Nonylphenol (NP) is a term used to refer to a group of isomeric compounds each consisting of a nine-carbon alkyl chain attached to a phenol ring, with the chemical formula $C_{15}H_{24}O$. The various isomers can differ both in the degree of alkyl chain branching and in the position on the phenol ring at which the alkyl chain is attached. Most NP produced commercially is in the form of 4-nonylphenol (i.e., with the alkyl chain attached at the *para*-position) with varied alkyl chain branching. The CAS registry number for a mixture of various branched isomers of NP is 84852-15-3. NP is a viscous liquid with a molecular weight of 220.3 g·mol^{-1}, a water solubility of 5.43 mg·L^{-1} at 20.5°C, a vapour pressure of 4.55 mPa at 25°C, and a Henry's law constant of 11.02 Pa·m^3·mol^{-1} (Reed 1978; Romano 1991; Ahel and Giger 1993; European Commission 1999). Synonyms for NP include nonyl phenol and isononylphenol. Major derivatives of NP are nonylphenol ethoxylates (NPEs) and nonylphenoxy acetic acids (also called nonylphenol ethoxycarboxylates [NPECs]).

NPEs consist of a phenol group attached to both a nine-carbon alkyl chain and an ethoxylate chain. NPEs have the general formula C_9H_{19}-$C_6H_4O(CH_2CH_2O)_nH$, where n may range from 1 to 100, but with most commercially produced NPEs containing between 6 and 12 ethoxylate groups. NPEs have an amphipathic nature, that is, the alkylphenyl moiety is hydrophobic and the ethoxylate chain is hydrophilic. Most commercial and industrial applications of NPEs utilize this characteristic surfactancy. Trade names for some commercial preparations of NPEs include Igepal, Imbentin, Lissapol, Marlophen, Surfonic, Tergitol, Terric, and Triton (Lee 1999).

NPECs have a chemical structure similar to NPEs, but with a carboxylate group (-COOH) on the end of the ethoxylate chain. The chemical formula for NPECs is C_9H_{19}-$C_6H_4O(CH_2CH_2O)_nCH_2COOH$, where n again refers to the number of ethoxylate groups. NPECs are formed during the aerobic biodegradation of NPEs (Ahel et al. 1994b).

NP, NPEs, and NPECs are synthetic compounds that do not occur naturally. Therefore, environmental concentrations can be solely attributed to human activities. The majority of NP in production is used to produce NPEs; however, it is also used as a formulant in pesticides, as a lubricating oil additive, and as a catalyst in the curing of epoxy resins (CIS 1990; Lorenc et al. 1992). In the form of tris(4-nonylphenyl) phosphite, it may be used as an antioxidant in the stabilization of rubber, vinyl polymers, polyolefins, and styrenics (Lorenc et al. 1992).

NPEs are present in many consumer products, including laundry detergents, shampoos, cosmetics, household cleaners, latex paints, and spermicides (Metcalfe et al. 1996). They have a broad range of industrial uses as surfactants, detergents, wetting agents, dispersants, defoamers, de-inkers, and antistatic agents. Major Canadian industrial users are textile mills and the pulp and paper industry; other applications include plastics and elastomer manufacturing, oil extraction and production, metal processing, leather processing, industrial and institutional cleaners, paint and protective coatings, and pesticides (Metcalfe et al. 1996).

NP and its ethoxylates may potentially enter the environment during production, use, storage, transportation, or through accidental spillage. They are primarily released to the environment through the discharge of municipal and industrial wastewaters into surface waters. Pathways to the terrestrial environment include the spraying of pesticides that contain NP or NPEs as formulants, landfilling of sludges, or the application of sewage sludge or pulp and paper mill sludge to agricultural soils. Runoff from these terrestrial sources is another pathway to aquatic systems. Although the NPEs with longer ethoxylate chains are nonpersistent in the environment and undergo a rapid primary biodegradation, their degradation products are considerably more persistent.

Table 1. Water quality guidelines for nonylphenol and its ethoxylates for the protection of aquatic life (Environment Canada 2002).

Aquatic life	Guideline value (µg·L^{-1})
Freshwater	1.0[*]
Marine	0.7[*†]

[*] Expressed on a TEQ basis using NP TEFs.
[†] Interim guideline.

Biodegradation is the most important process affecting the fate of NP and NPEs (Ahel et al. 1994b). NPEs undergo a two-stage degradation process. First, step-wise removal of ethoxy groups results in the formation of intermediate biodegradation products (short-chain NPEs and NPECs, and NP). The second stage involves the ultimate conversion of the molecules to CO_2, H_2O, and inorganic salts (Swisher 1987). The intermediate degradation products are more biorefractory, that is, they are less readily biodegraded than the parent NPEs, and therefore ultimate biodegradation occurs more slowly (Ahel et al. 1994a). Rates of biodegradation increase with increasing temperature (Ahel et al. 1994b; Manzano et al. 1999).

NP and NPEs are also removed from water by photolysis (Ahel et al. 1994c; Brand et al. 1998) and, to a lesser extent, volatilization (Dachs et al. 1999). Short-chain NPEs and NP are more hydrophobic than NPECs and longer-chain NPEs and therefore have a higher tendency to adsorb to sediments. The total organic carbon (TOC) content of the sediments has been shown to be an important determining factor in the adsorption of alkylphenols (Johnson et al. 1998) and short-chain NPEs (Urano et al. 1984; John et al. 2000). When released into soil, NP and NPEs tend to adsorb to the soil particles (Beigel et al. 1998), however, leaching and infiltration into groundwater have also been observed (Zoller et al. 1990; Ahel 1991; Rudel et al. 1998).

NP and NPEs with 1–3 ethoxylate groups show mild bioaccumulation in aquatic organisms, with the majority of calculated BAFs and BCFs ranging between 30 and 1000 (McLeese et al. 1981; Granmo et al. 1991; Ward and Boeri 1991c; Ahel et al. 1993; Brooke 1993b; Lewis and Lech 1996). In general, BAFs decrease with increasing ethoxylation. Under Canada's Persistence and Bioaccumulation Regulations (Government of Canada 2000), a substance is considered bioaccumulative if its BAF (or BCF) is equal to or greater than 5000. By this definition, NP and NPEs would not be considered bioaccumulative.

In fish, uptake of NP and NPEs occurs primarily through the gills, with transport to the various tissues/organs via the blood (Granmo and Kollberg 1976; Arukwe et al. 2000). Uptake is fairly rapid, with tissue concentrations reaching a steady state during the first 3–10 d of exposure (Granmo and Kollberg 1976; Ward and Boeri 1991c).

When fish exposed to NP and NPEs are transferred to clean water, elimination of the contaminants will occur, though at a slower rate than uptake (Coldham et al. 1998). The whole-body excretion half-life for juvenile Atlantic salmon exposed to NP was estimated at 4 d (McLeese et al. 1981). Metabolic degradation of NP in fish is thought to occur through oxidation and glucuronic acid formation in bile (Lewis and Lech 1996; Arukwe et al. 2000). The process of ω-oxidation followed by ß-oxidation has been proposed as the most likely biotransformation pathway (Thibaut et al. 1999). Some excretion is thought to occur in urine, via the kidney (Granmo and Kollberg 1976; Thibaut et al. 1999), but a biliary/fecal route has been suggested as the main pathway for excretion (Coldham et al. 1998).

It has been suggested that the mode of toxicity for NP and at least the lower chain length NPEs and NPECs is narcosis (Schüürmann 1991; Fay et al. 2000; Servos et al. 2000). Toxicity from longer chain length NPEs may be due to physical surfactancy, particularly at high concentrations above the critical micelle concentration. Nonylphenolic substances may also act as estrogen agonists to disrupt endocrine functions. Biomarkers of estrogenic activity, such as vitellogenin and zona radiata proteins, have been observed in fish exposed to NP (Arukwe et al. 1998; Korsgaard and Pedersen 1998). Other evidence of endocrine disruption, such as reduced gonadosomatic indices, histological effects on testicular structure, effects on smoltification, and occurrence of intersex, has also been observed (Madsen et al. 1997; Christiansen et al. 1998; Metcalfe et al. 2001).

NP and NPEs have been measured in Canadian fresh surface waters, freshwater and marine sediments, raw sewage, municipal and industrial wastewater effluents and sludge, and sludge-amended soils (see Environment Canada 2002). No data have been reported for concentrations in Canadian marine/estuarine waters or groundwater. Freshwater data are available from five provinces (British Columbia, Ontario, Quebec, Nova Scotia, and Prince Edward Island). Concentrations of NP found in Canadian fresh waters range from <0.01 to 1.7 $\mu g \cdot L^{-1}$ (Bennie et al. 1997; Rutherford 2001). Individual NPE ethoxamers may occur at concentrations up to 17 $\mu g \cdot L^{-1}$ (Rutherford 2001). NPECs have been measured at concentrations as high as 23 $\mu g \cdot L^{-1}$ (D. Berryman 2000, Direction des écosystèmes aquatiques, Ministère de l'Environnement du Québec, Quebec, pers. com.).

Water Quality Guideline Derivation

The Canadian water quality guidelines for NP and its ethoxylates for the protection of aquatic life were developed based on the CCME protocol (CCME 1991). For more information, see the supporting document (Environment Canada 2002).

Freshwater Life

Numerous acute and chronic toxicity data for NP are available for freshwater fish. Brooke (1993a) reported a 91-d LOEC of 10.3 $\mu g \cdot L^{-1}$ for growth reduction in rainbow trout, *Oncorhynchus mykiss*. A comparable value of 14 $\mu g \cdot L^{-1}$ was reported as the 33-d LOEC for survival with fathead minnows, *Pimephales promelas* (Ward and Boeri 1991b). Other reported toxic concentrations are generally an order of magnitude higher. For example, 28-d and 96-h LOECs for survival have been reported for *Lepomis macrochirus* at 126 and 211 $\mu g \cdot L^{-1}$, respectively, and for *P. promelas* at 193 and 230 $\mu g \cdot L^{-1}$, respectively (Brooke 1993b). Median lethal concentrations (96-h LC_{50}s) for *P. promelas* are cited at 128 $\mu g \cdot L^{-1}$ (Brooke 1993a) and 135 $\mu g \cdot L^{-1}$ (Holcombe et al. 1984), and values of 209 and 221 $\mu g \cdot L^{-1}$ are reported for *L. macrochirus* and *O. mykiss*, respectively (Brooke 1993a).

Considerable toxicity data also exist for freshwater invertebrates. A 96-h LC_{50} of 20.7 $\mu g \cdot L^{-1}$ was estimated for *Hyalella azteca* (Brooke 1993a). England and Bussard (1995) also reported a 96-h LC_{50} of 170 $\mu g \cdot L^{-1}$ and a 96-h EC_{50} for immobilization of 150 $\mu g \cdot L^{-1}$ for *H. azteca*. For *Daphnia magna*, concentrations of 84.8, 100, and 215 $\mu g \cdot L^{-1}$ have been reported for a 48-h immobilization EC_{50} (Brooke 1993a), a 21-d LC_{50} (Brooke 1993a), and a 21-d LOEC for reproduction (Comber et al. 1993), respectively. Numerous data points exist for the midge *Chironomus tentans*, including 14-d EC_{50}s of 95 $\mu g \cdot L^{-1}$ for both total adverse effects and larval growth (England and Bussard 1993), a 14-d LC_{50} of 119 $\mu g \cdot L^{-1}$ (England and Bussard 1993), a 20-d LOEC for survival of 91 $\mu g \cdot L^{-1}$ (Kahl et al. 1997), and a 14-d LOEC for larval growth of 150 $\mu g \cdot L^{-1}$ (England and Bussard 1993). Limited data are available for non-arthropod invertebrates. Brooke (1993a) reported 96-h LC_{50}s of 342 and 774 $\mu g \cdot L^{-1}$ for the annelid *Lumbriculus variegatus* and the snail *Physella virgata*, respectively.

Fewer data are available for the toxicity of NP to algae and aquatic macrophytes. The macrophyte *Lemna minor* exhibits reduced frond production after 96 h of exposure
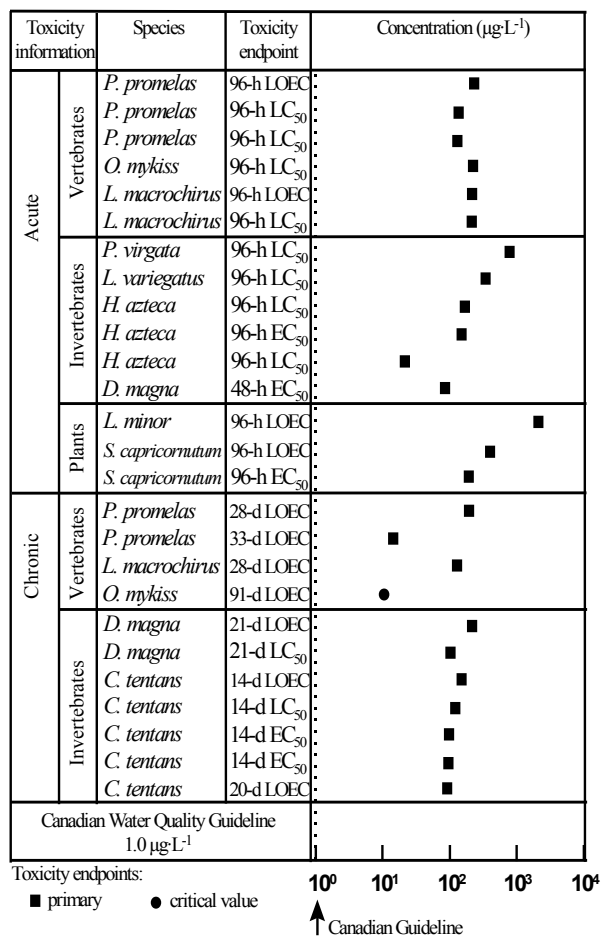
Toxicity information		Species	Toxicity endpoint	Concentration ($\mu g \cdot L^{-1}$)
Acute	Vertebrates	*P. promelas*	96-h LOEC	
		P. promelas	96-h LC_{50}	
		P. promelas	96-h LC_{50}	
		O. mykiss	96-h LC_{50}	
		L. macrochirus	96-h LOEC	
		L. macrochirus	96-h LC_{50}	
	Invertebrates	*P. virgata*	96-h LC_{50}	
		L. variegatus	96-h LC_{50}	
		H. azteca	96-h LC_{50}	
		H. azteca	96-h EC_{50}	
		H. azteca	96-h LC_{50}	
		D. magna	48-h EC_{50}	
	Plants	*L. minor*	96-h LOEC	
		S. capricornutum	96-h LOEC	
		S. capricornutum	96-h EC_{50}	
Chronic	Vertebrates	*P. promelas*	28-d LOEC	
		P. promelas	33-d LOEC	
		L. macrochirus	28-d LOEC	
		O. mykiss	91-d LOEC	
	Invertebrates	*D. magna*	21-d LOEC	
		D. magna	21-d LC_{50}	
		C. tentans	14-d LOEC	
		C. tentans	14-d LC_{50}	
		C. tentans	14-d EC_{50}	
		C. tentans	14-d EC_{50}	
		C. tentans	20-d LOEC	
Canadian Water Quality Guideline 1.0 $\mu g \cdot L^{-1}$				

Toxicity endpoints:
■ primary   ● critical value
10^0 10^1 10^2 10^3 10^4
↑ Canadian Guideline

Figure 1. Select freshwater toxicity data for nonylphenol.

to NP at a concentration of 2080 $\mu g \cdot L^{-1}$ (Brooke 1993a). The green algae *Selenastrum capricornutum* experiences growth reduction after 96 h of exposure to NP concentrations as low as 190.0 $\mu g \cdot L^{-1}$, and the corresponding median effective concentration (EC_{50}) is 410 $\mu g \cdot L^{-1}$ (Ward and Boeri 1990a).

The water quality guideline for the protection of freshwater life is 1.0 $\mu g \cdot L^{-1}$. It was derived by multiplying the 91-d LOEC of 10.3 $\mu g \cdot L^{-1}$ (Brooke 1993a) for the most sensitive organism, the rainbow trout, by a safety factor of 0.1 (CCME 1991).

Marine Life

A few chronic toxicity studies with NP are available for marine fish, however these all report unconventional endpoints for which the ecological relevance is unclear. For example, a 21-d LOEC of 24.5 $\mu g \cdot L^{-1}$ was reported

for an increased hepatosomatic index in flounder *(Platichthys flesus)* (Allen et al. 1999). A 21-d LOEC of 100 µg·L⁻¹ was reported for increased plasma concentrations of vitellogenin in the eelpout *Zoarces viviparus* (Korsgaard and Pedersen 1998). A 10-d LOEC of 2203 µg·L⁻¹ was reported for the induction of sublethal abnormalities in embryos of the killifish *Fundulus heteroclitus* (Kelly and Di Giulio 2000). Numerous acute toxicity tests with marine fish have been conducted. The 96-h LC_{50} for sheepshead minnows, *Cyprinodon variegatus*, has been estimated at 310.0 µg·L⁻¹ (Ward and Boeri 1990c) and 142.0 µg·L⁻¹ (Lussier et al. 2000). For inland silversides *(Menidia beryllina)*, a 96-h LC_{50} of 70.0 µg·L⁻¹ has been cited (Lussier et al. 2000). A 96-h LC_{50} of 17 µg·L⁻¹ has been measured in winter flounder *(Pleuronectes americanus)* (Lussier et al. 2000). In *F. heteroclitus*, 96-h LC_{50}s have been reported for embryos and for 2-week larvae at 5441 and 209 µg·L⁻¹, respectively (Kelly and Di Giulio 2000).

The lowest reported endpoint for a marine invertebrate comes from a secondary study by Billinghurst et al. (1998) in which the 48-h LOEC for reduced settlement in larvae of the barnacle *Balanus amphitrite* was 0.06 µg·L⁻¹. Several studies indicate that the mysid *Americamysis bahia* (recently renamed from *Mysidopsis bahia*) is also a sensitive marine invertebrate. Ward and Boeri (1991a) reported reductions in the growth of *A. bahia* after a 28-d exposure to NP concentrations as low as 6.7 µg·L⁻¹; reduced reproduction and survival were both observed at concentrations as low as 9.1 µg·L⁻¹. Ward and Boeri (1990b) also reported a 96-h LC_{50} for *A. bahia* of 43.0 µg·L⁻¹, and Lussier et al. (2000) reported a 96-h LC_{50} of 60.6 µg·L⁻¹ for this same species. Slightly higher 96-h LC_{50}s of 59.4, 61.6, 71.0, and >195 µg·L⁻¹ are reported for the grass shrimp *Paleomonetes vulgaris*, the amphipod *Leptocheirus plumulosus*, the lobster *Homarus americanus*, and the mudcrab *Dyspanopeus sayii*, respectively (Lussier et al. 2000). Lussier et al. (2000) also observed a 48-h EC_{50} of 37.9 µg·L⁻¹ for inhibition of fertilization in the coot clam, *Mulinia lateralis*. From a 53-d study on the copepod *Tisbe battagliai*, a LOEC of 41.0 µg·L⁻¹ has been reported for egg production, offspring survival, and intrinsic rate of increase (Bechmann 1999). For this same species, the 96-h LC_{50}s for nauplii and for adults are 31-62 µg·L⁻¹ and 500–1000 µg·L⁻¹, respectively (Bechmann 1999). For larvae of the Pacific oyster, *Crassostrea gigas*, exposure to 100 µg·L⁻¹ resulted in both a 48-h LOEC for various deformities and a 72-h LOEC for delayed development (Nice et al. 2000).

Ward and Boeri (1990d) reported a 96-h EC_{50} of 27.0 µg·L⁻¹ for growth inhibition in the marine alga *Skeletonema costatum*.

The most sensitive, nonlethal effect concentration is 0.06 µg·L⁻¹, based on reduced larval settlement in the barnacle *(Balanus amphitrite)* (Billinghurst et al. 1998). This study was not used for deriving the guideline, however, because it involved a short exposure time, used an unconventional endpoint, and was more than two orders of magnitude lower than any other endpoints reported in the literature. Confidence in this study was not high enough to base the guideline value on this LOEC. The interim water quality guideline for the protection of marine life is 0.7 µg·L⁻¹. It was derived by multiplying the 28-d LOEC of 6.7 µg·L⁻¹ for reduced growth in the mysid *(A. bahia)* (Ward and Boeri 1991a) by a safety factor of 0.1 (CCME 1991).
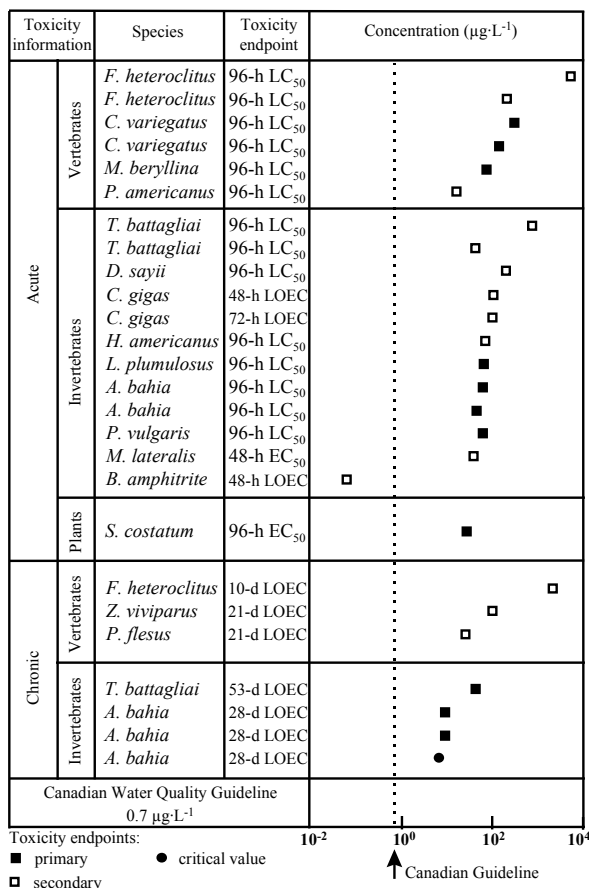

Toxicity information		Species	Toxicity endpoint	Concentration (µg·L⁻¹)
Acute	Vertebrates	*F. heteroclitus*	96-h LC_{50}	
		F. heteroclitus	96-h LC_{50}	
		C. variegatus	96-h LC_{50}	
		C. variegatus	96-h LC_{50}	
		M. beryllina	96-h LC_{50}	
		P. americanus	96-h LC_{50}	
	Invertebrates	*T. battagliai*	96-h LC_{50}	
		T. battagliai	96-h LC_{50}	
		D. sayii	96-h LC_{50}	
		C. gigas	48-h LOEC	
		C. gigas	72-h LOEC	
		H. americanus	96-h LC_{50}	
		L. plumulosus	96-h LC_{50}	
		A. bahia	96-h LC_{50}	
		A. bahia	96-h LC_{50}	
		P. vulgaris	96-h LC_{50}	
		M. lateralis	48-h EC_{50}	
		B. amphitrite	48-h LOEC	
	Plants	*S. costatum*	96-h EC_{50}	
Chronic	Vertebrates	*F. heteroclitus*	10-d LOEC	
		Z. viviparus	21-d LOEC	
		P. flesus	21-d LOEC	
	Invertebrates	*T. battagliai*	53-d LOEC	
		A. bahia	28-d LOEC	
		A. bahia	28-d LOEC	
		A. bahia	28-d LOEC	
Canadian Water Quality Guideline 0.7 µg·L⁻¹				

Toxicity endpoints:
■ primary ● critical value
□ secondary
↑ Canadian Guideline

Figure 2. Select marine toxicity data for nonylphenol.

Toxic Equivalency Factors

The guidelines in this fact sheet were developed based on toxicity data for NP; however, they should also be applied to NPEs and NPECs through the use of toxic equivalents.

NP, NPEs, and NPECs typically occur together in the aquatic environment as mixtures. Therefore, for the purpose of assessing acceptable levels of these substances in water, sediment, or soil, it is more useful to develop guidelines that consider their combined effects. This can be accomplished through the use of a toxic equivalency (TEQ) approach.

The TEQ approach is used to characterize the toxicity of a mixture of related compounds by expressing the toxicities of each individual compound in common terms and summing them. Application of the TEQ approach requires that all components of a mixture have a common mode of toxicity such that their effects are additive. Nonylphenolic substances meet this requirement. At typical environmental concentrations and for conventional toxicity endpoints, the mode of toxicity for NP and for at least the lower ethoxylate chain length NPEs and NPECs is narcosis (Schüürmann 1991; Fay et al. 2000; Servos et al. 2000). If these substances are all acting through narcosis, then additivity of their effects (as opposed to synergism or antagonism) is most likely (Servos et al. 2000).

Relative toxicity values, or NP toxic equivalency factors (TEFs), have been estimated for various nonylphenolic compounds (Table 2). These TEFs were derived based on a broad dataset that included both acute and chronic studies on a range of aquatic vertebrate and invertebrate species. Reported toxic concentrations for the various nonylphenolic compounds were matched with similar endpoints for NP from the same species and, where possible, from the same laboratory; then a relative toxicity ratio was calculated. From the resulting list of relative toxicity values for each group of compounds, a mean relative toxicity value (TEF) was calculated, with more weight given to those studies deemed to be of higher quality.

The total concentration of NP and NP equivalents in a sample can be calculated using the following equation:

$$\text{Total TEQ} = \sum_{i=1}^{n} (C_i \times TEF_i)$$

Table 2. Toxic equivalency factors (TEFs) for NP, NPEs, NPECs, OP, OPEs, and OPECs (Servos et al. 2000; Environment Canada 2002).

Chemical	TEFs (relative to NP)
NP	1
NPnEO ($1 \leq n \leq 8$)	0.5
NPnEO ($n \geq 9$)	0.005
NP1EC	0.005
NP2EC	0.005
OP	1
OPnEO ($1 \leq n \leq 8$)	0.5
OPnEO ($n \geq 9$)	0.005
OP1EC	0.005
OP2EC	0.005

where
TEQ = concentration of the mixture of nonylphenolic compounds expressed as toxic equivalent of NP
n = number of nonylphenolic compounds
i = 1, 2, 3, …, n
C_i = concentration of compound i
TEF_i = toxic equivalency factor for the compound i (unitless).

In the assessment of a mixture of nonylphenolic compounds, the environmental concentrations of NPEs and NPECs should be expressed in terms of NP equivalents, and the sum of these concentrations should then be compared against the guidelines developed in this document. If octylphenol (OP), octylphenol ethoxylates (OPEs), or octylphenol ethoxycarboxylates (OPECs) are present in environmental samples, it is recommended that these substances also be considered in the calculation of total NP equivalents. OP and OPEs are very similar in structure and behaviour to NP and NPEs and likely act through a similar mode of action.

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