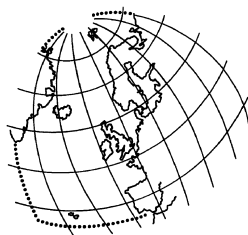


Octylphenol¹



OSPAR Commission 2003 (2006 Update)

¹ Secretariat's note: A review statement on octylphenol (Publication 402/2009) was adopted in 2009, highlighting new developments since the adoption of the Background Document.

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the "OSPAR Convention") was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

La Convention pour la protection du milieu marin de l'Atlantique du nord-est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.

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EXECUTIVE SUMMARY

The term "octylphenol" represents a large number of isomeric compounds of the general formula $C_8H_{17}.C_6H_4(OH)$. The octyl group (C_8H_{17}) may be branched in a variety of ways or be a straight chain and may be located at either the 2-, 3- or 4-position of the benzene ring. Of these potential isomers, 4-*tert*-octylphenol (CAS No. 140-66-9) is the most commercially important and has been included on the OSPAR List of Chemicals for Priority Action. Unless specified otherwise, the term "octylphenol" as used in this document refers to the substance 4-*tert*-octylphenol.

Octylphenol is very toxic to aquatic organisms, is not easily degraded in the environment, and has the potential to cause significant endocrine disruption effects and has been detected in surface waters.

The main areas of use of octylphenol are as an intermediate in the production of phenol/formaldehyde resins (98% of use) and in the manufacture of octylphenol ethoxylates (2% use). A small amount of the ethoxylates is used to produce ether sulphates. The end uses from the manufacture of these resins, ethoxylates and ether sulphates are various (e.g. a tackifier in rubber for tyres, water-based paints, pesticide formulations (as a dispersant) etc.), but the extent to which octylphenol reaches the environment from such products is not clear. It is also reported that octylphenol is present as an impurity in commercial grade nonylphenol and that this may account to some extent for its detection in the environment. Recent investigations have confirmed that nonylphenol is produced by the reaction of a commercial nonene feedstock with phenol and the feedstock may contain octene up to 10%. Consequently, a similar proportion of the "nonylphenol" produced will actually be octylphenol.

The action recommended is: to support the process of the development of appropriate measures to control discharges, emissions and losses of octylphenol through the implementation of the Water Framework Directive; to tackle impurities of octylphenol in nonylphenol through measures controlling discharges, emissions and losses of nonylphenols by the implementation of the Water Framework Directive 2000/60/EC and by the Marketing and Use Directive 76/769/EEC; Contracting Parties should finalise their implementation of PARCOM Recommendation 92/8 on Nonylphenol-Ethoxylates to ensure that any octylphenol compounds which may be impurities of nonylphenol ethoxylates (NPEs) are prevented from reaching the marine environment; to take national action to prevent the use of octylphenol ethoxylates as replacements for NPEs and to promote the development of substitutes for octylphenol where adequate substitutes are not currently available; OSPAR should publish, as a later supplement to this Background Document, the outcome of the exchanges of information within its Offshore Industry Committee on the presence of octylphenol as a production residue in ethoxylated resins and the possible effects of this; to invite industry to report how to improve emission estimates and derivation of effect values; OSPAR to communicate this background document to the European Commission and to other appropriate international organisations which deal with hazardous substances to take account of this background document in a consistent manner.

A monitoring strategy for octylphenol is annexed to this background document.

RECAPITULATIF

Le terme « octylphénol » désigne un grand nombre de composés isomères dont la formule générale est $C_8H_{17}.C_6H_4(OH)$. Le groupe octyle (C_8H_{17}) peut être ramifié de diverses manières ou constituer une chaîne droite et peut être situé dans la position 2-, 3- ou 4- sur l'anneau de benzène. Parmi ces isomères potentiels, c'est le 4-*tert*-octylphénol (N° CAS 140-66-9) qui est le plus important du point de vue commercial, et il a été inscrit sur la Liste OSPAR des produits chimiques devant faire l'objet de mesures prioritaires. Sauf indication contraire, tel qu'il est employé dans le présent document, le terme « octylphénol » désigne la substance dite 4-*tert*-octylphénol.

L'octylphénol est très toxique pour les organismes aquatiques, ne se dégrade pas facilement dans l'environnement, est susceptible de provoquer d'importantes perturbations du système endocrinien et a été décelé dans des eaux de surface.

Les principales applications de l'octylphénol sont comme intermédiaire dans la fabrication des résines phénoliques/de formaldéhyde (98 % de la consommation) ainsi que dans la fabrication des éthoxylates octylphénoliques (2 % de la consommation). Une petite quantité d'éthoxylates sert également à fabriquer des sulfates d'éther. Les applications finales des résines, éthoxylates et sulfates d'éther ainsi fabriqués sont diverses (p.ex. comme agents d'adhérence dans le caoutchouc des pneumatiques, dans les peintures à base aqueuse, dans les pesticides (comme dispersants) etc.) ; l'on ne sait toutefois pas en toute certitude dans quelle mesure l'octylphénol aboutit dans l'environnement par le biais de ces produits. Il est également signalé que de l'octylphénol est présent sous forme d'impuretés dans le nonylphénol de qualité commerciale, et que ceci explique dans une certaine mesure le fait qu'il ait été décelé dans l'environnement. Les résultats de récentes études ont confirmé que du nonylphénol était produit par la réaction d'une charge d'alimentation de nonène de qualité commerciale avec du phénol, et que la charge d'alimentation contient peut-être de l'octène dans une proportion pouvant atteindre 10 %. De ce fait même, une proportion analogue du « nonylphénol » produit est en fait de l'octylphénol.

Les actions recommandées sont les suivantes : soutien au processus d'élaboration de mesures propres à combattre les rejets, émissions et pertes d'octylphénol, ceci par l'application de la Directive-cadre sur l'eau ; supprimer les impuretés d'octylphénol dans le nonylphénol, par le biais de mesures combattant les rejets, émissions et pertes de nonylphénols en faisant appliquer la Directive-cadre sur l'eau (2000/60/CE) et la Directive relative à la commercialisation et l'utilisation (76/769/CEE) ; il convient que les Parties contractantes parachèvent la mise en oeuvre de la recommandation PARCOM 92/8 sur les éthoxylates nonylphénoliques, afin de faire en sorte qu'aucun composé d'octylphénol, pouvant être des impuretés d'éthoxylates nonylphénoliques (NPE) ne puisse atteindre le milieu marin ; prendre des mesures, à l'échelon national, pour empêcher que des éthoxylates octylphénoliques ne remplacent les NPE et favoriser la création de substituts de l'octylphénol lorsqu'il n'existe pas encore de succédanés adéquats ; il conviendrait qu'OSPAR publie, en supplément à posteriori au présent document de fond, le résultat des échanges d'informations au sein de son Comité industrie de l'offshore sur la présence d'octylphénol, comme résidu de fabrication, dans des résines éthoxylées ainsi que sur les effets éventuels de cette situation ; inviter l'industrie à indiquer comment améliorer les estimations des émissions et les calculs des valeurs des effets qui en sont déduits ; il convient aussi qu'OSPAR communique le présent document de fond à la Commission européenne et aux autres organisations internationales compétentes chargées des substances dangereuses, afin qu'elles tiennent compte du présent document de fond dans des conditions cohérentes.

Une stratégie de surveillance sur l'octylphénol est annexée à ce document de fond.

1. BASIS AND RATIONALE FOR ACTION

The objective stated in the OSPAR Strategy with regard to Hazardous Substances ('the Strategy'), which was adopted in Sintra in 1998² and endorsed by Ministers is:

"to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances".

Setting out the basis for OSPAR's work for achieving this objective, the Strategy also includes a timeframe which states that:

"every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020".

4-*tert*-octylphenol (CAS No.140-66-9) is on the OSPAR List of Chemicals for Priority Action, and the UK is the lead country for drawing up this background document on 4-*tert*-octylphenol.

This background document addresses this obligation and has the following aims:

- identifying the main sources of 4-*tert*-octylphenol and its various pathways into the marine environment;
- reviewing the various controls to limit discharges, emissions and losses of 4-*tert*-octylphenol;
- assessing the extent of the risk posed by octylphenol to the marine environment;
- assessing what further activities should be undertaken by OSPAR, or other relevant international organisations, in order to achieve the various OSPAR commitments.

This background document takes into account the "Interim Guidance on how to address Hazardous Substances for Priority Action" agreed at by the OSPAR Commission in 1999 (Annex 7 of the Summary Record OSPAR 99/15/1) and follows the basic structure for OSPAR background documents outlined in that document.

2. IDENTIFICATION OF ALL SOURCES OF THE SUBSTANCE AND PATHWAYS TO THE MARINE ENVIRONMENT

2.1 Properties of octylphenol

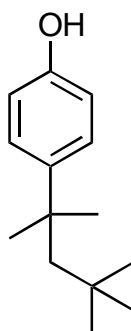
The term "octylphenol" represents a large number of isomeric compounds of the general formula C₈H₁₇.C₆H₄(OH). The octyl group (C₈H₁₇) may be branched in a variety of ways, or be a straight chain, and may be located at either the 2-, 3- or 4-position of the benzene ring. There are, therefore, many different potential octylphenol isomers.

Of these potential isomers, 4-*tert*-octylphenol (CAS Number 140-66-9) is the most commercially important and has been included on the OSPAR List of Chemicals for Priority Action (OSPAR, 2000).

CAS Number: 140-66-9
EINECS Number: 205-426-2
IUPAC Name: 4-*tert*-octylphenol

² Amended by the 2003 Ministerial meeting of the OSPAR Commission.

EINECS name: 4-(1,1,3,3-tetramethylbutyl)phenol
Molecular formula: C₁₄H₂₂O
Structural formula: HO-C₆H₄-C₈H₁₇ where C₆H₄ is a benzene unit substituted 1,4
Structure:



Octylphenol is very toxic to aquatic organisms, is not easily degraded in the environment, has the potential to cause significant endocrine disruption effects, and has been detected in surface waters. 4-*tert*-octylphenol has also been included in the Water Framework Directive list of priority substances (EU, 2001). The detailed properties of 4-*tert*-octylphenol, including numerical values for toxicity, persistence and bioaccumulation are set out in the fact sheet at Annex 2 which is available on the OSPAR web site (OSPAR List of Substances of Possible Concern).

Unless specified otherwise, the term “octylphenol” as used in this document refers to the substance 4-*tert*-octylphenol.

2.2 Identification of sources of octylphenol

The main areas of use of 4-*tert*-octylphenol are as an intermediate in the production of phenol / formaldehyde resins (98% of use) and in the manufacture of octylphenol ethoxylates (2% use). A small amount of the ethoxylates is used to produce ether sulphates. The end uses from the manufacture of these resins, ethoxylates and ether sulphates are as follows, but the extent to which octylphenol reaches the environment from such products is not clear. The ongoing risk assessment is attempting to clarify this question.

- a tackifier in rubber for tyres;
- ethoxylated resins, used in the recovery of oil in offshore processes;
- electrical insulating varnishes;
- niche applications such as in the paper and foundry industries;
- printing inks;
- pesticide formulations (as a dispersant);
- water-based paints;
- textile auxiliaries;
- emulsion polymerisation.

It is also reported that octylphenol is present as an impurity in commercial grade nonylphenol and that this may account to some extent for its detection in the environment. Recent investigations by the UK have confirmed that nonylphenol is produced by the reaction of a commercial nonene feedstock with phenol and the feedstock may contain 1-5% octene, 1% butene and 1% pentene. The level of octene can be up to 10%, although typically it is 3-5% (CEPAD, 2002). Consequently, a similar proportion of the “nonylphenol” produced will actually be octylphenol.

2.3 Pathways to the marine environment

Octylphenol is likely to reach the marine environment via one main route, namely industrial wastewaters from different land-based industrial activities where it is used as an intermediate. Other likely pathways investigated are the use of resins produced using octylphenol, the breakdown of ethoxylates to produce octylphenol, and the presence of octylphenol as an impurity in commercially produced nonylphenol. A possible pathway to the marine environment based on older reported uses is discharge waters from offshore production facilities. However, there are no current data which indicate that this is still a significant route. Octylphenol is not used by the offshore industry. OSPAR Contracting Parties are exchanging information on its presence as a production residue in ethoxylated resins. Octylphenol is a natural part of petroleum oil and may be found in produced water.

3. QUANTIFICATION OF SOURCES

3.1 Manufacture of octylphenol

4-*tert*-octylphenol is manufactured in the EU at quantities of around 23 000 tonnes per annum. The bulk of this tonnage is used within the EU with only a small percentage being exported. Production is currently carried out at six sites in Europe. Production plants are located in Germany, Belgium, Switzerland, France and the UK. Table 1 shows European production volumes, exports and imports in recent years.

Table 1: European production volume, exports and imports (CEPAD, 2002)

	Amount (tonnes/year)				
	1997	1998	1999	2000	2001
Production volume	17 520	18 259	19 626	22 215	22 633
Exports	234	104	6	0	150
Imports	1 035	1 337	1 240	1 308	375
Tonnage used	18 051	19 492	20 928	23 523	22 858
Captive use*	14 969	16 074	17 592	19 910	20 060

* used on-site to produce other substances

An additional source for production is during the production of nonylphenol. Nonylphenol is produced by the reaction of a commercial nonene feedstock with phenol and the feedstock may contain up to 10% of octene, although typically it contains 3-5% (CEPAD 2002). Consequently, a similar proportion of the nonylphenol produced will be 4-*tert*-octylphenol.

3.2 Quantification of uses

3.2.1 Use of phenolic resins

98% of octylphenol is used as an intermediate in the production of phenolic resins. The majority of the octylphenol resin produced and used in the EU is of the novolac type and is non-captive use. 4-*tert*-octylphenol/formaldehyde novolac resins are used as follows:

- **Rubber compounding** for tyre manufacture, to increase the tackiness of the rubber and improve adhesion of the different layers during vulcanisation. Tackifier resins are produced at four sites in Europe; two in France, one in Belgium and one in the UK. A very high proportion (up to 98%) of the octylphenol resin manufactured is used in rubber compounding for tyre manufacture in the EU (CEPAD, 2002). Resins are reported to be added to rubber in amounts

up to 1,5% of the rubber formulation (UBA, 2001), though the maximum figure for the percentage of resin in rubber used for tyres is 10% which results in a maximum concentration of 4-*tert*-octylphenol in tyres of 0,3% (CEPAD, 2002). The demand of octylphenol for this specific use was estimated to be 18 458 tonnes in 2001.

- **Electrical insulating varnishes** for secondary insulation of electric windings (e.g. in motors and transformers) to improve insulation and to bond windings together. These are stoving enamels, which are fully cured to form a thermosetting polymer, which is insoluble in water. The demand of octylphenol for this specific use was estimated to be 2 000 tonnes in 2001.
- **Printing inks** for most modern printing processes. The 4-*tert*-octylphenol resins enable toxic aromatic solvents to be replaced by far less toxic aliphatic alternatives. The inks are manufactured in high temperature processes where the resins are reacted with other resins, oils, etc. (leaving no significant trace of free alkylphenol), and are then diluted in ink solvents and pigmented. Again, the phenolic resin is typically around 7-8% of the ink formulation. No substitutes to alkylphenolic resins are currently available for this use. The demand of octylphenol for this specific use was estimated to be 1 000 tonnes in 2001.
- **Ethoxylated resins** for use as emulsifiers, to separate water from oil in oil recovery on offshore production platforms. They are added in very small amounts, often as low as a few parts per million, to oil/water emulsions produced during oil recovery and permit a high degree of separation. The residual 4-*tert*-octylphenol present in the ethoxylated resins is <0,01% (CEPAD, 2002). The demand for this specific use was estimated to be 200 tonnes in 2001.
- **Other uses.** Octylphenol/formaldehyde resins are used in some other applications like paper coating and the foundry industry. Another use mentioned by industry is in special paints used in marine applications because of the high resistance to saline waters that they provide. However no further data are available on this use at present. The demand of octylphenol for these uses is estimated to be 800 tonnes per annum, although the actual amounts per industry are not known. An overall tonnage of 800 has been used in the assessment.

3.2.2 Use of octylphenol ethoxylates (OPEs)

In the European Union production of octylphenol ethoxylates is currently only a secondary use, with a tonnage of 1 050 used in 2001 (CEPAD, 2002). 850 tonnes of the octylphenol ethoxylates (OPEs) were used directly and 200 tonnes were used to produce octylphenol ether sulphates (see section 3.2.4). There are about four or five companies producing OPEs in Europe.

OPEs are mainly used as emulsifiers for emulsion polymerisation by companies producing polymers (e.g. styrene-butadiene) with smaller uses as textile and leather auxiliaries (e.g. hot melts, textile printing, leather finishing), in pesticide formulations and in water-based paints. The amounts of OPEs used in these applications are as follows, with the corresponding tonnage of 4-*tert*-octylphenol (OP) used to make them shown in brackets:

- emulsion polymerisation = 550 tonnes OPE (220 tonnes OP);
- textiles/leather = 150 tonnes OPE (60 tonnes OP);
- pesticide formulations = 100 tonnes OPE (40 tonnes OP);
- water-based paints = 50 tonnes OPE (20 tonnes OP).

In leather and textile auxiliaries the OPEs are used as emulsifiers in finishing agents, which are mainly styrene-butadiene copolymers. Finishing agents cover leather and textiles with a thin polymer film to make the material more resistant to water, dust and light. They also give leather a shiny appearance. The OPE is physically bound in the polymer matrix which adheres to the substrate. Releases of OPEs from this insoluble polymer structure are unlikely.

In water-based paints, OPEs act as emulsifiers and dispersants, although the emulsifying properties are more dominant. They act in a similar manner when incorporated into pesticide formulations and also aid dispersion of the product over leaf surfaces.

A Norwegian survey of the use of alkylphenols and their ethoxylates in products in 1999 (NPCA, 2001) showed that no octylphenol and only about 4,4 tonnes of octylphenol ethoxylates were used (in 215 tonnes of products; 2,05%). The OPEs were used as follows:

- degreasing products 0,07 tonnes (in 3 tonnes of product; 2,3%);
- interior and exterior paint 0,03 tonnes (in 29 tonnes of product; 0,1%);
- other paint/varnish products 0,24 tonnes (in 61 tonnes of product; 0,4%);
- other products 3,6 tonnes (in 36 tonnes of products; 10%).

The Danish Product Register (Danish EPA, 2002) shows one further minor use for 4-*tert*-octylphenol mono-ethoxylate (octoxynol; CAS no. 9002-93-1) in paints, lacquers and varnishes and for surface treatment at less than 1 tonne per annum for each application. According to the Finnish Product Register, octylphenol is listed, but no products, production or imports are given for 2001. However, the use of products containing octylphenol ethoxylates (~40 tonnes in 2001) is indicated in the register as uses in paints, photographic chemicals and as an emulgator. The Swedish product register includes ten products corresponding to 3-4 tonnes of octylphenol in 2001.

The residual, unreacted octylphenol present in OPEs decreases with increasing extent of ethoxylation, ranging from 1% for OP3EO to 0,01% for OP10EO, and lower levels for greater degrees of ethoxylation (CEPAD, 2002). The majority of the ethoxylates on the market have 10 or more ethoxylate groups.

3.2.3 Use of octylphenol ether sulphates

Octylphenol ethoxylates can also be used to produce octylphenol ether sulphates (OPE-S). CEPAD is not certain that the production of OPE-S from the ethoxylates still occurs in the EU, but no data have been located to confirm this. It is considered that there may be 3 or 4 small companies in Europe producing around 250 tonnes of OPE-S per annum.

OPE-S are mainly used as an emulsifier in water-based paints. Another application is as an emulsifier or dispersant in pesticide or herbicide formulations. Due to the rather long chain length of the ethoxylate (EO) group (approximately 10 moles EO/mol) the dispersant properties are more dominant. In practice this means OPE-S act to disperse the pesticide emulsion as a very thin layer on the leaves of the plants.

The amounts of OPE-S used in these applications are as follows, with the corresponding tonnage of 4-*tert*-octylphenol used to make them shown in brackets:

- water-based paints = 200 tonnes OPE-S (80 tonnes OP);
- pesticide formulations = 50 tonnes OPE-S (20 tonnes OP).

Similarly to OPEs, the residual, unreacted octylphenol present in OPE-S decreases with increasing extent of ethoxylation, ranging from 1% for OP3EO sulphate to 0,01% for OP10EO sulphate, and lower levels for greater degrees of ethoxylation (CEPAD, 2002). The majority of the ethoxylates on the market have 10 or more ethoxylate groups. The market for OPE-S is declining gradually, but their substitution for use in water-based paints is considered to be very difficult.

4. MONITORING DATA ON DISCHARGES, EMISSIONS AND LOSSES

4.1 Aquatic inputs to the marine environment

No data are available on loads of octylphenol entering the OSPAR Convention waters and the Greater North Sea.

4.2 Atmospheric inputs

No data are available on atmospheric inputs of octylphenol but considering its low vapour pressure and tendency to adsorb to soils and sediments it can be expected that atmospheric concentrations will be extremely low. Any octylphenol released to the atmosphere is likely to be degraded rapidly by reaction with hydroxyl radicals (estimated half-life in air is ca. 3 hours) and deposition of the substance from the atmosphere is likely to be negligible with resulting rainwater concentrations being low. As the lifetime of octylphenol in the atmosphere is very short, it is unlikely to be transported a long distance from its point of emission and therefore concentrations due to atmospheric washout by precipitation from the atmosphere are likely to be greatest near the point of emission.

4.3 Concentrations in the marine environment (and other waters / sediments)

A compilation of measured concentrations of octylphenol in river and estuarine waters from the United Kingdom and other European countries is provided in Table 2. The available data show that water concentrations of octylphenol are typically below 1 µg l⁻¹.

Table 2: Summary of the measured octylphenol concentrations in river and estuarine surface waters

Location	Year	Octylphenol concentration (µg l ⁻¹)	Reference
Rivers			
River Lea (UK)	1994	0,4	Blackburn and Waldock (1995)
River Thames and tributaries (UK)	1994	<0,02-0,43	Britnell (1995)
River Dart (UK)	1994	<0,02-0,12	Warhurst (1995)
Manchester Ship Canal (UK)	1999	<0,2	Environment Agency (EA, 1999)
River Elbe and tributaries (Germany)	1998	0,0008-0,002	Working Group for the Cleanliness of the Elbe (2000)
Estuaries			
Tees Estuary (UK)	1994	13	Blackburn and Waldock (1995)
Tees and Tyne Estuaries (UK)	1997	n.d.*	Lye <i>et al</i> 1999
Wyre Estuary (UK)	1999	<0,2	Environment Agency (2001)
Elbe Estuary (Germany)	1998-1999	0,0013-0,018	Working Group for the Cleanliness of the Elbe (2000)
Coastal waters			
German Bight	1998-1999	0,0001-0,016	Working Group for the Cleanliness of the Elbe (2000)

*n.d. not detected; authors did not quote the detection limit.

Seawater samples from 14 sites around the Spanish coast were collected every two months from July 1999 to July 2000 and analysed for octylphenol and nonylphenol (Petrovic *et al*, 2002). Octylphenol was only detected at one site, near to the outfall of a chemical plant, at a concentration of 0,3 µg/l. The remaining sites were below the detection limit of 0,15 µg/l. Nonylphenol was found at seven of the sites, with average concentrations of 0,3 – 2,0 µg/l.

CEPAD, the sector arm of CEFIC dealing with alkylphenol ethoxylates, has stated that “in all likelihood the octylphenol and its derivatives measured in surface waters originate from the octylphenol present as an impurity in commercial grade nonylphenol and not from the use of octylphenol and derivatives as such, because the fraction of octylphenol derivatives is mostly constant at about 8-10% of the corresponding nonylphenol derivatives”. Consistent with this assertion are data from the River Elbe and its tributaries and the German Bight on the concentrations of 4-*tert*-octylphenol and its ethoxylates (OP1EO and OP2EO) and nonylphenol and its ethoxylates (NP1EO and NP2EO) (Working Group for the Cleanliness of the Elbe). These data are presented in Table 3. The proportion of octylphenol to nonylphenol measured at the 13 river and estuarine locations on the River Elbe ranged from 1,7 to 14,3% with a mean value of 8%, in keeping with the statement from CEPAD. However, no site-specific data have yet been located from the UK which would support nonylphenol production as being the main source of octylphenol in waters. Furthermore, it should be noted that the risk assessment of nonylphenol carried out under the EU Existing Substances Regulation does not mention octylphenol as an impurity of nonylphenol. However, the most recent evidence provided by CEPAD indicates that commercial nonylphenol is a definite source.

Table 3: Concentrations of 4-*tert*-octylphenol (and its ethoxylates) and nonylphenol (and its ethoxylates) measured in the water column of the River Elbe and the German Bight

Type of water sample	Water column concentrations measured in the River Elbe (nanogram l ⁻¹)					
	4-t OP	OP1EO	OP2EO	NP	NP1EO	NP2EO
Riverine	0,8-2,0	0,9-6,3	0,6-1,5	7,2-52	13-205	4,3-84
Estuarine	0,8-1,3	0,9-1,3	0,6-1,1	9,5-13	10-14	3,6-4,6
Coastal	0,1-16	0,1-11	0,1-19	0,3-63	0,7-29	0,2-10

A compilation of measured concentrations of octylphenol in wastewater discharges from industrial and municipal sewage treatment plants from the United Kingdom and other European countries is given in Table 4. It should be noted that all values are below the analytical detection limit. The Netherlands have also reported that in sewage sludge from municipal wastewater treatment plants in the Netherlands, octylphenol ethoxylates and octylphenol were measured in concentrations up to 28 µg/l and up to 2 µg/l respectively. The corresponding levels in industrial wastewater treatment plants in the Netherlands were measured in concentrations up to 50 µg/l and up to 24 µg/l respectively. A subsequent, more elaborate measurement programme in the Netherlands showed generally a (much) lower OP(E) presence, see RIZA/RIKZ report 2002.001 (http://www.riza.nl/publicaties/riza_rapporten/rr_2002_001.html). The highest OP concentration found in municipal effluent was 1,3 µg/l. OPE was not found at all (detection limit 0,7 µg/l). In sewage sludge OP(E) was not found, except in one case an OP concentration of 1,5 µg/g d.w. In the investigated surface waters and sediments OP(E) was not found.

Levels of octylphenol were measured in industrial waste waters in Canada (Lee *et al*, 2002). The concentrations found were generally low (below 1 µg/l) for most industries, although the chemical and chemical product industries waste waters had higher levels on occasions, up to 195 µg/l.

4.4 Sediments

Data on measured concentrations of 4-*tert*-octylphenol in sediments taken from a series of locations from the Tees and Tyne estuaries in the UK were found to be in the range 0,03 - 0,34 mg kg⁻¹ dry weight (for the Tees) and 0,002-0,02 mg kg⁻¹ dry weight (for the Tyne) (Lye *et al*, 1999). The octylphenol concentrations increased in the sediments in the vicinity of industrial and sewage works treatment discharges. 23 sediment samples taken from a number of European countries as part of the Pristine Project all showed octylphenol concentrations below the limit of detection (Pristine, 2000). Sediment samples from 26 locations around the Spanish coast were analysed for octylphenol (Petrovic *et al*, 2002a). The substance was only found at three sites, at concentrations from 17 to 145 µg/kg (limit of detection 10 µg/kg). For comparison, the levels of nonylphenol found were from the limit of detection (5 µg/kg) to 1 000 µg/kg.

Table 4: Summary of the measured octylphenol concentrations in wastewaters from industrial and municipal sewage treatment works

Effluent type and location	Year	Octylphenol concentration ($\mu\text{g l}^{-1}$)	Reference
Sewage treatment works receiving wool processing waste (UK)	1994	$\leq 0,36$	Warhurst (1995)
Sewage treatment works (UK)	1997	$\leq 3,3$	SEPA (1997)
Sewage treatment works (UK)	1999	n.d. ^a	Lye <i>et al</i> (1999)
Sewage treatment works (Spain) receiving domestic, textile and tannery waste waters		2,2 – 22 ^b	Petrovic <i>et al</i> (2002a)
Sewage treatment works (Switzerland)	2001	0,17 – 0,30	Espejo <i>et al</i> (2002)
Textile wastewater plant (Portugal)	2000	<9,0	Pristine (2000)
Wastewater treatment plant (Portugal)	2000	<9,0	Pristine (2000)
Wastewater treatment plants (Spain)	2000	<9,0	Pristine (2000)

^a n.d. not detected; authors did not quote the detection limit.

^b OP ethoxylates at 60 – 84 $\mu\text{g/l}$ in influent, <0,05 $\mu\text{g/l}$ in effluent

Table 5 provides data on a study of 4-*tert*-octylphenol and octylphenol ethoxylates concentrations in sediments from the River Elbe and its tributaries. Data are also given for the nonylphenol and nonylphenol ethoxylates (Working Group for the Cleanliness of the Elbe, 2000). The levels of octylphenol in the River Elbe were in the same range (0,021-0,086 mg kg^{-1} dry weight) as for the Tees and Tyne estuaries. At the 11 river and estuarine sites studied the proportion of octylphenol (OP) to nonylphenol (NP) ranged from 4,7 to 8,7%. Based on the mean value for the ratio of OP to NP in the raw materials, the expected sediment ratio estimated from the different partition coefficients would be 7,3%, which is very close to the mean measured ratio of 6,7%.

Table 5: Concentrations of octylphenol (and its ethoxylates) and nonylphenol (and its ethoxylates) measured in the sediments of the River Elbe

Type of water sample	Concentrations measured in the River Elbe (ng l^{-1})					
	4-t OP	OP1EO	OP2EO	NP	NP1EO	NP2EO
River	21-86	30-93	45-113	387-1 378	323-967	546-1 611
Estuarine	32-66	78-113	100-140	367-852	712-886	972-1 434

4.5 Concentrations in biota

There are a few tissue samples from aquatic organisms in European waters that have been collected and analysed for octylphenol to determine bioconcentration factors.

In order to ensure that any octylphenol used in production chemicals at offshore installations did not reach the food supply chain, a number of marine fish species (dab, haddock and herring) taken from around North Sea offshore installations were analysed for octylphenol as part of a preliminary UK Food Quality Assurance monitoring programme. The results of this study are reported by CEFAS (1997). This study showed that concentrations of octylphenol in liver and muscle were always below the limits of detection (i.e. <0,1 – 0,004 mg kg^{-1} depending on the species and tissue type tested).

Lye *et al* (1999) measured the accumulation of 4-*tert*-octylphenol (and nonylphenol and nonylphenol monoethoxylate) in juvenile and mature male flounder (*Platichthys flesus*) collected from the Tees and Tyne estuaries. Octylphenol (0,017 mg kg^{-1} wet weight) was detected in homogenised tissue of fish from

the Tees Estuary but was not detected in tissue from fish from the Tyne Estuary (<0,005 mg g⁻¹ wet weight). Octylphenol was not detected in water samples.

5. ASSESSMENT OF THE EXTENT OF THE PROBLEM

5.1 Introduction

In order to assess the extent of the problem, the UK has carried out a marine risk assessment based on the draft guidance developed by OSPAR and the EC in recent years. This involved two steps. Firstly, the preparation of a PBT assessment to ascertain whether the substance is so hazardous that measures should be developed solely on the basis of the information available on sources and pathways to the marine environment. This was followed by a more traditional risk assessment approach where the predicted environmental concentrations were compared with the predicted no effect concentrations to give a PEC/PNEC ratio for various scenarios. The PEC/PNEC ratios give a numerical indication of the degree of risk. The details of the marine risk assessment is given in Annex 1. However the marine risk assessment draws heavily on data and information in the UK RAR, which will be published in due course when it has been finalised. It is clear that the marine risk assessment would be greatly improved with the provision of better quality information. Currently a number of the PEC/PNEC estimates are based on default values.

5.2 PBT Assessment

The classification of octylphenol against the EC Technical Guidance Document PBT criteria gave the following results:

Persistence: octylphenol is considered to be not readily biodegradable in the risk assessment. Hence it meets the screening criteria for P or VP.

Bioaccumulation: the highest measured bioconcentration factor in fish is 297³. The predicted BCF from log K_{ow} is 634⁴. These are below the B cut-off, so octylphenol does not meet the B criteria.

Toxicity: the lowest NOEC is 6,1 µg/l. This is below the cut-off of 0,01 mg/l. Hence octylphenol does meet the T criteria.

Conclusion of the PBT Assessment: Overall octylphenol meets only two of the PBT criteria in the marine risk assessment. As it meets two of the criteria, the degree to which the third one is missed should be considered according to the TGD. In this case the measured BCFs are only just over 10% of the threshold, so octylphenol is some way from the criterion. Octylphenol does, however, exhibit endocrine disrupting properties and snails have been shown to be a potentially sensitive group of organisms (Oehlmann *et al.*, 2000), although the true values of the NOECs are not yet known.

5.3 PEC/PNEC ratios for the local marine risk assessment

The PEC/PNEC ratios for the local marine risk assessment⁵ are given below in Table 6. For details of the derivation of the PECs and PNECs and the various assumptions which have been used, see Annex 1.

³ Tsuda *et al* (2000).

⁴ A BCF value of 634 was calculated by EUSES (1997; equation also cited in the TGD) using the log K_{ow} of 4.12.

⁵ This risk assessment methodology has been formally agreed by the EC in April 2003 and has been adopted by the OSPAR Commission in June 2003 as the common EU/OSPAR risk assessment methodology for the marine environment.

5.4 Conclusion of the risk assessment for the marine compartment

There is at present a need for further information and/or testing. This would enable a number of the uncertainties due to the fact that estimated, rather than real, data have been used to be overcome. More information is needed on the actual emissions from the principal stages in the life-cycle, including an estimate of the contributions to emissions made by the known level of impurity in nonylphenol.

Table 6: Estimated PEC/PNEC ratios for 4-tert-octylphenol for the local marine risk assessment

Release source	Sea-water	Predator	Top predator
Production of 4-tert-octylphenol	180	2,85	0,57
Production of OP resins	246	3,9	0,78
Production of OPEs	0,34	4×10^{-4}	$7,6 \times 10^{-5}$
<i>Resin use:</i>			
Rubber for tyres	0,16	$2,5 \times 10^{-3}$	$5,1 \times 10^{-4}$
Varnishes	0,31	$3,2 \times 10^{-3}$	$6,3 \times 10^{-5}$
Ink formulation	2,5	0,038	$7,6 \times 10^{-3}$
Ethoxylated resins	21	0,044	$8,9 \times 10^{-3}$
Paper coating	0,41	$6,7 \times 10^{-3}$	$1,3 \times 10^{-3}$
<i>Ethoxylate use:</i>			
Formulation	2,1	$3,5 \times 10^{-3}$	$7,0 \times 10^{-4}$
Emulsion polymerisation	0,07	$1,1 \times 10^{-3}$	$2,2 \times 10^{-4}$
Textiles	4,8	0,015	$3,0 \times 10^{-3}$
Paint formulation	1,03	0,011	$2,2 \times 10^{-3}$
Paint use	0,02	$3,2 \times 10^{-4}$	$6,3 \times 10^{-5}$
Ether sulphate production	9,5	0,076	0,015

The large PEC/PNEC ratios produced for this assessment appear to indicate a significant risk to the marine compartment from the production and use of 4-tert-octylphenol in the EU. However, the values rely heavily on estimated PECs and freshwater toxicity values from a relatively small dataset for the PNECs. A revised exposure assessment is required in the first instance.

6. ACHIEVING THE DESIRED REDUCTIONS

6.1 OSPAR targets

The OSPAR Strategy with regard to Hazardous Substances sets out that the OSPAR objective with regard to hazardous substances is "to prevent pollution of the maritime area by continuing to reduce discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances."

The timeframe given in the Strategy states that "every endeavour will be made to move towards the target of cessation of discharges, emissions and losses of hazardous substances of concern by the year 2020."

At OSPAR 2002, OSPAR adopted guidance on the role of marine risk assessment, which gives, in particular, advice on the urgency of taking measures based on particular PEC/PNEC ratios (see Annex 6 of the OSPAR 2002 Summary Record). In attempting to apply this guidance the following conclusions were reached.

The estimated PEC/PNEC ratios for the production of 4-tert-octylphenol and the production of resins using the substance are greater than one for aquatic organisms and for predators through secondary poisoning. The use of resins in the formulation of inks and the ethoxylation of resins also give rise to

ratios above one. The formulation and use of OPEs in textiles and in paints, and the production of ether sulphates, give rise to ratios above one. However, these values are of limited use because the majority of the PEC values are derived from default emission estimates.

The guidance recognises, however, that where the uncertainties are high in the estimation of risk, this should be taken into account by the Contracting Parties when considering the actions necessary to achieve OSPAR's objectives. In this instance, the estimated PEC/PNEC ratios are subject to high levels of uncertainty due to the lack of reliable information on releases from most life-cycle stages and to the lack of long term toxicity information on seawater species.

Nevertheless, although it does not meet the PBT assessment in the EC Technical Guidance Document, 4-tert octylphenol may pose a risk to the marine environment, and it is therefore imperative from OSPAR's point of view that appropriate actions, commensurate with the estimated risks, and taking account of the uncertainties in their estimation, should be taken to achieve the 2020 cessation target.

6.2 OSPAR's role in achieving the desired targets

In order to meet the targets specified in the OSPAR objective and timeframe, it will be necessary to:

- assess the need for further reductions from the various sources and the practicability of such reductions;
- review existing regulations and controls in the light of the need for further reductions;
- decide which organisation is responsible and/or best placed for carrying out detailed assessments and/or implementing controls;
- inform the relevant organisation (if OSPAR sees fit) of the OSPAR Ministerial commitments with regard to hazardous substances and the need for action to address OSPAR concerns;
- set up mechanisms for monitoring the compliance with measures adopted in the relevant forum;
- set up mechanisms to monitor inputs to the marine environment and concentrations in the marine environment and biota to check that levels are falling at a satisfactory rate.

For a number of the sources of octylphenol, OSPAR may not be the most appropriate international body to instigate further controls or to assess whether the controls are practicable or necessary. Therefore, setting and achieving the desired reduction targets will need to be carried out through close co-operation with other international forums.

It will also be possible, through appropriate assessment and monitoring activities, to consolidate the values obtained in Tables 2, 3 and 4 and to determine whether octylphenol occurs in the marine environment at significant levels, and to assess whether the levels are falling due to the implementation of agreed actions, and whether values are approaching near to zero concentrations.

It will be of particular importance to take account of the proposed actions and monitoring requirements for octylphenol in the EC Water Framework Directive as well as in other international forums.

7. IDENTIFICATION OF POSSIBLE MEASURES

7.1 Review of existing OSPAR, EU and national measures

7.1.1 Measures in OSPAR

PARCOM Recommendation 92/8 on Nonylphenol-Ethoxylates is being progressively implemented by Contracting Parties and will be playing a part in ceasing discharges, emissions and losses of octylphenol compounds which may be present as impurities in nonylphenol ethoxylates.

7.1.2 Ongoing activities within the European Union

Within the Water Framework Directive a list of hazardous substances (including octylphenol) had been adopted as required by Article 16 of the Directive. 4-*tert*-octylphenol was included on this list as a "priority hazardous substance under review". Further assessment of this substance to determine whether this substance will be classified as a priority hazardous substance has taken place and the EC Technical Meeting II '02 concluded that it could advise the WFD Expert Advisory Forum that that 4-*tert*-octylphenol does not fulfil the PBT criteria. At the time of the publication of this background document a final decision on whether octylphenol will be added to the WFD list of priority hazardous substances for priority action had not yet been taken.

A draft proposal of a new Detergent Directive aims, *inter alia*, at restricting the use of alkylphenol ethoxylates (APEs) in detergents. Possible restrictions on the marketing and use of nonylphenol and nonylphenol ethoxylates are likely to be considered in the framework of Council Directive 76/769/EEC (marketing and use of dangerous substances).

Under the Existing Substances Regulation (EEC 793/93) the related alkylphenol "nonylphenol" has undergone risk assessment and risk reduction proposals have been suggested following this assessment. These proposals include the reduction in production and use of nonylphenol. As industry has confirmed that octylphenol is a contaminant of nonylphenol then it is likely that this reduction of nonylphenol production and use will have a significant effect on the levels of octylphenol reaching the environment.

4-*tert*-octylphenol has been included in the candidate list under the EC Community Strategy on Endocrine Disruptors⁶ as a endocrine disruptor of medium concern.

7.1.3 National initiatives within some Contracting Parties

The Environment Agency in the UK has published a strategy for endocrine-disrupting substances in the environment (EA, 2000), and octylphenol and its ethoxylates are included on the list of substances for which endocrine-disrupting effects have been reported. The action identified by the Agency for octylphenol and its ethoxylates is their phasing out for some uses (for example as industrial surfactants) in order to meet EQSs or targets which will be developed. The UK Government has recently asked industry to come forward with proposals for voluntary action on nonylphenol ethoxylates and octylphenol ethoxylates, in particular that octylphenol ethoxylates are not used as substitutes for nonylphenol ethoxylates when these chemicals are phased out.

The Norwegian government has announced in October 2001 that it has banned "most uses" of several common industrial surfactants known to disrupt human endocrine systems including octylphenol (and nonylphenol and nonylphenol ethoxylates). The prohibition takes effect from the end of 2001 and applies to the "production, use and sale of the substances in pure form or in compounds". Paint and shellac

⁶ Communication from the Commission to the Council and the European Parliament on the implementation of the Community Strategy for Endocrine Disruptors - a range of substances suspected of interfering with the hormone systems of humans and wildlife (COM (1999) 706); 14.06.2001; COM (2001) 262 final.

products and lubricants are exempt, however, because “satisfactory alternatives for these applications have not yet been developed” and because such products account for a relatively small proportion of releases to the environment. Resins coated with alkylphenol ethoxylates have not been used by the offshore industry since 1999.

According to the Swiss Ordinance of substances, detergents shall not contain octyl- and nonylphenol ethoxylates. Further restrictions are planned for applications such as industrial and institutional cleaning, textile and leather processing and metal finishing. A draft amendment of an ordinance will be circulated for comments in July 2003. The amendments are planned to cover both octylphenol and nonylphenol ethoxylates.

7.2 Alternatives

One of the guiding principles of the OSPAR Hazardous Substances Strategy is the principle of substitution (the substitution of hazardous substances or preferably non-hazardous substances where such alternatives are available).

Substitution has been discussed by various OSPAR subsidiary bodies in the 1999/2000 inter-sessional period. The substitution of hazardous substances used offshore has been addressed in OIC and is an essential element of the measures adopted at OSPAR 2000 with respect to the use and discharge of offshore chemicals.

The UK assessment has not yet revealed any definitive substitutes which have been used for octylphenol. Nevertheless substitutes such as long-chain alcohol ethoxylates have been recommended with respect to the phase out of nonylphenol ethoxylates, and these should therefore be considered regarding this use of octylphenol.

Substitution of octylphenol by another substance requires consideration of the following:

- that the substitute is less harmful and poses a lower risk;
- the physical behaviour of the substance and thus the nature of the processes used to produce these substances;
- the price differential between these substances and octylphenol, based on these processes and resulting performance of the product (such as ethoxylates);
- the efficacy of substitutes and the volumes required.

The physicochemical data for other alkylphenols (the most likely substitutes) indicate that there are only a small number of alkylphenols which could realistically be considered. These included 4-*tert*-pentylphenol, 2,4-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol and dodecyl phenol⁷. Long chain alcohols might also be considered. These potential substitutes would need to be investigated further from an environmental point of view to see if they pose a lower risk.

8. CHOICE FOR ACTIONS

8.1 Introduction

When considered in the light of the guidance on the role of risk assessment, the initial results from the risk assessment indicate that there should be concern over the production of octylphenol and the production of resins using the substance, which accounts for 98% of use. The use of the resins in the

⁷ This substance should not be confused with 2,4,6-tri-*tert*-butylphenol which is an OSPAR Substance for Priority Action.

formulation of inks and the ethoxylation of resins, the formulation and use of OPEs in textiles and in paints, and the production of ether sulphates also may give rise to concern. However, it should be noted that the majority of the PEC values are derived from default emission estimates and this should be taken into account in consideration of measures. A proper evaluation of the appropriate choices for action can only be made when all the relevant information has been collected and the UK risk assessment has been finalised in 2004 and the relevant risk reduction scenarios have been developed. Assessment will be required of possible additional measures, examining options against key criteria such as effectiveness, practicability and economic impact. In particular, there needs to be a better understanding of the risks posed by the various substitutes which are available to replace octylphenol. However, the following actions are already thought to be justified.

8.2 Action in the EC

The development of appropriate measures to control discharges, emissions and losses of octylphenol through the implementation of the Water Framework Directive is clearly a major instrument of control.

- OSPAR Contracting Parties that are also EU Member States should support this process.

The development of appropriate measures to control discharges, emissions and losses of nonylphenols (which are priority hazardous substances) through the implementation of the Water Framework Directive (WFD) and amendment to the Marketing and Use Directive 76/769/EEC will address any octylphenols which may be impurities of nonylphenols, and will support the OSPAR work on PARCOM Recommendation 92/8.

- OSPAR Contracting Parties that are also EU Member States should support this process.

To support these processes and ensure that the information in this background document and the conclusions reached by OSPAR are generally taken into account in the approach of the European Community,

- OSPAR should communicate this background document to the European Commission.

8.3 Action within OSPAR

Contracting Parties should finalise their implementation of PARCOM Recommendation 92/8 to ensure that any octylphenol compounds which may be impurities of nonylphenol ethoxylates are prevented from reaching the marine environment.

The substitution of octylphenol with safer substitutes which pose less risk to the environment should be encouraged. In this context,

- Contracting Parties should take national action to prevent the use of octylphenol ethoxylates as replacements for NPEs (for example, in emulsion polymerisation, in leather processing, in metal finishing, in the textile industry, in water-based paints and emulsion-coated papers and as a cleaning agent);
- Contracting Parties should encourage the development of substitutes for octylphenol in the manufacture printing inks, where adequate substitutes are not currently available.

OSPAR should publish, as a supplement to this Background Document, the outcome of the exchanges of information within its Offshore Industry Committee on the presence of octylphenol as a production residue in ethoxylated resins and the possible effects of this.

In recognition of the large uncertainties in the estimations of risk made,

- the relevant industries should be invited to work with Contracting Parties to improve the estimates of emissions, and if necessary, the estimation of PNEC values, to ensure the most effective risk reduction measures can be adopted.

OSPAR should review EC proposals under the WFD in order to check that the needs identified by this Background Document have been met, and to identify any necessary additional action.

OSPAR should re-evaluate the risks posed by octylphenol releases from resins when further information has been collected. Any associated measures which might be justified should be addressed through the background document review process.

8.4 Action in other forums

To ensure that the information in this background document can be considered in the context of other international agreements which deal with hazardous substances, and with which Contracting Parties are associated,

- OSPAR should send copies of this background document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are parties both to OSPAR and those other agreements to promote action to take account of this background document by those other international bodies in a consistent manner.

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ANNEX 1: MARINE RISK ASSESSMENT

1. INTRODUCTION

This section considers the risks to the marine environment from the production, use and disposal of 4-*tert*-octylphenol. The methodology used is based on the marine risk assessment chapter 4 of Part II of the TGD (published on the ECB website⁸ in April 2003).

2. DERIVATION OF MARINE PECS

2.1 Local assessment

The methodology outlined in the marine risk assessment guidance essentially assumes that the adsorption/desorption, degradation and accumulation behaviour in the marine environment can, in the absence of specific information for the marine environment, be adequately described by the properties of the substance relevant for the freshwater environment. The relevant properties for 4-*tert*-octylphenol will be discussed in the national UK risk assessment report (not yet published) and are summarised in Table A1.1.

Table A1.1: Adsorption and bioaccumulation properties for 4-*tert*-octylphenol

Property	Value
Log Kow	4,12
Organic carbon - water partition coefficient (Koc) l/kg	2 740
Solid-water partition coefficient in suspended matter (Kp _{susp}) l/kg	274
Suspended matter - water partition coefficient (K _{susp-water}) m ³ /m ³	69,4
Fish bioconcentration factor (BCF _{fish}) l/kg	634
Biomagnification factor in fish (BMF ₁) ^a	1
Biomagnification factor in predators (BMF ₂) ^a	1

Note: a) Taken from the marine risk assessment guidance section of the TGD, Table 29.

$$Clocal_{seawater} = \frac{Clocal_{eff}}{(1 + Kp_{susp} \cdot SUSP_{water} \cdot 10^{-6}) \cdot DILUTION}$$

Explanation of symbols:

Clocal _{eff}	concentration of the substance in the STP-effluent	[mg.l ⁻¹]	eq. (33)
Kp _{susp}	solids-water partitioning coefficient of suspended matter	[l.kg ⁻¹]	eq. (23)
SUSP _{water}	concentration of suspended matter in the seawater	[mg.l ⁻¹]	15
DILUTION	dilution factor		100
Clocal _{seawater}	local concentration in seawater during emission episode	[mg.l ⁻¹]	

Effluent from industrial sites is assumed to enter the marine environment without further waste water treatment. An exception to this is use of the substance in products that are used by the general public, where discharge via a wastewater treatment plant can be assumed, and so the effluent concentration from the wastewater treatment plant is used as a starting point for the assessment. This does not apply to any of

⁸ <http://ecb.jrc.it/existing-chemicals/>

the uses of octylphenol considered in this assessment. However, releases from 4-*tert*-octylphenol production were estimated after waste water treatment, and these have been used in the estimation of the marine PECs. Releases from the use of 4-*tert*-octylphenol ethoxylates have to be considered in a different way. The risk assessment considers that the degradation of the ethoxylates in waste water treatment plants leads to a release of 4-*tert*-octylphenol. Direct release of ethoxylates would not contain significant levels of 4-*tert*-octylphenol. In order to take into account the possible releases of 4-*tert*-octylphenol from these uses, it has been assumed that the effluents from waste water treatment plants serving these industries discharge into the marine environment with the same dilution factor of 100.

All of the emissions are estimated on a mass/day basis and in order to estimate concentrations, knowledge of the total aqueous effluent volume discharge from a site is needed. These data are not usually needed and were not available for the main risk assessment. The Technical Guidance document proposes that a volume of 2 000 m³/day should be assumed; this is the same volume as is assumed for freshwater scenarios as a default.

The effluent concentrations used as the starting point for the marine risk assessment are shown in Table A1.2 and were taken from the EUSES calculations (1997) for the local scenarios (in most cases they are the influent concentrations to the waste water treatment plants for the freshwater assessment, with the exceptions as noted above). Consequently these values are estimated (rather than measured) and have the same limitations as the other PECs estimated by EUSES. The Table also shows the resulting concentrations in seawater, marine sediment and marine biota. These have been estimated using the methods outlined in the draft marine risk assessment guidance and the properties for the adsorption and bioaccumulation behaviour of 4-*tert*-octylphenol.

For secondary poisoning, the concentrations in predators and top predators should be estimated using the following equations from the TGD.

$$\begin{aligned} \text{PEC}_{\text{oral, predator}} &= 0,5 \times (\text{PEC}_{\text{local, seawater, ann}} + \text{PEC}_{\text{regional, seawater, ann}}) \times \text{BCF}_{\text{fish}} \times \text{BMF}_1 \\ \text{PEC}_{\text{oral, top predator}} &= (0,1 \times \text{PEC}_{\text{local, seawater, ann}} + 0,9 \times \text{PEC}_{\text{regional, seawater, ann}}) \times \text{BCF}_{\text{fish}} \times \text{BMF}_1 \times \text{BMF}_2 \end{aligned}$$

It should be noted, however, that the model to calculate the regional concentrations for the marine assessment was not yet available. For this assessment, therefore, it has been assumed that the regional contribution to the PECs is negligible compared to the local contribution (see section 2.2 below).

2.2 Regional assessment

The marine risk assessment guidance proposes an approach for estimating a regional concentration in seawater based on a suggested scenario and recommends the use of fugacity modelling.

However, due to the lack of a suitable nested steady state distribution model (as in EUSES for the freshwater environment), it is not possible to estimate a regional concentration. Therefore, the calculations in Table A1.3 have assumed that the $\text{PEC}_{\text{regional, seawater}}$ is small compared with the $C_{\text{local, seawater}}$ and hence the $C_{\text{local, seawater}}$ is assumed to approximate to the $\text{PEC}_{\text{local, seawater}}$. These calculations should be reconsidered once a suitable model is available to estimate the true $\text{PEC}_{\text{regional, seawater}}$.

One possible pathway to the marine environment may occur from older reported uses in the offshore oil industry. Discharges from production or exploration platforms could lead to direct entry into marine waters. However, there are no current data that indicate this route to be significant. The use of 4-*tert*-octylphenol by the offshore oil industry was phased out by the UK in 1999.

Another possible pathway to the marine environment is the use of resins derived from 4-*tert*-octylphenol in special paints used in marine applications because of the high resistance to saline waters that they provide. The tonnage of resin used for this application is not known (except that it is less than 800 tonnes per annum), but the free 4-*tert*-octylphenol content of these resins is likely to be low (some 3-4%, though

awaiting confirmation of this by industry) so the maximum amount associated with this use is around 32 tonnes. No information is available at this time on the leaching characteristics of 4-*tert*-octylphenol from these paints, so no assessment has been made of the contribution from this source.

Table A1.2: Estimated PECs for 4-*tert*-octylphenol for the local marine risk assessment

<i>Release source</i>	<i>Clocal_{eff}</i> (µg/l)	<i>No. of days release</i>	<i>Clocal_{seawater}</i> (µg/l)	<i>Clocal_{seawater, ann}</i> (µg/l)	<i>PEC_{Clocal_{seawater}}</i> (µg/l)	<i>PEC_{Clocal_{seawater, ann}}</i> (µg/l)	<i>PEC_{Clocal_{sed}}</i> (µg/kg ww _t)	<i>PEC_{Coral_{predator}}</i> (mg/kg)	<i>PEC_{Coral_{top predator}}</i> (mg/kg)
<i>Production of 4-<i>tert</i>-octylphenol</i>	1 070	300	11	9,0	11	9,0	664	2,85	0,57
<i>Production of OP resins</i>	1 500	300	15	12,3	15	12,3	905	3,9	0,78
<i>Production of OPEs</i>	2,08	20	0,021	1,2x10 ⁻³	0,021	1,2x10 ⁻³	1,3	4x10 ⁻⁴	7,6x10 ⁻⁵
Resin use:									
<i>Rubber for tyres</i>	0,97	300	0,0097	0,008	0,0097	0,008	0,59	2,5x10 ⁻³	5,1x10 ⁻⁴
<i>Varnishes</i>	1,87	20	0,019	0,001	0,019	0,001	1,15	3,2x10 ⁻³	6,3x10 ⁻⁵
<i>Ink formulation</i>	15	300	0,15	0,12	0,15	0,12	9,1	0,038	7,6x10 ⁻³
<i>Ethoxylated resins</i>	131	40	1,3	0,14	1,3	0,14	78	0,044	8,9x10 ⁻³
<i>Paper coating</i>	2,5	300	0,025	0,021	0,025	0,021	1,5	6,7x10 ⁻³	1,3x10 ⁻³
Ethoxylate use:									
<i>Formulation</i>	12,5	30	0,13	0,011	0,13	0,011	7,8	3,5x10 ⁻³	7,0x10 ⁻⁴
<i>Emulsion polymerisation</i>	0,42	300	0,004	0,0035	0,004	0,0035	0,24	1,1x10 ⁻³	2,2x10 ⁻⁴
<i>Textiles</i>	29,3	60	0,29	0,048	0,29	0,048	17,5	0,015	3,0x10 ⁻³
<i>Paint formulation</i>	6,25	200	0,063	0,035	0,063	0,035	3,8	0,011	2,2x10 ⁻³
<i>Paint use</i>	0,13	240	0,001	0,001	0,001	0,001	0,06	3,2x10 ⁻⁴	6,3x10 ⁻⁵
<i>Ether sulphate production</i>	58,3	150	0,58	0,24	0,58	0,24	35	0,076	0,015

2.3 Derivation of marine PNECs

2.3.1 PNEC for water

For 4-*tert*-octylphenol there are valid acute saltwater data for invertebrates and fish (see main report for full details of the available toxicity data and its interpretation), the values being:

- 48-hour LC₅₀ (lethality) for adult *Acartia tonsa* (copepods) = 0,42 mg l⁻¹;
- 96-hour LC₅₀ (lethality) for larval *Fundulus heteroclitus* (estuarine fish) = 0,28-0,34 mg l⁻¹.

However, no long-term NOEC values are available for saltwater species. The lowest valid long-term NOEC for a freshwater species is 6,1 µg l⁻¹ for the growth of rainbow trout (*Oncorhynchus mykiss*). Long-term NOECs are also available for algae (based on growth in *Scenedesmus subspicatus* and *Selenastrum capricornutum*) and invertebrates (juvenile production in *Daphnia magna*), but these values were higher. Given the available dataset it is proposed that an assessment factor of 100 be applied (according to the marine risk assessment TGD) to the NOEC for growth inhibition of rainbow trout resulting in a saltwater PNEC_{saltwater} of 0,061 µg l⁻¹.

2.3.2 PNEC for sediment

The PNEC_{sediment} for the marine environment can be estimated from the PNEC_{saltwater} using the equilibrium partitioning method since no marine or freshwater sediment toxicity data are available for 4-*tert*-octylphenol. Since the log Kow for 4-*tert*-octylphenol is <5 it is not considered likely that significant uptake may occur via ingestion of sediment. Therefore, the saltwater PNEC_{sediment} can be derived by equilibrium partitioning from the PNEC_{saltwater} using the appropriate equation in Section 4.3.2.3 of the TGD, resulting in a value of 3,68 µg kg⁻¹.

2.3.3 PNEC for predators

The PNEC for secondary poisoning is derived in a similar manner to the main risk assessment report. The PNEC for secondary poisoning, PNEC_{orals}, is 1,0 mg kg⁻¹, based on a 28-day feeding study in rats with a NOEL of 15 mg/kg bw/day.

3. RISK CHARACTERISATION FOR THE MARINE ENVIRONMENT

The PEC/PNEC ratios for water, sediment and predators/top predators are shown in Table A1.3. Since the sediment PNEC and PECs were estimated using equilibrium partitioning, the PEC/PNEC ratios for local sediment and local seawater will be similar and so are not included in the table.

Table A1.3: Estimated PEC/PNEC ratios for 4-tert-octylphenol for the local marine risk assessment

Release source	Sea-water	Predator	Top predator
Production of 4-tert-octylphenol	180	2,85	0,57
Production of OP resins	246	3,9	0,78
Production of OPEs	0,34	4x10 ⁻⁴	7,6x10 ⁻⁵
<i>Resin use:</i>			
Rubber for tyres	0,16	2,5x10 ⁻³	5,1x10 ⁻⁴
Varnishes	0,31	3,2x10 ⁻³	6,3x10 ⁻⁵
Ink formulation	2,5	0,038	7,6x10 ⁻³
Ethoxylated resins	21	0,044	8,9x10 ⁻³
Paper coating	0,41	6,7x10 ⁻³	1,3x10 ⁻³
<i>Ethoxylate use:</i>			
Formulation	2,1	3,5x10 ⁻³	7,0x10 ⁻⁴
Emulsion polymerisation	0,07	1,1x10 ⁻³	2,2x10 ⁻⁴
Textiles	4,8	0,015	3,0x10 ⁻³
Paint formulation	1,03	0,011	2,2x10 ⁻³
Paint use	0,02	3,2x10 ⁻⁴	6,3x10 ⁻⁵
Ether sulphate production	9,5	0,076	0,015

3.1 PBT-assessment

The nature of the open sea is such that a PEC/PNEC comparison is not appropriate for risk assessment of this environmental compartment. A PBT-assessment has therefore been developed to take into account the unacceptably high uncertainty in predicting reliable exposure and/or effect concentrations, which hampers quantitative risk assessment.

3.1.1 Persistence

The degradation of 4-tert-octylphenol is discussed in the risk assessment, where it is concluded that although it is inherently biodegradable it is not readily biodegradable. No marine or freshwater standard simulation test data are available, but there is some non-standard simulation test data for degradation in river waters and river sediments (Johnson *et al.*, 2000). The freshwater half-lives varied from 7-50 days in laboratory microcosms and no degradation over 83 days in spiked sediments incubated under anaerobic conditions.

The data suggest that 4-tert-octylphenol fulfils the persistence criterion (half-life > 60 d in marine water or > 40 d in freshwater⁹ or half-life > 180 d in marine sediment or > 120 d in freshwater sediment) and, on the basis of the sediment data, probably also fulfils the very persistent criterion (half-life > 60 d in marine- or freshwater or >180 d in marine or freshwater sediment).

⁹ For the purpose of marine environment risk assessment half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

3.1.2 Bioaccumulation

Bioaccumulation data are discussed in the risk assessment. *In vivo* bioconcentration factors (BCFs) ranged from 46-297 and BCFs estimated from models ranged from 634-3 300. A conservative value of 634 estimated from a BCF model was preferred for use in the risk assessment and that value is below the bioaccumulation criterion (BCF > 2 000).

3.1.3 Toxicity

The toxicity of 4-*tert*-octylphenol is discussed in the risk assessment and the lowest chronic NOEC (growth) was 6,1 µg l⁻¹ from the 60 day post-hatch early life stage toxicity study with rainbow trout (*Oncorhynchus mykiss*). This value meets the toxicity criterion (chronic NOEC < 0,01 mg l⁻¹). In addition, adverse effect that are related to endocrine disruption may occur at lower concentrations.

3.1.4 Summary

4-*tert*-octylphenol exceeds the P and, potentially, vP criteria and the T criterion, but does not exceed the B criterion. Hence it can be considered to be potentially persistent or very persistent and potentially toxic. However, since the B criterion is not met, the draft TGD risk assessment guidance does not require further testing to be carried out to see if the vB criterion is met.

4. MARINE RISK ASSESSMENT CONCLUSIONS

The provisional risk assessment indicates a potential risk to water and sediment organisms for a number of applications for this substance. For predators, a risk is only indicated for two of the applications. No risk to top predators is indicated. The marine aquatic PNEC was derived from a limited dataset for toxicity test values for freshwater species, with only few saltwater organism toxicity test results available. Therefore further long-term testing with aquatic and/or sediment organisms, preferably marine species, would be helpful to revise the assessment.

It is noted that measured concentrations from marine biota have been shown to be relatively low and therefore the apparent risk to this compartment for predators may be overestimated. Only two of the applications (production of octylphenol and production of resins) give rise to a risk for predators. It would be advisable to seek more realistic data from which to derive PECs as a first refinement to the risk assessment, such as local emission data (as there are a limited number of companies involved in these activities) and marine water concentrations.

Result for marine compartment

There is at present a need for further information and/or testing.

The large PEC/PNEC ratios produced for this assessment appear to indicate a significant risk to the marine compartment from the production and use of 4-*tert*-octylphenol in the EU. However, the values rely heavily on limited freshwater data for PECs and freshwater toxicity values from a relatively small dataset for the PNECs. A revised exposure assessment is required in the first instance.

ANNEX 2: OSPAR FACT SHEET FOR OCTYLPHENOL

0	NAME	phenol, 4-(1,1,3,3-tetramethylbutyl)-		VERSION: 2002-04-15
1	IDENTIFICATION			
1.1	Cas No	140669		
1.2	EINECS/ELINCS	205-426-2		
1.3	Synonym	octylphenol		
1.4	Group/Function	phenol		
1.5	Initial selection	PBT NSDB(III), QSAR-DK(V),		
1.6	Prioritised for action	Date: OSPAR 2000; Lead Country: United Kingdom; Background document: OSPAR 2003		
	Parameter	Value	Source/Reference	Remarks
2	PHYSICAL/CHEMICAL PROPERTIES			
2.1	Molecular weight, g/mole	206,33	RAR-UK	
2.2	Water solubility, mg/l	1,90E+01	RAR-UK	Measured value
2.3	Vapour pressure, Pa	1,00E+00	RAR-UK	Measured value at 25C
3	ABIOTIC/BIOTIC DEGRADATION PROPERTIES			
3.1	Abiotic OH-oxidation t _{1/2} d	0,25	RAR-UK	Rate constant of 4,5e-11 cm ³ /molec/sec calculating using OH concentration of 500 000 molec/cm ³
3.2	Photolysis t _{1/2} d			
3.3	Ready Biodegradability	No	RAR-UK	Not readily biodegradable (<20%)
3.4	Half-life			
3.5	Inherent Biodegradability	No	RAR-UK	Not inherently biodegradable (<20%)
3.6	Biodeg-QSAR			
4	BIOACCUMULATION/BIOCONCENTRATION			
4.1	logKow	4	RAR-UK	Measured value
4.2	Bcf	297	RAR-UK	Highest measured value for fish; value of 634 calculated in RAR from log Kow and used in assessment
5	AQUATIC TOXIC PROPERTIES			
5.1	Acute toxicity algae IC50, mg/l	1,1	RAR-UK	72 h for <i>Scenedesmus subspicatus</i>
5.2	Acute toxicity daphnia EC50, mg/l	0,27	RAR-UK	Measured 96hr
5.3	Acute toxicity fish LC50, mg/l	0,25	RAR-UK	Measured 96hr for <i>Pimephales promelas</i> , range 0,25-2,2 mg/l

5.4	Chronic toxicity daphnia NOEC, mg/l	0,062	RAR-UK0	21 days reproduction test
5.5	Chronic toxicity fish NOEC, mg/l	0,0061	RAR-UK	60 days early life stage study with rainbow trout
5.6	Aquatox-QSAR			
5.7	Aquatic toxicity - other species			
6	HUMAN TOXIC PROPERTIES			
6.1	Acute toxicity			
6.2	Carcinogenicity			
6.3	Chronic toxicity			
6.4	Mutagenicity			
6.5	Reprotoxicity		The results of the two-generation study indicate that OP is not toxic to reproduction in mammals over a wide range of doses	Tyl, R.W. <i>et. al</i> (1999), Reg. Toxicol. Pharmacol., 30, 81-95
7	EXPOSURE			
7.1	Production Volume	22600	RAR-UK	Value for 2001
7.2	Use/Industry Category	Main use in production of phenol/formaldehyde resins, also used as intermediate for octylphenol ethoxylates and octylphenol ether sulphates		RAR-UK
7.3	Use in articles			
7.4	Environm. Occur. Measured		Surface water: up to 13 ug/l	RAR-UK
			Biota: freshwater fish up to 340 ug/kg dry weight	RAR-UK
7.5	Environm. Occur. Modelled		Surface water: local PEC 0,001-13,6 mg/l	RAR-UK
8	EU-LEGISLATION			
8.1	Dir 67/548/EEC (Classification)		Annex 1, Dir 67/548/EEC	
8.2	Reg 793/93/EEC (Existing substances)			
8.3	Dir 2000/60/EEC (WFD)	YES	Annex to 2000/60/EEC	
8.4	Dir 76/769/EEC (M&U)			
8.5	Dir 76/464/EEC (water)			
8.6	Dir 91/414/EEC (ppp)			
8.7	Dir 98/8/EEC (biocid)			
9	ADDITIONAL INFORMATION			
9.1	Hazard assessment-OECD	YES		www.oecd.org/ehs/sidstable/
9.2	Other risk assessments			

ANNEX 3: MONITORING STRATEGY FOR OCTYLPHENOL

As part of the Joint Assessment and Monitoring Programme (*reference number 2003-22*), OSPAR 2004 adopted an Agreement on monitoring strategies for OSPAR Chemicals for Priority Chemicals (*reference number 2004-15*) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (*reference number 2003-21*) with regard to octylphenol. The Monitoring Strategy for octylphenol will be updated as and when necessary, and redirected in the light of subsequent experience.

The sources of octylphenol are, in general, well characterised and have been set out in the OSPAR Background Document on octylphenol, the updated UK RAR on octylphenol and the EC WFD source inventory on octylphenol.

Octylphenol is present as an impurity in nonylphenol and any monitoring programmes for these chemicals should be coordinated.

The Background Document shows that octylphenol is subject to various controls by EC directives, and that measures for reporting on restrictions of use and of emissions, discharges and losses are either in place or under development. The most appropriate way to assess progress towards the OSPAR cessation target is therefore to periodically examine the amounts produced and used together with the implementation of the various directives and regulations.

OSPAR will, therefore examine evidence from reports on the implementation of the various directives and regulations to make an initial judgement of the extent to which the amounts of the substance emitted or discharged are likely to have been reduced.

There are currently no environmental monitoring programmes for octylphenol in the OSPAR framework. However, methodologies for monitoring octylphenol in the marine environment are generally well understood and the monitoring which has been done shows that detectable concentrations are only likely to be found at hotspots.

Octylphenol is a priority substance in the EC Water Framework Directive, and OSPAR will seek to compile data from monitoring in this context to assess progress towards its own objectives.

With respect to the offshore industry, OSPAR will organise an exchange of information on the presence of octylphenol in resins used offshore in 2006.

OCTYLPHENOL MONITORING STRATEGY	
Implementation of actions and measures	<ul style="list-style-type: none"> Examination of progress in the implementation of regulations on marketing and/or use or emission and/or discharge which have been agreed, or are endorsed, by the Background Document. Regulations on nonylphenol and nonylphenol ethoxylate are especially relevant to the reduction of discharges, emissions and losses of octylphenol
Production/use/sales/figures	<ul style="list-style-type: none"> The lead country will update information on production and use of octylphenol during review of the Background Document. The next review is planned for 2008/09
Inputs from offshore industry	<ul style="list-style-type: none"> Exchange information on presence in resins used which might contain alkylphenols
Maritime area:	
Concentrations in sediments	<ul style="list-style-type: none"> Where available, data will be periodically compiled from EC WFD monitoring
Concentrations in water	<ul style="list-style-type: none"> Where available, data will be periodically compiled from EC WFD monitoring

ANNEX 4: EXCHANGE OF INFORMATION ON OCTYLPHENOL IN RESINS

As a follow up to the chapter “Choice for actions”, this annex summarizes the outcome of the exchange of information within the Offshore Industry Committee (OIC) on the presence of octylphenol as a production residue in resins and the possible effects of this.

Information exchanged

Results of the following studies were presented at OIC 2004 and 2005 (OIC 05/3/9):

- a. The UK Department of Trade and Industry undertook a survey in 2004 to confirm the pattern of use of alkyl phenol (formaldehyde) resin (APR) on the United Kingdom continental shelf (UKCS);
- b. Studies commissioned by the European Oilfield Speciality Chemicals Association (EOSCA):
 - (i) Screen test for the presence of oestrogenic activity in chemicals for offshore use, 1999;
 - (ii) Testing 5 chemicals (oxyalkylated alkylphenolic resins) for oestrogenic activity, 2000;
 - (iii) A Review of the Degradation and Bioavailability of Phenol Formaldehyde Condensation Polymers (resins) as applied in the OSPAR Region;
 - (iv) Alkylphenol Based Demulsifier Resins and their Continued Use in the Offshore Oil and Gas Industry.

Conclusions of the studies

APR chemistry was introduced in the offshore oil and gas industry around 1990, and represented a step-change improvement in primary demulsifier technology. Alkyl phenols are reacted with formaldehyde to form condensation polymers, popularly referred to as resin demulsifiers. These products offered low ecotoxicity and, at that time, there were no concerns associated with their use. Since then, the move to a precautionary approach has led to some concerns about their use, on the grounds that they may contain, or degrade to, their precursors, the alkyl phenol ethoxylates, which have been reported as potential endocrine disruptors.

The United Kingdom survey showed that alkylphenol formaldehyde resins were present in a number of demulsifier formulations used on the UKCS, and were considered to be particularly important for the processing of certain types of oil. All of the operators currently using APRs confirmed that they were aware of the unsubstantiated concerns relating to their use, and that they had investigated alternative chemistries. The survey indicated that:

- a. alkyl phenol formaldehyde resins currently represent the best available chemistry to treat heavier cold crudes (i.e. crude oils) with a relatively high water cut (i.e. water content), and;
- b. that alternative chemistries offer no net environmental benefit, and may result in increased chemical use and discharge, greater environmental impact and increased operating costs.

The EOSCA studies indicated that:

- a. alkyl phenol formaldehyde resins do not exhibit endocrine disrupting properties;
- b. the resins do not contain any un-reacted precursors;
- c. it is unlikely that the resins would degrade to the precursors in the operating environments of offshore production;
- d. there is no evidence that alkyl phenol formaldehyde resins are environmentally damaging.

The United Kingdom chemical and offshore industries would continue to investigate alternative chemistries. The results of those investigations and the results of any further ecotoxicological studies relating to alkyl phenol formaldehyde resins would be reported to OIC.