Occurrence, fate and toxic effects of the industrial endocrine disrupter, nonylphenol, on plants - A review

Willeke de Bruin[a], Quenton Kritzinger[b], Riana Bornman[c], Lise Korsten [a,*]

[a] Department of Plant and Soil Sciences, Department of Science and Technology and National Research Foundation: Centre of Excellence in Food Security, University of Pretoria, Pretoria, 0002, South Africa

[b] Department of Plant and Soil Sciences, University of Pretoria, Pretoria, 0002, South Africa

[c] School of Health Systems and Public Health, University of Pretoria, Private Bag X323, Pretoria, 0001, South Africa

∗ Corresponding author. University of Pretoria, Plant and Soil Sciences, Department of Plant and Soil Sciences, Pretoria, 0002, South Africa. E-mail address: lise.korsten@up.ac.za (L. Korsten).

Highlights

• Nonylphenol can alter the morphological, physiological and ultrastructural status of plants.
• Nonylphenol can compromise the food safety status of edible crops.
• Nonylphenol has a different regulatory status across the world.

Abstract

Nonylphenol (NP) and its detrimental effects on the environment, humans, wildlife, fish and birds is an increasingly important global research focus. The number of investigations on the toxicity and metabolic fate of NP in plants is however limited. This paper reviews the prevalence and source of NP in plants and the effect it has on its morphological, physiological and ultrastructural status. Fruit and vegetables have been found to contain levels of NP that is twenty-fold exceeding the no observable effect level (NOEL) of freshwater algae. Apart from the potential risk this poses to the health of consumers, it can overburden the plant's natural defence system, leading to growth disorders. Plants exposed to NP show signs of overall growth reduction, changes in organelle structure and oxidative damage. These adverse effects may exacerbate the food security dilemma faced by many countries and impede their progress towards attaining the sustainable development goals.

Keywords: Nonylphenol; Plants; Toxicity

1. Introduction

Alkylphenol ethoxylates (APEO) are one of the most extensively used classes of surfactants (Chang et al., 2005). They are widely applied in the agricultural, food, industry and household sectors (Bergé et al., 2012) and are present in agricultural and food processing as well as other commonly used industrial and domestic formulated products (Bergé et al., 2012; Jubendradass et al., 2012; Yu et al., 2016). The most commonly used APEOs are the nonylphenol ethoxylates (NPEO), which account for 80% of total use (Bergé et al., 2012; Zgola-Grześkowiak et al., 2009).

Nonylphenol ethoxylates are incompletely biodegraded in the environment and wastewater treatment plants by the stepwise loss of ethoxy groups to form nonylphenol monoethoxylate (NPEO1), nonylphenol diethoxylate (NPEO2) and ultimately the completely de-ethoxylated product, nonylphenol (NP) (Belmont and Metcalfe, 2003; Chang et al., 2005; Croce et al., 2003; Mann and Boddy, 2000). The majority of NP is brought about by the biodegradation of NPEOs but it can also be produced industrially from cyclic intermediates in oil refining and tar (USA Environmental Protection Agency, 2010). Ever since its initial synthesis in 1940, the production and use of NP has been increasing exponentially. Globally, the NP market is anticipated to grow at a significant pace by 2025

with India and China representing the major production sites (https://www.persistencemarketresearch.com/market-research/nonylphenol-market.asp). It is hence classified as a high production volume (HPV) chemical (USA Environmental Protection Agency, 2010).

Nonylphenol mimics the female sex hormone oestrogen (Soares et al., 2008), thereby disrupting the normal functioning of the hormonal system in mammals (Jobling et al., 2006; Laws et al., 2000; Roy et al., 2009). Exposure to NP can also lead to long-term toxic effects. It has become an ever-present contaminant in the ecosystem (Pretorius and Bornman, 2005) where it negatively affects all forms of life. It has consequently become an important research topic for the sake of conserving the milieu and maintaining good health (Laufer et al., 2013; Zhu and Zuo, 2013; Zuo et al., 2015).

While many studies have provided comprehensive overviews on the effects of NP on mammals and its presence in different environments (Chokwe et al., 2017; Laufer et al., 2013; Noorimotlagh et al., 2018; Vandenberg et al., 2012; Lu and Gan, 2014; Zhu and Zuo, 2013), few have solely focussed on its uptake by and effect on plant species.

2. Sources of nonylphenol in the plant environment

Plants are exposed to NP from various sources (Bergé et al., 2012; Noorimotlagh et al., 2018). The main disposal route of NP into water systems is via sewage treatment works (STW) (Soares et al., 2008), whilst land amended with bio-solids or manure, run-off from pesticides and fertilizers in agricultural fields and livestock feeding operations can also contribute as sources for NP in the environment (Caballero-Gallardoa et al., 2016) **(**Fig. 1**).** In accordance with its physical-chemical properties, such as low solubility and high hydrophobicity, higher concentration of NP will be found in soil and sediments, followed by water and lastly air (Soares et al., 2008).

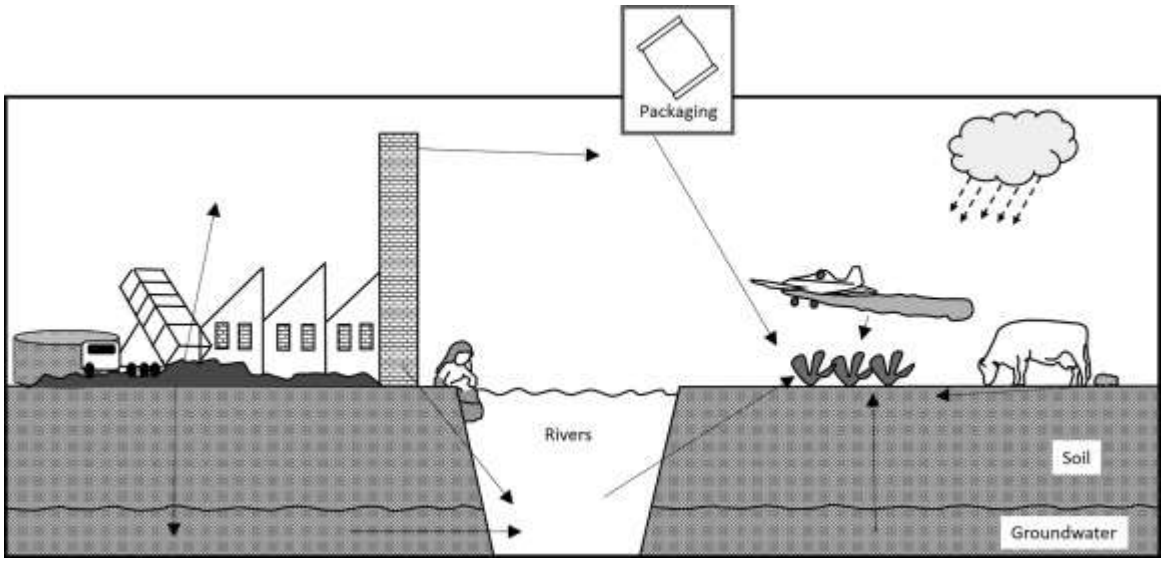

Fig. 1. Exposure of plants to difference sources of nonylphenol.

2.1. Water

Discharge from STW- and industrial wastewater effluents, landfill leachate, and agricultural activities can represent potential sources of NP in rivers and groundwater (USA Environmental Protection Agency, 2010; Zhu and Zuo, 2013). Rivers are often also important recreational sites and commonly used in developing countries for household activities such as bathing, washing of clothes and car wash businesses that serve local communities along the river (Barnhoorn et al., 2010; Sibali et al., 2010).

Surface water containing more than 10 µg/l NP is considered highly polluted, water containing 1–10 µg/l is polluted, while surface water containing <1 µg/l of NP has a low pollution level (Vazquez-Duhalt et al., 2005). From 164 groundwater samples tested of 23 European countries, 11% contained NP, which was also the most abundant industrial chemical in groundwater samples of Austria (Mao et al., 2012).

Recent intensification of agricultural production systems in less developed countries has increased the need for using untreated wastewater or greywater to irrigate vegetable crops (Castro-Rosas et al., 2012; Pachepsky et al., 2011). Greywater is defined as untreated household wastewater from showers, baths, laundry and kitchen and hand-wash basins. Greywater can be contaminated with toxic chemicals (Castro-Rosas et al., 2012) and surfactants such as NP which are considered to be the most abundant (Wiel-Shafran et al., 2006). Long-term irrigation with greywater may result in accumulation of surfactants in the soil, causing changes in soil properties and toxicity to plants (Al-Hamaiedeh and Bino, 2010).

2.2. Air

Nonylphenol is a semi-volatile compound that can vaporize into the atmosphere from various emission sources, including road traffic, industrial processes, waste incineration, wastewater treatment processes and domestic heating, (Bergé et al., 2012; Salapasidou et al., 2011). Once NP reaches the atmosphere, it can be returned to terrestrial and aquatic ecosystems by wet deposition (rain and snow) (Soares et al., 2008).

2.3. Soil

Nonylphenol ends up in soil through soil amendment with sewage sludge, spraying of pesticides that contain NP as formulant, wastewater used for irrigation, detergent use (by households or municipal services) or factory effluents (Cox, 1996). Due to its hydrophobic nature, NP adsorbs to the solid organic particles (Mailler et al., 2014) and eventually bio-accumulates to undesirable levels (from a few mg/kg up to several thousand mg/kg) (She et al., 2011). It can take months or years for NP to degrade in the soil. In studies of field soil amended with sewage sludge, residues of NP were still detected 301–322 days after application (Cox, 1996; Marcomini et al., 1989).

The application of sludge to agricultural land is a cost effective way to dispose of sewage (Ömeroğlu et al., 2015). In 2011 in the United States of America (USA), the average loading of NP to sewage sludge was 5510 metric tons, of which 3306 metric tons was introduced into the environment via land applications (Lu and Gan, 2014). In Europe, the primary pathway for sludge management is by way of land application (Mailler et al., 2017). In less developed countries there has also been an increased tendency to use sewage sludge as fertilizers in agriculture (Wang et al., 2008). Nonylphenol is frequently found in anaerobically degraded sewage sludge (Bokern and Harms, 1997). High concentrations can transfer from sludge to soil (Mailler et al., 2017) and eventually be taken up by plants, often only in small amounts (Dettenmaier and Doucette; 2007). The uptake is expressed as a bioconcentration factor (BCF) and is the ratio of NP concentration in plant vs. soil. Several studies have indicated that it is very low in different edible plant species such as broad bean, wheat, wheatgrass, barley and rape (Dettenmaier and Doucette; 2007; Havranek et al., 2016; Kirchmann and Tengsved, 1991; Mortensen and Kure, 2003; Roberts et al., 2006; Sjöström et al., 2008).

2.4. Agricultural pesticides and fertilizers

Nonylphenol ethoxylates are cost effective surfactants with outstanding performance (Soares et al., 2008) and account for the third largest industrial use of APEOs in the USA (Cox, 1996). Surfactants are commonly used as wetting, stabilising, emulsifying and dispersing agents (Knoche et al., 1992; Knoche and Noga, 1991). These surfactants are added to agricultural pesticides in order to increase droplet spreading, reduce surface tension and solvent evaporation rates, increase residence time on

plant surfaces, strengthen selectivity, enhance penetration of the active ingredient and/or to boost the product's storage characteristics (Davis et al., 1982; Björklund et al., 2009). Surfactants are also added to biocontrol products to enhance the effect of the biocontrol agent by contributing to adherence, spreading and enabling penetration (Singh et al., 2007). Following pesticide application, NP can still be detected on crops after 35 days (Fang et al., 2015).

3. Degradation of nonylphenol

Nonylphenol ethoxylates are degraded in two steps. The first process concerns the stepwise loss of ethoxy groups to form intermediate biodegradation products (short-chain NPEOs and NP) (Croce et al., 2003). This hydrolysis process is generally favoured under anaerobic conditions (Belmont and Metcalfe, 2003). During the second, aerobic stage, NP is degraded, resulting in the formation of CO_2, H_2O and inorganic salts (Bergé et al., 2012).

Biodegradation of NP can take place through the action of microorganisms, both in anaerobic and aerobic conditions (Soares et al., 2008). Anaerobic degradation exists in the presence of methanogens, eubacteria and sulphate-reducing bacteria (Chang et al., 2005) or the aquatic hyphomycete, *Calvariopsis aquatica*. Two ligninolytic enzymes, namely manganese peroxidase and laccase actively remove NP (Barlocher et al., 2011). Under aerobic circumstances, *Pseudomonas*, *Enterobacter* and *Stenotrophomonas* spp. have been shown to use NP as a carbon source (Chakraborty and Dutta, 2006; Kageyama and Marooka, 2005; Qhanya et al., 2017; Toyama et al., 2011; Yuan et al., 2004). The biodegradation of NP in soil may also be promoted by the presence of earthworms, as these improve soil aeration and nutritional status, or the earthworms themselves can accumulate NP in either free form or as bound residues (Shan et al., 2014).

Depth of the sludge layer, increased sunlight, oxygen availability, bioavailability of the NP to soil microflora and elevated temperatures are of major importance in NP degradation in soil. In water, other factors such as the sedimentation rate, river flow rate, and particle size also influence the rate of degradation (Soares et al., 2008; Mao et al., 2012).

Continuous exposure to NP can negatively impact the efficiency of microorganisms to eliminate this substance (Vazquez-Duhalt et al., 2005).

4. Presence on edible crops

Nonylphenol is becoming increasingly ubiquitous on vegetables and fruits (Fang et al., 2015). In fact, diet appears to be the major exposure route of NP to humans (USA Environmental Protection Agency, 2010). Contamination of edible plants is generally via exposure to sludge-amended soil, polluted water, the use of cleaning agents in the food processing industry and application of wax coats and pesticides on crops (Fang et al., 2015; Lu et al., 2007; Soares et al., 2008). Food packaging material may also contain NP or tris (nonylphenol) phosphate (TNPP) that are used as plasticisers or antioxidants (Lu et al., 2007; Votavová et al., 2009).

Previous studies reported the presence of NP on various fruits and vegetables in China, Germany, Taiwan and the USA (Fang et al., 2015; Guenther et al., 2002; Lu et al., 2007, 2013; Dodgen et al., 2013; She et al., 2012) (Table 1). All of these fresh products were obtained from producers or supermarkets, except for those analysed by Dodgen et al. (2013), where the presence of NP was as a consequence of fortified incubation in the laboratory. On average, NP concentrations varied from 2.6 to 27.4 μg/kg on fruit and 0.52–35.82 μg/kg on vegetables, with the highest concentration of 72.5 μg/kg, reported for maize (She et al., 2012). In China, where leafy vegetables account for a large portion of a person's diet, contamination with NP potentially elevate risks to human health. This is a matter of concern since long-term toxic effects of NP occur at concentrations as low as 3.3 μg/l in mammals (European Chemicals Bureau , 2002). It is however important to note that in studies where water or soil was spiked with NP, translocation of the latter from root-to-shoot was limited. In broad

bean, collard, lettuce, rape, wheat and wheat grass, the largest percentage of NP that was taken up by the roots remained there, with restricted distribution to the upper part of the plant (Dettenmaier and Doucette; 2007; Dodgen et al., 2013; Roberts et al., 2006; Sjöström et al., 2008) (Fig. 2).

Table 1. Concentrations of nonylphenol previously detected on edible fresh produce.

Source	Concentration	Location	Detection method	Reference
Apple	7.2–19.4 μg/kg	Germany	GC-MS/MS	Guenther et al. (2002); Lu et al. (2013)
Cabbage	0.52–31 μg/kg	China, Taiwan	HPLC-MS/MS; HPLC-fluorescence	Fang et al. (2015); Lu et al. (2007); She et al. (2012)
Carrot	5.1 μg/kg	USA	GC-MS/MS	Lu et al. (2013)
Citrus	11 μg/kg	USA	GC-MS/MS	Lu et al. (2013)
Collard	3.79–6.95 μg/kg	USA	LSC with ^{14}C-labeled NP	Dodgen et al. (2013)
Cucumber	33.39 μg/kg	China	HPLC-MS/MS	She et al. (2012)
Guava	24.3 μg/kg	Taiwan	HPLC-fluorescence	Lu et al. (2007)
Leek	1.66-35.82 5 μg/kg	China	HPLC-MS/MS	Fang et al. (2015); She et al. (2012)
Lettuce	1.18–7.5 μg/kg	Taiwan, USA	LSC; HPLC-fluorescence	Dodgen et al. (2013); Lu et al. (2007)
Maize	72.5 μg/kg	China	HPLC-MS/MS	She et al. (2012)
Pakchoy	21.46 μg/kg	China	HPLC-MS/MS	She et al. (2012)
Pineapple	2.6–27.4 μg/kg	Germany, Taiwan	GC-MS/MS; HPLC-fluorescence	Guenther et al. (2002); Lu et al. (2007)
Potato	0.6 μg/kg	Germany	GC-MS/MS	Guenther et al. (2002)
Pumpkin	5.3 μg/kg	USA	GC-MS/MS	Lu et al. (2013)
Spinach	1.3 μg/kg	Germany	GC-MS/MS	Guenther et al. (2002)
Soy bean	37.61 μg/kg	China	HPLC-MS/MS	She et al. (2012)
Tomato	18.5 μg/kg	Germany	GC-MS/MS	Guenther et al. (2002)
Watermelon	22 μg/kg	Taiwan	HPLC-fluorescence	Lu et al. (2007)

*GC-MS/MS = Gas chromatography–mass spectrometry; HPLC = High-performance liquid chromatography; LSC = Liquid scintillation counting; NP = nonylphenol

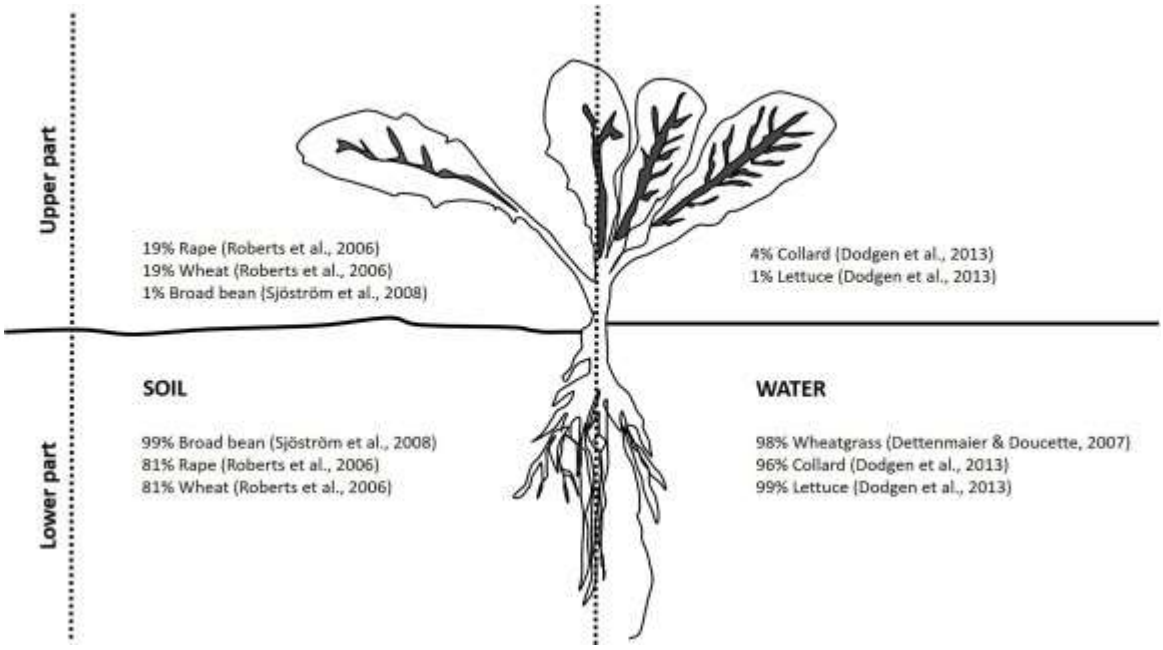

Fig. 2. Percentage distribution of nonylphenol in upper and below plant parts through uptake from artificially inoculated soil/water.

5. Analysis of nonylphenol in plant material

Bearing in mind that NP can cause adverse responses to the ecosystem at extremely low concentrations, it is imperative that detection equipment is particularly sensitive. The analytical procedures involved in determining the presence of NP in plants involve sample extraction/purification and detection (Belmont and Metcalfe, 2003; She et al., 2012).

Extraction of NP from solid matrices, such as plant material, requires effective sample pre-treatment due to various forms of interference during extraction and separation (De Araujo et al., 2018). The pre-treatment involves extra drying and extraction steps (Olujimi et al., 2010). Prior to extraction, the solid samples are dried and homogenised (Petrovic and Barceló, 2000) after which extraction is performed using steam distillation (Guenther et al., 2002), ultrasonication (Fang et al., 2015; Lu et al., 2015); solid phase (SPE) extraction (Fang et al., 2015); soxhlet extraction (Díaz-Cruz et al., 2003; Noppe et al., 2007; Ternes et al., 2002) or liquid-liquid extraction (Lu et al., 2007). The former uses methylene chloride (Lu et al., 2015) or mixtures of hexane and other solvents such as acetonitrile and isooctane (Guenther et al., 2002; Lu et al., 2007; Petrovic et al., 2002).

Following extraction of the compound, several types of equipment and techniques can be used for detection, and have most often included the use of high-performance liquid chromatography (HPLC), HPLC coupled with a fluorescence detector (HPLC-fluorescence), HPLC mass spectrometry (HPLC-MS/MS) (Fang et al., 2015; Lu et al., 2007) or gas chromatography-mass spectrometry (GC-MS/MS) (Guenther et al., 2002; Lu et al., 2015). Novel technologies focus on increasing signal intensity, reducing analysis time (e.g., liquid chromatography–mass spectrometry, ultra-performance liquid chromatography - tandem mass spectrometry, ultra-high performance supercritical fluid chromatography-tandem mass spectrometry), and attaining individual detection of NP isomers using an appropriate chromatographic column (e.g., chiral cyclodextrin GC capillary columns) followed by GC-MS (Li et al., 2018).

6. Metabolic fate of nonylphenol in plants

When plants are exposed to a xenobiotic such as NP, reactive oxygen species (ROS) (hydrogen peroxide and superoxide) are produced, thereby triggering an antioxidative defence response (Hasanuzzaman et al., 2012; Jiang and Yang, 2009). Accumulated NP is metabolized to hydroxylated and conjugated derivatives (Bokern and Harms, 1997). Chemical modification occurs through three sequential processes: phase I) Transformation of the compound, which usually involves hydrolysis or oxidation; phase II) Conjugation reactions; and, phase III) Compartmentalisation (Coleman et al., 1997). In phase I, chemical transformation involves enzyme-catalysed reactions that result in the conversion of the foreign molecule to a product that is more hydrophilic than the parent xenobiotic (Coleman et al., 1997; Sandermann, 1992). The enzymes responsible for this reaction include catalase (CAT), peroxidase (POD), and superoxide dismutase (SOD) that prepare NP for phase II reactions (Hasanuzzaman et al., 2012; Jiang and Yang, 2009; Chen and Yen, 2013). During phase II, the derivative from phase I is deactivated by linkage to a hydrophilic molecule, such as glucose, malonate or glutathione, to form water-soluble compounds. In phase III, the water-soluble conjugates, hydrogen peroxide (H_2O_2) and oxygen (O_2), are exported from the cytosol to the vacuole and apoplast where compartmentalisation and processing takes place. Compounds that are still insoluble at this stage, are stored in the cell wall (Coleman et al., 1997; Sandermann, 1992) whilst excessive amounts of H_2O_2 can cause many types of cell damage (Hasanuzzaman et al., 2012; Jiang and Yang, 2009).

7. Effect of nonylphenol on plants

Research studies on the effects and action of NP on higher plants are scarce and were mostly reported on in the 1980s and again from 2004 onwards. A summary of the effect of NP on plants, methods used to determine the extent of damage, plant species investigated and concentrations of NP it was exposed to, are summarized in Table 2**.** Of note is the fact that the results from Bokern and Harms (1997) were obtained using 4-n-NP (a linear isomer), whilst the most common commercial form of NP, technical 4-NP, was used in the other studies (a mixture of branched isomers). Recent findings have shown that the estrogenicity and metabolic pathways for these two compounds differ in fish (Pedersen et al., 1999), but whether this has relevance to the effect it has on plants remains unknown.

Table 2. Reported toxic effect of nonylphenol on plants.

Effect	Plant species	Nonylphenol exposure	Method used	Reference
Morphological				
Chlorosis and bleaching of plant tissue	*Salvinia molesta* (frond) *Lemna minor* (duckweed) *Lactuca sativa* (lettuce)	2.5, 10, 25 ppm 0.5, 2.5, 5 ppm 6400, 12 800 µg/l	Visual assessment Visual assessment Visual assessment	Prasad, 1986 De Bruin et al. (2017b)
Germination reduced	*Betula papyrifera* seeds (white birch)	100 ppm	Visual assessment	Weinberger & Vladut (1981)
	B. papyrifera seeds (white birch)	≥5 µg/ml	Visual assessment	Weinberger & Greenhalgh (1984)
	L. sativa (lettuce)	12 800 µg/l	Visual assessment	De Bruin et al. (2016)
	Lolium perenne (ryegrass) *Raphanus sativus* (radish)	1000 µg/l	Visual assessment	Gattullo et al. (2012)
	L. perenne (ryegrass) *Brassica rapa* (turnip)	>1 g/kg	Visual assessment	Domene et al. (2009)
	Triticum aestivum (wheat)	1000 µg/l	Visual assessment	Zhang et al. (2016)

Effect	Plant species	Nonylphenol exposure	Method used	Reference
Ion leakage	*B. papyrifera* seeds (white birch) *Avena fatua* (wild oat) *T. aestivum* (wheat) *L. sativa* (lettuce)	1500 µg/l >0.001% v/v 3200, 6400, 12 800 µg/l	Electrical conductivity Electrical conductivity Electrical conductivity	Weinberger & Greenhalgh (1984) Conlin et al. (1986) De Bruin et al. (2017b)
Mass reduced	*Beta vulgaris* (beetroot) *Glycine max* (soybean) *L. sativa* (lettuce) *Atriplex hortensis* (french spinach) *Hordeum vulgare* (barley) *T. aestivum* (wheat) *Chenopodium rubrum* (goosefoot) *Lycopersicon esculentum* (tomato) *Pennisetum americanum* (pearl millet) *Chenopodium quinoa* (quinoa) *Lupinus polyphyllus* (large-leaved lupine) *Daucus carota* (carrot)	0.01, 0.05, 0.10, 0.50, 1 mM	Weight measurement	Bokern and Harms (1997);
	L. sativa (lettuce) *L. sativa* (lettuce) *S. molesta* (frond) *L. minor* (duckweed) *T. aestivum* (wheat) *B. napus* (oil seed rape) *A. thaliana* (Arabidopsis) *L. perenne* (ryegrass) *B. rapa* (turnip)	12 800 µg/l 6400, 12 800 µg/l 2.5, 10, 25 ppm 0.5, 2.5, 5 ppm 10 000 mg/kg 100, 1000, 10 000, 50 000 µg/l >1 g/kg	Weight measurement Weight measurement Weight measurement Weight measurement Weight measurement Weight measurement Visual assessment	De Bruin et al. (2016) De Bruin et al. (2017b) Prasad, 1986 Roberts et al. (2006) Chen & Yen (2013) Domene et al. (2009)
Necrosis and browning of tissue	*A. thaliana* (Arabidopsis) *T. aestivum* (wheat) *Brassica napus* (oil seed rape)	≥10 000 µg/l 10 000 mg/kg	Visual assessment Visual assessment	Chen & Yen (2013) Roberts et al. (2006)
	S. molesta (frond) *L. sativa* (lettuce)	2.5, 10, 25 ppm 6400, 12 800 µg/l	Visual assessment Visual assessment	Prasad, 1986 De Bruin et al. (2017b)
pH change in rhizosphere	*A. fatua* (wild oat) *T. aestivum* (wheat) *L. sativa* (lettuce)	>0.001% v/v 800, 1600, 3200, 6400, 12 800 µg/l	Bromocresol agar pH meter	Conlin et al. (1986) De Bruin et al. (2017b)
Plant length reduced	*R. sativus* (radish) *P. banksiana seeds* (Jack pine) *B. papyrifera seeds* (white birch) *T. aestivum* (wheat) *B. napus* (oil seed rape) *L. sativa* (lettuce) *L. sativa* (lettuce) *T. aestivum* (wheat)	1 mg/l 20, 100 ppm 10 000 mg/kg 1600, 3200, 6400 µg/l 6400, 12 800 µg/l 1700–1800 µg/l	Visual assessment Visual assessment Visual assessment Visual assessment Visual assessment Visual assessment	Gattullo et al. (2012) Weinberger & Vladut (1981) Roberts et al. (2006) De Bruin et al. (2016) De Bruin et al. (2017b) Zhang et al. (2016)

Effect	Plant species	Nonylphenol exposure	Method used	Reference
Root/shoot ratio affected	*B. papyrifera* seeds (white birch) *L. sativa* (lettuce)	20, 100 ppm 3200, 6400, 12 800 µg/l	Visual assessment Visual assessment	Weinberger & Vladut (1981) De Bruin et al. (2016)
Root growth affected	*Lupinus hartwegii* (Hartweg's lupine) *L. polyphyllus* (large-leaved lupine) *P. banksiana seeds* (Jack pine) *A. thaliana* (Arabidopsis) *L. minor* (duckweed) *L. sativa* (lettuce) *L. sativa* (lettuce)	0.1 mM, 1 mM 20, 100 ppm 100, 1000, 10 000, 50 000 µg/l 0.5, 2.5, 5 ppm 6400, 12 800 µg/l 6400, 12 800 µg/l	Weight measurement Visual assessment Visual assessment Visual assessment Visual assessment Visual assessment	Bokern and Harms (1997) Weinberger & Vladut (1981) Chen & Yen (2013) Prasad, 1986 De Bruin et al. (2016) De Bruin et al. (2017b)
Water uptake reduced	*P. banksiana seeds* (Jack pine) *P. banksiana seeds* (Jack pine) *B. papyrifera seeds* (white birch) *L. sativa* (lettuce)	20, 100 ppm 5000-10 000 µg/l 800, 1600, 3200, 6400, 12 800 µg/l	Weight measurement Visual assessment Volume measurement	Weinberger & Vladut (1981) Weinberger & Greenhalgh (1984) De Bruin et al. (2017b)
Biochemical				
Antioxidant activities affected - Catalase - Peroxidase - Superoxide dismutase - Glutathione S-transferases - Ascorbate peroxidase	*T. aestivum* (wheat) *A. thaliana* (Arabidopsis) *T. aestivum* (wheat) *T. aestivum* (wheat) *A. thaliana* (Arabidopsis) *T. aestivum* (wheat) *A. thaliana* (Arabidopsis)	1000, 5000 µg/l 50 000 µg/l 1000, 5000 µg/l 1000, 5000 µg/l 10 000, 50 000 µg/l 1000, 5000 µg/l 10 000, 50 000 µg/l	Hydrogen peroxide degradation Hydrogen peroxide degradation Guaiacol oxidation Inhibition of nitroblue tetrazolium Inhibition of nitroblue tetrazolium Glutathione degradation Hydrogen peroxide degradation	Zhang et al. (2016) Chen & Yen (2013) Zhang et al. (2016) Zhang et al. (2016) Chen & Yen (2013) Zhang et al. (2016) Chen & Yen (2013)
ATP production disrupted	*Pinus banksiana seeds* (Jack pine) *B. papyrifera seeds* (white birch) *B. papyrifera seeds* (white birch) *Polystichum setiferum* spores	≥6250 µg/l 20, 100 ppm 0.002–0.02 µg/l	Luciferin-luciferase method Luciferin-luciferase method Tetrazolium assay	Weinberger & Greenhalgh (1984) Weinberger & Vladut (1981) Esteban et al. (2016)
Chlorophyll concentration affected	*Ocimum basilicum* (basil) *A. thaliana* (Arabidopsis) *T. aestivum* (wheat) *L. sativa* (lettuce)	3, 30, 300, 3000, 30000 µg/l 1000, 5000 µg/l 800, 12 800 µg/l	High-Performance liquid chromatography (HPLC) Spectrophotometry Spectrophotometry	Capota et al. (2004) Zhang et al. (2016) De Bruin et al. (2017b)
Lipid peroxidation increased	*T. aestivum* (wheat) *A. thaliana* (Arabidopsis)	1000, 5000 µg/l 100 µg/l	Malondialdehyde content Malondialdehyde content	Zhang et al. (2016) Chen & Yen (2013)
Malondialdehyde activity affected	*A. thaliana* (Arabidopsis)	50 000 µg/l	Tichloroacetic acid reaction	Chen & Yen (2013)
Photosynthesis reduced	*P. banksiana seeds* (Jack pine) *B. papyrifera seeds* (white birch) *A. thaliana* (Arabidopsis)	≥500 µg/l 100, 1000, 10 000, 50 000 µg/l	Fluorometer 2-D gel electrophoresis and Mass Spectrometry	Weinberger & Greenhalgh (1984) Chen & Yen (2013)

Effect	Plant species	Nonylphenol exposure	Method used	Reference
Phosphorous content increased	*Oryza sativa* (rice)	0.4% v/v	Colorimetric method	Rui-Chi et al., 1986
Proline activity affected	*A. thaliana* (Arabidopsis)	1000, 10 000, 50 000 µg/l	Ninhydrin chromogenic method	Chen & Yen (2013)
Ultrastructural				
Chloroplast	*L. sativa* (lettuce) *L. minor* (duckweed) *O. sativa* (rice)	3200, 6400, 12 800 µg/l 0.5, 2.5, 5 ppm 0.4% v/v	Transmission electron microscopy (TEM) TEM TEM	De Bruin et al. (2017b) Prasad, 1986 Rui-Chi et al., 1986
Endoplasmic reticulum	*L. sativa* (lettuce)	1600,3200, 6400, 12 800 µg/l	TEM	De Bruin et al. (2017b)
Lipid	*L. sativa* (lettuce)	1600, 3200, 6400, 12 800 µg/l	TEM	De Bruin et al. (2017b)
Mitochondria	*L. minor* (duckweed) *O. sativa* (rice)	0.5, 2.5, 5 ppm 0.4% v/v	TEM TEM	Prasad, 1986 Rui-Chi et al., 1986
Plasma membrane	*L. minor* (duckweed) *O. sativa* (rice) *L. sativa* (lettuce)	0.5, 2.5, 5 ppm 0.4% v/v 6400, 12 800 µg/l	TEM TEM Scanning electron microscopy (SEM)	Prasad, 1986 Rui-Chi et al., 1986 De Bruin et al. (2017a)
Vacuole	*L. sativa* (lettuce)	1600, 3200, 6400, 12 800 µg/l	TEM	De Bruin et al. (2017b)

One of the most common phytotoxic effects of NP on plants is through general growth inhibition (Bokern and Harms, 1997; Chen and Yen., 2013; Roberts et al., 2006; Zhang et al., 2016). This is manifested by reduced biomass (De Bruin et al., 2017b; Chen and Yen, 2013; Domene et al., 2009; Roberts et al., 2006) and length (Gattullo et al., 2012; Roberts et al., 2006; Wang et al., 2014; Weinberger and Vladut, 1981) and includes reduction in germinative capacity (De Bruin et al., 2016; Domene et al., 2009; Gattullo et al., 2012; Weinberger and Greenhalgh, 1984; Weinberger and Vladut, 1981). Esteban et al. (2016) alludes that the latter is likely related to a decrease in mitochondrial activity. This side-effect of NP, the authors state, is brought about by its ability to mimic natural allelochemicals and/or phytohormones, aptly referring to NP as a "phytoendocrine disruptor" (Esteban et al., 2016). Transmission electron microscopy (TEM) images of *Lemna minor* L. (duckweed) (Prasad, 1986) and *Oryza sativa* L. (rice) (Rui-Chi et al., 1986) reveal unidentifiable mitochondria. Disruption of this main site of ATP production is associated with depressed plant growth (Weinberger and Greenhalgh, 1984).

Damage to chloroplasts (De Bruin et al., 2017b; Prasad, 1986; Rui-Chi et al., 1986) can account for reduced chlorophyll levels and photosynthesis efficiency (Chen and Yen, 2013; Roberts et al., 2006; Wang et al., 2014; Weinberger and Greenhalgh, 1984) ultimately leading to stunted growth in plants exposed to NP (Chen and Yen, 2013; Zhang et al., 2016). Loss in chlorophyll is caused by pigment degradation, induced by the activity of POD, an antioxidant that also initiates lipid peroxidation (Zhang et al., 2016).

The collective operation of antioxidant enzymes, such as POD, CAT and SOD protect plants against oxidative damage (Chen and Yen, 2013; Zhang et al., 2016). Chen and Yen (2013) found that SOD and CAT levels in Arabidopsis increased when it was exposed to 10 000 and 50 000 µg/l NP, respectively. This correlates with findings related to enhanced POD, SOD and glutathione S-transferases activity in similar NP conditions (Zhang et al., 2016).

Malondialdehyde (MDA) reacts to oxidative stress and its content is commonly used as a membrane lipid peroxidation marker (Zhang et al., 2016). The compound's concentration increases with NP

exposure, indicating enhanced lipid peroxidation, which is usually followed by membrane damage (Chen and Yen, 2013; Pretorius et al., 2016). De Bruin et al. (2017a) used high-resolution scanning electron microscopy (SEM) to show that the plasma membrane of *Lactuva sativa* (lettuce) protoplasts that had been exposed to 6400 and 12800 μg/l NP had vesicle-like protrusions, accompanied by flattening in its direct vicinity. Changes in the morphology of membranes compromises its functionality and evidence of cellular injury is exemplified by electrolyte leakage (De Bruin et al., 2017b; Weinberger and Greenhalgh, 1984).

To gain a better understanding of the aforementioned, the inherent properties of a surfactant should be considered. Nonylphenol has an amphipathic nature, with the alkylphenyl being hydrophobic and the ethoxylate chain hydrophilic (Cox, 1996). This characteristic makes it an ideal surfactant. At low concentrations, surfactant molecules act as monomers, but at a critical concentration and temperature, the molecules self-associate to form aggregates known as "micelles" (Lichtenberg, 1985; Lichtenberg et al., 1983). These micelles bind to plant membranes and at the optimal concentration cause the membrane bilayer to open-up, causing an efflux of solutes (Knoche et al., 1992). Even at low concentrations the permeability of plant membranes is compromised by the production of pores in the membrane through which solutes can pass freely (Fletcher et al., 1980; Goñi and Alonso, 2000). This efflux of ions is dependent on the crop, type and dose of surfactant, duration of exposure, droplet/leaf interface area and pH (Fletcher et al., 1980; Knoche et al., 1992; Schuck et al., 2003; St John et al., 1974).

Nonylphenol has moderately high hydrophobicity with an octanol–water partition coefficient (log Kow) greater than four (Dodgen et al., 2013). Movement of organic compounds within plants mainly decreases with increasing hydrophobicity (Trapp and Legind, 2011). Previous studies have linked this property with higher concentrations of NP found in roots that have a higher lipid content relative to shoots (Briggs et al., 1982; Collins et al., 2011; De Bruin et al., 2016, 2017a, 2017b; Lu et al., 2015). Exposed plant roots show reduced root hair growth (De Bruin et al., 2016; Weinberger and Vladut, 1981) and thickening of the roots themselves (De Bruin et al., 2017b; Roberts et al., 2006), ultimately affecting the absorption of water and nutrients (De Bruin et al., 2016).

8. Regulatory aspects

As a result of the endocrine disruptive and toxic bioaccumulative effects of NP compounds, developing countries have restricted the production, marketing and use of NP. In Europe and North America, regulations banning products that contain NP have been implemented since 2000. Nonylphenol and its ethoxylates were designated as one of the 33 priority hazardous substances in the European Water Framework Directive (Directive 2008/105/EC, 2008) that recommends a maximum allowable concentration of 2 μg/L for surface water and a 50 mg/kg NPEO limit to sewage sludge intended for agricultural use (3rd draft Working Document on Sludge) (Directorate-General Environment, 2000). As a co-formulant in pesticides and biocides, NP is restricted from being placed on the market or used as substances or in mixtures in concentrations equal to or greater than 0.1% by weight. The Environmental Protection Agency of the USA prepared a guideline that recommends NP concentrations in freshwater to be below 6.6 μg/L and in saltwater, below 1.7 μg/L, although drinking water is not mentioned (Soares et al., 2008; USA Environmental Protection Agency, 2010). In Canada and Japan the use and production of NPEOs are strictly monitored (Mao et al., 2012) while they are completely banned for use in detergents by the 2000 OSPAR convention (legal instrument guiding international cooperation on the protection of the marine environment of the North-East Atlantic) (OSPAR, 2001).

Whereas developed countries have taken measures to restrict the production of NP, an increase in its use has been observed in many emerging countries such as those in Asia and Africa (Bergé et al., 2012; Gao et al., 2014; Mao et al., 2012). Enormous amounts of NP and its ethoxylates are imported from developed nations who are constrained from manufacturing it for local use. South Africa, for example, imported 12 000 tons of NPEOs and NP in 2013 (Official correspondence, senior policy

advisor of South African Department of Environmental Affairs, Ms Noluzuko Gwayi). No action has been taken by any of these countries to reduce or eliminate their usage (Soares et al., 2008) although there have been attempts at limiting its use inert ingredients in pesticides (South African Act No 36 of 1947, Department of Agriculture, Forestry and Fisheries, 2015). Control of the application of these compounds in agriculture remains a challenge, since the labelling on commercial products often do not declare the type of surfactant used.

9. Conclusion

Nonylphenol has a different regulatory status across the world and the extent of its presence in aquatic, terrestrial and urban ecosystems varies between countries and sources. Owing to its moderately high hydrophobicity, it tends to accumulate in organic rich materials such as plants. This paper provides, to the best of our knowledge, the first systematic review of NP in the plant environment.

In plants, the presence of NP can lead to reduction in germinative capacity, disruption of ATP production, changes in photosynthesis, and reduction in plant biomass and length. Apart from the potential negative impact this can have on yield, it could also compromise the food safety status of edible crops. In assessing potential dietary intake of NP through edible crops, it is important to note that NP accumulation in roots is higher compared to above-ground tissues. Due to a low translocation factor of NP from roots to upper tissues, the potential human health risk may therefore be significantly greater for root vegetables such as onions, carrots and radishes (Dodgen et al., 2013; Sjöström et al., 2008). Specific studies should address the effect of NP on critical root crops that are irrigated with contaminated water such as potatoes, carrots and onions. This would be particularly useful to understanding the translocation of NP in the edible parts and the risk for humans due to their consumption.

The detrimental effect NP poses to the wellbeing of the earth's natural resources is enhanced by increased industrialisation and agricultural intensification, substantiating the urgent intervention needed into current water management practices. The development of standards and regulations aimed at restricting the production and use of NP should therefore be encouraged and informed by research that takes plant ecosystems into account. Particular attention ought to be paid to reducing NP levels in the human diet through an effective regulatory framework that is supported by exposure risk assessment studies. Finally, further studies into the link between NP levels in water or soil to humans via consumption of fresh produce should be prioritized.

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