USA	75–340	32–320	30–200	54–159		74	Rice et al., 2003
USA	5.8–15.3						Kannan et al., 2003
Korea	25.4–932						Li et al., 2004
The Netherlands	ND–1 222	ND–51.9	ND–221	ND–1 151[a]			Verslycke et al., 2005
Spain	13–225						Lara-Martin et al., 2006
Italy	47–192						Pojana et al., 2007
USA				1800–11 000[b]			Loyo-Rosales et al., 2007
Brazil	1–10						Fiedler et al., 2007
South Africa						1.94–941[c]	Sibali et al., 2010
Germany	ND–1 364						Grund et al., 2011
China	16.6–203.8				ND–2.6		Wang et al., 2012
Nigeria	1.1–79.4				2.2–24.5		Oketola and Fagbemigun, 2013
Poland	1.46–2.31				6.56–13.1		Koniecko et al., 2014
South Africa	ND	6.4–51	13–82	24–38	ND–46		Chokwe et al., 2016

[a] *Sum of NPE3–16*

[b] *Sum of NPE0–14*

[c] *Sum of OPE1–3*

Biota

Alkylphenols are lipophilic and thus accumulate in fatty tissues (Vazquez-Duhalt et al., 2005; Uguz et al., 2003; Abdulla Bin-Dohaish, 2012). Uptake occurs mainly through two pathways: water (gill ventilation) and diet. Generally, high concentrations of APEs are expected to be found in the liver relative to muscle because of the liver's role in storage, detoxification and regulation of all metabolic process (Uguz et al., 2003). However, most of the analysed publications limited their studies to APE levels in muscle and this will therefore be discussed in this section.

Fish, mussel and shellfish are the most common biosamples because they are typical aquatic organisms that might be sensitive to APs and APEs in surface water. The ability of these organisms to accumulate APs and APEs depends on their feeding strategy (David et al., 2009). A higher portion of APEs and APs were detected in organisms with higher exposure to sediments, suggesting that the main source of APEs and APs may not be the water column, but sediments and dietary uptake, both depending on their distribution in the aquatic environment (Ferreira-Leach and Hill, 2001; David et al., 2009).

NP, NPE1 and NPE2 were detected in all shellfish samples obtained from rivers flowing into Lake Biwa, Japan with concentration ranges of 2.8–19.3, 7.7–23.3, 2.0–5.3 ng/g wet wt., respectively (Tsuda et al., 2002). Datta et al. (2002) reported the concentration of NP and NPEs in trout, common carp and yellow perch from various locations in the USA Great Lakes region. Concentrations of NP, NPE1, NPE2, and NPE3 from fish samples ranged from 18–2 075 ng/g wet weight. In the Cuyahoga River, USA the concentration of NPE0–2 in carp ranged from 32–920 ng/g (Rice et al., 2003). A concentration range of 151–300 ng/g for NP was reported in 6 fishes (i.e., weever, catfish, bartail flathead, white flower croaker, wolfish, and mullet) from Bohai Bay by Hu et al. (2005). Wang et al. (2007) reported NP in mussels from the Masan Bay of Korea, where concentrations ranged from 50.5–289.2 ng/g dry wt. In the Venice lagoon, NP in mussels was detected with a concentration range of 115–211 ng/g dry wt (Pojana et al., 2007). Concentrations ranging from 32.6–47.2 ng/g were detected in carp and moggel (*Labeo umbratus*) from South Africa (Chokwe et al., 2015b).

Sludge

Sorption to sludge, as a consequence of a high affinity for organic matter, and biological degradation are major removal mechanisms for APEs during wastewater treatment (Scrimshaw and Lester, 2002; Shao et al., 2003; Soares et al., 2008; Stasinakis et al., 2008). It has also been reported that treatment plants that treat wastewater of industrial origin, or from areas with high population densities indicative of an urban area, exhibit high concentration of APEs (Langford and Lester, 2002). Few studies have been reported the presence of APEs in sludge. La Guardia et al. (2001) investigated concentrations of APE degradation products (NP, NPE1, NPE2) in sludge from 11 US WWTPs and found that concentrations were highest in the anaerobically digested samples (721 000–981 000 ng/g dry wt). In the majority of samples, NP was the most abundant. NP concentrations of 242 000 ng/g (sludge before anaerobic digestion) and 308 000 ng/g (sludge anaerobically stabilized) were reported by Bruno et al. (2002) in a sludge sample from Italy. Concentrations ranging from 3 600–93 000 ng/g and 12 800–233 500 ng/g for NP and NPEO, respectively, were reported by Fountoulakis et al. (2005) in three WWTPs (Athens, Patras and Heraklion) in Greece. NP, NPE1 and NPE2 concentrations (110, 1 010 and 2 890 ng/g, respectively) were reported by Gatidou et al. (2007) from Mytilene City WWTPs, Greece. In Spain, the concentrations of NP, NPE1 and NPE2 were determined from biological wastewater treatment plants and ranges from 3 200–199 000 ng/g were reported (Fernández-Sanjuan et al., 2009). A concentration range of between ND and 642 ng/g was reported by Chokwe et al. (2015c) for sludge samples from three WWTPs in South Africa.

EXPOSURE PATHWAYS TO APES

According to human exposure assessments, as shown in Fig. 4, non-occupational exposure to APEs can occur through a variety of exposure pathways including inhalation of air, ingestion of food and indoor dust, and by drinking contaminated water (Ying et al., 2002; Erickson, 2002; Lu et al., 2007; Salapasidou et al., 2011; Zhou et al., 2011). Another source of exposure might be via the cleaning agents used in the food-processing industry, or plastic packaging materials from which NP, used in tris(nonylphenol) phosphite as an oxidant, could migrate into food (Inoue et al., 2001; Loyo-Rosales et al., 2004). When animals ingest NP, its absorption from the gastrointestinal tract is initially rapid, and probably extensive. NP is distributed widely throughout the body, with the highest concentrations in fatty tissues (WHO, 2004).

Exposure through food

NP levels were measured in 39 foods and beverages, including fruits and vegetables, dairy products, fish and meat, pasta, beer, coffee and chocolate, from German supermarkets, by Güenther et al. (2002), who found a concentration range of 0.1–19.4 µg/kg. These findings suggest that food may be an important route of exposure to endocrine-disrupting compounds (EDCs) like APEs in humans. A similar study was conducted by Lu et al. (2007) in Taiwan by sampling 25 types of food consumed by locals, including two freshwater fish, two saltwater fish, two shellfish, two other seafoods, poultry, livestock, vegetables, rice and noodles, three other proteins and fruits. The foodstuff samples were analysed for NP, OP, butylphenol (BP), NPE1 and NPE2. NP was detected in 243 samples from the total of 318 samples (76.4%), with an average concentration of 235.8 ± 90.7 µg/kg. NP in vegetables can likely be attributed to pesticides (Güenther et al, 2002). Both branched and linear NP were detected in the tissues of pumpkin, carrot, and citrus purchased from Florida, with the highest concentration, of 18.5 µg/kg, reported for citrus (Lu et al., 2013). NP concentration ranged from 1.18 to 4.31 µg/kg (lettuce) and 3.79 to 6.95 µg/kg (collard) in the stems and leaves while the concentrations in the roots of lettuce and collard were 926.9 µg/kg and 339.2 µg/kg, respectively (Dodgen et al, 2013). Monitoring studies by Dodder et al. (2014) reported NP levels exceeding 50 µg/kg and a detection frequency of more than 50% in mussel tissues collected along the Californian coast. The data supported the trend that NP levels increase with increasing urbanization of the sampling site (Careghini et al., 2014; Luo et al., 2014).

Exposure through air and other pathways

Exposures to APEs are not always exclusively through food. Other exposure pathways to these compounds may include non-dietary ingestion, dermal absorption from product use, drinking contaminated water and inhalation (Rudel and Perovich, 2009). A day-care study concluded that dietary ingestion was the primary exposure pathway for toddlers to a group of phenolic compounds that included nonylphenol, though inhalation was found to be a secondary route of exposure (Wilson et al., 2001). Short-chain alkylphenol polyethoxylates have been found in drinking water and groundwater in the US (White et al., 1994; Rudel et al., 1998; Swartz et al., 2006) indicating that drinking of contaminated water is another exposure pathway to NP.

TOXICITY

Exposure to APE degradation products can result in acute and/or chronic toxicity to aquatic organisms (Langston et al., 2005; Vazquez-Duhalt et al., 2005). Studies have demonstrated that APEs compete for the binding site of natural oestrogen receptors in vertebrates and can elicit a variety of responses, including stimulation of vitellogenin, an egg-yolk protein in males; modification of testicular structure and decreased sperm counts thus leading to both intersex fish and altered sex ratios in populations, and induction of both liver damage and mortality (Servos, 1999; Ackermann et al, 2002; Bakke, 2003; Staples et al., 2004; Rempel and Schlenk, 2008; Amaro et al., 2014; Chen et al., 2014). Among marine organisms, gastropods and bivalves appear to be most sensitive to the effects of NP and OP, followed by fish, other invertebrates and then algae (Staples et al., 2004; Van Miller and Staples, 2005; Wang et al., 2010; Gao et al., 2014; Hsu et al., 2016). In general, decreasing exothylate chain length has been correlated with increasing toxicity (Servos et al., 2003). Chronic toxicity values and no-observed-effect concentrations (NOEC) are as low as 6 µg/L in fish and 3.7 µg/L in invertebrates, respectively (Servos, 1999). Lowest-observed-effect concentration (LOEC) was at a nominal dose of 4 µg/kg body weight of AP for effects on the timing of puberty, while the delay effect in mature fish was at 20 µg/kg body weight (Meier et al., 2011). A study by Bellingham et al. (2010) demonstrated that the developing foetus during pregnancy was sensitive to environmentally relevant concentrations of EDCs that may have a serious impact on the future development of the reproductive system. Xie et al. (2013) showed that nonylphenol and tert-octylphenol bind with human serum albumin during transport and metabolic processes in vitro. The USEPA guideline for ambient water quality designates nonylphenol concentrations of below 6.6 µg/L and 1.7 µg/L in freshwater and saltwater, respectively (USEPA, 2005; Brooke and Thursby, 2005). In the European Union (EU) risk assessment report on NP of 2001 a no-observable-effect concentration (NOEC) of 0.33 µg/L was derived (WHO, 2004).

MAJOR KNOWLEDGE GAPS FOR ALKYLPHENOL ETHOXYLATES

Wastewater effluents were identified as a major source of APEs and their degradation by-products in the environment; thus, more studies should be undertaken to measure the levels of APEs at WWTP outfalls, and terrestrial environments close to agricultural, mining and chemical industries, as the concentration are expected to be highest there. Within effluent studies, as these pollutants are directly linked to urbanization (Falconer et al., 2006), the impact of population increases in metropolitan areas need to be assessed for APEs pollution. As sewage is known to be released into wetlands and oceanic waters, studies of APE levels in these compartments' inhabitants (such as birds, frogs, algae, daphnia, dolphins, etc.) need to be undertaken in order to assess the impact of APEs on biodiversity of such bodies. Indoor dust has been implicated as an important exposure route for other persistent organic pollutants (POPs) such as TBBPA (Abdallah et al., 2008; Harrad et al., 2010), PBDEs (Ali et al., 2013; Abafe and Martincigh, 2015) and PCBs (Abafe and Martincigh, 2015); an accurate assessment (occurrence and fate) of alkylphenol ethoxylates in the indoor environment is of major importance for developing countries as the use of these endocrine-disrupting chemicals is suspected to be on the rise.

There were two studies considered in this review which reported on degradation of NPE0–16 (Verslycke et al., 2005; Loyo-Rosales et al., 2007). Though these studies confirmed NP as the major product, more information on the behaviour and degradation of the longer-chain NPE6–16 in different environmental matrices and biota becomes of utmost importance. In addition, the fate and transport of the longer-chain NPE in the environment is still not well understood. Also, there is a paucity of data on the adverse health impacts of NPE1–3. Hence, studies should be undertaken to establish the minimum health risk concentration for each isomer as well as to investigate the synergic health effect of a combination of different environmentally relevant concentrations of APEs. There is a scarcity of data on human biological monitoring for APEs around the globe and more research also needs to be directed toward NPE isomer identification, as the available studies determined exposure to technical mixtures of OPs and NPs (Calafat et al., 2005; 2008; Faniband et al., 2014).

NPE (1–3) as emerging environmental contaminant should be studied systematically to evaluate their potential threat to environmental and human health. To accomplish this goal, research activities should look into, among others: (i) developing analytical methods to measure these pollutants in a variety of matrices down to trace levels; (ii) fate and transport of NP and NPE (1–3) in air; (iii) more toxicity data to assess the effects on terrestrial organisms such as plants; and (iv) potential effects on wildlife due to long-term exposure to low concentrations of NP and NPEs.

CONCLUSIONS

Irrespective of sources, APEs have become ubiquitous in the environment. The occurrence of APEs and APs has been reported around the globe in wastewater effluents, surface waters, sediments, biota and air. Discharges from WWWTPs were found to be a major source of these compounds in the environment, though atmospheric deposition, urban runoff and direct discharge, such as application of pesticides to aquatic vegetation, may also be important sources of these compounds in the environment and humans. There were few results cited in the review that showed concentrations of NP above the USEPA guideline for ambient water quality, thus indicating moderate to high risk from contamination by NP of surface waters around the globe. Exposure pathways to these compounds include: contaminated foods, ingestion, inhalation and water.

Thus, the presence of APEs in the food chain, indoor air, dust and water should be continuously monitored. More studies are required to further understand the fate and transport of NPE (6–16) in the environment and biota as well as adverse health impacts of NPE (1–3) isomers in wildlife and humans.

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