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Nonylphenol: Properties, legislation, toxicity and determination

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ABSTRACT

This paper aims to gather and discuss important information about nonylphenol, such as physical chemistry properties, toxicity and analytical methods in various matrices. As a degradation product of ethoxylated alkylphenols, nonylphenol presents a higher degree of reactivity than its precursor. Due to its harmful effects on the environment, use and production of nonylphenol has been banned in European Union countries, alongside their precursors. The guide on quality of drinking water (USEPA) recommends a maximum concentration of 28 µg L^{-1} for fresh water. In Brazil, there is no clear legislation containing values of maximum concentration of nonylphenol. Due to this lack of regulation, a continuous monitoring is necessary of this pollutant in environmental samples. This paper aims to encourage further studies on nonylphenol, seen as a critical environmental pollutant. For proper monitoring is necessary to have reliable analytical methods and easy to perform in routine analysis.

Key words: nonylphenol, endocrine disrupter, pollutant, water analysis.

INTRODUCTION

Nowadays, the growing concern over water resources availability is justified by its key role in the socioeconomic development of humanity. Availability which is affected not only by water scarcity in some regions, or the increase in world demand, but also by the depreciation of its quality. Considering the uncontrolled growth of cities and human activities in the surrounding watershed, it is worth noticing the increased pollution of surface and groundwater (Rebouças 2001, Vianna 2015, Tundisi 2008). In Brazil, even with investments in sewage systems and treatment plants, only a small portion of the sewage volume generated by cities is effectively treated before reaching the rivers. The release of sewage into water bodies without any treatment is one of the main causes for depreciation of water quality. The absence of adequate basic sanitation compromises the primal use of this resource, the public supply. Such context imposes a continuous need for finding even further sources, more complex and more expensive chemical treatments to ensure availability of drinking water (Tucci 2008).

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A general concern has been raising worldwide about the contamination of the environment (air, soil, forests, animals, rivers and oceans by chemicals from industrial activities, mineral exploration and agricultural exploitation) and its relation to the recent increase of congenital malformations, asthma, cancer and neurological and behavioral disorders in children (Godoi et al. 2003, Mello-da-Silva and Fruchtengarten 2005).

The concern about the contamination of surface and underground water systems with pesticides has grown in the world. In industrialized countries, the Green Revolution of the 1960s significantly increased agricultural productivity due to the expansion of sown area, mechanization, pest control, among others. For pest control, the massive use of pesticides was necessary, dangerous chemicals used to repel or kill rodents, fungi or insects potentially harmful to intensive agriculture. These extensively used chemicals, at first sight, bring a great benefit to human health, by increasing agricultural productivity. On the other hand, many of those first-generation pesticides are harmful to the environment. Some of them can persist in soils and aquatic sediments, bioaccumulate in the tissues of invertebrates and vertebrates, moving in trophic chains, and affect top predators (Mnif et al. 2011).

After the Second World War the sale and trading of chemicals, such as fertilizers, pesticides and insecticides increased sharply. This increase was justified by industrial development and the need to supply the demand of the population for food and to improve the quality of crops (Colborn et al. 1994, El-Shahawi et al. 2010). Meanwhile, the problem of environmental pollution has emerged, particularly regarding water, soil and air The organic compounds released into the environment, or formed from the degradation of other compounds, generally present a high toxicity that may chronically alter the development and reproduction of aquatic life (Ghiselli and Jardim 2007).

Water resources pose as the final destination of the main pesticides, considering surface and underground resources. Soil and water operate interactively and any action that causes adverse effect in one of these will affect the other. In some cases, less than 0.1% of the amount of applied pesticides reaches the target species while the remaining (99.9%) has the potential to move to other environmental compartments, such as surface water and groundwater through natural processes as leaching, volatilization, degradation, sorption and plant uptake (Ribeiro et al. 2007).

The formulation of the pesticide contains components such as adjuvants and usage modifiers, in addition to the active ingredient. Amongst the adjuvants, there are the surfactants, stickers-spreaders, wetting agents, to name but a few. Regarding utility modifiers, there are buffering agents to alter and stabilize solution`s pH and enhance active ingredient solubility; and there are also compatibility agents, to mitigate compatibility problems arising from the mix of multiple pesticides, or pesticides and fertilizers (Fraga 2012).

Surfactants are compounds able to change the surface and interfacial properties of a liquid mixture. They form aggregates, called micelles, usually in low concentrations in solution, decreasing the surface tension of the system and contributing to the stability of the mixture. These compounds are classified into four types, which takes into account the nature of the hydrophilic group: non-ionic, anionic, cationic and amphoteric (Fernandes Providello et al. 2006). After use, residual surfactants are directly released into the sewage system or directly to surface waters, causing pollution of the aquatic system and forming degradation products (Aloui et al. 2009).

The alkylphenol ethoxylate (APEO), non-ionic surfactants has been widely used in phenolic resins, plastics additives, detergents, emulsifiers, pesticides formulations among others. The most relevant APEO is nonylphenol ethoxylate

(NPnEO), representing approximately 80% of production, of which 60% has the environment as a final destination (Renner 1997, Solé et al. 2000, Zgola- Grześkowiak et al. 2009).

Nonylphenol is formed during anaerobic breakdown of the ethoxylated alkylphenols (APEO). In the absence of oxygen, nonylphenol formation is favored (4 to 8 times) when compared to aerobic. Under aerobic conditions, the APEO degrade through either the loss of ethylene oxide units to form low-molecular weight ethoxylates or through the formation of carboxylated ethoxylates ultimately terminating in CO_2 and water. Studies have demonstrated that derivatives of ethoxylated alkylphenols are more persistent and toxic than the parent substances also having the ability to cause disruption of natural hormones to interact with the estrogen's receptor (Renner 1997). It has also been demonstrated (Ahel et al. 1994) that nonylphenol can be degraded by photochemical processes. In bright summer sun, nonylphenol near the water surface has a half-life of 10-15 hr. Another study by Ahel et al. (1996) demonstrated that nonylphenol can be reduced in ground water. The authors suggest that biological processes are responsible provided that the ground water temperature does not become too cold for biological degradation. The authors suggested that this reduction involves biological processes occurring in the part nearest to the river aquifer, provided the groundwater temperature is not low enough for biological degradation (Solé et al. 2000, Zgola- Grześkowiak et al. 2009, Ahel et al. 1994, 1996).

Due to the rapid biodegradation of the alkylphenol ethoxylate, generating more toxic metabolites with potential endocrine disruption, the European Commission, through Directive nº 2003/53/EC banned their use in the European Union. However, the control of the application of these compounds in agriculture is not easy, since many of the products commercially available carry in restricted or no label information about the presence of surfactants in their formulation (Zgola-Grześkowiak et al. 2009).

NATIONAL AND INTERNATIONAL LEGISLATION ON ENDOCRINE DISRUPTERS IN WATER

Over the past few years, a great number of studies trend a growing concern about exposure to chemicals that can interact with the endocrine system and cause adverse effects on wildlife and humans. Studies indicate the presence of these chemicals, called endocrine disruptors in wastewater treatment plants, surface water and groundwater due to the low efficiency of the water treatment process. That is, even after conventional treatment, the water body receptor may still be contaminated (Meyer et al. 1999, Bila et al. 2007). The shortage of water resources is an issue faced by many countries, including Brazil. Highlighting the increasingly imperative need for new studies on the impacts of these disruptors in all beings included in this scenario, studies on water quality among others.

Table I shows the maximum allowed values of some EDs according to the regulation currently enforced both in Brazil and the United States, for surface water and supply as well as the guidance value provided by the Drinking Water Quality Guide World Health Organization Health. Some compounds recently characterized as endocrine disruptors, such as bisphenol a, are not included in the regulations presented in this table.

The guidelines on the quality of US water consumption is given by the Safe Drinking Water Act, establishing the maximum level of contaminants that may be acceptable in drinking water, and the goal of the maximum level of contaminants. Although not enforced as a law, the guide regulates the concentration below which risks to human health are not presented. In addition, another guide is the National Recommendation of Water Quality Criteria (USEPA 2015).

TABLE I
Maximum concentration (μg L^{-1}) of endocrine disruptors in drinking water (1) and surface water (2) in accordance with national and international laws.

	Maximum concentration (μg L^{-1})				
	Brazil		USA		WHO
Composto	1[a]	2[b]	1[c]	2[d]	1[e]
Benzopyreno	0.7	0.018[e]	0.2	n.m.[f]	0.7
Nonylphenol	n.m.	n.m.	n.m.	28[g]/7[h]	n.m.
Pentachlorophenol	9	3	1	19[g]/13[h]	9
Dihexyl-phthalate	20	n.m	6	n.m.	8

a: Portaria MS 2914/2011 (BRASIL 2011); b: Resolução CONAMA 357/2005 (BRASIL 2005); c: Safe Drinking Water Act, SDWA(USEPA 2004); d: National recommendation of water quality criteria (USEPA 2009); e: World Health Organization; f: not mentioned value; g: fresh water; h: salty water.

Brazilian regulation is cosisted of basically two guides: Resolution 357/2005 from CONAMA (National Environmental Agency) (Brasil 2005), for water bodies contamination assessment; and Resolution 2914 from the National Ministry of Health, to stablish and ensure drinkability in public suply.

PHYSICOCHEMICAL PROPERTIES OF NONYLPHENOL

Nonylphenol has a molecular formula $C_{15}H_{24}O$ (M.M= 220 g mol^{-1}). In environmental conditions, it is a viscous liquid, slightly soluble in water (4.90 mg L^{-1} at 25 °C) and soluble in common organic solvents such as acetonitrile and methanol. It has melting point of -10 °C, boiling point of 304 °C, density of 0.6 g mL^{-1} at 20 ºC, the vapor pressure of 1.33 Pa (20 °C) and log P in the range of 4.36 to 4.60. In aqueous solution, it behaves as a weak acid with pKa = 10,7.

TOXICITY

After establishing that nonylphenol brings risk to people, the use of its precursor was banned in many countries and replaced by other surfactants, providing more safety for the population and the environment (Soares et al. 2008).

The US Environmental Protection Agency defines an endocrine disrupter compound as “an exogenous agent that interferes with the synthesis, secretion, transport, metabolism, binding or elimination of the body’s natural hormones, which are responsible for homeostasis, reproduction, development and / or behavior” (USEPA 1998).

To assess the toxicity of environmental contaminants in aquatic organisms, ecotoxicity tests using algae, bacteria, aquatic invertebrates, zooplankton and fish as test organisms are available. In these tests, not only parameters of toxicity are evaluated, but also biochemical, physiological and behavioral parameters. The acute toxicity of nonylphenol for freshwater animals can vary from 20.7 μg L^{-1} for the amphipod *Hyalella azteca* to 774 μg L^{-1} for snail *Physella virgate*. At last, chronic toxicity of nonylphenol for freshwater animals ranges from 10.18 μg L^{-1} for the fish species *Pimephales promelas* to 157.9 μg L^{-1} for the crustacean *Daphnia magna* (USEPA 2005). Azevedo et al. (2001), mentions that the range of concentrations commonly found in rivers is between 0.2 e 12 μg L^{-1}, values that are already likely to cause problems for some organizations (Azevedo et al. 2001).

SAMPLE PREPARATION

For the determination of analytes in environmental matrices becomes generally required isolation, pre-concentration and possibly a cleaning step (clean-up) due to the complexity of the matrix. Among the applied extraction methods for the determination of nonylphenol in water are liquid-liquid extraction (LLE), the solid phase extraction (SPE) solid-phase micro extraction (SPME) and dispersive liquid-liquid micro extraction (DLLME). In solid matrices or sewage sludge extractors type soxhlet and extraction assisted by ultrasound, extraction accelerated solvent (ASE) and pressurized liquid extraction (PLE) are most widely used. Table II presents an overview of nonylphenol extraction methods, liquid and solid matrices described more recently.

The efficiency of the extraction process is directly related to the pH of the matrix where nonylphenol is found. The interference of the liquid matrix pH is given by the fact that nonylphenol may have a nonpolar character in the pH range from 0 to approximately 10 and a polar character in pH above 10.7. Consequentially, nonylphenol has greater solubility in the matrix with more alkaline character, because in this pH condition, nonylphenol presents greater ionic character, thereby increasing its water affinity.

For liquid samples the predominantly used method was SPE. The most commonly used solid phase was the nonpolar character (C18) (Liu et al. 2004, Cai et al. 2003, Ciofi et al. 2014, Souza, 2011 Fabregat-Cabello et al. 2013, Petrie et al. 2013, Martinez and Peñuela 2013, de Sousa Leite et al. 2010, Gatidou et al. 2007, Petrovic et al. 2003, Jeannot et al. 2002, Díaz et al. 2002, Fiedler et al. 2007, Su et al. 2012), but also observed in works which deployed solid phase of polymeric nature, with retention capability of polar and nonpolar analytes together (Azevedo et al. 2001, Jeannot et al. 2002, Terzopoulou et al. 2014, Kuch and Ballschmiter 2001, Montagner and Jardim 2011, Sodré et al. 2010b, Huerta et al. 2015, Cruceru et al. 2012). The major part of SPE uses cartridges containing 500 mg of solid phase and 6 ml volume capacity, but there are also works describing cartridges used with different stationary phase masses, such as 1000 mg, 60 mg and 200 mg. Other techniques used for extraction of nonylphenol in liquid samples are liquid-liquid extraction (Cruceru et al. 2012, Oketola and Fagbemigun 2013), the addition of ultrasound with SPE (Huerta et al. 2015), use of DLLME (Sun et al. 2013), and use of SPME (Díaz et al. 2002, Hernández et al. 2007).

In some protocols shown in Table II, there is the inclusion of yet another step, cleaning (clean-up). This step has the purpose of removing any interferences that may have been trapped on the solid phase cartridge and cause problems to the other stages. For this step, it is necessary to select a solvent in which such interferences are soluble (to promote desorption of the solid phase), although the washing solvent must not desorb the analyte. In the analyte desorption step, a great variety of solvents are used, such as methanol (Ciofi et al. 2014, Fabregat-Cabello et al. 2013, Petrovic et al. 2003, Fiedler et al. 2007, Montagner and Jardim 2011, Sodré et al. 2010a), ethyl acetate (Liu et al. 2004), dichloromethane (Martinez and Peñuela 2013), mixture of methanol and water (Cai et al. 2003), acetonitrile and dichloromethane (Azevedo et al. 2001), ethyl acetate and methanol (Souza 2011), dichloromethane and methanol (de Souza Leite et al. 2010, Su et al. 2012), dichloromethane e hexane (Gatidou et al. 2007, Terzopoulou et al. 2014), acidified methanol and dichloromethane (Díaz et al. 2002), methanol and ethyl ether (Jeannot et al. 2002), acetone and methanol (Kuch and Ballschmiter 2001, Sodré et al. 2010b) and methanol, acetic acid and acetone mixture with dichloromethane (Petrie et al. 2013).

The extraction procedure for solid phase involves two steps: one sorption stage where

TABLE II
Nonylphenol extraction methods in liquid and solid matrices.

Sample	Extraction method	Steps			Recovery	Reference
		Cartridgde	Clean-up[a]	Elution[b]		
Líquid	SPE	C18	H_2O / MeOH (9:1)	AcOEt	>80%	Liu et al. 2004
			X	MeOH / H_2O (1:9)	≈95%	Cai et al. 2003
			H_2O / MeOH (8:2) pH= 2.5	MeOH	Uninformed	Ciofi et al. 2014
			MeOH / H_2O (1:9)	AcOEt / MeOH (6:4)	≈80%	Souza 2011
			X	MeOH	≈70%	Fabregat-Cabello et al. 2013
			X	ACET; HOAc 0.1 % MS MeOH / DCM	50%	Petrie et al. 2013
			H_2O	DCM	> 90%	Martinez and Peñuela 2013
			HEX / DCM (1:4)	MeOH / DCM (9:1)	Uninformed	De Souza Leite et al. 2010
			H_2O	DCM / HEX (4:1)	35%	Gatidou et al. 2007
			X	MeOH	85%	Petrovic et al. 2003
			X	HEX / DCM (9:1) + MeOH / DCM (9:1)	92%	Jeannot et al. 2002
			X	DCM / MeOH c/ HOAc (9:1)	Uninformed	Díaz et al. 2002
			Na_2SO_4 + DCM	MeOH	65% - 84%	Fiedler et al. 2007
		C18 + Zr doped TiO_2	H_2O	DCM / MeOH (1:9)	93%	Su et al. 2012
		Polymeric	H_2O	HEX / DCM (1:1)	80%	Terzopoulou et al. 2014
			MeOH / H_2O (4:6) + H2O + MeOH / MH_4OH / H_2O (10:2:88)	MeOH / ETHER (1:9)	≈50%	Jeannot et al. 2002
			X	ACET + MeOH	89% - 92%	Kuch and Ballschmiter 2001
			H_2O	ACN / DCM (1:1)	73%	Azevedo et al. 2001
			X	MeOH (3 ciclos)	70%	Montagner and Jardim 2011
			X	MeOH	≈72%	Sodré et al. 2010a
			X	ACET + MeOH	70%	Sodré et al. 2010b
	Ultrasound + SPE	OSTRO™ 96	Ultrasound: 3 cycles 120 s ACN/H_2O (3:1)	MeOH	80%	Huerta et al. 2015
	LLE	X	Column with Na_2SO_4 anhydrous	Solution aqueous / organic solvent (20:1) pH=3 / 20 min	81% - 87%	Cruceru et al. 2012
		X	Syringe with Silica gel + wool + Na_2SO_4	1) DCM + HEX 2) MeOH	86%	Oketola and Fagbemigun 2013
	DLLME	Disperser solvent: 0.5 mL MeOH Extractor solvent: 50 µL 1-hexyl-3-methylimidazolium hexafluorophosphate Separation: Centrifugation (3 minutes, 6000 rpm)			93.5%	Sun et al. 2013
	SPME	Sample + NaCl + magnetic stirring NaOH + internal standard + derivatization reagent (DMS + DES + MNNG) thermostated water bath 60 ºC + fiber (CW/DVB) + stirring (900 rpm) Desorption fiber (headspace) 250 ºC for 3 minutes			Uninformed	Díaz et al. 2002
		Sample + NaCl + magnetic stirring + fiber (CW/DVB) Desorption fiber (headspace) 250º C for 5 minutes			Uninformed	Hernández et al. 2007

TABLE II (continuation)

Sample	Extraction method	Steps			Recovery	Reference
		Cartridgde	Clean-up[a]	Elution[b]		
Solid	Soxlet		4 hours ; 90 °C; HEX		54%	Bernacka et al. 2009
			4 hours; MeOH; Dilution of the methanolic extract in H_2O / MeOH (7:3) and extraction by cartridge C18		72%	Jeannot et al. 2002
	Ultrasound		30 minutes; 50 °C; MeOH / H_2O (2:1)		63%	Gatidou et al. 2007
			5 minutes; ACET		≈65%	Lara-Marín et al. 2012
			5 g dry sample + 25 mL DCM / HEX (2:1) 15 minutes Centrifugation: 1500 rpm 5 minutes Concentration and drying with Na_2SO_4		78%	Oketola and Fagbemigun 2013
	Ultrasound + SPE		3 cycles de 30 minutes; 50 °C; MeOH Cartridge: polymeric; Clean-up: H_2O; Elution: MeOH / DCM		≈98%	Ömeroğlu et al. 2015
	PLE		sample + Na_2SO_4 Extractor solvent: ACET / MeOH (1:1 Temperature: 75 ºC and pressure 1500 psi per 5 minutes Concentration of the extract by rotary evaporator Purification: cartridge C18		81%	Petrovic et al. 2003
	ASE		2 cycles de 12 minutes Solvent: MeOH (60% vol extraction cell) Argon purge cycles of 1 minute Purification: Na_2SO_4 + 15 mL MeOH		65% - 84%	Fiedler et al. 2007

ACET = acetone; ACN = acetonitrile; DCM = dichloromethane; HEX = hexane; H_2O = water; MeOH = Methanol; DMS = dimethyl sulfate; DES = diethyl sulfate; MNNG = 1-methyl-3-nitro-1-nitrosoguanidina; ETHER = ethyl ether;
AcOEt = ethyl acetate; HOAc = acetic acid.

a solid phase presents similar character with the analyte, thereby increasing the value of the partition coefficient. The other step involves the desorption of the analyte, which requires a solvent having high affinity with the analyte to promote the desorption of the solid phase, so that the partition coefficient is the lowest possible. The selection of solid phase and eluting solvent influences considerably the analyte recovery results, as shown in Table I. For nonylphenol, most studies use solid phase hydrophobic character (C18), as the solid phase has a similar character to the analyte (nonpolar), increasing the sorption in phase and causing increased coefficient of analyte solid-phase partition. Regarding elution solvent, it must present characteristics similar to the analyte, thus providing sufficient strength to promote the desorption of the analyte from the solid phase. As a consequence of these two factors, an erroneous choice of solid phase and / or the eluting solvent will cause the extraction procedure to present low recovery values.

Regarding solid matrices, there is a scarce number of works to be found, and the predominantly used method of extraction was the ultrasound (Gatidou et al. 2007, Oketola and Fagbemigun 2013, Lara-Martin et al. 2012). It is also observed the use of soxhlet (Jeannot et al. 2002, Bernacka et al. 2009), ultrasound and SPE (Ömeroğlu et al. 2015), PLE (Petrovic et al. 2003) e ASE (Fiedler et al. 2007). In these extraction methods for solid matrices, it is also observed the use of large amounts of sample, reaching 500 g of sample, and exceedingly lengthy protocols. The use of methanol or acetone in the procedures with ultrasound and the use of the extraction using hexane due to the structural similarity with the analyte can also be observed.

ANALYTICAL METHODS FOR THE QUANTIFICATION OF NONYLPHENOL

Given the low polarity of nonylphenol molecule, methods of analysis based on high-performance liquid chromatography (HPLC) and gas chromatography (GC) have been developed. Due to this fact, most investigations reported in the literature refers to these analytical techniques. For most cases, independent of matrix, the use of mass spectrometry (MS) for the detection of nonylphenol is observed, but also observed is the usage of other detectors such as molecular absorption spectrophotometry in ultra-violet (UV) and fluorescence (FLU).

The chromatographic analytical methods for determination of nonylphenol in liquid and solid matrices are shown in Tables III and IV respectively.

For liquid samples, there is use of GC-MS (Azevedo et al. 2001, Liu et al. 2004, Martinez and Peñuela 2013, Jeannot et al. 2002, Terzopouliu et al. 2014, Kuch and Ballschmiter 2001, Sodré et al. 2010b, Oketola and Fagbemigun 2013, Díaz et al. 2002, Hernández et al. 2007, Planas et al. 2002), HPLC-FLU (Zgola-Grześkowiak et al. 2009, Cai et al. 2003, Lou et al. 2012, Marcomini and Giger 1987, Ahel et al. 2000), HPLC-UV (Montagner and Jardim 2011, Marcomini and Giger 1987, Fytianos et al. 1997, Cao et al. 2013) and HPLC-MS (Ciofi et al. 2014, Petrovic et al. 2003, Jeannot et al. 2002, Sodré et al. 2010a, Sun et al. 2013). Among the methodologies using HPLC, most make use of a reverse phase column, including columns with eighteen carbon bonded silica (C18) (Zgola-Grześkowiak et al. 2009, Petrovic et al. 2003, Jeannot et al. 2002, Montagner and Jardim 2011, Sodré et al. 2010a, Sun et al. 2013, Lou et al. 2012, Fytianos et al. 1997, Cao et al. 2013), columns with 8 carbons attached to silica (C8) (Cai et al. 2003, Marcomini and Giger 1987, Ahel et al. 2000) and columns with pentafluorophenyl as stationary phase (Ciofi et al. 2014).

Regarding the detection limit and quantification values found by the authors, there is value in the concentration range of ng mL^{-1} (Cai et al. 2003), ng L^{-1} (Liu et al. 2004, Martinez and Peñuela 2013, Petrovic et al. 2003, Jeannot et al. 2002,

TABLE III
Chromatographic analytical methods for determination of nonylphenol in liquid matrices.

Technique	LQ[a] e LD[b]	Analyhtical Conditions[c]	Detection[d]	Reference
HPLC	LD = 0.02 µg L^{-1} LQ = 0.13 µg L^{-1}	Column: C18 (250 mm x 4.6 mm i.d , 13 Å) Mobile phase: H_2O/THF (1:1) Flow rate: 1 mL min^{-1} Elution: Isocratic Time of analysis: 15 minutes	Fluorescence λexi = 225 nm λemi= 300 nm	Zgoła-Grześkowiak et al. 2009
	LD = 0.018 ng mL^{-1}	Column: C8 (150 mm x 4.6 mm i.d, 3 µm) Mobile phase: ACN/H_2O (75:25) Flow rate: 1 mL min^{-1} Elution: Isocratic Time of analysis: 10 minutes	Fluorescence λexi = 220 nm λemi= 315 nm	Cai et al. 2003
	LD = 0.44 µg L^{-1} LQ = 1.47 µg L^{-1}	Column: C18 Mobile phase: ACN/H_2O (70:30) Flow rate: 1 mL min^{-1} Elution: Isocratic Time of analysis: 20 minutes	Fluorescence λexi = 233 nm λemi= 302 nm	Lou et al. 2012
	LQ < 4 µg L^{-1}	Column: C8 and aminossílica C8 - (250 mm x 4.6 mm i.d, 10 µm, with guard column 30 mm x 4 mm i.d Amino - 100 mm x 4 mm i.d, 3 µm Mobile phase: A/B (45:55) Phase A: isopOH/H_2O/ ACN Phase B: ACN:H_2O (45:55) Flow rate: 1.2 mL min^{-1} Elution: gradient Time of analysis: 25 minutes	UV λreverse phase= 225 nm λnormal phase = 277 nm Fluorescence λexi = 230 nm λemi= 295 nm	Marcomini and Giger 1987
	Not available	Column: C18 (250 mm x 4.6 mm i.d, 10 µm) Mobile phase: HEX/THF (8:2) + isopOH/H_2O (9:1) Flow rate: 1.0 mL min^{-1} Eluition: gradient	UV λ= 277 nm	Fytianos et al. 1997
	LD = 18 ng L^{-1} LQ = 59 ng L^{-1}	Column: C18 (250 mm x 4.6 mm i.d) Mobile phase: ACN/H_2O (75:25) Flow rate: 0.8 mL min^{-1} Elution: gradient Time of analysis: 40 minutes Injection volume: 40 µL	UV= 278 nm	Montagner and Jardim 2011
	LD = 0.03 µg L^{-1} LQ = 0.08 µg L^{-1}	Column: C8 (125 mm x 3 mm i.d, 5 µm) Mobile phase: HEX/2-propOH (98,5:1,5) Flow rate: 0,4 mL min^{-1} Elution: Isocratic Time of analysis: 10 minutes	Fluorescence λexi = 228 nm λemi= 305 nm	Ahel et al. 2000
	LD = 1 ng L^{-1}	Column: C18 (55 mm x 2 mm i.d, 3 µm) Mobile phase: MeOH / H_2O Flow rate: 0.4 mL min^{-1} Elution: gradient Time of analysis: 24 minutes Injection volume: 10 µL	MS	Petrovic et al. 2003
	Not available	Column: C18 (250 mm x 4.6 mm i.d, 5 µm) Mobile phase: MeOH/H_2O (75:25) Flow rate: 0.8 mL min^{-1} Eluition: Isocratic	UV = 225 nm	Cao et al. 2013
	LQ = 0.1 µg L^{-1}	Column: C18 (150 mm x 4.6 mm i.d, 5 µm) Mobile phase: MeOH + ACN (1:1) / H_2O Flow rate: 0.8 mL min^{-1} Elution: gradient Injection volume: 20 µL Time of analysis: 15 minutes	MS	Jeannot et al. 2002
	Not available	Column: pentafluorfenil Mobile phase: H_2O c/ HCOOH + ACN/THF (1:9) Flow rate: 0.4 mL min^{-1} Elution: Gradient Time of analysis: 25 minutes	MS	Ciofi et al. 2014

TABLE III (continuation)

Technique	LQ[a] e LD[b]	Analyhtical Conditions[c]	Detection[d]	Reference
HPLC	LD = 0.76 µg L^{-1}	Column: C18 (150 mm x 2.1 mm i.d, 5 µm) Mobile phase: H_2O + MeOH (4:6) Flow rate: 0.3 mL min^{-1} Elution: Isocratic Time of analysis: 10 minutes Injection volume: 10 µL	MS	Sun et al. 2013
	LD = 0.04 ng L^{-1} LQ = 0.1 ng L^{-1}	Column: C18 (30 mm x 2.1 mm i.d, 3,5 µm) Mobile phase: H_2O c/ NH_4OH (1% v/v) + MeOH Flow rate: 0.3 mL min^{-1} Elution: gradient Time of analysis: 10 minutes Injection volume: 10 µL	MS	Sodré et al. 2010a
GC	LD = 42 ng L^{-1} LQ = 140 ng L^{-1}	Gas: He Column: ZB-5 Temperature: 100 °C – 320 °C Time of analysis: 20.4 minutes Derivatization: (MSTFA)	MS	Martinez and Peñuela 2013
	LD = 0.01 µg L^{-1}	Gas: He Column: HP-5MS Temperature: 60 °C – 300 °C Time of analysis: 24 minutes	MS	Azevedo et al. 2001
	LD = 0.8 ng L^{-1} LQ = 2.6 ng L^{-1}	Gas: He Column: ZB-5 Temperature: 100 °C – 300 °C Time of analysis: 25 minutes Derivatization: pyridine + BSTFA	MS	Liu et al. 2004
	LQ = 2 ng L^{-1}	Gas: He Column: BPX-5 Temperature: 85 ºC – 300 ºC. Derivatization: BSTFA	MS	Jeannot et al. 2002
	LQ = 0.05 µg L^{-1}	Gas: He Column: HP-5MS Temperature: 90 °C – 300 °C Time of analysis: 35 minutes	MS	Hernández et al. 2007
	LD = 0.05 ng L^{-1}	Gas: He Column: DB-5MS Temperature: 80 °C – 300 °C Time of analysis: 75 minutes Derivatization: PFBCl	MS	Kuch and Ballschmiter 2001

TABLE III (continuation)

Technique	LQ[a] e LD[b]	Analyhtical Conditions[c]	Detection[d]	Reference
GC	LD = 10.9 ng L^{-1} LQ = 36 ng L^{-1}	Gas: He Column: TR-5MS Temperature: 60 °C – 320 °C Time of analysis: about 100 minutes	MS	Terzopoulou et al. 2014
	LD = 0.1 μg L^{-1}	Gas: He Column: DB-5MS Temperature: 70 °C – 285 °C Time of analysis: about 27 minutes Derivatization: DMS + DES + MNNG	MS	Díaz et al. 2002
	LD = 10 ng L^{-1}	Gas: He Column: DB-5 Temperature: 80 °C – 310 °C Time of analysis: about 50 minutes	MS	Planas et al. 2002
	LD = 2.0 ng L^{-1} LQ = 7.0 ng L^{-1}	Gas: He Column: HP-5 Temperature: 50 °C – 300 °C Time of analysis: about 25 minutes Derivatization: 1) NaHCO3 + NaOH +stirring 2) HEX + HAc anhydrous +stirring	MS	Oketola, Fagbemigun 2013
	LD = 0.11 μg L^{-1} LQ = 0.36 μg L^{-1}	Gas: He Column: DB-5MS Temperature: 80 °C – 300 °C Time of analysis: 38 minutes Derivatization: MTBSTFA + 1% TBDMCS	MS	Sodré et al. 2010b

a- Limit of detection (LD).
b- Limit of quantification (LQ).
H2O = water; C8 = octil group bonded silica; C18 = octadecil group bonded silica; isopOH =Isopropyl Alcohol; BSTFA = bis (trimethylsilyl) trifluoroacetamide; THF = tetrahydrofuran; DCM = dichlorometane; He = helium; ACN = acetonitrile; HEX = hexane; HCOOH = formic acid MTBSTFA = N-methyl-N-(tert-butyl dimethyl silicon) tri fluoroacetamide; TBDMCS = tert-butyl dimethyl chlorosilane; $NaHCO_3$ = sodium bicarbonate; HOAc = acetic acid; DMS = dimethyl sulfate; DES = diethyl sulfate; MNNG = methyl-3-nitro-1-nitrosoguanidine; PFBCl = pentafluorobenzyl chloride.
For fluorescence technique λexi λemi and refers to wavelengths of excitation and emission, respectively. MS refers to mass spectrometry.

TABLE IV

Chromatographic analytical methods for determination of nonylphenol in solid matrices.

Technique	LQ[a] e LD[b]	Analytical Conditions[c]	Detection[d]	Reference
HPLC	LD = 0.005 mg kg^{-1} LQ = 0.01 mg kg^{-1}	Column: C18 (250 mm x 4.6 mm i.d , 5 µm) Mobile phase: ACN/H_2O Elution: gradient Time of analysis: 40 minutes	Fluorescence λexi = 275 nm λMSi= 300 nm	Bernacka et al. 2009
	Not available	Guard-column: C18 (4 mm x 3 mm i.d, 3.2 µm) Mobile phase: H_2O/MeOH Flow rate: 0.2 mL min^{-1} Elution: gradient Time of analysis: 18 minutes	MS	De Sousa Leite et al. 2010
	LD = 30 µg kg^{-1}	Column: C18 (150 mm x 4,6 mm i.d, 5 µm) Mobile phase: ACN/H_2O Flow rate: 1 mL min^{-1} Elution: gradient Time of analysis: 40 minutes	MS	Andreu et al. 2007
	LD = 0.5 µg kg^{-1}	Column: C18 (55 mm x 2 mm i.d, 3 µm) Mobile phase: MeOH / H_2O Flow rate: 0.4 mL min^{-1} Elution: gradient Time of analysis: 24 minutes Injection volume: 10 µL	MS	Petrovic et al. 2003
	LQ = 1 ng g^{-1}	Column: C18 (150 mm x 4.6 mm i.d, 5 µm) Mobile phase: MeOH + ACN (1:1) / H_2O Flow rate: 0.8 mL min^{-1} Elution: gradient Injection volume: 20 µL Time of analysis: 15 minutes	MS	Jeannot et al. 2002
UPLC	LD = 2.2 ng g^{-1}	Column: C18 (50 mm x 2 mm i.d, 1.8 µm) Mobile phase: ACN/(HCOOH/$NH4HCO_2$) Flow rate: 0.4 mL min^{-1} Elution: gradient Time of analysis: 4 minutes	MS	Lara-Martín et al. 2012
GC	LD = 0.04 µg g^{-1} LQ = 0.13 µg g^{-1}	Gas: He Column: DB5MS Temperature: 80 °C – 280 °C Time of analysis: 22 minutes Derivatization: pyridine + BSTFA	MS	Gatidou et al. 2007
	LQ = 0.1 µg kg^{-1}	Gas: He Column: HP-5MS Derivatization: anthracene deuterated Temperature: 50 °C – 290 °C Time of analysis: 23 minutes	MS	Fiedler et al. 2007
	LD = 0.3 ng g^{-1} LQ = 0.3 ng g^{-1}	Gas: He Column: HP-5 Temperature: 50 °C – 300 °C Time of analysis: about. 25 minutes Derivatization: 1) $NaHCO_3$ + NaOH + stirring 2) HEX + HOAc anhydrous + stirring	MS	Oketola, Fagbemigun 2013

a- Limit of detection (LD).

b- Limit of quantification (LQ).

c- ACN = acetonitrile; BSTFA = bis (trimethylsilyl) trifluoroacetamide; HCOOH= formic acid; NH4HCO2 = ammonium formiato; HEX = hexane; HOAc = acetic acid; NaHCO3 = sodium bicarbonate.

d - For fluorescence technique λexi λemi and refers to wavelengths of excitation and emission, respectively. MS refers to mass spectrometry.

Terzopoulou et al. 2014, Kuch and Ballschmiter 2001, Montagner and Jardim 2011, Sodré et al. 2010a, Oketola and Fagbemigun 2013, Planas et al. 2002) and also in the concentration range µg L^{-1} (Zgola-Grześkowiak et al. 2009, Azevedo et al. 2001, Jeannot et al. 2002, Sodré et al. 2010b, Sun et al. 2013, Díaz et al. 2002, Hernández et al. 2007, Lou et al. 2012, Marcomini and Giger 1987, Ahel et al. 2000).

For solid samples, it can be observed using HPLC-FLU (Bernacka et al. 2009), GC-MS (Gatidou et al. 2007, Fiedler et al. 2007, Oketola and Fagbemigun 2013), HPLC-MS (de Souza Leite et al. 2010, Petrovic et al. 2003, Andreu et al. 2007) and UPLC-MS (Lara-Martin et al. 2012). The detection and quantification limit values have a concentration range from ng g^{-1} (Jeannot et al. 2002, Oketola and Fagbemigun 2013, Lara-Martin et al. 2012), µg g^{-1} (Gatidou et al. 2007), µg kg^{-1} (Petrovic et al. 2003, Fiedler et al. 2007, Andreu et al. 2007) to mg kg^{-1} (Bernacka et al. 2009).

As it may be observed in the tables above, the type of matrix and machinery, together with the type of detector, provide a detection limit of quantification and lower values than others. It can be observed in tables III and IV how these factors can greatly interfere with the detection and quantification limit values, causing works that use the same hyphenated techniques to find distinct detection and quantification limit values. Tables 3 and 4, show that in the vast majority of studies published detection limit values and quantification below the maximum level of contaminants recommended by the USEPA as shown in Table I. Thus, demonstrating that the methods already developed and validated by the authors, have great use in environmental monitoring of nonylphenol in liquid and solid matrices. Tables III and IV list the following works which were carried out in Brazil (Azevedo et al. 2001, de Souza Leite et al. 2010, Fiedler et al. 2007, Montagner and Jardim 2011, Sodré et al. 2010a, b). These studies were carried out both in liquid and solid matrices and set quantification limits for liquid samples in the range of ng L^{-1} to µg L^{-1}. As for solid samples, the limit of quantification reported by the brazilian authors were in the range of concentration mg kg^{-1}.

CONCLUSIONS

Nonylphenol has endocrine disrupting capacity and is characteristically prone to accumulating on the environment with high organic matter content. It has low solubility in water, which can cause difficulty in their monitoring in environmental samples. Although there is a significant amount of studies involving determination of nonylphenol in environmental samples, there are few studies in Brazil. The lack of national publications combined with lack of legislation setting nonylphenol limits in Brazil underscores the need to develop analytical methods with analytical reliability for determination of this analyte, and the implementation of monitoring programs to better assess the quality of the environment.

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