Ministerie van Verkeer en Waterstaat

Directoraat-Generaal Rijkswaterstaat

Rijksinstituut voor Kust en Zee/RIKZ

Chemical study on alkylphenols

Report: RIKZ/2001.029
1 juli 2001

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Preface

In the framework of the project "Investigating for chemicals in the future", the North Sea Directorate has put the department of Rijkswaterstaat Institute for Coastal and Marine Management (RIKZ) in charge, to start a study on unknown chemicals. The object of this project is to identify the most important contaminants, which present a threat to the North Sea and the identification of gaps in policy, management and knowledge. In the project monitoring data are evaluated and a number of "new" substances are proposed as a potential threat for the North Sea.

On 30th of June 2000 BKH Consulting Engineers has received the order to make a study on a selection of the Alkylphenols. This study will be directed on the whole track of octyl, nonyl and decylphenols in the environment. From production and emission to immission, waste and effects.
The project is co-ordinated by Mrs drs A.M.C.M. Pijnenburg of RIKZ. The project-leader of BKH is Mrs drs C.P. Groshart. The authors of the report are: Mr drs P.C. Okkerman, W.B.A. Wassenberg and Mrs drs C.P. Groshart.

Summary

General
Alkylphenols are mainly used as raw material in the production of a variety of industrial products such as surfactants, detergents, phenolic resins, polymer additives and lubricants. Private and commercial use of alkylphenols does not occur. Current world demand is estimated at approximately 400,000 tonnes/y, with nonylphenol as the most widely used compound (market share: 80- 90%). Octyl-, dibutyl-, decyl- and dodecylphenols are produced in total quantities of 60,000 tonnes/year.

Nonylphenol production in Western Europe amounts to 75,000- 80,000 tonnes/year. Octylphenol production is estimated at approx. 7,000 tonnes/year. In the Netherlands, there are no production sites for alkylphenols. Nonylphenol demand in The Netherlands is estimated at 1300- 1400 tonnes/year. For the next few years, world demand will grow 1-2 % per year.

Alkylphenol ethoxylates are primarily used as surfactants, detergents and emulsifiers in a wide range of applications in the industry (auxiliaries) and as commercial product (cleaning agents, wetting agents, dispersants, lubricants, etc) in many end use sectors. Current world demand is estimated at 600,000 tonnes/y, with nonylphenol (85%) and octylphenol ethoxylates (15%) as most widely used compounds. World demand growth is estimated at 2-3 %/year. In the EU, due to voluntary and regulatory initiatives, the use of these substances is to be limited in order to minimise alkylphenol emissions to the environment.

In Western Europe, nonylphenol ethoxylates production is about 120,000 tonnes/year. Demand in the EU varies from 65,000 to 80,000 tonnes, while export amounts to 35,000- 45,000 tonnes/year. In the Netherlands, there is no production of alkylphenol ethoxylates. Annual nonylphenol ethoxylates demand in 1997 was estimated at approx. 1,500 tonnes, coming down from 4,900 tonnes/year in 1986.

Sources and emissions
Nonylphenol emissions due to use in the chemical and polymer industry in the Netherlands (<15 kg/ year) are negligible compared to emissions from nonylphenol ethoxylates degradation in municipal wastewater (14.1 tonnes/year; see table 1). Nonylphenol ethoxylates emissions to surfacewater in the Netherlands are estimated at 45 tonnes (1997). From table 1 can be seen that the first 6 use sectors are responsible for the total nonylphenol and nonylphenol ethoxylates emissions to surfacewater. On European scale, emissions of nonylphenol and nonylphenol ethoxylates amount to 1065 and 3400 tonnes/year.

Environmental characteristics and toxicity in aquatic systems
Environmental characteristics
Alkylphenols are characterised by low solubility in water (< 15 mg/l) and low vapour pressures (< 10 Pa). Log K_{ow} values vary from 4.1 for octylphenol to 4.5 for nonylphenol. Octyl- and nonylphenol will be non-volatile and will adsorb strongly onto solids. Alkylphenol ethoxylates with many ethoxylate groups (n>10), are very soluble in water, making these compounds potentially mobile. However, once released in water, they are easily hydrolysed to compounds with few ethoxylate groups (n<3), which behave more or less the same as the core alkylphenol compounds (strong adsorption to solids).

Environmental data for nonylphenol indicate that this compound is strongly concentrated in freshwater algae and fish. (BCF = 6000- 7000 and 200- 600 l/kg respectively). Nonylphenol was not found to bio-accumulate in the food chain. BCF values for short chained nonylphenol ethoxylates (n<3) show the same tendency to accumulate in aquatic biota, but BCF values are somewhat lower (1000- 5000 l/kg for algae and 80- 150 l/kg for fish). Half-life for excretion from fish is short (< 1 day). BCF data in marine biota were found to be in the same range as for freshwater organisms.

Table 1:
Nonylphenol (NP) and nonylphenol ethoxylates (NPEO) emissions (1997)

	The Netherlands			European Union		
	NPEO Use	Emissions to water		NPEO use	Emissions to water	
		NPEO	NP		NPEO	NP
Agrochemicals	95	9.5	3.0	5000	500	155
Various niche applications	235	15.3	4.8	12300	800	250
Industrial cleaning	180	11.6	3.6	23000	1500	470
Leather processing	60	3.8	1.2	3100	200	65
Metal processing	50	3.4	1.1	2000	45	14
Pulp and paper industry	15	1.0	0.3	800	55	18
Chemical industry	470	0.2	0.07	7000	3	0.9
Paints & lacquer manufacture	235	0.1	0.03	4000	2	0.6
Domestic use of paints	60	0.1	0.03	3200	5	1.6
Textile processing	-	-	-	4800	290	90
Total	1400	45.0	14.1	65200	3400	1065

Nonylphenol is resistant to hydrolysis but is susceptible to photolysis in water. Nonylphenol ethoxylates (n>10) are easily hydrolysed to short chained ethoxylate compounds (n<3), which show significant resistance to photolysis in water. In atmosphere, however, all selected compounds have a short photochemical half-life (< 1 day).

Primary biodegradation of nonylphenol in fresh water occurs at half-life values of 15- 20 days. Half life in sea water is 50- 70 days. In both cases, adaptation (20-30 days) is required. Mineralisation occurs solely on the nonyl chain. Primary degradation of nonylphenol ethoxylates (n=9) in fresh water had an half-life of < 4 days. Mineralisation half-live for the major degradation product (NP2EO) in river water is 20- 30 days. In sewage sludge, nonylphenol ethoxylates degradation is fast (half-life < 6 days). In both river water and sewage sludge, degradation of the phenolic ring is observed. Half-lives for primary nonylphenol ethoxylates degradation in brackish and salt water were 3-4 days and 14-35 days respectively and depends strongly on the water temperature. Major degradation product, NP2EO, was found to mineralise slowly, but without substantial formation of nonylphenol.

Nonylphenol mineralisation in soil is fast (half-life of 10-15 days) after adaptation of 15-20 days. Mineralisation occurs solely on the nonyl chain. Half-life for mineralisation of nonylphenol ethoxylates in sludge-amended soils was 5- 10 days and 50 days in non-amended soils. Nonylphenol, produced from nonylphenol ethoxylate mineralisation, is fully degraded.

Toxicity in aquatic systems
Octyl- and nonylphenol are capable of binding to the estrogen receptor thus disturbing the endocrine system. The order of estrogenic potency is octylphenol > nonylphenol > nonylphenol ethoxylate. Octylphenol and nonylphenol ethoxylates are metabolized to octyl- and nonylphenol. Numerous ecotoxicity data are available on nonylphenol. There are no data on the ecotoxicity of octylphenol ethoxylates. From the available data on octylphenol is appears that octylphenol is extremely toxic to aquatic organisms but seems to be less toxic to algae and bacteria. Nonylphenol is also very toxic to most aquatic organisms. Nonylphenol ethoxylate is moderately to very toxic to aquatic organisms.

The iMPCs are derived for octylphenol (0.122 µg/l and 16.08 µg/kg ds), nonylphenol (0.35 µg/l and 1186 µg/kg ds) and nonylphenol ethoxylate (0.044 µg/l and 5.67 - 11.31 µg/kg ds). Comparing the iMPC with the actual measured concentrations the iMPCs for nonylphenol and nonylphenol ethoxylate are exceeded in the Netherlands. The iMPCs for octylphenol is not exceeded in the Netherlands but concentrations in other countries in Europe do exceed the iMPC.

Occurrence and behaviour in aquatic systems
Significantly increased levels of alkylphenols and alkylphenol ethoxylates are found in sediments near wastewater treatment plants and specific user sites, with highest levels for nonylphenol and its ethoxylates. Levels in water are significantly lower. In the middle and late 1980's, sediment/water concentration ratios for nonylphenol ranged from 300- 5,000, at concentrations of 500- 15,000 µg/kg (dw) in sediment and 1- 10 µg/l in water. Concentrations for short chained nonylphenol ethoxylates (NP1EO and NP2EO) varied from 3,000- 12,000 µg/kg (dw) in sediment and 10-100 µg/l in water. Comparison of 1984 and 1996 nonylphenol concentrations in Swiss river waters revealed that levels in water have decreased by roughly a factor 10. Similar data for comparison of sediment concentrations were not available.

In the Netherlands, 1997 values for nonylphenol in fresh waters were below detection (< 0.07 µg/l), whereas concentrations of nonylphenol ethoxylates were only a little higher (0.14 µg/l). Nonylphenol levels in fresh water sediments (1,500-1,700 µg/kg dw) were lower than for nonylphenol ethoxylates (3,000- 8,000 µg/kg dw). Concentrations of nonylphenol and nonylphenol ethoxylates were < 0.07 µg/l in Dutch estuarine surfacewaters. For both nonylphenol and nonylphenol ethoxylates, levels in Dutch estuarine sediments were approximately 2-3 times lower than in fresh water sediments.

Policy
In several countries policy has been made on octylphenol and nonylphenol ethoxylates. Virtually all domestic uses of nonylphenol ethoxylates as cleaning agents have been phased out. In the Netherlands the use of nonylphenol ethoxylates as cleaning agents for industrial uses is reported as terminated.

Prognosis
Further to voluntary industry initiatives to minimise the use of nonylphenol ethoxylates as much as possible, the nonylphenol ethoxylates demand in the EU is expected to decline in the coming years. Quantitative data for future reduction targets are not available, however. Within the framework of PARCOM, national authorities in various Western European countries will shortly review the progress of current voluntary initiatives, in order to assess the necessity of further regulatory use restrictions.

Conclusions and recommendations

From the study results can be assessed that due to wide spread use of nonylphenol ethoxylates in industrial and non-industrial applications, selected compounds are abundantly present in fresh water environments, mainly due to biodegradation of nonylphenol ethoxylates in municipal wastewater. Major emissions to surfacewater are coming from end-use applications where used products are integrally discharged with wastewater. Physico-chemical data of selected compounds indicate that, due to sorption onto sediments, mobility in aquatic environments will be low. Environmental data for release verification and distribution in marine sediments and biota are however scarce.

In the Netherlands, due to restricted use in non-industrial applications, many nonylphenol ethoxylates have been replaced in the last decade and their use has decreased by approx. 70%. National data for historical evaluation of emissions are not available, but from foreign figures it is expected that lower use will have lead to lower nonylphenol and nonylphenol ethoxylates levels in environments.

Further it is assessed that alkylphenols are moderately to very toxic to aquatic organisms. Alkylphenols also exert endocrine disrupting effects and are widely observed in the environment at concentrations exceeding the derived iMPCs. Although degradation in the environment occurs (inherently biodegradable) the substances present a considerable risk to the environment. Based on the fact that alkylphenols are carcinogenic and exert endocrine disrupting effects, it is recommended to derive an ADI or TDI in order to facilitate a comparison between human exposure and the concentrations in the environment.

From comparison of iMPC values with concentrations in the environment it follows that the iMPC are exceeded in most cases. It is therefore advised to derive an official MPC. There are for the moment no data available on octylphenol ethoxylate. Although octylphenol ethoxylate use is minor and their occurrence is scarcely monitored in the environment, it is recommended to gather more information on these substances because it is closely related to nonylphenol ethoxylates.

1 Introduction

1.1 Backgrounds

Alkylphenols are phenol-derivatives that have one or more alkyl groups connected with the aromatic ring structure. The complete group consists of approximately 130 different structures. This study will be restricted to the octyl- and nonylphenols, which exert endocrine disrupting effects. In this respect of special interest are the alkylphenol ethoxylates (APEO). These substances are emitted into the environment and may biodegrade to alkylphenol. As the APEO group mainly consists of octyl- and nonylphenol ethoxylates these substances are also included in the study.

About the effects of alkylphenols on the aquatic environment at present little information is available. This is alarming because several alkylphenols and alkylphenol ethoxylates are found in the aquatic environment. To get an opinion on the consequences of the occurrence of these chemicals in the aquatic environment, the underlying report is composed. This report gives an overview of the available knowledge on alkylphenol and alkylphenol ethoxylates in regard to the aquatic environment. Important criteria for selecting these chemicals were:

- they are used and/or produced in the Netherlands;
- they are on several attention lists;
- they are expected to be persistent and bioaccumulative;
- they are expected to present a danger to the environment.

This report is produced in the framework of the project "Investigating for chemicals in the future".

1.2 Objectives

The objectives of this study with regard to the alkylphenols and alkylphenol ethoxylates are:

To give an analysis of the problems in the aquatic environment: a description of the load, occurrence, behaviour and effects and a analysis of the problems which indicate how the presence of the alkylphenols and alkylphenol ethoxylates may disturb the functioning of the different water systems by effects on sensitive organisms. Furthermore giving an overview of the national and international policy.

In this study the most recent information on alkylphenols and alkylphenol ethoxylates has been used. It is possible that in some attention areas the essential information is not yet available. In these cases recommendations for further research will be done.

The study is broadly set up. The next aspects will be handled. In chapter 2 the chemical characteristics of the alkylphenols and alkylphenol ethoxylates are described. In chapter 3 the production process is clarified and the use of these chemicals is described. In chapter 4 the sources of emissions, primarily to the aquatic environment, are estimated and specified. In chapter 5 and 6 the behaviour in the environment and the occurrence in the environment are described, respectively. In chapter 7 and 8 an overview is given of the toxicity data and the policy, respectively.

1.3 Limitations

In principle the study conforms itself to information that has a relation to aquatic systems. The situation around air or soil will be briefly described. Furthermore the emphasis lies on the situation in the Netherlands. In some cases the situation of the basins of Rhine, Meuse and Schelde will be commented. The information will be presented briefly. For more extensive information referred is to the concerned sources.

2 Physical chemical properties

2.1 Identification

In regard to the current environmental concern about their extensive use and endocrine effects the following groups are studied:
- octylphenols
- nonylphenols
- octylphenol ethoxylates
- nonylphenol ethoxylates

Octyl- and nonylphenols are alkylphenols with a C_8- and C_9-alkyl rest. The alkyl rest can be branched in several ways. Alkylphenols are mainly used as intermediate for the production of alkylethoxylates (nonionic surfactants) (80%), and antioxidant additives for rubber and plastics (10%), miscellaneous, including lube oil additives and phenol resins (10%). Of all alkylphenols only the octyl- and nonylphenols are ethoxylated as from the other alkylphenols the alkyl group is too short or too long for a good tenside function.

Nonylphenol and its ethoxylates are considered as the most important group of alkylphenols and alkylphenolethoxylates.

Octylphenol (CAS No: 67554-50-1) and nonylphenol (CAS No: 25154-52-3) as originally defined by CAS covered all octyl and nonylphenols. However, subsequent revisions redefined it to cover only straight chain octyl and nonylphenol, other isomers having different CAS numbers. We found 20 isomers and 11 salts for octylphenol and 14 isomers and 38 salts and derivatives of nonylphenol (Annex 2).

This assessment covers four alkylphenols: octylphenol (CAS no: 67554-50-1) and phenol, 4-octyl-, branched (CAS no: 99561-03-2), nonylphenol (CAS No: 25154-52-3) and Phenol, 4-nonyl, branched (CAS No: 84852-15-3).

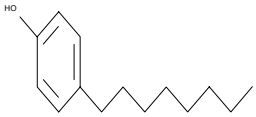
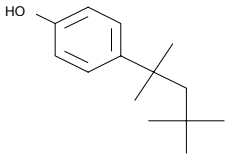
Other alkylphenols of commercial significance are dodecylphenol and dinonylphenol.

Alkylethoxylates are derived from the reaction of alkylphenol with ethylene oxide. The resulting product is not pure but a mixture of different alkylphenolethoxylates (APEO) with a variable number of ethoxylate (EO) groups. In Annex 2 is included a list of 20 Commercial alkylphenolethoxylates.

2.1.1 Octylphenols

The physical properties and chemical structure of octylphenol and branched octylphenol are given in table 2.1.

Table 2.1:
Physical characteristics of octylphenol

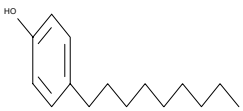
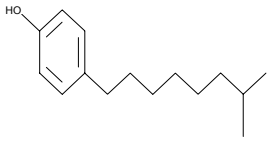
Substance	**Octylphenol**	**4-Octylphenol Branched**
CAS number	67554-50-1	99561-03-2
Chemical formula	C_{14}-H_{22}-O	C_{14}-H_{22}-O
Molecular mass	206.33	206
Physical state	White or pink flakes	
Chemical structure		
Technical products		
Synonyms	OP, Octylphenol 1-Hydroxy-4- octylbenzene	1,1,3,3-Tetramethyl-1 (4-hydroxyphenyl)-butane; 4-(1,1,3,3-Tetramethylbutyl) phenol; p-t-Octylphenol); Diisobutylphenol

2.1.2 Nonylphenols

Technical nonylphenol (isononylphenol) is a mixture of a number of isomers and homologues. The alkyl group is attached to the para (p) or orth (o) position with a 9:1 distribution. Branching is possible at several positions.

The purity has been reported as 90% w/w. The following impurities are reported as being present in nonylphenol:
2-nonylphenol 5% w/w, 2,4-dinonylphenol 5% w/w

Table 2.2:
Physical characteristics of nonylphenol

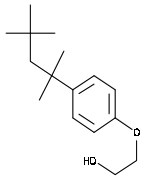
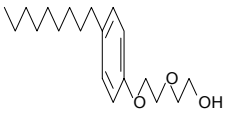
Substance	**Nonylphenol**	**4-Nonylphenol Branched**
CAS number	25154-52-3	84852-15-3
Chemical formula	$C_{15}H_{24}O$	$C_{15}H_{24}O$
Molecular mass	220	220
Physical state	Thick light yellow, straw colour liquid, slight phenolic odour	pale yellow viscous liquid, slight phenolic odour
Chemical structure		
Synonyms	NP	4-NP
Technical products		industrial nonylphenol
Synonyms		
Technical products		

2.1.3 Alkylphenolethoxylates

The most common alkylphenol ethoxylates are the tri and tetra-ethoxylates of p-octylphenol and p-nonylphenol. Exemplary ethoxylated alkylphenols used as the surfactant component of the mixtures are: p-octylphenol EO(3), p-nonylphenol EO(5) and p-decylphenol EO(4) and are used as clothes dryer additive for fabric softening and crisping.
Others have a higher number of ethylene oxide (EO) molecules, such as Tergitol NP40 (CAS nr. 127087-87-0) a nonylphenol with EO(7, 9, 10, 35 or 40) and a molecular weight up to 1900 to 2100. NP-35 is no longer produced. Nonylphenolethoxylates with EO > 7 are water soluble, whereas EO35 and 40 are solids.

The alkylphenol ethoxylates surfactants are manufactured by reacting alkylphenol with ethylene oxide. The reaction results in a very low level of unethoxylated hydrophobe and a narrow distribution of ethylene oxide adducts. Commercial alkylphenolethoxylates contain 1-4% glycol ethers and <10 ppm ethylene oxide.

Table 2.3:
Physical characteristics of alkylphenolethoxylates

Substance	**Octylphenolethoxylates**	**nonylphenol ethoxylates**	**Tergitol**
CAS number	9002-93-1	26027-38-3	127087-87-0
Chemical formula	$[C_{16}H_{26}O_2]n$	$[C_{19}H_{32}O_3]n$	
Molecular mass	250.38	308	1900-2100
Physical state	viscous, colourless liquid	pale yellow viscous liquid, slight phenolic odour	white solid with a "mild characteristic odour"
Chemical structure			
Synonyms	Alkylaryl polyether alcohol, Octoxynol; Poly(oxy-1,2-ethanediyl), .alpha.-(octylphenyl)-.omega.-hydroxy-	Nonylphenol polyoxyethylene ether; Glycols, polyethylene, mono-(p-nonylphenyl) ether; Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-.omega.-hydroxy- [1]	
Technical products	Triton X-100	Tergitol	

[1] For a more extensive listing of synonyms and products see annex 2

2.2 Physico-chemical characterisation

In table 2.4 and 2.5 the chemical and physical data for nonyl and octylphenol are presented. The characteristics of the different alkylphenols are basically the same. All alkylphenols have a low water solubility and a low volatility (low Henry coefficient). The octanol water partitioning coefficient (log Kow) is relatively high and indicates bioaccumulative properties and affinity for adsorption to soil and sediment.

Table 2.4:
Chemical and physical data of octyl and nonylphenols (EU, 1999; IUCLID, 1996)

Compound	Octylphenol	4-Octylphenol Branched	Nonylphenol	4-Nonylphenol Branched
CAS no	67554-50-1	99561-03-2	25154-52-3	84852-15-3
Commercial product	-	-	-	-
Molecular formula	C_{14}-H_{22}-O	C_{14}-H_{22}-O	$C_{15}H_{24}O$	$C_{15}H_{24}O$
Molecular mass	206.33	206.33	220	220
Melting point (°C)	79-82	-	2 -10**	-8, -8, -10, 10 <20,
Boiling point (°C)	277	-	315* 293-297**	-
Flash Point (°C)	145 (open cup)	-		-
Vapour Pressure (Pa, 20°C)	1	-	10 2.4 E-5 mm HG at 25°C**	10
Density (g cm^{-3}, 20°C)	0.95	-	-	
Henry constant (Pa m^3 mol^{-1})	-	-	-	0.16
Solubility H_2O (25°C ; mg /1)	12.6	-	5	5
Log K_{ow}	3.7; 4.12 at 20.5ºC; 4.5 at 23ºC	-	-	3.28 - 4.48

* Verschueren, 1983
** HSDB, 2000

Table 2.5:
Chemical and physical data of octyl- and nonylphenols ethoxylates (EU, 1999; IUCLID, 1996)

Substance	**Octylphenol ethoxylates**	**Nonylphenol ethoxylates**	**Tergitol**
CAS number	9002-93-1	-	127087-87-0
Commercial product	Triton X-100	-	Tergitol NP-40
Molecular formula	$[C_{16}H_{26}O_2]n$	$[C_{19}H_{32}O_3]n$	-
Molecular mass	250.38	-	1600-2100
Melting point (°C)	27	-	44
Boiling point (°C)	270	-	-
Decomposition Point (°C)	-	-	-
Specific gravity	1.04	-	1.07
Log K_{ow}	4.86 (estimated)	-	
Vapour Pressure (Pa, 20°C)	0 mm Hg	-	<0.01 mm Hg
Vapour density (air = 1)	21,0	-	-
Henry constant (Pa m^3 mol^{-1})	-	-	1.2E-7 atm (estimated)
Solubility H_2O (25°C ; mg /1)	Complete	-	20% (w/w)
Critical micelle conc (CMC) in water (25°C)	-	-	0.2 g/l

Distribution air is of no importance as indicated by the low vapour pressure. As alkylphenol ethoxylates - in comparison with alkylphenols - have high water solubility, indicates that water is the main route of transport through the environment. Degradation of the alkyl groups of the ethoxylates induces decreasing solubility and increasing affinity for organic phase (soil, sediment, biological material). A theoretical distribution of nonylphenol in the environment is >60% in sediment, > 10% in soil and approx. 25% in water (TemaNord, 1996).

2.3 References

- EU (1999) European Union. Risk assessment of 4-nonylphenol (branched) and nonylphenol. Final Draft Report, September 1999
- IUCLID, 1996 International Uniform Chemical Information database, EC
- Sniffer, 1998. Proposed Environmental Quality Standards for Octylphenol in water. Environmental Agency Scotland & Northern Ireland Forum for Environmental Research (SNIFFER), WRc plc, R&D Technical report P59/i688
- TemaNord (1996). Chemicals with Estrogen-like Effects. Nordic Council of Ministers, Copenhagen 1996. ISBN 92 9120 918 X

3 Production and use

3.1 General

Alkylphenols are produced in high volumes and are basically used as an intermediate for the chemical industry in the production of alkylphenol ethoxylates (nonionic surfactants and detergents), phenolic resins (plastics) and phenolic oximes (anti-oxidants). They are further used as heat stabilizers and curing agents in various industrial applications. Commercial use is non-existing. Nonylphenol and octylphenol make up >95% of the market. Only minor amounts of butyl-, decyl- and dodecylphenols are produced for specific applications. In the environment, alkylphenols are further produced in biodegradation of surfactants in domestic and industrial wastewater. As such, their occurrence in the environment is related to wide spread use and emissions to surfacewater (EU, 1999; Leisewitz, 1997; TemaNord, 1996).

Alkylphenol ethoxylates (APEOs) are basically used as nonionic surfactants, detergents and stabilisers which have a wide range of applications as wetting agents, dispersants, emulsifiers, solubilizers and foaming agents. APEOs are of major importance for wet processing of industrial materials and are therefore widely used in the production of pulp and paper, textiles, coatings, agricultural pesticides, lubricant oils and fuels and in the metal finishing and plastics industry. As a constituent of industrial and commercial products, it is further used in a wide variety of medium and small companies (niche markets) as detergent and as wetting and cleaning agents. In Europe, industrial applications have a major market share (>70%) since the use in domestic cleaning has been abandoned since the 1990's. Use in non-industrial applications (<30%) include mainly institutional cleaning products, paints, lacquers and wetting agents for agricultural chemicals.

3.2 Major producers

3.2.1 Alkylphenols

The production industry in Western Europe currently consists of 10 major companies which produce butyl-, octyl-, nonyl- and dodecylphenols, which are exclusively used as industrial intermediates. A summary of major producers is given in table 3.1 (Leisewitz, 1997)

Table 3.1:
Major producers of alkylphenols in Western Europe

Country	Producer	Location
Germany	Huls AG (nonylphenol) BASF (octylphenol) Bayer (butylphenol)	Marl Ludwigshafen Leverkussen
France	Great Lakes Chemicals (octylphenol)	Presan
Switzerland	Schenectady (octylphenol)	Pratteln
Sweden	AKZO Nobel (nonylphenol)	Molndal
Great Britain	ICI (nonylphenol) BP Chemicals (dodecylphenol)	Wilton London
Italy	SISA (nonylphenol) Enichem (nonyl- and dodecylphenol)	Pioltello Mantova

Total production capacity for nonyl- and octylphenol is at around 110,000 and 7,000 tonnes/year, respectively. Annual production is strongly depending on the market demand, but fluctuates between 60 and 70% of the installed capacity. Major part of the nonylphenol production is used in nonylphenol ethoxylate and phenolic resin production (see table 3.2).

Table 3.2:
Production and demand of nonylphenol in Western Europe

	1995 (tonnes/y)	1997 (tonnes/y)
Production capacity	110,000	110,000
Production	77,000	73,500
Import	5,000	8,500
Export	18,000	3,500
Use in Western Europe	64,000	78,500
Use as intermediate for		
Phenolic resins/plastics/additives	33,700	32,800
Nonylphenolethoxylates	27,900	43,200
Phenolic oximes	2,400	2,500

Sources: EU, 1999; UBA 1997; Leisewitz 1997; Leisewitz 1999

3.2.2 Nonylphenol ethoxylates

In 1997, the production of nonylphenol ethoxylates in the EU amounted to 118,000 tonnes. Nonylphenol ethoxylates are being produced by a large number of companies at various sites in the EU, amongst there are thought to be 10 large production sites. Details about producers and production sites were not publicly available, but from specific industry profiles it is known that nonylphenol ethoxylates are produced in multi-purpose ethoxylation plants. Overall ethoxylation capacity in the EU was estimated at 1,300,000 tonnes per year, with the major companies located in Germany (BASF, Hoechst and Huls). A large fraction of the nonylphenol ethoxylate production is being exported. Depending on the actual demand, production and export can fluctuate from year tot year (EU, 1999; Leisewitz, 1997).

Table 3.3:
Production and demand of nonylphenol ethoxylates in the EU

	1994 (tonnes/y)	1995 (tonnes/y)	1997 (tonnes/y)
Production	100,400	109,800	118,000
Import	0	400	5,600
Export	35,400	35,400	46,000
Use in the EU	65,000	74,800	77,600
Industrial and institutional cleaning	-	22,700	23,000
Emulsion polymerisation	-	9,700	9,000
Textile auxiliaries	-	8,000	8,000
Captive use in chemical industry	-	6,700	7,000
Leather auxiliaries	-	6,200	6,000
Agriculture chemicals	-	5,000	5,000
Paints	-	3,500	4,000
Metal industry	-	2,000	2,000
Pulp and paper	-	1,000	1,000
Various niche markets	-	10,000	12,200

Sources: EU, 1999; UBA 1997; Leisewitz 1997; Leisewitz 1999

3.3 Production processes

In the EU some 90% of the production and use of alkylphenols and alkylphenol ethoxylates is related to nonylphenol and its ethoxylates, therefore descriptions in this chapter are focused only on the production and use of nonylphenol and nonylphenol ethoxylates.

3.3.1 Nonylphenol

Production of nonylphenols is based on the reaction of phenols with olefines at elevated temperatures and in presence of a catalyst. Phenol is mixed with tripropylene (isononene) in a molar ratio of 1:1,7. The catalysed reaction leads to a mixture of nonylphenol isomeres, dominated by branched chain congeners. By-products and non-reacted materials are removed from the product by means of multi-stage vacuum distillation. Non-reacted phenol and isononene are recycled to the production process. The overall nonylphenol yield is typically >98% (Leisewitz 1997).

As generally applied by nonylphenol producers, there are three main processes for the production of nonylphenol:

1. Phenol and mixed nonenes are reacted in the presence of a catalyst in a batch process. The catalyst used is montmorillonite clay/fulcat and phosphoric acid.
2. Phenol and mixed nonenes are reacted in the presence of a sulphonated ion exchange resin in a batch process. The catalyst/precoat system can be reused for 40-500 batches.
3. Phenol and isononene react in a continuous process (two-stage fixed bed reactor) with ion exchange resin as catalyst. The catalyst has a life of about three months.

At present, 80-85% of the total nonylphenol production is achieved in continuous fixed bed reactors. Due to the fully closed production process, emissions to surface water and atmosphere are negligible (EU, 1999; Leisewitz 1997).

3.3.2 Nonylphenol ethoxylates

Nonylphenol ethoxylates are produced by reaction of nonylphenol with ethylene oxide. Nonylphenol is heated with an alkali catalyst (potassium hydroxide). Water, produced at this stage, is removed at 120° C under vacuum. Subsequently ethylene oxide is added which quantitatively reacts with free nonylphenol. Reaction mixture is subsequently neutralised to pH 6 to 8 using acetic acid. The reaction is exothermic and reaction mixtures can become explosive above optimal temperatures and ethylene oxide addition rates. The length of the ethoxylate chain can be controlled by the nonylphenol to ethylene oxide ratio and the reaction time. Any residual water will lead to the formation of polyethylene glycol, which is present in most nonylphenol ethoxylates as inert by-product). (EU, 1999).

Mainly, in the EU there are two methods for producing nonylphenol ethoxylates. In the loop reactor process, nonylphenol circulates in a continuous cycle while ethylene oxide is added in excess under controlled temperature and pressure conditions. Because nonylphenol is more reactive than ethoxylate, the product and rinsing waters are virtually nonylphenol free. Batches of nonylphenol ethoxylate are produced in quantities of 6-40 tonnes and are then usually pumped directly into road tankers for delivery or storage. The other method used is the "stirred tank" process. Details of this method were not available. (EU, 1999).

Rinsing water from reaction vessels is usually treated on site by mechanical (flotation, oil skimmers, sedimentation) and biological treatment. Treated effluent is discharged to the sewer or surface water. Oil residues from mechanical separation and sludge from biological treatment are usually incinerated without emissions to the atmosphere. Emissions from treated effluent are negligible in comparison with the nonylphenol emissions from surfactant degradation in municipal wastewater treatment (EU, 1999).

3.4 Major applications

3.4.1 Nonylphenol

Besides the use in production of nonylphenol ethoxylates, nonylphenol is further applied as intermediate in the polymer industry for the production of phenolic resins, plastics and stabilisers and in the production of mineral ore extraction chemicals (phenolic oximes).

Nonylphenol ethoxylate production

In 1997, the nonylphenol use as an intermediate in the production of nonylphenol ethoxylate amounted to 40,000-45,000 tonnes (see table 3.2.). Major release to the environment is expected from nonylphenol ethoxylate biodegradation due to discharge of surfactants and other nonylphenol ethoxylate products in domestic and industrial wastewater. European nonylphenol ethoxylate producers estimate that 60-70% of the overall nonylphenol ethoxylate use will finally end up in wastewaters (Leisewitz 1997).

Polymer industry

The main use of nonylphenol in the plastics industry is as a monomer in the production of phenol/formaldehyde resins, which are subsequently used in the production of paints and adhesives and as additive in the rubber industry. The total amount of nonylphenol used in this application was approximately 22,500 tonnes in 1997. There are reported to be around 50 producers of phenol/formaldehyde resins within the EU, of which some 20 are thought to use nonylphenol. It is estimated that nonylphenol is used in the production of phenol/formaldehyde resins at 25 sites within the EU. From information of phenol/ formaldehyde

producers in the EU it was assessed that the nonylphenol release to effluent was <0.001 % of the amounts used, which is in agreement with standard emissions for this type of industry. Wastewater from the production process is treated off-site. (EU, 1999).

Other applications include the use of nonylphenol as an intermediate in the production of tri (4-nonylphenyl) phosphite (TNPP). The total amount of nonylphenol used in TNPP production is 4,000 tonnes/year. Information from TNPP producers indicate that releases to the environment are typically zero, since all waste produced in production processes is incinerated (EU, 1999). Annual use of nonylphenol as a catalyst in curing of epoxy resins production amounts to about 1,500 tonnes. Releases of nonylphenol from this process are likely to be similar to those from the production of nonylphenol/formaldehyde resins, although nonylphenol makes up a much smaller part of the total resin than in the case of nonylphenol/formaldehyde resins. Nonylphenol releases to wastewater are estimated at 0.01 % of the nonylphenol amounts used. Use in other plastic stabilisers is estimated at approximately 1,000 tonnes. Nonylphenol releases to wastewater are estimated at 0.05 % of the nonylphenol amounts used. Further it is indicated that in the production of resins, plastics and stabilisers nonylphenol is only used as reactive compound. Nonylphenol releases from product use are therefore negligible (EU, 1999; Leisewitz 1997).

Phenolic oxime production
Nonylphenol is used by one company within the EU to manufacture phenolic oximes, which are used as a reagent for the extraction and purification of copper from ore. Total quantity of nonylphenol used in this application is 2,500 tonnes/year, being used at one production site. In the EU, phenolic oximes are not used for this application. All phenolic oximes produced are exported to customers outside of the EU. Wastewater is treated on-site in an activated sludge treatment plant. After treatment the nonylphenol emission to surface water was < 0.004 % of the nonylphenol amounts used. Sludge produced from the on-site waste water treatment plant is disposed to landfill (EU, 1999).

3.4.2 Nonylphenol ethoxylates

Nonylphenol ethoxylates are being produced in a wide class of substances, predominantly by variation of the number ethoxylate groups, making these substances very versatile for dissolving nonpolar substances in polar solvents and vice versa. Most nonylphenol ethoxylates further exhibit a low surface tension, making them excellent wetting agents for rinsing, cleaning and dispersion purposes (see table 3.4).

Table 3.4:
Industrial use of nonylphenol ethoxylates (CEFIC, 1996)

Industrial use in the EU (1994)	annual use (tonnes/year)	as nonylphenol (tonnes/year)	%
Agricultural industry	4900	1750	7.9
Chemicals industry (in synthesis)	4600	1650	7.4
Electrical/electronic engineering	100	30	0.2
Public domain (cleaning)	22700	8770	36.7
Leather processing industry	6300	2450	10.2
Metal refining and processing	100	30	0.2
Mineral oil and fuel industry	100	30	0.2
Photographic industry	100	30	0.2
Polymers industry	4700	1900	7.6
Pulp, paper and board industry	800	280	1.3
Textile processing industry	4800	1650	7.8
Paints, lacquers and varnishes	4000	1400	6.5
Civil and mechanical engineering	100	30	0.2
Other	8500	3000	13.8
Total	61800	23000	100

Nonylphenol ethoxylates with low number of ethoxylate molecules are rather hydrophobic and are frequently used as dispersants in oil related applications, whereas nonylphenol ethoxylates with high number of ethoxylate molecules are highly soluble in water. Latter compounds are normally used as cleaning agent for dissolving organics, fats and grease into water or as dispersant of organics as in water based (epoxy resin) paints and lacquers. Both types of nonylphenol ethoxylates are further used as wetting agents to improve flowing properties of water, thereby the reducing rinsing water amounts in various industrial and non-industrial applications.

Table 3.5:
Use of nonylphenol ethoxylates

Functional use in the EU	%
Surface active agents	46.1
Cleaning/washing agents	44.7
Foaming agents	2.8
Flotation agents	1.7
Construction materials and additives	1.4
Cosmetics	1.5
Dust binding agents	1.4
Intermediates	0.2
Plant protection products, agricultural	0.1
Others	0.1

Sources (CEFIC, 1996; EU, 1999)

Industrial and institutional cleaning
Nonylphenol ethoxylates are used in laundries, for floor and surface cleaning in buildings, as vehicle cleaners, anti-static cleaners and metal cleaning. Nonylphenol ethoxylates typically account for <5% by weight of the final formulation. Domestic use of nonylphenol based cleaning products will be virtually zero within the EU due to voluntary bans and agreements with industry. Voluntary agreements with industry should further lead to additional decrease of nonylphenol ethoxylates use in industrial based cleaners in the next few years.

Textile auxiliaries
As auxiliaries for several textile manufacture processes such as scouring, fibre lubrication and dye levelling. Main use is in wool scouring where natural fats are removed from the wool. Nonylphenol ethoxylates are used due to their detergent and fibre lubricating properties and because they do not adsorb into wool like anionic surfactants.

Leather auxiliaries
Nonylphenol ethoxylates are applied in wet degreasing of hides in the leather industry.

Agriculture
Used as wetting agent in agrochemical formulations for increase spraying efficiency and to reduce the amount of active ingredient that needs to be applied. They may also be incorporated as dispersants and emulsifiers or added to the spray tank at the time of application. Nonylphenol ethoxylates are further used in veterinary medicinal products as surfactants in teat dips and as an aid in the control of mastitis.

Emulsion polymers
Nonylphenol ethoxylates are added to acrylic esters used for specialist coatings, adhesives and fibre bonding. They act as dispersants and maintain the stability of the formulation. Nonylphenol ethoxylates are also used in polymer solutions used in wastewater treatment.

Paints and lacquers
Used in paint resins (polyvinyl acetates) and as a resin stabiliser in oil and water based paints. Formulations contain typically 0.6-3% nonylphenol ethoxylates.

Pulp and paper
Nonylphenol ethoxylates are used in wetting of pulp fibres.

Metal industry
Main use is in metal cleaning processes (iron and steel manufacture), steel phosphating, electronics cleaning (for metal contacts) and cleaning of metal products prior to storage. Nonylphenol ethoxylates are also used in the formulation and usage of cutting and drilling oils. Cutting and drilling oils are mainly emulsions of white spirit, water and hydrophobic surfactants.

Miscellaneous uses
Particularly for military use in gearboxes, nonylphenol ethoxylate phosphate esters are used as additives in lubricating oil. These products prevent aggregation of metal fragments in engine boxes and reduce the impact of water contamination. In some cosmetic formulations nonylphenol ethoxylates are thought to be used as surfactant, while in the developing of photographic film it is used as a wetting agent. Possible products used in the public domain containing possible

nonylphenol ethoxylate include vehicle and office cleaning agents, correction fluids and inks and non-agricultural pesticides.

3.5 Demands in the EU

3.5.1 Nonylphenol

In 1997, nonylphenol use in Western Europe was approximately 80,000 tonnes. Figures from 1995 to 1997 illustrate that demand in the EU varies, largely due to the demand of nonylphenol in nonylphenol ethoxylate production (see table 3.2). Overall nonylphenol production and demand in other sectors were nevertheless stable, indicating that the lower domestic demand is compensated by increased export outside the EU. A summary of nonylphenol production in the EU and other parts of the world is given in table 3.6. From this table can be seen that the EU has a 25 % market share in global demand.

Table 3.6:
Production of major alkylphenols and alkylphenol ethoxylates (tonnes/y)

1997	EU	USA	Japan	Other	World
NP	80000	145000	40000	70000	335000
OP	7000	35000	5000	13000	60000
Total	87000	180000	45000	83000	395000
NPEO	120000	240000	65000	105000	530000
OPEO	12000	60000	8000	20000	100000
Total	132000	300000	73000	125000	630000

Sources: EU, 1999; CMR 1999; Japan 1997; Chemexpo 1998; UBA 1997; Leisewitz 1997; Leisewitz 1999

Reliable data for evaluation of market growth (or decline) in the EU were not available. Nonylphenol ethoxylates producers in the USA, on the other hand, estimated that the EU market for nonylphenol ethoxylates will decrease 4 to 5% per year over the following 5 years, contrary to a annual market growth in the USA of 2-3% over the same period. Based on relative stable nonylphenol production levels in years when nonylphenol ethoxylates use significantly decreased, it is assumed that in the following 5 years overall nonylphenol demand will remain more or less constant (CMR, 1999).

3.5.2 Nonylphenol ethoxylates

Nonylphenol ethoxylate demand in the EU in 1997 was 78,000 tonnes, with the industrial and institutional cleaning product sector as the largest user (see table 3.3). The use in this sector is still significant despite voluntary agreements between member states and industry to phase out the use of these substances in these products, as was achieved for the use nonylphenol ethoxylates in domestic cleaning products (EU, 1999; Leisewitz, 1999).

In order to obtain an indication of the effect of the banning of nonylphenol ethoxylates in domestic cleaning products, national demand figures for several Western European countries from 1986 and 1995 were compared (see table 3.7). From the data in table 3.7 can be assessed that banning of nonylphenol ethoxylates use in domestic cleaning products (e.g. intentions to phase out overall use) were most effective in the Netherlands and Nordic States.

Further it can be seen that the 1986 use in Germany was already lower than in other countries, which can be explained by the fact that restrictive actions in

Germany were initiated earlier than in other countries. In 1995, however, the overall nonylphenol ethoxylates demands in the Netherlands and Nordic States have fallen below the German value (see figures 3.1 and 3.2). From figure 3.3 it is further assessed that nonylphenol ethoxylates are typical consumer chemicals and that between 1986 and 1995 the overall use in Western Europe decreased by approx. 40%.

Table 3.7:
Use of nonylphenol ethoxylates in Western Europe

		1986 Tonnes/y	1995 Tonnes/y	1986 kg/inh/y	1995 Kg/inh/y	Decrease %
Germany	D	15000	9200	0.237	0.143	38.7
Switzerland	CH[a]	2900	1700	0.405	0.233	41.4
Italy	I[a]	21300	10800	0.383	0.191	49.3
Netherlands	NL	4900	1300	0.336	0.083	72.9
United Kingdom	UK[a]	23700	12900	0.415	0.222	45.6
Denmark	DK	1900	750	0.370	0.143	60.5
Sweden	S	3100	1200	0.360	0.136	61.3
Norway	N	1600	550	0.372	0.125	65.6
Finland	SF	1900	750	0.379	0.146	60.5
Nordic states	NC	8500	3250	0.368	0.138	61.8
EU-states	-	71800	37400	0.343	0.175	47.9
EU-total	EU	120000	67700	0.347	0.192	43.6

[a]: 1995 value extrapolated on basis of 1986 and 1989 values
Sources: EU, 1999; UBA 1997; Leisewitz 1997; Leisewitz 1999; Warhurst 1995

For Switzerland, Italy and United Kingdom no reliable 1995 demand data were available. The 1995 values were therefore based on extrapolation of the 1986 and 1989 figures as assessed by the Swedish EPA in 1991 (TemaNord, 1996). It is not known to what extent these extrapolated data represent the actual 1995 figures in these countries.

Figure 3.1 NPEO consumption in Western Europe

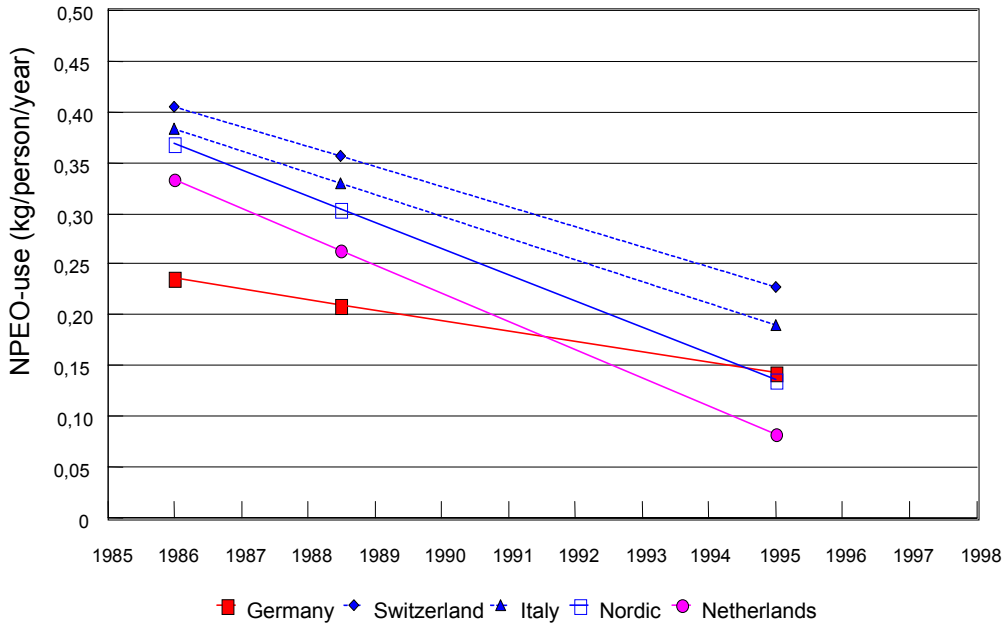


Figure 3.2 Nominal NPEO consumption in Western Europe

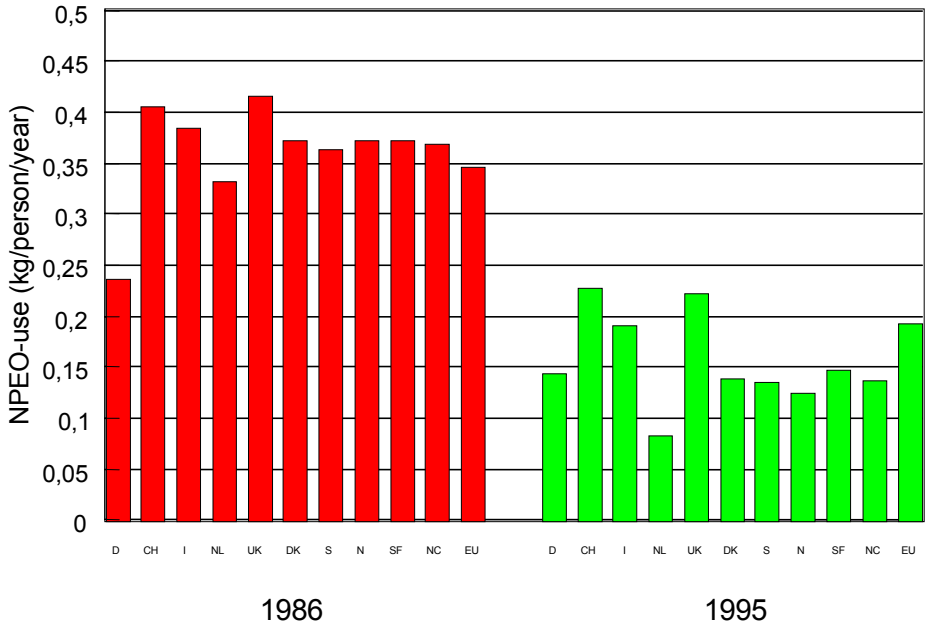
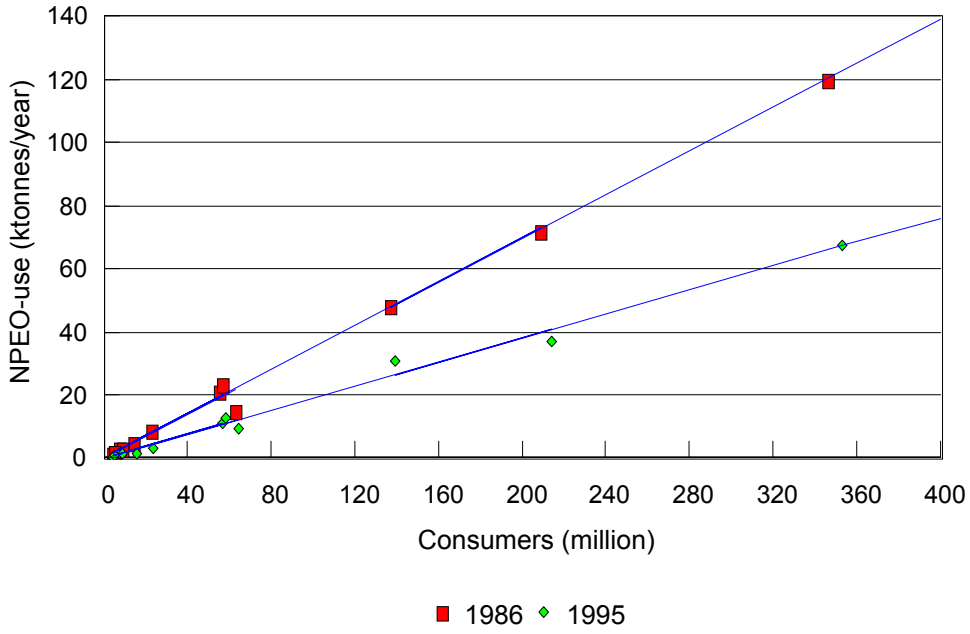


Figure 3.3 NPEO consumption in Western Europe



From data in table 3.8 it further can be assessed that the nominal use (in kg/person/year) of nonylphenol ethoxylates in EU is significantly lower than in the USA and Canada.

Table 3.8:
Use rates of nonylphenol ethoxylates

1997	EU	USA	Canada	
Consumers	375	275	30	Million
NPEO use	77000	100000	12200	Tonnes/y
NPEO use	0.205	0.364	0.407	kg/person/y

Sources: Chemexpo 1998; CMR, 1999; Leisewitz 1997; Canada 2000

3.6 Demands in the Netherlands

3.6.1 Nonylphenol

There no nonylphenolethoxylates producers situated in the Netherlands (RIZA, 2000). Quantitative data for captive nonylphenol use in production of phenolic resin polymers and oximes were not available for the Netherlands situation. Neither information was available for verification phenolic resin polymers and oximes producers in the Netherlands. In order to obtain an average estimate for the nonylphenol use in the Netherlands, EU figures for the nonylphenol use in 1997 are extrapolated on Gross Domestic Product (GDP) basis. The extrapolated use figures are presented in table 3.9.

Table 3.9:
Estimated nonylphenol in the Netherlands

Nonylphenol use (1997)	EU	NL
Phenol / formaldehyde resin production	22500	1100
TNPP production	4000	200
Catalyst in epoxy resins production	1000	50
Total	27500	1350

Source: EU, 1999

3.6.2 Nonylphenol ethoxylates

In 1995, a national survey was performed for quantification of industrial use of alkylphenol ethoxylates in the Netherlands. In this survey the use of alkylphenol ethoxylates in major industrial applications was studied. On basis of the study results, the industrial alkylphenol ethoxylates use was estimated at maximally 1000 tonnes in 1995. Further it was established that there were many initiatives within the industrial user groups to find technical and environmentally safe alternatives for currently used alkylphenol ethoxylates (Westra, 1995).

In applications where technical alternative products were available, alkylphenol ethoxylates were largely replaced. In the remaining applications, replacement of alkylphenol ethoxylates containing products was either technically impossible or it required too many (technical) process changes to facilitate the use of alternative products. For the latter cases it further was established that when current production and treatment processes are to be replaced, new process technology will be based on alkylphenol ethoxylates free products (Westra, 1995).

Use sectors not included in the study were agriculture, small and medium companies (niche applications) and domestic use of paints. Taking these use sectors into consideration on basis of extrapolated EU figures, then overall alkylphenol ethoxylates use in 1995 would total 1400 tonnes, from which >90% is expected to be nonylphenol ethoxylates (1250 tonnes). An estimate for the updated use of nonylphenol ethoxylates in 1997, based on the observed EU growth in nonylphenol ethoxylates use, is given in table 3.10.

Table 3.10:
Nonylphenol ethoxylates use in the Netherlands

1997	NPEO use tonnes/y	NPEO use %
Agriculture use	96	6.5
Various niche applications	236	16.0
Industrial cleaning	179	12.0
Leather processing	60	4.0
Metal working	52	3.5
Pulp and paper industry	14	0.9
Chemical industry	469	33.0
Paints & lacquer manufacture	235	16.0
Domestic use of paints	61	4.1
Pesticide formulation	83	5.6
Textile processing	Negligible	Negligible
Total	1485	100.0

From table 3.10 can be concluded that the chemical industry and paint industry are the major user sectors (together ca 50% of the overall use), followed by the use in niche applications and industrial cleaning. Comparison with EU figures for nonylphenol ethoxylates use (table 3.4) demonstrate that that use in cleaning applications in the Netherlands (12%) is significantly lower than in the EU (36,7%). With regard to the figures in table 3.10, it further should be noted that the figures are partly based on extrapolated figures from 1995. They therefore do not account for any decreases in nonylphenol ethoxylates use as a consequence of intermediate measures to limit the use of substances in industrial and niche applications.

3.7 Waste disposal

3.7.1 Nonylphenol

Waste materials containing nonylphenols can be generated at nonylphenol production sites, production plants where it is used as an intermediate, at formulation companies or by final product disposal after service life. For nonylphenol releases at nonylphenol production sites and other production processes, it is established that nonylphenol emissions from (treated) wastewater discharge to surface water are negligible (EU, 1999).

Liquid and solid wastes, produced from wastewater treatment (oily residues and sewage sludge) are either sent off for disposal at controlled landfills or incinerated on-site without emissions to the environment. Landfilled sewage sludge, containing high levels of nonylphenol, can be a source for release of nonylphenol to leachate and groundwater. Environmental data at landfill sites showed that only traces of nonylphenol were found in leachate or groundwater, indicating that nonylphenol is preferentially bound to solids and is not subject to significant leaching (EU, 1999; TemaNord 1996).

Products containing nonylphenol being disposed off after service life are mainly products containing epoxy/formaldehyde polymers. As indicated earlier, nonylphenol is only used as a reactive compound in these products, therefore nonylphenol releases from these products can be excluded (EU, 1999; Leisewitz, 1997).

3.7.2 Nonylphenol ethoxylates

Nonylphenol ethoxylates are generally used in liquid form, as detergent or surfactant in cleaning agents, auxiliary in industrial processes or as additive in industrial and commercial products such as paints and lacquers. Main release pathway for nonylphenol ethoxylates will be in municipal wastewater after use (see chapter 4). Other potential nonylphenol ethoxylate releases are landfilling or incineration of nonylphenol ethoxylates containing products such as paints and industrial wastes, for which separate regulatory disposal methods apply.

From experiences at production sites with nonylphenol ethoxylates waste incineration, it can be concluded that incineration of nonylphenol ethoxylate wastes will not lead to significant emissions. For landfilling of nonylphenol ethoxylates containing wastes it is expected that under anaerobic conditions, nonylphenol ethoxylates will be largely converted to nonylphenol, which is bound to solids thus hardly will be released (EU, 1999; TemaNord 1996).

3.8 Potential alternatives

3.8.1 Nonylphenol

From an environmental point of view there is no urgent need for replacement of nonylphenol, because various risk assessment studies have shown that nonylphenol releases from production are virtually zero and commercial use of nonylphenol does not occur. Environmental concern is mainly caused by nonylphenol production from nonylphenol ethoxylates biodegradation in aquatic environments. Furthermore, nonylphenol and nonylphenol based products (resins, additives etc) are a basic chemicals group with specific properties and performance with major advantages over the other alkylphenols, resulting in their dominant market position, making them hard to replace. Accordingly, until now no efforts have been made to replace these chemicals.

3.8.2 Nonylphenol ethoxylates

The question whether nonylphenol ethoxylates are strictly necessary for a specific application depend on various factors, such as the specific performance compared to alternatives and the price/performance ratio. Presently, nonylphenol ethoxylates are significantly cheaper than other surfactants, but given enough time, money and knowledge, it is should be possible to find a suitable alternatives (Westra, 1995).

It further may be assumed that the price of the substitutes will decrease as their demand will increase. The general impression is that in a number of branches of industry already a considerable effort has been invested in order to find suitable replacements for nonylphenol ethoxylates. However, the ease with which the nonylphenol ethoxylates can be replaced depends on the specific application (Westra, 1995).

Colloid systems

Nonylphenol ethoxylates possess excellent physio-chemical properties, i.e. they are good emulsifiers, dispersants, wetting agents and emulsion-stabilizers. This specific material thus provides a combination of several useful properties. According to representatives of the paint and polymer industry mostly nonylphenol ethoxylates are used because they act as a combined emulsifier, dispersant, stabilizer and wetting agent. A colloid system like paint must be stable for a long period of time, the combination of emulsifying and stabilizing properties is found to be of crucial importance. In these systems nonylphenol ethoxylates are clearly more difficult to replace. However, according to a representative of a paint-producing company, nonylphenol ethoxylates will not be applied in all newly developed products (Westra, 1995).

Metal degreasing and metalworking fluids
In another important application, degreasing agents and working fluids for the metal-processing industry, nonylphenol ethoxylates have been replaced to a large extent. In these applications nonylphenol ethoxylates are predominantly used because of their emulsifying properties. In case of degreasing fluids, the emulsifying properties define the 'cleaning properties of the fluid', i.e. oily and greasy materials are removed as a result of the emulsifying power of the alkylphenol ethoxylates. In this particular application the long-term stability of the emulsions is not technically required.

In these applications the wetting properties are also of importance. The surface tension of the cleaning solution has to be low enough in order to wet the entire surface of the material to be degreased. The alternatives used, (fatty) alcohol ethoxylates, seem to have emulsifying and wetting properties which are satisfactory to the users. According to producers of these new degreasing agents, the technical performance of their product was equivalent to the performance of nonylphenol ethoxylates. In these applications, where nonylphenol ethoxylates still are used, there is no technical reason for maintaining current products (Westra, 1995).

In case of metal-working fluids similar arguments are valid. Again, the emulsion has to be stable for a comparatively short period of time. Furthermore the applied surfactant should have good wetting properties. Nonylphenol ethoxylates have been substituted in most metal-working fluids, only a small amount is still being used. Nonylphenol ethoxylates are usually replaced by (fatty) alcoholethoxylates. In one application, the so-called rolling fluids, nonylphenol ethoxylates are still applied. The substitution for this application was found to be more difficult. Ethoxylated alcohols were found to result in increased foaming and decreased wetting properties. Other substitutes are currently under investigation (Westra, 1995).

Industrial degreasing agents
For industrial degreasing agents, e.g. for the degreasing of engine parts, similar arguments hold as for the metal degreasing fluids. There seems to be no reason not to replace the nonylphenol ethoxylates by other emulsifiers. According to a representative of a degreasing agent producing company, substitution of nonylphenol ethoxylates by ethoxylated alcohols still is problematic. It is found that these surfactants result in longer wetting times and the surface tension of the degreasing solution is lowered to a smaller extent. Nevertheless, more and more products have been substituted over the years (Westra, 1995).

Other uses
In the formulation of pesticides, the substitution of nonylphenol ethoxylates by (fatty) alcohol ethoxylates was found not to be satisfactory. The formulations containing ethoxylated alcohols were found to be less stable. However, other emulsifiers are currently being tested. A manufacturer of defoaming products for the paper industry claims that no technically equivalent replacement for nonylphenol ethoxylates is available.

3.9 Conclusions and recommendations

From production and specific use figures for alkylphenols and alkylphenol ethoxylates in the EU and the Netherlands over the period 1985-1997 can be assessed that:

1. Nonylphenol production in Western Europe amounts to 75.000- 80.000 tonnes/year. Octylphenol production is estimated at approx. 7.000 tonnes/year. Captive use of nonylphenol in production of phenolic resins and

oximes amounts to 35.000 tonnes/y and is relatively stable, whereas use in nonylphenolethoxylates (28.000- 42.000 tonnes/year) and export of nonylphenol (3.500- 18.000 tonnes/year) fluctuate from year to year. Commercial use of nonylphenol does not exist. Octylphenol use patterns are not known but are expected to resemble the use of nonylphenol.

2. Nonylphenol ethoxylates production in Western Europe amounts to 100,000-120,000 tonnes/ year, accounting for 90% of the overall alkylphenol ethoxylates demand in the EU. Nonylphenol ethoxylates demand within the EU varies from 65,000 to 80,000 tonnes, while export of nonylphenol ethoxylates is estimated at 35,000- 45,000 tonnes/year. Octylphenol ethoxylates production is not known, but is estimated at approx. 10,000 tonnes/year.

3. Main use of nonylphenol ethoxylates is in application as surfactant and detergent, making up 90% of the total market. Main use sectors for nonylphenol ethoxylates in the EU are industrial and institutional cleaning (30%), chemical industry (25%), textile industry (10%) and leather industry (10%). The remaining use is in various commercial applications (niche markets; 25%).

4. Corresponding use sectors for nonylphenol ethoxylates in the Netherlands are chemical and paint manufacture industry (50%) and industrial cleaning (12%). Remaining use is in various commercial applications (niche markets; 38%).

5. Due to voluntary industry initiatives to phase nonylphenol ethoxylates in non-industrial applications, the overall nonylphenol ethoxylates use of the Netherlands has decreased by 73%, from 4,900 tonnes/year in 1986 to 1,300 tonnes in 1995. Overall use in Western Europe was estimated at 120,000 tonnes/year in 1986 and 68,000 in 1995, equivalent to a decrease of 43%.

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4 Emissions to aquatic environment

Because production and use of alkylphenols and alkylphenol ethoxylates is related for 90% to nonylphenol and its ethoxylates, this chapter will only describe the emissions associated with production and use of nonylphenol and nonylphenol ethoxylates.

4.1 Industrial sources

4.1.1 Production

In the Netherlands there are no production facilities for alkylphenols and alkylphenol ethoxylates (RIZA, 2000).

4.1.2 Use as an industrial intermediate

Nonylphenol

There are no nonylphenol ethoxylates producers situated in the Netherlands. Information for verification of the presence of phenolic resin polymers and oximes producers in the Netherlands was not available (RIZA, 2000). In order to obtain nevertheless an average estimate for the nonylphenol use in the Netherlands, EU figures for nonylphenol use in 1997 are extrapolated for the Netherlands situation on a comparative Gross Domestic Product (GDP) basis. The extrapolated figures for intermediate use in the industry are presented in table 4.1.

Table 4.1:
Nonylphenol use in the Netherlands (EU, 1999)

Nonylphenol use (1997) *	
Phenol / formaldehyde resin productions	1100
TNPP production	200
Catalyst in epoxy resins production	50
Total	1350

* : Extrapolated from overall use in EU

Emissions factors for the nonylphenol use as an intermediate were derived from the EU Technical Guidance Document for risk assessment (TGD). According to this document the nonylphenol release factors to wastewater is 0.01% for use in the phenol/formaldehyde resin production, 0% for use in TNPP production (due to integral incineration of wastewater) and 0.04% for use as a catalyst in epoxy resins production (EU, 1999).

For quantification of final emissions to surface water from the phenol/formaldehyde resin and epoxy resins production it is assumed that the wastewater from both industries is either treated on-site or treated in municipal wastewater treatment plants, consisting of primary (sedimentation) and secondary (active sludge) treatment. Removal rates for nonylphenol in such treatment plants is typically >90%. With a "worst case" removal rate of 90%, nonylphenol emissions to surface water from phenol/formaldehyde resin and epoxy resins production will be 11 and 2 kg/year, respectively (EU, 1999).

Nonylphenol ethoxylates

Nonylphenol ethoxylates are not used as intermediates in industrial production processes, but only as additive in the chemical and paint industry (captive use), in washing and cleaning products, and as additive in industrial and commercial products (auxiliaries).

4.2 Formulation

4.2.1 Nonylphenol

Nonylphenol is not used as a commercial product. For use as a industrial intermediate in the polymer and oximes production, formulation is not required. As such, nonylphenol formulation can be excluded as a potential emission source to the aquatic environment.

4.2.2 Nonylphenol ethoxylates

For use in industrial and institutional cleaning products and in industrial and commercial auxiliaries, nonylphenol ethoxylates need to be formulated. According to the EU risk assessment, formulation of nonylphenol ethoxylates occurs at other locations than the production and processing sites. Releases from formulation are however minor compared to releases from production (EU, 1999).

In the Netherlands, only for one application (agrochemicals) formulation activities could be identified. For other uses in the Netherlands it is unknown whether nonylphenol ethoxylates are imported as raw material and are formulated in the Netherlands, or that formulated nonylphenol ethoxylates products are imported (Westra, 1995). As a worst case for the potential emissions to the aquatic environment, it is assumed that the total Netherlands use of nonylphenol ethoxylates (ca 1500 tonnes) is formulated in the Netherlands. With an estimated emission factor of 0.003 tonne/tonne, annually some 4.5 tonnes will be released with wastewater to the sewer e.g. wastewater treatment plants. Assuming secondary treatment of these wastewaters, 90-95% of the incoming nonylphenol ethoxylates loads will be removed by biodegradation and adsorption to sewage sludge, resulting to an average release to surface water of 340 kg/year. Corresponding nonylphenol releases will be 110 kg/year to surface water and 990 kg/year to sewage sludge (EU, 1999).

4.3 Captive use and service life

In the Netherlands, it is estimated that in 1997 roughly 700 tonnes nonylphenol ethoxylates were applied in the chemical and paint industry (captive use) and some 800 tonnes were used in auxiliary and commercial products. A specification of used amounts is given in table 4.2.

Table 4.2:
NPEO use and emissions to surface water in the Netherlands (1997)

		NPEO use tonnes/y	NPEO to wastewater kg/kg	NPEO to wastewater tonnes/y	NPEO to surface water tonnes/y	as NP surface water tonnes/y
1.	Agrochemicals use	96	0.1000	-	9.6	3.4
2.	Various niche applications	236	0.9000	210	15.2	4.8
3.	Industrial cleaning	179	0.9000	160	11.5	3.6
4.	Leather processing	60	0.9000	54	3.8	1.2
5.	Metal working	52	0.9000	47	3.4	1.0
6.	Pulp and paper industry	14	1.0000	14	1.0	0.30
7.	Chemical industry	469	0.0070	3,3	0.2	0.07
8.	Paints & lacquer manufacture	235	0.0070	1,6	0.1	0.04
9.	Domestic use of paints	61	0.0200	1,2	0.1	0.03
10.	Pesticide formulation	83	0.0035	0,3	0.0	0.01
11.	Textile processing	Negligible	-	-	-	-
Total		1485	0.33	495	45.0	14.4

Sources: EU, 1999 and Westra, 1995; NPEO: nonylphenol ethoxylates: NP: nonylphenol

With respect to the use and emissions of agrochemicals it is noted that the release to surface water (10% to ditches) is caused by drift losses during spraying. For all other use, the emissions to wastewater are based on actual emission factors from the industry or from the TGD for risk assessment (EU, 1999). From table 4.2 can be concluded that, mainly due to commercial applications, about 33% of the overall nonylphenol ethoxylate use ends up in wastewater. For quantification of emissions to surface water, it is assumed that waste water from the various applications is either treated on-site or in a municipal wastewater treatment.

Typical removal rates for nonylphenol ethoxylates (NPEO) range from 90 to 95%. For calculation of the final emission to the surface water, an average value of 92.5% removal is generally used. As a consequence of biological degradation, nonylphenol ethoxylates are partly converted to nonylphenol. On average, some 25% of the incoming nonylphenol ethoxylates load is converted to nonylphenol, from which >90% is adsorbed onto sewage sludge. Correspondingly, the net nonylphenol emission factor to the surface water will be 0.025 tonne/tonne discharged NPEO. For nonylphenol release from formulated agrochemicals, the average nonylphenol content (35%) is taken.

From table 4.2 can be concluded that after wastewater treatment, some 45 tonnes (partly degraded) nonylphenol ethoxylates and 14 tonnes nonylphenol are discharged to surface water. From the specific emissions in table 4.2 can further be calculated that 97% of the overall emission load to the surface water is caused by the first six use sectors, representing only 43% of the overall nonylphenol ethoxylates use. Aqueous discharge of used products containing nonylphenol ethoxylates (service life: 35 tonnes NPEO/ year) account for 78% of the total emission load to the surfacewater. The use of agrochemicals (9.6 tonnes NPEO/year) is largely responsible for the remainder of the emissions to surface water.

Table 4.3:
NPEO use and emissions to surface water in the EU (1997)

		NPEO use	NPEO to wastewater	NPEO to wastewater	NPEO to surface water	as NP to surface water
		tonnes/y	kg/kg	tonnes/y	tonnes/y	tonnes/y
1.	Agriculture use	5000	0.1000	500	500	175
2.	Industrial&institutional cleaning	23000	0.9000	20700	1480	463
3.	Various niche applications	12300	0.9000	11070	792	247
4.	Textile processing	4800	0.8500	4080	292	91
5.	Leather processing	3100	0.9000	2790	199	62
6.	Pulp and paper industry	800	1.0000	800	57	18
7.	Metal extraction	2000	0.3160	632	45	14
8.	Domestic use of paints	3200	0.0200	64	5	1
9.	Captive use in chemical industry	7000	0.0070	49	4	1
10.	Paints and lacquer manufacture	4000	0.0050	20	1	0
Total		65200	0.6250	40705	3375	1073

Source: EU, 1999; NPEO: nonylphenol ethoxylates; NP: nonylphenol

From corresponding figures for use and emissions in the EU (table 4.3) can be concluded, that the overall nonylphenol ethoxylates release in the EU (62.5%) is significantly higher than in the Netherlands and that after wastewater treatment, on a relative basis, 70% more NPEO and nonylphenol is released to the surfacewater.

4.4 Transboundary emissions

4.4.1 Atmospheric deposition

Empirical data on the atmospheric deposition of gaseous and dust-borne nonylphenol ethoxylates and nonylphenol emissions in the Netherlands were not available. Neither is known to what extent gaseous and dust-borne emissions are susceptible to wet and dry deposition. On basis of the low volatility of these substances, it is however estimated that gaseous emissions will be insignificant.

4.4.2 Hydrological transport

Empirical data on emission levels or emission loads in rivers, entering or leaving the Netherlands were not available.

4.5 Evaluation

4.5.1 Basic production and use data

For estimation of industrial emissions of nonylphenol in the Netherlands, data about the actual nonylphenol use in the industry were not available. Based on extrapolated use figures and industrial emission factors for nonylphenol, the predicted emissions are insignificant compared to nonylphenol emission loads from service life.

Further, it should be noted that actual data about use and emission in the Netherlands of other alkylphenol ethoxylates were not available, mainly due to the fact that in most applications (ca 90%) nonylphenol ethoxylates are being used. Correspondingly, nearly all information on the use and environmental concern of alkylphenol ethoxylates is related to the use of nonylphenol ethoxylates. As rule of thumb, the use of these other alkylphenol ethoxylates may be estimated at 10%, basically consisting of octylphenol ethoxylates. For the emission factors as well as

for the behaviour in wastewater treatment, it can be assumed that the actual situation for other alkylphenol ethoxylates will be basically the same as for nonylphenol ethoxylates (EU, 1999; Leisewitz, 1997; TemaNord, 1996).

4.5.2 Emission factors

Basic use data and emission factors have been retrieved from a large series of environmental assessment studies and surveys, which are based on verified data from various industries and which are generally recognised to be representative for the industrial use. Data for the environmental behaviour in wastewater treatment are based on detailed process data, which have been confirmed in various environmental research projects (EU, 1999; Leisewitz, 1997; TemaNord, 1996).

4.6 Conclusions and recommendations

From emission estimates and wastewater treatment results for nonylphenol and nonylphenol ethoxylates, the following conclusions can be drawn with respect to release of nonylphenol and nonylphenol ethoxylates in the Netherlands and the EU:

1. Major emissions of nonylphenol and nonylphenol ethoxylates in the Netherlands and the EU are caused by discharge of used products (mainly cleaning agents and auxiliaries) to domestic and industrial wastewater.
2. In secondary (mechanical/biological) wastewater treatment, nonylphenol ethoxylates are largely removed (90-95%).
3. In biological wastewater treatment, nonylphenol ethoxylates are partially converted to nonylphenol (25% of ingoing nonylphenol ethoxylates loads). Major part of the nonylphenol produced (90%) is adsorbed onto sewage sludge, leading to a net release to surface water of 0.025 tonne /tonne of nonylphenol ethoxylates discharged.
4. Major discharge sources for nonylphenol ethoxylates to wastewater and surfacewater are use sectors that do not apply source-oriented pollution control or wastewater recovery. In the Netherlands, these use sectors represent approx. 35% of the total nonylphenol ethoxylates amount, but are responsible for 77% of the total emission load to surfacewater. The remainder of the emissions (23%) is coming from nonylphenol ethoxylates in formulated agrochemicals.

4.7 References

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5 Behaviour in the aquatic environment

5.1 Introduction

The behaviour of organic micropollutants in the aquatic environment is determined by the properties of the compound (solubility, hydrophobicity, volatility,) and by the characteristics of the water system of concern (residence time of the water, sedimentation area, organic matter content, etcetera). These compound and system specific properties also determine to what extent a compound will accumulate in organisms.

5.2 Solubility and volatilisation

The water solubility of a compound is a good indication of the extent to which this compound can be transported with water. In general poorly soluble compounds have a high affinity for silt particles in a water system. This is the reason that the compound will settle together with the sediment and suspended particles and thereby the transport along with the water stream will be slowed down. Solubility and vapour pressure further determine whether a compound will evaporate out of water. The volatility of a compound is characterised by its Henry constant.

5.2.1 Octylphenol and octylphenol ethoxylates

The solubility of octylphenol in water has been reported as 12 mg/l, from which can be concluded that octylphenol is poorly soluble in water (IUCLID, 1996). Experimental data for octylphenol ethoxylates, and their major environmental degradation products, were not available. From qualitative comparison with nonylphenol ethoxylates, it can be expected that the solubility of octylphenol ethoxylates with few ethoxylate groups (n= 1- 5) will be in the range of the solubility of octylphenol, whereas octylphenol ethoxylates with 10- 100 ethoxylate groups are shown to be completely miscible with water.

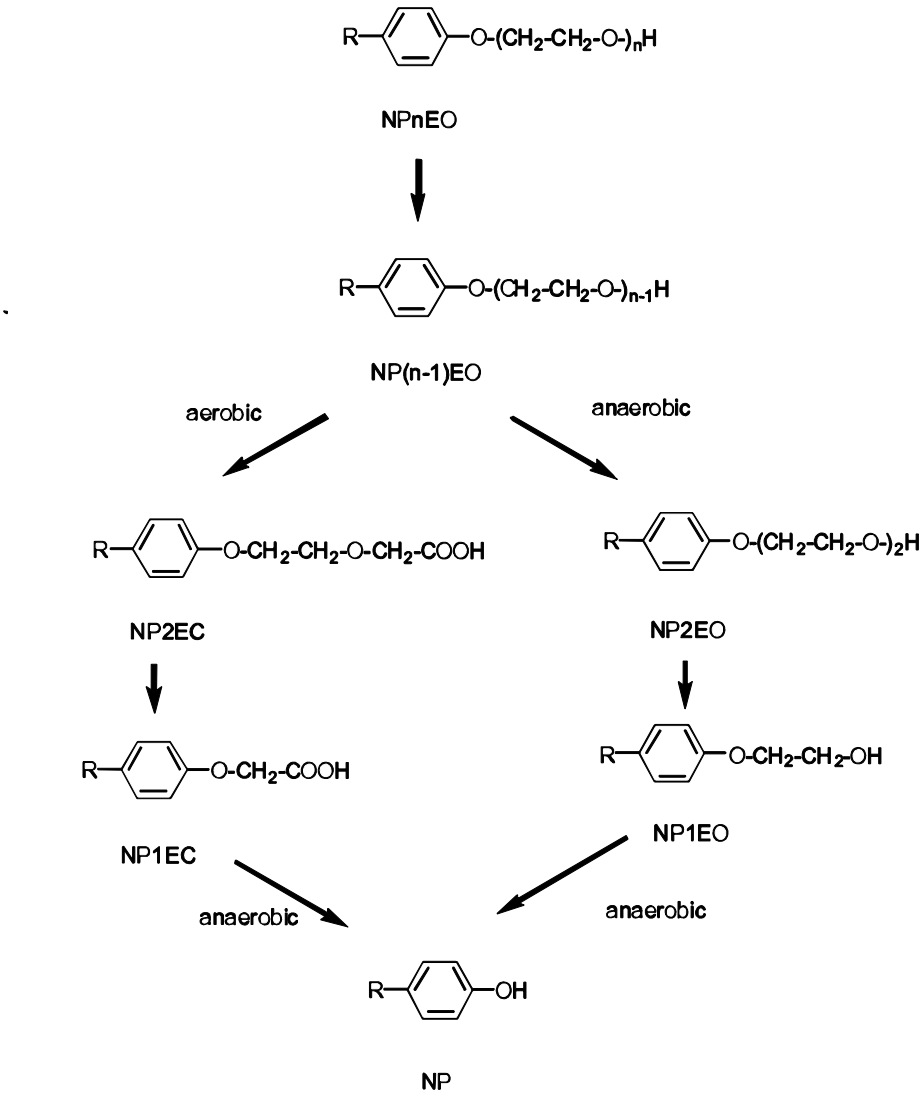
The vapour pressure of octylphenol at 20 °C was estimated as 1 Pa (IUCLID, 1996). From this value can be concluded that octylphenol will hardly be volatile. Experimental vapour pressure data for octylphenol ethoxylates were not available, due to the fact that vapour pressures of these compounds are not commonly measured. Generally it is assumed that, based on the low vapour pressure of octylphenol and the high molecular weight and good solubility of octylphenol ethoxylates, the volatility of octylphenol ethoxylates will be negligible. A summary of water solubility and vapour pressure values is given in table 5.1.

5.2.2 Nonylphenol and nonylphenol ethoxylates

The solubility of nonylphenol in water was determined as 5- 11 mg/l, which means that nonylphenol is poorly soluble in water (EU, 1999; KEMI, 1994). Solubility data for nonylphenol ethoxylates and major environmental degradation products, were not available. From qualitative information, it is assessed that nonylphenol ethoxylates with 10- 100 ethoxylate groups are completely miscible with water. Comparison of log *K*ow values (ca 4.2) for lower nonylphenol ethoxylates (n= 1- 5) with the value for nonylphenol (log *K*ow 4- 4.5) indicates that solubilities will be comparable (Ahel et al., 1994a). A review of environmental degradation products is given in figure 5.1.
For nonylphenol, vapour pressure at 20 °C is measured as 7- 10 Pa. From these values can be concluded that nonylphenol hardly will evaporate from water and

soil. Vapour pressure data for nonylphenol ethoxylates were not available. Based on the low volatility of nonylphenol and high molecular weight and good solubility of nonylphenol ethoxylates in water, vapour pressures of nonylphenol ethoxylates are expected to be low (EU, 1999; KEMI, 1994).

Figure 5.1:
Biological degradation pathways for nonylphenol ethoxylates (Ball, 1989)



NPnEO	Nonylphenol ethoxylate with n ethoxylate groups. Usually mixtures; average value for n is 9-10, within a range of 1-20
NP2EC	Carboxylic acid of NP2EO formed by oxidation of terminal hydroxyl group
NP1EC	Carboxylic acid of NP1EO formed by oxidation of terminal hydroxyl group
NP2EO	Nonylphenol diethoxylate
NP1EO	Nonylphenol monoethoxylate
NP	Nonylphenol

Table 5.1:
Solubility and volatility parameters of selected compounds

	Mole weight (g/mole)	Solubility (mg/l)	Solubility (mol/m^3)	P_{vapour} (Pa)	Henry coefficient[a] ($atm.m^3/mol$)
Octylphenol	206	12	0,061	1,0	$0,16* 10^{-3}$
Octylphenol ethoxylate	250- 4600[b]	10- high[b]	0,40-high[b]	*	*
Nonylphenol	220	5-11	0,027	7 - 10	$3,1* 10^{-3}$
Nonylphenol ethoxylate	264- 4600[b]	10- high[b]	0,40-high[b]	*	*

[a] : vapour pressure/solubility ratio; [b]: for n > 40 *: not available

5.3 Sorption

The extent of sorption of a compound strongly depends on the compound's hydrophobicity and the availability of organic matter in soil, sediment or suspended particles. The hydrophobicity of a compound is characterised by its octanol water partition coefficient (K_{ow}). To what extent the compound will adsorb onto soil, sediment or suspended solids further depends on the organic matter e.g. organic carbon content of these media.

The specific affinity of a compound can be directly related to organic carbon content by means of the K_{oc} value. For various media, the organic carbon content is known. Detailed measurements have been performed on adsorption of organic compounds onto these media. According to the TGD for risk assessment, partition coefficients of hydrophobic chemicals in organic carbon / water systems (K_{oc}) can be derived from the following equation:

$\log K_{oc} = 0.81 * \log K_{ow} + 0.10$ for $1.0 < \log K_{ow} < 7.5$

With a standard fractional organic carbon content of soil, sediment and suspended solids taken as 2, 5 and 10% respectively, specific adsorption constants (Kp) for soil, sediment and suspended sediment can be calculated directly from the K_{oc} or K_{ow} value.

5.3.1 Octylphenol and octylphenol ethoxylates

The octanol-water partitioning (log *K* ow) for octylphenol was determined as 4.1 (IUCLID, 1996). From this value can be concluded that octylphenol will preferentially be bound to suspended solids, sewage sludge, sediment and soil. Experimental log K_{ow} values for octylphenol ethoxylates and their major degradation products in the environment, OP1EO, OP2EO (octylphenol mono- and di- ethoxylate), OP1EC and OP2EC (octylphenol mono- and di-carboxylic acid) were not available.

From log K_{ow} data for nonylphenol ethoxylates, it is estimated that the solubility of octylphenol ethoxylates with few ethoxylate groups (n= 1- 5) will be low, e.g. the log *K* ow value will be in the same range as for octylphenol. The same applies for the major environmental degradation products OP1EO, OP2EO (octylphenol mono- and di-ethoxylate), OP1EC and OP2EC (octylphenol mono- and di-carboxylic acid). All these compounds will be preferentially be bound to suspended solids, sewage sludge, sediment and soil.

Octylphenol ethoxylates with 10- 100 ethoxylate groups are completely miscible with water. These compounds will hardly have any affinity for suspended solids, sewage sludge, sediment and soil. With regard to the environmental occurrence of these substances should be noted that once released in the aquatic environment, they will be largely hydrolysed e.g. converted to octylphenol ethoxylates with few ethoxylate groups (n= 1- 5).

5.3.2 Nonylphenol and nonylphenol ethoxylates

Experimental data indicate that nonylphenol is a hydrophobic compound, with a log *K*ow value of 4.48. For technical products, containing various nonylphenol isomers, log *K*ow values can vary from 3.3- 6.4 (SEPA, 1998), indicating that nonylphenol will be preferentially bound to suspended solids, sewage sludge, sediment and soil. Experimental log K_{ow} data for nonylphenol ethoxylates with high number of ethoxylate groups (10- 100) were not available. Based on their high inherent water solubility, it is expected that these compounds will hardly interact with suspended solids, sewage sludge, sediment and soil.

From log K_{ow} values for the major degradation products NP1EO and NP2EO (nonylphenol mono- and diethoxylate) in table 5.2 can be concluded that they will preferentially be sorpted onto suspended solids, sewage sludge, sediment and soil (Ahel and Giger, 1993).

Table 5.2:
Summary of calculated partition coefficients

	log K_{ow} -	log K_{oc} -	Kp-soil l/kg	Kp-sediment l/kg	Kp-susp. sed. l/kg
Octylphenol	4,10	3,42	55	135	270
Nonylphenol	4,48	3,73	110	270	540
NP1EO and NP2EO	4,17- 4,20	3,50	65	160	320

NP1EO and NP2EO : nonylphenol mono- and diethoxylate

For three surface soils, Roy F. Weston Inc (1990) determined the soil adsorption isotherm of nonylphenol. Characteristics of the tested soils are given in table 5.3. Adsorption of nonylphenol was determined by equilibrating aqueous nonylphenol solutions with a known amount of soil. At equilibrium, the distribution between the water and soil was measured and sorption constants (Kp_{soil}) were calculated using the Freundlich equation.

Table 5.3:
Soil characteristics and Kp values for nonylphenol

Parameter	Soil 1	Soil 2	Soil 3
Cation exchange capacity (meq/100 g)	28.4	46.2	24.6
Exchangeable bases (meq/100 g)	27.8	45.8	17.2
Exchangeable acids (meq/100 g)	0.6	0.4	7.4
Total organic carbon (%)	0.82	10.2	8.6
pH	7.1	7.3	6.4
Kp_{soil} (l/kg)	4 009	2 301	5 164
Kp_{soil} (calculated, TGD)	44	547	462
Koc (l/kg)	490 000	22 600	60 000

From the experimental Kp values can be concluded that nonylphenol adsorbs significantly stronger to soils than is expected on basis of the empirical TGD relation. The large difference in adsorption coefficients is probably caused by nonylphenol adsorption onto non-organic soil constituents (EU, 1999). In another nonylphenol adsorption test, a K_{oc} value of 68.000 l/kg was determined (HSDB, 2000).

Ahel et al. (1996) studied the infiltration of nonylphenol from river water into groundwater in the Glatt River region of Switzerland. Table 5.4 shows the concentration profile of nonylphenol in groundwater. Decaying nonylphenol concentrations in groundwater indicate significant nonylphenol removal along the passage through the aquifer.

Table 5.4:
Nonylphenol concentrations in groundwater

Sampling Point	Concentration (µg/l)	
	Mean	Range (n=16)
Glatt River (surfacewater)	2.7	0.7- 26
Groundwater 2.5 m from river	0.96	<0.1- 29
Groundwater 5 m from river	0.40	<0.1- 4.4
Groundwater 7 m from river	0.44	<0.1- 3.4
Groundwater 13 m from river	0.20	<0.1- 33

Ahel et al. (1994a) further reviewed levels of nonylphenol ethoxylates and their degradation products in surface water and sediments in the Glatt River. The ratio of nonylphenol concentrations in sediment and water ranged from 364 to 5100, indicating preferential association of nonylphenol to sediments. In another study, wastewater/sewage sludge partition coefficients were evaluated for nonylphenol, NP1EO and NP2EO (nonylphenol mono- and diethoxylate). Values ranged from 10500 l/kg for nonylphenol to 1800 and 900 l/kg for NP1EO and NP2EO. K_{oc} values for nonylphenol, NP1EO and NP2EO were calculated as 30000, 5200 and 2600 l/kg.

5.4 Transformations in freshwater and marine environments

5.4.1 Hydrolysis

Alkylphenols
Based upon the complete lack of biodegradation in control experiments of various laboratory studies, it is expected that hydrolysis will not play a significant role in the removal of alkylphenols in aquatic environments (Corti et al., 1995; Trocmé et al., 1988).

Alkylphenol ethoxylates
From the composition of nonylphenol ethoxylates in municipal wastewater it was calculated that 20-30 mole-% of nonylphenol ethoxylate is hydrolysed during anaerobic transport in sewers. Hydrolysis occurs exclusively via release of ethoxylate groups. Main hydrolysis products are NP1EO and NP2EO (63%) and nonylphenol (21%). The remaining 16% consist of NP1EC and NP2EC, formed by partial oxidation of NP1EO and NP2EO (Ahel, 1994).

5.4.2 Photolysis

Alkylphenols
In addition to microbial breakdown, Ahel et al. (1994b) confirmed that NP is susceptible to photochemical degradation. Using natural (filtered) lake water, it was found that under summer sun conditions, nonylphenol had a half life of approximately 10-15 hours in the top waterlayer. Conversion rates at 20-25 cm below the surface were about 1.5 times slower. Degradation products were not identified. Based on chemical analogy between nonyl- and octylphenol, it is estimated that the photochemical behaviour of octylphenol will be similar. For photochemical degradation in general, it is further mentioned that high removal rates are restricted to a small fraction of the overall surface water.

Nonylphenol released to the atmosphere is likely to be degraded by reaction with hydroxyl radicals. The rate constant for this reaction has been estimated using the AOP program (Syracuse, 1991). The estimated rate constant is 54×10^{-12} $cm^3.mol^{-1}.s^{-1}$. The pseudo first-order rate constant for degradation in air (k_{air}) can be calculated from this rate constant using the following equation:

$k_{air} = k_{OH} \times [OH]_{air} \times 24 \times 3600 = 7.0\ day^{-1}$

k_{air} Pseudo first order rate constant for degradation in air [day^{-1}]
k_{OH} Specific degradation rate constant with OH-radicals [5.4×10^{-11} $cm^3.molec^{-1}.s^{-1}$]
$[OH]_{air}$ Concentration of OH radicals in the atmosphere [15×10^5 $molec.cm^{-3}$]

From this rate constant, a half-life in the atmosphere is calculated of 0.2 days. Accordingly, nonylphenol is unlikely to be transported far through the atmosphere. Because the absorbed nonylphenol fraction on aerosol particles is also low, the potential for transport in the atmosphere is nearly zero. Additionally, nonylphenol is unlikely to move from the troposphere to the stratosphere and contribute to ozone depletion (EU, 1999).

Alkylphenol ethoxylates
From simultaneous measurements during photolysis experiments with nonylphenol, for nonylphenol ethoxylates it was found that photolysis rates were significantly

slower. Therefore it is estimated that photolysis will only a minor role in the overall removal of alkylphenol ethoxylates in aquatic environments. (Ahel et al.,1994b). Similar to the high photochemical reaction rates for nonylphenol in the atmosphere, the photolysis half-life for nonyl- and octylphenol ethoxylates in atmosphere is expected to be short.

5.4.3 Biodegradation and mineralisation

Octylphenol and octylphenol ethoxylates
Ball et al. (1989) carried out an extensive study to investigate the biodegradation of octylphenol ethoxylates (OPnEO) and octylphenol ethoxylate carboxylic acids (OPnEC) under a variety of aerobic and anaerobic conditions. OPnEO and OPnEC mixtures contained ethoxy oligomers with n ranging from 1 to 5. The following test environments were investigated:

1. OPnEO in water seeded with activated sludge from domestic wastewater treatment;
2. OPnEO and OPnEC in water incubated at 20oC with settled primary effluent from domestic waste water treatment;
3. OPnEO and OPnEC in water incubated at 35oC with anaerobic organisms, fed on a mixture of primary effluent and activated sludge.

Periodically, media were analysed for the presence of degradation products.

Results from experiments using activated sludge solids (system 1) clearly showed that OPnEO degrade to OPnEC (mainly OP2EC). The total mass balance indicates that little or no degradation to mineralised products (CO_2) was occurring in the system. Primary sludge tests (system 2) demonstrated that longer chain OPnEO (n≥ 3) degraded rapidly (within 2 days) under formation of mainly OP2EO. Primary degradation of OP1EO and OP2EO required an adaptation period of minimal 5 and 17 days respectively. Only slight oxidation of OPnEO to OPnEC occurred for OPnEO with n>3. Corresponding data for degradation of OPnEC indicate that OPnEC with n<2 are largely degraded; for OPnEC with n>2 only slight degradation occurred (EU, 1999).

Under anaerobic conditions, OPnEO was fully degraded to OP1EO within 10 days. OP1EO was subsequently converted to octylphenol (system 3). OPnEC was generally stable under anaerobic conditions, with exception of OP1EC which was rapidly degraded to octylphenol.

These results clearly show that under aerobic conditions OPnEO are transformed to relatively stable OP2EO and OPnEC (n=2-3) which are subsequently transformed to unidentified products. Under anaerobic degradation conditions, octylphenol was the major product. These results were found to be in good agreement with the environmental behaviour of nonylphenol ethoxylates in domestic wastewater treatment (EU, 1999) Lashan et al. (1966) carried out tests using 20 mg/l radiolabelled p-tert. octylphenol ethoxylate (n=10) in bench-scale activated sludge units. The compound used was ^{14}C-labelled in the ethoxylate chain and ^{3}H-labelled on the phenol ring. In shake-flask cultures, inoculated with acclimated activated sludge, >90% primary biodegradation was seen in 7 days. In bench-scale activated sludge units, operating with hydraulic retention times of either 3 or 6 hours, acclimation required 5-11 days and 90-95% primary degradation was seen.

Radiolabelling further revealed that degradation of the octylphenol ethoxylate reflected primarily the loss of ethoxylate groups, with little or no degradation of the phenolic ring. In a another experiment, radiolabelled octylphenol ethoxylate was fed into an anaerobic septic tank-percolation system for several months. The hydraulic residence time was 67 hours. The octylphenol ethoxylate showed overall

degradation of 84-93% based on loss of foaming tendency and cobalt thiocyanate analysis, with an average loss of ^{14}C of 46%. Again, no loss of aromatic ^{3}H was observed (EU, 1999).

Nonylphenol and nonylphenol ethoxylates
Below, a summarised description is given of biodegradation results for nonylphenol and nonylphenol ethoxylates in water, wastewater and soil. Detailed information on the biodegradation experiments is given in Annex 3.

Nonylphenol

A) Degradation in water

The biodegradability of nonylphenol has been determined in the modified Sturm test (EEC Directive 79/831 ENV/283/80). The experiments were carried out both with and without an emulsifier (20 mg C/l). Control experiments were conducted with sodium benzoate and with emulsifier. The control substance (sodium benzoate) achieved complete degradation within 20 days, indicating that the inoculum had sufficient biological activity. Neither nonylphenol, with or without emulsifier, nor the emulsifier itself achieved any degradation (Hüls, 1996b). In a second study, primary degradation of nonylphenol was studied in the modified Sturm test (EEC Directive 79/831 ENV/283/80) with adapted activated sludge as inoculum. In tests without emulsifier no degradation occurred within 40 days. Nonylphenol in combination with an emulsifier resulted in 78% degradation (Hüls, 1996c).

Gaffney (1976) studied the biodegradation of nine chemicals (including nonylphenol) in domestic and municipal wastewater. No degradation of nonylphenol was observed in tests with domestic wastewater. In tests with municipal wastewater, nonylphenol levels decreased by 45% in 135 hours, probably because inoculum in municipal wastewaters was already adapted to nonylphenol and a variety of other pollutants.

Two other ready biodegradation tests have been carried out with nonylphenol. The test results have been reported by Williams and Varineau (1996). In both tests, nonylphenol was of commercial grade and contained a highly branched alkyl chain. Biodegradation of nonylphenol (10 mg C/l) was by monitored of CO_2 production. Some 10% biodegradation was seen after 10 days incubation, rising to 53% by day 28.

In an OECD 301F test, nonylphenol biodegradation (31 mg/l) at 22°C was monitored by oxygen consumption (no emulsifiers were used in the test). The control substance (sodium benzoate) showed >94% degradation within 28 days. For nonylphenol 19% primary biodegradation was seen in 10 days, rising to 62% in 28 days. In all OECD tests, nonylphenol shows significant biodegradation but fails to meet the criteria for ready biodegradability (10 day window). These results lead to the conclusion of rather inherent than ready biodegradability (Williams and Varineau, 1996).

Table 5.5:
Biodegradation rates of nonylphenol in aquatic environment

Test environment	Identification	Period (days)	Removal (%)	DT-50 (days)	Reference
Sturm degradation test with Inoculated medium	CO_2	32	None	-	Huls, 1996b

Activated sludge - without emulsifier - with emulsifier	CO_2	 40 40	 None 78	 - 18	Huls, 1996c
Activated sludge from Domestic WWTP	CO_2	0-10 10-40	10 48	65 28	Williams et al., 1996c
OECD 301F test with Inoculated medium	O_2 –demand	0-10 10-28	19 53	33 20	Williams et al., 1996c
Seawater with sediment Seawater without sediment	$^{14}CO_2$	0-28 0-28 28-56	34 1,7 25	47 960 68	Ekelund et al., 1993
Primary degradation - industrial wastewater - domestic wastewater	 GC- FID / ECD	 5-6 5-6	 45 none	 6,5 -	 Gaffney 1976
Primary degradation - river water - lake water	 HPLC	 44 44	 84 85	 16,5 16,3	 Sundaram et al., 1976

Ekelund et al. (1993) studied the biodegradation of 4-nonylphenol in seawater and sediment, in which ^{14}C uniformly ring-labelled nonylphenol (containing a mixture of branched isomers) was used. The experiments were performed with filtered seawater and seawater with sieved soft bottom sediment. In absence of sediment, degradation (as $^{14}CO_2$ production) was 0.06% per day up to 28 days, and then 1% per day after 28 days, suggesting a period of adaptation. In presence of sediment the degradation rate was 1.2% per day. Increased biodegradation in sediment was attributed to the higher number of micro-organisms present. In low oxygen experiments, the reaction rate was slow. Mineralisation half-life was approx. 56 days. Low recoveries for total ^{14}C (45-64%) indicate that actual biodegradation may have been higher than based on $^{14}CO_2$ measurements.

Nonylphenol degradation in stream and pond water was studied by Sundaram and Szeto (1981) under simulated field conditions Water and sediments were taken from Northland Creek and Hargraft Lake, Ontario, Canada. Samples were analysed for nonylphenol by HPLC analysis. Half-lives for nonylphenol was found to be 16.5 days in stream water and 16.3 days in pond water. Unidentified transformation products (more polar than the parent nonylphenol) were formed and it was thought that these could be formed by microbial degradation or photo-oxidation. In pond water/sediment experiments, nonylphenol rapidly adsorbed onto sediment. The sediment phase showed a maximum nonylphenol concentration after 10 days, decreasing to only 20% of the nonylphenol added after 70 days.

B) Degradation in soil

Trocmé et al. (1988) studied the fate of nonylphenol in a simplified soil system at 100 and 1000 mg/kg and its effect on microbial activity. Nonylphenol persistence was further studied under aseptic conditions. In the 1000 mg/kg sample, CO_2 evolution was initially strongly depressed and a decrease was noted in the ATP (adenosine triphosphate) content in the 1000 mg/kg sample after 5 days. In the control and 100 mg/kg samples such effects were absent.
After 40 days, 89% nonylphenol was degraded in the 100 mg/kg sample and 62% in the 1000 mg/kg sample. In all tests, volatilisation was insignificant. Nonylphenol was more persistent under the semi-sterile conditions with only 24% degradation in 24 days, from which was concluded that nonylphenol only undergoes microbial degradation after a period of induction. Chromatographic results for nonylphenol indicated that certain isomers of nonylphenol degraded more easily than others.

Marcomini et al. (1992) studied the fate of nonylphenol in sludge amended soil. Initial concentration of nonylphenol in the soil was 4.7 mg/kg and dropped to 0.46

mg/kg dry weight after 322 days. Disappearance of nonylphenol was fast in the first two weeks followed by a slow disappearance from days 30-90. Half-lives for primary degradation were estimated as 8 days for initial degradation and 90 days for the second stage.

Kirchman et al. (1991) studied the biodegradation of 4-n-nonylphenol in soil (the substance had a straight alkyl chain rather than a branched chain, usually found in technical products). Nonylphenol degradation was tested at concentrations of 10 or 500 mg/kg and incubated in sealed flasks for 3 months. Degradation was monitored by chromatographical analysis of the parent compound and by CO_2 evolution. Parent compound analysis revealed that less than 10% remained after 10 days. Nonylphenol was not detected (<0.02 mg/kg) after 20 days. At the higher concentration tested, roughly 60% of the nonylphenolic carbon was converted to CO_2 in 94 days. In 10 mg/kg test samples, CO_2 evolution was similar to that in the controls.

Further evidence for biodegradation of nonylphenol in soil was reported in BUA (1988). In this report the results of an unpublished study were given that indicated that around 95% removal of nonylphenol occurred with partial degradation of the aromatic ring occurred after 48 days at 275 mg/kg. Giger et al. (1987) observed 80-90% nonylphenol reduction in 104 days after manure application. Reduction in the soil concentration was initially rapid.

C) Summary

From above test results can be concluded that nonylphenol undergoes significant biodegradation in water, sediment and soil. Results from standard biodegradation tests indicate that nonylphenol is rather inherently than readily biodegradable. Some deviating test results can be explained by toxicity of nonylphenol for micro-organisms at tested concentrations. Results by Corti et al. (1995) seem to support the assumption that micro-organisms exclusively grown on nonylphenol exhibit a longer lag phase than control cultures. Further it is important that micro-organisms need a period of adaptation as shown by Ekelund et al. (1993) in the degradation of nonylphenol in seawater and by Gaffney (1976) who observed enhanced biodegradation in municipal wastewaters that already contained nonylphenol and so may have been adapted (EU, 1999).
Another factor that needs to be considered is that the nonylphenol is usually a mixture of isomers with variable branching in the nonyl chain. It is known in general, that increased branching in alkyl chains causes a reduction in biodegradability and so it is expected that in technical nonylphenol, some of the components of the mixture degrade faster than others. Trocmé et al. (1988) demonstrated with intermediate chromatographic nonylphenol analyses that some nonylphenol peaks decreased faster than others. (EU, 1999).

Finally, it should be noted that nonylphenol itself contains 9 carbon atoms on the alkyl chain and 6 carbon atoms on the aromatic ring. When CO_2 evolution is used as endpoint for mineralisation, theoretically 60% CO_2 evolution would results from the alkyl chain only, without any degradation of the aromatic ring. However, there are several tests (both for nonylphenol and nonylphenol ethoxylates) using ring-labelling that clearly show that CO_2 production over 60%, indicating that the aromatic ring undergoes mineralisation to CO_2.

Nonylphenol ethoxylates

A) Biodegradation testing

An extensive literature survey was performed by the EU Risk Assessment Rapporteur on the biodegradation of nonylphenolethoxylates (NPnEO) under various environmental conditions. Most of the data refers to branched chain p-nonylphenol groups. In the research projects studied, the following classes of intermediate degradation products were identified:

NPnEO : Nonylphenol ethoxylate with n ethoxylate groups. For commercial products, usually mixtures of straight and branched oligomers, average value for n is 9-10, within a range of 1-20.

NP1EO : Nonylphenol monoethoxylate.

NP2EO : Nonylphenol diethoxylate.

NP1EC : Carboxylic acid of NP1EO formed by oxidation of the terminal hydroxyl group.

NP2EO : Carboxylic acid of NP2EO formed by oxidation of the terminal hydroxyl group.

An indicative schedule for aerobic and anaerobic degradation pathways for nonylphenol ethoxylates is given in figure 5.1.

For evaluation of the biodegradability of surfactants various standard biodegradation tests have been developed. In the OECD Screening Test, nonylphenol ethoxylates are used as sole carbon source and primary degradation is monitored with a Bismuth Active Substance (BiAS), which is used to indicate to what extent nonylphenol ethoxylate are degraded to compounds with less than 5 ethoxylate groups. The OECD Confirmatory Test is used to verify on laboratory scale the behaviour of a surfactant under domestic wastewater treatment conditions. In this test the surfactant is added to synthetic sewage and fed to a vessel containing activated sludge. The average residence time is 3 hours. The final effluent (after sedimentation) is analysed for BiAS. Nonylphenol ethoxylates have also been tested in biodegradation tests (e.g. OECD) that measure the ultimate biodegradation (Gerike, 1987). Indicative biodegradation test results are shown in table 5.6.

Table 5.6:
Results from standard biodegradation tests (Gerike, 1987)

Substance	OECD Screening (BiAS removal)	OECD Confirm. Test (BiAS removal)	Closed Bottle Test (COD removal)	Modified OECD Test (DOC removal)
NP9EO	6-78%	97%	5-10%	8-17%
Alkylphenol ethoxylates	84%	96%	29%	-

The BIAS results indicate that primary biodegradation is occurring. From the low COD and DOC removal in the closed bottle and modified OECD test it is clear that after primary degradation, refractory intermediates are being formed. Varineau and Williams (1997) recently reported however that NPnEO (n=9) showed 53-58% ultimate degradation (measured as % CO_2 generation in 28 days) in a OECD 301B ready biodegradation test.

Narkis and Schneider-Rotel (1980) further found that ozonation of NPnEO (n=10-15) prior to a modified OECD screening test increased markedly the TOC removal (62.5% TOC removal versus 22.9% TOC removal with no ozonation). Ozonation

was thought to cause changes to the aromatic ring that facilitated biodegradation. Rudling and Solyom (1974) studied degradation of several NPnEO (n=8, 10 and 14) using the OECD Screening Test (at 15 and 20°C instead of 25°C). All three compounds were found to degrade for >90% within 12 days (primary degradation). Gas chromatographic analysis indicated that after 4 days at 20°C, NP2EO was the major degradation product. NP2EO itself was degraded for 50% after 28 days. At 15°C, secondary NP2EO degradation was completely absent.

B) Removal in wastewater treatment

Various detailed field studies on aquatic behaviour of nonylphenol ethoxylates and their degradation products refer to wastewater treatment plants in Switzerland and were carried out before regulatory controls were introduced to limit the use of nonylphenol ethoxylates in domestic products. Concentrations shown below do therefore not reflect the current situation in Europe, but the results are still useful for evaluation of the overall behaviour of nonylphenol ethoxylates during wastewater treatment.

Formation of nonylphenol during anaerobic sludge digestion in Switzerland was studied by Giger et al. (1984). Levels of nonylphenol in 30 anaerobically digested sewage sludges were in the range 450-2500 mg/kg dry weight (mean 1.01 g/kg dry weight). In sewage treatment plants, primary and secondary sedimentation sludges showed much lower levels of nonylphenol (90-150 and 40-140 mg/kg dry weight, respectively). Levels were also lower in aerobically stabilised sewage sludge (80-500 mg/kg dry weight; mean: 280 mg/kg dry weight). In anaerobic digestion primary and secondary sludges, a 4-8 fold increase in nonylphenol content was observed.

Brenner et al. (1988) studied the fluxes of nonylphenol, nonylphenol mono- and diethoxylate (NP1EO and NP2EO) in sewage treatment plants in Switzerland, focusing on the digestion/ stabilisation of the sewage sludge. High levels of nonylphenol (640-2200 mg/kg dry weight) were found in samples of anaerobically digested sewage sludge. Significantly lower levels of nonylphenol were found in samples of aerobically stabilised sludge (mean 300 mg/kg dry weight). Both NP1EO and NP2EO were thought to be precursors of nonylphenol. Based on detailed measurements at one plant, it was estimated that 50% on a molar basis of the total NPnEO entering into the plant was converted to nonylphenol in final sewage sludge.

Ahel et al. (1994c) reported results from surveys of 11 mechanical-biological wastewater treatment plants in the highly urbanised Glatt Valley, Switzerland. Wastewater treatment plants typically consisted of a primary clarifier, aeration tank and secondary clarifier for biological treatment. Sewage sludge was treated in an anaerobic digester. Main components in untreated sewage and primary effluent were NPnEO (n=3-20) which accounted for 82.4% of the nonylphenol derivatives present, followed by NP1EO/NP2EO (11.5%), NP1EC + NP2EC (nonylphenol mono- and dicarboxylic acid) (3.1%) and nonylphenol (3%). In secondary effluent, composition of nonylphenol compounds changed markedly. NP1EC and NP2EC were predominant (46.1%), followed by NP1EO + NP2EO (21.8%) and nonylphenol (3.9%). NPnEO were only present in traces.

Overall removal of NPnEO (n>2) was around 92%. On basis of overall mass balances of secondary treatment, it was shown that approximately 37% of the

ingoing NpnEO loads were degraded and that nonylphenol compounds were released to the environment in the following composition:

- 8% as untransformed NPnEO
- 11% as NP1EO and NP2EO
- 19% as NPnEC
- 25% as nonylphenol (of which >90% is adsorbed onto digested sewage sludge).

Most of the nonylphenol was found to be formed during anaerobic sludge digestion.

Di Corcia et al. (1994) studied the behaviour of nonylphenol and its ethoxylates in a mechanical/ biological wastewater treatment plant in Italy over a period of 1 year. Mean removal of nonylphenol ethoxylate was 94.3%. Nonylphenol concentrations in influent and effluent indicate that the removal was around 93%, mainly by adsorption onto sludge.

Results for nonylphenol ethoxylates in sewage treatment plants in the United States show that removal of nonylphenol ethoxylate was generally >92%. (Naylor et al., 1992). Nonyl phenol was found in digested sludge at levels of 1,800-2,800 mg/kg (see table 5.7).

Table 5.7:
Removal of nonylphenol ethoxylates in wastewater treatment in the United States

Location	NPnEO source	Period	Nonylphenol ethoxylate (µg/l)		
			Influent	Effluent	Removal
South-eastern United States	Textile/furniture	May 1988	1780	103	94.1 %
	Domestic sewage	May 1988	2400	71	97.0 %
Midwest United States	Domestic wastewater and Detergent manufacture	August 1990 March 1991	1540 1130	43 85	97.2 % 92.5 %
Northwest United States	Wood pulp mill 1	June 1990	4700-12200	170- 250	97.5 %
	Wood pulp mill 2	September 1989	13400	2170	84.3 %

Measurements of nonylphenol concentrations in other sewage sludge from the United States showed also an increase in the nonylphenol concentration during anaerobic digestion. At 4 treatment works, levels of nonylphenol were measured in ingoing sludges and at the outlet of the anaerobic digester. Ingoing levels were 21-64, 3, 180 and 960 mg/kg. After digestion, levels were 380, 1030, 940 and 540 mg/kg respectively. Levels of nonylphenol in aerobic sludges at 5 other treatment plants were 1-175 mg/kg (Williams and Varineau, 1996).

From the results above can be concluded that primary biodegradation of nonylphenol ethoxylates appears to occur rapidly under wastewater treatment conditions, especially with acclimated microorganisms. The first degradation step for NPnEO (n>3) is rapid hydrolysis of ethoxylate groups to form NP1EO and NP2EO. Once formed, these compounds are partially oxidised to NP1EC and NP2EC. Under anaerobic conditions, however, NP1EO and NP2EO are preferentially converted to nonylphenol. A summary of the relevant degradation behaviour during wastewater treatment is shown in table 5.8.

Table 5.8:
Fate of nonylphenol ethoxylates in wastewater treatment

NPnEO	Type of test	Results	Reference

n=9	Coupled Units test	48.6% DOC removal; 97% primary degradation (OECD test)	Gerike (1987)
n=9	Semi-continuous Activated sludge test	Overall 93% removal of the NPnEO; 26% in effluent as NPnEC; 20.8% was mineralised to CO_2; 23.1% highly degraded metabolites; Nonylphenol formation 4.5% of NPnEO	Varineau (1996a)
n=8, 10, 14, 16, and 30	Lab-scale activated sludge system	82-96% removal of the original surfactant	Rudling (1974)
n=9	Lab-scale bioreactors at sewage treatment plant, United States	>95% NPnEO removal; 35-50% as NPnEO/NPnEC	Kravetz (1982).
Influent	Sewage treatment plants, Switzerland	50 mole % of the NPnEO was estimated to form nonylphenol in anaerobic digestion.	Brenner (1987)
Influent	Sewage treatment plants, Switzerland	Overall NPnEO (n>2) removal: 92%. 19% in effluent as NPnEC 11% in effluent as NP1EO + NP2EO 22.5% as nonylphenol, adsorbed onto digested sludge < 2.5% in effluent as nonylphenol 8% released untransformed	Ahel (1994c)
Influent	Sewage treatment plants in the United States	>92% removal of the original surfactant	Naylor (1992); Kubeck and Naylor (1990).

NPnEO : Nonylphenol ethoxylates
NPnEC: Nonylphenol carboxylic acids
NP1EO/NP2EO: Nonylphenol mono/diethoxylate

On basis of overall wastewater treatment results, the average mass balance for nonylphenol ethoxylates in mechanical/biological wastewater treatment was calculated (see table 5.9).

Table 5.9:
Nonylphenol ethoxylates mass balances in wastewater treatment

	%-weight	%-mole
Removal from wastewater		
Mineralised to CO_2	45	13
Adsorption onto sludge	19.5	40
Released to surfacewater		
NP1EC / NP2EC (nonylphenol mono- and dicarboxylic acid)	17	23
NP1EO / NP2EO (nonylphenol mono- and diethoxylate)	8	11
Nonylphenol	2.5	5.1
NPnEO (n>2) (nonylphenol ethoxylates)	8	8

As shown above, NPnEO is removed in secondary wastewater treatment by 92 %, but other short chain nonylphenol ethoxylates and carboxylic acids (NP1EO, NP2EO, NPnEC) can still undergo degradation after discharge. Anaerobic degradation of these compounds can potentially lead to a 8-fold increase of the released nonylphenol loads. Information from river die-away tests and soil tests however indicate that nonylphenol was found to be a minor degradation product from these compounds (EU, 1999). Accordingly, it is assumed that the release NPnEO to the sewage treatment plants , will result in nonylphenol emissions equal to 2.5 weight-% of the ingoing NPnEO loads. The complete mineralisation of NP1EO, NP2EO, NPnEO, and NPnEC is likely to have a half-life, of 100 days in surfacewater and 30 days in sediment.

C) Biodegradation in surfacewater

Degradation behaviour of NPnEO similar to that in anaerobic digesters was also observed in the Glatt River, Switzerland (Ahel et al., 1994c). Main input of nonylphenol compounds into the river was thought to come from secondary effluents from municipal wastewater treatment plants. From 1983 to 1986, daily composite samples were collected from several parts of the river and from secondary wastewater treatment effluent along the river. Most abundant compounds were NP1EC and NP2EC (carboxylic acids), followed by NP1EO and NP2EO, nonylphenol and finally NPnEO (n>3). The hydraulic residence time of the river was 10-15 hours. From overall mass balances it was found that:

- 85% of the NPnEO (n>3);
- 70% of the NP1EO and NP2EO and
- 62% of the nonylphenol

were eliminated by biodegradation and/or adsorption to sediment. Further, a 27% increase in NP1EC and NP2EC was observed. Nonylphenol was the major component in sediment.

The degradation of ^{14}C ring-labelled NPnEO (average n=9) has been studied in river die-away tests. The river water for the tests was from the Missouri River, several miles downstream from a wastewater treatment plant. The water was spiked with 1% of secondary effluent from a domestic wastewater treatment plant to ensure sufficient adaptation to NPnEO (bacterial activity was similar to that in the Missouri River ($1\text{-}10\times10^4$ cfu/ml)).

For the die-away tests, samples of the water were spiked with 200 µg/l of the ^{14}C-labelled NPnEO and were incubated at 20°C with slow stirring and a gentle airflow over the surface. Primary degradation (defined as degradation into species not identifiable as nonylphenol and NPnEO) was monitored and 89% primary degradation occurred after 28 days and 96% after 128 days. At the end of the

experiment (128 days) >95% of the original NPnEC was converted. Ultimate biodegradation (conversion to $^{14}CO_2$) measurements indicated that some 50% of the ^{14}C-labelled nonylphenol was converted to $^{14}CO_2$ in the first 60 days of the test, with an additional 10% nonylphenol conversion to $^{14}CO_2$ in days 60-128. The reduced rate of mineralisation during the second half of the experiment is probably due to a loss of biomass viability (Varineau et al., 1996b and CMA, 1997).

Aerobic biodegradation of a ^{14}C ring-labelled nonylphenol 9-mole ethoxylate (^{14}C-NPE9) was also examined in laboratory semi-continuous activated sludge (SCAS) and river water environments (Naylor et al., 1998). In the SCAS experiments, primary effluent from a local wastewater treatment plant was dosed with ^{14}C NPE (n = 9), and levels of ^{14}C in clarified effluent, settled sludge solids, and CO2 were monitored. A significant portion of the ^{14}C consisted of soluble metabolites that degraded beyond the phenol ring. Dosing of the SCAS system ended after 29 days. Dissipation of residual radioactivity was followed for another 19 days. CO2 evolution and decline of radioactivity in the sludge solids both followed first order rate kinetics, with half-lives of 2.8 days and 5.8 days, respectively. In a river die-away experiment, the $^{14}CO2$ evolution from river water dosed with ^{14}C NPE was monitored for 128 days. After an induction period of 21 days, $^{14}CO2$ evolution followed first order kinetics; half-life was 22 days. It was shown that the NPE phenolic ring is mineralized under activated sludge and die-away conditions (Naylor et al., 1998).

In brackish and saline water, the degradation of a NPnEO (n=10, range 1-18) was studied using a static die-away method. The water was collected from Šibenik Harbour which receives a significant amount of municipal wastewater (nonylphenol ethoxylates emission was estimated at 5 tonnes/year). The water in the harbour is highly stratified with a brackish layer overlaying the saline layer. Both water types were collected in March, September, October and November. Die-away tests were carried out at seasonal temperatures, ranging from 13°C in March to 22.5°C in September. Water samples (0.1 or 1 mg/l) were incubated in the dark. The disappearance of the total nonylphenol ethoxylates in the samples were found to occur faster in brackish water than in saline water. This was thought to be due to higher adaptation of the brackish water to NPnEO compared to the saline layer.

The half-life for disappearance of the NPnEO was found to be longer in winter (> 1 month at 13°C) than in summer (2.5-4 days in brackish and 14-35 days in saline water respectively). Changes in oligomer distribution of the parent NPnEO was also investigated. NPnEO was found to be relatively unchanged during the first 3 days incubation. After 8 days there was a clear shift from higher oligomers (all NPnEO with n>5 had disappeared) to lower oligomers (increase in NPnEO with n<4, with the biggest increase in NP2EO). NP2EO subsequently degraded at a slower rate than seen for the higher oligomers, with low residual amounts of NP2EO after 30 days. Nonylphenol was absent in all cultures (Kveštak and Ahel, 1995).

D) Degradation in soil

The degradation of nonylphenol ethoxylates in soil was examined by Küchler et al. (1994). Over a period of one year, 10 land compartments were treated with two types of sewage sludges or sanitary effluent containing nonylphenol ethoxylate and nonylphenol. The sewage sludge was mixed into the top 5 cm of the soil. Soil

samples from various depths (0-10, 10-20 and 20-30 cm) were analysed for presence of nonylphenol and nonylphenol ethoxylates. Nonylphenol ethoxylate levels decreased rapidly in time, with no compound being detected after 20 days. No leaching of nonylphenol ethoxylate was seen from the 0-10 cm layer, indicating that removal was fully by biodegradation. In the first 10 days, nonylphenol levels increased, indicating that it was formed by degradation of nonylphenol ethoxylate. After 20 days however, no nonylphenol was detected, indicating that it had been degraded.

The biodegradation of nonylphenol ethoxylate and a commercial spray adjuvant containing 76% nonylphenol ethoxylate in soil was studied in lab-scale tests. The system consisted of flasks with 50 g of dry soil, to which 10 mg (as carbon) test substance in solution was added. The flasks were incubated in the dark at 22±3°C for 64 days. Mineralisation to CO_2 was compared to controls. In some instances, parent compound analysis was carried out. After 64 days, 57% of the nonylphenol ethoxylates and 64% of the adjuvant had degraded to CO_2. Samples on day 63 showed that no compound containing an aromatic ring or ethoxylate chain was present in the soil, indicating that significant mineralisation had occurred.

5.5 Bioconcentration

Bioconcentration is the process in which micro contaminants are taken up by organisms. The contaminant is concentrated to higher internal concentrations in case it is not metabolised by the organism as compared to the case that it is metabolised. Bioconcentration is considered to be a partition process between water and organisms and comparable with for example sorption and octanol-water partitioning. Bioconcentration of compounds in aquatic organisms can occur through uptake of compounds directly from the water (bioaccumulation) or through food (biomagnification). Bioaccumulation can be measured in different ways. Organisms can be exposed to water with contaminants until equilibrium is attained (internal contents do not increase anymore). The bioconcentration factor (BCF) can be calculated from the ratio between the content in organisms and water: BCF = $C_{organism}$ / C_{water}. The BCF can be expressed on dry weight, lipid weight and wet weight basis.

5.5.1 Octylphenol and octylphenol ethoxylates

From data searches and literature reviews it was established that all bioconcentration data were related to nonylphenol and nonylphenol ethoxylates. Based on the chemical similarities between the environmental behaviour of octyl- and nonylphenolic compounds, bioconcentration data for nonylphenol and nonylphenol ethoxylates compounds are expected to be representative for octylphenol and octylphenol ethoxylates.

5.5.2 Nonylphenol and nonylphenol ethoxylates

Nonylphenol

Ahel et al. (1993) studied the bioaccumulation potential of nonylphenol in freshwater biota in the Glatt river and one of its tributaries, the Chriesbach, in Switzerland. Samples of microphytic algae were collected in the summer and autumn and quantified by HPLC, with a detection limit of 0.03 mg/kg dry weight. Nonylphenol concentrations in *Cladophora glomerata, Fontinalis antipyretica* and *Potamogeton crispus* were 38, 4.2 and 2.5 mg/kg dry weight respectively. The

average concentration of nonylphenol in the river was 3.9 µg/l. Concentrations of nonylphenol in *Cladophora glomerata* were found to vary depending upon location and season with higher concentrations being observed in summer than autumn and nearer to the sewage outfall. BCFs values varied between 6600-7700 l/kg dry weight.

Fish samples collected in the Glatt river contained nonylphenol concentrations organs up to 1.6 mg/kg dry weight (see table 5.10). Average concentration of nonylphenol in the river was 3.9 µg/l. Based on average concentrations of nonylphenol in water, BCF in fish was calculated as 13-408 l/kg dry weight for individual organs (Ahel et al., 1993).

Table 5.10:
Nonylphenol bioconcentration factor in fish (l/kg dry weight)

Organs	Squalius cephalus	Barbus barbus L	Oncorhynshus mykiss
- muscle	45	100	38
- gut	120 – 300	13	410
- liver	250 – 350	250	-
- gills	250 - 350	< 10	-

Granmo et al. (1991) studied the bioaccumulation of nonylphenol in field tests using caged mussels (*Mytilus edulis*). The mussels were exposed to nonylphenol near to a wastewater outlet from a chemical plant producing surfactants between August and October 1984. The measured BCFs found were around 340 on a fresh weight basis, with highest concentrations near the outfall. A much lower BCF of 10 has been measured in mussel by McLeese et al. (1980a). In this experiment, mussels were exposed to a pesticide formulation, reportedly containing around 50% nonylphenol and the uptake (over 4 days) and excretion (over 8 days) was determined. Excretion from the organism was rapid (half-life of 0.3 days).
Lewis and Lech (1996) studied uptake, disposition, and persistence of nonylphenol from water in rainbow trout (*Oncorhynchus mykiss*). Juvenile fish (40-60g) were exposed under static conditions to 36 µg/l ^{14}C-nonylphenol. ^{14}C-nonylphenol was detected in the following tissues in descending concentrations: bile, liver, kidney, fat, gill, heart, muscle. Bioconcentration of ^{14}C-nonylphenol was determined by static exposure to 18 µg/l ^{14}C-nonylphenol for 24 hours. The bioconcentration factor for the viscera was 110 (after 24 hours). Depuration half-lives from fat, muscles and livers were 20, 18.6 and 5.9 hours respectively.

Table 5.11:
Bioconcentration factors of nonylphenol in freshwater biota

Organism	BCF (l/kg)	Conc.(µg/l)/ duration / type	Reference
Algae			
Cladophora glomerata	6600-7700 (dw)	3.9 / - / - (25 mg/kg dw)	Ahel, et al., 1993 in Warhurst, 1995 and in HSDB, 2000
Mollusc			
Mytilus edulis	280-400 (ww)	40 / 50 d / -	Granmo, et al., 1990 in HSDB, 2000
Mytilus edulis	10		McLeese, et al., 1980 (1864)*
Fish			
Squalius cephalus	358	3.9 /-/- (1.4 mg/kg dw in liver)	Ahel, et al., 1993 in Warhurst, 1995
Onchorhynchus mykiss	110.09 (ww)	18 / 1d / Static	Lewis, et al., 1996 in AQUIRE
Lepomis macrochirus	192- 332 (ww) 220 (ww)	14 / 14d / Static 28 / 28d / Static	Brooke (1993) in EU, 1999
Pimephales promelas	313- 859 535- 947	9- 193 / 14d / Static 6- 126 / 28d / Static	Brooke (1993) in EU, 1999
Pimephales promelas	271 (ww) 344 (ww)	4.9 mg/l 20 d / flow through (uptake rate = 133 ml/g w-d; depuration rate = 0.49/d) 22.7 mg/l 20 d / flow through (uptake rate = 193 ml/g w-d; depuration rate = 0.56/d)	Ward and Boeri (1991) in EU, 1999

* in Verschueren, 1983 ww: wet weight dw: dry weight

Brooke (1993b) determined bioconcentration factors for fathead minnow (*Pimephales promelas*) and bluegills (*Lepomis macrochirus*) over 28 days exposure to 5 concentrations of nonylphenol. For fathead minnows exposed to concentrations of 9, 19, 38, 78 and 193 µg/l, mean BCF value were 586±273 after 14 days and 741±206 after 28 days (wet weight basis). The BCF was found to be independent of concentration at 28 days but not after 14 days. Reduced growth was seen at the two highest concentrations tested.

For bluegill exposed to concentrations of 5.6, 12.4, 27.6, 59 and 126 µg/l, the mean BCF was 262±70 after 14 days and 220 after 28 days (wet weight basis). The BCF value was found to be independent of exposure at the three lowest concentrations. The BCF at the two higher concentrations were lower, particularly at 14 days, than the values obtained at lower concentrations.

The bioconcentration of nonylphenol in the fathead minnow (*Pimephales promelas*) has also been studied by Ward and Boeri (1991). Fathead minnow (0.5-1 g wt) were exposed to nominal concentrations of 5 and 25 µg/l nonylphenol in an intermittent flow-through system for 20 days. The exposure period was followed by 7 days depuration. The system was monitored for nonylphenol, dissolved oxygen content, temperature and pH. Levels of nonylphenol were 4.9 µg/l and 22.7 µg/l respectively. Acetone was added to increase the solubility of nonylphenol in the water. Samples were extracted with hexane and quantified by HPLC. The concentration of nonylphenol in tissues increased from background concentrations to steady state concentrations during the first 3-10 days of exposure.

Uptake and depuration of nonylphenol appeared to be independent of the concentration of the test substance in water. After 20 day exposure to 4.9 µg/l, the BCF was 271 l/kg fresh weight with an uptake rate constant of 133 day^{-1} and a depuration rate constant of 0.49 day^{-1}. Exposure to 22.7 µg/l nonylphenol for 20

days resulted in a BCF of 344 l/kg fresh weight with an uptake rate constant of 193 day^{-1} and depuration rate constant of 0.56 day^{-1}. Analysis of viscera and carcass collected on the last day indicated that nonylphenol concentration in the viscera was 1.6 to 7.1 times the concentration in the carcass.

Ekelund et al. (1990) studied the bioaccumulation of ^{14}C-labelled p-nonylphenol in marine animals. ^{14}C- labelled p-nonylphenol was synthesised from uniformly labelled phenol and unlabelled nonene for use in the bioaccumulation studies. Acetone (20 mg/l) was used as a solvent for the nonylphenol added to the seawater. Three marine species were used:

- common mussel (*Mytilus edulis* L.);
- common shrimp (*Crangon crangon* L.) and
- three spined stickleback (*Gasterostrus aculeatus* L.)

All animals were exposed to the ^{14}C-nonylphenol in flow-through systems. The flow through each tank was approximately 85 ml/min. Each tank contained 10 ltr water and 110 animals (60 g soft tissue mussels, 45 g shrimps and 85 g sticklebacks respectively). Nonylphenol concentrations in the test ranged from 4.9-6.4 µg/l. Exposure was for 16 days followed by an elimination period of 32 days. Samples were taken at regular intervals throughout the experiment, and stored at -20^{0}C for analysis. For shrimp and fish it was found that steady state bioaccumulation had been reached by the end of the exposure period, whereas for mussel steady state had not been achieved by 16 days. Nonylphenol concentrations in individual tissues and BCF values on wet weight and fat basis are given in table 5.12.

Table 5.12:
Nonylphenol accumulation in marine biota

	Nonylphenol (µg/kg wet weight)	BCF (l/kg wet weight)	BCF (l/kg fat)
Mussel (Mytilus edulis L.)	16260 - 25600	2740 - 4120	169300 - 216600
Shrimp (Crangon crangon L.)	670 - 680	90 - 110	7500
Stickleback (Gasterostrus aculeatus)	5730 - 6300	1200 - 1300	16700 - 17800

Elimination of nonylphenol was observed to be rapid from fish. For mussels a significant proportion of the nonylphenol in mussel tissue remained after the 30 day elimination period. Since the BCFs are based on total ^{14}C measurements, the presence of metabolites may have led to an overestimate of the accumulation of nonylphenol seen, particularly for fish. However for mussels, TLC analysis after 4, 8 and 16 days exposure showed that >80% of the radioactivity present co-chromatographed with nonylphenol (BCF corrected for this would be 2190-3300 on a wet weight basis).

Table 5.13:
Bioconcentration factors of nonylphenol in marine biota (on wet weight basis)

Organism	BCF (l/kg)	Conc.(µg/l)/ duration / type	Reference
Mollusc			
Mytilus edulis	1.4 7.9 7.9 8.5 9 11 12 13	1130 / 4d / Static 1130 / 2d Static 100 / 4d Static 1130 / 2d / Static 100 / 1d / Static 1130 / 1d / Static 1130 / 1d / Static 100 / 2d / Static	McLeese, et al., 1980 in AQUIRE
Fish			
Salmo salar	75 190 235	170 / 4d renewal 250 / 2d / renewal 310 / 1d renewal (54.91 mg/kg ww in org.)	McLeese, et al., 1981 in AQUIRE

* in Verschueren, 1983

The bioconcentration of nonylphenol in juvenile Atlantic salmon (*Salmo salar*) was studied by McLeese et al. (1981) over 4 days exposure. The uptake rate constant was measured to be 45 day^{-1} and the excretion rate constant was 0.16 day^{-1}, giving a wet weight bioconcentration factor of around 280. The excretion half-life was estimated to be around 4 days.

Nonylphenol concentrations in duck organs from the Glatt river area contained up to 1.2 mg/kg dry weight. Biomagnification factor in duck was calculated as 26 - 308 l/kg dry weight for the individual organs (see table 5.14 ; Ahel et al., 1993).

Table 5.14:
Nonylphenol accumulation in duck

Anas boscas	mg/kg dry wght	BAF (l/kg)
- muscle	1.20	308
- gut	0.54	138
- liver	0.10	26
- stomach	0.24	62

From the data reviewed, it is clear that nonylphenol bioconcentrates to a significant extent in aquatic species, with BCFs (fresh weight basis) of around 2,000-3,000 l/kg in mussels and up to 1,300 l/kg in fish. The latter value for fish may overestimate the BCF, because most values were measured within a range of 200-600 l/kg. Lower concentrations in fish than in algae further indicate that little bio-accumulation through the food chain occurs.

In a Danish EPA report bioaccumulation in plants was reviewed. It was observed that background concentrations of nonylphenol in spring barley grains (10.1 µ g/kg) did not increase after the soil was contaminated with nonylphenol (12.5 mg/kg). No increase in 3 plant species (clover, wheat and potatoes) was found upon application of nonylphenol containing sludge. Nonylphenol content in grains did not increase when sludge contaminated with 2.5 g nonylphenol/kg (dry weight) was applied (EU, 1999).

Nonylphenol ethoxylates

Table 5.15 shows the approximate bioconcentration factors of NPnEO that were calculated for various biota by Ahel et al. (1993). He studied the bioconcentration of nonylphenol and nonylphenol ethoxylates in mussels incubated in lake water 1 km downstream from a waste water treatment plant. The treatment plant received wastewater containing a high level of nonylphenol ethoxylate surfactants. In higher organisms, bioconcentration may include biomagnification through the food chain and uptake of sediment, usually containing higher levels than in the water. In addition, there may also be metabolism within the organism, for example of NP2EO to NP1EO and NP1EO to NP respectively.

Table 5.15:
Bioconcentration and biomagnification factors of nonylphenol ethoxylates

Organism	BCF (l/kg dry)	Concentration	Reference
Algae			
Cladophora glomerata	3500-5000 (80 mg/kg dw)	23 µg/l NP1EO	Ahel, et al., 1993 in Warhurst, 1995
Cladophora glomerata	1000-1800 (29 mg/kg dw)	9.4 µg/l NP2EO	Ahel, et al., 1993 in Warhurst, 1995
Fish			
Squalius cephalus	78 (1.8 mg/kg dw)	23 µg/l NP1EO	Ahel, et al., 1993 in Warhurst, 1995
Squalius cephalus	149 (1.4 mg/kg dw)	9.4 µg/l NP2EO	Ahel, et al., 1993 in Warhurst, 1995
Birds			
Anas boscas	91 (2.1 mg/kg dw)	23 µg/l NP1EO	Ahel, et al., 1993 in Warhurst, 1995
Anas boscas	37 (0.35 mg/kg dw)	9.4 µg/l NP2EO	Ahel, et al., 1993 in Warhurst, 1995
Anas boscas	7 (0.16 mg/kg dw)	23 µg/l NP2EO	Ahel, et al., 1993 in Warhurst, 1995

NP1EO : Nonylphenol monoethoxylate
NP2EO : Nonylphenol diethoxylate

The bioconcentration factor of nonylphenol in mussels was calculated as 2000 on a dry weight basis. BCF values for NP1EO and NP2EO observed in *Cladophora glomerata* (3500- 5000 and 1000- 1800 l/kg respectively) indicate that the tendency to accumulate in algae is high and that their BCF values are in the same range as for nonylphenol (6600- 7700 l/kg). Further can be established that NP1EO accumulates more strongly than NP2EO, which is caused by to the higher hydrophobicity of NP1EO.

5.6 Distribution in water systems

The behaviour of a substance and its distribution in the environment is primarily governed by properties such as solubility in water, volatility and biodegradability. To what extent these properties are favoured or hindered, depends further on the environmental conditions. The influence of environmental circumstances on the substance's behaviour, can be simulated through modelling of the relevant mass transfer processes. Two modelling programmes, EPIWIN from the Syracuse Research Corporation and EUSES from the EU, have been used to compute the volatilisation from surface water and the substance distribution over air, water and sewage sludge during wastewater treatment.

With the EPIWIN estimation program it is possible to estimate environmental properties from the compound's chemical structure (chemical bond estimation method). Computed values are subsequently used to calculate basic emission

distributions between water, air and soil, or the (a)biotic degradation in water and atmosphere. For compounds without experimental data for relevant environmental properties, this estimation method can provide a first indication of the required properties and behaviour in the environment. However, calibrations computations for compounds with reliable data show that sometimes computed values for K_{ow}, K_{oc} and Henry's Law coefficient significantly differ from experimental values and that accordingly, emission distributions will deviate substantially from results obtained with experimental data. EUSES (EU System for Estimation of Substances; developed by RIVM and extensively used in EU Risk Assessments) is a multi-functional, modelling programme for estimation of emission factors and emission distributions from industrial pollution sources. It contains various emissions scenarios and large databases with relevant technical data about emission sources, operating characteristics of wastewater treatment plants, meteorological data, etc.

For the selected compounds, the environmental behaviour in lakes, rivers and wastewater treatment plants was quantified. Furthermore, a theoretical half-life value was computed for atmospheric photolysis in order to obtain an indication of the persistence of compound after it is released into the atmosphere. Basic conditions for volatilisation from river and lake are given in table 5.16.

Table 5.16:
Basic parameters for volatilisation (EPIWIN)

	River	Lake
Water depth (m)	1	1
Wind velocity (m/s)	3	0.5
Water current velocity (m/s)	1	0.05

For computation of the emission distribution during wastewater treatment, an activated sludge plant was chosen with a regular set-up consisting of primary sedimentation, aeration and secondary sedimentation. Under these conditions, the biodegradability of the selected compounds was assumed to be negligible.

The modelling results are summarised in table 5.17. From the volatilisation results for river and lake, it shows that compounds with high Henry's Law coefficients such as octyl- en nonylphenol are rapidly removed from surface waters. Lower nonylphenol ethoxylates (NP1EO and NP2EO) and nonylphenol diethoxycarboxylic acid (NP2EC) are not volatile. Half life values for reaction with hydroxyl radicals indicate that all compounds are readily degraded in atmosphere. From removal results in wastewater treatment plants can be concluded that octyl- en nonylphenol are partially stripped to air. Further it shows that emissions to surface water (via effluent) increase with descending log K_{oc}-value.

Table 5.17:
Results of EPIWIN and EUSES estimation programmes for environmental distribution of selected brominated compounds

Property	Octylphenol	Nonylphenol	NP1EO	NP2EO	NP2EC
Log Kow (measured)	4.10	4.49	4.21	4.12	-
Log Koc (measured)	3.42	4.63	3.71	3.41	3.16
H (estimated) (atm m^3/mole)	$0.16.10^{-3}$	$3.1.10^{-3}$	negligible	negligible	negligible
Volatilisation half-life from river	0.5 days	0.2 days	48 days	66 yrs	65 yrs
Volatilisation half-life from lake	7.9 days	6.1 days	350 days	480 yrs	470 yrs
Half-life for reaction with hydroxyl radicals	2.6 hrs	2.5 hrs	2.7 hrs	2.1 hrs	2.3 hrs
Removal in WWTP (%)					
To effluent	59.7	10.5	62	76	85
To sludge	23.2	67.9	38	24	15
To air	17.1	21.6	0	0	0

H: Henry's law constant; WWTP: Wastewater Treatment Plant; TGD: Technical Guidance Document

5.7 Conclusions and recommendations

With respect to the environmental properties and behaviour in aquatic systems and soil the following conclusions can be drawn for the selected compounds:

1. On basis of log K_{ow}-values of the selected compounds (4.0- 4.5), it is assessed that octyl- and nonylphenol as well as the lower alkylphenol ethoxylates (n<3) are highly hydrophobic and will preferentially be bound to solid phases (sediment, soil, suspended solids and sewage sludge). Higher alkylphenol ethoxylates (n>10), on the contrary, are highly soluble in water, but once released into the environment, they are easily hydrolysed to lower e.g. more hydrophobic ethoxylates.
2. Nonylphenol and the lower alkylphenol ethoxylates are strongly bound to soil, sediment and sewage sludge with Koc-values of 20,000- 70,000 l/kg for nonylphenol and 2,500 and 5,000 l/kg for nonylphenol mono- and diethoxylate (NP1EO and NP2EO) respectively. Once sorpted onto soil and sludge, nonylphenol and NP1EO and NP2EO are steadily fixed and hardly leach.
3. Nonylphenol and NP1EO and NP2EO were found to be resistant to hydrolysis, nonylphenol was easily photolysed in surfacewater with a half-life of 10- 15 hours, whereas NP1EO and NP2EO hardly showed any reaction to sunlight. Under atmospheric conditions, all alkylphenols and alkylphenol ethoxylates are estimated to be degraded easily by photolysis with estimated half-lives of < 1.0 day.
4. Primary biodegradation of nonylphenol in fresh water occurs at half-lives of 15- 20 days in presence of adapted micro-organisms. Primary biodegradation in marine environments is significantly slower with half-lives of 50- 70 days. Adaption takes usually 20- 30 days. In all degradation experiments extensive mineralisation was observed, but only from the side chain and not from the phenolic ring structure. Nonylphenol mineralisation in soil is fast with half-lives of 10- 15 days after an induction period of 15- 20 days.
5. Primary biodegradation of nonylphenol ethoxylates (n=9) in fresh water is relatively fast with half-life of < 4 days, with nonylphenol diethoxylate (NP2EO) being the major degradation product. Mineralisation half-live of NP2EO in river water varies between 20- 30 days, after an induction phase of 20 days. Nonylphenol ethoxylates degradation in sewage sludge is much

faster at half-lives < 6 days. In both test environments, partial degradation of the phenolic ring structure was observed.
Half-lives for primary nonylphenol ethoxylates degradation in brackish and salt water were 3-4 days and 14-35 days respectively, after an induction period of 8 days. Major degradation product, NP2EO, mineralises slowly without formation of nonylphenol. Mineralisation of nonylphenol ethoxylates in soil occurs at half-lives of 5- 10 days in sludge-amended soils to 50 days for non-amended soils. In both environments nonylphenol was found to be fully degraded.

6. In biological wastewater treatment, nonylphenol ethoxylates are hydrolysed to NP1EO and NP2EO, which are subsequently partially bound to sludge solids and oxidised to nonylphenol mono-ethoxyl and diethoxyl carboxylic acid (NP1EC and NP2EC). Overall nonylphenol ethoxylates removal on is 53% (mole), with 13% in the form of ultimate biodegradation. Sludge bound NP1EO and NP2EO is converted to nonylphenol under anaerobic conditions. Remaining 47% in effluent consist largely of NP1EO, NP2EO, NP1EC and NP2EC, which are slowly mineralised in receiving surfacewater.
7. Environmental concentrations in fresh and marine biota indicate that nonylphenol, NP1EO and NP2EO readily accumulate. In fresh water algae, BCF values range from 6600- 7700 l/kg for nonylphenol to 3500- 5000 and 1000- 1800 l/kg for NP1EO and NP2EO respectively. BCF values for nonylphenol in fish vary generally between 200- 600 l/kg, indicating that little bioaccumulation in the food chain occurs. BCF values for NP1EO and NP2EO in fish amounted to 80- 150 l/kg.

With respect to these findings should be noted that most of the environmental data presented above correspond with nonylphenol ethoxylates releases to the environment before voluntary measures were taken to reduce the use of nonylphenol ethoxylates in non-industrial applications. With the emissions reductions, discussed in chapter 4, current concentrations in the aquatic environment will be significantly lower.

Data for evaluation of the impact of emission reductions on environmental concentrations are not available. To facilitate such a verification, it is recommended to perform additional measurements to determine to what extend environmental concentrations have changed over the years.

5.8 References

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6 Occurrence in the aquatic environment

6.1 Analytical techniques

A variety of extraction techniques and quantification methods may be used in determining concentrations of nonylphenol, depending upon the type of sample to be analysed. The most frequently used extraction technique for environmental samples appears to be steam distillation; other techniques employed use hexane and methylene chloride as extraction solvent. Quantification of samples is usually by HPLC (High Performance Liquid Chromatography) or GC (Gas Chromatography) using either UV or MS (Mass Spectrometer) detectors. Where appropriate, details are given about the analytical techniques employed and the detection limits.

When analysing samples of nonylphenol, the low solubility of nonylphenol in water needs to be taken into account. Nonylphenol may also be adsorbed onto the surface of glassware thereby reducing the concentration measured in solution. Varineau (1996) reports the results of a round robin analysis to determine the effect of analytical methodology on reported nonylphenol/ nonylphenol ethoxylate levels in the environment. Blind samples were sent to principal researchers in the nonylphenol area for analysis. The overall conclusion of the study is that analytical methodology is not a likely source for the variation seen in the levels of NP/NPE in environmental samples (EU, 1999).
A summary of widely used analytical methods for nonylphenol and nonylphenol ethoxylates in various environmental matrices is presented in table 6.1 (EU, 1999).

Table 6.1: Analytical methods for nonylphenols and nonylphenol ethoxylates

Sample	Extraction method	Separation and detection	Detection Limit	Reference
Soil	Extraction with hexane	HPLC / UV	20 µg/kg (dw)	Marcomini et al. (1992)
Soil	Steam distillation	HPLC / UV	20 µg/kg (dw)	Kirchman et al. (1991)
Soil	Steam distillation	HPLC / UV	µg/kg (dw)	Kuchler et al. (1994)
Sediment	Steam distillation	HPLC / UV	0,5 µg/kg (dw)	Suoanttila (1996)
Sediment	Steam distillation	HPLC / UV	1 µg/kg (dw)	Marcomini et al. (1990)
Sewage sludge and sediments	Steam distillation	HPLC / UV	2.93 µg/kg.	Naylor et al. (1992a)
Sewage sludge and sediment	Steam distillation	HPLC / UV	3 µg/kg.	Williams & Varneau (1996)
Sewage sludge and sediment	C18 solid phase column	GCMS	20 µg/kg (dw)	Zellner and Kalbfus (1997)
Sewage sludge and sediment	In-situ acetylation	GCMS	100 µg/kg (dw)	Lee and Peart (1995)
Bioata in fresh water	Extraction with hexane	HPLC / UV	20 µg/kg (dw)	Ward and Boeri, 1991
Bioata in fresh water	Extraction with cyclohexane	HPLC / UV	30 µg/kg (dw)	Ahel et al. (1993)
Groundwater	Steam extraction	HPLC / UV	0.10 µg/l	Ahel et al. (1996)
Surfacewater	Steam distillation	HPLC / UV	0.10 µg/l	Naylor et al. (1992a)
Surfacewater	Steam distillation	HPLC / UV	0.50 µg/l	Ahel and Giger (1985)
Surfacewater	C18 solid phase column	GCMS	0.03-0.2 µg/l	Blackburn&Waldock (1995)
Surfacewater	C18 solid phase column	GCMS	0.001 µg/l	Zellner and Kalbfus (1997)
Surfacewater	In-situ acetylation	GCMS	0.10 µg/l	Lee and Peart (1995)
Surfacewater	Steam extraction	HPLC / UV	0.01 µg/l	Suoanttila (1996)

dw: dry weight

6.2 Occurrence in freshwater environment

In the reviewed literature, a wide variety of measured levels of nonylphenol in various water systems were available, but reliable data about the environmental occurrence of octylphenol and octylphenol ethoxylates were scarce. Below descriptions are therefore largely restricted to the environmental occurrence of nonylphenol and nonylphenol ethoxylates. Some nonylphenol levels reflect rather concentrations near point sources (e.g. wastewater treatment plants) and application sites than the overall situation. Given the fact that use of nonylphenol ethoxylates in domestic detergents in most European countries has been reduced in recent years (due to industry led voluntary agreements), some of the older measurements (notably data from the Glatt River in Switzerland) may not reflect the current levels of nonylphenol, particularly where the major source was thought to be from nonylphenol ethoxylate use in detergents.

6.2.1 Surface water

Nonylphenol
A great number of research projects have been focused on the nonylphenol occurrence in the Glatt river, located in a highly urbanised area in Switzerland. Water and sediment samples were extracted by steam distillation and quantified by HPLC. The detection limit for the method used was 0.5 µg/l (Ahel and Giger, 1985). Ahel et al. (1981) reported nonylphenol concentrations in the Glatt river of 1 to 2.8 µg/l (mean: 1.8 µg/l). One year later, Schaffner et al. (1987) reported an average concentration of 4.1 µg/l. Ahel et al. (1986) reported an average value of 2.7 µg/l, with maximum values up to 26 µg/l. In a later study, nonylphenol levels were reported between ≤0.3 µg/l and 45 µg/l. Unpublished work by Giger (1997 in UK,1999) indicates that levels of nonylphenol in the Glatt river decreased significantly due to the banning of nonylphenol ethoxylates in domestic purposes. Average nonylphenol concentrations in surfacewater was found to have decreased to 0.1-0.3 µg/l (see table 6.2).

Blackburn and Waldock (1995) measured the concentration of nonylphenol in 6 rivers in the United Kingdom. The rivers were chosen to give a wide range of potential nonylphenol emissions and concentrations. Nonylphenol concentrations were measured as total extractable nonylphenol (TENP). The highest concentration of nonylphenol was measured in the River Aire, which receives a high input of industrial surfactants from textile industries. In 1996 an additional water quality survey was performed in the Northeast Region in order to evaluate industrial emissions to surface waters. Average levels ranged from 0,6 to 100 µg/l with peak concentrations of 50-730 µg/l at specific wastewater discharge points (Sniffer, 1998). In River Lea octylphenol was found in significantly lower concentrations than nonylphenol (see table 6.3).

The concentration of nonylphenol and nonylphenol ethoxylates have further been measured in a lake in Eastern Finland. The lake receives inputs from a sewage treatment plant which treats wastewater from a car import and washing business which uses nonylphenol ethoxylate surfactants. The concentration of nonylphenol in the lake water 1 km from the sewage treatment plant was 0.1-0.8 µg/l. Background concentration of nonylphenol in the lake was reported as 0.01 µg/l. (Suoanttila, 1996).

In 1995 the 'Bund-/Länderausschuß für Umweltchemikalien' (BLAU, 1995) reviewed the available information on nonylphenol concentrations in the environment in Germany. The nonylphenol concentration in the river Main was monitored throughout the years 1989-1991. The nonylphenol concentration in the

water (March 1990) was in the range of 0.007 to 3.3 µg/l One year later (June 1991) the concentrations were in the range of 0.009 to 1.3 µg/l.

Table 6.2:
Nonylphenol in fresh water (µg/l)

Surfacewater	Year	Nonylphenol	Reference
River Glatt	Switzerland		
Range in surfacewater	1980	0.1- 0.64	Ahel et al., 1981
Range in surfacewater	1984	1.0- 2.8	Ahel et al., 1985
Range in surfacewater	1984	1- 10	Ahel et al., 1985
Near WWTP	1984	3.0	Ahel et al., 1985
average value	1985	4.1	Schaffner et al., 1987
range in surfacewater	1986	0.7- 26	Ahel et al., 1996
range in surfacewater	1996	0.1- 0.3	Giger et al., 1997
Various rivers (TENP)*	United Kingdom		
River Aire	1994	1.6- 180	Blackburn et al., 1995
River Thames	1994	0.8- 2.3	Blackburn et al., 1995
River Lea	1994	0.5- 12	Blackburn et al., 1995
River Ouse	1994	0.6- 53	Blackburn et al., 1995
Various rivers (TENP)*	United Kingdom		
- Northeast region (average)	1996	0.6- 100	Sniffer 1998
- near emission discharges	1996	50- 730	Sniffer 1998
Lake Eastern Finland	Finland		
- near WWTP	1995	0.1- 0.8	Suoanttila,1996
- rural area	1995	0.01	Suoanttila,1996
River Main	Germany		
average	1989	0.38	BLAU, 1995
average	1990	0.52	BLAU, 1995
average	1991	0.12	BLAU, 1995
range in surfacewater	1990	0.01- 3.3	BLAU, 1995
median 90%	1990	0.08	BLAU, 1995
range in surfacewater	1991	0.01- 1.3	BLAU, 1995
median 90%	1991	0.18	BLAU, 1995
Bavarian rivers	Germany		
- range in surfacewater	1995	0.01- 0.08	Zellner et al., 1997
- near WWTP	1995	0.1- 0.4	Zellner et al., 1997
Various rivers	United States		
- range in surfacewater	1990	0.11- 0.64	Naylor,1992
- average	1990	0.12	Naylor,1992
Various surfacewaters	The Netherlands		
Nieuwe Waterweg	1997	< 0.07	LOES, 1999
Kanaal Gent-Terneuzen	1997	< 0.07	LOES, 1999

* TENP: Total Extractable Nonyl Phenol

Zellner and Kalbfus (1997) published monitoring data from a survey in Bavarian rivers. For monitoring of nonylphenol in water, as well as in sediments and sludge from wastewater treatment plants, a specific analytical method using gas chromatography/mass spectrometry was used. The detection limit of the method was 1 ng/l. Downstream of wastewater treatment plants the nonylphenol concentrations were found to be in the range of 0.1-0.4 µg/l, depending on population density and level of industrialisation. At other locations of the rivers the concentrations were much lower, i.e. in the range of 0.01-0.08 µg/l.

Table 6.3: Nonyl- and octylphenol in fresh water (µg/l)

Surfacewater	Year	Nonylphenol	Octylphenol	Reference
Various rivers (TENP)*	United Kingdom			
River Lea	1994	0.5- 12	0.4	Blackburn, 1995

* TENP: Total Extractable Nonyl Phenol

In the USA a representative survey of nonylphenol concentrations in 30 rivers has been conducted (Naylor et al., 1992a; Radian Corporation, 1990). Samples for analysis were extracted by steam distillation and formalin added as a preservative. Quantification was by HPLC and the detection limit for the method used was 0.107 µg/l. In 17 of the 30 rivers investigated, nonylphenol concentrations ranged from 0.11-0.64 µg/l. Levels in the other rivers were below the detection limit.

Recently, an indicative monitoring programme was started in the Netherlands for identification of suspected endocrine disruptive substances in surfacewater. Within the framework of this programme, nonylphenol and its ethoxylates were monitored in surfacewater and sewage treatment effluents at various locations throughout the Netherlands. At the investigated locations, nonylphenol levels in surfacewater were all below the detection limit (<007 µg/l.; LOES,1999).

Nonylphenol ethoxylates
Near outlets of municipal wastewater treatment plants in the Glatt river area, nonylphenol ethoxylates levels in surfacewater were reviewed by Ahel et al. (1994). Main nonylphenol ethoxylates found in water were NP1EO and NP2EO. Other major compounds were NP1EC and NP2EC (carboxylates). Measurements by Blackburn (1999) showed that NPxEO levels in certain industrial areas in the UK are still considerably high (see table 6.4). Nonylphenol ethoxylates levels in Netherlands surfacewaters were only slightly above the detection limit (0.14 µg/l; LOES, 1999).

Table 6.4: Nonylphenolethoxylates in fresh water (µg/l)

Surfacewater	Year	NPnEO	NPnEC	Reference
River Glatt	Switzerland			
- range in surfacewater	1984	3-110	2-115	Ahel et al., 1994
Various rivers	United Kingdom			
River Aire	1995	15-76	-	Blackburn et al., 1999
River Mersey	1995	6-11	-	Blackburn et al., 1999
River Tees	1995	76	-	Blackburn et al., 1999
Various rivers	United States			
- range in surfacewater	1990	0.13- 1.8	-	Naylor,1992
Various surfacewaters	The Netherlands			
Kanaal Gent-Terneuzen	1997	0.14	-	LOES, 1999

NPnEO: Nonylphenol ethoxylate with n ethoxylate groups
NPnEC: Carboxylic acid of NPnEO formed by oxidation of the terminal hydroxyl group
n = 1, 2

6.2.2 Sediment

Nonylphenol
Ahel et al. (1994) measured nonylphenol concentrations in sediments in the Glatt river in Switzerland. The range of concentrations found was between 510-5600 µg/kg dw (see table 6.5).

In 1995 the 'Bund-/Länderausschuß für Umweltchemikalien' (BLAU, 1995) reviewed nonylphenol concentrations in the environment in Germany. In March 1991, nonylphenol concentrations in sediments were 56-14800 µg/kg dry weight (mean: 9500 µg/kg). In June 1991 levels were 22-13200 µg/kg dw (average: 7700 µg/kg dry weight). In 1994, the nonylphenol concentration in the suspended matter in the river Main and several other Hessian surface waters was 170-3300 µg/kg dry weight (mean: 800 µg/kg dry weight). In June 1991, sediment of the Lake Constance contained nonylphenol in the range of <3 to 214 µg/kg dry weight (mean: 50 µg/kg dry weight).

Concentrations of nonylphenol and their ethoxylates were also measured in sediments in a lake in Eastern Finland, which receives treated wastewater from a car import and washing company using nonylphenol ethoxylate surfactants. Levels of nonylphenol in sediment 1 km from the sewage treatment plant were 180-890 µg/kg (dry weight). Background nonylphenol level in sediment was 0.43 µg/kg (dw). (Suoanttila, 1996). Blackburn et al. (1999) found, in addition to aqueous measurements, that nonylphenol levels in the Aire Mersey river were still high in 1995. Naylor et al. (1992a) analysed sediment samples from 30 rivers in the USA. The average concentration of nonylphenol in sediment was 162 µg/kg and the range of concentrations was <2.9 to 2960 µg/kg dw. Nonylphenol was not detected in 6 of the rivers sampled.

Table 6.5:
Nonylphenol in fresh water sediments and suspended solids (µg/kg dry weight)

Surfacewater	Year	Nonylphenol	Reference
River Glatt	Switzerland		
range in sediment - maximum in sediment	1984 1985	510- 5600 13100	Ahel et al., 1985 Ahel et al., 1994
Lake Constance	Germany		
range in sediment - average value	1991 1991	3- 210 50	BLAU,1995 BLAU,1995
Various rivers (TENP)	United Kingdom		
River Aire River Mersey	1995 1995	15000 1000	Blackburn, 1999 Blackburn, 1999
Lake Eastern Finland	Finland		
- near WWTP - rural area	* *	180- 890 0,43	Suoanttila,1996 Suoanttila,1996
River Main	Germany		
range in sediment average value range in sediment average value range in suspended solids - average value	1991a 1991a 1991b 1991b 1994 1994	56- 14800 9500 22- 13200 7700 170- 3300 800	BLAU, 1995 BLAU, 1995 BLAU, 1995 BLAU, 1995 BLAU, 1995 BLAU, 1995
Hessian rivers	Germany		
Average in suspended solids	1995	2500	UBA 1998/66
Bavarian rivers	Germany		
range in sediment	1995	1000- 10000	Zellner,1995
Various rivers	United States		
range in sediment - average value	1990 1990	<2,9- 2960 162	Naylor,1992 Naylor,1992
Pulp and paper mill site	Canada		
downstream - effluent discharge point	* *	290- 1280 12900- 41100	Lee and Peart, 1995 Lee and Peart, 1995
Various surfacewaters	The Netherlands		
Noordzeekanaal Amsterdam Kanaal Gent-Terneuzen	1997 1997	1520 1670	LOES, 1999 LOES, 1999

TENP: Total Extractable Nonyl Phenol a: March b: June

Lee and Peart (1995) measured concentrations of octyl- and nonylphenol in sediment samples taken downstream from a pulp and paper mill outflow and near a sewage treatment plant in Canada. Nonylphenol concentrations in sediment downstream from a pulp and paper mill outflow were 290-1280 µg/kg dw. The nonylphenol concentrations in sediment near the sewage treatment plant were significantly higher (1290-41100 µg/kg dw). Measurements further showed that octylphenol concentrations were significantly lower than nonylphenol concentrations (see table 6.6).

Table 6.6:
Nonyl and octylphenol in fresh water sediments (µg/kg ds)

Surfacewater	Year	Nonylphenol	Octylphenol	Reference
Pulp and paper mill site	Canada			
- downstream - near effluent discharge	* *	290- 1280 12900- 41100	5- 70 400	Lee and Peart, 1995 Lee and Peart, 1995

At the several sites, concentrations of nonylphenol ethoxylates were measured. Results are shown in table 6.7. Nonylphenol ethoxylate concentrations in Netherlands sediment were found to be significantly higher than the corresponding nonylphenol concentrations (LOES, 1999).

Nonylphenol ethoxylates

Table 6.7:
Nonylphenolethoxylates in fresh water sediments (µg/kg ds)

Surfacewater	Year	NPnEO	NPnEC	Reference
River Glatt	Switzerland			
- at effluent discharge - average value	1984 1984	11600 7600	6800 4500	Ahel et al., 1994 Ahel et al., 1994
River Rhine	Germany			
Average value	1987	1500	-	TemaNord, 1996
Various surfacewaters	The Netherlands			
Nieuwe Waterweg Noordzeekanaal Amsterdam Kanaal Gent-Terneuzen	1997 1997 1997	8100 5700 2980	- - -	LOES, 1999 LOES, 1999 LOES, 1999

NPnEO: Nonylphenol ethoxylate with n ethoxylate groups
NPnEC: Carboxylic acid of NPnEO formed by oxidation of the terminal hydroxyl group
n = 1,2

6.2.3 Wastewater treatment and sewage sludge

Ahel et al. (1981) measured nonylphenol concentrations in secondary sewage effluent in Switzerland. Nonylphenol concentrations in the effluent were 14-63 µg/l (mean 40 µg/l) and 13-42 µg/l (mean 26 µg/l), from the two sites surveyed. The higher values were from a municipal sewage treatment plant serving a heavily populated area.

Ahel and Giger (1985) surveyed municipal wastewaters and sewage sludges from the Zürich area in Switzerland. The concentration of nonylphenol in the raw wastewater was 14 µg/l. The concentration of nonylphenol in the effluent was 8 µg/l and the concentration in receiving waters was 3 µg/l. The concentration in digested sludge was measured as 1000 mg/kg (dry weight).

Blackburn and Waldock (1995) measured the concentration of nonylphenol in wastewater treatment plant effluent in the UK. The concentration of nonylphenol in the effluent from a sewage treatment plant receiving industrial wastewaters was 330 µg/l total extractable nonylphenol (TENP). Concentration in effluents from sewage treatment plants receiving mainly domestic wastewaters and operating secondary treatment was 0.2-2.9 µg/l TENP. The concentration of nonylphenol in effluents from domestic sewage treatment plants with only primary treatment (sedimentation) was 6.7 µg/l TENP.

In Eastern Finland effluent from a sewage treatment plant receiving wastewater from a car import and washing business was monitored. The concentration of nonylphenol before treatment was 100-200 µg/l and nonylphenol ethoxylate concentration 30,000-70,000 µg/l. After treatment concentrations dropped to 4-34 µg/l nonylphenol and 4,600-12,900 µg/l nonylphenol ethoxylate. (Suoanttila, 1996).

The concentrations of several substances in Hessian rivers, sewage and sewage sludge including nonylphenol have been measured from 1991 to 1995 by the 'Hessian Landesanstalt für Umwelt' (Fooken et al., 1995). The mean concentration of nonylphenol in sewage sludge of domestic WWTP was about 25 mg/kg dw (range 6-52.1 mg/kg dw). The concentration of nonylphenol in 3 effluents of industrial wastewater treatment plants ranged from 1.5 to 2.9 µg/l.

Naylor et al. (1992a) measured the concentration of nonylphenol in influent, effluent and sludge of sewage treatment plant in the USA. All the sewage treatment plants studied used activated sludge digestion. Nonylphenol levels in influent of a WWTP which receives water from a nonylphenol production site, were 400-800 µg/l. Concentrations in the effluent were between 23-74 µg/l. Nonylphenol concentrations in sludge were highest (2800 and 1800 mg/kg respectively) for sewage treatment plants receiving wastewater from cleaning product manufacture and domestic wastewater.

Concentrations of octylphenol, nonylphenol and their ethoxylates were monitored in domestic and industrial wastewaters and wastewater treatment plants in the Netherlands (see table 6.8 a and b). All levels in urban wastewater were considerably lower than in industrial wastewater, although effluent levels did not differ much.

Table 6.8a:
Levels in various urban wastewaters in the Netherlands

1997	OP	NP	OPEO	NPEO
Influent (µg/l)	< D – 0.1	< D - 23	< D – 27	2.1 – 170
Effluent(µg/l)	< D – 0.2	< D - 1	< D – 1.3	< D – 17
Sludge (µg/g)	< D – 2	< D - 125	< D – 28	0.7 – 880

D: Detection level

Table 6.8b:
Levels in various industrial wastewaters in the Netherlands

1997	OP	NP	OPEO	NPEO
Influent (µg/l)	< D – 100	< D - 400	< D - 5350	< D – 2270
Effluent(µg/l)	< D – 0.13	< D – 1.2	< D – 8.7	< 0.9 – 15
Sludge(µg/g)	< D – 24	< D – 2500	< D - 50	< D – 2400

D: Detection level

Mass balances for removal in one specific industrial wastewater treatment plant further showed that all pollutants were removed to great extent (> 98%). Low concentrations in sewage sludge indicate that biodegradation and/or volatisation are the major removal pathways (see table 6.9).

Table 6.9:
Removal in industrial wastewater treatment in the Netherlands

1997	OP	NP	OPEO	NPEO
Influent (µg/l)	100	400	5350	2270
Effluent (µg/l)	1.2	< D	2.2	8,8
Sludge (µg/l)	0.95	6.5	50	86
Adsorption (%)	0.4	0.7	0.3	1.5
Degradation *(%)	98.4	99.4	99.6	98.1
Effluent (%)	1.2	0	0.1	0.4

D: Detection level *: and/or volatilisation

The Danish EPA has conducted a study on the use of sewage sludges in agriculture in which concentrations of nonylphenol and nonylphenol ethoxylates (with 1 or 2 ethoxylate groups) were measured. Nonylphenol was detected in only 3 out of 20 samples. Average concentration in solids was 34 µg/kg dry weight with a maximum level of 130 µg/kg dry weight. Nonylphenol ethoxylates were detected in all 20 samples, at average levels of 15200 µg/kg dry weight with a range of 300 - 67,000 µg/kg dry weight. Nonylphenol ethoxylates were further detected in 18 out of 19 aqueous leachate samples. The average concentration was 0,041 mg/l with the highest concentration at 520 mg/l (EU, 1999).

6.2.4 Organisms

Ahel et al. (1993) reviewed the bioaccumulation potential of nonylphenol in freshwater organisms in the Glatt river and one of its tributaries, the Chriesbach, in Switzerland. The average concentration of nonylphenol in the river was 3.9 µg/l. Samples of microphytic algae were collected in the summer and autumn and frozen (-20°C) until analysis. Fish and duck samples were also collected and dissected, specific organs and tissues were deep frozen until analysis. Nonylphenol was detected in the following concentrations in microphytic algae; *Cladophora glomerata* 38 mg/kg dry weight, *Fontinalis antipyretica* 4.2 mg/kg dry weight and *Potamogeton crispus* 2.5 mg/kg dry weight. The concentrations of nonylphenol in fish organs are shown in tables 6.10.

Table 6.10:
Nonylphenol in fish organs

Squalius cephalus	mg/kg dry wght
- muscle	0.18
- gut	0.46- 1.20
- liver	1.0- 1.40
- gills	0.98- 1.40
Barbus barbus L	
- muscle	0.38
- gut	0.05
- liver	0.98
- gills	<0.03
- heart	0.30
- roe	0.09
Oncorhynshus mykiss	
- muscle	0.15
- gut	1.60

Concentrations in specific organs of a wild duck are shown in table 6.11.

Table 6.11:
Nonylphenol in duck organs

Anas boscas	mg/kg dry wght
- muscle	1.20
- gut	0.54
- liver	0.10
- stomach	0.19- 0.24
- heart	<0.03
- brain	0.19

6.2.5 Groundwater

Ahel et al. (1996) reported the concentration of nonylphenol in groundwater near the River Glatt as a consequence of river water infiltration into the soil. River water was found to be the major nonylphenol source. Average nonylphenol concentration in river water was 2.7 µg/l. Concentrations of nonylphenol in ground water were 1.0 µg/l, 0.5 µg/l, and 0.3 µg/l at 2.5m, 7m and 14 m respectively from the river. The decay of the concentration in the groundwater illustrate that nonylphenol is removed due to strong binding to soil.

6.2.6 Rainwater

For none of the considered compounds measurement data were available with respect to the presence in rainwater. Nonylphenol is relatively short lived in the atmospheric environment, based upon the reaction with hydroxyl radicals. Nonylphenol is not very volatile and so it is unlikely to enter the atmosphere in large amounts. Removal of nonylphenol from the atmosphere by precipitation is therefore to be negligible with resulting rain water concentrations being low. As the lifetime of nonylphenol in the atmosphere is relatively short it is unlikely to be transported a long distance from its point of emission. Concentrations due to precipitation of nonylphenol from the atmosphere are therefore likely to be greatest near the point of emission.

6.3 Occurrence in marine environment

6.3.1 Surface water

Blackburn and Waldock (1995) measured the concentration of nonylphenol in estuarine waters around the UK. Nonylphenol concentrations were measured as total extractable nonylphenol (TENP). The highest concentrations were observed in the heavily industrialised Tees estuary at 0.09-5.2 µg/l TENP. In other estuaries concentrations were between <0.08 and 0.32 µg/l TENP. The concentration of nonylphenol in sea water near the outfall from a tanker washing operation was reported as 27 µg/l.

6.3.2 Sediment

Marcomini et al. (1990) measured nonylphenol levels in sediment samples taken from the Lagoon of Venice in Italy. The mean concentration of nonylphenol in the sediment samples was 14 µg/kg (dry weight) at a range 5 to 42 µg/kg (dry weight). Concentrations in Netherlands estuarine environments ranged from 200-630 µg/kg (dry weight) for nonylphenol and 700- 2600 µg/kg (dry weight) for nonylphenol ethoxylates (see table 6.12; LOES, 1999).

Table 6.12:
Alkylphenol and alkylphenol ethoxylates in Netherlands estuaries

Westerschelde	OP	NP	OPEO	NPEO
Surface water (µg/ltr)	-	-	-	-

Suspended solids (µg/kg dw)	< D	210	< D	705
Sediment (µg/kg dw)	-	-	-	-
IJmuiden				
Surface water (µg/ltr)	< D	< D	< D	< D
Suspended solids (µg/kg dw)	< D	620	< D	1370
Sediment (µg/kg dw)	< D	630	< D	2600

D: Detection level

6.3.3 Organisms

No environmental data were observed for selected compounds in marine biota.

6.4 Conclusions

Based on the findings of this chapter, the following conclusions can be drawn with respect to the occurrence of selected compounds in the aquatic environment:

1. Most environmental data observed in literature and reviews is generally related to the occurrence of nonylphenol and nonylphenol ethoxylates, and in particular to the period 1985-1995, when the use of nonylphenol ethoxylates were considerably higher than nowadays. Only for the Netherlands, actual data were available. Most of the described concentrations therefore will overestimate current occurrence in aquatic environment.
2. Comparison of aqueous concentrations and levels in sediments provides useful information about distribution and behaviour in of selected compounds in aquatic environments. From the environmental concentrations can be concluded that nonylphenol and nonylphenol ethoxylates are preferentially bound to sediments, with highest concentrations near discharges of municipal an industrial wastewater treatment plants, receiving high nonylphenol ethoxylate inputs.
3. Historical data for occurrence of nonylphenol in Swiss river waters between 1985 and 1995 indicate that due to the banned use of nonylphenol ethoxylates in domestic applications has lead to a significant decrease of aqueous nonylphenol concentrations. Data about the historical development of nonylphenol concentrations in sediments were however not available.
4. Comparison of nonylphenol concentrations in fresh water algae and fish to aqueous nonylphenol levels confirm that this compound readily bioaccumulates in aquatic biota. Similar data about nonylphenol ethoxylates concentrations in fresh water biota were not available. For none of the selected compounds environmental concentrations in marine organisms could be retrieved.
5. Incidental measurement results in estuarine surfacewater and sediments further indicate that the concentrations in the aqueous phase were slightly higher or below the detection limit. In sediment still significant concentrations of selected compounds were present.
6. Incidental data for octylphenol and octylphenol ethoxylates show that their occurrence is considerably lower than for nonylphenol and nonylphenol ethoxylates, which is in good agreement with the relative low use of octylphenol and octylphenol ethoxylates.

6.5 References

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7 Toxity in the aquatic environment

7.1 Mechanism of toxicity

The direct estrogenic substances may act in at least 3 different ways. At first they may bind to the estrogen receptor, in which case the mechanism of action is identical to 17ß-oestradiol. The second mechanism is based on stimulation of the endogenous production of 17ß-oestradiol. A third mechanism could be the diminishing of 17ß-oestradiol degradation. Furthermore there are substances that may bind to the estrogen receptor but do not cause an estrogenic effect in organisms. These substances are anti-estrogenic, because they prevent the binding of endogenous oestradiol and thereby cause endocrine disruption. There are also substances that influence the hormone regulation in an indirect way, e.g. because they influence the metabolism or the excretion of 17ß-oestradiol (RIKZ, 1996).

Octylphenol and nonylphenol are capable of displacing 17ß-estradiol from estrogen receptor in rainbow trout and activate transcription in estrogen receptor transfected MCF-7 cells (White, et al., 1994 in Sepa, 1998). The action of these compounds appeared to be mediated by the estrogen receptor, since their effects depended on its presence and were blocked by estrogen antagonists. Alkylphenols have estrogenic effects and have also been shown to bind directly to the estrogen receptor (White et al., 1994 in Sepa, 1998). Nonylphenol is the most used/studied of the alkylphenols and is together with octylphenol determined to be among the most potent estrogenic compounds within this group of chemicals (White et al., 1994 in Sepa, 1998). Soto, et al. (1991 in Sepa, 1998) showed that the para-substituted tert-butylphenol had estrogenic properties in MCF-7 cells whereas the ortho- and meta-substituted tert-butylphenols were inactive (SEPA, 1998).

7.1.1 Metabolism

Major metabolites of nonylphenol are hydroxylated in only one position on the alkyl chain. This indicates that only one P450 isoenzyme is responsible for the metabolism of these nonylphenol isomers in rainbow trouts. The primary metabolites are 2-(4-hydroxyphenyl)-8-hydroxy-nonane, 3-(4-hydroxyphenyl)-8-hydroxy-nonane and 4-(4-hydroxyphenyl-8-hydroxy-nonane) (Meldahl, et al. 1996).

In rats, nonoxynol-9 (nonylphenol with 9 ethoxy-groups) is metabolized to nonylphenol and subjected to glucuronidation. Radiolabelled nonoxynol-9 has been shown to be cleared from rat liver and kidneys within 48 h (Nimrod & Benson, 1996 in SEPA, 1998).

7.2 Toxic effects in the aquatic environment

7.2.1 General

This paragraph describes the data on toxicity retrieved from the literature. Toxic effects for species in the aquatic environment are distinguished into acute and chronic effects. Furthermore a distinction is made between (pelagic) water organisms and ((epi) bentic) sediment organisms. It is not possible to base this distinction on the larger taxonomic groups. Within every group there are representatives of a typical bentic and a typical pelagic way of living. Even within one species there can be a shift of one compartment to the other during the

development from larvae to adult. The placing of a taxonomic group under pelagic or bentic organisms is therefore arbitrar.

In this report the available toxicity data are presented per group of species. The retrieved toxicity data are not evaluated, except for the lowest values, which are to be used to derive iMPCs. However, when available, the test methodology used is reflected, which gives an indication about the quality of the data. The level of toxicity of the alkyl phenols is classified according to the classification system in Annex 4.1.

7.2.2 Toxic effects in freshwater aquatic environment

General
In this report the Daphnids, are incorporated with the pelagic freshwater environment. The other freshwater crustaceans and insect larvae are incorporated with the bentical environment. Algae, bacteria, protozoa and fish are incorporated with the pelagic environment. Data from tests with sediment with several organisms are also incorporated with the bentical environment.
The decision whether a test is acute or chronic depends on the generation time of the specific species (group) and in principal chronic tests should enclose more than 1 generation. In this report the toxicity tests on insects, crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae, bacteria and protozoa the EC_{50} values at 96 h and less are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are regarded per test. Tests on early life stages (ELS) are regarded as chronic. In table 7.2 to 7.5 all retrieved acute and chronic toxicity data of the alkyl phenols for freshwater organisms are presented. Table 7.1 gives an overview of the level of toxicity. In this table the data from crustaceans of pelagic and bentic environments are combined.

Table 7.1:
Overview of the toxicity data on alkyl phenols in the freshwater environment classified according to the classification system in Annex 4.1
0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic.

Chemical	CAS no	Bacteria/ Protozoan		Algae		Insects/Worms/ Molluscs		Crustaceans		Fish		Amphibian	
		Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron
Octylphenol	67554-50-1	*	-	**	-	-	-	***	**	***	***	-	-
Octylphenol ethoxylate	9002-93-1	-	-	***	-	-	-	-	-	-	-	-	-
Nonylphenol	25154-52-3	**[c] ***[a]	-	***	*	***[b] ***[e] ***[d]	**[b] 0[d]	***	***	***	***	**[f]	**
Nonylphenol ethoxylate	26027-38-3	-	-	***	0	-	-	***	0	**	**[g]	-	-

a. Protozoan
b. Insects
c. Bacteria
d. Molluscs
e. Worms
f. Based on a NOEC
g. Based on a LOEC (growth)

Octyl phenol
In table 7.2 the lowest ecotoxicity data per group of species are given. In Annex 4.4 all data are given.

The tables 7.2a and b on acute and chronic toxicity data show that there are acute data for water and sediment organisms. Chronic toxicity data are only available on water organisms.
Octylphenol is acute very toxic to crustaceans and fish and moderately toxic to algae. To bacteria octylphenol is slightly toxic. Chronic data on octylphenol show that octylphenol is very toxic to fish and moderately toxic to crustaceans.
Octylphenol is acute also very toxic to crustaceans in sediment. Data on endocrine effects indicate that the effect levels for these data are around the same level as chronic toxicity data.
The toxicity data are generally far below the limit of the water solubility of 5-12.6 mg/l.

Table 7.2.a
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Bacteria	Octylphenol	>10	3 h	EC50	Act.sewage sludge org.	OECD 204	IUCLID, 1996 in WRC, 1998
Algae	Octylphenol	0.3 n 1.1 n 4.2 n	72 h	EC10 EC50 EC90	Scenedesmus subspicatus		IUCLID, 1996 in WRC, 1998
Crustaceans	Tetramethyl butyl phenol	0.09	2 d	LC50	Daphnia magna	Static	Zou, et al., 1997
Fish	Octylphenol	0.084 0.12 0.17	14 d 14 d 6 d	NOEC LC50 LC50	Oncorhynchus mykiss	Flow through, GLP, 12 °C, pH=8-8.2	IUCLID, 1996 in WRC, 1998
Estrogenic effects							
Mollusc	Octylphenol	<0.001	5 m	LOEC induction superfemales	Marisa cornuarietis	renewal, tap water, 22 C	Oehlmann, et al., 2000
Fish	Octylphenol	0.003	-	LOEC increased vitellogenin production	Salmo gairdneri Males		Jobling, et al., 1996 in WRC, 1998
Amphibian	4-octylphenol	78320 nM (16.9 mg/l)	-	IC50 binding affinity to ER	Xenopus laevis Liver cells	-	Lutz, et al., 1999
Sediment organisms							
Crustaceans	Octylphenol	0.0133 0.0196 m	96 h	EC50 Immobilisation LC50	Gammarus pulex	Semi-static	Sims and Whitehouse, 1998 in WRC, 1998

* m=measured, n=nominal

Table 7.2b:
Retrieved chronic effect concentration (NOEC) (mg/l) of octyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Crustaceans	Octylphenol	0.03 0.1	21 d	NOEC Reproduction rate LOEC	Daphnia magna	-	IUCLID, 1996 in WRC, 1998
Fish	Octylphenol	0.0061 m 0.011 m	60 d	NOEC LOEC	Oncorhynchus mykiss	Flow through, GLP, Post-hatch early life study	IUCLID, 1996 in WRC, 1998

* m=measured, n=nominal

Octyl phenol ethoxylate
In table 7.3a the data on the ecotoxicity of octylphenol ethoxylate are given. There are only data on acute toxicity.
There are only 2 data (from 1 study) on the ecotoxicity of octylphenol ethoxylate on algae. These data indicate that octyl phenol ethoxylate is acute very toxic to moderately toxic to algae.

Table 7.3a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	OP11EO	0.21	96 h	EC50 growth	Selenastrum capricornutum	-	Lewis, 1986 (in TemaNord, 1996)
Algae	OP11EO	7.4	96 h	EC50 growth	Microcystis aeruginosa	-	Lewis, 1986 (in TemaNord, 1996)

Nonyl phenol
In table 7.4 the lowest ecotoxicity data per group of species are given. In Annex 4.5 all data are given.
The tables 7.4a and b on acute and chronic toxicity data show that there are toxicity data of nonyl phenol for water and sediment organisms. Nonylphenol is acute very toxic to protozoans, algae, crustaceans, fish and the sediment organisms insects, worms, molluscs and crustaceans. To amphibians and bacteria nonylphenol is acute moderately toxic. Based on the chronic data nonylphenol is very toxic to crustaceans and fish, moderately toxic to insects and amphibians, slightly toxic to algae and very slightly toxic to molluscs.
Data on endocrine effects indicate that the effect levels for these data are around the same level or higher as the other toxicity data.
The toxicity data are generally below the limit of the water solubility of 5-7 mg/l.

Table 7.4.a:
Retrieved acute effect concentration (mg/l) of nonyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Concentra-tion (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Bacteria	4-nonylphenol	10 32 >40	2 h 2 h 24 h	50% inhibition of spore germination >99% inhibition of spore germination no inhibition	Bacillus megaterium		Lewis & Jurd, 1972 in EU, 1999
Flagellate	Nonylphenol	0.5 0.75	-	55% inhibition of photosynthesis 100% inhibition of photosynthesis	Chlamydomonas reinhardii	-	Moody & Weinberger, 1983 in EU, 1999
Algae	Nonylphenol CAS 25154-52-3	0.0033 0.0563	72 h	EC10 Biomass EC50 Biomass	Scenedesmus spicatus	EN 28692/ISO 8692, DIN 38412-9, valid for risk assessment	Kopf, 1997 in EU, 1999
Molluscs	Nonylphenol	0.0005 – 0.005 0.010	3-7 d	Ceased production of egg mass, death of adults Reduced egg mass production, hatching affected	Lymnaea stagnalis		Smith, et al., 2000 in SETAC 2000
Crustaceans	Nonylphenol CAS 84852-15-3 (>95% 4-nonylphenol)	0.069 m 0.276 m	96 h	EC50 LC50	Ceriodaphnia dubia	24-25°C, Static, pH=8.3-8.6, valid	England, 1995 in EU, 1999
Fish	Nonylphenol	0.096 m 0.128 m	96 h	EC50 LC50	Pimephales promelas	Flow through, valid	Brooke, 1993a in EU, 1999
Endocrine effects							
Crustaceans	Nonylphenol	0.05 0.1	48 h	NOEC LOEC increased accumulation of 14C testosterone= decrease in production of testosterone elimination product (testosterone-glucose)	Daphnia magna	Exp 48 h and then 16 h to 14C testosterone, conc-related effect	Baldwin, et al., 1997 in EU, 1999
Fish	Nonylphenol	0.03	35 d (+431 d)	LOEC Reduced mean body weight and length, ovosomatic index (OSI) elevated	Oncorhynchus mykiss female	Flow through, exposed from hatch to sexual maturity, pH=6.5, 7-13°C, aerated	Ashfield, et al, 1998 in EU, 1999
Amphibian	4-nonylphenol	33666 nM (7.4 mg)	-	IC50 binding affinity to ER	Xenopus laevis Liver cells	-	Lutz, et al., 1999
Sediment organisms							

Class	Substance	Concentra-tion (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Worms	Nonylphenol CAS 25154-52-3	0.268 m 0.342 m	96 h	EC50 Inactivity LC50	Lumbriculus variegatus	Flow through, valid	Brooke, et al., 1993a in EU, 1999
Insects	4-nonylphenol	0.057 m	96 h	EC50	Ischnura elegans	Static, renewal	Sims, et al., 1997 in wrc
Molluscs	Nonylphenol CAS 25154-52-3	0.378 m 0.774 m	96 h	EC50 Inactivity LC50	Physella virgata	Flow through, valid	Brooke, et al., 1993a in EU, 1999
Crustaceans	4-nonylphenol	0.0127 m	96 h	EC50	Gammarus pulex	Static, renewal	Sims, et al.,1997 in wrc

* m = measured, n = nominal , valid = valid for risk assessment (EU, 1999)

Table 7.4.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	Nonylphenol CAS 25154-52-3	0.694 m 1.48 m	96 h	NOEC LOEC Cell production	Selenastrum capricornutum	Valid	Brooke, et al., 1993a, in EU, 1999
Crustaceans	Nonylphenol	0.001 n	21 d	NOEC Reproduction	Daphnia magna	Static, use with care	Kopf, 1997 in EU, 1999
Molluscs	Nonylphenol	5	6 d	LC50	Anodonta cataractae		McLeese, et al., 1980 in wrc
Fish	Nonylphenol	0.0074 m 0.014 m 0.0102 m	33 d	NOEC survival LOEC survival MATC survival	Pimephales promelas	Flow through GLP, unaerated	CMA, 1991 in wrc
Amphibian	Nonylphenol CAS 25154-52-3	0.025 0.050	14 d	NOEC development LOEC development	Xenopus laevis	Renewal	Fort, et al, 1997 in AQUIRE, 2000
Sediment organisms							
Insects	Nonylphenol CAS 104-40-5	0.0125-0.2	20 d	NOEC growth, mortality, development and reproduction	Chironomus tentans		Kahl, et al., 1997 in AQUIRE
Amphibian	Nonylphenol	155 mg/kg (dosed sed.) 220 mg/kg (dosed sed.) 260 mg/kg (dosed sed.) 390 mg/kg (dosed sed.) 250 mg/kg (dosed sed.)	30 d	NOEC weight & Mortality EC50 weight & Mortality LC50 LOEL weight & Mortality MATC	Rana catesbiana	GLP	CMA, 1992 in wrc

* m = measured, n = nominal, valid = valid for risk assessment (EU, 1999)

Nonyl phenol ethoxylate

The tables 7.5a and b show the lowest toxicity data of nonyl phenol ethoxylate for waterorganisms. In Annex 4.6 all data are given.

There are no data on sediment organisms.
Nonylphenol ethoxylate is acute very toxic to algae and crustaceans and moderately toxic to fish. Based on the chronic data nonylphenol ethoxylate is moderately toxic to fish and very slightly toxic to algae and crustaceans.
Data on endocrine effects indicate that the effect levels for these data are around the same level as the other toxicity data.
The toxicity data are generally below the limit of the water solubility of >10 mg/l.

Table 7.5.a: Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	NPEO	0.09	96 h	EC50	Selenastrum capricornutum		Argese, et al., 1994 in Warhurst, 1995
Crustaceans	NP2E	0.148	48 h	LC50	Daphnia magna	-	Maki et al, 1998 in CEPA, 2000
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	1	96 h	LC50	Salmo trutta		Reiff et al., 1979 in Verschueren, 1983
Endocrine effects							
Crustaceans	Nonylphenol polyethoxylate (NPPG=nonylphenol polyethylene glycol)	5	-	LOEC Inhibition of elimination of testosterone	Daphnia magna		Baldwin, et al., 1998 in Chemweb, 2000
Fish	NP1EC	0.02	-	LOEC Production of female egg yolk protein	Salmo gairdneri males		Jobling, 1996 in Friends of the earth, 2000

* m = measured, n = nominal

Table 7.5b:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	NP9EO	8	-	NOEC growth	Selenastrum capricornutum	-	Dorn, et al, 1993 in CEPA, 2000
Crustaceans	NP1EC	2.2	7 d	NOEC reproduction	Ceriodaphnia dubia	-	Naylor, et al, 1997 in CEPA, 2000
Insects	NP1EO	80	-	EC50	Culex pipiens	-	Maxwell & Piper 1968 in CEPA, 2000
Fish	NP2EO	0.010 0.030	35 d	Growth reduction No growth reduction	Salmo gairdneri		Ashfield, et al., 1995 in wrc

* m = measured, n = nominal

Overview of the toxicity data for fresh water organisms

In table 7.6 and 7.7 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in **mg/l.**

Table 7.6:
Overview of the lowest retrieved acute effect concentrations ($L(E)C_{50}$) (in mg/l) of the alkyl phenols in the freshwater environment

Substances	Bacteria/ Protozoan	Algae	Insects/ Worms	Molluscs	Crustaceans	Fish	Amphibian
Octylphenol	>10[a]	1.1	-	-	0.09 0.0133 (sed)	0.12	-
Octylphenol ethoxylate	-	0.21	-	-	-	-	-
Nonylphenol	10[a] 0.5[b]	0.0563	0.057[c] 0.268[d]	0.010 (LOEC) 0.378 (sed)	0.069 0.0127 (sed)	0.096	0.025 (NOEC)
Nonylphenol ethoxylate	-	0.09	-	-	0.148	1	-

a. Bacteria c. Insects
b. Protozoan d. Worms

Table 7.7:
Overview of the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of the alkyl phenols in the freshwater environment

Substances	Bacteria/ Protozoan	Algae	Insects/ Worms	Molluscs	Crustaceans	Fish	Amphibian
Octylphenol	-	-	-	-	0.03	0.0061	-
Octylphenol ethoxylate	-	-	-	-	-	-	-
Nonylphenol	-	0.694	0.0125 - 0.2[c]	5 (LC50)	0.001	0.0074	0.025
Nonylphenol ethoxylate	-	8	80[c](EC50)	-	2.2	0.01 (LOEC)	-

a. Bacteria c. Insects
b. Protozoan d. Worms

Tables 7.6 and 7.7 show that most data are available on fish and crustaceans and that ecotoxicity data on alkylphenols are scarce except for nonylphenol.

7.2.3 Effects observed in the environment

There are 3 field studies on the effects of alkylphenols to fish, zooplankton and benthic macroinvertebrates in mesocosms: Liber, et al. (1998), O'Halloran, et al. (1998) and Schmude, et al. (1998). The studies are shortly summarized.

In the study of O'Halloran zooplankton in enclosures were studied. Zooplankton were collected at regular intervals from 9 days before the first nonylphenol application until day 83. After collection, the abundances of the various organisms were determined by counting and the effects of the nonylphenol on the zooplankton community were assessed based on changes observed in population abundances and taxonomic composition.

In the experiment, a total of 45 taxa were identified from the 18 enclosures over the 9 sampling dates. The most abundant group present was Cladocera (dominated by Chydoridae and Daphnidae). Copepods were dominated by cyclopoids. The peak abundance of both cladoceran and copepod populations occurred between days 34 and 51 (August 12-27) of the experiment. Of the 45 taxa identified, 32 were found at high enough abundance on several sampling days to carry out a statistical analysis.

All cladoceran and copepod taxa were significantly ($p<0.05$) reduced in number in the enclosures exposed to 243 µg/l nonylphenol when compared to controls, and some of the more sensitive taxa were significantly reduced in number at two lower nonylphenol concentrations (76 µg/l and 23 µg/l). Ostracod and rotifer taxa

appeared to be less sensitive, with effects being seen at nonylphenol concentrations of 243 µg/l and ≥76 µg/l respectively. The maximum reduction in abundance generally occurred within 1 to 7 days of the last nonylphenol application, and recovery to control abundance generally occurred within 7 to 28 days of the last nonylphenol application. However, some particularly sensitive taxa e.g. Acroperus and Calanoida did not recover in the 76 µg/l or 243 µg/l treatments by the end of the study. The maximum acceptable toxicant concentration (MATC) for the study was derived as ~10 µg/l (O'Halloran et al., 1998).

In the study of Schmude et al. (1998) benthic macroinvertebrates were studied. The detection limit for the sampling method used was 37-55 organisms/m^2 and a total of 25 taxa were identified. The most abundant groups present in the enclosures were Chironomidae, Oligochaeta and Mollusca, with Chironomidae generally representing >90% of the organisms found. The first sampling date for the treated enclosures was day 25 i.e. 5 days after the last application of nonylphenol. Generally, the oligochaete and chironomid groups showed a similar sensitivity to nonylphenol, with both being significantly reduced in number following 243 µg/l treatments and the abundance of both groups generally recovered to control levels within 4-6 weeks. Molluscs were found to be significantly reduced in number throughout most of the study in the 243 µg/l treatments. The NOEC and LOECs derived from the experiment were 23 µg/l and 76 µg/l based in the mean water concentrations in the enclosures over the first 20 days of the test (Schmude, et al., 1998).

The study of Liber et al. (1998) looked at the effects on nonylphenol on the growth and survival of juvenile bluegill sunfish (Lepomis machrochirus). This species was not native to the pond and so 150 juvenile bluegills were added to each enclosure after the removal of the endemic fish population. The bluegill populations in the various enclosures were sampled (minimum of 10 fish per sample) once before the first nonylphenol application and seven times after the first nonylphenol application (days 5-6, 13-14, 19-20, 26-27, 40, 54 and 70-71) and growth was used as the main endpoint for assessing effects. No significant ($P<0.05$) difference was found in mean lengths and weights of fish from the nonylphenol-treated enclosures when compared to controls at any time during the study. Capture success was used as an indication of reduced bluegill survival. Capture success in the 243 µg/l treated enclosures was lower (although not statistically significant ($p>0.05$)) than in controls from day 19 onwards, and by day 54 the mean capture success in this group was 88% lower (significant at $p<0.001$) than in controls. These findings indicated that at the end of the assessment period (day 70-71), the bluegill populations in the 243 µg/l treatment (83% reduction compared with controls) and also possibly the 76 µg/l treatment (56% reduction compared with controls) had been adversely effected, but the reductions in capture success seen were not significantly different from controls ($p<0.05$) due to low capture success in one of the control groups. The cumulative mortality seen in the enclosures supported these findings as 74 dead fish were found in the 243 µg/l treatments, with 68 of these occurring between days 11 to 22, and the mean mortality seen in the 76 µg/l group was also greater (but not statistically significant) than in controls. Bioconcentration factors of 10-614 (mean 87±124) were determined on a fish wet weight basis for fish from the 5 µg/l and 23 µg/l groups (Liber et al., 1998).

Table 7.8:
Effects observed on zooplankton and macroinvertebrate populations

Taxon	NOEC[a]	LOEC[a]	Maximum reduction relative to controls	Time to recovery (days after last nonylphenol application)
ZOOPLANKTON				
Cladocera	76	243	77	14
Alona	76	243	48	8
Chydorus	76	243	79	14
Pleuroxus	76	243	99	31
Ceriodaphnia	23	76	91	43
Simocephalus	76	243	96	14
Acroperus	23	76	99	>63
Bosmina	76	243	98	1
Kurzia	76	243	99	43
Copepoda	76	243	86	31
Acanthocyclops	76	243	94	31
Eucyclops	76	243	92	31
Macrocyclops	76	243	97	43
Calanoida	5	23	90	>63
Mesocyclops	76	243	98	31
Diacyclops	76	243	92	31
Paracyclops	5	23	91	43
Harpacticoid	76	243	98	31
Rotifera	243	>243	-	-
Monostyla	243[b]	>243	-	-
Polyarthra	243	>243	-	-
Lecane	243[b]	>243	-	-
Trichocerca	23	76	73	63
Keratella	76	243	80	28
Euchlanis	76[b]	243	88	34
Pleosoma	243	>243	-	-
Conochilus	243	>243	-	-
Colurella	76	243	85	31
Platyias	76	243	91	43
Lepadella	243[b]	>243	-	-
Testudinella	76	243	95	≥31
Trichotria	76	243	82	1
Brachionus	243[b]	>243	-	-
Notholca	76	243	93	1
Myytilina	243[b]	>243	-	-
Ostracoda	76	243	82	14
All zooplancton	76	243	67	28
Macroinvertebrates				
Chironomidae Tanytarsini	76	243		53
Chironomini	243	>243		-
Oligochaeta				
Naididae	23	76		75
Tubificidae	243	>243		-
Mollusca				-
Bivalvia	23	76		>399
Gastropoda	76	243		>111 but ≤299

Notes for table 7.8:

a) based on average concentration measured in water during the 20 day exposure period - exposure may have occurred via other phases.
b) showed a significant increase in abundance relative to controls within 7-30 days of last application.

Overall, the lowest NOEC derived in the study was 5 µg/l (for two species of Copepod). Generally the effect levels determined in the study for the various organisms agree reasonably well with the laboratory generated data (Liber et al., 1998).

Taken has a whole, the field studies provides good supporting data for that generated in the laboratory studies.

7.2.4 Estrogenic potencies

White et al., 1994 (in UK, 1998) investigated the estrogenicity of various alkylphenolic compounds in a variety of different in vitro bioassays. The order of estrogenic potency was Octylphenol > Nonylphenol acetic acid > Nonylphenol = Nonylphenol diethoxylate. Octylphenol was active in many of the bioassays at 0.1 µM (20 µg/l) and was 1000 times less potent than ethinyl estradiol.
The oestrogenic potency of various compounds on rainbow trout hepatocytes (Jobling and Sumpter, 1993 in Warhurst, 1995) is 0.000009 for 4-nonylphenol, 0.00016 for 4-t-butylphenol, 0.000037 for 4-t-octylphenol, 0.000006 for NP2EO, 0.0000002 for NP9EO and 0.0000063 for NP1EC related to 17ß-Oestradiol (=1).

Alkylphenol polyethoxylates (APEs) have been shown to be estrogenic both in vitro and in vivo (WRC, 1998). The ethoxylate chain length varies (typically 10-30). In sewage treatment, the ethoxylate chain is degraded rapidly to form short-chain APEs, alkylphenol carboxylates and alkylphenols (APs). Estrogenic activity and toxicity increases with decreasing chain length, with the short chain nonylphenol-1-ethoxylate (NP1EO) and nonylphenol-1-carboxylate (NP1EC) being the two most active forms in vitro and in vivo. Overall, they are weak estrogens, with activities of less than one thousanth the potency of 17ß-Oestradiol (WRC, 1998). Alkylphenol polyethoxylates with more than 3 ethoxylates in the chain hardly have any estrogenic activity(RIVM, 1996).

Alkylphenols (APs) have greater estrogenic activity than the APEs. For example octylphenol is one five hundredth of the potency of 17ß-Oestradiol, representing one of the more potent estrogenic substances (WRC, 1998). It may not be excluded that additivity of estrogenic activity occurs by the separate alkyl phenols (RIVM, 1996).
Nonylphenol is the most commonly used member of the alkylphenol group. Recent research on Daphnia magna suggests that, as well as estrogenic effects, one of the consequences of exposure to nonylphenol is a decrease in the elimination of testosterone and an increase in accumulation of androgenic derivatives. This mechanism, termed metabolic androgenisation, may contribute to the reproductive toxicity of nonylphenol in addition to any estrogenic effects (WRC, 1998). Nonylphenol induced vitellogenin production, an egg yolk protein, in male rainbow trout (Lech, et al., 1996). Chronic exposures to nonylphenol induced testis-ova (an intersex condition characterized by the formation of ovarian tissue, including oocytes, within normal testicular tissue) in Japanses medaka (Gray & Metcalfe, 1997).

7.2.5 Comparing exposure concentrations to environmental criteria

Until now no environmental criteria are set for the alkyl phenols. Therefore a comparison with exposure concentrations can not be made. However, at the moment the derivation of environmental criteria has started.

7.2.6 Toxic effects in marine aquatic environment

General
In table 7.10 to 7.13 the retrieved acute and chronic toxicity data of the alkyl phenols for marine organisms are reproduced. In this report the toxicity tests on crustaceans and molluscs with a testing time of 96 h and less, are regarded as acute. The other tests are regarded as chronic. For algae the EC_{50} values at 96 h are regarded as acute and the NOEC values at 96 h as chronic. For fish the data are per test. Tests on early life stages (ELS) are regarded as chronic. No distinction is made between water and sediment organisms. Table 7.9 gives an overview of the level of toxicity.

Table 7.9:
Overview of the toxicity data on alkyl phenols in the marine environment classified according to the classification system in Annex 4.1
0 = very slightly toxic; * = slightly toxic; ** = moderately toxic; *** = very toxic

Chemical	CAS no	Bacteria/ Protozoan		Algae		Molluscs		Crustaceans		Fish		Amphibian	
		Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron	Acute	Chron
Octylphenol	67554-50-1	***[a]	-	***	-	-	-	***	-	-	-	-	-
Octylphenol ethoxylate	9002-93-1	-	-	-	-	-	-	**	-	-	-	-	-
Nonylphenol	25154-52-3	-	-	***	-	***	**[e]	***	***	***	**[b]	-	-
Nonylphenol ethoxylate	26027-38-3	-	-	***	-	**	0[c]	***	0[c]	**	***[d]	-	-

a. Diatom
b. LOEC behaviour
c. LOEC
d. LOEC avoidance
e. behaviour

Octyl phenol
The table 7.10 shows the lowest toxicity data of octyl phenol for marine organisms. In Annex 4.7 all data are given.
There are no data on chronic toxicity except for 1 endocrine effect.
Octylphenol is acute very toxic to protozoans, algae and crustaceans.
The toxicity data are generally below the limit of the water solubility of 5-12.6 mg/l.

Table 7.10.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol for groups of species from the marine aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	Tetramethyl butyl phenol	0.14	3 d	EC50 population decrease	Skeletonema costatum		Walsh, et al., 1988 (AQUIRE)
Diatom	Tetramethyl butyl phenol	0.09	2 d	EC50 Population decrease	Bellerochea polymorpha		Walsh, et al., 1988 (AQUIRE)
Crustaceans	Tetramethyl butyl phenol	0.0479 – 0.1131	4 d	LC50	Mysidopsis bahia	Static, fed	Cripe et al., 1989 (AQUIRE; in UK, 1998)
Fish	Tetramethyl butyl phenol	81-175 mg/kg	1.83 d	Mortality	Cyprinus carpio	Dose	Loeb, et al., 1963
Endocrine effect							
Mollusc	Octylphenol	<0.001	3 m	LOEC Enlarged accesssory pallial sex glands + enhanced oocyte production; reduced penis and prostate gland length	Nucellus lapillus	renewal, 35 ‰, 14 C	Oehlmann, et al., 2000

Octyl phenol ethoxylate
In table 7.11 the data on the ecotoxicity of octylphenol ethoxylate are given. Data are only available on acute toxicity.
There is only 1 data on the toxicity of octylphenol ethoxylate to algae and there are 2 data on the toxicity to crustaceans. The limited data indicate that octyl phenol ethoxylate is acute moderately toxic to crustaceans.

Table 7.11:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Concentration (mg/l)*	Testing time	Effect type	Organism	Method	Literature(source)
Waterorganisms							
Algae	$OP9.5^{E}O$	-	-	50% depression of growth at 15 mg/l and 10 mg/l	Nitzschia holsatica	-	Nyberg, 1976 (in TemaNord, 1996)
Crustaceans	OP5EO	1.83	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 (in TemaNord, 1996)
Crustaceans	OP1.5EO	6.51-7.07	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 (in TemaNord, 1996)

Nonyl phenol
The tables 7.12.a and b show the lowest toxicity data of nonyl phenol for marine organisms. In Annex 4.8 all data are given.

Nonylphenol is acute very toxic to algae, crustaceans, molluscs and fish. Based on the chronic data nonylphenol is very toxic to crustaceans and moderately toxic to fish and molluscs (based on a LOEC behaviour).
The toxicity data are generally below the limit of water solubility of 5-7 mg/l.
Table 7.12.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol for groups of species from the marine aquatic environment

Class	Substance	Concentra-tion(mg/l)[a]	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	Nonylphenol CAS 84852-15-3 (95% 4-nonylphenol)	0.027 m	96 h	EC50 Cell growth	Skeletonema costatum	21-22°C, pH=7.9-8.1 to 8.3-9.6, 30‰, valid	Ward & Boeri, 1990a in EU, 1999
Molluscs	4-nonylphenol CAS 84852-15-3	0.038 n	96 h	LC50	Mulinia lateralis	Static, use with care	Lussier et al., in EU, 1999
Crustaceans	Nonylphenol CAS 84852-15-3 (4-nonylphenol, branched)	0.018 m 0.030 m 0.043 m	96 h	NOEC LOEC LC50	Mysidopsis bahia	Flow through, 23.8-25.3°C, pH=7.3-8.2, 20‰, valid	Ward & Boeri, 1990c in EU, 1999 (CMA, 1990 in wrc)
Fish	4-Nonylphenol CAS 84852-15-3	0.017 n	96 h	LC50	Pleurnectus americanus	Static, use with care	Lussier, et al., in EU, 1999
Endocrine effects							
Fish	4-p-nonylphenol (>98%)	0.003 n 0.0016 m		LOEC*	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al., 1999

* Increased severity scores of testes of males (=relative or absolute nr of Sertoli cells); also necrotic spermatozoa and germ cell syncytia. Valid = valid for risk assessment (EU, 1999)
a. m = measured; n = nominal

Table 7.12.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol for groups of species from the marine aquatic environment

Class	Substance	Concentration(mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Crustaceans	Nonylphenol CAS 84852-15-3 (4-nonylphenol, branched)	0.0039 m 0.0067 m 0.0051 m 0.0091 m 0.0078 m >0.021 m	28 d	NOEC,Length LOEC,Length MATC, Length LOEC survival F1 MATC Survival F1 LC50	Mysidopsis bahia	Static, 23.3-26.4°C, pH=7.5-8.2, 20-21‰, valid	Ward & Boeri, 1991c in EU, 1999 (CMA, 1991a in wrc)
Molluscs	Nonylphenol CAS 25154-52-3	0.018-0.1	13-30 d	Behaviour	Mytilus edulis	Flow through	Granmo, et al., 1989 in AQUIRE
Fish	Nonylphenol	0.1 1	4 w	NOEC Histology gills NOEC Histology gonads	Platichthys flesus		Banning et al, 1996 in Vethaak RIKZ, 1996
Endocrine effects							
Fish	4-p-nonylphenol (>98%)	0.003 n 0.0016 m		LOEC*	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al, 1999

* Increased severity scores of testes of males (=relative or absolute nr of Sertoli cells); also necrotic spermatozoa and germ cell syncytia. valid= valid for risk assessment (EU, 1999). a. m=measured; n= nominal

Nonyl phenol ethoxylate
The table 7.13a and b show the lowest toxicity data of nonyl phenol ethoxylate for marine organisms. In Annex 4.9 all data are given.

Nonylphenol ethoxylate is acute very toxic to algae and crustaceans and moderately toxic to fish and molluscs. Based on the chronic data nonylphenol ethoxylate is very toxic to fish and very slightly toxic to molluscs and crustaceans. The toxicity data are generally below the limit of the water solubility of >10 mg/l.

Table 7.13.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol ethoxylate for groups of species from the marine aquatic environment

Class		Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae		0.009-0.0122	72 h	EC_{50} growth	Thalassiosira sp.	-	Walsh, 1987 (AQUIRE)
Molluscs	NP10EO	1.5-10	96 h	LC50	Balanus balanoides	-	Swedmark, 1986 in TemaNord, 1996
Crustaceans	NP1.5EO	0.11	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Fish	NP9EO	2.5	96 h	LC50	Gadus morrhua	-	Swedmark, 1971 in CEPA, 2000
Endocrine effects							
Fish	Nonylphenol ethoxylate	>0.010 n >0.0055 m	-	NOEC Mortality, no differences in gonads or secondary sex characteristics or gonads of males and females	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al., 1999

a. m = measured; n = nominal

Table 7.13.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol ethoxylate for groups of species from the marine aquatic environment

Class	Substance	Concentration (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Crustaceans	NP10EO	5	-	LOEC Cirral activity	Balanus balanoides		Lewis, 1991 in Warhurst, 1995
Molluscs	APEO	2.4	21 d	LOEC Larval growth and development	Mytilus edulis		Lewis, 1991 in Warhurst, 1995
Fish	NP10EO	0.002	-	LOEC avoidance	Gadus morrhua		Lewis, 1991 in Warhurst, 1995

Overview of toxicity data for marine organisms
In the Tables 7.14 and 7.15 an overview is given of the lowest retrieved acute and chronic effect concentrations. The concentrations are reflected in **mg/l.**

Table 7.14:
Overview of the lowest retrieved acute effect concentrations ($L(E)C_{50}$) (in mg/l) of the alkyl phenols in the marine environment

Substances	Bacteria/ Protozoan	Algae	Insects/ Worms	Molluscs	Crustaceans	Fish	Amphibian
Octylphenol	0.09 protozoan	0.14	-	-	0.0479-0.1131	-	-
Octylphenol ethoxylate	-	-	-	-	1.83	-	-

Nonylphenol	-	0.027	-	0.038	0.043	0.017	-
Nonylphenol ethoxylate	-	0.009-0.0122	-	1.5-10	0.11	2.5	-

Table 7.15:
Overview of the lowest retrieved chronic effect concentrations (NOEC) (in mg/l) of the alkyl phenols in the marine environment

Substances	Bacteria/ Protozoan	Algae	Insects/ Worms	Molluscs	Crustaceans	Fish	Amphibian
Octylphenol	-	-	-	-	-	-	-
Octylphenol ethoxylate	-	-	-	-	-	-	-
Nonylphenol	-	-	-	0.018-0.1 LOEC [a]	0.0039	0.1[c]	-
Nonylphenol ethoxylate	-	-	-	2.4 LOEC	5 LOEC[d]	0.002 LOEC [b]	

a. LOEC behaviour
b. LOEC avoidance
c. NOEC histology gills
d. LOEC cirral activity

From the tables 7.14 and 7.15 it is clear that marine toxicity data on the alkylphenols are scarce. From the available data it seems that these substances are very toxic to marine organisms.

7.3 Standards and derivation of iMPCs

In MilBoWa (1999) harmonized standards are derived for several environmental compartments for a number of chemicals. The purpose of MilBoWa (1999) is to create a system of limit- and target values for soil and surface water.
A limit value is a quality level that minimally should be achieved or maintained. A target value is a quality level at which no adverse effects are to be expected. The limit value is based upon the "maximal permissible concentration" (MPC), the target value on the "negligible risk level" (NR). At time it could be possible that different MPCs were operative for the same substance because there were also MPCs derived in the framework of the admission of plant protection products and biocides. In 1999 (Kalf, et al., 1999) the procedure for the derivation of MPCs for admission policy of plant protection products and biocides and the setting of environmental quality standards are harmonised.
As a starting-point it is formulated that a MPC is comparable to the concentration at which at least 95% of the species in the ecosystem will be protected (method of Van Straalen and Denneman (1989), modified to the model of Aldenberg and Slob (1991; 1993). There is also formulated that the negligible risk level is comparable to 1% of the MPC.

For the alkylphenols there are no standards derived yet.

For the derivation of MPCs directly from ecotoxicological endpoints two different methods are used: the refined effect assessment method and the preliminary effect assessment method. Because longterm chronic data are preferred above shortterm acute data the aim is to apply the refined effect assessment method. However application of this method is based on data availability: at least four NOEC values are needed for four different taxonomic groups of organisms. If these data are not available the preliminary effect assessment method is applied. In this case in principle the TGD is applied. In figure 7.1 the direct method for MPC derivation is presented.

MPC derivation direct method

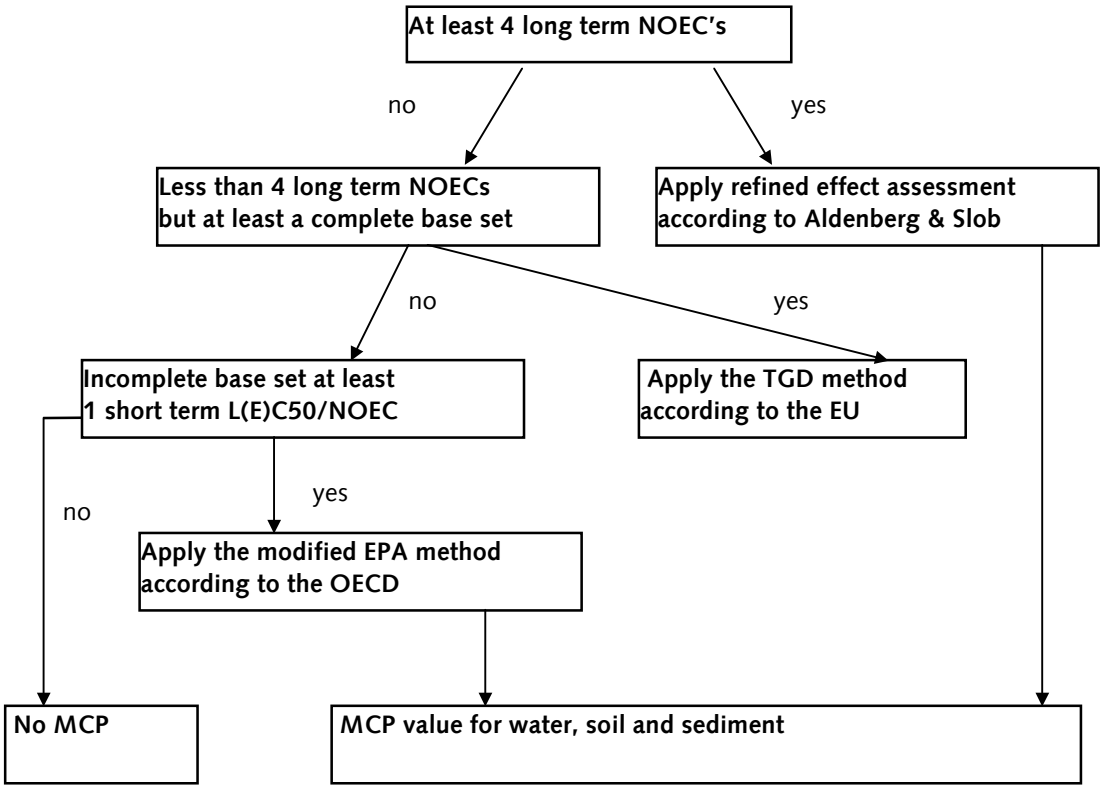

Figure 7.1: Scheme for the derivation of the MPC: direct method

The aim of the environmental quality standards is that the MPC is set at a level that protects all species in an ecosystem. However, in order to be able to use extrapolation methods like the one of Aldenberg & Slob, a 95% protection level is chosen as a sort of cut-off value.
The 95% protection level can be defined for an individual substance if there are NOEC values for at least four different groups of species (e.g. fish, mollusc, crustacean and algae) available. The method of Aldenberg & Slob assumes that the NOECs used for estimating distribution, fit the log-logistic distribution.
If there are not enough data to apply the method of Aldenberg & Slob, the preliminary effect assessment method is used. In principle the assessment factors of the ECB (1996), laid down in the Technical Guidance Documents (TGD), are used. The application of the TGD assessment factors is presented in table 7.16.

Table 7.16:
Assessment factors for aquatic toxicity data following EU/TDG (ECB, 1996) according to EUSES (EC, 1996)

Available valid data	Assessment factor to be applied to the lowest L(E)C50 or long-term NOEC
At least one short-term L(E)C50 from each of 3 trophic levels of the base-set (fish, Daphnia and algae)	1000[a]

One long-term NOEC (either fish or Daphnia)	100[b]
Two long-term NOECs from species representing two trophic levels (fish and/or Daphnia and/or algae)	100[b] 50[c]
Long-term NOECs from at least 3 species (normally fish, Daphnia and algae) representing three trophic levels	50[c] 10[d]
Field data or model ecosystems	Reviewed on a case by case basis

- Base set= 3 L(E)C50 values from acute aquatic toxicity tests, carried out with 3 organisms each representing a different trophic level (algae, Daphnia and fish).
- NOEC should be from long term test and L(E)C50 form short test.

a. Except for substances with intermittent release under no circumstances should a factor lower than 100 be used in deriving a iMPCwater from short-term toxicity data.
b. An assessment factor of 100 applies to a single long-term NOEC (fish or Daphnia) if this NOEC was generated for the trophic level showing the lowest L(E)C50 in short-term tests.
   An assessment factor of 100 applies also to the lowest of two long-term NOECs covering two trophic levels when such NOECs have not been generated from that showing the lowest L(E)C50 of short-term tests.
c. An assessment factor of 50 applies to the lowest of two NOECs covering two trophic levels when such NOECs have been generated covering that level showing the lowest L(E)C50 in the short-term tests. It also applies to the lowest of 3 NOECs covering three trophic levels when such NOECs have not been generated from that level showing the lowest L(E)C50 in the short-term tests.
d. An assessment factor of 10 will normally only be applied when long-term toxicity NOECs are available from at least three species across three trophic levels (e.g. fish, Daphnia, and algae or a non-standard organism instead of a standard organism). The PNECwater should be calculated from the lowest available NOEC. This is only sufficient, however, if the species tested can be considered to represent one of the more sensitive groups. This is particularly important of the substance does not have the potential to bioaccumulate. If it is not possible to make this judgement, then an assessment factor of 50 should be applied to take into account any interspecies variation in sensitivity.
e. For compounds with a high log Kow no short term toxicity may be found. Also, even in long term tests this may be the case or steady state may still not have been reached. For tests with fish for non-polar narcosis the latter can be substantiated by the use of long-term QSARs. It can be considered to use a higher assessment factor in such cases where steady state seems not to have been reached.
f. For substances for which no toxicity is observed in short term tests a long term test has to be carried out if the log Kow > 3 (or BCF > 100) and if PEClocal/regional is > 1/100th of the water solubility. The NOEC from this test can then be used with an assessment factor of 100. If in addition another NOEC from an algae test of the base set is determined, an assessment factor of 50 is applied.

There are two exceptions to the use of the TGD method:

1 Only when long term NOECs on three trophic levels are available, a comparison with data from the (complete) base set is no longer demanded.
2. It is inferred that for more hydrophobic compounds, short term toxicity data may not be representative, since the time span of an acute test may be too short to reach a toxic internal level. In those cases, base set completeness is not

demanded and an assessment factor of 100 may be applied to a chronic test, which should not be an alga test if this is the only chronic test available.

If the base set is incomplete, the TGD method cannot be applied, abitrar safety factors are used (the modified EPA-method (OECD, 1992)): a factor 10 and/or 1000 wille be applied to the NOEC and/or L(E)C50, respectively, to derive the MPC. It should be stressed here that this exception may only be used if the TGD can not be applied.
In Table 7.17 the safety factors of the modified EPA method, dependent on the number of available toxicity data, are presented.

The calculated MTR in this report will be defined as "indicative MPC" (iMPC).
In contradiction to the limit and target values the derived iMPCs have only a technical status and no political value. They are not legally set and may change as soon as more toxicity data become available and/or an MTR is derived by the INS-project.

Table 7.17:
Safety factors for the derivation of iMPCs in surface water (modified EPA method)

Available toxicity data	Safety factor
Lowest acute L(E)C_{50} or QSAR estimation for acute toxicity	1000
Lowest acute L(E)C_{50} or QSAR estimation for acute toxicity for at least algae, crustaceans and fish	100
Lowest NOEC or QSAR estimation for chronic toxicity	10*
Lowest NOEC or QSAR estimation for chronic toxicity For at least algae, crustaceans and fish	10

* this value will be compared with the value based on acute L(E)C_{50} values. The lowest value will be selected.

Based on the retrieved toxicity data the iMPCs are derived using the procedure described by Kalf (1999). For the derivation of the iMPCs the fresh and saltwater toxicity data are combined just as the data concerning pelagic and bentic organisms (based on the assumption that bentic organisms are exposed through the same medium as the pelagic organisms). Biomagnification is not included in this calculation. The toxicity data used for the derivation
of the iMPCs are reflected in Annex 4.2. The iMPCs are in table 7.18.

The iMPCs for sediment are calculated using the equilibrium partition (EP) method (see Slooff, 1992; Beek, 1993).

MTR sed = MTR water x Kp

The equilibrium partition coefficient is calculated with the K_{oc} (see chapter 5, table 5.2) using the following formula:

$Kp = K_{oc}$ x foc ($l.kg^{-1}$)

In the calculation the standard soil is assumed to contain 5% organic carbon.

Table 7.18:

iMPCs for surface water (µg/l) and sediment (µg/kg dry soil)

Substance	Surface water (µg/l)		Sediment (µg/kg ds)	
	iMPC	Method	IMPC	Method
Octylphenol	0.122	TGD/50	16.08	EP (log Kp=2.12)
Octylphenol ethoxylate	-	-	-	-
Nonylphenol	0.239	Ald/Sbb	810	EP (log Kp=3.53)
Nonylphenol ethoxylate	0.044	TGD/50	11.31 5.67	EP (log Kp=2.41 NP1EO) EP (log Kp=2.11 NP2EO)

As no limit values are derived for the alkyl phenols there is no comparison possible with the iMPCs. However a comparison with the concentrations in the environment can be made.
In table 7.19 and 7.20 the concentrations in surface water and sediment from chapter 6 are summarized. Data are available on octylphenol, nonylphenol and nonylphenol ethoxylate.
The iMPC of octylphenol in water is 0.122 µg/l and 16.08 µg/kg ds in sediment. Octylphenol concentrations in surface water in the Netherlands are not measured. Concentrations in the UK are 0.4 µg/l. This indicates that the iMPC is exceeded in the UK. Concentrations of octylphenol in sediment are only measured in Canada: 5-400 µg/kg ds. This means the iMPC is exceeded.
The iMPC for nonylphenol in water is 0.35 µg/l and in sediment 1186 µg/kg ds. Nonylphenol concentrations in surface water in the Netherlands are <0.07 µg/l. Based on the available concentrations the iMPC is not exceeded in the Netherlands. However maximum concentrations in Switzerland, UK, Finland, Germany and the USA all exceed the iMPC for nonylphenol. Nonylphenol concentrations in sediment in the Netherlands are 1520-1670 µg/kg ds. This means the iMPC sediment is exceeded. The same goes for all other maximum values of the measurements in other countries.
The iMPC for nonyphenol ethoxylate is 0.044 µg/l and in sediment 5.67 to 11.31 µ g/kg ds. Nonylphenol ethoxylate concentrations in the Netherlands are 0.14 µg/l. This means the iMPC is exceeded in the Netherlands as well as in Switzerland, the UK and the USA. Nonylphenol ethoxylate concentrations in the Netherlands are 2980-8100. This meams the iMPC sediment is exceeded. The same goes for the measured concentrations in Switzerland and Germany.

Table 7.19:
Concentration ranges in surface water in µg/l on several locations based on data from chapter 6

Location	Year	Octylphenol in surfacewater In µg/l	Nonylphenol in surfacewater In µg/l	Nonylphenol ethoxylate In surfacewater In µg/l
Switzerland	1980	-	0.1-0.64	-
	1984	-	1-10	3-110
	1985	-	4.1	-
	1986	-	0.7-26	-
	1996	-	0.1-0.3	-
UK	1994	0.4	0.5-180	-
	1995	-	0.6-730	6-76
	1996	-	0.01-0.8	-
Finland	1995	-	0.01-0.8	-
Germany	1989	-	0.38	-
	1990	-	0.01-3.3	-
	1991	-	0.01-1.3	-

	1995	-	0.01-0.4	-
USA	1990	-	0.11-0.64	0.13-1.8
Netherlands	1997	-	<0.07	0.14

Table 7.20:
Concentration ranges in sediment and suspended solids in µg/kg ds on several locations based on data from chapter 6

Location	Year	Octylphenol in sediment In µg/kg ds	Nonylphenol in sediment In µg/kg ds	Nonylphenol ethoxylate In sediment In µg/kg ds
Switzerland	1984	-	510-5600	7600-11600
	1985	-	13100	-
UK	1995	-	1000-15000	-
Finland	-	-	0.43-890	-
Germany	1987	-	-	1500
	1991	-	3-14800	-
	1994	-	170-330	-
	1995	-	1000-10000	-
USA	1990	-	<2.9-1280	-
Canada	-	5-400	290-41100	-
Netherlands	1997	-	1520-1670	2980-8100

7.4 Human toxicity

General effects
The alkyl phenols are listed as endocrine disrupters (Colborn, 1993) and may cause estrogenic effects and effects on thyroid hormones.

p-Nonylphenol and p-octylphenol induced cell proliferation in vitro and increased progesterone receptor levels in human breast tumour MCF-7 cells (Soto, et al., 1991, White et al., 1994 in WWF-OSPAR). In vivo nonylphenol induced uterine cornification and endometrial growth in immature rats (Odum, et al., 1997; Lee &Lee, 1996 in WWF-OSPAR). Chronic exposures to octylphenol greatly reduced sperm quantity, and adversely influenced the sizes, weights, and histological structures of the testes, epididymis, ventral prostate glands, seminal vesicles, and coagulating glands in adult male rats (Boockfor & Blake, 1997 in WWF-OSPAR).

No data have been found on interaction of APs with either the thyroid hormone or retinoid pathways (SEPA98).

Octyl phenol and ethoxylate
Octylphenol was not found to be mutagenic in a bacterial Ames test and in a Salmonella typhimurium test (IUCLID, 1996 in WRC, 1998).

Table 7.21:
Acute toxicities to mammalians

Chemical	Species	LD50 (mg/kg)	Reference
o-octylphenol	Rat	2800	NIOSH, 1996 in WRC, 1998
p-tert-octylphenol	Rat	>2000	IUCLID, 1996 in WRC, 1998

p-tert-octylphenol	Rat	2160	NIOSH, 1996 in WRC, 1998
p-tert-octylphenol	Rat	2760	IUCLID, 1996 in WRC, 1998
p-tert-octylphenol	Rat	4040	IUCLID, 1996 in WRC, 1998
p-tert-octylphenol	Mouse	3210	NIOSH, 1996 in WRC, 1998

Octylphenol is readily absorbed and excreted by rats following oral administration. Octylphenol is of low acute toxicity in rodents, with acute LD50 values above 2000 mg/kg (see Table 7.21). In a 90-day study in rats, a NOAEL of 30 ppm and a LOAEL of 300 ppm have been reported based on reduced body weight gain (IUCLID, 1996 in WRC, 1998). In another 90-day study in rats, a much higher NOAEL of 2500 mg/kg bw has been reported. However the quality of the study is uncertain. No other data were located on its chronic toxicity, carcinogenicity or reproductive toxicity.
Octylphenol has been shown to be weakly oestrogenic in a number of in vitro tests and is considered to be more potent than nonylphenol. It has generally been shown to be about 1000 times lower in potency than the synthetic hormone, ethinyl estradiol.
The estrogenicity of octylphenol in rats in vivo was studied in rats in vivo by giving daily oral doses of either 100 – 400 mg/kg for 3 days. No significant effect was seen on absolute uterine weight. There was a statistically significant increase in relative uterine weight at each dose level which ranged from 1.18-fold at 100 mg/kg to 1.31 fold at 400 mg/kg (CTL, 1996 cited in IUCLID, 1996b in WRC, 1998) of which the biological importance is unclear. Considering this it is concluded that octylphenol does not possess estrogenic activity in vivo based on this study (WRC, 1998).

Nonyl phenol and ethoxylate
The acute dietary LC50, lowest-lethal concentration (LLC) and no-observable effect concentration (NOEC) for mortality of nonylphenol ethoxylate 9 (NPE9) administered via the diet to Northern Bobwhite Quail were derived. It appears there were no effects up to 5,000 ppm, which was the highest dose tested.

Exposure routes in the aquatic environment.
Contamination of the aquatic environment (surface water and sediment) can pose a threat to public health. The hazards can be caused by direct and/or indirect contact with the contaminants.
In principle, uptake of contaminants by humans can take place by ingestion (oral), dermal contact (via the skin) and inhalation (via the lungs).

Human health risk assessment evaluation with exposure to sediment
BKH (1991) has conducted a study into the human health risks of recreants potentially exposed to contaminants in sediment. Because children are seen as the most vulnerable group, recreating children are used as a starting point for the derivation of a human-toxicologic based advisory value (HTBA-value) for contaminations in sediment.
Above this value adverse health effects may be expected. In Annex 4.3 the human health assessment evaluation-method is described. The HTBA-values are based on ADI-values (Acceptable Daily Intake) from the literature and the K_{ow}-values. For the alkylphenols there are no ADIs or TDIs available.

7.5 Conclusions

Mechanism of toxicity
Octylphenol and Nonylphenol are capable of binding to the estrogen receptor thus disturbing the endocrine system. The order of estrogenic potency is octylphenol > nonylphenol > nonylphenol ethoxylate.

Metabolism
Octylphenol and nonylphenol ethoxylates are metabolized to octyl- and nonylphenol. The major metabolites of nonylphenol are hydroxylated to hydroxyphenyl hydroxy alkanes.

Toxicity in freshwater environment
From the available data on octylphenol it appears that octylphenol is very toxic to crustaceans and fish and less toxic to algae and bacteria. There are very limited data on the ecotoxicity of octylphenol ethoxylate. These data indicate that octyl phenol ethoxylate is acute very toxic to algae. Abundant data are available on nonylphenol. Nonylphenol is also very toxic to most aquatic organisms. Nonylphenol ethoxylate is very toxic to algae and moderately toxic to crustaceans and fish.

Toxicity in saltwater environment
From the available data on octylphenol it appears that octylphenol is very toxic to aquatic organisms. There are very limited data on the ecotoxicity of octylphenol ethoxylate. These data indicate that octyl phenol ethoxylate is acute moderately toxic to algae. Nonylphenol is very toxic to most aquatic organisms. Nonylphenol ethoxylate is also very toxic to fish and amphibians but very slightly toxic to crustaceans and molluscs.

Limit values and indicative MPCs
The iMPCs are derived for octylphenol (0.122 µg/l and 16.08 µg/kg ds), nonylphenol (0.35 µg/l and 1186 µg/kg ds) and nonylphenol ethoxylate (0.044 µg/l and 5.67 - 11.31 µg/kg ds). Comparing the iMPC with the actual measured concentrations the iMPCs for nonylphenol and nonylphenol ethoxylate are exceeded in the Netherlands. The iMPCs for octylphenol is not exceeded in the Netherlands but concentrations in other countries in Europe do exceed the iMPC.

Humane toxicity
The alkylphenol are acute very slightly toxic to mammalians but are carcinogenic and exert endocrine disrupting effects in mammals. The HTBA-values could not be derived.

7.6 Recommendations

Based on the fact that alkylphenols are carcinogenic and exert endocrine disrupting effects it should be advised to derive an ADI or TDI in order to make a comparison between human exposure and the concentrations in the environment possible.
From comparison of the iMPC with the concentrations in the environment it follows that the iMPC are exceeded in most cases. It is therefore advised to derive an official MPC.
There are for the moment no data available on octylphenol ethoxylate. Although octylphenol ethoxylate is less produced and less measured in the environment, it is recommended to gather more information on these substances because it is closely related to nonylphenol ethoxylates.

7.7 References

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8 Policy overview

8.1 National environmental policy

8.1.1 Netherlands

In the National Environmental Policy Plan (NMP, 1989) and the more recently published National Environmental Policy Plan-3 (NMP-3, 1997) the general environmental policy is described.
In the year 2010 the environmental targets and target values must be reached. Concerning the reverse of the risks caused by high concentrations of chemicals, specific policy targets have been set in the National Environmental Policy Plan of 1989. These targets imply the aim to not exceed the Maximum Permissible Concentrations (MPCs) and the Negligible Concentrations (NCs) in 2010, by means of prevention and reconstruction. These values are guidelines but not legally binding. When the environmental quality standards are set, other aspects, such as political and technical feasibility, are also taken into account. Target values are either set at the NC or at the background value. The derivation of MPCs and NCs is explained in chapter 7.3.
In the report on integral standardisation on substances (INS, 1997) environmental quality standards have been derived. For the alkylphenols and alkylphenol ethoxylates no specific quality standards, MPCs or NCs have been set.
The current water policy is reflected in the Fourth Note on Watermanagement (1997). In this note the targets and headlines of the policy for the national water management are given.

8.1.2 Other country specific policy

PARCOM
Information on nonylphenol has been gathered by Sweden on the implementation of PARCOM Recommendation 92/8 by a number of contracting parties. From the information obtained it appears that virtually all domestic uses of nonylphenol ethoxylates as cleaning agents have been phased out. In most countries this has been achieved by either voluntary action or as a negotiated agreement. The phase out of nonylphenol ethoxylates as cleaning agents for industrial uses varies between different countries (EU, 1999).

Switzerland and Italy
In Switzerland the use of octylphenol ethoxylates and nonylphenol ethoxylates in washing agents and washing auxiliary substances was banned in September 1987. In Switzerland the use of nonylphenol ethoxylates as cleaning agents for industrial uses, has been banned(EU, 1999). In Italy also a general bann has been placed on the use of NPEs.

Netherlands and Belgium
In the Netherlands the use of nonylphenol ethoxylates as cleaning agents for industrial uses is reported as terminated. In Belgium use has strongly decreased, and a screening study of the use and discharge in all sectors in Belgium is due to be executed (EU, 1999).

Sweden
In Sweden use of nonylphenol ethoxylates in cleaning agents was reduced by 70-80% during the period 1990-1995. This reduction is a result of both administrative

actions and voluntary actions from industry (EU, 1999). In Sweden the recommended limit value for nonylphenol in sludge for agricultural use was 100 mg/kg dw this was reduced to 50 mg/kg dw in 1997.

Germany
In Germany, manufacturers and processors of nonylphenol ethoxylates entered into a voluntary agreement in January 1986 to phase-out the use of alkylphenol ethoxylates (nonylphenol and di-isobutylphenol ethoxylates) in domestic laundry detergents and cleansers as well as for detergents used in commercial laundry by the end of 1986, and in aerosol-filled cleansers and disinfectant cleansers from November 1987. They also agreed to look into possible substitution of nonylphenol ethoxylates in industrial uses (wetting agents and detergents in the textile industry by January 1989; use in leather and fur, paper, textiles and industrial cleaners by January 1992) (BUA, 1988). Based on these voluntary commitments, the use of alkylphenol ethoxylates in detergents and cleaning agents was reduced by about 85% from 1986 to 1997. Germany found that the target of a complete phase out in the area of washing and cleaning agents by 1992 was not achieved. Among the reasons given for this failure were a number of low to medium size companies involved which probably were not members of the associations having suscribed to the voluntary agreement; foreign manufacturers and importers continuing to sell products containing alkylphenols in Germany; voluntary commitments were found not to cover all areas of application; the competitive position of alkylphenols compared to alternative products (EU, 1999).

Finland
In Finland PARCOM Recommendation 92/8 has not yet been implemented. However the amount of nonylphenol ethoxylates used in household cleaning agents has decreased sharply during the last few years but the use has not completely phased out (EU, 1999).

Denmark
In Denmark limit values for nonylphenol in sludge to be applied to farmland have been set. From 1 July 1997 the limit value for nonylphenol and nonylphenol ethoxylates (with 1 or 2 ethoxylate groups) in soil is 50 mg/kg dw. This limit value is due to be reduced on the 30 June 2000 to 10 mg/kg dw. Based upon a limited data set of effects data on terrestrial species Denmark have set a soil quality criteria for nonylphenol of 0.01 mg/kg (EU, 1999).

UK
In the UK there is not any specific legislation aimed at nonylphenol or nonylphenol ethoxylates. However, they are covered indirectly by legislation such as integrated control (IPC). Under IPC, releases are required to meet environmental quality standards (EQSs). An operational EQS has been developed for nonylphenol of 1 µg/l.
In 1976 UK industry agreed a voluntary action to phase out the use of nonylphenol ethoxylates in domestic cleaning products. This agreement covered all key manufacturers and, companies, which belonged to a recognised trade association. In 1996/97, the British Association for Cleaning Specialities (BACS) and the Soap and detergent Industry Association (SDIA) reached a voluntary agreement to remove all alkylphenol ethoxylates from industrial and institutional detergent in 1998. This agreement does not cover solvent degreasers (EU, 1999).

8.2 European Commission

In Europe, a voluntary ban on the use of nonylphenol ethoxylates in domestic detergents has been agreed by all the major manufacturers of detergents (EU, 1999).

8.3 International policy

8.3.1 OSPAR

PARCOM Recommendation 92/8 requires Member States to achieve the phase out of nonylphenol ethoxylates in domestic detergents by 1995 and in all detergent applications by 2000 (EU, 1999).

Nonylphenol/ethoxylates (NP/NPEs) and related substances, were identified for priority action in 1998, when the Commission adopted the OSPAR Strategy with regard to Hazardous Substances (cf. Annex 2 of this strategy).

Because octylphenol is considered to show significant endocrine disrupting effects, it is included in the OSPAR 1998 List of Candidate Substances (cf. List 6 in Annex 3 of the OSPAR Strategy with regard to Hazardous Substances) (OSPAR, 2000).

8.4 References

- European Community (1983), Official journal OJ L 147, 6.6
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- NMP (1989) Nationaal Milieubeleidsplan, VROM
- NMP-3 (1997) Nationaal Milieubeleidsplan 3, VROM 97591/b/2-98
- OSPAR (2000) http://www.ospar.org/eng/html/final_OSPAR_2000pressrelease.htm
- OSPAR (1997) Provisional priority list of hazardous substances, DIFF 97/19/1 Annex 5
- UN, PIC, prior informed consent, http://irptc.unepch/pic
- UN, POP, persistent organic pollutants, http://irptc.unepch/pops
- UK (1999) Risk assessment on nonylphenol

Annex 1: Abbreviation list

ADI	Acceptable daily intake
AOP	Aerobic oxidation programme (Syracuse)
APEO	Alkylphenol Ethoxylates
ATP	Adenosine triphosphate
BCF	Bioconcentration factor
BiAS	Bismuth Active Substance
BKH	BKH Consulting Engineers
BUA	Umwelt Bundes Amt
CAS	Chemical Abstract Services
CEFIC	European Chemical Industry Council
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
EC	European Commission
EC50	Effect concentration with 50% effect
ECD	Electron capture detector
EO	Ethoxylate
EPA	Environmental Protection Agency
EPIWIN	Estimation Programme for Microsoft Windows v2.2 (Syracuse)
ER	Estrogen receptor
EU	European Union
EUSES	EU System for estimation of substances
Foc	Fraction organic matter in soil
GC	Gas chromatography
GC/MS	Gas chromatography/ Mass Spectrometry
GDP	Gross Domestic Product
GLP	Good laboratory practice
HPLC	High performance liquid chromatography
HTBA	Human toxicologic based advisory value
iMPC	Indicative Maximum Permissible Concentration
IMTR	Indicative MTR
IUCLID	International uniform chemical information database
KEMI	Swedish national chemicals inspectorate
Koc	Organic carbon content
Kom	organic matter content
Kow	Octanol water partitioning coefficient
Kp	Equilibrium partition coefficient
Kp soil	Equilibrium partition coefficient for soil
LC50	Effect concentration with 50% mortality
LD50	Effect dosis with 50% effect
LOEC	Lowest observed effect concentration
MPC	Maximum Permissible Concentrations
MS	Mass spectrometry
MTR	Maximal tolerable risk
NC	Negligible concentration
NOEC	No observed effect concentration
NP	Nonylphenol
NPE	Nonylphenol ethoxylates
NPnEC	Carboxylic acid of NPnEO formed by oxidation of terminal hydroxyl group
NPnEO	Nonylphenol ethoxylate with n ethoxylate groups
NP1EC	Carboxylic acid of NP1EO formed by oxidation of terminal hydroxyl group
NP2EC	Carboxylic acid of NP2EO formed by oxidation of terminal hydroxyl group

NP1EO	Nonylphenol monoethoxylate
NP2EO	Nonylphenol diethoxylate
NR	Negligible risk
OECD	Organisation for Economic Cooperation and Development
OP	Octylphenol
OPE	Octylphenol etoxylates
OPEO	Octylphenol ethoxylates
OPnEC	Carboxylic acid of OPnEO formed by oxidation of terminal hydroxyl group
OPnEO	Octylphenol ethoxylate with n ethoxylate groups
OP1EC	Carboxylic acid of OP1EO formed by oxidation of terminal hydroxyl group
OP2EC	Carboxylic acid of OP2EO formed by oxidation of terminal hydroxyl group
OP1EO	Octylphenol monoethoxylate
OP2EO	Octylphenol diethoxylate
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PEC	Predicted effluent concentration
PIC	Prior informed consent
PNEC	Predicted no effect concentration
POP	Persistent organic pollutants
QSAR	Quantitative structure analysis r
RIKZ	Rijkswaterstaat Institute for Coastal and Marine Management
RIVM	National institute for human health and environment
RIZA	Institute for Inland Water Management and Waste Water Treatment
SCAS	Semi-Continuous Activated Sludge
SD	Standard deviation
TDI	Tolerable daily intake
TENP	Total extractable Nonyl Phenol
TGD	Technical Guidance Document
TLC	Thin layer chromatography
TOC	Total Organic Carbon
VROM	Ministry of spatial planning and environment
WWTP	Wastewater treatment plant

Annex 2: List of commercially used products

Commercial alkylphenolethoxylates

	CASNR	NMCHEM	MCFORMBRT
1	99561-03-2	Phenol, 4-octyl-, branched	C14-H22-O
2	67554-50-1	Phenol, octyl-	C14-H22-O
3	949-13-3	Phenol, 2-octyl-	C14-H22-O
4	1806-26-4	Phenol, 4-octyl-	C14-H22-O
5	11081-15-5	Phenol, isooctyl-	C14-H22-O
6	27013-89-4	Phenol, 4-isooctyl-	C14-H22-O
7	93891-78-2	Phenol, sec-octyl-	C14-H22-O
8	26401-75-2	Phenol, 2-sec-octyl-	C14-H22-O
9	27214-47-7	Phenol, 4-sec-octyl-	C14-H22-O
10	140-66-9	4-(1,1,3,3-Tetramethylbutyl) phenol	C14-H22-O
11	1818-08-2	Phenol, 4-(1-methylheptyl)-	C14-H22-O
12	3307-00-4	Phenol, 4-(1-ethylhexyl)-	C14-H22-O
13	3307-01-5	Phenol, 4-(1-propylpentyl)-	C14-H22-O
14	3884-95-5	Phenol, 2-(1,1,3,3-tetramethylbutyl)-	C14-H22-O
15	17404-44-3	Phenol, 2-(1-ethylhexyl)-	C14-H22-O
16	18626-98-7	Phenol, 2-(1-methylheptyl)-	C14-H22-O
17	27193-28-8	Phenol, (1,1,3,3-tetramethylbutyl)-	C14-H22-O
18	27985-70-2	Phenol, (1-methylheptyl)-	C14-H22-O
19	37631-10-0	Phenol, 2-(1-propylpentyl)-	C14-H22-O
20	1331-54-0	Phenol, (2-ethylhexyl)-	C14-H22-O
21	30259-97-3	Phenol, octyl-, barium salt	C14-H22-O .1/2 Ba
22	84878-51-3	Phenol, octyl-, cadmium salt	C14-H22-O .1/2 Cd
23	84878-50-2	Phenol, octyl-, calcium salt	C14-H22-O .1/2 Ca
24	26762-90-3	Phenol, octyl-, dihydrogen phosphate	C14-H23-O4-P
25	84878-49-9	Phenol, octyl-, zinc salt	C14-H22-O .1/2 Zn
26	41157-62-4	Phenol, 4-octyl-, barium salt	C14-H22-O .1/2 Ba
27	84394-98-9	Phenol, 4-octyl-, lead(2+) salt	C14-H22-O .1/2 Pb
28	58288-41-8	Phenol, 4-octyl-, potassium salt	C14-H22-O .K
29	78899-79-3	Phenol, 4-octyl-, sodium salt	C14-H22-O .Na
30	93922-02-2	Phenol, isooctyl-, sodium salt	C14-H22-O .Na
31	93922-03-3	Phenol, isooctyl-, potassium salt	C14-H22-O .K
1	25154-52-3	Phenol, nonyl-	C15-H24-O
2	136-83-4	Phenol, 2-nonyl-	C15-H24-O
3	139-84-4	Phenol, 3-nonyl-	C15-H24-O
4	104-40-5	Phenol, 4-nonyl-	C15-H24-O
5	11066-49-2	Phenol, isononyl-	C15-H24-O
6	27938-31-4	Phenol, 2-isononyl-	C15-H24-O
7	26543-97-5	Phenol, 4-isononyl-	C15-H24-O
8	90481-04-2	Phenol, nonyl-, branched	C15-H24-O
9	91672-41-2	Phenol, 2-nonyl-, branched	C15-H24-O
10	84852-15-3	Phenol, 4-nonyl-, branched	C15-H24-O
11	17404-66-9	Phenol, 4-(1-methyloctyl)-	C15-H24-O
12	30607-37-5	Phenol, methyloctyl-	C15-H24-O
13	30784-30-6	Phenol, 4-(1,1-dimethylheptyl)-	C15-H24-O
14	52427-13-1	Phenol, 4-(1-ethyl-1-methylhexyl)-	C15-H24-O
15	28987-17-9	Phenol, nonyl-, barium salt	C15-H24-O .1/2 Ba
16	84878-48-8	Phenol, nonyl-, cadmium salt	C15-H24-O .1/2 Cd
17	30977-64-1	Phenol, nonyl-, calcium salt	C15-H24-O .1/2 Ca
18	83970-30-3	Phenol, nonyl-, cobalt(2+) salt	C15-H24-O .1/2 Co
19	1322-83-4	Phenol, nonyl-, hydrogen sulfate	C15-H24-O4-S

20	72586-00-6	Phenol, nonyl-, lead(2+) salt	C15-H24-O .1/2 Pb
21	27936-43-2	Phenol, nonyl-, potassium salt	C15-H24-O .K
22	54181-64-5	Phenol, nonyl-, sodium salt	C15-H24-O .Na
23	31291-42-6	Phenol, nonyl-, strontium salt	C15-H24-O .1/2 Sr
24	77194-15-1	Phenol, nonyl-, zinc salt	C15-H24-O .1/2 Zn
25	34332-96-2	Phenol, 4-nonyl-, dihydrogen phosphate	C15-H25-O4-P
26	41157-58-8	Phenol, 4-nonyl-, barium salt	C15-H24-O .1/2 Ba
27	54628-06-7	Phenol, 4-nonyl-, sodium salt	C15-H24-O .Na
28	74230-03-8	Phenol, 4-nonyl-, zinc salt	C15-H24-O .1/2 Zn
29	68081-86-7	Phenol, nonyl derivs.	
30	68081-87-8	Phenol, nonyl derivs., phosphosulfurized	
31	68442-67-1	Barium, carbonate 4-nonylphenol complexe	
32	68515-89-9	Barium, carbonate nonylphenol complexes	
33	68515-91-3	Phenol, nonyl derivs., barium salts	
34	68515-93-5	Phenol, nonyl derivs., sulfides	
35	68515-94-6	Phenol, nonyl derivs., sulfides, barium	
36	68515-95-7	Phenol, nonyl derivs., sulfides, calcium	
37	68605-30-1	Barium, nonylphenol tall-oil fatty acids	
38	85665-51-6	Phenol, 4-nonyl-, compd. with 1-piperazine	C15-H24-O .C6-H15-N3
39	90481-05-3	Phenol, nonyl-, manuf. of, by-products	
40	91672-42-3	Phenol, nonyl-, branched, sulfurized	
41	91783-02-7	Phenol, nonyl-, branched, barium salts	
42	93028-52-5	Phenol, nonyl-, barium salt, basic	
43	93384-93-1	Phenol, nonyl-, branched, sodium salt	
44	93762-64-2	Phenol, 4-isononyl-, reaction products	
45	93776-65-9	Phenol, 2-nonyl-, zinc salt	C15-H24-O .1/2 Zn
46	93778-54-2	Phenol, 2-nonyl-, barium salt	C15-H24-O .1/2 Ba
47	93894-07-6	Phenol, 2-nonyl-, cadmium salt	C15-H24-O .1/2 Cd
48	93894-08-7	Phenol, 4-nonyl-, cadmium salt	C15-H24-O .1/2 Cd
49	97811-33-1	Phenol, nonyl-, hydrogen sulfate, ammonium	C15-H24-O4-S.H3-N
50	100209-07-2	Phenol, 4-nonyl-, hydrogen sulfate, branched	
51	100209-08-3	Phenol, 4-nonyl-, hydrogen sulfate, branched	
52	100209-09-4	Phenol, 4-nonyl-, hydrogen sulfate, branched	
	27157-66-0	Decylphenol	C16-H26-O
	27193-86-8	Dodecylphenol	C18-H30-O
	104-43-8	p-Dodecylphenol, 4-docecyl phenol	C18-H30-O

Commercial alkylphenolethoxylates

	CASNumber	Chemical	EO Units
		octylphenolethoxylates	
1	1322-97-0	Octylphenol monoethylene oxide	1
2	2315-67-5	p-Octylphenol monoethoxylate; 2-(4-(1,1,3,3-tetramethylbutyl)phenoxy) ethanol	1
3	9002-93-1	p-tert-Octylphenoxy polyethoxy ethanol; Polyethylene glycol mono(p-(1,1,3,3-tetramethyl butyl)phenyl)ether	> 1
4	9004-87-9	Iso-octylphenyl polyethylene glycol ether	> 1
5	9036-19-5	Octylphenoxy poly(ethoxythanol)	>1
6	68987-90-6	(C8) Branched alkylphenol ethoxylate	>1
7	2315-61-9	p-Octylphenol diethoxylate	2
8	2315-62-0	p-Octylphenol ethoxylate	3
9	2315-63-1	p-Octylphenol ethoxylate	4
10	2315-64-2	p-Octylphenol ethoxylate	5
		nonylphenol ethoxylates	
1	104-35-8	4-Nonyl phenoxy ethanol	1
2	9016-45-9	Poly(oxy-1,2-ethanediyl), .alpha.-(nonylphenyl)-.omega.-hydroxy-	1

	CASNumber	Chemical	EO Units
3	27986-36-3	Nonylphenoxyglycol; (Nonylphenoxy) ethanol; Nonylphenol monoethoxylate	1
4	20427-84-3	4-Nonylphenol diethylene glycol ether; 4-Nonylphenoxy ethoxy ethanol; 2-(2,4-nonylphenoxy)ethoxy ethanol	2
5	27176-93-8	Nonylphenoxy diglycol	2
6	7311-27-5	4-Nonylphenol polyethylene glycol ether	4
7	27177-05-5	Nonylphenol hepta(oxyethylene) ethanol; Nonylphenol octaethoxylate; Nonylphenol octaglycol ether	8
8	26571-11-9	Nonylphenol octa(oxyethylene) ethanol	9
9	27177-08-8	Nonylphenol nona(oxyethylene) ethanol; Nonylphenol decaethylene glycol ether	10
10	68412-54-4	(C9) Branched alkylphenol ethoxylate	>1
11	9016-45-9	Nonylphenol polyethylene glycol ether; Nonylphenol polyethylene oxide; Nonylphenol polyglycol ether; Nonylphenol polyethylene glycol ether; Nonylphenoxy poly(oxyethylene) ethanol	> 1
12	26027-38-3	p-Nonylphenol polyethylene glycol ether; a-(p-Nonylphenyl)-w-hydroxipoly(oxyethylene)	> 1
		Dodecylphenol ethoxylates	
1	9014-92-0	Dodecylphenol polyethylene glycol ether	> 1
2	26401-47-8	Mono(p-dodecylphenyl)polyethylene glycol ether	> 1
		Alkylphenolethoxy acetic acids	
1	108241-00-5	p-Octylphenoxyethoxy acetic acid	-
2	121057-06-5	p-Octylphenoxydiethoxy acetic acid	-
3	121057-07-6	p-Octylphenoltriethoxy acetic acid	-
4	3115-49-9	p-Nonylphenoxy acetic acid	-
5	106807-78-7	4-Nonylphenoxyethoxy acetic acid	-
6	108149-59-3	4-Nonylphenoxydiethoxy acetic acid	-

Listing of synonyms and trademarks of octyl- and nonylphenolethoxylates:

Polyoxyethylene Nonylphenol CAS # [9016-45-9]
Synonyms: Polyethylene Mono(nonylphenyl)ether Glycols; Polyoxyethylene (9) Nonylphenyl Ether; nonyl phenol ethoxylate; nonylphenyl polyethyleneglycol ether, nonionic; polyethylene glycol 450 nonyl phenyl ether, nonionic surfactant; Tergitol NP-9; polyethylene glycol 450 nonyl phenyl ether; Ethoxylated nonylphenol; alpha(nonylphenyl)-omega-hydroxypoly(oxy-1,2-ethanediyl); polyethylene glycols mono(nonylphenyl)ether; macrogol nonylphenyl ether; nonoxinol; polyoxyethylene(n)-nonylphenyl ether; nonylphenoxypolyethoxyethanol; nonylphenyl polyethylene glycol ether; nonoxynol; Makon; ; T-DET-N; surfionic n; sterox; arkopal N-090; carsonon N-9; igepal co-630; neutronyx 600; PEG-9 nonyl phenyl ether; protachem 630; rewpol hv-9; polyoxyethylene nonyl phenol; Glycols, polyethylene, mono(nonylphenyl) ether; Nonylphenol polyethylene glycol ether; Nonylphenol, polyoxyethylene ether; Nonylphenoxypoly(ethyleneoxy)ethanol; POE nonylphenol; Polyoxyethylene nonylphenol; POE (10) nonylphenol;

Triton®X-100 CAS # [9002-93-1]
Synonyms: Alkylaryl polyether alcohol; Octyl phenol ethoxylate; Triton X-100 Surfactant; Polyoxyethylated octyl phenol; alpha-[4-(1,1,3,3-tetramethylbutyl)phenyl]-omega-hydroxypoly(oxy-1,2-ethanediyl); Octoxinol; Triton X 100; Triton X 102; Ethylene glycol octyl phenyl ether; Polyoxyethylene octyl phenyl ether; p-(1,1,3,3-Tetramethylbutyl)phenol ethoxylate; Octylphenoxypolyethoxyethanol; Polyethylene glycol mono [4-(1,1,3,3-tetramethylbutyl)phenyl] ether; Poly(oxyethylene)-p-tert-octylphenyl ether; POE octylphenol; polyoxyethylene (10) octylphenol; POE (10) octylphenol; POE(10) Octyl Phenyl Ether; Octoxynol-10; POE(3) Octyl Phenyl Ether; Octoxynol-3; POE(30) Octyl Phenyl Ether; Octoxynol-30

Trademarks
Accosoft®, Alpha Foamer®, Alpha-Step®, Amidox®, Ammonyx®, Amphosol®, Bio-Soft®,Bio-Step®, Bio-Terge®, Btc®, Btc 2125®, Catigene®, Cedepal®, Cedephos®, Drewmulse®, Drewpol®, Drewpone®, Drewsorb®, Dual-Quat®, Kessco®, Lathanol®, Makon®, Maprosyl®, Micro-Step®, Microfoam®, Nacconol®, Neobee®, Neutronyx®, Ninate®, Ninex®, Ninox®, Ninol®, Nipol®, Onyxide®, Polystep®, So/San®, Steol®, Stepan®, Stepan-Mild®, Stepanate®, Stepanflo®, Stepanflote®, Stepanfoam®, Stepanform®, Stepanlube®, Stepanol®, Stepanpol®, Stepanquat®, Stepantan®, Stepantex®, Stepfac®, Stepflow®, Steposol®, Stepsperse®, Stepwax®, Stepwet®, Toximul®, Wecobee®, EMULPHOPAL®, EMULPHOR®, IGEPAL*

In Europe:
amphosol®, bactistep®, catigene®, secosol®, secoster®, stepanquat®, stepantex®

Annex 3: Degradation of nonylphenol and nonylphenol ethoxylates

Nonylphenol

The biodegradability of nonylphenol has been determined in the modified Sturm test (EEC Directive 79/831 ENV/283/80). In this study nonylphenol (22.8 mg/l) was added to a liquid inoculated medium which was aerated at a temperature of 21-23°C for 32 days. The inoculum used in the test was activated sludge from a municipal sewage plant and had a bacterial count of 18×10^5 CFU/ml (colony forming units/ml). The experiments were carried out both with and without an emulsifier (20 mg C/l) present in the nonylphenol test solution. Two control experiments were conducted with only sodium benzoate and with only emulsifier (Hüls, 1996b).

Degradation was monitored by measuring the actual CO2 evolution compared with the theoretical amount that would be evolved if the substance was completely oxidised. The control substance (sodium benzoate) achieved complete degradation within 20 days, indicating that the inoculum used had sufficient biological activity. Neither nonylphenol, with and without emulsifier, nor the emulsifier itself achieved degradation within 32 days.

In a second study the biodegradability of nonylphenol was studied in the modified Sturm test (EEC Directive 79/831 ENV/283/80) with adapted activated sludge as inoculum. Activated sludge was adapted prior to use in the test by incubation with nonylphenol at a concentration of 5 mg/l for 13 days and then 50 mg/l for a further 5 weeks. Test conditions were the same as in the previous test with the exception that the duration of the test was 40 days. Nonylphenol (22.8 mg/l) was tested with and without an emulsifier (20 mg C/l) and sodium benzoate was used as a control substance. Nonylphenol without emulsifier did not achieve any degradation within 40 days. Nonylphenol in combination with emulsifier achieved however a degradation level of 78% within the 40 day period, whereas the control test with emulsifier alone did not show any degradation (Hüls, 1996c).

The results obtained in the two modified Sturm tests indicate that nonylphenol is not readily biodegradable. Fed to adapted micro-organisms, nonylphenol may undergo biodegradation and is therefore considered to be inherently biodegradable. The difference in nonylphenol degradability seen in the second test with and without the emulsifier is difficult to explain other than in the absence of the emulsifier the availability of nonylphenol to the micro-organisms may be reduced (UK, 1999).

Two other ready biodegradation tests have been carried out with nonylphenol. The results of these have been reported by Williamson and Varineau (1996). In both tests the nonylphenol used was a commercial grade and contained a highly branched alkyl chain. Inocula for the tests were derived from sewage treatment plants receiving predominantly municipal wastewater. In an OECD 301 B test, biodegradation of nonylphenol (10 mg C/l) was monitored by the amount of CO2 generated. Some 10% biodegradation was seen after 10 days incubation, rising to 53% by day 28 (UK, 1999).

In an OECD 301F test oxygen consumption was used to determine the extent of biodegradation. Nonylphenol was tested at a concentration of 31 mg/l (92.4 mg ThOD/l) at 22oC and no emulsifier solvents were used in the test (the test

substance was added directly to the dilution water). The purity of the nonylphenol used was given as 95.6% p-nonylphenol, with the rest as o-nonylphenol, which is in line with the purity of typical commercial products. The average bacterial population of the inoculum used was 106 CFU/ml. The control substance (sodium benzoate) showed >94% degradation within 28 days. For nonylphenol 19% biodegradation was seen in 10 days, rising to 62% in 28 days.
In both the OECD 301B and 301F tests, nonylphenol shows significant biodegradation but fails to meet the criteria for ready biodegradability (10 day window). These results lead to the indication of inherent biodegradability rather than ready biodegradability (Williamson and Varineau, 1996).

Ekelund et al (1993) studied the biodegradation of 4-nonylphenol in seawater and sediment, in which 14C uniformly ring-labelled nonylphenol (containing a mixture of branched isomers) was used. The experiment were performed with contained seawater and seawater with sieved soft bottom sediment. Formalin was added to four flasks containing seawater. Half of the flasks, containing seawater and sediment were bubbled with nitrogen gas prior to the start of the experiment. Subsequently 11 µg 14C ring-labelled nonylphenol was dissolved in acetone and added to small glass plates. After the solvent was evaporated, the glass plates were added to the reaction flasks, and were incubated at 11 ± 2°C in the dark for 16 weeks.

In flasks containing formalin no 14CO2 was recovered. In absence of sediment, degradation (as measured by 14CO2 production) was very slow at 0.06% per day up to 28 days then 1% per day after 28 days, suggesting a period of adaptation is required. In presence of sediment the degradation rate was 1.2% per day. In low oxygen experiments the reaction rate was slow. The increase in degradation rate in the sediment system was attributed to the higher number of micro-organisms present. In flasks without sediment, overall 14C recovery was around 64% (with 44% in the CO2 fraction) and 49% in the flasks with sediment (with 46% in the CO2 fraction). Thus around 45% of the ring-label was converted to CO2 in 8 weeks, giving a mineralisation half-life of slightly longer than 56 days. However, the low overall recovery of 14C-label in the experiments indicates that the actual extent of biodegradation may be higher (with a resulting shorter half-life) than based on 14CO2 measurements, for example due to incorporation of 14C into biomass.

Table 1:
Biodegradation rates of nonylphenol in aquatic environment

Test environment	Identification	Period (days)	Removal (%)	DT-50 (days)	Reference
Sturm degradation test with Inoculated medium	CO_2	32	None	-	Huls, 1996b
Activated sludge Without emulsifier With emulsifier	CO_2	 40 40	 None 78	 - 18	Huls, 1996c
Activated sludge from domestic WWTP	CO_2	0-10 10-40	10 48	65 28	Williamson et al, 1996c
OECD 301F test with inoculated medium	O_2 –demand	0-10 10-28	19 53	33 20	Williamson et al, 1996c
Seawater with sediment Seawater without sediment	$^{14}CO_2$	0-28 0-28 28-56	34 1,7 25	47 960 68	Ekelund et al, 1993
Primary degradation - industrial wastewater - domestic wastewater	 GC- FID / ECD	 5-6 5-6	 45 none	 6,5 -	Gaffney 1976
Primary degradation - river water - lake water	HPLC	 44 44	 84 85	 16,5 16,3	Sundaram et al, 1976

Gaffney (1976) studied the biodegradation of a standard mixture of nine chemicals (including nonylphenol) in domestic wastewater and municipal wastewater. The test concentration was 1 mg/l. Hexane and acetone were used as carrier solvents and allowed to evaporate before the tests were performed. Samples were extracted with hexane and analysed by GC with FID/ECD. No degradation of nonylphenol was observed in tests with only domestic wastewater. In tests with municipal wastewater, nonylphenol levels decreased by 45% in 135 hours, probably due to the fact that municipal wastewaters contained nonylphenol and a variety of other pollutants, and so may have been adapted.

Nonylphenol degradation in stream and pond water was studied by Sundaram and Szeto (1981) under simulated field conditions Water and sediments used were taken from Northland Creek and Hargraft Lake, Ontario, Canada. Degradation experiments of up to 44 days were carried out by incubating water and water/sediment samples (100 g sediment in 200 ml water) with nonylphenol (1 mg/l) in either open or closed flasks at 16oC under artificial light (16 hours light and 8 hours dark per day). Periodically samples were analysed for the presence of nonylphenol by HPLC analysis.

When incubated in either pond (pH 7.3) or stream water (pH 6.9), in open flasks nonylphenol was found to disappear from solution rapidly with an half-life of around 2.5 days for both systems. No degradation products were detected in the water during the experiment and it was thought that the removal from solution was due to volatilisation rather than degradation. When nonylphenol was incubated in pond water or stream water in sealed flasks, the half-life for nonylphenol was found to be 16.5 days in stream water and 16.3 days in pond water. Unidentified transformation products (more polar than the parent nonylphenol) were also shown to be formed in the experiment and it was thought by the authors that these could be formed by microbial degradation or photo-oxidation. In pond water with sediment test flasks, most of the nonylphenol rapidly adsorbed onto the sediment phase. The sediment phase showed a maximum nonylphenol concentration after 10 days, decreasing to only 20% of the nonylphenol added after 70 days. This removal was thought to be due to microbial

degradation as concentrations in autoclaved samples remained constant over the same time period.

Corti et al (1995) studied the microbial degradation of nonylphenol in axenic cultures using a yeast related to the species Candida maltosa strain LMAR1 isolated from sludge samples collected at a treatment plant of textile industry wastewaters. A pure isomer, 4-(1-nonyl)phenol, with a linear alkyl chain was synthesised and used as the sole source of carbon and energy in the experiments. The yeast strain LMAR1 was shown to able to grow when incubated in yeast broth at 28oC with nonylphenol (at a concentration of 100 mg/l) as the sole source of carbon and energy. In presence of nonylphenol, the number of colony forming units (CFU) increased from 4.5×106 cells/ml to 5.6×108 cell/ml at day 21, compared to only a small increase from 1.7×106 cells/ml to 3.8×106 cells/ml in control experiments.

Periodic extracts of the cultures were analysed by GLC. The extracts showed a disappearance on the nonylphenol peak signal after 7 days incubation, with at least four new peaks appearing in the trace representing various degradation products. No significant abiotic degradation was observed in the control experiments. The authors concluded that Candida maltosa is capable of biodegrading nonylphenol. Growth of the yeast suggesting that nonylphenol is at least partially utilised as a carbon and energy source. 4-Acetyl phenol was suggested as a possible metabolite. However, as this experiment was carried out with a single isomer of nonylphenol with a linear alkyl chain, it is not clear if branched chain nonylphenols would behave similarly (Corti et al (1995)).

Trocmé et al (1988) studied the fate of nonylphenol in a simplified soil system and its effect on microbial activity. The soil system was made up of sewage sludge compost (1/3 dry matter) and sandstone (2/3 dry matter) and had the following characteristics: pH 6.8, total nitrogen 0.5%, organic carbon 11%, carbon:nitrogen ratio 20, total phosphorus 1%, cation exchange capacity 22.1 meq/100g, water holding capacity 51%. Two concentrations of nonylphenol were applied (100 and 1000 mg/kg). Nonylphenol persistence was also studied under aseptic conditions. CO2 production was determined by thermal conductivity. Possible volatilisation was measured by phenol traps.

CO2 evolution was significantly depressed by the 4th day in the 1000 mg/kg spiked sample, and a decrease was noted in the ATP (adenosine triphosphate) content in the 1000 mg/kg sample after 5 days. In the control and 100 mg/kg samples such effects were absent. After 40 days 89% nonylphenol was degraded in the 100 mg/kg sample and 62% in the 1000 mg/kg sample. In all tests volatilisation was insignificant. Nonylphenol was more persistent under the semi-sterile conditions with some 24% degradation after 24 days, from which can be concluded that nonylphenol only undergoes microbial degradation after a period of induction. Chromatographic results for nonylphenol indicated that certain isomers of nonylphenol degraded more easily than others.

Marcomini et al (1992) studied the fate of nonylphenol in sludge amended soil. Soil samples were collected from the upper 5 cm of grassland that received anaerobically digested sludge by means of a liquid spread, 4-6 times a year. Nonylphenol was analysed by extraction with hexane and quantified by HPLC with UV-fluorescence detector. The initial concentration of nonylphenol in the soil was 4.7 mg/kg and this had dropped to 0.46 mg/kg dry weight after 322 days. Disappearance of nonylphenol was fast in the first two weeks followed by a slow disappearance from days 30-90. Half-lives for primary degradation were 8 days for initial degradation and 90 days for the second stage.

Kirchman et al (1991) studied the biodegradation of 4-n-nonylphenol in soil (the substance tested had a straight alkyl chain rather than a branched chain usually found in commercial products). In the test, nonylphenol was added to soil at concentrations of 10 or 500 mg/kg and incubated in sealed flasks for 3 months. Degradation was monitored by chromatographical analysis of the parent compound and CO2 evolution. Based on parent compound analysis, less than 10% remained after 10 days. Nonylphenol was not detected (<0.02 mg/kg) after 20 days incubation. At the higher concentration tested, roughly 60% of the nonylphenolic carbon was converted to CO2 after 94 days In the 10 mg/kg test sample, CO2 evolution was similar to that in the controls.

Further evidence for biodegradation of nonylphenol in soil was reported in BUA (1988). In this report the results of an unpublished study were given that indicated that around 95% removal of nonylphenol occured with partial degradation of the aromatic ring occurred after 48 days at 275 mg/kg. Giger et al (1987) observed a 80-90% reduction in nonylphenol soil concentrations 104 days after manure application. Reduction in the soil concentration was initially rapid.

From the test data above can be concluded that nonylphenol undergoes biodegradation in water, sediment and soil. The results from standard biodegradation tests are variable but nevertheless indicate that nonylphenol is inherently biodegradable. Explanation of some deviating test results can be explained by the toxicity of nonylphenol for micro-organisms at used test concentrations.

Results by Corti et al (1995) seem to support the assumption that micro-organisms exclusively grown on nonylphenol exhibit a longer lag phase than control cultures. Further seems to be important that micro-organisms need a period of adaptation as was shown by Ekelund et al (1993) in the degradation of nonylphenol in seawater and by Gaffney (1976) who observed enhanced biodegradation in municipal wastewaters that already contained nonylphenol and so may have been adapted (UK, 1999).

Another factor that needs to be considered is that the nonylphenol supplied is a mixture of compounds with differing degrees of branching/isomers in the nonyl chain. It is known in general, that increased branching in alkyl chains causes a reduction in biodegradability and so it may be expected that in technical nonylphenol, some of the components of the mixture would degrade faster than others.
Trocmé et al (1988) found some direct evidence for this in intermediate chromatographic analyses of nonylphenol during the test (some nonylphenol peaks decreased faster than others). Such an effect may explain why in many of the tests the degradation of nonylphenol appears to follow an initial rapid removal of nonylphenol followed by one or more slower phases (UK, 1999).

Finally, it should be noted that nonylphenol itself contains 9 carbon atoms on the alkyl chain and 6 carbon atoms on the aromatic ring. When CO2 evolution is used as endpoint to show mineralisation, theoretically 60% CO2 evolution would be seen from the alkyl chain only, without any degradation of the aromatic ring. However, there are several tests (both for nonylphenol and nonylphenol ethoxylates) using ring-labelling that clearly show that the aromatic ring undergoes degradation to CO2.

Nonylphenol ethoxylates
An extensive literature survey was performed by the EU Risk Assessment Rapporteur on the biodegradation of nonylphenolethoxylates (NpnEO) under

various environmental conditions. Most of the data refers to branched chain p-nonylphenol groups. A summary of the study results is given below, whereas detailed information is given in ANNEX . In the research projects studied, the following classes of intermediate degradation products were identified:

NPnEO : Nonylphenol ethoxylate with n ethoxylate groups. For commercial products, usually mixtures of straight and branched oligomers, average value for n is 9-10, within a range of 1-20.

NP1EO : Nonylphenol monoethoxylate.

NP2EO : Nonylphenol diethoxylate.

NP1EC : Carboxylic acid of NP1EO formed by oxidation of the terminal hydroxyl group.

NP2EO : Carboxylic acid of NP2EO formed by oxidation of the terminal hydroxyl group.

For evaluation of the biodegradability of surfactants various standard biodegradation tests have been developed. In the OECD Screening Test, which is carried out for 19 days, nonylphenol ethoxylates are used as sole carbon source and primary degradation is monitored by using a Bismuth Active Substance (BiAS). Degradation results based on BiAS analysis indicate to what extent nonylphenol ethoxylate are degraded to compounds with less than 5 ethoxylate groups. Pass mark is 80% removal in the 19 day period (Gerike, 1987).

The OECD Confirmatory Test is used to verify on laboratory scale the behaviour of a surfactant under domestic wastewater treatment conditions. In this test the surfactant is added to synthetic sewage and fed to a vessel containing activated sludge. The average residence time in the vessel is 3 hours. The final effluent (after sedimentation) is analysed for BiAS. Nonylphenol ethoxylates have also been tested in biodegradation tests (e.g. OECD) that measure the ultimate biodegradation (mineralisation). Indicative results from standard biodegradation tests are shown in table 1.

Table 1:
Results from standard biodegradation tests (Gerike, 1987)

Substance	OECD Screening (BiAS removal)	OECD Confirm. Test (BiAS removal)	Closed Bottle Test (COD removal)	Modified OECD Test (DOC removal)
NP9EO	6-78%	97%	5-10%	8-17%
Alkylphenol ethoxylates	84%	96%	29%	-

The BIAS results indicate that primary biodegradation is occurring. From the partial COD and DOC removal in the Closed Bottle and Modified OECD Test it is clear however that after primary degradation refractory intermediates are being formed. Varineau and Williams (1997) recently reported however that NPnEO (n=9) showed 53-58% ultimate degradation (measured as % CO_2 generation in 28 days) in a OECD 301B ready biodegradation test.

Narkis and Schneider-Rotel (1980) further found that ozonation of NPnEO (n=10-15) prior to a modified OECD screening test increased markedly the TOC removal (62.5% TOC removal versus 22.9% TOC removal with no ozonation). Ozonation was thought to cause changes to the aromatic ring that facilitated biodegradation.

Rudling and Solyom (1974) studied degradation of several NPnEO (n=8, 10 and 14) using the OECD Screening Test (at 15 and 20°C instead of 25°C). All three compounds were found to degrade for >90% within 12 days (primary degradation). Gas chromatographic analysis of the test media indicated that after 4 days at 20°C, NP2EO was the major degradation product. NP2EO itself was degraded for 50% after 28 days. At 15°C, however, secondary NP2EO degradation was absent.

Various detailed field studies on aquatic behaviour of nonylphenol ethoxylates and their degradation products refer to wastewater treatment plants in Switzerland and were carried out before regulatory controls were introduced to limit the use of nonylphenol ethoxylates in domestic products. Concentrations shown below do therefore not reflect the current situation in Europe, but the results are still useful for evaluation of the overall behaviour of nonylphenol ethoxylates during wastewater treatment.

Ahel et al (1994b) reported results from surveys of 11 mechanical-biological wastewater treatment plants in the highly urbanised Glatt Valley, Switzerland. Wastewater treatment plants typically consisted of a primary clarifier, aeration tank and secondary clarifier for biological treatment. Sewage sludge was treated in an anaerobic digester. Main components in untreated sewage and primary effluent were NPnEO (n=3-20) which accounted for 82.4% of the nonylphenol derivatives present, followed by NP1EO/NP2EO (11.5%), NP1EC + NP2EC (3.1%) and nonylphenol (3%). In secondary effluent, composition of nonylphenol compounds changed markedly. NPnEO were only present in trace amounts. NP1EC and NP2EC were predominant (46.1%), followed by NP1EO + NP2EO (21.8%) and nonylphenol (3.9%).
Overall removal of NPnEO (n>2) was around 92%. After secondary treatment, nonylphenol compounds were released to the environment in the following composition:

- 8% as untransformed NpnEO
- 11% as NP1EO and NP2EO
- 19% as NPnEC
- 25% as nonylphenol (of which >90% is adsorbed onto digested sewage sludge)

Most of the nonylphenol is found to be formed during anaerobic sludge digestion.

Brenner et al (1988) studied the fluxes of nonylphenol, NP1EO and NP2EO through sewage treatment plants in Switzerland, focusing on the digestion/stabilisation of the sewage sludge at the plants. High levels of nonylphenol (640-2200 mg/kg dry weight) were found in samples of anaerobically digested sewage sludge from 24 plants. Significantly lower levels of nonylphenol were found in samples of aerobically stabilised sludge from 5 plants (mean 300 mg/kg dry weight). Both NP1EO and NP2EO were thought to be precursors to the formation of nonylphenol.

Based on detailed measurements at one plant with anaerobic sludge digestion it was estimated that 50% on a molar basis or 17% on weight basis of the total NPnEO entering into the plant was converted to nonylphenol in the final sewage sludge.

In another Swiss research project, the NPnEO behaviour in 4 wastewater treatment plants was studied in the various stages of treatment. In all plants NPnEO (n=3-20) was largely eliminated (81.3-99.4%). Concentrations of NP1EO and NP2EO were usually slightly lower in secondary effluent. Concentrations of nonylphenol were always lowered by activated sludge (secondary treatment), while the concentration

of NP1EC and NP2EC increased in the effluent after secondary treatment. Tertiary treatment (anaerobic sludge digestion) was shown to further reduce the concentration of nonylphenol, NP1EO and NP2EO in the effluent, but had little effect on the concentration of NP1EC and NP2EC. Analysis results from sludge digestion showed that nonylphenol was concentrated in sludge by a factor of 15, while the concentration of NP1EC and NP2EC in sludge reduced slightly (Giger et al, 1987).

Results for nonylphenol ethoxylates in sewage treatment plants in the United States (see table 2) show that removal of nonylphenol ethoxylate was generally >92%. (Naylor et al, 1992). Nonyl phenol was found in digested sludge at levels of 1,800-2,800 mg/kg.

Table 2:
Removal of NPnEO in wastewater treatment in the United States

Location	NpnEO source	Period	Nonylphenol ethoxylate (µg/l)		
			Influent	Effluent	Removal
South-eastern United States	Textile/furniture	May 1988	1780	103	94.1 %
	Domestic sewage	May 1988	2400	71	97.0 %
Midwest United States	Domestic wastewater and Detergent manufacture	August 1990 March 1991	1540 1130	43 85	97.2 % 92.5 %
Northwest United States	Wood pulp mill 1	June 1990	4700-12200	170- 250	97.5 %
	Wood pulp mill 2	September 1989	13400	2170	84.3 %

Di Corcia et al (1994) studied the behaviour of nonylphenol and its ethoxylates in a mechanical/ biological wastewater treatment plant in Italy over a period of 1 year. Mean removal of nonylphenol ethoxylate was 94.3%. Nonylphenol concentrations in influent and effluent indicate that the removal was around 93%, mainly by adsorption onto sludge.

Formation of nonylphenol during anaerobic sludge digestion in Switzerland was studied by Giger et al (1984). Levels of nonylphenol in 30 anaerobically digested sewage sludges were in the range 450-2500 mg/kg dry weight (mean 1.01 g/kg dry weight). Primary and secondary sewage sludges showed much lower levels of nonylphenol (90-150 and 40-140 mg/kg dry weight, respectively). Levels were also lower in aerobically stabilised sewage sludge (80-500 mg/kg dry weight; mean: 280 mg/kg dry weight). When raw and anaerobic sludges were evenly mixed and digested for 40 days, a 4 to 8 fould increase in nonylphenol content was observed.

Measurements of nonylphenol concentrations in sewage sludge from the United States also show a similar increase in the nonylphenol concentration during anaerobic digestion (Williams and Varineau, 1996). At 4 treatment works, levels of nonylphenol were measured in ingoing sludges and at the outlet of the anaerobic digester. Ingoing levels were 21-64, 3, 180 and 960 mg/kg. After digestion, levels were 380, 1,030, 940 and 540 mg/kg respectively. In contrast, the levels of nonylphenol measured in aerobic sludges at 5 other treatment plants were in the range 1-175 mg/kg.

Degradation behaviour of NPnEO simular to that in anaerobic digesters was also observed in the Glatt River, Switzerland (Ahel et al, 1994c). Main input of nonylphenol compounds into the river was thought to come from secondary effluents from municipal wastewater treatment plants. From 1983 to 1986, daily composite samples were collected from several parts of the river and from

secondary wastewater treament effluent along the river. Most abundant compounds were NP1EC and NP2EC, followed by NP1EO and NP2EO, nonylphenol and finally NPnEO (n>3), which made up only a small fraction. The hydraulic residence time of the river was 10-15 hours. From overall mass balances it was found that:

- 85% of the NPnEO (n>3);
- 70% of the NP1EO and NP2EO and
- 62% of the nonylphenol

were eliminated by biodegradation and/or adsorption to sediment. Further, a 27% increase in NP1EC and NP2EC was observed. Nonylphenol was the major component in sediment.

The degradation of ^{14}C ring-labelled NPnEO (average n=9) has been studied in river die-away tests. The river water for the tests was from the Missouri River, several miles downstream from a wastewater treatment plant. The water was spiked with 1% (w/w) of secondary effluent from a domestic wastewater treatment plant to ensure that the bacteria present in the water had been previously exposed to NPnEO (total number of bacterial colony forming units (cfu) in the test was around 1×10^4 cfu/ml, which is similar to the number found in the Missouri River ($1\text{-}10\times10^4$ cfu/ml)).

For the die-away tests, samples of the water were spiked with 200 µg/l of the ^{14}C-labelled NPnEO and were incubated at 20°C with slow stirring and a gentle airflow over the surface. Primary degradation (defined as degradation into species not identifiable as nonylphenol and NPnEO) was monitored and 89% primary degradation occurred after 28 days and 96% after 128 days. At the end of the experiment (128 days) >95% of the original NPnEC was converted. Ultimate biodegradation (conversion to $^{14}CO_2$) measurements indicated that some 50% of the ^{14}C-labelled nonylphenol was converted to $^{14}CO_2$ in the first 60 days of the test, with an additional 10% nonylphenol conversion to $^{14}CO_2$ in days 60-128. The reduced rate of mineralisation during the second half of the experiment is probably due to a loss of biomass viability (Varineau et al, 1996b and CMA, 1997).

The aerobic biodegradation of a ^{14}C ring-labeled nonylphenol 9-mole ethoxylate (^{14}C-NPE9) was examined in laboratory semi-continuous activated sludge (SCAS) and river water environments (Naylor et al, 1998). In the SCAS experiments primary effluent from a local wastewater treatment plant was dosed with ^{14}C NPE9 and fed into SCAS systems, and levels of ^{14}C in clarified effluent, settled sludge solids, and CO2 were monitored. A significant portion of the ^{14}C consisted of soluble metabolites that had degraded beyond the phenol ring. Dosing of the SCAS system ended after 29 days. Dissipation of residual radioactivity was followed for another 19 days. CO2 evolution and decline of radioactivity in the sludge solids both followed first order rate kinetics, with half-lives of 2.8 days and 5.8 days, respectively. In a river die-away experiment, the $^{14}CO2$ evolution from river water dosed with ^{14}C NPE was monitored for 128 days. After an induction period of 21 days, $^{14}CO2$ evolution followed first order kinetics; half-life was 22 days. It was shown that the NPE phenolic ring is mineralized under activated sludge and die-away conditions (Naylor et al, 1998).

In brackish and saline water, the degradation of a NPnEO (n=10, range 1-18) was studied using a static die-away method. The water was collected from Šibenik Harbour which receives a significant amount of municipal wastewater (the input of nonylphenol ethoxylates to the harbour was estimated at 5 tonnes/year). The water in the harbour is highly stratified with a brackish layer overlaying the saline layer, and both water types were collected in March, September, October and November. The die-away tests were carried out at the temperature at the time of

sampling, which ranged from 13°C in March to 22.5°C in September. The test NPnEO was added to the water samples (0.1 or 1 mg/l) and incubated in the dark. The disappearance of the total nonylphenol ethoxylates present in the sample was monitored, and this was found to occur faster in the brackish water than the saline water. This was thought to be due to an increased amount of pre-exposure of the brackish water to NPnEO compared to the saline layer.

The half-life for disappearance of the NPnEO was found to be longer in winter (> 1 month at 13°C) than in summer (2.5-4 days in brakish and 14-35 days in saline water respectively). Changes in oligomer distribution of the parent NPnEO was also investigated. NPnEO was found to be relatively unchanged during the first 3 days incubation. After 8 days there was a clear shift from higher oligomers (all NPnEO with n>5 had disappeared) to lower oligomers (increase in NPnEO with n<4, with the biggest increase in NP2EO). NP2EO subsequently degraded at a slower rate than seen for the higher oligomers, with low residual amounts of NP2EO after 30 days. Nonylphenol was absent in all cultures (Kveštak and Ahel, 1995).

From the results above can be concluded that primary biodegradation of nonylphenol ethoxylates appears to occur rapidly under wastewater treatment conditions, especially with acclimated microorganisms. The first degradation step for NPnEO (n>3) is rapid hydrolysis of ethoxylate groups to form NP1EO and NP2EO. Once formed, these compounds are partially oxidised to NP1EC and NP2EC. Under anaerobic conditions, however, NP1EO and NP2EO are preferentially converted to nonylphenol. A summary of the relevant degradation behaviour during wastewater treatment is shown in table 3.

Table 3:
Fate of nonylphenol ethoxylates during wastewater treatment

NpnEO	Type of test	Results	Reference
n=9	Coupled Units test	48.6% DOC removal; 97% primary degradation (OECD test)	Gerike (1987)
n=9	Semi-continuous Activated sludge test	Overall 93% removal of the NpnEO; 26% in effluent as NpnEC; 20.8% was mineralised to CO_2; 23.1% highly degraded metabolites; Nonylphenol formation 4,5% of NpnEO	Varineau (1996a)
n=8, 10, 14, 16, and 30	Lab-scale activated sludge system	82-96% removal of the original surfactant	Rudling (1974)
n=9	Lab-scale bioreactors at sewage treatment plant, United States	>95% NpnEO removal; 35-50% as NpnEO/NpnEC	Kravetz (1982).
Influent	Sewage treatment plants, Switzerland	50 mole % of the NPnEO was estimated to form nonylphenol in anaerobic digestion.	Brenner (1987)
Influent	Sewage treatment plants, Switzerland	Overall NPnEO (n>2) removal: 92%. 19% in effluent as NpnEC 11% in effluent as NP1EO + NP2EO 22,5% as nonylphenol, adsorbed onto digested sludge < 2.5% in effluent as nonylphenol 8% released untransformed	Ahel (1994b)
Influent	Sewage treatment plants in the United States	>92% removal of the original surfactant	Naylor (1992); Kubeck and Naylor (1990).

On basis of the results from table 8, the average mass balance for nonylphenol ethoxylates in mechanical/biological wastewater treatment would be as follows:

	%-weight	%-mole
Removal from wastewater		
• Mineralised to CO_2	45 %	13 %
• Adsorption onto sludge	19.5 %	40 %
Released to surfacewater as:		
• NP1EC / NP2EC	17 %	23 %
• NP1EO / NP2EO	8 %	11 %
• Nonylphenol	2.5 %	5,1 %
• NPnEO (n>2)	8 %	8 %

From the results above can be concluded that some 50-55 mole-% of the ingoing ethoxylates are being removed from the wastewater. Major removal mechanism is adsorption onto sludge (75 % of overall removal). Ultimate degradation accounts for the rest (25 %). The load of nonylphenolic compounds to surfacewater largely consists of NP1EC/NP2EC (50 %) and NP1EO/NP2EO (25 %).

The difference between the weight and molar based results are caused by the fact that in the weight based results, mineralisation to CO_2 is related to the overall mass loss, largely due to oxidation of hydrolysed EO molecules. The molar based results are however normalised to the basic amounts of nonylphenolic compounds and therefore present directly to what extent ultimate degradation of phenolic compounds has occured.

As shown above, NPnEO is removed in secondary wastewater treatment by 92 %, but the other nonylphenol ethoxylates (NP1EO, NP2EO, NPnEO, NPnEC) released

with the effluent can still undergo degradation after discharge. Anaerobic degradation of these compounds can potentially lead to a 9-fold increase of the originally released nonylphenol loads. Information from river die-away tests and soil tests however indicate that nonylphenol was found to be a minor degradation product from these compounds (often only traces of nonylphenol were seen in river sediments and soil).

As a worst case scenario, it can be assumed that the release NPnEO to the aquatic environment from secondary treated wastewater effluents, will result in nonylphenol emissions equal to 2.5 weight-% of the ingoing NpnEO loads. The overall conversion of the other nonylphenolic compounds (NP1EO, NP2EO, NPnEO, NPnEC) is likely to have a fairly long half-life, probably of the order of 100 days in water and 30 days in soil.

The degradation of nonylphenol ethoxylates in soil has been examined in field trials (Küchler et al (1994). Over a period of one year, 10 land compartments were treated with two types of sewage sludges or with sanitary effluent containing nonylphenol ethoxylate and nonylphenol. The sewage sludge was mixed into the top 5 cm of the soil. Soil samples collected from various depths (0-10 cm, 10-20 cm and 20-30 cm) were analysed for presence of nonylphenol and nonylphenol ethoxylates. Nonylphenol ethoxylate levels decreased rapidly in time, with no compound being detected after 20 days. No leaching of nonylphenol ethoxylate was seen from the top (0-10 cm layer) indicating that removal was fully by biodegradation. In the first 10 days of the test, the nonylphenol concentration increased, indicating that it was formed by degradation of nonylphenol ethoxylate. After 20 days however, no nonylphenol was detected, indicating that this itself had been degraded.

The biodegradation of nonylphenol ethoxylate and a commercial spray adjuvant product containing 76% nonylphenol ethoxylate in soil has been studied in lab-scale tests. The system used consisted of flasks containing 50 g of dry soil, to which 10 mg (as carbon) of test substance in solution was added. The flasks were incubated in the dark at 22 ± 3°C for 64 days and biodegradation (mineralisation) was measured by CO_2 evolution from the system compared with controls. In some instances, parent compound analysis was also carried out. By day 64 of the experiment, 57% of the nonylphenol ethoxylate and 64% of the adjuvant had degraded to CO_2 (Hughes et al, 1996).

The pass mark for complete mineralisation in the test is usually 50% (based on the fact the microorganisms generally assimilate a significant amount of the available carbon) but for the nonylphenol ethoxylate tested, a third of the carbon in the was associated with the alkylphenol chain, and so the CO_2 evolution seen was not sufficient to confirm that the entire parent compound had degraded. However samples analysed on day 63 showed that no compound containing an aromatic ring or ethoxylate chain was present in the soil, indicating that complete mineralisation had occurred.

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Annex 4: Background information on aquatic toxicity

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Annex 4.1 Used classification systems for aquatic toxicity

Toxicity to algae (96-h, EC_{50}), crustaceans (48-h, LC_{50}) and fish (96-h, LC_{50}):

Class $E(L)C_{50}$ (mg/l)

very toxic		< 1	
moderately toxic	1	-	10
slightly toxic	10	-	100
very slightly toxic		> 100	

Toxicity to aquatic organisms: chronic tests:

Class NOEC (mg/l)

very toxic		< 0.01	
moderately toxic	0.01	-	0.1
slightly toxic	0.1	-	1
very slightly toxic		> 1	

Toxicity to birds: acute oral LD_{50} (mg/kg body weight)

Class LD_{50} (mg/kg)

very toxic		< 5	
moderately toxic	5	-	50
slightly toxic	50	-	500
very slightly toxic		> 500	

Annex 4.2 Overview of the toxicity data per group of organisms (freshwater and marine) used for the derivation of iMPCs in surface water

Table 1:
Acute toxicity data (mg/l)[a]

Substance	Taxonomic group	L(E)C50 (mg/l)	EPA Safety factor
Octylphenol	Bacteria	>10	-
	Protozoan	0.09	-
	Algae	0.14	-
	Crustaceans	0.0479	-
	Fish	0.12	-
Octylphenol ethoxylate	Algae	0.21	-
	Crustacean	1.83	-
Nonylphenol	Bacteria	10	-
	Protozoan	0.5	-
	Algae	0.027	-
	Worms	0.268	-
	Insects	0.057	-
	Mollusc	0.038	-
	Crustaceans	0.0127	-
	Fish	0.017	-
Nonylphenol ethoxylate	Algae	0.009 –0.0122	-
	Mollusc	1.5-10	-
	Crustaceans	0.11	-
	Fish	1	-

a. QSAR calculations using the equations given for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document have not been used because of the high log Kow which makes the QSAR unreliable.
b. Field study (not used for derivation of iMPC).

Table 2:
Chronic toxicity data (mg/l)[a]

Substance	Taxonomic group	NOEC (mg/l)	EPA or TGD Safety factor
Octylphenol	Crustaceans	0.03	-
	Fish	0.0061	50/TGD
Nonylphenol[c]	Algae	0.694	Aldenberg/Slob
	Insect	0.0125	Aldenberg/Slob
	Mollusc	0.2	Aldenberg/Slob
	Crustaceans	0.0039	Aldenberg/Slob
	Crustaceans	0.001	Aldenberg/Slob
	Crustaceans	0.01	Aldenberg/Slob
	Crustacean	0.0887	Aldenberg/Slob
	Fish	0.0005	Aldenberg/Slob
	Fish	0.001	Aldenberg/Slob
	Fish	0.0074	Aldenberg/Slob
	Fish	0.025	Aldenberg/Slob
	Fish	0.0595	Aldenberg/Slob
	Amphibian	0.025	Aldenberg/Slob
Nonylphenol ethoxylate	Algae	8	-
	Molluscs	2.4[b]	-
	Crustaceans	2.2[e]	50/TGD
	Fish	0.01 [b, d]	-

a. QSAR calculations using the equations given for non-polar narcosis in Appendix II of Chapter 4 in the Technical Guidance Document have not been used because of the high log Kow which makes the QSAR unreliable.

b. LOECs.
c. Not all data from the articles are checked.
d. Unreliable value.
e. Article could not be checked.

Annex 4.3 Human health risk assessment evaluation method

Human health risk may occur by direct contact of recreating people with contaminants in the aquatic environment (water, sediment). Playing children (1.5 - 4.5 years old with a body weight of 14 kg) are seen as the most vulnerable groups based on age-bound factors. The relevant exposure routes are through oral intake and dermal contact. The intake (in mg/day) can be calculated for the separate exposure routes for 1 day of playing at the waterside in a worst-case scenario (for a detailed description see BKH, 1991):

Oral intake through sediment

The oral intake through sediment is:

$I_{o,sed} = S_1 * 10^{-6} *$ level B

in which:

$I_{o,sed}$	daily oral intake of contaminants via sediment (mg/kg bw)
S_1	sediment intake in mg dw/day (1020 mg dw/day)
10^{-6}	conversion factor for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

Oral intake through suspended matter

The oral intake through suspended matter is:

$I_{o,susp} = I * S_2 * 2 * 10^{-9} *$ level B

$I_{o,susp}$	daily oral intake of contaminants via suspended matter (mg/kg bw)
I	intake surface water (50 ml/day)
S_2	concentration in suspended matter (300 mg dw/l)
2	correction factor for higher concentrations in suspended matter
10^{-9}	conversion factor for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

Oral intake through surface water

The oral intake through surface water is:

$I_{o,wat} = W_i * 10^{-3} * (10^{0.21}/f_{oc}*K_{ow}) *$ level B

$I_{o,wat}$	daily oral intake of contaminants via water (mg/kg bw)
W_i	intake of surface water (50 ml/day)
10^{-3}	conversion factor for units in the given dimensions
f_{oc}	organic carbon fraction in sediment (0.05)
K_{ow}	partition coefficient octanol/water
B	level of contamination in soil material in mg/kg dw

Dermal contact with sediment

The dermal contact with sediment is:

$I_{d,sed} = O_{skin} * B_{b,skin} * A * M * 10^{-6} *$ level B

$I_{d,sed}$	daily dermal intake of contaminants via sediment (mg/kg bw)
O_{skin}	surface of skin exposed (2800 cm^2)
$B_{b, skin}$	area of skin covered with sediment parts (0.5 mg dw/cm^2)
A	absorption coefficient (0.12/day)
M	matrix effect: the effect of the binding of contaminants to soil particles on body intake (0.15)
10^{-9}	conversion factors for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

Dermal contact with suspended matter

Dermal contact with suspended matter is negligible compared to dermal contact with sediment.

Dermal contact with water

Dermal contact with water is:

$I_{d,wat} = O_{skin} * t * A'' * B_{w,skin} * 10^{-9} * C_w$

$I_{d,wat}$	daily dermal intake of contaminants via water (mg/kg bw)
O_{skin}	exposed skin surface (4560 cm^2)
t	exposure time (3 hours/day)
A''	absorption coefficient (0.01/hour)
$B_{w, skin}$	area of skin covered with water (0.5 µg/cm^2)
10^{-9}	conversion factors for units in the given dimensions
C_w	concentration in water; this is:

$Cw = 2*(10^{0.21})/(f_{oc} * K_{ow}) * 10^3 *$ level B

with:

f_{oc}	organic carbon fraction in sediment (0.05)
K_{ow}	partition coefficient octanol/water
10^3	conversion factor for units in the given dimensions
B	level of contamination in soil material in mg/kg dw

For the calculation of the yearly-averaged daily intake, the daily intake should be multiplied with a factor 30/365; the number of playing days at the water side is estimated at 30 per year.
For the calculation of concentrations of individual contaminants in sediment, the yearly-averaged daily total intake through the above-mentioned exposures routes are compared to a human health guidance value, at which there is a maximal tolerable risk (MTR, ADI). This means the ADI should be multiplied by 14 kg body weight and 0.05 (MTR) to derive the maximum intake per day for a child of 14 kg. In this way HTBA-values may be derived.

In the report of BKH (1991) the level at which there is a maximal tolerable risk (MTR) is linked to the intervention-value-level, an environmental quality level that is established in view of direct measures and at which there is a "serious risk for human health". For the derivation of the HTBA-values for sediment, above which there is a "serious risk", the total contribution of exposure to sediment is set at a maximum of 5% of the MTR. Using this percentage, it is expected that other sources as well as the contribution of other substances, which comparable effects, are sufficiently encountered for.

Annex 4.4 Data on the ecotoxicity of octylphenol to freshwater organisms

Table 4.4.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Bacteria	Octylphenol	**>10**	**3 h**	**EC50**	Act.sewage sludge org.	OECD 204	IUCLID, 1996 in WRC, 1998
Bacteria	Octylphenol	>1700 n	6 h	EC50 Inhibition of oxygen consumption	Pseudomonas putida	GLP	IUCLID, 1996 in WRC, 1998
Algae	Octylphenol	0.3 n **1.1 n** 4.2 n	**72 h**	EC10 **EC50** EC90	Scenedesmus subspicatus		IUCLID, 1996 in WRC, 1998
Algae	Octylphenol	1.9	96 h	EC50	Selenastrum capricornutum	GLP, Static, 24-25°C	IUCLID, 1996 in WRC, 1998
Crustacean	Tetramethyl butyl phenol	0.01-0.04	<5 d	NOEC Development	Daphnia magna	Renewal	Zou, et al, 1997
Crustacean	Tetramethyl butyl phenol	**0.09**	**2 d**	**LC50**	Daphnia magna	Static	Zou, et al, 1997
Crustacean	Octylphenol	0.17 n	24 h	LC50	Daphnia magna		IUCLID, 1996 in WRC, 1998
Crustacean	Octylphenol	0.11 m 0.26 m 0.27 m	- 24 h 48 h	NOEC LC50 LC50	Daphnia magna	Flowthrough, 20°C, pH 8.3-8.4	IUCLID, 1996 in WRC, 1998
Crustacean	4-tert octylphenol, 95%	0.586-0.916 µM	96 h	NOEC survival	Daphnia magna	DSWL water, pH 7.8-7.4, 28, DO>60%	Gerritsen, et al., 1998
Fish	Octylphenol	0.084 **0.12** 0.17	14 d **14 d** 6 d	NOEC **LC50** LC50	Oncorhynchus mykiss	Flowthrough, GLP, 12 °C, pH=8-8.2	IUCLID, 1996 in WRC, 1998
Fish	Octylphenol	0.077 m 0.25 m 0.29 m	96 h 96 h 24 h	NOEC LC50 LC50	Pimephales promelas	Flowthrough, 22°C, pH= 8-8.2, GLP	IUCLID, 1996 in WRC, 1998
Fish	Octylphenol	0.21 m 0.26 m 0.39 m	96 h	LC0 LC50 LC100	Leuciscus idus	Semi-static, GLP	IUCLID, 1996 in WRC, 1998
Fish	Octylphenol	0.6 n	48 h	LC50	Leuciscus idus		IUCLID, 1996 in WRC, 1998
Fish	p-Octylphenol	1.05	48 h	LC50	Cyprinus carpio	-	MITI, 1992 in TemaNord 1996
Sediment organisms							
Crustacean	Octylphenol	0.0133 **0.0196 m**	**96 h**	EC50 Immobility **LC50**	Gammarus pulex	Semi-static	Sims and Whitehouse, 1998 in WRC, 1998

* m = measured, n = nominal
GLP = Good Laboratory Practice

Table 4.4.b:
Retrieved estrogenic effects with concentration (mg/l) of octyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Con.c (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Estrogenic effects							
Mollusc	Octylphenol	**<0.001**	5 m	**LOEC induction superfemales**	Marisa cornuarietis	renewal, tap water, 22 C	Oehlmann, et al., 2000
Mollusc	Octylphenol	<0.001	12 m	LOEC induction superfemales	Marisa cornuarietis	renewal, tap water, 22 C, life cycle test	Oehlmann, et al , 2000
Fish	Octylphenol	**0.003**	-	**LOEC increased vitellogenin production**	Salmo gairdneri Males		Jobling, et al, 1996 in WRC, 1998
Fish	4-tert-octylphenol >97%	0.02	21 d	LOEC increased vitellogenin in serum, % fertlized eggs, survival of embryo's, inhibition spermatogenesis	Oryzias latipes Male	Flow through	Gronen, et al, 1999
Fish	Octylphenol	0.03	3 w	LOEC inhibition of testicular growth, histology of testes (inhibition of spermatogenesis)	Salmo gairdneri Males	Exposure during sexual development	Jobling, et al, 1996 in WRC, 1998
Fish	Octylphenol	0.03	35 d	LOEC Increased vitello-genin levels in males and females and modified skin structure in males, decreased mucus cell numbers, epidermal and dermal thickness, increased relative fecundity and egg volume in females	Salmo gairdneri		Ashfield, et al, 1995 in WRC, 1998
Fish	Tert-octylphenol	0.150	9 d	LOEC Increased plasma vitellogenin		Water exposure	Pedersen, et al, 1999 in Chemweb, 2000
Fish	n-octylphenol	0.150	9 d	NOEC Increased plasma vitellogenin		Water exposure	Pedersen, et al, 1999 in Chemweb, 2000
Fish	4-tert Octylphenol	0.434 (2.11 µ M)	4 d	ED50 Vitellogenin production	Salmo gairdneri hepatocytes	Rel potency 0.000037, in vitro	Jobling & Sumpter, 1993 in Warhurst, 1995; Epa, 1997; DHC99
Fish	4-tert Octylphenol	0.003 M	-	Binding affinity, 50% displacemnet of oestradiol	Salmo gairdneri plasma	RBA<0.01 relative to 100% oestradiol	Milligan, et al., 1998
Fish	Tert-octylphenol	50 mg/kg	12 d	LOEC Increased plasma vitellogenin		injection	Pedersen, et al, 1999 in Chemweb, 2000
Fish	n-octylphenol	50 mg/kg	12 d	NOEC Increased plasma vitellogenin		injection	Pedersen, et al, 1999 in Chemweb, 2000
Amphibian	4-octylphenol	**78320 10^{-9}M**	-	**IC50 binding affinity to ER**	Xenopus laevis Liver cells	-	Lutz, et al, 1999

* m = measured, n = nominal

Table 4.4c:

Retrieved chronic effect concentration (NOEC) (mg/l) of octyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature(source)
Waterorganisms							
Crustaceans	Octylphenol	**0.03** 0.1	**21 d**	**NOEC Reproduction rate** LOEC	Daphnia magna		IUCLID, 1996 in WRC, 1998
Crustaceans	Octylphenol	0.34 >0.037 <0.062	21 d	EC50 Survival young/adults, adult mean length MATC	Daphnia magna	Flow through, GLP, meas.	IUCLID, 1996 in WRC, 1998
Fish	Tetramethyl butyl phenol	0.001-0.03 0.001-0.05	24 d 22 d	NOEC growth LOEC decr. growth	Oncorhynchus mykiss		Ashfield, et al, 1998 in AQUIRE
Fish	Tetramethyl butyl phenol	0.001-0.03	35 d	NOEC Changed morphology	Oncorhynchus mykiss		Ashfield, et al, 1998 in AQUIRE
Fish	Octylphenol	0.001 0.01	35 d	Increased growth Decreased growth	Oncorhynchus mykiss		Ashfield, et al, 1995 in WRC, 1998
Fish	Octylphenol	**0.0061 m** 0.011 m	**60 d**	**NOEC** LOEC	Oncorhynchus mykiss	Flow through, GLP, post-hatch Early life stage	IUCLID, 1996 in WRC, 1998
Fish	> 97% 4-tert Octylphenol	0.005	21 d	NOEC reproduction, embryo survival	Oryzias latipes	Preliminary test 27C, pH 8.7	Gronen, et al., 1999

* m = measured, n = nominal
GLP = Good Laboratory Practice

Annex 4.5 Data on the ecotoxicity of nonylphenol to freshwater organisms

Table 4.5.a:
Retrieved acute effect concentration (µg/l) of nonyl phenol for Bacteria and flagellates from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Bacteria	4-nonylphenol	>10	30 min	EC10 Oxygen consumption	Pseudomonas putida		Knie, et al, 1983 in UK, 1999
Bacteria	4-nonylphenol	16	-	EC10 Oxygen consumption	Pseudomonas putida		Trenel & Kuehn, 1982 in wrc, 1998
Bacteria	4-nonylphenol	**10** 32 >40	2 h 2 h 24 h	**50% inhibition of spore germination** >99% inhibition of spore germination no inhibition	Bacillus megaterium		Lewis & Jurd, 1972 in UK, 1999
Flagellate	Nonylphenol	**0.5** 0.75	-	**55% inhibition of photosynthesis** 100% inhibition of photosynthesis	Chlamydomonas reinhardii		Moody & Weinberger, 1983 in UK, 1999
Flagellate	Nonylphenol	0.5-0.7	1 h	Cell membrane disorganisation, distorted flagellae	Chlamydomonas reinhardii		Weinberger & Rea, 1981 in UK, 1999; WRC, 1998
Flagellate	Nonylphenol	0.5 0.75	-	75% inhibition of photosynthesis 100% inhibition of photosynthesis	Chlamydomonas reinhardii		Moody et al 1983 in wrc, 1998

* m = measured, n = nominal

Table 4.5.b:
Retrieved acute effect concentration (mg/l) of nonyl phenol for aquatic plantae and algae from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Plantae	Nonylphenol CAS 25154-52-3	0.901 m 2.08 m	96 h	NOEC LOEC Frond production	Lemna minor	Valid	Brooke, et al, 1993a in UK, 1999
Plantae	Nonylphenol	0.5	2 d	Inhibition of frond production	Lemna minor		Prasad, 1989 in UK, 1999
Plantae	Nonylphenol	0.125	4-9 d	LOEC Reduction in growth	Lemna minor		Prasad, 1989 in UK, 1999; WRC, 1998
Plantae	Nonylphenol	0.5	4-9 d	EC100 Bleaching, chlorosis, mortality	Lemna minor		Prasad, 1989 in UK, 1999; WRC, 1998
Plantae	Nonylphenol	2.5	3 d	Inhibition of frond production	Salvinia molesta		Prasad, 1989 in UK, 1999
Plantae	Nonylphenol	2.5-25	6-9 d	Phytotoxic: mortality	Salvinia molesta		Prasad, 1989 in UK, 1999
Algae	branced NP	0.027	96 h	EC50 Growth	Selenastrum capricornutum		CMA, 1990d in TemaNord, 1996
Algae	Nonylphenol CAS 25154-52-3	0.0033 **0.0563**	72 h	EC10 Biomass **EC50** **Biomass**	Scenedesmus spicatus	EN 28692/ISO 8692, DIN 38412-9, valid	Kopf, 1997 in UK, 1999
Algae	Nonylphenol CAS 25154-52-3	0.0251 0.323	72 h	EC10 Growth rate EC50 Growth rate	Scenedesmus spicatus	EN 28692/ISO 8692, DIN 38412-9, valid	Kopf, 1997 in UK, 1999
Algae	Nonylphenol CAS 84852-15-3 (95% 4-nonylphenol)	0.41 m	96 h	EC50 Cell growth	Selenastrum capricornutum	23.2-23.7°C, pH=7.4-7.5 to 8.2-8.9, valid	Ward &Boeri, 1990b in UK, 1999
Algae	Nonylphenol	0.5 1.3	72 h	EC10 Cell growth EC50 Cell growth	Scenedesmus spicatus	GLP, valid	Hűls, 1996d in UK, 1999
Algae	Nonylphenol CAS 104-40-5	1.5 25 0.025-7.5	24 h 24 h -	EC50 LC100 Growth reduction	Chlorella pyrenoidosa		Weinberger & Rea, 1982 in UK, 1999
Algae	Nonylphenol CAS 25154-52-3	2.5	0.33-0.58 d	Biochemical effects	Chlamydomonas reinhardtii	Static	Weinberger, et al, 1987 in AQUIRE
Algae	Nonylphenol CAS 25154-52-3	>0 - < 10	0.08 d	Biochemical effects	Chlamydomonas reinhardtii	Static	Brack, et al, 1998 in AQUIRE, 2000

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.5.c:
Retrieved acute effect concentration (mg/l) of nonyl phenol for molluscs and crustaceans from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Molluscs	Nonylphenol	**0.0005 – 0.005** **0.010**	3-7 d	**Ceased production of egg mass, death of adults** **Reduced egg mass production, hatching affected**	Lymnaea stagnalis		Smith, et al, 2000 in SETAC 2000
Molluscs	Nonylphenol	0.005	10 d	Delay in development and reduction in number of hatchlings	Lymnaea stagnalis		Smith, et al, 2000 in SETAC 2000
Crustaceans	Nonylphenol CAS 104-40-5	0.025-0.1	2.67 d	Changed hormone levels	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE, 2000
Crustaceans	Nonylphenol CAS 84852-15-3 (>95% 4-nonylphenol)	**0.069 m** 0.276 m	96 h	**EC50** LC50	Ceriodaphnia dubia	24-25°C, Static, valid pH=8.3-8.6,	England, 1995 in UK, 1999
Crustaceans	Nonylphenol	0.085	48 h	EC50	Daphnia magna	Static, valid	Brooke, 1993a in UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.09 n	24 h	EC0	Daphnia magna	Static, 20°C, pH=8, use with care	Bringmann & Kűhn, 1982 in AQUIRE, 2000; UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.14 n 0.218 n	48 h 24 h	EC50 immobilisation	Daphnia magna	Static, 20°C, pH=7.5, valid	Hűls, 1992c in UK, 1999
Crustaceans	Nonylphenol CAS 104-40-5	0.14-0.19	24 h	EC50	Daphnia pulex	25°C,	Ernst, et al, 1980 in UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.15	2 d	Increased mortality (100%)	Daphnia galeata mendotae	Static	Shurin, et al, 1997 in AQUIRE, 2000
Crustaceans	Nonylphenol CAS 104-40-5	0.18 n	24 h	EC50	Daphnia magna	PH=8, use with care	Bringmann & Kűhn, 1982 in UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.19 m	48 h	EC50 Intoxication	Daphnia magna	Static, pH=8.25, 20°C, valid	Comber, et al, 1993 in AQUIRE, 2000; UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.3 m	24 h	EC50 Intoxication	Daphnia magna	Static, pH=8.25, 20°C, valid	Comber, et al, 1993 in AQUIRE, 2000; UK, 1999
Crustaceans	Nonylphenol CAS 25154-52-3	0.34 n	24 h	EC100	Daphnia magna	Static, pH=8, 20°C, use with care	Bringmann & Kűhn, 1982 in AQUIRE, 2000; UK, 1999
Crustaceans	Nonylphenol	0.44	48 h	EC50	Daphnia magna		Monsanto, 1985 in UK, 1999
Crustaceans	Nonylphenol	Mean 0.47 n	48 h	EC50	Ceriodaphnia dubia	25°C, use with care	Ankley, et al, 1990 in UK, 1999
Crustaceans	Nonylphenol	> 0.3 n	48 h / 96 h	L(E)C50	Ceriodaphnia dubia	Static, renewal	CMA, 1995 in wrc, 1998
Crustacean	4-nonylphenol, 85%	0.617-1.37 µM	96 h	NOEC survival	Daphnia magna	DSWL water, pH 7.8-7.4, 28, DO>60%	Gerritsen, et al., 1998

* m = measured, n = nominal
Valid: valid for risk assessment (UK, 1999).
Table 4.5.d:

Retrieved acute effect concentration (mg/l) of nonyl phenol for fish from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Fish	Nonylphenol CAS 104-40-5	0.05-0.22 µ g/l	4 d	NOEC decreased biochemical in Brain	Salmo gairdneri	Static	Jones, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 104-40-5	0.08-0.22 µ g/l	4 d	NOEC decreased biochemical in Brain	Pimephales promelas	Static	Jones, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 104-40-5	0.08-0.22 µ g/l	4 d	NOEC decreased biochemical in Brain	Ptychocheilus lucius	Static	Jones, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.01414	3 d	EC50 Genetic	Salmo gairdneri	Flow through	Lech, et al, 1996 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.018-0.036	0.33-0.58 d	Increased accumulation in multiple organs	Onchorhynchus mykiss	Static	Lewis, et al, 1996 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.060-0.187	96 h	Behaviour	Pimephales promelas	Flow through	Holcombe, et al, 1984 in AQUIRE, 2000
Fish	Nonylphenol	0.0831 m 0.23 m	96 h	NOEC Mortality LOEC mortality	Pimephales promelas	Flow through, valid	Brooke, 1993b, in UK, 1999
Fish	Nonylphenol	0.0865 m 0.211 m	96 h	NOEC Mortality LOEC mortality	Lepomis macrochirus	Flow through, valid	Brooke, 1993b, in UK, 1999
Fish	Nonylphenol CAS 25154-52-3	0.098-0.187	96 h	Physiologic effects	Pimephales promelas	Flow through	Holcombe, et al, 1984 in AQUIRE, 2000
Fish	Nonylphenol	**0.096 m** 0.128 m	96 h	**EC50** LC50	Pimephales promelas	Flow through, valid	Brooke, 1993a in UK, 1999
Fish	Nonylphenol	0.109 0.221	96 h	EC50 LC50	Onchorhynchus mykiss	Flow through, valid	Brooke, 1993a in UK, 1999
Fish	Nonylphenol CAS 104-40-5, (4% 2-nonylphenol 91% 4-nonylphenol 5% dinonylphenol)	0.135 0.187 m 0.098 m	96 h 96 h 96 h	LC50 LOEC lethargy LOEC loss of equilibrium	Pimephales promelas	Flow through, pH=6.9-7.7, 24.6°C	Holcombe, et al, 1984 in AQUIRE, 2000; UK, 1999
Fish	Nonylphenol CAS 25154-52-3 (91% 4nonylphenol 4% 2-nonylphenol; 2% nonylphenol)	0.137	72 h	LC50	Pimephales promelas	Flow through, pH=6.9-7.7, 26.4°C	Holcombe, et al, 1984 in HSDB, 2000
Fish	Nonylphenol CAS 104-40-5	0.14	96 h	LC50	Pimephales promelas	24.5°C, pH=7.29	Geiger, et al, 1985 (II)
Fish	Nonylphenol CAS 104-40-5	0.145	96 h	LC50	Salvelinus		McLeese, et al, 1980b in kemi, 1989
Fish	Nonylphenol	0.145	96 h	LC50	Salvelinus fontinalis		Armstrong & Kingsbury, 1979, in UK, 1999
Fish	Nonylphenol CAS 25154-52-3 (91% 4nonylphenol 4% 2-nonylphenol; 2% nonylphenol)	0.164 (0.145-0.186)	48 h	LC50	Pimephales promelas	Flow through, pH=6.9-7.7, 26.4°C	Holcombe, et al, 1984 in HSDB, 2000
Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)

Fish	Nonylphenol CAS 25154-52-3	0.19365	3 d	LC50	Salmo gairdneri	Flow through	Lech, et al, 1996 in AQUIRE, 2000
Fish	Nonylphenol	0.203 m 0.209 m	96 h	EC50 LC50	Lepomis macrochirus	Flow through, valid	Brooke, 1993a in UK, 1999
Fish	Nonylphenol	0.23	96 h	LC50	Onchorhynchus mykiss		Armstrong & kingsbury, 1979 in UK, 1999
Fish	Nonylphenol	0.3	96 h	LC50	Pimephales promelas		Monsanto, 1985b in wrc, 1998
Fish	4-nonylphenol	0.4	96 h	LC50	Oryzias latipes	Static	Yoshimura, 1986 in UK, 1999
Fish	Nonylphenol	0.48	24 h	LC50	Oncorhynchus mykiss		Ernst et al, 1980 in UK, 1999
Fish	Nonylphenol CAS 104-40-5	0.48-0.92	96 h	LC50	Salmo gairdneri		Ernst, et al, 1980 in kemi, 1989
Fish	Nonylphenol	0.51	96 h	LC50	Pimephales promelas		Waldock & Thain, 1991 in UK, 1999
Fish	Nonylphenol	0.56 n	48 h	LC50	Leuciscus idus melanotus	Static,20° C pH=7.2-7.3, Use with care	Hűls, 1996f in UK, 1999
Fish	Nonylphenol	0.95	48 h	LC50	Leuciscus idus melanotus	Static	Huels, 1988 in wrc, 1998
Fish	NP	0.95	48 h	LC50	Cyprinus carpio	-	MITI, 1992 (in TemaNord, 1996)
Fish	Nonylphenol	1.4	48 h	LC50	Gasterosteus aculeatus		Granmo, 1991 in UK, 1999
Fish	Nonylphenol CAS 104-40-5	1.3	-	LC50	Leuciscus idus		Knie, et al, 1983 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	4.370	2 d	LC50	Oryzias latipes	-	Yoshioka, et al, 1986 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	5	0.58 d	Behaviour	Petrpmyzon marinus	Static	Appelgate, 1957 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	5	0.17 d	Behaviour	Onchorhynchus mykiss	Static	Appelgate, 1957 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	10	24 h	Behaviour, mortality	Onchorhynchus kisuth	Static	MacPhee, et al, 1969 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	10	24 h	Behaviour, mortality	Onchorhynchus tshawytscha	Static	MacPhee, et al, 1969 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	10	24 h	Mortality	Ptychocheilus oregonensis	Static	MacPhee, et al, 1969 in AQUIRE, 2000

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.5.e:
Retrieved acute effect concentration (mg/l) of nonyl phenol for sediment organisms from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Sediment organisms							
Worms	Nonylphenol CAS 25154-52-3	**0.268 m** 0.342 m	96 h	**EC50 Inactivity** LC50	Lumbriculus variegatus	Flow through, valid	Brooke, et al, 1993a in UK, 1999
Insects	Nonylphenol	0.097 m	96 h	MATC	Chironomus tentans	GLP	CMA, 1993 in wrc, 1998
Insects	4-nonylphenol	**0.057 m**	96 h	**EC50**	Ischnura elegans	Static, renewal	Sims, et al, 1997 in wrc, 1998
Insects Insects	4-nonylphenol Nonylphenol	0.108 m 0.16 m	96 h 96 h	LC50 EC50	Ischnura elegans Chironomus tentans	Static, renewal GLP	Sims, et al, 1997 in wrc, 1998 CMA, 1993 in wrc, 1998
Insects	Nonylphenol CAS 25154-52-3	0.596 m	96 h	EC50 Loss of equilibrium	Ophiogomphus sp.	Flow through, valid	Brooke, et al, 1993a in UK, 1999
Molluscs	Nonylphenol CAS 25154-52-3	**0.378 m** 0.774 m	96 h	**EC50 Inactivity** LC50	Physella virgata	Flow through, valid	Brooke, et al, 1993a in UK, 1999
Crustaceans	4-nonylphenol	**0.0127 m**	96 h	**EC50**	Gammarus pulex	Static, renewal	Sims, et al,1997 in wrc, 1998
Crustaceans	Nonylphenol CAS 25154-52-3	0.0207 m	96 h	EC50 Loss of equilibrium	Hyalella azteca	Flow through, valid	Brooke, et al, 1993a in UK, 1999
Crustaceans	4-nonylphenol	0.0246 m	96 h	LC50	Gammarus pulex	Static, renewal	Sims, et al,1997 in wrc, 1998
Crustaceans	Nonylphenol CAS 84852-15-3 >95% 4-nonylphenol)	0.15 m 0.17 m	96 h	EC50 LC50	Hyalella azteca	Flow through, 21°C, pH=7.9-8.7, valid	England & Bussard, 1994 in UK, 1999
Crustaceans	Nonylphenol	0.15 m	96 h	EC50	Hyalella azteca	GLP	CMA, 1994 in wrc, 1998
Crustaceans	Nonylphenol	0.17 m	96 h	LC50	Hyalella azteca	GLP	CMA, 1994 in wrc, 1998

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.5.f:
Retrieved endocrine effect concentration (mg/l) of nonyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Endocrine effects							
Crustacean	Nonylphenol	0.01	30 d	LOEC deformed offspring: curled tail spines and no terminal setae: reduced swimming ability	Daphnia galeata mandotae	Renewal every 48 h, dose-related	Shurin &Dodson, 1997 in UK 1999
Crustacean	Nonylphenol	**0.05** **0.1**	48 h	**NOEC** **LOEC increased accumulation of 14C testosterone= decrease in production of testosterone elimination product (testosterone-glucose)**	Daphnia magna	Exp 48 h and then 16 h to 14C testosterone, conc-related effect	Baldwin, et al, 1997 in UK, 1999
Crustacean	Nonylphenol	0.050 >=0.1	30 d	LOEC Increased daily production of female offspring NOEC Daily production of male offspring	Daphnia galeata mandotae	Renewal every 48 h, dose-related	Shurin &Dodson, 1997 in UK 1999
Crustacean	Nonylphenol	>0.1 0.1 0.071	3 w	NOEC Survival LOEC reduced number of off-spring 50 % elimination of testosterone	Daphnia magna	Exp 48 h and then 16 h to 14C testosterone, conc-related effect	Baldwin, et al, 1997 in UK, 1999
Fish	Nonylphenol	0.001 0.01 **0.03** 0.01 0.01	22 d (+86 d) 35 d (+431 d)	LOEC Reduced body weight NOEC Reduced body weight **LOEC** **Reduced mean body weight and length, ovosomatic index (OSI) elevated** NOEC Reduced body weight LOEC Reduced length	Oncorhynchus mykiss female	Flow through, exposed from hatch to sexual maturity, pH=6.5, 7-13°C, aerated	Ashfield, et al, 1998 in UK, 1999
Fish	Nonylphenol	0.01 0.01 0.05 0.1	3 mo	LOEC Mean body weight and length NOEC Sex reversal, developed testis-ova LOEC sex-reversal, developed testis-ova LOEC changed sex-ratio	Oryzias latipes	Static renewal (every 72 h 1^{e} month and then every 48 h)	Gray & Metcalfe, 1997 in UK, 1999

Class	Substance	Conc. (mg/l)*	Testing time	Effect type	Organism	Method	Literature (source)
Fish	4-nonylphenol	0.01414	-	EC50 Increased vitellogenin synthesis	Salmo gairdneri	-	Ren, 1996 in EU, 2000; UBA, 1998
Fish	4-nonylphenol	0.014	-	LOEC Vitellogenin production	Salmo gairdneri Hepatocytes	Potency= 0.000071	Hansen, 1998 in EU, 2000
Fish	Nonylphenol	0.00502 0.0203	3 w	NOEC Stimulation of vitellogenin production LOEC	Oncorhynchus mykiss males	Flow through, exposure in Nov	Jobling et al, 1996 in UK, 1999
Fish	Nonylphenol	0.0203 0.0543	3 w	NOEC Reduction in testis size (GSI) LOEC	Oncorhynchus mykiss males	Flow through, exposure in Nov	Jobling et al, 1996 in UK, 1999
Fish	Nonylphenol	0.03 n	3 w	Stimulation of vitellogenin production, reductions in testis size (GSI), higher proportion of spermatogonia type A	Oncorhynchus mykiss males	Flow through, exposure in May	Jobling et al, 1996 in UK, 1999
Fish	Tech-nonylphenol	0.150	9 d	LOEC Increased plasma vitellogenin	-	Water exposure	Pedersen, et al, 1999 in Chemweb, 2000
Fish	n-nonylphenol	0.150	9 d	NOEC Increased plasma vitellogenin	-	Water exposure	Pedersen, et al, 1999 in Chemweb, 2000
Fish	Nonylphenol	>=0.22 (10^{-6} M)	-	Stimulation of vitellogenin production	Oncorhynchus mykiss hepatocytes		White, et al, 1994 in UK, 1999
Fish	Nonylphenol	0.96	28 d	LOEC decreased GSI, testis histology	Xiphophorus maculatus	Aerated, tap water, 28C	Kinnberg, et al., 2000
Fish	Tech. Nonylphenol	1 µM	96 h	LOEC Induction of vitellogenin-mRNA	Salmo gairdneri Hepatocytes	-	Islinger, et al, 1999
Fish	Nonylphenol	10 µM	5-10 h	Maximum level of ER mRNA and a slight induction of vitellogenin mRNA	Salmo gairdneri Hepatocytes	In vitro	Flouriot, et al, 1995 in sepa, 1998
Fish	4-nonylphenol	16.15 µ M	4 d	ED50 Vitellogenin production	Salmo gairdneri hepatocytes	Potency = 0.0000090 (17β estradiol)	Jobling & Sumpter, 1993 in Warhurst, 1995; Epa, 1997; UK,1999
Fish	Tech. Nonylphenol	100 µM	96 h	Maximum rate of vitellogenin gene expression	Salmo gairdneri Hepatocytes	Same rate as observed by 10-100 nM oestradiol	Islinger, et al, 1999
Fish	Nonylphenol	10 mg/kg ww	2 w	Increased vitellogenin in plasma, plasma lipids, protein and ninhydrin positive substances	Platichthys flesus	4 intraperitoneal injections	Christensen, et al, 1995 in UK, 1999
Fish	Nonylphenol	10 mg/kg/ week	25 d	LOEC Increase in plasma vitellogenin concentration, reduction in gonadosomatic index	Zoarces viviparus Males	Injections, dose-related effect	Christiansen, et al, 1998
Fish	Tech. Nonylphenol	50 mg/kg	12 d	LOEC Increased plasma vitellogenin		injection	Pedersen, et al, 1999 in Chemweb, 2000

Fish	n-nonylphenol	50 mg/kg	12 d	NOEC Increased plasma vitellogenin		injection	Pedersen, et al, 1999 in Chemweb, 2000
Fish	Nonylphenol	79 mg/kg 237 mg/kg	7 d	NOEC LOEC Induction of serum vitellogenin	Ictalurus punctatus	Potency 5000 lower than 17β-estradiol	Nimrod & Benson, 1996 in UK, 1999
Amphibian	4-nonylphenol	**33666 10^{-9}M**	-	**IC50 binding affinity to ER**	Xenopus laevis Liver cells	-	Lutz, et al, 1999

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.5.g:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	Nonylphenol CAS 25154-52-3	**0.694 m** 1.48 m	**96 h**	**NOEC** LOEC Cell production	Selenastrum capricornutum	Valid	Brooke, et al, 1993a, in UK, 1999
Crustacean	Nonylphenol	**0.001 n**	**21 d**	**NOEC** **Reproduction**	Daphnia magna	Static, use with care	Kopf, 1997 in UK, 1999
Crustacean	Nonylphenol CAS 104-40-5	0.0062-0.025	21 d	Increased reproduction	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE, 2000
Crustacean	Nonylphenol CAS 104-40-5	0.0062 0.025 0.05-0.1	21 d	NOEC mortality Increased mortality (10%) 50% decreased live offspring	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE, 2000
Crustacean	Nonylphenol CAS 25154-52-3	0.010-0.1	30 d	Changed reproduction, increased development	Daphnia galeata mendotae	Renewal	Shurin, et al, 1997 in AQUIRE, 2000
Crustacean	Nonylphenol CAS 25154-52-3	0.024-0.071m	21 d	NOEC Reproduction (surviving offspring)	Daphnia magna	Renewal 20°C, pH=8.25, OECD 202, valid	Comber, et al, 1993 in AQUIRE, 2000; UK, 1999
Crustacean	Nonylphenol CAS 104-40-5	0.025-0.100	21.67 d	LOEC Changed hormone levels	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIR, 200E
Crustacean	Nonylphenol CAS 25154-52-3, 98% nonylphenol, 86.1% 4-nonylphenol	0.039 m	21 d	NOEC Growth (length)	Daphnia magna	Renewal, OECD 202, Static, 20°C, pH=8,25, valid	Comber, et al, 1993 in AQUIRE + UK, 1999
Crustacean	Nonylphenol CAS 104-40-5	0.050 0.1	21 d	NOEC Reproduction LOEC Reproduction	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE
Crustacean	Nonylphenol CAS 104-40-5	0.062-0.1	21 d	Changed mortality (0% / 10%)	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE
Crustacean	Nonylphenol CAS 104-40-5	0.071	21 d	MATC Reproduction	Daphnia magna	Renewal	Baldwin, et al, 1997 in AQUIRE
Crustacean	Nonylphenol CAS 84852-15-3 (>95% 4-nonylphenol)	0.0887 m 0.202 m	7 d	NOEC Reproduction LOEC Reproduction	Ceriodaphnia dubia	24-25°C, Static, pH=8.3-8.6, valid	England, 1995 in UK, 1999
Crustacean	Nonylphenol	0.027 n 0.1 n 0.3 >0.3 n 0.17	7 d	EC50 Mortality & size NOEC reproduction LOEC LC50 MATC Reproduction	Ceriodaphnia dubia	Static renewal	CMA, 1995 in wrc, 1998
Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)

Crustacean	Nonylphenol CAS 25154-52-3	0.1 m	21 d	LC50	Daphnia magna	Renewal?? (Static), 20°C, pH=8.25, OECD 202, valid	Comber, et al, 1993 in AQUIRE + UK, 1999
Crustacean	Nonylphenol CAS 25154-52-3	>=0.1 n	21 d	NOEC Reproduction	Daphnia magna	Semistatic, 20°C, valid	Hűls, 1992a in UK, 1999
Crustacean	Nonylphenol CAS 25154-52-3	0.1 n 0.14 n	21 d	NOEC Reproduction LOEC Reproduction	Daphnia magna	Semistatic, 20°C, valid	Hűls, 1992b in UK, 1999
Crustacean	Nonylphenol CAS 25154-52-3	0.120	7 d	LC50	Daphnia magna	Renewal, 20°C, pH=8.25, OECD 202, valid	Comber, et al, 1993 in AQUIRE, 2000; UK, 1999
Crustacean	Nonylphenol CAS 25154-52-3	0.120	14 d	LC50	Daphnia magna	Renewal, 20°C, pH=8.25, OECD 202, valid	Comber, et al, 1993 in AQUIRE, 2000; UK, 1999
Crustacean	Nonylphenol CAS 25154-52-3	0.13	21 d	NOEC Mortality	Daphnia magna	Renewal	Comber, et al, 1993 in AQUIRE, 2000
Crustacean	Nonylphenol CAS 84852-15-3 (>95% 4-nonylphenol)	0.0992 m 0.258 m	7 d	EC50 LC50	Ceriodaphnia dubia	Static, 24-25°C, pH=8.3 -8.6, valid	England, 1995 in UK, 1999
Crustacean	Nonylphenol CAS 84852-15-3 (>95% 4-nonylphenol)	0.202 m 0.377 m	7 d	NOEC Survival LOEC Survival	Ceriodaphnia dubia	24-25°C, Static, pH=8.3-8.6, valid	England, 1995 in UK, 1999
Molluscs	Nonylphenol	**5**	6 d	**LC50**	Anodonta cataractae	-	McLeese, et al, 1980 in wrc, 1998
Fish	Nonylphenol CAS 25154-52-3	0.0005 –0.0019	28 d	NOEC Changed morphology	Oryzias latipes	Flow through	Nimrod, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.0005 –0.0019	28 d	Changed reproduction and population growth, changed growth and morphlogy	Oryzias latipes	Flow through	Nimrod, et al, 1998 in AQUIRE, 2000
Fish	NP	0.001 0.010	35 d	NOEC Growth suppression LOEC Growth suppression	Salmo gairdneri		Ashfield, et al, 1995 in wrc, 1998
Fish	Nonylphenol	**0.0074 m** 0.014 m 0.0102 m	**33 d**	**NOEC survival** LOEC survival MATC survival	Pimephales promelas	Flow through GLP, unaerated	CMA, 1991 in wrc, 1998
Fish	Nonylphenol, 4-branched, CAS 84852-15-3	0.0074 m 0.014 m	33 d 33 d	NOEC Survival LOEC survival	Pimephales promelas	Flowthrough, 25°C, pH=7.4-8.1, valid	Ward & Boeri, 1991b in UK, 1999
Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)

Fish	Nonylphenol CAS 25154-52-3	0.010	21 d	NOEC Biochemical changes in plasma	Onchorhynchus mykiss	Renewal	Tremblay, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.025-0.1	21 d	Changed hormone level in plasma	Onchorhynchus mykiss	Renewal	Tremblay, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.025	21 d	LOEC Increased biochemical effects in plasma	Onchorhynchus mykiss	Renewal	Tremblay, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol CAS 25154-52-3	0.025-0.1	21 d	NOEC Growth, morphology	Onchorhynchus mykiss	Renewal	Tremblay, et al, 1998 in AQUIRE, 2000
Fish	Nonylphenol	0.0595 m 0.126 m	28 d	NOEC Mortality LOEC mortality	Lepomis macrochirus	Flow through, valid	Brooke, 1993b, in UK, 1999
Fish	Nonylphenol	0.0775 m 0.193 m	28 d	NOEC Mortality LOEC mortality	Pimephales promelas	Flow through, valid	Brooke, 1993b, in UK, 1999
Fish	Nonylphenol CAS 104-40-5	0.010-0.1	90 d	Changed growth	Oryzias latipes	Renewal	Gray, et al, 1997 in AQUIRE, 2000
Fish	Nonylphenol CAS 104-40-5	0.010-0.1	90 d	Changed histology (0-86) in testis	Oryzias latipes	Renewal	Gray, et al, 1997 AQUIRE, 2000
Fish	Nonylphenol CAS 104-40-5	0.1	Sub-acute/ chronic	LOEC Subletal effects	Fish		Holcombe, et al, 1984 in kemi, 1989
Fish	Nonylphenol CAS 104-40-5	0.46	17 d	LC50	Oryzias latipes		Gray, et al, 1997 in AQUIRE, 2000
Amphibian	Nonylphenol CAS 25154-52-3	**0.025** **0.050**	14 d	**NOEC development** **LOEC development**	Xenopus laevis	Renewal	Fort, et al, 1997 in AQUIRE, 2000

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.5.h:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol for sediment organisms from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Sediment organisms							
Insects	Nonylphenol CAS 104-40-5	**0.0125-0.2**	**20 d**	**NOEC growth, mortality, development and reproduction**	Chironomus tentans		Kahl, et al, 1997 in AQUIRE, 2000
Insects	Nonylphenol CAS 104-40-5	0.042	20 d	NOEC increased mortality (23%)	Chironomus tentans		Kahl, et al, 1997 in AQUIRE, 2000
Insects	Nonylphenol CAS 104-40-5	0.091	20 d	LOEC increased mortality (62%)	Chironomus tentans		Kahl, et al, 1997 in AQUIRE, 2000
Insects	Nonylphenol	0.119 (water) 0.075->0.252 (interstitial water) >34 mg/kg (sediment)	14 d	LC50	Chironomus tentans	Flow through, 20°C, pH=7.7-8.3, valid	England & Bussard, 1993 in UK, 1999 (CMA, 1993 in wrc, 1998)
Amphibian	Nonylphenol	**155 mg/kg (dosed sed.)** 220 mg/kg (dosed sed.) 260 mg/kg (dosed sed.) 390 mg/kg (dosed sed.) 250 mg/kg (dosed sed.)	**30 d**	**NOEC weight Mortality** EC50 weight, Mortality LC50 LOEL weight Mortality MATC	Rana catesbiana	GLP	CMA, 1992 in wrc, 1998
Amphibian	Nonylphenol	155 mg/kg dw 390 mg/kg dw	10, 20, 30 d	NOEL LOEL	Rana catesbiana	Valid, sediment test	Ward & Boeri, 1992 in UK, 1999
Amphibian	Nonylphenol	220 mg/kg dw 260 mg/kg dw	30 d	EC50 LC50	Rana catesbiana	Valid, sediment test	Ward & Boeri, 1992 in UK, 1999

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Annex 4.6: Data on the ecotoxicity of nonylphenol ethoxylate to freshwater organisms

Table 4.6.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	NPEO	**0.09**	96 h	**EC50**	Selenastrum capricornutum		Argese, et al, 1994 in Warhurst, 1995
Algae	NP4EO	6	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Algae	NP9EO	12	-	EC50	Selenastrum capricornutum	-	Dorn, et al, 1993 in CEPA, 2000
Algae	NP9EO	10	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Algae	NP9EO	16	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Algae	APEO	20-50	72 h	LOEC growth	Selenastrum capricornutum		Lewis, 1990 in Warhurst, 1995
Algae	NP9EO	31	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Algae	NP9EO	125	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Algae	NP9EO	5000	-	Lethal treshold values	Scenedesmus subspicatus	-	Janicke, et al, 1969 in TemaNord, 1996
Crustaceans	NP2E	**0.148**	48 h	**LC50**	Daphnia magna	-	Maki et al, 1998 in CEPA, 2000
Crustaceans	NpnEO Mix 1,2	0.626	-	LC50	Ceriodaphnia dubia	-	Weeks et al, 1996 in CEPA, 2000
Crustaceans	NP2EC	0.99	-	LC50	Daphnia magna	-	Maki et al, 1998 in CEPA, 2000
Crustaceans	NP1EO + NP2EO	1.04	48 h	LC50	Ceriodaphnia dubia		Ankley, et al, 1990 in wrc, 1998
Crustaceans	NPEO	1.5	48 h	EC50	Daphnia magna		Argese, et al, 1994 in Warhurst, 1995
Crustaceans	NP9E	14	48 h	LC50	Daphnia magna	-	Dorn et al, 1993 in CEPA, 2000
Crustaceans	NP1EC	14	48 h	LC50	Daphnia magna	-	Naylor et al, 1997 in CEPA, 2000
Crustaceans	NP1EC	17	96 h	LC50	Ceriodaphnia dubia	-	Naylor et al, 1997 in CEPA, 2000
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	**1**	96 h	**LC50**	Salmo trutta		Reiff et al, 1979 In Verschueren, 1983
Fish	NPEO	2.7	48 h	LC50	Salmo trutta		Argese, et al, 1994 in Warhurst, 1995
Fish	NP3.3EO	2.5	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	NP1EO	3	48 h	LC50	Oryzias latipes	-	Yoshimura, 1986 in CEPA, 2000
Fish	NP5EO	3.6	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	NP9E	4.6	96 h	LC50	Pimpehales promelas	-	Dorn et al, 1993 in CEPA, 2000
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	4.9	48 h	LC50	Carassius auratus		Reiff et al, 1979 in Verschueren, 1983
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	5	96 h	LC50	Gasterosteus aculeatus		Swedmark, 1986 in Kemi, 1989
Fish	NP10EO	5.4	48 h	LC50	Carassius auratus	-	Kurata, et al, 1997 in TemaNord, 1996
Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)

Fish	NP6.4EO	5.4	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	8.6	96 h	LC50	Rasbora heteromorpha		Reiff et al, 1979 in Verschueren, 1983
Fish	Nonylphenol ethoxylate (3 EO) CAS 9016-45-9	7-11.2	96 h	LC50	Idus idus		Reiff et al, 1979 in Verschueren, 1983
Fish	NP2EC	8.9	48 h	LC50	Gasterosteus aculeatus		Yoshimura, 1986 in wrc, 1998
Fish	NP1EC	9.6	48 h	LC50	Gasterosteus aculeatus		Yoshimura, 1986 in wrc, 1998
Fish	NP8.4EO	11.6	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	NP8.9EO	11.2	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	NP13.1EO	48.0	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996
Fish	NP16.6EO	110	48 h	LC50	Oryzias latipes		Yoshimura, 1986 in TemaNord, 1996

Table 4.6.b:
Retrieved endocrine effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Crustaceans	Nonylphenol polyethoxylate (NPPG=nonylphenol polyethylene glycol)	**5**	-	**LOEC Inhibition of elimination of testosterone**	Daphnia magna		Baldwin, et al, 1998 in Chemweb, 2000
Fish	NP1EC	**0.02**	-	**LOEC Production of female egg yolk protein**	Salmo gairdneri Males		Jobling, 1996 in Friends of the earth, 2000
Fish	NP2EO	0.02	-	LOEC Production of female egg yolk protein	Salmo gairdneri Males		Jobling, 1996 in Friends of the earth, 2000
Fish	4 nonylphenol nona ethoxylate	0.03	-	Increased plasma vitellogenin level	Salmo gairdneri		Harries, 1995 in EU, 2000
Fish	NP2EO	0.03	-	Increased plasma vitellogenin level	Salmo gairdneri		Harries, 1995 in EU, 2000
Fish	NP1EC	0.03 n	3 w	Stimulation of vitellogenin production, reductions in testis size (GSI), higher proportion of spermatogonia type A	Oncorhynchus mykiss males	Flow through, exposure in May	Jobling et al, 1996 in UK, 1999
Fish	NP2EO	0.03 n	3 w	Stimulation of vitellogenin production, reductions in testis size (GSI), higher proportion of spermatogonia type A	Oncorhynchus mykiss males	Flow through, exposure in May	Jobling et al, 1996 in UK, 1999
Fish	NP1EC	15.25 µM	-	ED50	Salmo gairdneri hepatocytes	Rel potency 0.0000063	Jobling & Sumpter, 1993 in Warhurst, 1995; in Epa, 1997
Fish	NP2EO	17.27 µM	-	ED50	Salmo gairdneri hepatocytes	Rel potency 0.000006	Jobling & Sumpter, 1993 in Warhurst, 1995; in Epa, 1997
Fish	NP9EO	82.31 µM	-	ED50	Salmo gairdneri hepatocytes	Rel potency 0.0000002	Jobling & Sumpter, 1993 in Warhurst, 1995; in Epa, 1997

* m = measured, n = nominal

Table 4.6.c:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol ethoxylate for groups of species from the freshwater aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Algae	NP9EO	**8**	-	**NOEC growth**	Selenastrum capricornutum	-	Dorn, et al, 1993 in CEPA, 2000
Crustaceans	NP1EC	**2.2**	7 d	**NOEC reproduction**	Ceriodaphnia dubia	-	Naylor, et al, 1997 in CEPA, 2000
Crustaceans	NP9EO	10	7 d	NOEC	Daphnia magna	-	Dorn, et al, 1993 in CEPA, 2000
Crustaceans	NPnEO, mix 1,2	0.28	7 d	NOEC	Ceriodaphnia dubia	-	Weeks, et al, 1996 in CEPA, 2000
Insects	NP1EO	**80**	-	**EC50**	Culex pipiens	-	Maxwell & Piper 1968 in CEPA, 2000
Fish	NP1EC	**0.010** **0.030**	35 d	**Accelerated growth** **No growth acceleration**	Salmo gairdneri		Ashfield, et al, 1995 in wrc, 1998
Fish	NP2EO	0.010 0.030	35 d	Growth reduction No growth reduction	Salmo gairdneri		Ashfield, et al, 1995 in wrc, 1998
Fish	NP9EO	1	7 d	NOEC	Pimephales promelas		Dorn, et al, 1993 in CEPA, 2000
Fish	NP1EC	1	7 d	NOEC	Pimephales promelas	-	Williams, 1997 in CEPA, 2000

Annex 4.7 Data on the ecotoxicity of octylphenol to marine organisms

Table 4.7.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of octyl phenol for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	Tetramethyl butyl phenol	**0.14**	**3 d**	**EC50 population decrease**	Skeletonema costatum		Walsh, et al, 1988 in AQUIRE, 2000
Diatom	Tetramethyl butyl phenol	**0.09**	**2 d**	**EC50 Population decrease**	Bellerochea polymorpha		Walsh, et al, 1988 in AQUIRE, 2000
Crustaceans	Tetramethyl butyl phenol	**0.0479 – 0.1131**	**4 d**	**LC50**	Mysidopsis bahia	Static, fed	Cripe et al, 1980 in AQUIRE, 2000; Cripe et al, 1989 in UK, 1998
Crustaceans	Tetramethyl butyl phenol	1.1	4 d	LC50	Crangon septemspinosa	Renewal	McLeese, et al, 1981 in AQUIRE, 2000
Crustaceans	Tetramethyl butyl phenol	2-10	3-7 d	Mortality	Uca pugilator	Renewal	Zou, et al, 1999 in AQUIRE, 2000
Crustaceans	Tetramethyl butyl phenol	2-10	3-7 d	Enzymes	Uca pugilator	Renewal	Zou, et al, 1999 in AQUIRE, 2000
Fish	Tetramethyl butyl phenol	**81-175 mg/kg**	1.83 d	**Mortality**	Cyprinus carpio	Dose	Loeb, et al, 1963

Table 4.7.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of octyl phenol for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Endocrine effect							
Mollusc	Octylphenol	**<0.001**	3 m	**LOEC Enlarged accesssory pallial sex glands + enhanced oocyte production; reduced penis and prostate gland length**	Nucellus lapillus	renewal, 35 ‰, 14 C	Oehlmann, et al , 2000

Annex 4.8 Data on the ecotoxicity of nonylphenol to marine organisms

Table 4.8.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	Nonylphenol CAS 84852-15-3 (95% 4-nonylphenol)	**0.027 m**	96 h	**EC50 Cell growth**	Skeletonema costatum	21-22°C, pH=7.9-8.1 to 8.3-9.6, 30‰, valid	Ward & Boeri, 1990a in UK, 1999
Algae	4-Nonylphenol (branched)	0.03 m	72 h	EC50 Growth	Skeletonema costatum	Static, unaerated, GLP	CMA, 1990a, in wrc, 1998
Algae	Nonylphenol CAS 25154-52-3	0.46	24 h	EC50 Reproduction/ Growth	Tetrahymena pyriformis	Static	Yoshioka, et al, 1985 in Nikunen, 1990; AQUIRE, 2000
Molluscs	Nonylphenol CAS 25154-52-3	0.018-0.320	1-3 d	Reproduction	Mytilus edulis	Renewal	Granmo, et al, 1989 in kemi, 1989; AQUIRE, 2000
Molluscs	4-nonylphenol CAS 84852-15-3	**0.038 n**	**96 h**	**LC50**	Mulinia lateralis	Static, use with care	Lussier et al, in UK, 1999
Molluscs	Nonylphenol CAS 25154-52-3	5 n 1.7 m	6 d	LC50	Anadonta cataracta	Renewal, 10°C, use with care	McLeese, et al, 1980 in AQUIRE, 2000; UK, 1999
Molluscs	Nonylphenol CAS 104-40-5	3 n	96 h	LC50	Mytilus edulis	Renewal, 17°C, 32‰, use with care	Granmo, et al, 1989 in AQUIRE, 2000; UK, 1999
Crustaceans	Nonylphenol CAS 84852-15-3 (4-nonylphenol, branched)	0.018 m 0.030 m **0.043 m**	**96 h**	NOEC LOEC **LC50**	Mysidopsis bahia	Flow through, 23.8-25.3°C, pH=7.3-8.2, 20‰, valid	Ward & Boeri, 1990c in UK, 1999 CMA, 1990 in wrc, 1998
Crustaceans	4-Nonylphenol CAS 84852-15-3	0.059	96 h	LC50	Palaemonetes pugio	Flow through, use with care	Lussier et al, in UK, 1999
Crustaceans	4-nonylphenol CAS 84852-15-3	0.06 m	96 h	LC50	Mysidopsis bahia	Flow through, use with care	Lussier, et al, in UK, 1999
Crustaceans	4-nonylphenol CAS 84852-15-3	0.062 m	96 h	LC50	Leptocheirus plumulosus	Flow through, use with care	Lussier, et al, in UK, 1999
Crustaceans	4-Nonylphenol CAS 84852-15-3	0.071 n	96 h	LC50	Homarus americanus	Static, use with care	Lussier et al, in UK, 1999
Crustaceans	Nonylphenol	0.118 0.139	96 h	LC50	Nitrocra spinipes	Not valid	Wahlberg, et al, 1990d in UK, 1999
Crustaceans	Nonylphenol CAS 104-40-5	0.2 n 0.17 m	96 h	LC50	Homarus americanus	Renewal 10°C, use with care	McLeese, et al, 1980b in kemi, 1989; AQUIRE, 2000; UK, 1999
Crustaceans	nonylphenol	0.19	48 h	LC50	Acartia tonsa	Static, natural brackish water seawater, 18‰, 20°C,	Kusk, et al, 1999
Crustaceans	4-nonylphenol CAS 84852-15-3	0.2 m	96 h	LC50	Dyspanopeus sayi	Flow through, use with care	Lussier, et al, in UK, 1999
Crustaceans	nonylphenol	0.28 n	48 h	LC50	Acartia tonsa	Static, Synthetic medium, 20°C, 18‰,	Kusk, et al, 1999
Crustaceans	Nonylphenol	0.4 n 0.3 m	4 d	LC50	Crangon septemspinosa	Renewal 10°C, use with care	McLeese, et al, 1980, 1981 in AQUIRE, 2000; UK, 1999; kemi, 1989

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Crustaceans	nonylphenol	0.36 n	48 h	LC50	Acartia tonsa	Static, Red sea commercial salt mixture, 20°C, 18‰,	Kusk, et al, 1999
Crustaceans	Nonylphenol	0.42	96 h	LC50	Crangon crangon		Waldock & Thain, 1991 in UK, 1999
Crustaceans	4-Nonylphenol	0.6	96 h	LC50	Crangon crangon		Granmo, 1991 in UK, 1999
Fish	4-Nonylphenol CAS 84852-15-3	**0.017 n**	**96 h**	**LC50**	**Pleurnectus americanus**	Static, use with care	Lussier, et al, in UK, 1999
Fish	4-Nonylphenol CAS 84852-15-3	0.069 m	96 h	LC50	Menidia beryllina	Flow through, use with care	Lussier, et al, in UK, 1999
Fish	Nonylphenol	0.1	15 d	LC50	Gadus morhua	17°C	Swedmark, et al, 1971 in UK, 1999
Fish	Nonylphenol CAS 104-40-5	0.13-0.16	96 h	LC50	Salmo salar	Flow through, use with care	McLeese, et al, 1981 in kemi, 1989; UK, 1999
Fish	4-Nonylphenol CAS 84852-15-3	0.142 m	96 h	LC50	Cyprinodon variegatus	Flow through, use with care	Lussier, et al, in UK, 1999
Fish	Nonylphenol CAS 104-40-5	0.19	96 h	LC50	Salmo salar	Static, use with care	McLeese, et al, 1981 in AQUIRE, 2000; UK, 1999
Fish	Nonylphenol	0.3	96 h	LC50	Agonus cataphractus		Etnier, 1985 in UK, 1999
Fish	Nonylphenol, 4-branched CAS 84852-15-3	0.24 m 0.31 m	96 h	NOEC LC50	Cyprinodon variegatus	Flow through, 22°C, 15-17‰, pH=7.4-8.1, valid	Ward &Boeri, 1990d in UK, 1999
Fish	4-nonylphenol	0.18 n 0.44 n	96 h	NOEC LC50	Poecilia reticulata	Static, 25°C, 28‰, pH=8, use with care	? in UK, 1999
Fish	Nonylphenol	0.51 0.36	96 h 7 d	LC50	Agonus cataphractus		Waldock & Thain, 1991 in wrc, 1998
Fish	Nonylphenol	0.4 0.6	96 h	NOEC Mortality LOEC Mortality	Platichthys flesus		Banning et al, 1996 in Vethaak RIKZ, 1996
Fish	Nonylphenol CAS 25154-52-3	0.9	96 h	LC50	Salmo salar	Renewal	McLeese, et al, 1980 in Nikunen, 1990; AQUIRE, 2000
Fish	Nonylphenol	3	96 h	LC50	Gadus morrhua	17°C	Swedmark, et al, 1971 in UK, 1999
Fish	Nonylphenol	3	96 h	LC50	Gadus morrhua		Argese, et al, 1994 in Warhurst, 1995

* m = measured, n = nominal
GLP = Good Laboratory Practice
Valid: valid for risk assessment (UK, 1999).

Table 4.8.b:
Retrieved endocrine effect concentration (LC_{50} and/or EC_{50}) (mg/l) of nonyl phenol for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Endocrine effects							
Fish	4-p-nonylphenol (>98%)	**0.003 n** **0.0016 m**		**LOEC** **Increased severity scores of testes of males (=relative or absolute nr of Sertoli cells); also necrotic spermatozoa and germ cell syncytia**	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al, 1999
Fish	4-p-nonylphenol (>98%)	>0.010 n >0.0024-0.0034 m		NOEC Mortality, size of secondary sex characteristics or gonads of males, proportions of eggs	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al, 1999
Fish	Tech. Grade 4-nonylphenol (4-t-nonylphenol hydroxyl)	10 mg/kg /week	2 w	LOEC Increased vitellogenin induction (thickness of vitellogenin band)	Platichthys flesus Males	Injection intraperitoneal, half doses 2 x week, dose-related effects, 25‰, 13°C,	Christensen, et al, 1999
Fish	Nonylphenol, 85% para-isomers, 8-13% phenol, 1% tripropylene, 1% dinonylphenol	1 mg/kg bw 25 mg/kg bw 125 mg/kg bw	2 w	LOEC Increase in 6β-hydroxylase activities of liver microsomes LOEC decrease 6β-hydroxylase activity of liver microsomes LOEC Decrease in 6β, 16α, 17α-hydroxylase activity and EROD activity, also increased vitellogenin in plasma	Salmo salar	Intraperitoneal injection, 34‰, 10°C, in vivo	Arukwe, et al, 1997 in UK, 1999
Fish	Nonylphenol CAS 104-40-5	25 mg/kg 125 mg/kg	14 d	NOEC Decrease in enzymes in liver LOEC Decrease in enzymes in liver	Salmo salar	Injection	Arukwe, et al, 1997 in AQUIRE, 2000
Fish	Tech. Grade 4-nonylphenol (4-t-nonylphenol hydroxyl)	100 mg/kg /week	2 w	LOEC Increased conc. of calcium in plasma, increased GPT activity in plasma	Platichthys flesus Males	Injection intraperitoneal, half doses 2 x week, dose-related effects, 25‰, 13°C,	Christensen, et al, 1999

* m = measured, n = nominal

Table 4.8.c:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Crustaceans	Nonylphenol CAS 84852-15-3 (4-nonylphenol, branched)	**0.0039 m** 0.0067 m 0.0051 m 0.0091 m 0.0078 m >0.021 m	28 d	**NOEC Length** LOEC Length MATC Length LOEC survival F1 MATC Survival F1 LC50	Mysidopsis bahia	Static, 23.3-26.4°C, pH=7.5-8.2, 20-21‰, valid	Ward & Boeri, 1991c in UK, 1999 CMA, 1991a in wrc, 1998
Crustaceans	Nonylphenol	0.34	7 d	LC50	Crangon crangon		Waldock & Thain, 1991 in wrc, 1998
Molluscs	Nonylphenol CAS 25154-52-3	**0.018-0.1**	13-30 d	**Behaviour**	Mytilus edulis	Flow through	Granmo, et al, 1989 in AQUIRE, 2000
Molluscs	Nonylphenol CAS 25154-52-3	0.018-0.56	30 d	Behaviour	Mytilus edulis	Renewal	Granmo, et al, 1989 in AQUIRE, 2000
Molluscs	Nonylphenol	0.056 0.1	15-30 d	LOEC byssus strength No byssus thread formation	Mytilus edulis		Granmo, et al, 1989, 1991 in wrc, 1998
Molluscs	Nonylphenol CAS 104-40-5	0.14 n	850 h = 35 d	LC50	Mytilus edulis	Renewal, 17°C, 32‰, use with care	Granmo, et al, 1989 in kemi, 1989; AQUIRE, 2000; UK, 1999
Molluscs	Nonylphenol	0.2	35 d	NOEC fertilisation	Mytilus edulis		Granmo, et al, 1989, 1991 in wrc, 1998
Molluscs	Nonylphenol CAS 104-40-5	0.5 n	15 d	LC50	Mytilus edulis	Renewal 17°C, 32‰, use with care	Granmo, et al, 1989 in AQUIRE, 2000; UK, 1999
Molluscs	Nonylphenol CAS 25154-52-3	1 n >0.7 m >1 n	15 d	Mortality LC50 LC50	Mya arenaria	Renewal 10°C, use with care	McLeese, et al, 1980 in AQUIRE, 2000; UK, 1999
Fish	Nonylphenol	**0.1** 0.2 0.4 1	4 w	**NOEC Histology kieuw** LOEC Histology kieuw, no effect on liver LOEC Histology liver NOEC Histology gonads	Platichthys flesus		Banning et al, 1996 in Vethaak RIKZ, 1996

* m = measured, n = nominal
Valid: valid for risk assessment (UK, 1999).

Annex 4.9 Data on the ecotoxicity of nonylphenol ethoxylate to marine organisms

Table 4.9.a:
Retrieved acute effect concentration (LC_{50} and/or EC_{50}) (ng/l) of nonyl pheno, ethoxylate for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Algae	-	**0.009-0.0122**	**72 h**	**EC_{50} growth**	Thalassiosira sp.	-	Walsh, 1987 in AQUIRE, 2000
Algae	-	0.040-0.380	72 h	EC_{50} growth	Skeletonema costatum	-	Walsh, 1987 in AQUIRE, 2000
Algae	-	>1.5	96 h	EC_{50} growth	Chlorella sp.	-	Walsh, 1987 in AQUIRE, 2000
Molluscs	NP10EO	**1.5-10**	96 h	**LC50**	Balanus balanoides	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	<5	96 h	LC50	Pecten operculans	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	5	96 h	LC50	Cardium edule	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	12	96 h	LC50	Mytilus edulis	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	18	96 h	LC50	Mya arenaria	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	>100	96 h	LC50	Carcinus maenas	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	>100	96 h	LC50	Crangon crangon	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	>100	96 h	LC50	Hyas araneus	-	Swedmark, 1986 in TemaNord, 1996
Molluscs	NP10EO	>100	96 h	LC50	Eupagurus berngardus	-	Swedmark, 1986 in TemaNord, 1996
Crustaceans	NP1.5EO	**0.11**	48 h	**LC50**	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Crustaceans	NP1EO/NP2EO	0.11	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in CEPA, 2000
Crustaceans	NP9EO	0.71-2	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Crustaceans	NP1EO	0.9	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in CEPA, 2000
Crustaceans	NP15EO	2.57	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Crustaceans	NP1EC	9.4	48 h	LC50	Mysidopsis bahia	-	Naylor, et al, 1997 in CEPA, 2000
Crustaceans	NP40EO	>100	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Crustaceans	NP50EO	>4110	48 h	LC50	Mysidopsis bahia	-	Hall, et al, 1989 in TemaNord, 1996
Fish	NP9EO	**2.5**	96 h	**LC50**	Gadus morrhua	-	Swedmark, 1971 in CEPA, 2000
Fish	NPE (4EO)	5-9	96 h	LC50	Marine fish	-	Swedmark, 1986 in kemi
Fish	NPE (10EO)	6	96 h	LC50	Gadus morrhua	-	Swedmark, 1986 in kemi
Fish	NP40EO	>400	96 h	LC50	Gadus morrhua	-	Swedmark, 1971 in TemaNord, 1996
endocrine effects							
Fish	4 NP acetic acid: NP1EC	0.003 M	-	Binding affinity, 50% displacemnet of oestradiol	Salmo gairdneri plasma	RBA<0.1 relative to 100% oestradiol	Milligan, et al., 1998
Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)

Fish	Nonylphenol ethoxylate	**>0.01 n >0.0055 m**		**NOEC Mortality, no differences in gonads or secondary sex characteristics or gonads of males and females**	Pimephales promelas	Continuous flowing, aerated, 25-26°C	Miles-Richardson, et al, 1999

* m = measured, n = nominal

Table 4.9.b:
Retrieved chronic effect concentration (NOEC) (mg/l) of nonyl phenol ethoxylate for groups of species from the marine aquatic environment

Class	Substance	Conc. (mg/l)	Testing time	Effect type	Organism	Method	Literature (source)
Waterorganisms							
Crustaceans	NP10EO	**5**	-	**LOEC Cirral activity**	Balanus balanoides	-	Lewis, 1991 in Warhurst, 1995
Molluscs	NP10EO	2.0	-	LOEC Burrowing	Astarte montagui	-	Lewis, 1991 in Warhurst, 1995
Molluscs	APEO	**2.4**	21 d	**LOEC Larval growth and development**	Mytilus edulis	-	Lewis, 1991 in Warhurst, 1995
Molluscs	NP10EO	5.0	-	LOEC Byssal thread formation, adductor muscle closing	Mytilus edulis	-	Lewis, 1991 in Warhurst, 1995
Fish	NP10EO	**0.002**	-	**LOEC Avoidance**	Gadus morrhua	-	Lewis, 1991 in Warhurst, 1995
Fish	NP10EO	2.0	-	LOEC Swimming activity	Gadus morrhua	-	Lewis, 1991 in Warhurst, 1995