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REVIEW

Nonylphenol occurrence, distribution, toxicity and analytical methods in freshwater

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Abstract

Nonylphenol is a typical endocrine-disrupting chemical that has received considerable attention from government officials, scientists and the public due to its estrogenicity and ubiquitous occurrence in water environments. Here we review the current knowledge on nonylphenol occurrence, distribution, toxic effects and water quality criteria related to the protection of freshwater organisms. Nonylphenol enters the water ecosystem mainly via wastewater treatment plant effluents, agricultural runoff, groundwater discharge from air, soil, water and agricultural sources. Toxic effects of nonylphenol on aquatic organisms include acute toxic effects, growth and development effects, estrogenic effect and reproductive effects, neurotoxicity, liver toxicity and immunotoxicity.

Keywords Endocrine-disrupting chemicals · Nonylphenol · Toxic effects · Water quality criteria · Freshwater organisms

Abbreviations

PNEC	Predicted no-effect concentration
SWQC	Short-term water quality criteria
LWQC	Long-term water quality criteria
NOEC	No observable effects concentration
CCME	Canadian Council of Ministers of the Environment
USEPA	United States Environmental Protection Agency
LC_{50}	50% of the lethal concentration
EC_{50}	50% of the effective concentration
EC_{10}	10% of the effective concentration
EE_2	17 alpha-ethinyl estradiol
HC_5	Hazardous concentration for 5% of species

Introduction

In recent years, one of the issues concerning the quality of drinking water is the presence of contaminants of emerging concern, including endocrine-disrupting chemicals, pharmaceuticals and personal care products, microplastics, and other chemical products (Padhye et al. 2014; Tijani et al. 2016; Kaur and Goyal 2019; Padervand et al. 2020), some

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of which have adverse effects on the normal reproductive fitness functions of aquatic organisms and humans, by means of disrupting secretion of endogenous hormones, and thus have attracted considerable attention from environmental scientists and experts (Desbrow et al. 1998; Silva et al. 2002; Huang et al. 2012a; Wang et al. 2016, 2018). The ecotoxicological impact of endocrine-disrupting chemicals not only on vertebrates but also on invertebrates is a currently worldwide concern, particularly in terms of the impact of pollution on entire ecosystems (Hirano et al. 2009; Chang et al. 2007), including coatings and latex paint, adhesives, inks, detergents, emulsifiers, solubilizers, dispersing agents, petroleum recovery chemicals and personal care products (Ying et al. 2002; Soares et al. 2008). The most commonly used alkylphenol ethoxylates are nonylphenol ethoxylates, which account for 80% of the total use (Zgola-Grześkowiak et al. 2009). Nonylphenol ethoxylates are the incompletely biodegraded product in the environment and wastewater treatment plants, due to the stepwise loss of ethoxy groups, thereby forming nonylphenol monoethoxylate and nonylphenol diethoxylate, and completely degraded to the deethoxylated product, nonylphenol (Mann and Boddy 2000).

Nonylphenol, as an endocrine-disrupting chemical, has become a great concern in recent years and has been found to be persistent in environmental areas, bio-accumulative in biotas, and toxic to organisms (Ekelund et al. 1993; Corvini et al. 2005; Riefer et al. 2011a, b; Dsikowitzky and Schwarzbauer 2014; Zhou et al. 2018). Nonylphenol has been found worldwide in wastewater discharge, wastewater treatment plant effluents, surface water, groundwater, and in sediments at ng/mL or ng/g levels (Ying et al. 2002; Fawell et al. 2001; Nowak et al. 2008; Vieira et al. 2020). A great number of studies have revealed that the frequent occurrence of cancerous tumors, obesity and impaired reproductive function in humans may be caused by drinking nonylphenol contaminated water (Chen et al. 2013; Michałowicz 2014). Additionally, it has been confirmed that the environmental exposure level of nonylphenol is the most significant factor of affecting the structural changes, species composition and quantity of ecosystems (Arnon et al. 2008; Nie et al. 2014). Due to endocrine-disrupting chemicals' estrogenic activity, several compounds classified as alkylphenols have been included among a list of priority contaminants. Notably, nonylphenol and nonylphenol monoethoxylate are well-known micro-pollutants with potential risks to the environment, as well as the health of animals and humans. These compounds have been identified as priority hazardous substances in the Water Framework Directive and the third draft of the Working Document on Sludge by the European Union (European Companian 2008; Soares et al. 2008), including the endocrine-disrupting chemicals Group. In Japan, nonylphenol is designated as a parameter in the environmental quality standard of water pollution. Therefore, many countries have restricted the use of these substances. However, some countries persist on using nonylphenol due to their high capacity as chemical product. Previous investigations have indicated that nonylphenol produces multiple toxic effects, such as acute toxic effects, growth and development toxic effects, estrogen effect and reproductive toxic effects, through nuclear hormone receptors such as estrogen, androgen, and progesterone, both in vivo and vitro (Zha et al. 2008). Furthermore, recent studies have observed some other mechanisms such as functioning on membrane receptors, and enzymes in steroid biosynthesis pathways (Baravalle et al. 2018; Rosenfeld and Cooke 2019). More specifically, nonylphenol induces the production of the female-specific, egg-yolk precursor vitellogenin in the livers of males, and is related to testis-ova, and decreases fecundity and fertility (Zha et al. 2008), thus has aroused widespread concern among environmental scientists over the past decade (Kanaki et al. 2007; Huang et al. 2012a, b; Goeppert et al. 2014).

Water quality criteria are the threshold limits for contaminants in water environment which have harmful effects on human health, aquatic ecosystems and use functions (Feng et al. 2012a, 2013a; Yang et al. 2014a). Water quality criteria have been established for the protection of aquatic organisms based on scientific experiments and extrapolations. The function of water quality criteria is to provide guidance and a scientific basis for formulating water quality standards. In addition, water quality criteria are an essential part of ecological risk assessment; ecological restoration; environmental crisis management; environmental damage identifications and assessments; and related policies, laws, and regulations. Water quality criteria play a decisive role in environmental protection and management programs, including developed and developing countries (Wu et al. 2012; Feng et al. 2012a, b, 2019). Assessment factor and statistical extrapolation for species sensitivity distribution method are the two basic methods for derivation of water quality criteria (Jin et al. 2015; Liu et al. 2016a). The predicted no-effect concentration (PNEC) is the most important step in ecological risk assessment to determine the short-term water quality criteria (SWQC) and long-term water quality criteria (LWQC) of detecting contamination of substance to protect certain ecosystems (Jin et al. 2011, 2012; Wu et al. 2014; Jin et al. 2014; Feng et al. 2013b, 2019). To date, some organizations at the national level and other governmental agencies have derived PNEC or no observable effects concentration (NOEC) for nonylphenol. For instance, the European Union had established a toxicity threshold of 0.33 μg/L with species sensitivity distribution based on the potential toxic effect of nonylphenol on freshwater fish (ECB 2001). The Canadian Council of Ministers of the Environment (CCME) issued the water quality guidelines of nonylphenol employing the assessment factor method to derive the value of 1.00 μg/L in 2002 (CCME 2002). In addition, the United States Environmental Protection Agency (USEPA) determined that the value of water quality criteria was 6.60 μg/L for nonylphenol using species sensitivity rank in 2005 (USEPA 2005).

Many studies have summarized the toxicity effects, fate and biodegradation of nonylphenol, yet few of the existing studies have reviewed the water quality criteria of nonylphenol in freshwater and seldom focused on the water quality criteria difference considering different research methods and toxicity endpoints. Based on this, in order to protect aquatic organisms comprehensively, the occurrence, distribution, toxic effects and water quality criteria of nonylphenol in water environment are summarized. The review can improve the understanding of the mechanisms of nonylphenol toxicity and its water quality criteria research methods. Moreover, this review could provide theory and data support for environmental risk assessment and management of these contaminants of emerging concern.

Occurrence and distribution of nonylphenol in the environment

Nonylphenol enters the water ecosystem via wastewater treatment plant effluents, agricultural runoff, groundwater discharge from air, soil, water and agricultural sources. Nonylphenol can both accumulate in sediments and in organisms. Municipal wastewater treatment plant effluents are considered as a main source of nonylphenol to surface waters (Söffker and Tyler 2012; Li et al. 2020; Xin et al. 2019). The sources of nonylphenol exposure to the water ecosystem are shown in Fig. 1.

Previous studies have reported that nonylphenol has been detected in lakes, rivers, oceans, sediments, sludge, soil and even in drinking water, food and air (Cheng et al. 2017; Zhou et al. 2015), among which water ecosystem pollution is the most serious. The main forms of nonylphenol in water environmental include: dissolved in water, and adsorbed on suspended solid particles or sediments. The results show that the solubility of hydrophobic organic compounds in water is negatively correlated with adsorption, and nonylphenol with low solubility in water is easily absorbed by particles. In addition, due to the relatively weak degradation ability of microorganisms to nonylphenol under anaerobic conditions, nonylphenol is continuously accumulated in the sediment, and there is a long-term risk of re-release to the water (Means et al. 1980). The distribution of dissolved nonylphenol in the water environments of China and several other countries is shown in Table 1 and Fig. 2.

The concentration level of nonylphenol in China's surface water was rather high, i.e., the mean concentration of nonylphenol in the Liao River is the highest, at 1094.05 ng/L. Meanwhile, the nonylphenol exposure concentration in some other countries is equivalent to China, while the concentration level of nonylphenol in freshwater is higher than that in seawater, i.e., the Daliao River Estuary's freshwater (430.50 ng/L), Daliao River Estuary seawater (350 ng/L), Sishili Bay and Taozi Bay freshwater (208 ng/L), Sishili Bay and Taozi Bay seawater (39.50 ng/L). The reason may be that the concentration of nonylphenol in the seawater is relatively low, and when a great quantity of freshwater

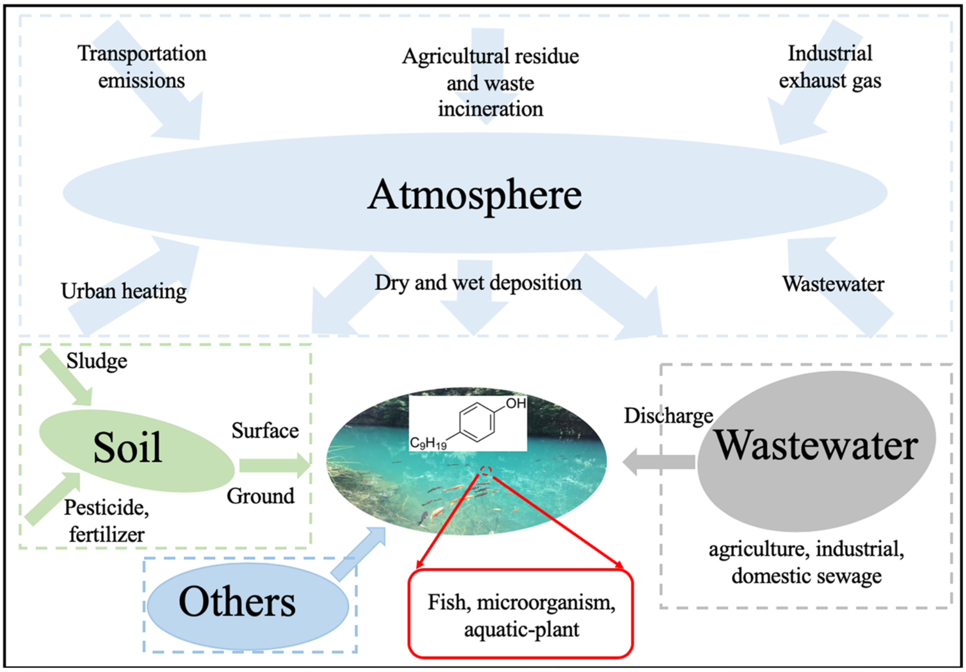

Fig. 1 Sources of nonylphenol exposure in water ecosystems. Nonylphenol enters the water ecosystem via wastewater treatment plant effluents, agricultural runoff, groundwater discharge from air, soil, water and agricultural sources

Table 1 Distribution of nonylphenol in water environments

Country	Site	Sample type	Concentration level of nonylphenol (ng/L)	Mean concentration of nonylphenol (ng/L)	References
China	Yangtze River (Nanjing Section)	River	1.4–858	429.70	Liu et al. (2017)
	Yangtze River	River	100.21–288.75	194.48	Jin et al. (2014)
	Yellow River	River	165.8–1187.6	676.70	Wang et al. (2012)
	Liao River	River	122.4–2065.7	1094.05	Wang et al. (2011)
	Liao River	Reservoir	30.05–54.27	42.16	Jin et al. (2014)
	Pearl River	River	117–685	401	Yang et al. (2014b)
	Pearl River	Reservoir	58.33–85.16	71.75	Jin et al. (2014)
	Haihe	River	106–561	333.50	
	Haihe	Reservoir	96.85–121.59	109.22	Jin et al. (2014)
	Daliao River Estuary	Seawater	25–675	350	Li et al. (2013)
	Daliao River Estuary	Freshwater	84–777	430.50	
	Sishili Bay and Taozi Bay	Seawater	3–76	39.50	Huang et al. (2012a, b)
	Sishili Bay and Taozi Bay	Freshwater	120–296	208	
	Taihu Lake	Lake	0.36–1442.7	721.53	Zhou et al. (2014)
	Chaohu Lake	Lake	38.6–86.1	62.35	Liu et al. (2016b)
Japan	Tokyo Bay	Seawater	ND–147	73.50	Ahrens et al. (2010)
Singapore	Singapore's coastal	Seawater	20–2760	1390	Bayen et al. (2013)
Italy	Tiber river	River	0.5–1589	794.75	Pojana et al. (2007)
Canada	St. Lawrence River	River	13–920	203	Bennie et al. (1997)
Nigeria	two major rivers in Lagos	River	43.9–79.4	61.65	Oketola and Fagbemigun (2013)
Spain	Ría de Arousa; Ría de Vigo; Ría de Pontevedra; Ría de A Coruña	Seawater	0.037–0.24	0.14	Salgueiro-González et al. (2015)
Greece	Les Voss	Seawater	12–210	111	Kanaki et al. (2007)
Korea	Masan Bay	Seawater	101–928	514.50	Li et al. (2008)
France	Seine River	River	57–153	105	Cladière et al. (2014)

ND not detected

flows into the sea water, it is diluted again. Additionally, previous research documented that among 164 groundwater samples tested from throughout 23 European countries, 11% contained nonylphenol, which was also the most abundant industrial chemical in groundwater samples taken from Austria (Mao et al. 2012). Nevertheless, due to the fact that nonylphenol and nonylphenol ethoxylates have not been effectively limited in China, the usage of these compounds is greater than in other countries, and the exposure concentrations of nonylphenol detected in various water bodies of China were greater than other regions (Jin et al. 2014).

Toxicity mechanisms of nonylphenol to aquatic organisms

Extensive previous studies have demonstrated estrogen effect, biological toxicity and strong bioaccumulation effect that had been resulted from exposure to nonylphenol (Diamanti-Kandarakis et al. 2009; Wu et al. 2014) (Supplementary Material S1). The toxic effect of nonylphenol is multifaceted and can produce a toxic effect through non-estrogen pathways. Animal-based experiments have confirmed that nonylphenol bears different degrees of damage to the reproductive systems of animals (Sharma et al. 2009). It is necessary to further study the long-term chronic toxicity of nonylphenol at low concentrations. The toxic effects of nonylphenol on aquatic organisms were varied as observed by different scientists, but in general, it can be divided into the following aspects:

Acute toxic effects

The larval stage of an organism is the most sensitive in organism's development, as the larval stage has weak resistance to the outside world, and may suffer from growing slowly or even dying easily when poisoned by pollutants. Therefore, the larval stage is often used for acute toxicity research (Liney et al. 2005). Nonylphenol has strong acute toxicity to phytoplankton, zooplankton, amphibians, invertebrates and fish.

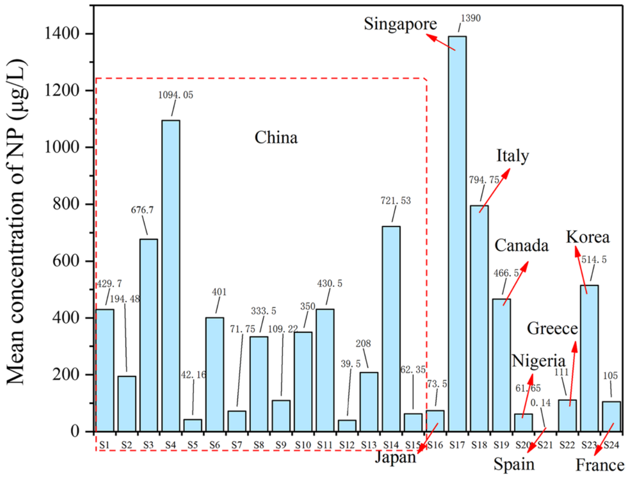

Fig. 2 Distribution of nonylphenol in water environment of China and other countries. NP: nonylphenol. (S1: Yangtze River (Nanjing Section), S2: Yangtze River, S3: Yellow River, S4: Liao River–River, S5: Liao River-Reservoir, S6: Pearl River–River, S7: Pearl River-Reservoir, S8: Haihe-River, S9: Haihe-Reservoir, S10: Daliao River Estuary-Seawater, S11: Daliao River Estuary-Freshwater, S12: Sishili Bay and Taozi Bay-Seawater, S13: Sishili Bay and Taozi Bay-Freshwater, S14: Taihu Lake, S15: Chaohu Lake, S16: Japan, S17: Singapore, S18: Italy, S19: Canada, S20: Nigeria, S21: Spain, S22: Greece, S23: Korea, S24: France)

The research results of Staples et al. (2004) have revealed that 50% of the lethal concentration (LC_{50}) or 50% of the effective concentration (EC_{50}) of nonylphenol on microalgae, invertebrates and fish were 27–2500 μg/L, 21–3000 μg/L, and 17–3000 μg/L, respectively. Teneyck and Markee (2007) introduced three phenolic compounds, nonylphenol, nonylphenol monoethoxylate and nonylphenol diethoxylate, to evaluate their toxicity on the freshwater species *Pimephales promelas* and *Ceriodaphnia dubia*, and found that the LC_{50} of 96 h for *Pimephales promelas* of nonylphenol and 48 h for *Ceriodaphnia dubia* of nonylphenol were 136 and 92.6 μg/L, respectively. Furthermore, the USEPA (2005) reported that the larvae of *Cyprinodon variegates* were more tolerant to nonylphenol, while those of *Paralichthysolivaceus* were less tolerant, with the 24 h LC_{50} being 310 and 17 μg/L, respectively.

Growth and development toxic effects

Fish embryonic gonads are bidirectional and can develop into both testes and ovaries. Nonylphenol may interfere with the endocrine system and hinder the growth and development of organisms, manifesting in ways such as shorter body size or lighter body weight. Nonylphenol can cause embryonic development of adverse toxic effects on the fish and amphibians (Chaube et al. 2013).

Willey and Krone (2001) found that nonylphenol could change the distribution of primordial germ cells along the anterior and posterior axis in 24 h embryos of *Danio rerio*, thereby changing the gonadal structure of juveniles and adults. Sone et al. (2004) reported that nonylphenol mainly affected the late development of *Xenopus laevis* embryos, thus resulting in short bodies, small heads, spinal curvature, abdominal enlargement and digestive tract coiling. In addition, it was also found that nonylphenol at a concentration of 6.8 nmol/L significantly shortened the body length of *Danio rerio* embryos, and also shortened the tail length and head width of *Danio rerio* embryos (Kinch et al. 2016).

Estrogen effect and reproductive toxic effects

Nonylphenol has a similar chemical structure to that of estrogen, which has been proven to be a type of mimic-estrogen substance that can affect the reproductive system of organisms. Nonylphenol can induce the formation of vitellogenin, testis degeneration, the formation of ovum and testis in amphoteric organs, the feminization of males, and the decline in hatching ability of fertilized eggs (Karen et al. 2003; Kobayashi et al. 2005).

Nonylphenol has an estrogen effect and reproductive toxic effects on aquatic organisms' reproductive cells, sexual differentiation, gonadal tissue structure, endocrine system genotoxicity related to reproduction, and so on (Giesy et al. 2010). Gray and Metcalfe (1997) found that *Oryzias latipes* exposed to 100 μg/L nonylphenol could increase the apoptosis of spermatocytes, Sertoli cells and stromal cells by six times as compared with that of the control group. Schwaiger et al. (2002) found that fibrosis was present in the testis, while 10 μg/L nonylphenol could induce mixed gonads in the offspring (both male and female) of the parents. After 28 days of exposure to nonylphenol (80–1280 μg/L), the relative weight of gonads in male *Xiphophorus helleri* decreased with the increase in nonylphenol dose. Besides, the testicular tissue structure changed, as manifested in such ways as Sertoli cell hypertrophy, and there was a sign of transformation to output tubular cells (Kinnberg et al. 2000). Exposure to nonylphenol during the sensitive development of fish can mimic or block the secretion of endogenous hormones and other chemicals, thereby affecting or destroying the sexual differentiation of fish. Yu et al. (2008) found that nonylphenol could induce the down-regulation of the Glutathione S-transferase-Mu gene in the gonads of *Kryptolebias marmoratus*. In addition, at the concentrations of nonylphenol exposed from 1 to 10 μg/L, luciferase detection showed that the estrogen-related receptor gene of *Chironomus riparius* was up-regulated (Park and Kwak 2010).

Other toxic effects

Nonylphenol also has additional toxic effects such as neurotoxicity, liver toxicity, immunotoxicity (Matozzo et al.

2008; Kitagawa et al. 2009). Nonylphenol exhibits many effects on the development of brain tissue, mainly by means of interfering with the ion channels of cells, affecting the energy metabolism of cells, reducing the synthesis and release of neurotransmitters, reducing the function of neurotransmitter receptor, and ultimately affecting the development and differentiation of neurons. However, at present, most studies have focused on mammals such as rats (Chitra et al. 2002; Mao et al. 2010).

In summary, although the existing research data have fully shown that nonylphenol has certain toxic effects on aquatic organisms' reproduction, the results have not been consistent with one another, and its toxic mechanism requires further exploration. Substantial evidence has confirmed that the traditional endpoints, such as survival, development and growth, for the assessment of toxicity effects cannot provide comprehensive protection for aquatic organisms, due to the fact that nonylphenol can affect the reproductive fitness of life at a concentration of 1 μg/L or even less (Ackermann et al. 2002; Caldwell et al. 2008). Furthermore, Jin et al. (2014) also indicated that the effect based on reproduction at concentrations was lower than those based on lethality, growth, biochemical and molecular biology from the species sensitivity distribution curve. Similar results were observed by Li et al. (2019), Lei et al. (2012), and Gao et al. (2015), as shown in Fig. 3.

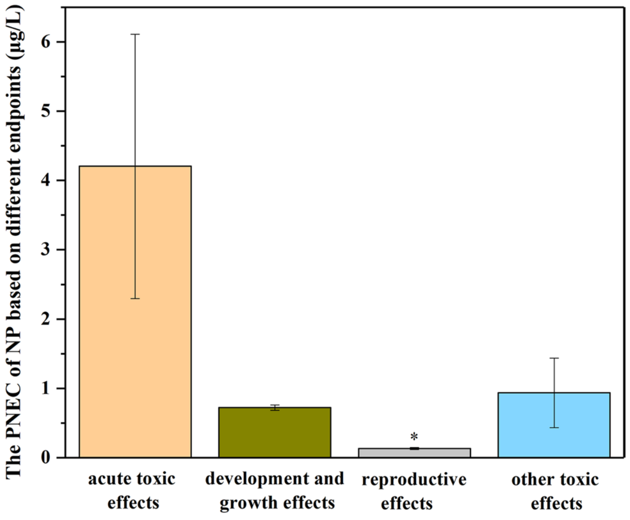

Fig. 3 The predicted no-effect concentration (PNEC) of nonylphenol based on different endpoints (μg/L). The "*" represents that the effect based on reproduction at concentrations was lower than those based on lethality, growth, biochemical and molecular biology from the species sensitivity distribution curve. Here NP: nonylphenol. Data collected from Jin et al. (2014), Li et al. (2019), Lei et al. (2012), Gao et al. (2015)

Water quality criteria research of nonylphenol for the protection of aquatic organisms

Water quality criteria for the protection of aquatic organisms can be derived through the methodologies which are primarily used, namely assessment factor, species sensitivity rank and species sensitivity distribution. The commonly selected toxicity endpoints were traditional endpoints that generally lead to lethal effect or growth inhibition effect data for some conventional pollutants in the study progress of water quality criteria. The contaminants of emerging concern and endocrine-disrupting chemicals have lethal effects, but in addition also have some adverse effects on reproduction and development, and thus the endpoints were selected to differentiate the conventional pollutants to some extent. Therefore, more sensitive genotoxicity, aromatics receptor effects and endocrine interference effects should be selected to derive the water quality criteria of nonylphenol. Many countries, agencies and researchers have obtained the derivation of water quality criteria for nonylphenol based on different research methods and endpoints. The derivations of water quality criteria for nonylphenol from different countries and researchers are listed in Table 2. The derivation of water quality criteria for nonylphenol difference can be seen when considering different methodologies and toxic effects endpoints.

Difference of water quality criteria for nonylphenol based on different toxicological endpoints

The selection of different endpoints will affect the test species determination, toxic data screening and criteria value derivation. In 2001 the European Union utilized the species sensitivity distribution method to derive the predicted no-effect concentration (PNEC) of 0.33 μg/L nonylphenol for freshwater organisms based on the endocrine disruptive toxic effect for freshwater fish (ECB 2001). This was much lower than the value derived by the USEPA for the nonylphenol freshwater criterion continuous concentration, namely 6.60 μg/L, using the species sensitivity rank method based on the traditional endpoint (LC_{50} and EC_{50}) in 2005 (USEPA 2005). Lei et al. (2012), Jin et al. (2014) and Gao et al. (2015) established the different values of water quality criteria for nonylphenol based on traditional endpoints, such as death, survival, growth, which were 2.21, 6.01 and 4.29 μg/L lower than the USEPA water quality criteria, but at the same order of magnitude, they were 6.70, 18 and 13 times higher than the European Union water quality criteria, respectively. Based on the

Table 2 Studies of water quality criteria for nonylphenol from different countries and researchers

Country (researcher)	Methodology	Endpoints	PNEC or NOEC (μg/L)	References
EU	SSD	EC_{10}	0.33	ECB (2001)
Canada	AF	LC_{50}	1.00	CCME (2002)
USA	SSD	LC_{50}	5.90	Staples et al. (2004)
	SSR	LC_{50}, EC_{50}	6.60	USEPA (2005)
	SSD	LC_{50}	0.57 (base data sets)	Hahn et al. (2014)
	SSD	LC_{50}	0.93 (full data sets)	
Japan	PMM	population growth rate	0.82–2.10	Lin et al. (2005)
China	AF	death	0.74	Lei et al. (2012)
	AF	reproductive	0.10	
	SSD	death	2.21	
	SSD	reproductive	1.34	
	SSD	survival	6.01	Jin et al. (2014)
	SSD	growth	0.75	
	SSD	biochemical and molecular biology	1.29	
	SSD	reproductive	0.12	
	SSD	traditional	4.29	Gao et al. (2015)
	SSD	reproductive	1.37	
	SSD	LC_{50}, EC_{50}	1.85	Zhang et al. (2017)

Here EU European Union, *SSD* species sensitivity distribution, *AF* assessment factor, *SSR* species sensitivity rank, *PMM* population matrix model, *PNEC* predicted no-effect concentration

reproductive endpoint, they were 1.34, 0.12 and 1.37 μg/L (Lei et al. 2012; Jin et al. 2014; Gao et al. 2015), respectively, which were much lower than the USEPA water quality criteria of 4.90, 54.90 and 4.80 times, at the same order of magnitude with the value of European Union. However, some differences did exist, the reason for which may be the difference sensitive species selection between them, and the fact that the native species varied among different geographical distributions (Jin et al. 2015). Similar results were also reported by Caldwell et al. (2008) that the PNEC derived for a synthetic estrogen 17 alpha-ethinyl estradiol (EE_2) based on a reproductive endpoint was 100 times lower than that based on a traditional endpoint. Therefore, the nontraditional endpoint selection in the derivation of the water quality criteria is equal to significance for the protection of aquatic organisms.

Difference of water quality criteria for nonylphenol based on different methodologies

Different research methodologies selected will affect the derivation of water quality criteria. The assessment factor method used by Canada is based on the most sensitive species, and thus it shows a high degree of uncertainty, despite the fact that it is feasible when the toxicity data are not available. In brief, the assessment factor method is more protective, conservative and sometimes arbitrary (Chapman et al. 1998). The species sensitivity rank method adopted by USEPA may exhibit some uncertainty as the species sensitivity rank method is considered on four toxicity data, and the cumulative probabilities are adjacent to 0.05. The species sensitivity distribution method, which is employed by most researchers and increased sharply in the derivation of water quality criteria, offers more reliability, reasonability, certainty and adaptability, as the species sensitivity distribution method is based on an established distribution of a full set of toxicity data (Gao et al. 2015; Lei et al. 2012). However, some limitations also existed when adopting the species sensitivity distribution method to derive the water quality criteria, since the value derived from the species sensitivity distribution method protects 5% of the species (hazardous concentration for 5% of species, HC_5), and if all of the organisms in a certain water body require protection, then it is not suitable. Furthermore, when and how to use the SWQC and LWQC derived from the species sensitivity distribution method must be determined more clearly. The endocrine and reproductive system differs drastically among different organisms, and the functional mechanism is varied among different individuals, and thus the water quality criteria value derived based on reproductive endpoints also differs among researchers.

Perspectives

The toxic effects mechanisms involved in nonylphenol exposure have not been reported comprehensively and accurately, and the currently studies are no available relevant research or standard to quantitatively assess the toxicity and environmental risk of nonylphenol. Besides, nonylphenol is different from conventional pollutants, such as heavy metals and nutrients. Nonylphenol has multiple toxic effect endpoints, including acute death, growth and development toxicity, estrogen effect, endocrine interference toxicity and other toxicity. The traditional endpoints such as survival, development and growth, for the assessment of toxicity effects cannot provide comprehensive protection for aquatic organisms, due to the fact that nonylphenol can affect the reproductive fitness of life at a concentration of 1 μg/L or even less. And previous researches have indicated that the effect based on reproduction at concentrations was lower than those based on lethality, growth, and development. When formulating the water quality criteria of traditional pollutants, only SWQC and LWQC should be considered, while the establishment of water quality criteria for nonylphenol needs to consider more about how to protect the function of fish reproduction effectively (Vandenberg et al. 2012). It may be a great challenge to derivation water quality criteria of nonylphenol for protecting freshwater organisms.

Since endocrine-disrupting chemicals such as nonylphenol are different from conventional pollutants, nonylphenol should be treated differently when formulating water quality criteria, to find a more suitable toxic effect dose relationship and toxic effect endpoint, and to select more suitable theoretical methodology of the water quality criteria for the formulation of endocrine-disrupting chemicals such as nonylphenol. The basic modes of action of endocrine-disrupting chemicals are triaxial, gonad-reproductive toxicity, thyroid, adrenal, and others interfere with exogenous metabolism, glucose metabolism, retinoic acid and have more modes of action. A general summary of nonylphenol and endocrine-disrupting chemicals may not be appropriate. Since nonylphenol is most related to reproductive toxicity, the water quality criteria for nonylphenol can be considered from the perspective of the gonadal axis.

In the process of deriving the water quality criteria of nonylphenol, the following suggestions should be considered: (1) Since plants and lower invertebrates have no endocrine system, in order to reduce unnecessary waste of experiments, fish reproductive toxicity test can be used, with other species as auxiliary; (2) since nonylphenol is a kind of substance with reproductive toxicity, it is prior to formulate the water quality criteria based on reproductive toxicity of nonylphenol; (3) considering the low-dose and nonlinear effects response of nonylphenol, in deriving the reproductive toxicity criteria of nonylphenol, there is no necessary to consider the SWQC, only use the LWQC; (4) the possible endpoints of hypothalamus–pituitary–gonadal axis in vertebrates including: biochemical indexes, such as vitellogenin, estradiol and testosterone, histopathological indexes, such as the proportion of spermatogonia, the proportion of androgyny, the morphological indexes, such as the secondary sexual characteristics, and the behavioral indexes, and these toxicity endpoints can be used to derive the aquatic ecological criteria for nonylphenol.

Conclusion

In order to protect the freshwater aquatic organisms better and manage nonylphenol effectively, the following advice is given for future consideration: (1) More sensitive and explicitly toxic endpoints based on reproductive toxicity must be considered, i.e., spawning rate, fertilization rate, hatchability and multi-generation effect; (2) the toxicity effect mechanism of nonylphenol on aquatic organisms' hypothalamus-pituitary–gonadal axes should be given more attention; and (3) native sensitive species and international common species should be selected as much as possible. Additionally, a set of systematic theories and methodologies, considering a set of ecological factors as possible, is required for nonylphenol water quality criteria and standards. The theory and methodology of nonylphenol should be continuously explored, and the key scientific problems of the existing water quality criteria should continue to be systematically studied.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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