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Environmental risk evaluation report: *para*-C_{12}-alkylphenols (dodecylphenol and tetrapropenylphenol)

SCHO0607BMVN-E-P

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Executive summary

This risk assessment covers any branched chain *para*-C_{12}-alkylphenol in commercial use in Europe, but particularly “phenol, (tetrapropenyl) derivatives” (CAS no. 74499-35-7) (tetrapropenylphenol) and “dodecylphenol, mixed isomers (branched)” (CAS no. 121158-58-5).

para-C_{12}-alkylphenols are primarily used as chemical intermediates in the production of oil and lubricant additives for petrol- (gasoline) and diesel-powered road vehicles and marine diesel engines. They are also used to make phenolic resins for printing inks, rubber compounding for tyres and varnishes. There is a production facility in the United Kingdom, although not all the industrial applications take place in this country. European consumption of *para*-C_{12}-alkylphenols is around 50,000 tonnes per year (2004).

para-C_{12}-alkylphenols are viscous oily liquids at 20°C. Their variable composition means that properties also vary and can be difficult to determine experimentally. The values for the key physico-chemical properties selected for this assessment are a vapour pressure of 0.009 Pa at 20ºC; a water solubility of 31 µg/L at 22ºC for the main components (2.1 mg/L for the bulk commercial material); and a log octanol-water partition coefficient (log K_{ow}) of 7.14.

The substance is not readily or inherently biodegradable in the aquatic environment, and can accumulate in aquatic organisms (the measured fish bioconcentration factor is 823). The substance is expected to partition mainly to soil and sediment when it is released to the environment, where it is likely to be persistent. Atmospheric transport and deposition to soil are expected to be negligible.

The emissions of *para*-C_{12}-alkylphenols have been predicted for each stage of the life cycle using the assumptions of a European Technical Guidance Document for industrial chemical risk assessment, supplemented where possible with industry specific information (including emission scenario documents).

A limited amount of validated information is available to assess the environmental hazard potential of *para*-C_{12}-alkylphenols. The substance is acutely toxic to aquatic organisms, and may cause long-term adverse effects in the aquatic environment. The predicted no-effect concentration (PNEC) for freshwater aquatic organisms selected for the environmental risk assessment is 0.04 µg/L. Further long-term toxicity testing on suitable species could refine this value. The PNECs in other compartments are largely derived from the surface water PNEC, with the exception of a PNEC of 3.3 mg/kg body weight/day for predators exposed through food.

para-C_{12}-alkylphenols do not meet the European criteria for consideration as a persistent, bioaccumulative and toxic (PBT) chemical, since the substance does not meet the bioaccumulation criterion. However, they do meet the UK Chemical Stakeholder Forum’s PBT criteria for a substance of concern.

Overall, the assessment identifies potential environmental risks from production, use as an intermediate, and most end-uses of the derivatives and resins (which all contain some *para*-C_{12}-alkylphenols as impurities). The risks are to the freshwater and marine aquatic (including sediment) compartments and soil. Predators are potentially at risk if exposed via the terrestrial food chain; there are also potential risks to humans following environmental exposure for some resin uses. The substance does not pose a risk to WWTP micro-organisms, the atmosphere or to predators exposed via the aquatic food chain based on the information available.

More detailed data on emissions and measured concentrations in the environment would enable the conclusions to be re-assessed. There is also scope to refine the toxicity assessment for all compartments through further testing, particularly for sediment- and soil-dwelling organisms.

The major uses of *para*-C_{12}-alkylphenols are quite different from those of other alkylphenols which have been the subject of major risk assessments (specifically nonylphenol and octylphenol) and so restrictions on the uses of these other substances are unlikely to impact the use pattern of *para*-C_{12}-alkylphenols.

Acknowledgements

The Environment Agency would like to formally acknowledge the helpful assistance of member companies of the Risk Assessment Task Group (RATG) of the American Chemistry Council's Petroleum Additives Panel; the Conseil Européen des Phénols Alkylés et Derivés (CEPAD); and the European Phenolic Resins Association (EPRA). These organisations voluntarily and openly submitted detailed information, including test data. The Advisory Committee on Hazardous Substances also provided input as this assessment progressed.

Colleagues at the Health and Safety Executive wrote the human health effects assessment and the risk characterisation for human exposure via the environment. Helen Jordinson, Paul Eccles and Anne O'Neil from the Environment Agency provided valuable assistance in the re-interpretation of the aquatic toxicity data.

The Environment Agency would like to thank all contributors to this report, especially the peer reviewers (including the Danish Environmental Protection Agency, the Dutch National Institute of Public Health and the French National Institute for Industrial Environment and Risks). A list of all the organisations consulted is provided in Appendix 4.

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Preface

In 2005 a study by the Environment Agency (EA, 2005a) found that octylphenol and dodecylphenol were both potential substitutes for nonylphenol, a substance now subject to restricted marketing and use in Europe. The two alternatives were highlighted as priorities for environmental risk assessment. Dodecylphenol was also identified as a potentially "persistent, bioaccumulative and toxic (PBT)" substance, both by the Chemicals Stakeholder Forum (CSF) in the UK (CSF, 2003) and by the European Commission.

The substance is both manufactured and used in the United Kingdom (UK), so environmental exposure is possible. However, there are no existing reviews of the substance's hazards or risk.[1] The UK Government therefore decided that more information was needed on the potential risks to the environment and to human health following releases of the substance to the environment. This report clarifies the substance's identity and properties, and the concentrations that might lead to environmental or human health concerns. It also highlights the points in the life cycle where risks might be occurring, or could occur in the future. Assessment of the human health risks following exposure of either consumers or workers is beyond the scope of this report.

The assessment has relied on the voluntary provision of data from industry. Information on uses and supply levels is only available at the European level. However, given the nature of the open market in Europe, the assessment assumes that any use of the substance at the European level could take place in the UK, unless there is reliable evidence to suggest that this not the case (e.g. if only a small number of non-UK locations are know to use a particular process).

During the course of this review, industry representatives volunteered to perform additional studies and to prepare a Screening Initial Data Set (SIDS) Initial Assessment Report (SIAR). This type of report is a comprehensive hazard assessment under the auspices of the Organisation for Economic Co-operation and Development (OECD) SIDS programme[2]. The SIDS documents were discussed at an international review meeting in April 2006, under the UK's sponsorship (SIAR, 2006). The meeting agreed that the substance is a candidate for further work based on its hazards to human health and the environment. At the same time, the substance was added to the list of chemicals being considered under the UK Co-ordinated Chemical Risk Management Programme (for further details of this programme, see http://www.defra.gov.uk/environment/chemicals/ukrisk.htm).

Given that the OECD assessment will be published in due course, only the key data are summarised in this report. However, all of the data provided by industry for the CSF, OECD and EU PBT initiatives have been taken into account.

The layout of this report follows the format (with a few small modifications) of an assessment carried out under Council Regulation (EEC) 793/93, known as the Existing Substances Regulation (ESR). Readers familiar with such assessments should quickly find the information they are seeking. The data collection and peer review process is described in Appendix 4.

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[1] A substance initially called 'dodecylphenol' was identified by the Oslo and Paris Convention for the Protection of the Marine Environment of the Northeast Atlantic (OSPAR) as a hazardous substance for priority action (OSPAR, 2000). However, the listed substance is actually 2,4,6-tri-*tert*-butylphenol (CAS no. 732-26-3).

[2] See http://oecd.org/.

Note that the possibility of additive or synergistic effects with other alkylphenols has not been considered in this report. Such an approach is more suited to site-specific assessments because of the differences in use pattern of the chemicals involved.

Note: Whilst detailed information has been provided by industry for lubricant applications, the assessment still relies on default assumptions for resin applications. The scenarios described in this report may be, therefore, unrealistic. There may also be some other uses of the substance that are not reflected in the use pattern provided by the main trade associations. Nevertheless, this report has been in preparation for some considerable time; its draws its conclusions on the basis of current knowledge. The information it contains should be read with care to avoid possible misinterpretations or misuse of the findings. Anyone wishing to cite or quote this report should contact the Environment Agency beforehand.

1 General substance information

The term 'dodecylphenol' represents any compound with the general formula $C_6H_4(OH)C_{12}H_{25}$. The dodecyl group is a chain of 12 carbon atoms, which may be branched or linear. The chain can be located at the 2-, 3- or 4-position of the benzene ring. This complexity means that there are potentially lots of individual isomers, and the commercial substance has been described differently in various chemical inventories. For example, the European Inventory of Existing Commercial Chemical Substances (EINECS) has four entries for dodecylphenol, listed in Table 1.1. The CAS registry also lists other related substances.

Table 1.1 Relevant substances listed as 'existing' under EU law

EINECS name	CAS no.	EINECS no.	Supply level according to ESIS[a]
Phenol, dodecyl-, branched	121158-58-5	310-154-3	LPV
Dodecylphenol	27193-86-8	248-312-8	LPV
p-Dodecylphenol (synonym: 4-laurylphenol)	104-43-8	203-202-9	Not HPV or LPV
Isodecylphenol	11067-80-4	234-287-0	LPV

Notes: a) The European Chemical Substances Information System (ESIS), part of the European Chemicals Bureau website (http://ecb.jrc.it). High production volume (HPV) chemicals were manufactured or imported at ≥1,000 tonnes/year at least once by a company in 1990-1994. Low production volume (LPV) chemicals were supplied at ≥10 tonnes/year.

Consultation with the Conseil Européen des Phénols Alkylés et Derivés (CEPAD) and the Risk Assessment Task Group (RATG) of the American Chemistry Council has established that the commercial substance is in fact identified more appropriately with the names listed in Table 1.2. The main ones are highlighted in bold (CEPAD, personal communication, 2000; RATG, 2005).

Table 1.2 Branched C_{12}-alkylphenols considered as part of the life cycle analysis

Name	CAS number	EINECS number
Phenol, tetrapropylene	57427-55-1	-
Phenol, (tetrapropenyl) derivatives	74499-35-7	-
Dodecylphenol, mixed isomers (branched)	121158-58-5	310-154-3
Phenol, 4-dodecyl, branched	210555-94-5	-

For the purpose of this assessment these products are referred to collectively as ***para*-C_{12}-alkylphenols**. Where relevant, the name 'tetrapropenylphenol' has been used as the principal commercial name, but the report uses the names from the original information sources to avoid further confusion. Information clearly related to a more specific isomer or component is identified. **The conclusions of the assessment are considered to be representative for all branched chain *para*-C_{12}-alkylphenols.**

Both CEPAD and the RATG believe that the other substances listed in Table 1.1 are predominately straight-chained. As such, they are unlikely to have ever been supplied in any significant volume, and are not considered to be commercially relevant in Europe today.

Further background information on the development of the terminology is given in the SIAR (2006).

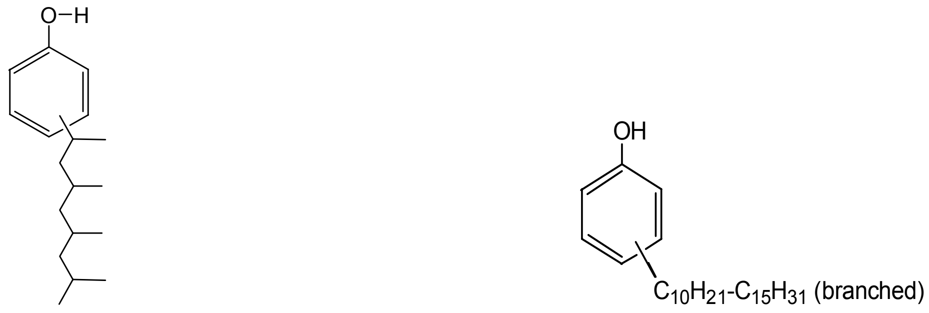
1.1 Identification of the substance

As discussed in the general introduction to this section, various names and identifying codes have been used to describe this substance. Table 1.3 and Figure 1.1 present the information that the main manufacturers and users of the substance consider to be most relevant to the commercial product.

Table 1.3 Identification of the principal commercial *para*-C_{12}-alkylphenols

Descriptor	Substance	
CAS number	74499-35-7	121158-58-5
EINECS number	No entry	310-154-3
Common name	Phenol, (tetrapropenyl) derivatives	Dodecylphenol, mixed isomers (branched)
EINECS name	No entry	Phenol, dodecyl-, branched
Molecular formula	$C_{16}H_{26}O$ to $C_{21}H_{36}O$	See main text
Structural formula	$HO-C_6H_4-C_{10}H_{21}$ to $HO-C_6H_4-C_{15}H_{31}$ where C_6H_4 is a benzene unit (typically substituted at the 1,4-position)	See main text
SMILES code	Oc1ccc(cc1)C(C)CC(C)CC(C)CC(C)C for isomer given in Figure 1.1	See main text
Molecular weight	234.38-304.51 g/mole (262.43 g/mole for the C_{12}-alkyl derivative)	See main text
Synonyms	See the general introduction. Tetrapropenylphenol may also be called 'dodecylphenol T' (SASOL, 2000) or T-DET (IUCLID, 1995). *para-C*$_{12}$-alkylphenols is used as a generic term referring to both types of compound for the purposes of this assessment.	

The term 'tetrapropenyl' represents a large number of highly branched isomeric alkyl olefins ranging from $C_{10}H_{20}$ to $C_{15}H_{30}$. Therefore, the chemical name tetrapropenylphenol represents both the presence of branched alkyl groups that may be located at either the 2-(*ortho*), 3-(*meta*), or 4-(*para*) position on the benzene ring and a range of alkyl chain lengths as well. The predominant nominal $C_{12}H_{25}$ side chain alkyl group has a typical continuous carbon chain length of eight carbons with four methyl branches.



C$_{12}$ derivative

Figure 1.1 Structure of tetrapropenylphenol

The chain shown for the C$_{12}$ derivative is an idealised branched structure – other branching patterns are possible. The substance derived from butylene trimer is likely to have a different branching pattern and mixture of chain lengths (see Section 1.2).

1.2 Purity/impurities, additives

1.2.1 Purity/impurities

The following information was provided by RATG (2005) (see also the SIAR, 2006).

Tetrapropenylphenol is made up of >99% w/w single alkyl-substituted phenols, the majority of which (>95% w/w) are substituted at the 4(*para*)- position on the benzene ring. There is a very small amount of 2(*ortho*)- and 3(*meta*)- substitution. The di-alkylphenol is the only expected reaction impurity at <0.1% w/w. Other impurities may include starting materials such as phenol (CAS no: 108-95-2) (0.02-0.60% w/w) and water (≤0.05% w/w) (SASOL, 2000; SIAR, 2006).

The quoted purity relates only to total alkylphenol content. Tetrapropenylphenol is produced from complex olefin feedstocks with a range of alkyl chain lengths and branching patterns. The data in Table 1.4 and Figure 1.2 represent the carbon range distribution of three samples of commercial material. The C$_{12}$-alkyl content is around 70%, but there are significant amounts of lower and higher molecular weight substances.

Table 1.4 Alkyl chain length distribution in commercial tetrapropenylphenol, per cent w/w

Alkyl chain length	Sample			Average
	1	2	3	
C$_3$	0.00	0.09	0.19	0.09
C$_4$	0.04	0.17	0.30	0.17
C$_5$	0.27	0.23	0.34	0.28
C$_6$	0.31	0.18	0.30	0.26
C$_7$/C$_8$	0.24	0.08	0.20	0.17
C$_9$	0.39	0.07	0.65	0.37
C$_{10}$/C$_{11}$	21.70	19.50	16.27	19.16
C$_{12}$	**68.55**	**69.00**	**68.50**	**68.68**
>C$_{12}$	8.41	9.90	12.91	10.41
Total[1]	**99.91**	**99.22**	**99.66**	**99.59**

Notes: [1]The values are ranges from different suppliers and so do not add up to 100%.

In addition to variations in alkyl chain length, extensive branching also occurs during the acid-catalyzed alkylation process. Every conceivable methylene analogue is observed when the substance is analyzed by electrospray ionization mass spectroscopy (as if the starting olefin were a mixture of branched olefins in the range of C_{10}-C_{15} with the vast majority of olefin in the C_{12} fraction).

The detailed distribution of chain lengths in the substance made with butylene trimer (tri n-butene) as the source of the alkyl group has not been sought. However, the trimer mixture contains various isomers with different branching to that found in propylene tetramer (SASOL Germany GmbH, personal communication, 2005). Nevertheless, C_{12}-alkyl material will also be the major component.[3]

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[3] Note that the related substance 4-*tert*-octylphenol is made with dimerized isobutene. Isobutene is pure, and so the finished product only has a single chain length, with a clearly defined branch structure.

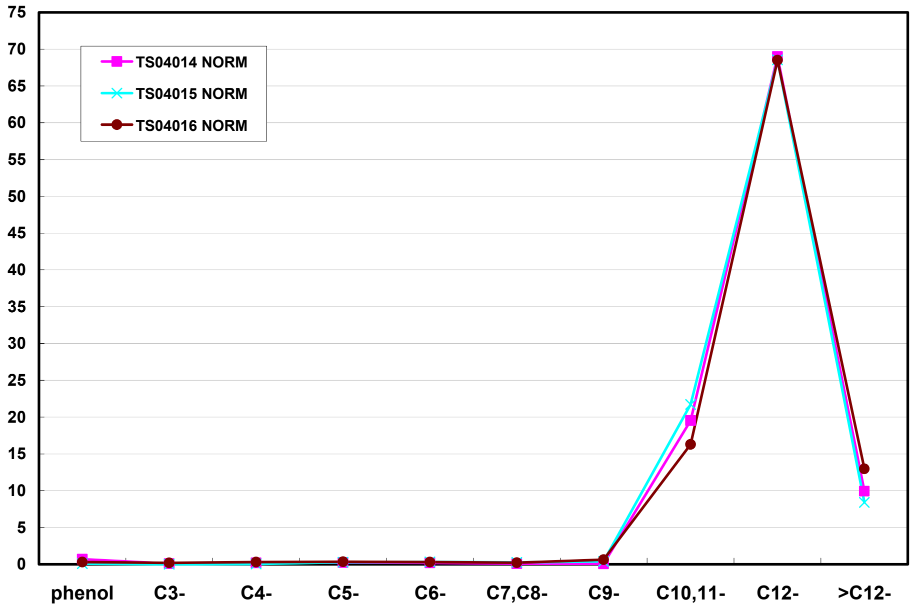

Figure 1.2 Alkyl chain length distribution in three samples of commercial tetrapropenylphenol

Most of the available data have been generated using commercial material rather than specific components, and expressed as an overall value rather than a range. **For the sake of simplicity, this assessment assumes that the commercial substance behaves as a single component material (i.e. the major C_{12}-alkylphenol content) in the environment for the purposes of exposure and hazard assessment.** This C_{12}-alkylphenol content is also a mixture; the properties of the different components will vary, but they are expected to vary less than across the range of chain lengths present in the commercial material.

1.2.2 Additives

In general the substance does not require stabilisation with additives, although in some cases colour stabilisers may be used (especially for purer technical grades) (Schenectady International, personal communication, 2006).

1.3 Physico-chemical properties

The following section provides a summary of the chemical and physical properties of the substance. The complex nature of the substance makes the choice of physico-chemical parameters for modelling purposes difficult. For this assessment, a single representative value has been chosen for each end-point based on the available data, and a sensitivity analysis is presented in Appendix 1. Further details are provided in the SIAR (2006).

1.3.1 Physical state (at n.t.p.)

Commercially produced *para*-C_{12}-alkylphenols are viscous oily liquids at 20°C and 101.3 kPa (as described in the test reports summarised in Section 4).

1.3.2 Melting point

Pour points around -3°C or lower have been reported. This parameter refers to the lowest temperature at which movement of the substance is observed, which is an appropriate measurement for oily substances of this type.

1.3.3 Boiling point

The substance will boil over a temperature range because of the number of components it contains. Various boiling ranges have been reported, depending on the purity and origin of the material and methods used. RATG (2005) comment that the expected boiling point range is from below 300ºC to over 350ºC at normal atmospheric pressure.

1.3.4 Relative density

The relative density is reported to be around 0.93 at 20°C.

1.3.5 Vapour pressure

The product information datasheets (SASOL, 2000) quote a measured value of 4.0 hPa at 160ºC for 'dodecylphenol T' and 5.7 hPa at 160ºC for 'dodecylphenol'. A measured value of 9.19×10^{-3} Pa has also been reported in an industry specification sheet, determined using ASTM D 323 on a commercial sample of tetrapropenylphenol (>99% purity).

The reliability of these results is difficult to determine in the absence of a test report. However, the latter result does provide a standard method that is appropriate for this type of substance. The company that made the measurement has confirmed that the commercial material was tested. The measured value is consistent with room temperature vapour pressures of nonylphenol (0.3 Pa, from EC, 2002) and octylphenol (0.21 Pa, from EA, 2005b). The comparison also suggests that the measured value does not represent the more volatile minor components of the substance.

It is also helpful to consider predicted values for the vapour pressure in this case. IUCLID (1995) reports an estimated value of 9.24×10^{-6} kPa at 25ºC generated by the United States Environment Protection Agency's (US EPA's) PC Graphical Exposure Modelling System (dated 1989). It is unclear which method was used for this calculation. The MPBPWIN v1.41 model (US EPA, 2000) derives three predicted values at 25ºC using the idealised isomer structure from Section 1.1, as follows:

- 1.6×10^{-4} mm Hg (0.021 Pa) (Mackay method);
- 2.47×10^{-5} mm Hg (3.3×10^{-3} Pa) (modified Grain method);
- 1.36×10^{-5} mm Hg (1.8×10^{-3} Pa) (Antoine method).

The validity of these predictions is uncertain, given that the same model predicts that the substance will be a solid at room temperature. However, they are all consistent with the measured value.

The measured value of 9.19 x 10^{-3} Pa (assumed to be at 25ºC) has been used in the risk assessment. Although limited details of the study are available, the value is in good agreement with predicted values and is consistent with data from analogous substances.

1.3.6 Water solubility

The bulk water solubility of tetrapropenylphenol was determined to be 1.54 mg/L at 20ºC using the shake flask method (OECD test guideline 105) (Mullee, 2004). The concentration was measured using HPLC. Although the column elution method is recommended for poorly soluble materials, the viscous liquid nature of the test substance risked plugging the column. However, the results from experiments using the flask method may be somewhat uncertain because the substance could adsorb to glassware (see Section 4.1).

The water solubility of a commercial sample of tetrapropenylphenol was determined by ASTM method E1148-02 (Dutta, 2003a). The substance was shaken with HPLC water for two minutes every hour for seven hours, and allowed to stand for 72 hours. The saturated water was filtered three times (0.45 μm filter) and a drop checked under a microscope for undissolved material. The water was extracted with methylene chloride, the solvent separated and evaporated, and the residue dissolved in acetonitrile for HPLC analysis with fluorescence detection. Peaks due to C_3-, C_4-, C_5-, C_6- and C_{12}-alkyl chain lengths were quantified. The results were:

C_3	0.448 mg/L
C_4	0.862 mg/L
C_5	0.721 mg/L
C_6	0.060 mg/L
C_{12}	0.016 mg/L

The solubility of the bulk material was 2.11 mg/L as the sum of the components.

A second measurement was carried out following the same procedure, but using a distilled sample of the commercial product. The distillation was carried out under vacuum, and the eighth of 10 fractions taken as containing predominantly C_{12} or higher material. Field ionisation mass spectroscopy showed this fraction to contain 91% of C_{12} and higher alkyl chain isomers. The solubility of this distilled fraction (based on the C_{12} peak only) was 0.031 mg/L.

These data confirm that the water solubility varies with the chain length of the alkyl group. The bulk product has an apparent water solubility of ~2 mg/L, with a large contribution from lower molecular weight components. This lower molecular weight fraction is more soluble than the C_{12}-alkyl fraction, which is expected to be more soluble than the C_{13-15} fraction.

For comparison, the WSKOW v1.41 model (US EPA, 2000) estimates a water solubility of 58 μg/L at 25ºC using the idealised structure from Section 1.1. This value is in good agreement with the measured results. This method is based on the predicted octanol-water partition coefficient (see Section 1.3.7). An alternative value of 0.37 mg/L is estimated using the WATERNT v1.01 model in the same software suite. This latter model uses a fragment method, but the value is an overestimate of around one order of magnitude compared to the measured result for the C_{12} component.

Some other data have been found, although their validity is uncertain due to a lack of supporting information. A water solubility of 1 mg/L at 20°C for dodecylphenol (CAS no. 27193-86-8) is cited in IUCLID (1995). Product information datasheets quote a value of about 26 mg/L at 20°C for 'dodecylphenol' and a value of <0.3 mg/L at 20°C for 'dodecylphenol T' (SASOL, 2000). The higher value could be related to larger amounts of lower alkyl chain length material.

The measured value of 31 µg/L for the distilled fraction has been used in this assessment to represent the main components of the substance. Clearly, interpretation of the aquatic toxicity and degradation results needs to allow for the different solubilities of the various components. Solubility studies at concentrations up to the bulk solubility of around 2 mg/L are therefore also potentially useful in assessing the fate and effects of the substance.

1.3.7 n-Octanol–water partition coefficient (log K_{ow})

A log K_{ow} value of 5.5 was measured for p-dodecylphenol (CAS no. 104-43-8) using high performance liquid chromatography on a Whatman Partisil-10 ODS-2 reverse phase column with methanol containing 15% water as the solvent (applied at a flow rate of 2 ml/min) (McLeese *et al.*, 1981). The method appears to be valid. However, the composition of the substance is not given and the influence of varying chain lengths has not been considered. The reliability of this result is therefore unknown.

For comparison, a log K_{ow} of 7.17 was calculated from the idealised structure from Section 1.1 using the KOWWIN (v1.67) model (US EPA, 2000).

Consequently, Dutta (2003b) determined the log K_{ow} of the C_{12} component of a commercial sample of tetrapropenylphenol using three methods. Analysis was by HPLC with UV or fluorescence detection. The results from the three methods were in close agreement:

- OECD slow stirring method: 7.14;
- OECD HPLC method: 7.96;
- dialysis method: 7.33.

A log K_{ow} value of 8.05 was determined for a distilled fraction (as described in Section 1.3.6) using the HPLC method.

The log K_{ow} of 7.14 determined by the slow-stir method is preferred for the risk assessment because it is a direct measurement. This is in excellent agreement with the predicted value.

1.3.8 Hazardous physico-chemical properties

These are relevant to this assessment from the point of view of laboratory hazards that might limit testing options, or require controls on process equipment (e.g. to exclude air if a substance is pyrophoric).

The flash point is around 150°C. No information could be located for autoflammability. The chemical structure of this compound does not suggest a likelihood of explosivity or oxidising properties.

1.3.9 Other relevant physico-chemical properties

Acid dissociation constant (pKa)

A pK_a value of 12.19 is reported in IUCLID (1995), but the substance is described as 2,4,6-tri-*tert*-butylphenol and so this entry is presumably in error. Nevertheless, the pK_a value for phenol is reported to be 9.9 (ECB, 2002) and an alkyl-substituted phenol would be slightly less acidic and have a higher pK_a value (due to the electron donating properties of the alkyl group). Consequently, it is not considered necessary to provide a more accurate value, since *para*-C_{12}-alkylphenols would be undissociated at typical environmental pH.

1.3.10 Summary of physico-chemical properties

Table 1.5 summarises the key physico-chemical data used for this assessment.

Table 1.5 Physico-chemical properties used in the risk assessment

Property	Value and comment
Physical state at n.t.p.	Oily liquid
Molecular weight	262.43 g/mol (main component)
Vapour Pressure	9.19×10^{-3} Pa at 25°C
Water solubility	31 µg/L at 20°C (main component) ~2 mg/L (bulk solubility)
n-Octanol-water partition coefficient, log K_{ow}	7.14
Acid dissociation constant (pK_a)	>9.9

2 General information on exposure

The primary information summarised in this section has been provided by industry for commercial tetrapropenylphenol (RATG, 2005). CEPAD (2002) provided the information on resin uses. The 'EU' refers to the 15 European Union Member States (EU-15) prior to expansion in May 2004 unless stated otherwise. However, this assessment does account for known production in new Member States when estimating the overall level of use.

2.1 Production

2.1.1 Production processes

Commercial manufacture began in the mid-1940s. Tetrapropenylphenol is produced in a closed constant flow reactor using solid phase acid catalysis to promote the alkylation of phenol with propylene tetramer (CAS no. 6842-15-5). The reactants are pumped up through the catalyst bed in a continuous mode and the crude alkylphenol is fractionally distilled to remove any un-reacted olefin and phenol. The un-reacted olefin and phenol are re-cycled and the purified tetrapropenylphenol is pumped to dedicated storage tanks to await further chemical processing. The reactions are illustrated schematically in Figure 2.1.

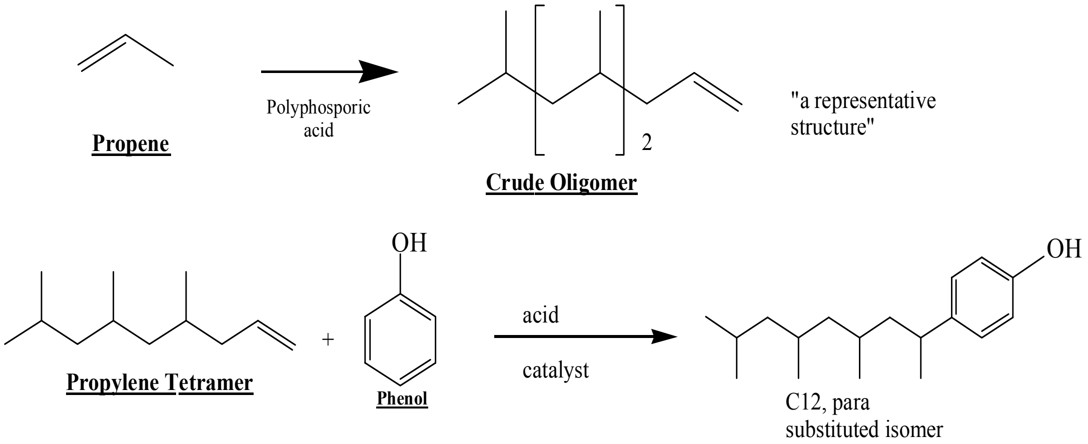

Figure 2.1 Tetrapropenylphenol manufacturing process

A similar process would produce butylene trimer (tri-n-butene) and hence *para*-C_{12} alkylphenol by this route. IUCLID (1995) provides some additional details, stating that the reaction is catalysed by an ion exchange resin, and takes place at 80-130°C and 101.3 kPa.

2.1.2 Scale of consumption

The ESIS database indicates that there were three producers/importers of *para*-C_{12}-alkylphenols in Europe in the early 1990s, and these are indicated in Table 2.1.

Table 2.1 EU producers/importers in the early 1990s

EINECS name	CAS no.	Producer/importer
Phenol, dodecyl-, branched	121158-58-5	Hüls AG, Marl, Germany (now SASOL Germany GmbH)
Dodecylphenol	27193-86-8	ENICHEM S.p.A., Milano, Italy (now Polimeri Europa)
Isodecylphenol	11067-80-4	Schenectady Pratteln AG, Pratteln, Switzerland

Consultation for this report indicates that production was carried out at four sites in Europe in 2005, in Germany, Poland, France and the UK (the locations are provided in a confidential annex to this report). The former Italian producer has indicated that despite offering the substance for sale on its website, it has not supplied it for a number of years, and has no plans to recommence production (Polimeri Europa, personal communication, 2005). Other producers exist in Singapore and the USA (SIAR, 2006).

CEPAD and RATG members have provided European production and import quantities for the period 1998–2002; these figures have been used in the calculations later in the assessment. The individual tonnages and capacities are confidential, but the overall level of production is around 50,000 tonnes/year (mostly as tetrapropenylphenol).

2.1.3 Trends in supply volumes

The substance has been on the market for several decades. The available data suggest that the level of production and use for *para*-C_{12}-alkylphenols in the EU is generally stable.

2.2 Uses

2.2.1 General information on uses

Around 99% of the consumption volume is used in the production of oil and lubricant additives (primarily calcium alkyl phenate sulphides). A relatively small amount is used to produce phenol/formaldehyde resins for printing inks and rubber tyre manufacturing.

2.2.2 Production of oil and lubricant additives

Tetrapropenylphenol is mainly used in the EU as an intermediate to produce more chemically complex detergent and inhibitor additives for oil and lubricants. The primary lubricant additive products manufactured from tetrapropenylphenol are various calcium alkyl phenate sulphides (phenates). These are made by companies in the EU, and are also imported from the USA.

Lubricant additives are complex mixtures of synthetic chemicals. They are combined with highly refined lubricant base oils to blend lubricants or are added to petroleum fuels to achieve a particular end use or level of performance (e.g. two-cycle oils).

Current automotive and industrial finished oils owe their performance mainly to the lubricant additive systems added to them.

The additive packages sold by additive manufacturers to lubricant manufacturers have a mixture of components that together perform certain distinctive functions such as detergency (deposit control), dispersancy (prevention of settling and agglomeration of soot and organic oxidation products), oxidation inhibition, anti-wear, anti-rust and corrosion inhibition. Additive detergents also neutralize sulphuric acids – which can be formed in the combustion process – and prevent deposits forming on engine parts such as pistons. There are many different formulating approaches for each of these basic performance functions. Each requires different additive components or combinations of components that may provide the necessary performance characteristics in the finished lubricant.

The major lubricant producers buy additive packages from lubricant additive manufacturers and formulate finished oils that provide all the performance characteristics they require. Additives based on tetrapropenylphenol derivatives are most widely used in:

- Gasoline-powered cars and trucks;
- High speed diesel engines used in on-road passenger cars and trucks and off-road construction and farm equipment;
- Medium speed diesel engines (1,000-10,000 horsepower (HP)) used in railway engines, tugboats, ferries and power generation stations;
- Slow speed large marine diesel engines (10,000-50,000 HP);
- Air-cooled two-cycle engines such as snowmobiles, motorcycles, chainsaws, lawn mowers, weed cutters, etc.

Tetrapropenylphenol-based additives are **not** used in hydraulic, cutting and drilling fluids, or in oil-based or aqueous metalworking fluids.

The total volume of detergent/dispersant lubricant additive sold in the UK has been estimated at 101,820 tonnes (EA, 2003). The UK represents approximately 15% of the total EU market (Ozimek, 1999). Around 680,000 tonnes of detergent/dispersant mix are therefore used in the EU. In an industry review paper, dispersants accounted for 60% of the total dispersant/detergent mix, implying that around 270,000 tonnes of detergent are used in use in the EU (ATC, 1993). Ozimek (1999) estimates that 40% of this amount (approximately 108,000 tonnes) is based on calcium phenate sulphides. About 60% of this phenate volume is active material (65,000 tonnes), the rest being highly refined lubricating oil diluent. This quantity is greater than that which could be made from the *para*-C_{12}-alkylphenols produced or imported in the EU. There is therefore a net import of phenates into the EU. This imported product has been taken into account in the calculations of emissions of *para*-C_{12}-alkylphenols.

Calcium alkyl phenate sulphides4

Calcium alkyl phenate sulphide lubricant components are oligomeric mixtures of alkyl phenate molecules that are linked by one to three sulphur atoms. The tetrapropenyl group is the most common alkyl chain occurring in many of the members of the

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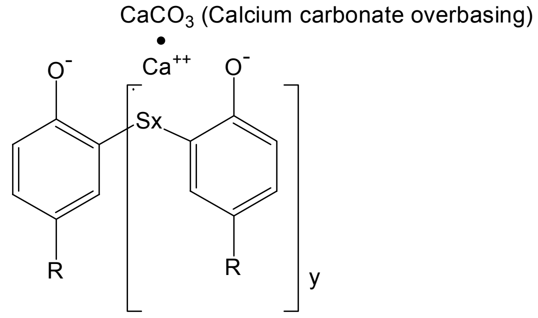
[4] A hazard assessment for 'alkyl phenate sulfides' is currently underway as part of a voluntary industry-led initiative that feeds into the OECD SIDS programme (see http:/www.iccahpv.com). The UK is the sponsor country for this assessment, and final documents are expected in 2007.

phenate category, but other alkyl groups of this category can contain saturated linear C_{18}-$_{30}$ (alpha-olefin) alkyl groups attached primarily at the para-ring position. These substances are prepared by sulphurizing alkylphenol in a highly refined lubricating base oil medium in the presence of calcium hydroxide. The calcium alkyl phenate sulphides may be further reacted with additional calcium hydroxide and carbon dioxide to form a calcium carbonate 'overbased' derivative. The calcium carbonate overbasing step does not represent a structural modification of the alkyl phenate sulphide molecule but is better described as a loose ionic association with the phenate moiety. An idealized structure of a calcium alkyl phenate sulphide is illustrated in Figure 2.2.



R = Primarily C12 (branched) with some C9 (nonyl or C18-30 (linear)
x = 1-3 bridging sulfur molecules
y = 1-3 alkyl phenate molecules

Figure 2.2 Calcium alkyl phenate sulphide chemical structure

The polar nature of the overbasing is efficiently stabilized by the non-polar alkyl phenate carbon chains present in the derivatives. The inherent oil solubility of these highly branched alkyl moieties in the highly refined lubricating base stocks contributes to the long-term stability of these substances.

Phenates are only manufactured (and therefore distributed in commerce) diluted in highly refined lubricating base oils because:

- they are used to dissolve the starting raw materials;
- they act as a solvent for the manufacturing process;
- they are critical for optimizing the reaction kinetics used in the manufacture of functional alkyl phenate sulphides, which can not be produced apart from the base oil medium;
- highly refined lubricating base oils are required to control viscosities during the blending of these lubricant additives with other components to make finished lubricants.

The base oil content is typically around 40% for calcium alkyl phenate sulphides, and 50% for the overbased substances. Alkyl phenate sulphides are never isolated from their highly refined lubricant base oils during the component life cycle. The CAS number assigned to each substance is in reference to the active calcium alkyl phenate sulphide ingredient and does not reflect the identity of the highly refined lubricant base oils used in the manufacture. These base oils are typified by the CAS numbers 64742-54-7 and 64741-88-4. The base stocks used in manufacturing are High Viscosity Index (HVI) oils produced from the distillation of crude oil followed by solvent extraction and/or hydro-refining to increase viscosity and reduce polycyclic aromatic content.

Commercial calcium alkyl phenate sulphides contain levels of un-reacted alkylphenol. Analysis of seven commercial products showed a range of alkylphenol content from 3.7 to 26%, with a mean content of 11.7% and a 95th-percentile value of 19% (RATG, 2005). As this is a relatively small sample, the results provide only a rough estimate of the residual content. In the estimates of emissions in Section 3, the 95th percentile value will be used for the estimation of local emissions, while the mean level will be used for the regional and continental emission estimates.

The calcium alkyl phenate sulphides are blended with other components to make the final lubricant products. Levels of the sulphides in commercial products are 0.5-1.0% for air-cooled two-cycle oils, 1-10% for automotive diesel and gasoline cars, and 10-30% for marine diesels.

Alkyl phenol sulphides can also be produced. These materials are not neutralized with calcium hydroxide during their manufacture, but are the product of simple sulphurization of tetrapropenylphenol. These materials have not been used to formulate lubricants since the late 1980s and are not produced or imported into Europe any longer.

Dialkaryl zinc dithiophosphates

Today, zinc dialkyldithiophosphates (ZnDTPs) are widely used as multi-functional lubricant additives used to formulate primarily automotive and diesel engine oils and all types of industrial hydraulic fluids. Thirty or more years ago, most high performance diesel engine oils contained dialkaryl zinc dithiophosphates made from tetrapropenylphenol as their primary additive to provide anti-wear and oxidation control. Figure 2.3 gives the chemical structure.

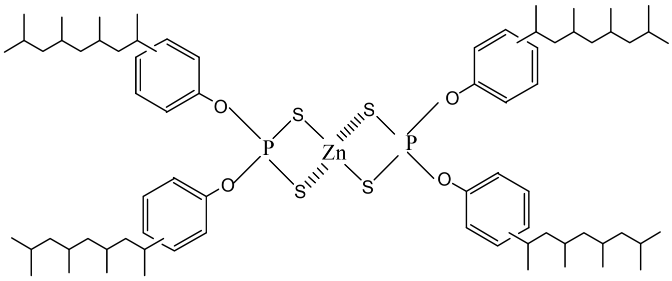


Figure 2.3 Tetrapropenyl zinc dithiophosphate

Due to poor train wear performance, tetrapropenyl-based ZnDTPs have been almost completely phased out in the EU, and replaced with non-aromatic C_{3-8} alkyl alcohol variants. The amount of tetrapropenylphenol still used to make ZnDTPs is thought to be small, with all of the products being exported to Africa, Eastern Europe and/or the former Soviet States.

Tetrapropenylphenol ethoxylates

A very small proportion (<1%) of the overall tonnage of tetrapropenylphenol is used to make ethoxylates (see Figure 2.4). These are used as anti-rust agents in finished lubricants at levels of 0.05-0.30% w/w. The number of ethoxy units is 10-15. Since the tetrapropenylphenol molecule has high oil solubility, its ethoxylate derivatives are never used in water-based applications. The volume of these materials used in lubricants has been dropping since the late 1980s and this is a continuing trend. The industry believes they will eventually be totally phased out. The residual content of free alkylphenol in the ethoxylates is unknown but most probably <1%.[5]

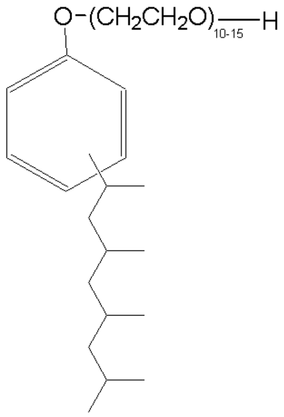


Figure 2.4 Ethoxylated tetrapropenylphenol

Ethoxylate and propoxylate derivatives of tetrapropenylphenol are also used at part per million levels as cleaning agents in fuel.[6] Such use appears to be limited, and will be considered as similar to the use of the ethoxylate derivatives in lubricants within this assessment. This will probably over-estimate emissions from this source, since fuel additives will be destroyed in the combustion process.

Other derivatives

Tetrapropenylphenol can be used to make 2,4-di-*tert*-butyldodecylphenol (CAS no. 68025-37-6). This substance is also used to make lubricant additives. No specific information on the production or use of this substance has been obtained.

There are no known salicylates made from tetrapropenylphenol, as all are made from C_{14}-$_{18}$ or higher alpha-olefin-derived alkylphenols.

2.2.3 Phenolic resins and lacquers

A small fraction of the *para*-C_{12}-alkylphenols supplied in Europe (around 280 tonnes/year) is used to make phenolic resins (CEPAD, 2003). Butylene trimer (tri-n-butene)-derived substance is more relevant to this use than tetrapropenylphenol (SASOL Germany GmbH, personal communication, 2005). The following information has been supplied by CEPAD (2002 & 2003).

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[5] For comparison, the residual, unreacted alkylphenol present in octylphenol ethoxylates decreases with increasing extent of ethoxylation, ranging from 1% for OP3EO to 0.01% for OP10EO, and lower levels for greater degrees of ethoxylation. The majority of the octylphenol ethoxylates on the market have 10 or more ethoxylate groups (see EA, 2005b).

[6] http://apps.kemi.se/flodessok/floden/kemamne_eng/dodecylfenol_eng.htm, and www.icso.com.pl/en/Processes/-phenols.htm

Production process

Phenol/formaldehyde (Bakelite) resins are one of the oldest-known thermosetting/thermoplastic synthetic polymers. The initial production step is the base-induced reaction of the phenolic compound and formaldehyde to give a hydroxybenzyl alcohol. With *para*-C_{12}-alkylphenol the addition takes place at the *ortho*- position. The next step is the formation of a dihydroxydiphenylmethane derivative with elimination of water (condensation). Continuation of these reactions leads to a two-dimensional polymer.

Production of these polymers is based almost exclusively on discontinuous batch processes using a traditional reactor or 'kettle'. The phenol/formaldehyde resins may be made with *para*-C_{12}-alkylphenols alone or, more commonly, in admixture with other phenols depending on the properties desired for the final resin. Most of the starting material in the resins is chemically bound and cannot be released even on subsequent chemical or biological degradation, but the resins may also contain a small proportion (up to 3%) of unreacted *para*-C_{12}-alkylphenols.

There are two main types of phenolic resin, both of which are heat reactive:

- novolacs are made with a molecular excess of phenolic substance and are usually catalysed with acid (e.g. hydrochloric, sulphuric or oxalic acid);
- resoles are made with a molecular excess of formaldehyde and are usually catalysed with alkali (e.g. sodium hydroxide, ammonia or amines).

There were fewer than 10 resin-producing companies in the EU (with at least one in the UK) in 2001. It is not known how many of these sites were actually using *para*-C_{12}-alkylphenols.

Phenolic resin use

Printing inks

According to CEPAD, printing inks account for the bulk of resins produced from *para*-C_{12}-alkylphenols, although user industry-specific information is unavailable.

Phenolic resins are essential components of modern printing inks. They make it possible to apply inks and coatings to paper, plastic, metal and other surfaces more quickly and accurately and with faster drying. Printing ink carriers are fluids and gels, that enable lithographic and letterpress printing inks to carry colour onto a variety of printing surfaces. The ink carriers also help printing presses to

- run at higher speeds;
- use inks with less pigment;
- produce less waste;
- offer better performance characteristics such as gloss, brightness and rub or scratch resistance.

No substitutes for alkylphenolic resins are currently available for these applications.

The inks are manufactured in high-temperature processes in which the resins are reacted with other resins and oils (leaving no significant trace of free alkylphenol). They are then diluted in ink solvents and pigmented. The phenolic resin typically makes up around 7-8% of the ink formulation. The weight of ink as a percentage of a printed page is very small.

Rubber compounding for tyres

Novolac resins are an essential ingredient of rubber compounding for tyre manufacture. They increase the tackiness of the rubber and improve adhesion of the different layers during vulcanisation. Resins are generally added to rubber in amounts up to 1.5% of the rubber formulation (Emission Scenario Document for rubber in the Technical Guidance Document – see also Section 3.2.4.2.2 of this report), though the maximum figure for the percentage of resin in rubber used for tyres is 10%.

CEPAD reports that only small quantities of *para*-C_{12}-alkylphenol were used for this application. Consultation with the user industry also suggests that this substance is of minor importance in the tyre manufacturing industry (European Rubber Chemicals Association and International Institute of Synthetic Rubber Manufacturers, personal communication, 2006).

The maximum concentration of free *para*-C_{12}-alkylphenols in the resins used to make tyres is assumed to be 3% (CEPAD, 2002). Due to the impermeable nature of the rubber, the alkylphenol is not available to the aqueous environment except as a result of tyre wear through abrasion.

Tackifier resins were produced at four sites in Europe in 2001: two in France, one in Belgium and one in the UK. The UK manufacturing unit did not make resins using this substance, and has since closed (Schenectady International, personal communication, 2006).

Other uses of resins

CEPAD/EPRA have a reported minor use of *para*-C_{12}-alkylphenol-based resins as a binder in varnishes. Very little information is available about this application.

No other significant European resin uses have been identified by CEPAD (2002), although some sources suggest that there could be a few niche applications (e.g. carbonless copy paper coatings and adhesives (Kirk-Othmer, 1999)). These are not considered further in this report.

2.2.4 Other potential uses

Information from product registers

The SPIN (Substances in Preparations in Nordic Countries) database (http://www.spin2000.net/spin.html) provides data on the use of chemical substances in Norway, Sweden, Denmark and Finland. The information comes from the Product Registries of the contributing countries. Results of database searches in October 2005 summarised in Table 2.2.

Table 2.2 Information from Nordic product registers

Substance name	CAS number	EINECS number	Use information
Phenol, 4-dodecyl-	104-43-8	203-202-9	Confidential use in Denmark in 2000.
Phenol, dodecyl-	27193-86-8	248-312-8	Use reported in Sweden (highest tonnage was 45 tonnes in 2001), and Denmark (0.2 tonnes/year), in ‘lubricants and additives’, and ‘fuel additives’.
Formaldehyde, polymer with 4-dodecylphenol and 1,2-ethanediamine	67953-78-0	-	Confidential use in Norway in 2001, but use confidential.
Phenol, bis(1,1-dimethylethyl)dodecyl-	68025-37-6	268-192-0	Reported from all four countries. Up to 50 tonnes per year in Sweden, used in ‘lubricants and additives’.
Rosin, fumarated, polymer with dipentaerythritol, dodecylphenol and formaldehyde	68152-51-2	-	Reported in Denmark (2001) and Sweden (1999-2003). No information on uses, but used in up to 50 preparations, at up to 180 tonnes in a year in Sweden.
Phenol, (tetrapropenyl) derivatives	74499-35-7	-	Used in ‘lubricants and additives’ in Sweden (no tonnage given).
Phenol, 4,4'-(1-methylethylidene)bis-, polymers with 2-(2-aminoethoxy)ethanol, branched dodecylphenol, N,N-dimethyl-1,3-propanediamine, epichlorohydrin and polypropylene glycol, acetates (salts)	174819-73-9	-	Confidential use in Sweden in 2003.
Formaldehyde, reaction products with distn. residues from manuf. of phenol (tetrapropenyl) derivs., methylamine and phenol (tetrapropenyl) derivs., calcium salts	220795-04-0	-	Confidential use in Sweden in 2003.
Phenol, 2(or 4)-C20-30-sec-alkyl derivs., reaction products with carbon dioxide, distn. residues from manuf. of phenol (tetrapropenyl) derivs. and phenol (tetrapropenyl) derivs., calcium salts	220795-13-1	-	Confidential use in Sweden in 2003.
Phenol, 2(or 4)-C20-30-sec-alkyl derivs., reaction products with carbon dioxide, distn. residues from manuf. of phenol (tetrapropenyl) derivs., phenol (tetrapropenyl) derivs. and sulphur, calcium salts	220795-16-4	-	Confidential use in Sweden in 2003.

Most of the reported uses are the same as those described in the preceding sections. The low tonnage of dodecylphenol (CAS no. 27193-86-8) use as a fuel additive in Denmark and Sweden is presumably due to ethoxylate alternatives (see Section 2.2.2.3).

Other reported uses

An Internet search suggests that there is (or was) a use of *para*-C_{12}-alkylphenol ethoxylates as speciality surfactants[7], some of which may be used in agrochemicals (e.g. either as an emulsifier or active substance in pesticide formulations). However, according to CEPAD, their higher production costs and poorer surfactant performance make them generally unsuitable as substitutes for the nonylphenol ethoxylate surfactants that are now phased-out in the EU.

The Pesticide Safety Directorate has confirmed that there are currently no plant protection products on the UK market known to contain dodecylphenol ethoxylates (personal communication to the Environment Agency, October 2005). Similarly, the Health and Safety Executive confirmed that there are no biocidal products on the UK market containing dodecylphenol ethoxylates, and the Veterinary Medicine Directorate has no products containing dodecylphenol ethoxylates in its database (both personal communications to the Environment Agency, October 2005)

Such uses therefore do not appear to be relevant to the UK at present, and are not addressed in this assessment.

An EINECS search has identified several other derivatives that have not been specifically mentioned above. These are listed in Appendix 2. Given the extent of the consultation to date, it is likely that these are of low commercial importance, or are variants of derivatives used for the applications already described. However, the existence of additional derivatives shows that there could be some uses of *para*-C_{12}-alkylphenols that have not been properly accounted for.

2.3 Life cycle in the UK

There was one production site in the UK in 2005. *para*-C_{12}-alkylphenols may also be present as an impurity in derivatives and final products:

- Around five facilities produce lubricant additive packages in the EU, but none is located in the UK. The UK does not produce or import calcium phenate sulphides. Some final lubricant blending does take place in the UK, at an unknown number of presumably small sites (there are around 150 blending sites in the EU). There is widespread use of the finished lubricants.
- The situation concerning resins is less clear. It is assumed that such resins are not made in the UK, but they might still be used, at least for printing inks.

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[7] For example, http://www.huntsman.com lists a series of dodecylphenol ethoxylate surfactants, including their SURFONIC®_DDP series and TERIC®_DD series. No use is given on the website. These products have applications as rewetting agents, solvent cleaners, degreasers, detergents, solubilizing agents, emulsifiers, penetrants and dispersants, but they are made in the USA and are not supplied in the EU (personal communication from Huntsman to the Environment Agency, 2006).

2.4 Other sources

There is no known natural source of *para*-C_{12}-alkylphenols. Some higher molecular weight alkylphenols have been produced commercially (e.g. 4-hexadecylphenol (CAS no. 2589-78-8) is listed on the ESIS database as an LPVC in the EU, although production in Europe may have stopped some years ago). It may be possible that they contain some components in common with this substance. However, in the absence of more detailed information on the composition and supply volumes of these products, this source is considered hypothetical and has been ignored in this assessment.

2.4.1 Degradation of derivatives

para-C_{12}-alkylphenols are chemical intermediates used to make other substances. The possibility of their reformation in the environment following the degradation of these derivatives needs to be considered.

Calcium alkyl phenate sulphides are made in oil. For hydrolysis to their conjugate acid alkylphenols to occur, they must be extracted from oil, and the sulphur bridge must be removed. At normal environmental pH calcium alkyl phenate sulphides are most likely to remain as their calcium salts.

The following information is taken from the draft OECD SIAR in preparation for the alkyl phen(ol)ate sulphides category:

There are no published or unpublished data on the oxidative stability of alkyl phen(ol)ate sulphides. However, should they be accidentally released into the environment, several factors mitigate the oxidation of the sulphur bridge in commercial preparations of these substances. The physico-chemical properties of alkyl phen(ol)ate sulphides, such as high lipophilicity and extremely low water solubility, strongly favour retention of these substances in the oil phase. Environmental oxidants are generally water soluble and would thus be excluded from the oil phase, suggesting that those oxidants would be inaccessible to the alkyl phen(ol)ate sulphides. Furthermore, ambient environmental temperatures are unfavourable to the oxidation of the sulphur bridges. Furthermore, alkyl phen(ol)ate sulphides are manufactured at temperatures exceeding 230°C, with no special effort to exclude air (an oxidizing environment) from the operation. It is therefore reasonable to conclude that alkyl phen(ol)ate sulphides are resistant to degradation due to environmental oxidation.

2.5 Regulatory initiatives

No substance-specific legislative controls currently exist. *para*-C_{12}-alkylphenols are, however, classifiable as a ‘dangerous substance’ for the environment under Directive 67/548/EEC (see Section 4.6), and this has consequences for several other pieces of legislation (e.g. relating to hazardous waste).

para-C_{12}-alkylphenols are not listed under any name or CAS number in an EU review of 564 potential endocrine disrupting substances (EC, 2000). The Japanese government reports that the substance with the CAS number 104-43-8 may have an estrogen agonist potential at a high dose level, but in the absence of a definitive study (see Section 4.1.4), was unable to establish an actual endocrine disrupting effect. It is therefore ‘grey’-listed, with low priority for review as its production volume is low in Japan (K Kawahara, personal communication, November 2005).

The Integrated Pollution Control (IPC)[8] and Integrated Pollution Prevention and Control Regulations (IPPC, due to have totally replaced IPC by the end of 2007) will apply to some parts of the substance's life cycle[9]. Releases are restricted under the general principles that all installations and mobile plant should be operated in such a way that:

- all the appropriate preventative measures are taken against pollution, in particular through application of the best available techniques;
- no significant pollution is caused.

In practice, if releases of *para*-C_{12}-alkylphenols or derivatives from an IPPC process were sufficiently high to cause concern then release limits would be imposed, or an improvement condition would be set requiring a reduction in releases over an agreed period of time.

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[8] Statutory Instrument 2000 No. 1973 The Pollution Prevention and Control (England and Wales) Regulations 2000 Part I (11).

[9] The production of the substance itself, phenol/formaldehyde resins and lubricant additives are all covered by Section 4.1 (Organic Chemicals) of the PPC Regulations. They are 'part A' activities, and are regulated by the Environment Agency in England and Wales. In general, activities involving rubber are 'part B' activities under the Regulations, and are consequently regulated by local authorities. In general terms, formulation and blending are excluded.

3 Environmental exposure

This assessment has been prepared in accordance with the principles and methods laid down in Commission Regulation (EC) 1488/94[10], which is supported by a technical guidance document (TGD, 2003) and associated computer program[11] (EUSES v2.0.3[12]). This assessment is generic in that it represents a *realistic worst-case approach* for a hypothetical environment that broadly reflects average European conditions. Further details can be found in the TGD. Given that tonnage data were supplied for the EU market, the following discussion is applicable across Europe.

3.1 Environmental fate and distribution

3.1.1 Environmental degradation

Atmospheric degradation

No measured data are available. *para*-C_{12}-alkylphenols released to the atmosphere in the vapour phase are likely to be degraded rapidly by reaction with hydroxyl (OH) radicals. The AOP program (v1.91, in EPIWIN v3.12 (US EPA, 2000)) estimates the rate constant for this fate process as 5.6×10^{-11} $cm^3/(molec.s)$, using the idealised structure in Figure 1.1 as input (the degree of branching in fact makes little difference to the rate constant calculated). The pseudo first-order rate constant for degradation in air can be calculated from this rate constant using the following equation as found in the TGD:

$$kdeg_{air} = k_{OH} \times OHCONC_{air} \times 24 \times 3600 = 2.4\ d^{-1}$$

$kdeg_{air}$	Pseudo first-order rate constant for degradation in air [d^{-1}]
k_{OH}	Specific degradation rate constant with OH radicals [$cm^3.molecule.^{-1}s^{-1}$]
$OHCONC_{air}$	Concentration of OH radicals in the atmosphere [5×10^5 molecule. cm^{-3}]

From this rate constant the estimated half-life for the reaction of OH radicals with *para*-C_{12}-alkylphenols in the atmosphere is calculated to be 6.8 hours. The reaction rate for this process means that *para*-C_{12}-alkylphenols are unlikely to be transported far from their emission source before they degrade.

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[10] Official Journal No. L 161, 29/06/1994 p. 03–11.

[11] Available from the European Chemicals Bureau, http://ecb.ei.jrc.it/.

[12] One of the main differences from the EUSES 1 model (as used for nonylphenol) is that it is now assumed that 100% of the activities involving a substance take place in the region, unless there is a good reason to consider a more dispersed distribution. One effect of assuming that the activity takes place wholly within the region is that the default amount calculated to be used at a local site is increased in comparison to the default estimates from EUSES 1. Although the numbers of days for use may also increase, the usual consequence is that the resulting PEC values are increased.

Aquatic degradation

Abiotic degradation

No data are available. In general, hydrolysis and photolysis are believed to be negligible removal processes for *para*-C_{12}-alkylphenols in the aquatic environment, on the basis of evidence from similar substances (e.g. nonylphenol (EC, 2002)).

Biodegradation

In a modified Sturm test (Hüls, 1992a), 'dodecylphenol T' was added to a liquid mineral medium at concentrations of 10 and 20 mg/L, which was inoculated and aerated at a temperature of 21-23ºC for 28 days. The inoculum used in the test was activated sludge from a municipal sewage plant and had a bacterial count of 3.3×10^4 CFU/ml (colony forming units per ml). The experiments were carried out without an emulsifier present. A positive control experiment was conducted using sodium benzoate. Degradation was monitored by measuring the actual CO_2 evolution compared with the theoretical amount that would be evolved if the substance was completely oxidised. The control substance (sodium benzoate) achieved a degradation level of 95% within 28 days, reaching the threshold for ready biodegradability within 14 days. This indicated that the inoculum used had sufficient biological activity.

The substance achieved a degradation level of 25% at 10 mg/L and 6% at 20 mg/L within a period of 28 days. This result indicates that this substance is not readily biodegradable. The lack of biodegradation is unlikely to be a function of toxicity towards the bacterial culture, in view of the results reported in Section 4.1.6 and below.

The low level of degradation observed in the ready biodegradability study could have been due to the poor availability of the substance to the micro-organisms in the test medium. A study has recently been performed therefore to investigate the inherent biodegradation potential of tetrapropenylphenol in aerobic aqueous conditions (Mead and McKenzie, 2005). The study was carried out in accordance with the draft OECD test guideline 302D (CONCAWE test), which has been specifically developed for use with poorly water soluble substances. The test material was prepared by applying a test solution in acetone to a glass fibre filter paper and evaporating the solvent (thereby increasing the surface area exposed to the micro-organisms), to give a test concentration of 24.3 mg/L, equivalent to 20 mg carbon/L. This was exposed to a composite microbial inoculum derived from soil and a waste water treatment plant (treating predominantly domestic sludge) in the dark for 56 days (following pre-exposure of the inoculum over 14 days to enhance its biodegradation potential). Degradation was determined by both CO_2 evolution and compound-specific analysis using HPLC. Abiotic test vessels were also prepared and analysed to correct for any losses of test material in the inoculated test vessels due to adsorption to glassware. A toxicity control was also included.

Based on CO_2 production, 10% degradation was achieved over 56 days. The results of compound specific analysis showed that no significant chemical or biological degradation of the test material occurred. The toxicity control showed that the test material was not toxic to the micro-organisms used in the study. Consequently, tetrapropenylphenol is not inherently biodegradable. The level of degradation was even lower than observed in the more stringent ready biodegradation test, but this might have been due to subtle differences in test substance composition.

Degradation in soil

No experimental data are available on the degradation of *para*-C_{12}-alkylphenols in soil.

Evaluation of environmental degradation data

para-C_{12}-alkylphenols are likely to be rapidly degraded (with a half-life of around 7 hours) by reaction with OH radicals if released to the atmosphere in the vapour phase. Abiotic degradation processes in water are probably negligible, and the results of biodegradation tests indicate that the substance is neither readily nor inherently biodegradable. The limited biodegradation observed in the two available studies is consistent with the branched structure of the substance.

In comparison, nonylphenol is inherently biodegradable (EC, 2002). Indeed, the widespread use of nonylphenol and its ethoxylates until recently may mean that the wider environment has an enhanced capacity to degrade alkylphenols in certain circumstances. There is some evidence of limited mineralisation from the ready biodegradation study, although this was not reflected in the inherent test, perhaps owing to differences in test substance composition (e.g. the degree of branching and purity).

No information is available on the degradation of *para*-C_{12}-alkylphenols in the terrestrial environment.

For the purpose of EUSES modelling, *para*-C_{12}-alkylphenols are considered not to be biodegradable.

3.1.2 Environmental partitioning

Adsorption

The organic carbon-water partition coefficient (K_{oc}) can be estimated from the octanol-water partition coefficient (log K_{ow} of 7.14). There are two equations in the TGD and EUSES that were derived for chemical types including phenols, and these give predicted K_{oc} values of 2.5×10^5 and 1.41×10^5. However, both of these are considered valid only for log K_{ow} values up to 5.0 or 5.5, so their use for this substance has a higher degree of uncertainty.

There are also two more general equations in the TGD and EUSES. One of these is the default equation, for non-hydrophobics, which is considered valid for log K_{ow} values up to 8.0 and predicts a K_{oc} value of 5.4×10^4. The second is a general equation for predominantly hydrophobics, which is considered valid up to log K_{ow} values of 7.5 and predicts a K_{oc} value of 7.65×10^5. Although *para*-C_{12}-alkylphenols are expected to be hydrophobic, this latter equation does not include any oxygen-containing substances in its training set. Hence all four equations have some limitation regarding their applicability when used for this substance.

As the K_{oc} is not a property which has a clear worst case value (higher values mean higher concentrations in solid phases but lower ones in water) the geometric mean value of the four predictions (1.1×10^5) has been used here as a representative value. The effect of the possible range of values will be considered in the uncertainty analysis in Appendix 1. All the values suggest that *para*-C_{12}-alkylphenols will be strongly adsorbed to soils, sludges and sediments and will not leach to water from soils and sludges.

The following partition coefficients have been calculated using EUSES, based on the K_{oc} of 1.1 x 10^5:

Kp_{susp}	11,000 L/kg	Partition coefficient for solids/water in suspended matter
Kp_{sed}	5,500 L/kg	Partition coefficient for solids/water in sediment
Kp_{soil}	2,200 L/kg	Partition coefficient for solids/water in soil
$K_{soil-water}$	3,300	Soil/water partitioning coefficient
$K_{susp-water}$	2,750	Suspended matter/water partitioning coefficient
$K_{sed-water}$	2,750	Sediment/water partitioning coefficient

Given that *para*-C_{12}-alkylphenols are weak acids, pH might also have an effect on their adsorptive behaviour. However, the pK_a is above 10, meaning that in most situations encountered in the environment the substance will be present in the undissociated and hence more hydrophobic form.

Volatilisation and precipitation

para-C_{12}-alkylphenols are not highly volatile and so are unlikely to enter the atmosphere in large amounts. The substance is expected to be relatively short-lived in the atmosphere, based upon the reaction with OH radicals (Section 3.1.1.1). The fraction that will adsorb to aerosol particles is low (<20% estimated by EUSES). Therefore the potential for transport of *para*-C_{12}-alkylphenols in the atmospheric environment is also likely to be low. With the low water solubility of the substance, removal of *para*-C_{12}-alkylphenols from the atmosphere through precipitation is not likely to be a significant process and rainwater concentrations are likely to be low. Concentrations due to precipitation of *para*-C_{12}-alkylphenols from the atmosphere are therefore likely to be greatest near the point of release.

The volatilisation of *para*-C_{12}-alkylphenols from surface water to air may be estimated from the Henry's Law Constant.

The Enichem Computation Model estimates the Henry's Law Constant as 78.75 hPa.m^3/mol at 20°C (IUCLID, 1995). The methodology used to generate this value is unclear. The Henry's Law Constant has been estimated for the purposes of this report using the idealised structure in Section 1.1. Values of 1.42 or 3.51 Pa.m^3/mol (bond or group method respectively) are predicted at 25°C using the HENRYWIN (v3.10) model (US EPA, 2000).

The Henry's Law Constant may also be calculated from the vapour pressure, molecular weight and water solubility of the substance. Using a vapour pressure of 9.19 x 10^{-3} Pa, a molecular weight of 262.43 g/mol and a water solubility of 31 µg/L, a Henry's Law Constant of 78 Pa.m^3/mol can be calculated. **This value is preferred for the risk assessment**, as it is based on two measured properties, and the water solubility at least relates to a major component of the substance. Nevertheless, both the vapour pressure (in particular) and water solubility values are somewhat uncertain (and will vary between the components of the substance).

An air-water partitioning coefficient ($K_{air-water}$) may be derived from the Henry's Law Constant and is calculated as 0.033 m^3/m^3.

The $K_{air-water}$ and Henry's Law Constant suggest that volatilisation may be a significant transfer mechanism for *para*-C_{12}-alkylphenols from water systems. For example, based on the Henry's Law Constant of 77.8 Pa m^3/mol, the volatilisation half-life from a model river (1 m deep flowing at 1 m/sec with a wind velocity of 3 m/sec) can be estimated to be about 3 hours (EPIWIN v3.12 (US EPA, 2000)). However, the low concentrations of *para*-C_{12}-alkylphenols expected in water means that this is not an important process in the overall fate of the substance.

Fugacity modelling

Fugacity modelling shows how a substance may be distributed in the environment following release to a specific compartment (air, water, soil or sediment). The potential environmental distribution of *para*-C_{12}-alkylphenols has been assessed using a Mackay generic level III fugacity model (EQC v1.01, May 1997[13]) that is accessible via the OECD HPV programme. After release to a specific environmental compartment, the substance is predicted to move mostly to solid phases, as indicated in Table 3.1.

Table 3.1 Environmental distribution of *para*-C_{12}-alkylphenols

Compartment	Mass %		
	Release to air	Release to water	Release to soil
Air	0.03	0.001	<0.001
Water	0.005	0.91	0.003
Soil	99.5	4.54	94.7
Sediment	0.49	94.5	0.32

The wastewater treatment plant (WWTP) model used in EUSES estimates the proportion of a substance entering the WWTP that will be directed to air, water and sludge. For *para*-C_{12}-alkylphenols, the proportions are 6.1% to air, 11.3% to water and 82.6% to sludge, with no biodegradation.

3.1.3 Bioaccumulation and metabolism

Measured data

The bioconcentration of tetrapropenylphenol in rainbow trout (*Oncorhynchus mykiss*) was measured in a study following a protocol based on US EPA, ASTM and OECD guidelines (Wildlife International, 2006). This study was not finalised in time for inclusion in the OECD SIAR (2006), but a draft report has been made available for this risk assessment. Fish were exposed to two concentrations of tetrapropenylphenol (nominal levels 2 µg/L and 20 µg/L) in flow-through systems in stainless steel aquaria for a 27-day uptake period, which was followed by a 15-day depuration period. The environmental conditions (temperature, pH, dissolved organic carbon, hardness, alkalinity, conductivity, and total organic carbon) were monitored throughout the test and were within acceptable limits.

The test substance was a mixture of radiolabelled tetrapropenylphenol (uniformly ring-labelled) and non-labelled commercial material. The purity of both was 100% tetrapropenylphenol; the radiolabelled material contained 63% carbon-14. No analyses of the composition of the source materials were included. Stock solutions were made up in dimethyl formamide (DMF). There was 0.1 mL/L of DMF in all exposures and in the solvent control.

The concentration of total radiolabel in the water was measured at intervals throughout the test by liquid scintillation counting; the mean measured concentrations on this basis

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[13] Model available from http://webdomino1.oecd.org/comnet/env/models.nsf

were 1.1 µg/L and 11 µg/L for the uptake phase. A number of samples were also analysed by HPLC, with fluorescence detection, for different fractions (C_{5}-$_{10}$, C_{11}-$_{12}$ and C_{13+}). The fraction that eluted before the C_{5}-$_{10}$ fraction was also measured and described as 'polar metabolites'. The sum of these four fractions was at least 75% of the concentration on the basis of total radioactivity in almost all samples. The concentrations are presented in Table 3.2.

Table 3.2 Mean measured substance concentrations in water during uptake phase

Component	**Exposure series I 2 µg/L (nominal)**		**Exposure series II 20 µg/L (nominal)**	
	Concentration (µg/L)	**% nominal**	**Concentration (µg/L)**	**% nominal**
Total radiolabel[1]	1.1	55	11	55
Polar metabolites[1]	0.06	-	0.51	-
C_{5-10}	0.21	11	2.1	11
C_{11-12}	0.51	25	5.2	26
C_{13+}	0.10	5	1.2	6

Notes: [1] Values not included in the study report, but derived from the data for this summary.

Fish were sampled on days 0, 1, 3, 7, 11, 14, 21 and 24 of the uptake phase, and days 1, 3, 8 and 11 of the depuration phase. Two fish were taken at each time for the controls, and four for each exposure level. The fish were dissected into non-edible (head, fins and viscera) and edible tissues. The total radioactivity was determined in the individual samples by liquid scintillation counting. In addition, methanol extracts of pooled tissue samples (combining the four edible tissue samples at each time, etc.) were analysed by HPLC for the same four fractions as above. Again, the combined fractions gave a similar overall concentration to that determined on the basis of total radioactivity. The relative proportions of the four fractions in edible tissues were similar to those in water. In non-edible tissues, the proportion of polar metabolites was notably increased. The concentrations in fish did not increase further above the levels reached after three days at either exposure concentration. The steady state concentrations were taken as the mean of the measured concentrations over the period from 3 to 24 days. The concentrations are presented in Table 3.3, along with the concentrations of each of the fractions as determined by HPLC.

Table 3.3 Steady state concentrations in fish tissues (µg/kg wet weight)

Component	**Nominal 2 µg/L**			**Nominal 20 µg/L**		
	Edible	**Non-edible**	**Whole fish**	**Edible**	**Non-edible**	**Whole fish**
Total radiolabel	317	1,762	905	3,184	15,707	8,237
Polar metabolites[1]	31.6	1,139	-	270	9,221	-
C_{5-10}	43.9	114	-	455	1,266	-
C_{11-12}	185	401	-	2,018	4,396	-
C_{13+}	42.6	98.7	-	508	1,123	-

Notes: 1Values not included in study report, derived from data for this summary

A number of bioconcentration factor (BCF) values were derived from the above results. Values were calculated for the steady state concentrations based on the total radioactivity measurements for edible tissues, non-edible tissues and whole fish. Steady state values were also calculated for the individual fractions for edible and non-edible tissues. Values for whole fish by fractions were not calculated in the study report. Values have been estimated for this summary using the average ratio of edible:non-edible tissues at each exposure level; these were 1.46:1 for the 1.1 µg/L exposures and 1.49:1 for the 11 µg/L exposures. The concentrations at each sampling time in the uptake and depuration phases were used to calculate uptake and depuration rate constants, and hence kinetic BCF values. All of the BCF values are in Table 3.4.

Table 3.4 Bioconcentration factors

Component		1.1 µg/L exposure			11 µg/L exposure		
		Edible	Non-edible	Whole fish	Edible	Non-edible	Whole fish
Total radiolabel	- steady state	289	1,601	823	289	1,428	749
	- kinetic	328	1,787	920	329	1,611	844
C_{5-10}		209	544	345	217	603	372
C_{11-12}		362	786	534	388	845	572
C_{13+}		426	987	654	423	936	629

Notes: Whole fish values for fractions calculated for this summary.

The study is considered to be valid. The metabolites were not identified, so it is not possible to conclude anything about their potential effects. As a result, the BCF based on total radioactivity in whole fish is taken to be the most appropriate from this study. The steady state values are preferred since they are based on direct calculation from the data rather than derived from data fitting, although in this case the kinetic values agree well. As a worst case the higher of the two steady state BCF values (823) is the preferred value for use from this study.

Other data

Limited data are available for p-dodecylphenol (no composition given, but presumed to be linear for the purposes of this assessment). Bioconcentration was measured in juvenile Atlantic salmon (*Salmo salar*) by McLeese *et al.* (1981) over four-day exposure and four day depuration periods. The concentration of p-dodecylphenol in water was below the apparent water solubility limit (but see comments below). Analytical data on body concentrations were obtained from groups of fish after 1, 2 and 4 days' exposure and in groups which were then held in clean water for 1, 2 and 4 days. These data were used to determine equilibrium concentration factors using a one-compartment model, taking into account the exponential decrease in p-dodecylphenol measured in the study. The uptake rate constant (k_1) was measured to be 6 day^{-1} and the excretion rate constant (k_2) was 0.001 day^{-1}, giving a wet weight bioconcentration factor (BCF) (k_1/k_2) of around 6,000 (log BCF of 3.78 [BCF = 6,026]). The excretion half-life was estimated to be around 690 days.

This measured BCF value suggests that bioconcentration of (linear) dodecylphenol in aquatic organisms may occur to a significant extent. However, this particular study is considered invalid due to a number of inadequacies.

First, there is inadequate validation of the analytical methodology for the recovery of dodecylphenol from water and fish tissue. The reliability of the analytical methodology was not established over the range of concentrations (especially the very low levels) experienced in the study. The recovery efficiencies for dodecylphenol in water (56%) and fish tissue (35%) were unsatisfactory. To account for this poor recovery, correction factors were applied to the water and tissue dodecylphenol concentrations, which contributed to the uncertainty in the derivation of the BCF. Furthermore, no data were presented on the relative extraction efficiency between the water and tissue methods.

Second, bioaccumulation studies are typically conducted at a low and high exposure concentration equivalent to 1/10th – 1/100th of the median lethal concentration (LC_{50}) for acute effects. This ensures that the concentrations selected do not result in acute toxic effects to the test organisms. The study indicates that the average exposure concentration of dodecylphenol at days 1, 2 and 4 were 0.24, 0.19 and 0.13 mg/L respectively. These concentrations are of the same order of magnitude as the 96-hour LC_{50} value reported in the study (i.e. 0.14 mg/L).

Third, in the uptake and excretion portions of the study, only two fish were sampled at 24, 48 and 96 hours to determine the BCF. This test organism sample size was insufficient to provide statistical validity.

Finally, the observation that the exposure concentrations decreased exponentially during the uptake period (0.24, 0.19 and 0.13 mg/L at 1, 2 and 4 days respectively) indicates that a constant exposure concentration was not maintained during the uptake phase. The observed fall in exposure concentration may have been due to adsorption of the substance to the glass surface of the test vessel. Alternatively, the falling apparent concentration may have resulted from variability of an analytical methodology that had not been validated for reliability at low concentrations of dodecylphenol in water. Whatever the cause, a decreasing measured dodecylphenol concentration in the exposure system will result in an artificial increase in the uptake rate constant.

Calculated data

A bioconcentration factor (BCF) of 44,400 can be calculated from the log K_{ow} of 7.14 using one of the quantitative structure-activity relationships (QSARs) recommended in the TGD (i.e. the quadratic equation for substances with a log K_{ow} greater than 6). However, the phenolic group can be metabolised, so this value may represent a worst case estimate.

The bioconcentration factor for earthworms can be calculated as 166,000 using the TGD equation.

Comparison with other alkylphenols

The BCF value used in the Environment Agency's octylphenol risk assessment is 634, calculated from the log K_{ow} value (EA, 2005b). Although the available experimental data were not considered sufficiently reliable, they include measured values of 41 to 297 from field measurements, and 261 and 471 from laboratory studies. BCF values of 800 to 1,000 were found in some specific tissues (these were based on soluble residues, and so may include components other than the test substance). Although the data are sparse, they are of the same order as the whole body values for C_{5-10}-alkylphenols from the study with tetrapropenylphenol.

The published EU risk assessment for nonylphenol (EC, 2002) reports the mean measured BCF from reliable studies (on a fresh weight basis) as 741. Measured whole fish BCF values were 220, 262, 271, 280, 344, 586 and 741, but there was also a BCF of 1,200-1,300 in marine fish based on total radioactivity. Levels were higher in viscera than the carcass. The assessment used a BCF of 1,280 calculated from the log K_{ow} of 4.48 as a reasonable worst case estimate.

Most of the measured values for nonylphenol are similar to those obtained for the C_{5-10} alkylphenol fraction in the tetrapropenylphenol study (when considering these on a whole body basis). There are also similar indications of higher levels in some fish tissues than in others.

Summary of bioaccumulation

A recent study is available, and is considered to be fully valid. It is consistent with findings for similar substances, with the same pattern of accumulation (including higher levels in some organs). **A BCF of 823 will therefore be used in the assessment.** This indicates a moderate bioaccumulation potential, and is considered to be representative of all *para*-C_{12}-alkylphenols, regardless of branching pattern.

This BCF is clearly much lower than the QSAR estimate, and the implication is that processes such as metabolism are very important mitigating factors for this type of substance.

The predicted BCF for earthworms of 166,000 will be used in the assessment. It is recognised that this could be over-predicted based on the evidence with fish. However, there is no information on the possible metabolism of this type of substance in worms. Jager (2003) commented that the activity of some enzyme systems in worms is lower than in fish, mammals or birds, and that the relationship between log BCF in worms and log K_{ow} remained linear even with very hydrophobic chemicals. Therefore the predicted value will be used in the exposure assessment as a worst case.

3.1.4 Summary of environmental fate and distribution

The available data suggest that *para*-C_{12}-alkylphenols are of low volatility and low water solubility, and will adsorb strongly to organic matter in soils, sediments and sludges. Consequently, the substance will be relatively immobile in soil and sediment (notwithstanding movement of particles). Degradation processes within these media (biotic and abiotic) are predicted to be extremely slow. If released directly to the atmosphere, hydroxyl radicals are likely to degrade the substance quickly; transport from the site of release will be limited. Bioaccumulation is expected to be moderate in fish and potentially high in earthworms.

3.2 Environmental releases

3.2.1 General introduction

To effectively assess potential releases of *para*-C_{12}-alkylphenols to the environment, all aspects of the life cycle of both the substance and the main products of chemical processing need to be taken into account, namely:

- production of *para*-C_{12}-alkylphenols;
- releases of *para*-C_{12}-alkylphenols during processing into products (e.g. lubricant additive and resin manufacture);
- releases from residual substance in these products when used in further steps (e.g. lubricant formulation and resin use in tyres and inks);
- releases at the regional level through private use of the end products, such as tyres or lubricants.

Estimates of the releases from these steps have been made using a combination of information from the relevant industry (mainly for production and for the production of lubricant additives), the emission scenario document for lubricants (OECD, 2004) and default values from the TGD.

3.2.2 Releases from production of the substance and lubricant additive package manufacture

This section addresses releases from the production of tetrapropenylphenol and from its use as an intermediate in the production of lubricant additives (including the blending of additive packages). The two steps are considered together because there are only a limited number of companies and sites involved in these activities, and they are often involved in several of the operations. Information has been provided on emissions from three sites, which cover the majority of the activities. However, if the specific combinations of activities were reported here it might be possible to identify the individual sites. Therefore the specific information has been included in a confidential annex, available to regulatory authorities on request.

As several of the activities take place at the same locations, it is not possible to present total emissions for each individual process. Instead, an overall total combining emissions from these processes has been estimated: 4.67 kg/year, to surface water (i.e. after wastewater treatment, which can include oil-water separation and biological treatment). This estimate is based on measurements made at two sites operating the above processes during periods when the processes were active. The measurements also included maintenance periods for the production process (during which the catalyst was changed and the reactor vessel cleaned) and periods when the substance was delivered to sites using it as an intermediate. Hence the data are considered to be representative of the normal range of activities.

The oil separated from water at the sites is in all cases sent for recycling. Where biological treatment is used, the sludges are dried and then incinerated, so there are no emissions to land through sludge application.

3.2.3 Releases from lubricants

Releases from lubricant blending

For this section the emission scenario document (ESD) on lubricants and additives has been used (OECD, 2004) to estimate reasonable worst case releases from blending sites. The information relates to the calcium alkyl phenate sulphides (referred to as phenates in this section) in general, but is taken to cover the ethoxylate and other additives as well. Blending activity is known to take place in the UK.

Phenates made from tetrapropenylphenol can contain a range of concentrations of unreacted substance (see Section 2.2.2.1). For the purpose of this assessment a content of 19% (the 95th-percentile value from measurements) is used in calculations for the local scale (as a reasonable worst case), and a content of 11.7% (the mean value) used for calculations on larger scales.

The phenates are used in crankcase lubricants and in marine lubricants. In crankcase lubricants, the phenate can make up 1-10% of the lubricant, and an average of 5% is assumed here. Hence the final lubricant contains 0.95% tetrapropenylphenol as a reasonable worst case for the local calculations, and 0.59% for the larger scale calculations. In marine lubricants the phenate makes up 10-30% of the final lubricant (20% assumed as the average here). Hence the lubricant contains 3.8% of tetrapropenylphenol for the local calculations and 2.3% for the larger scale calculations.

From the ESD the emissions are estimated for a site blending 30,000 tonnes of lubricant per year. It is assumed that all of the production contains phenate.

Using the ESD, the emission to air from blending crankcase lubricants is estimated as 1.3 g/day, or 0.38 kg/year. For marine lubricants the figures are 5.2 g/day, or 1.6 kg/year.

Using the ESD the emission factor to water from blending crankcase lubricants is estimated as 4.8 x 10^{-6} kg/tonne lubricant, which includes emissions in both the water and oil phases[14]. For production of 100 tonnes of lubricant per day (assuming 300 days of operation) the emissions to water are 4.8 x 10^{-4} kg/day, or 480 mg/day. The factor for marine lubricants is calculated as 1.9 x 10^{-5} kg/tonne, giving a daily emission of 1.9 g/day.

The calculations above are based on the 95th percentile content of tetrapropenylphenol. The mean content of 11.7% is used for the regional and continental calculations. For crankcase lubricants the emission factor for release to air is calculated as 7.9 mg/tonne of lubricant produced, and the factor for release to water is calculated as 3 mg/tonne. The equivalent factors for marine lubricants are 31 mg/tonne to air and 11.7 mg/tonne to water.

For crankcase lubricants the annual amount of tetrapropenylphenol used to make the additives is 24,000 tonnes. This produces 28,800 tonnes of phenates. At an average content of 5%, this amount could be used in 576,000 tonnes of lubricants per year. Applying the crankcase factors above to this quantity, the overall emissions from blending are 4.6 kg/year to air and 1.7 kg/year to waste water. There are a large number of lubricant blenders in the EU, so the regional emissions are assumed to be 10% of the total. The emissions for crankcase lubricant blending are therefore:

	Air	Waste water
local:	1.3 g/day	0.48 g/day
regional:	0.46 kg/year	0.17 kg/year
continental:	4.14 kg/year	1.53 kg/year

For marine lubricants, the annual amount of tetrapropenylphenol used is 14,574 tonnes, equivalent to 17,490 tonnes of phenates. At an average content of 20%, this could produce 87,444 tonnes of lubricants. Applying the marine factors above to this amount, the overall emissions from blending marine lubricants are estimated as 2.7 kg/year to air and 1 kg/year to waste water. The total quantity of lubricant is less than three times the size of the local site used in the calculations, and so for marine lubricants it is assumed that all blending takes place in the region. The emissions are therefore:

	Air	Waste water
local:	5.2 g/day	1.9 g/day
regional:	2.7 kg/year	1 kg/year

The marine lubricant blending emissions are higher than those for the crankcase lubricants, so they will be used for the local emissions. The combined emissions from

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[14] Lubricant blending does not involve process water. The releases are related to other processes such as the handling of raw materials and products.

blending are: regional, 3.16 kg/year air, 1.2 kg/year waste water; and continental 4.14 kg/year air, 1.53 kg/year waste water.

Releases from use and disposal of lubricants

The ESD on lubricants and additives (OECD, 2004) provides information on the losses of crankcase lubricants to the environment from their use and end of life stages. This data has been used to estimate releases of tetrapropenylphenol. The amount of tetrapropenylphenol used in crankcase lubricants in the EU is 24,000 tonnes, which corresponds to 28,800 tonnes of phenates. The mean level of unreacted tetrapropenylphenol in the phenates is 11.7%, so the amount of residual tetrapropenylphenol in crankcase lubricants is 3,370 tonnes per year. It is assumed that the market for lubricants is at a steady state, so that new production matches the quantity that is lost, degraded or disposed of. Thus, the annual amount of tetrapropenylphenol that is lost, degraded or disposed of is 3,370 tonnes.

Measurements have been carried out on the level of tetrapropenylphenol present in lubricating oils at the end of their service life or a simulated service life (RATG, 2005). Different results were found for gasoline engines and for diesel engines. For gasoline engines, 98% of the tetrapropenylphenol was destroyed, while for diesel engines the figure was 93%. These figures have been used to adjust the amount of tetrapropenylphenol released from the use and disposal of lubricants. For losses related to used oil, the full degradation values have been applied. For losses during use, it has been assumed that on average half of the degradation would have taken place, and so the amounts remaining would be 51% for gasoline engines and 54% for diesel. The split between gasoline and diesel use is approximately 40% gasoline to 60% diesel.

The releases calculated using the methods in the ESD are presented in Table 3.5.

Table 3.5 Fate of crankcase lubricants during use and disposal

Source	Quantity (tonnes/year)		% of total[a]	Comments
	Gasoline engines	Diesel engines		
Spillage losses on charging/oil left in containers[b]	1.7	2.5	0.125	Wastewater
	13.5	20.2	1	Landfill
	5.1	7.6	0.375	Waste oil for re-use
Consumed in use[c]	324	485	24	Exhaust emissions to air, largely combusted
	2.6	4.1	1	Leakages to soil/surface water[e]
Used oil[d]	6.7	35.4	25	Re-used as fuel oil in house
	3.7-7.1	19.5-37.5	13.75-26.5	Re-used as fuel oil after treatment
	4.8-9.2	30.5-48.4	21.5-34.25	Home use: disposed to wastewater/soil/landfill[f]

Notes: [a] the percentage figures apply to the overall lubricant and so do not include any degradation.

[b] the quantities here assume no degradation of tetrapropenylphenol has occurred.

[c] the quantities here take account of degradation of tetrapropenylphenol in oil in use, assuming half the degradation at end of life as average (so 51% remaining for gasoline and 54% for diesel).

[d] the quantities here take account of degradation of tetrapropenylphenol in oil in use, using the end of life values (2% remaining for gasoline engines and 7% for diesel).

[e] releases divided equally between soil and surface water.

[f] releases divided equally between the three areas.

The total releases from this stage of the lifecycle are therefore 23.4 tonnes to waste water, 3.35 tonnes to surface water and 22.6 tonnes to soil (taking the highest figure for home use of used oil). These are divided between the region (10%) and the continent (90%) to give the following releases: waste water, 2.3 tonnes/year regional; 21 tonnes/year continental; surface water, 0.34 tonnes/year regional, 3.0 tonnes/year continental; soil, 2.3 tonnes/year regional, 20 tonnes/year continental.

There is no similar information on the fate of marine lubricants. However, RATG (2005) have provided a description of the way in which these lubricants are used. In large slow speed marine diesel engines the lubricant is injected into the cylinders directly to lubricate the piston, cylinder and rings, and as a result the lubricant will be burned with the fuel. Hence there should be negligible emission from this use. The oils in large medium speed marine engines are only changed in the course of major overhauls, which occur only every few years. The oil removed from the engines is recycled, so there should be no emissions from this use either. It is therefore concluded that the releases from the use of lubricants in marine engines are negligible.

3.2.4 Releases from resin applications

Production of resins

In this life cycle step, *para*-C_{12}-alkylphenols are used as a monomer in a polymerisation process. Water is present in the process – in the stock formaldehyde solutions, and as a reaction product. The default emission factors from the TGD (Table 3.10, Appendix 1, wet process) are 10^{-5} for emissions to both air and water.

There are no specific emission data for *para*-C_{12}-alkylphenols. In the EU risk assessment of nonylphenol (EC, 2002), one site provided data to estimate a water emission factor of 8 x 10^{-6}, which is close to the default value for nonylphenol of 10^{-5}. The default emission factors will therefore also be used for *para*-C_{12}-alkylphenols. As there are only a small number of companies producing these resins (around 10 in the EU, not all of which may be processing this substance), this assessment assumes that all of the tonnage used in this life cycle step (280 tonnes per year) is used in a single region. Using the total tonnage with the B table (Table B3.9) in the TGD, the fraction of main source (i.e. the relative amount that the largest regional site will use) is 0.25, so that 70 tonnes are used at the site, and the number of production days is 28.

The estimated emissions are:

	Air	Waste water
local:	0.025 kg/day	0.025 kg/day
regional:	2.8 kg/year	2.8 kg/year

This assessment assumes resins are made using *para*-C_{12}-alkylphenol as the sole phenol (i.e. it is not mixed together with other phenols). This assumption affects the estimation of how much resin is manufactured at a site, but not the emission estimates themselves.

Releases from the use of resins

No specific information is available about releases from any resin use. This assessment therefore assumes that the content of residual substance in the resin is 3% of the amount used (as described in Section 2.2.3). The consumption volume for this application is 280 tonnes, so the total amount of residual *para*-C_{12}-alkylphenol is 8.4 tonnes.

Inks

The bulk of the resins produced from *para*-C_{12}-alkylphenols (210 tonnes) are used to make printing inks. The production process is essentially a formulation step, as the resin is mixed with a number of other components. The resin makes up 7-8% of the ink concentrate, excluding the solvent. There is no specific information on this process. The default TGD emission factor for air is 2.5 x 10^{-3}, and for water is 0.003 (Table A2.1). The relevant B table for this process in the TGD is B2.8.

As the tonnage is low it is assumed that it is all used in the region. Taking the average resin content in ink as 7.5%, the amount of ink produced from 210 tonnes is 2,800 tonnes. The fraction of main source from the TGD B Table is 0.4, which gives a use of 84 tonnes of resin at the site, going into 1,120 tonnes of ink containing *para*-C_{12}-

alkylphenol resins each year. The number of emission days is 300. The estimated emissions are:

	Air	Waste water
local:	0.021 kg/day	0.025 kg/day
regional:	16 kg/year	19 kg/year

The ink production process actually involves some reaction between the components. There are no significant traces of *para*-C_{12}-alkylphenols left in the finished inks. Hence releases from the printing process, or from the recycling of paper printed with these inks, are negligible. These two steps in the ink life cycle are not considered further in this assessment.

Tyres

Tyre production

This process is a minor application of this substance. The Emission Scenario Document (ESD) for Additives in the Rubber Industry included in the TGD provides information on the releases to water from the combined formulation and processing stages and so covers the tyre production process. This information has been used to estimate emissions from this life cycle step, as specific data are unavailable. The calculation is performed for the resin, and then adjusted for the content of unreacted phenol in the resin (3% assumed). The estimation assumes that the residual phenol is retained in the rubber to the same degree as the resin. The retention factor from the ESD is 0.995 (i.e. 0.5% is not retained).

There is no specific information on the level of use of tackifier resins in the ESD, so the value for processing aids of 1-5 parts per hundred rubber (phr) has been taken and the middle value of 3 phr has been used. This equates to around 1.5% by weight.

The amount of tyre production at a site is taken as the ESD's default value of 26.4 tonnes per day, equivalent to the consumption of around 400 kg of resin per day. It is assumed that the resin is used over 90 days.

The resulting emission of resin is calculated as 2.0 kg/day; the corresponding emission of *para*-C_{12}-alkylphenols is 0.06 kg/day to water. Assuming that all of the resin is used in the region, the regional emissions are 5.3 kg/year.

The default emission factor to air is taken from the TGD and is 5×10^{-4} (Table A2.1, Appendix 1, dedicated equipment, little cleaning). The amount of *para*-C_{12}-alkylphenols in the resin used per day from the estimates above is 12 kg, so the daily emission to air is 6×10^{-3} kg/day. The regional emissions are 0.53 kg/year. The estimated emissions from tyre production are therefore:

	Air	Waste water
local:	6×10^{-3} kg/day	0.06 kg/day
regional:	0.53 kg/year	5.3 kg/year

Tyres in use

Losses from tyres in use need to be considered, through abrasive wear of the material rather than through leaching or volatilisation. Information from Schenectady International, Inc. (a major producer of phenol-based resin for tyre consumption), shows the resin is used in the interior portion of the tyre and is therefore not subject to abrasion and loss during use (APERC and CEPAD, 2005). Consequently, losses from tyres in use might be expected to be insignificant. However, there is some evidence to show the presence of the related substance 4-*tert*-octylphenol in road runoff (EA, 2005b). The following discussion is therefore provided as an illustration of the potential significance of this source, *recognising that it might not be wholly realistic for* para-C_{12}-*alkylphenols.*

Information from Australia suggests that an average new tyre weighs 10 kg and a used tyre weighs about 9 kg. The weight of rubber is 85% of the total tyre weight, so about 12% of the rubber is lost in use during the service life of the tyre (SA EPA, 2002). An Environment Agency report (EA, 1998) suggests losses of 10-20% of tyres by weight over their lifetime, with a total loss in the UK of 53,000 tonnes of rubber per year. This total corresponds to 14% of the weight of tyres disposed of each year. An average value of 15% is used to estimate losses of rubber per year. Assuming that the new rubber processed into tyres goes to replace that withdrawn from use at the end of the tyre service life, the equivalent of 15% of new rubber is released each year.

It is assumed that the resin and the unreacted *para*-C_{12}-alkylphenols are lost at the same rate as the rubber. The amount of residual *para*-C_{12}-alkylphenols in resins is estimated as 1.05 tonnes. Hence the amount of resin abraded per year is 15% of 1.05 tonnes, or 158 kg. This release is assumed to be split equally between surface water and industrial soil (e.g. roadside verges), with 10% release to the region. The emissions are:

	Surface water	Industrial soil
regional:	7.9 kg/year	7.9 kg/year
continental:	71 kg/year	71 kg/year

Even if the abraded material contained *para*-C_{12}-alkylphenols, not all of it might be available to the environment. However, the particles will break down over time, and so complete availability has been assumed for the remainder of this discussion as a worst case. This source makes only a small contribution to the regional emissions.

Tyre disposal

There may be possible releases from the tyre rubber at the end of the service life as a tyre. The disposal of tyres into landfills is no longer allowed. Council Directive 1993/31/EC[15] (the EU Landfill Directive) banned the disposal of whole tyres to landfill in July 2003. The ban was completed for all tyres (including tyre crumb) during 2006. The use of whole tyres in landfill engineering applications is still allowed.

A number of other civil engineering applications for used tyres have been investigated as a way to use up the waste material (e.g. as part of flood defence measures, and surfacing for playgrounds, sports arenas and roads). The risk assessment on 4-*tert*-octylphenol discusses the possible leaching of that substance from tyre residues after disposal (EA, 2005b). That assessment concluded that the overall contribution of tyre disposal, re-use or use in other areas to the overall emissions of 4-*tert*-octylphenol is likely to be negligible. As the use of *para*-C_{12}-alkylphenols in tyres is at a much lower level than that of 4-*tert*-octylphenol, a similar conclusion can be made here.

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[15] Official Journal No. L 182, 16/07/1999 p. 01-19. More information can be obtained from http://www.tyredisposal.co.uk/Landfill.asp.

Varnishes

It is understood that *para*-C_{12}-alkylphenol-based resins can be used as a binder in varnishes, but no other information is available. It is assumed that releases from resin production cover any releases from varnish formulation. The application and curing of the varnish is analogous to a coatings use, but heat curing involves further cross-linking and reaction, and so this application is essentially a polymer-processing step (the resin acts as a cross-linking agent). The default TGD emission factors for polymer processing (Table A3.11, Type V) are therefore considered to be more relevant for this scenario, and are 0.075 to air and 5×10^{-5} to water.

The tonnage of resin used in this application is low, and so all use is assumed to take place in the region. The default fraction used at a site is 0.35 (Table B3.9), which gives12 tonnes of resin used over 12 days per year. This amount of resin contains 360 kg of *para*-C_{12}-alkylphenols, or 30 kg/day. The estimated emissions are:

	Air	Waste water
local:	2.25 kg/day	1.5×10^{-3} kg/day
regional:	79 kg/year	0.053 kg/year

3.2.5 Summary of releases

The release estimates from the sections above are summarised in Table 3.6. These data are used in the EUSES program to calculate the PEC values.

Table 3.6 Summary of releases to environment

Life cycle stage	Local (kg/d)	Regional (kg/year)	Continental (kg/year)
Production of the substance and lubricant additive manufacture	Site specific – see confidential annex	sw: 4.67	
Lubricant blending	a: 5.2×10^{-3} ww: 1.9×10^{-3}	a: 3.16 ww: 1.2	a: 4.14 ww: 1.53
Lubricant use and disposal		ww: 2,300 sw: 340 soil: 2,300	ww: 21,000 sw: 3,000 soil: 20,000
Phenol/formaldehyde resin production	a: 0.025 ww: 0.025	a: 2.8 ww: 2.8	
Resins – ink formulation	a: 0.021 ww: 0.025	a: 16 ww: 19	
Resins – tyre production	a: 6x10-3 ww: 0.06	a: 0.53 ww: 5.3	
Resin – tyres in use		sw: 7.9 soil: 7.9	sw: 71 soil: 71
Resins – varnish use	a: 2.25 ww: 1.5×10^{-3}	a: 79 ww: 0.053	

Note: a – release to air; ww – release to waste water; sw – direct release to surface water; soil – release to industrial soil.

3.3 Environmental concentrations

3.3.1 Aquatic compartment (surface water, sediment and wastewater treatment plant)

Estimated aquatic environmental concentrations

The predicted environmental concentrations (PECs) for water local to the point of release (PEC_{local}) are calculated using the environmental releases detailed in Section 3.2 and the equations set out in Chapter 3 of the TGD.

The local PEC is made up of a local water concentration (C_{local}) resulting from the relevant process emission, and a background concentration that results from emissions in the regional environment ($PEC_{regional}$). This regional PEC is itself a result of direct emissions from industrial processes using the substance and its derivatives, and diffuse emissions as a consequence of the use of end products. In the absence of specific information, sewage effluent is assumed to be diluted in river water by a factor of 10.

The PEC for sediment can be derived from the PEC_{local} for surface water using the suspended matter–water partitioning coefficient, assuming equilibrium partitioning.

The results are presented in Table 3.7. As described in Section 3.2.2, specific information on releases was provided by three sites (A-C), representing production of the substance, and its use as an intermediate in lubricant additive manufacturing (one site does both). This information has been used to calculate PEC values for these three sites. Two of the sites involved in lubricant additive production (A and B) have discharges at estuarine locations and are therefore included in the marine risk assessment in Appendix 3 (site B appears not to use biological treatment of its waste effluent, and so a PEC for WWTP is only provided for site A).

No aqueous process effluents are expected to arise from the production process used at the third site (site C in Table 4.7), and the substance has not been detected in the site effluent. Calculations have been performed based on the detection limit of the analytical method, and the results are presented as “less than” values (the actual level of exposure from this site could be substantially lower). (No information is available about WWTP influent concentrations at this site, and so a PEC for WWTP has not been estimated given the uncertainty in the effluent levels.

No information has been provided about the locations of the remaining two or three sites in Europe, although they are not in the UK. A freshwater scenario has therefore been omitted from the assessment of this life cycle stage.

Table 3.7 Local aquatic PECs

Life-cycle stage		PECs for WWTP organisms (mg/L)	PECs for surface water (mg/L)	PECs for sediment (mg/kg wwt)
Production of the substance	Site C	-	<5.8×10^{-3}	<13.9
Production of the substance and lubricant additive manufacture	Site A	3.3×10^{-3}	-	-
Lubricant blending		1.1×10^{-4}	1.6×10^{-5}	3.9×10^{-2}
Phenol/formaldehyde resin production		1.4×10^{-3}	1.3×10^{-4}	0.31
Resins – ink formulation		1.4×10^{-3}	1.3×10^{-4}	0.31
Resins – tyre production		3.4×10^{-3}	3.0×10^{-4}	0.72
Resins – varnish use		8.7×10^{-5}	1.5×10^{-5}	3.5×10^{-2}
Regional		-	7.0×10^{-6}	3.3×10^{-2}

All of the calculated concentrations are below the solubility of the major component of the substance.

Measured aquatic environmental concentrations

A variety of extraction techniques and quantification methods may be used in determining concentrations of alkylphenols, the techniques used being dependent upon the type of sample being analysed. Quantification of samples is usually by high performance liquid chromatography (HPLC) or gas chromatography (GC) using either UV or mass spectrometer detectors. Details about the analytical techniques employed and the detection limits are provided in the following sections where appropriate. The Environment Agency has recently developed a method for analysing *para*-C_{12}-alkylphenols in river water. The substance is extracted and derivatized to its pentafluorobenzoyl chloride ester and measured using a gas chromatograph fitted with a mass selective detector in negative chemical ionisation mode. The limit of detection is 5 ng/L.

When analysing samples of *para*-C_{12}-alkylphenols, its low solubility in water must be considered. As with nonylphenol, *para*-C_{12}-alkylphenols may also be adsorbed onto the surface of glassware thereby reducing the concentration measured in solution.

Although there has been considerable monitoring of certain alkylphenols and their ethoxylates in European waters over the past decade, this work has been limited primarily to nonylphenol and to a lesser extent octylphenol. There has been less extensive monitoring for other shorter or longer chain alkylphenols.

Freshwaters, wastewater treatment and industrial effluents

IVL (2005) analysed a small number of surface water samples taken from locations in Sweden close to industrial sites (paint and resin producers) and to WWTPs treating household waste water. The samples were taken in 2003. The analysis looked for a range of phenolic compounds including 4-dodecylphenol (CAS No. 27193-86-6, but described as an isomer mixture, mostly branched). Extraction and clean up of the samples were followed by derivitization (acetylation) using acetic anhydride. The derivatized phenols were separated using silica gel chromatography and analysed using GC-MS. 4-dodecylphenol was not detected at any of the locations, with a detection limit of 4-6 ng/L.

Analyses were also carried out on samples of effluent from treatment plants at industrial sites and from domestic WWTPs. The substance was not found, with detection limits varying from 3-10 ng/L.

Sludge samples were analysed from the same WWTPs, and 4-dodecylphenol was detected in around 20% of the samples. The mean concentration was ~0.05 µg/g dw, with a range of 0.03-1.4 µg/g (mg/kg).

Measured concentrations have been reported in a confidential report relating to two sites involved in the production and/or use as an intermediate of *para*-C_{12}-alkylphenols. The range of concentrations found in the effluent from the sites after treatment was 0.2-10.6 µg/L.

Groundwater

No data have been located.

1.1.1.1.1 Sediment

IVL (2005) analysed sediment samples from 19 locations in urban and industrial areas in Sweden. The general analytical method is described in Section 3.3.1.2.1. 4-Dodecylphenol was detected in ~30% of the samples, with a mean concentration of 5 ng/g dw and a range of 3.4-38 ng/g dw (detection limit range 1-39 ng/g (µg/kg) dw).

Comparison of measured and estimated aquatic concentrations

Only limited measured data are available. The substance was not detected in surface water samples at 4-6 ng/L, which is about the level of the estimated regional concentration. The predicted surface water concentrations for local scenarios are higher than this, which may suggest some over-estimation. However, the measurements do not relate specifically to the scenarios considered in this assessment. Measurements in effluents at real sites engaged in the production and/or use of the substance as an intermediate are of the same order as those calculated for (other) local scenarios.

For sediment, the measured values are presented on a dry weight basis, and so need to be converted to wet weight for comparison with the calculated values. Assuming the TGD standard water content for sediment, a conversion factor of 2.6 is applied, giving measured values in the range 1.3-15 ng/g wwt. The upper end of this range is similar to the calculated regional sediment concentrations, but lower than the calculated local sediment levels.

In light of the limited availability of measured data, the estimated concentrations will be used in the risk characterisation. These may be conservative, but this is taken into account in the risk characterisation.

3.3.2 Terrestrial compartment

The TGD covers direct releases to soil, the application of sewage sludge containing the chemical, and atmospheric deposition. No direct releases to soil are expected. Concentrations caused by atmospheric deposition are expected to be negligible due to the atmospheric behaviour of *para*-C_{12}-alkylphenols and the small amounts that are released to the air. The calculated soil concentrations therefore stem principally from the application of sewage sludge (this is to be expected when the behaviour of *para*-C_{12}-alkylphenols in WWTP is considered – see Section 3.1.5). There is no land spreading of sludge from any of the three sites that provided specific release data (sites A-C, covering production of the substance and production of lubricant additives). This life cycle step is therefore assumed not to give rise to significant concentrations of the substance in soil.

Three different soil PECs are calculated depending on the protection goal. These vary in terms of the depth of soil considered and the duration and/or route of exposure. The 30-day average for soil represents the PEC for soil organisms, while the 180-day averages for agricultural and grassland are used to estimate exposure of animals and humans through the food chain.

At the regional level the soil concentration in unpolluted or 'natural' soil must be used as a background concentration. It is added to the local contribution to avoid double counting of application through sludge. The PECs for the terrestrial compartment are given in Table 3.8.

Table 3.8 Local terrestrial PECs

Life-cycle stage	**PEC_{soil} (mg/kg wwt)**			**$PEC_{porewater}$ (µg/L) (agricultural soil)**
	30-d average	**Agricultural**	**Grassland**	
Lubricant blending	2.8×10^{-2}	2.8×10^{-2}	1.1×10^{-2}	1.5×10^{-2}
Phenol/formaldehyde resin production	3.7×10^{-1}	3.7×10^{-1}	1.4×10^{-1}	0.2
Resins – ink formulation	3.7×10^{-1}	3.7×10^{-1}	1.4×10^{-1}	0.2
Resins – tyre production	8.9×10^{-1}	8.8×10^{-1}	3.4×10^{-1}	4.6×10^{-1}
Resins – varnish use	2.3×10^{-2}	2.3×10^{-2}	9.7×10^{-3}	1.2×10^{-2}
Regional	3.0×10^{-4}	5.0×10^{-2}	-	2.6×10^{-2}

Note: The WWTP sludge from site C is incinerated, so there is no release to soil for this site. The sludge from sites A and B (covering lubricant additive manufacture) are also incinerated. This assessment thus assumes that sludge incineration occurs at all remaining sties for this life cycle stage.

Only one report of measured concentrations in soil has been located. IVL (2005) analysed natural soil samples from three locations in Sweden. They did not detect 4-dodecylphenol in any sample, with a detection limit of 0.002 mg/kg dw. The detection limit is equivalent to 1.75 µg/kg wet weight. The estimated regional concentration is 0.3 µg/kg wet weight, which is not inconsistent with the measured value. The estimated concentrations will be used in the risk characterisation.

3.3.3 Atmospheric compartment

Considering the low vapour pressure of *para*-C_{12}-alkylphenols, their reaction with hydroxyl radicals and their tendency to adsorb to soils and sediments, atmospheric concentrations of the substance are likely to be low. PECs for the air compartment have been estimated for each use pattern using EUSES. The calculated regional background concentration is 0.08 ng/m^3. IVL (2005) reported that 4-dodecylphenol was not detected in air samples from Sweden from locations described as background, industrial and urban, at a detection limit of 0.3 ng/m^3. The calculated and measured results are not in disagreement. Although this work does not provide any confirmation of the calculated values; it is clear that the levels in air will be low.

3.3.4 Dietary exposure of wildlife

para-C_{12}-alkylphenols are expected to be relatively persistent and have a moderate potential to bioconcentrate in fish. Accumulation of the substance in food chains is therefore possible; it might reach a concentration in food that could cause toxic effects in a predator that eats that food. This is known as secondary poisoning.

PECs for piscivores have been calculated using the measured fish BCF value of 823 along with the estimated PECs for the aquatic compartment. PECs for earthworms have been estimated using the PECs for soil and pore water. These are shown in Table 3.9. The calculations follow the procedures outlined in the TGD, and include a default biomagnification factor for the aquatic food chain; for *para*-C_{12}-alkylphenols this is 1 (BCF <2,000).

Table 3.9 PECs for secondary poisoning

Life-cycle stage		PECs for fish eaten by predators (mg/kg wwt)	PECs for worms eaten by predators (mg/kg wwt)
Production of the substance	Site C	<2.0	-
Lubricant blending		0.009	3.0
Phenol/formaldehyde resin production		0.01	16
Resins – ink formulation		0.047	16
Resins – tyre production		0.11	36
Resins – varnish use		0.006	2.8

Note: The WWTP sludge from Site C is incinerated, so there is no release to soil for this site. The same is assumed to apply for all sites making lubricant additives.

A contribution of 50% is made to each PEC value by both the regional and local concentrations. This calculation step accounts for some species of animal foraging for food over a wide area (i.e. half of the dietary intake for both aquatic and terrestrial food chains is assumed to come from local and half from regional sources). In the case of *para*-C_{12}-alkylphenols, the local aquatic surface water concentrations provide a significantly higher percentage of the overall value than do the regional concentrations.

Only one report that included measurements for the substance in biota has been located. IVL (2005) analysed fish samples from lakes in Sweden, and did not find 4-dodecylphenol at a detection limit of 10 ng/g (µg/kg). The estimated concentration in fish from the regional concentration in water of 7 x 10^{-6} mg/L is 6 µg/kg, which is not inconsistent with this finding. The calculated concentrations will be used in the risk characterisation.

3.3.5 Human exposure via the environment

Concentrations of *para*-C_{12}-alkylphenols in human intake media have been calculated using EUSES 2, and the results are presented in Table 3.10. These have been converted into daily doses using the standard intake figures from the TGD; these and the overall estimated daily dose are presented in Table 3.11. The production and intermediate use scenarios have not been included in the tables because these scenarios are based on real site information, which suggests that there should be no significant local exposure of humans via the environment.

Table 3.10 Predicted concentrations of the substance in human intake media

Life cycle stage	Drinking water (mg/L)	Fish (mg/kg)	Leaf crops (mg/kg)	Root crops (mg/kg)	Meat (mg/kg)	Milk (mg/kg)	Air (mg/m^3)
Lubricant blending	1.5×10^{-5}	0.012	2.6×10^{-3}	1.26	0.014	4.5×10^{-3}	1.3×10^{-6}
Phenol/formaldehyde resin production	1.9×10^{-4}	0.013	1.3×10^{-3}	16.4	0.013	4.0×10^{-3}	6.1×10^{-7}
Resins - ink formulation	1.9×10^{-4}	0.089	9.8×10^{-3}	16.6	0.059	0.019	4.9×10^{-6}
Resins - tyre production	4.6×10^{-4}	0.20	3.0×10^{-3}	39.4	0.03	9.6×10^{-3}	1.5×10^{-6}
Resins - varnish use	1.2×10^{-5}	6.0×10^{-3}	0.042	1.04	0.23	0.072	2.1×10^{-5}
Regional	2.6×10^{-5}	5.8×10^{-3}	1.6×10^{-4}	2.24	2.8×10^{-3}	9.0×10^{-4}	7.8×10^{-8}

The TGD method uses the natural soil concentration as the background to the local concentrations, to avoid double counting of chemical application in sludge to soil. For this substance the regional agricultural soil concentration is much higher than the natural soil concentration. As a result the level in root crops, which depends on the soil level, is higher in the regional scenario than in some of the local scenarios.

The root crop levels dominate the dose for the scenarios with the highest total doses. However, the accuracy of these estimates is uncertain, as the log K_{ow} value for *para*-C_{12}-alkylphenols is well above the range of values that were used to develop the prediction model used to calculate these concentrations.

Table 3.11 Predicted daily human doses (all mg/kg bw/day)

Life cycle stage	Drinking water	Fish	Leaf crops	Root crops	Meat	Milk	Air
Lubricant blending	4.2×10^{-7}	2.0×10^{-5}	4.4×10^{-5}	6.9×10^{-3}	6.1×10^{-5}	3.6×10^{-5}	3.6×10^{-7}
Phenol/formaldehyde resin production	5.4×10^{-6}	2.2×10^{-5}	2.2×10^{-5}	9.0×10^{-2}	5.5×10^{-5}	3.2×10^{-5}	1.8×10^{-7}
Resins - ink formulation	5.5×10^{-6}	1.5×10^{-4}	1.7×10^{-4}	9.1×10^{-2}	2.5×10^{-4}	1.5×10^{-4}	1.4×10^{-6}
Resins - tyre production	1.3×10^{-5}	3.3×10^{-4}	5.1×10^{-5}	2.2×10^{-1}	1.3×10^{-4}	7.7×10^{-5}	4.1×10^{-7}
Resins - varnish use	3.4×10^{-7}	9.8×10^{-6}	7.3×10^{-4}	5.7×10^{-3}	9.8×10^{-4}	5.8×10^{-4}	6.0×10^{-6}
Regional	7.4×10^{-7}	9.5×10^{-6}	2.8×10^{-6}	1.2×10^{-2}	1.2×10^{-5}	7.2×10^{-6}	2.2×10^{-8}

4 Effects assessment

Only the key studies listed in the SIAR (2006) are summarised in this Section, together with some results from additional studies for related compounds that are not mentioned in the SIAR. Where a study is classed as 'use with care', it is not considered to be fully valid, but may be used as supportive evidence if other data are available. The data refer to the branched substance unless otherwise stated.

4.1 Aquatic compartment (including sediment)

Table 4.1 lists the key data, with further details in the text. *para*-C_{12}-alkylphenols have low water solubility and a high potential for adsorption to test vessels. Nominal levels may therefore misrepresent actual exposures, so analyses to confirm exposure concentrations are usually necessary for aquatic studies to be considered valid.

4.1.1 Toxicity to fish

Acute toxicity

Freshwater species

A 96-hour acute toxicity test comparable with OECD test guideline 203 was performed with the golden orfe (*Leuciscus idus*) using 'dodecylphenol T' (Hüls AG, 1992b). No effects on mortality were evident, and a 96-hour NOEC of ≥0.5 mg/L was recorded. However, although a semi-static test design was used with analytical monitoring of the test concentration, no test substance was actually detected at any time period because the detection limit of the analytical method was rather high (0.5 mg/L). The study therefore provides no information about actual dissolved concentrations. In addition, it gives no details about the test solution preparation method, or the steps taken to minimise adsorption to glassware and filters, etc. Whilst the study implies that the substance is not acutely toxic to fish up to the water solubility limit of the main component, the results cannot be considered fully valid.

A 96-hour LC_{50} of 0.14 mg/L is reported for p-dodecylphenol (CAS number and purity not reported) with the Atlantic salmon (*Salmo salar*) at a temperature of 10ºC (McLeese *et al.*, 1981). The exposure concentration decreased exponentially during the test (the paper states that a static system was used, but that toxicant solutions were changed at 48 hours). The result is therefore reported as the geometric mean of the highest concentration without, and the lowest concentration with, 50% mortality. The study is not valid since the number of test organisms used was too small (three per exposure).

In conclusion, no fully valid acute fish toxicity tests are available.

Table 4.1 Toxicity of *para*-C_{12}-alkylphenols to freshwater aquatic organisms – summary of key studies

Species	Chemical tested	Age/Size	Renewal regime	Temp (°C)	Dissolved oxygen	Hardness (mg $CaCO_3$/L) or salinity (‰)	pH	Endpoint	Concentration (mg/L)	Reference	Validity
Fish											
Leuciscus idus (Golden orfe)	Dodecylphenol T (CAS no.121158-58-5) Purity = 99.9%	6 ± 2 cm	Semi-static	20	No data	No data	8.1	96-h NOEC	≥0.5 (m)	Hüls AG, 1992b	Use with care
Invertebrates											
Daphnia magna (Water flea)	Tetrapropenylphenol (CAS no. 74499-35-7) Purity not reported	<24 h	Static	21	≥89%	No data	7.9	48-h EC_{50}	0.037 (n)	Sewell and McKenzie, 2005a	Valid, but results recalculated – see main text
								48-h NOEC	0.011 (n)		
	Tetrapropenylphenol (CAS no. 74499-35-7) Purity not reported	<24 h	Semi-static	21	≥87%	120-132	7.7-7.9	21-d NOEC	0.0037 (n)	Sewell and McKenzie, 2005b	Valid, but results recalculated – see main text
								21-d LOEC	0.012 (n)		
								21-d EC_{50}	0.0086 (n)		
Algae											
Scenedesmus subspicatus	Tetrapropenylphenol (CAS no. 74499-35-7) Purity not reported	Growth phase	Static	24	N/A	N/A	7.2-7.5	72-h E_rC_{50}	0.36 (n)	Vryenhoef and McKenzie, 2005	Valid, but results recalculated – see main text
								72-h NOEC	0.070 (n)		

Notes:

Notes:	m	measured (concentration)
	n	nominal (concentration)

The SIAR (2006) reports a 96-h LL_{50} of 40 mg/L for tetrapropenylphenol with fathead minnows (*Pimephales promelas*) using a water-accommodated fraction. Although actual test concentrations were measured by total organic carbon (TOC) analysis, the relation of TOC to test substance concentration was not provided, which means the results cannot be used for PNEC derivation.

Saltwater species

No data are available.

Chronic toxicity

No long-term fish toxicity data are currently available in either fresh or salt water. A comparison with related substances is made in Section 4.1.5.

4.1.2 Toxicity to aquatic invertebrates

Acute toxicity

Freshwater species

An acute toxicity test has recently been conducted on *D. magna* in accordance with OECD test guideline 202 (Sewell and McKenzie, 2005a). The test solutions were prepared using a stock solution of tetrapropenylphenol in acetone, and glassware was pre-conditioned with the appropriate test solution for approximately 24 hours prior to the initiation of the test to try to minimise the effects of adsorption. The study was performed over 48 hours, on a range of nominal concentrations up to the limit of (bulk) water solubility, including a solvent control. Filtration of the test solutions prior to analysis was not considered appropriate since preliminary investigations indicated that a significant amount of the test material adsorbed to the filter matrix. Test concentrations were therefore determined at 0 and 48 hours, both untreated and following centrifugation at 40,000 g for 30 minutes.

A 48-h EC_{50} of 37 µg/L and a 48-h NOEC of 11 µg/L were generated based on nominal concentrations. However, analytical recovery in untreated solutions at 0 and 48 hours was variable, suggesting that some material may have desorbed from the pre-treated glassware in some cases. The analytical method (HPLC) also might be less reliable for the two lowest test concentrations, since these were close to the limit of quantitation (4.8 µg/L). Analysis of centrifuged test samples at 0 hours showed measured concentrations 27-78% of nominal; concentrations at 48 hours were 23-49% of nominal. An exception occurred with the lowest test concentration (1.1 µg/L), with recovery at 150% and 149% of nominal at 0 and 48 hours respectively.

Whilst steps were taken to minimise the effects of adsorption, the analytical monitoring demonstrates that the actual exposure concentrations were variable, and this complicates the interpretation of the data. The results of the study have been recalculated based upon geometric mean measured concentrations for the purposes of this assessment. The 48-h EC_{50} is calculated to be 17 µg/L and the 48-h NOEC is calculated to be 18 µg/L (note that this NOEC is higher than the EC_{50}; this is an artefact caused by the highly variable analytical measurements).

The overall result (in terms of both nominal and corrected concentrations) is slightly lower than an earlier result obtained by Hüls AG, but is of a similar order of magnitude.

Saltwater species

The SIAR (2006) reports a 96-h EL_{50} of 0.58 mg/L (nominal) for the shrimp *Mysidopsis bahia* (now known *as Americamysis bahia*) using a water accommodated fraction. This value is not useful for risk assessment since there is no information about dissolved concentrations.

A 96-hour LC_{50} value of 0.15 mg/L was determined for p-dodecylphenol (CAS no. and purity not reported) with adult saltwater sand shrimp *Crangon septemspinosa* (McLeese *et al.*, 1981). A static exposure system was used, at 10ºC. The result is reported as the geometric mean of the highest concentration without, and the lowest concentration with, 50% mortality. The result should be treated with caution, since it suffers from the same problems as those described for the acute fish study by the same authors.

Chronic toxicity

Freshwater species

A 21-day reproduction study has been carried out with *D. magna* in accordance with OECD test guideline 211 (Sewell and McKenzie, 2005b). The test solutions were prepared using a stock solution of tetrapropenylphenol in acetone, and glassware was pre-conditioned with the appropriate test solution for approximately 24 hours prior to the start of the test to minimise the effects of adsorption. The test solutions were renewed three times per week. Concentrations were monitored analytically using HPLC at intervals throughout the study, following centrifugation at 40,000 g for 30 minutes.

Based on nominal concentrations, a 21-d NOEC of 3.7 µg/L, a 21-d LOEC of 12 µg/L and a 21-d EC_{50} for reproductive output of 8.6 µg/L were found. Nevertheless, as for the acute test, the analytical measurements make the results difficult to interpret with confidence. For example, measured concentrations were variable throughout the test for the lower dose groups, with a declining trend over the renewal periods. Measurements of concentration for the lowest dose group (0.37 µg/L) were below the limit of quantitation of the analytical method, and the method was also considered less reliable for the very low concentrations determined in some of the centrifuged samples. In view of the very low concentrations involved, there is also a possibility of both desorption and absorption of the test substance to vessel walls during the analytical procedure, despite the precautions that were taken.

In view of these findings, the nominal concentrations might not accurately reflect the actual exposure concentrations. Therefore this assessment uses re-calculated results based on time-weighted mean. The values used in this assessment are therefore a 21-d NOEC of 2.0 µg/L, a 21-d LOEC of 2.7 µg/L (based on parental immobilisation and reproduction) and a 21-d EC_{50} for reproductive output of 2.4 µg/L. These values are slightly lower than the nominal concentrations, but are preferred for the risk characterisation.

Saltwater species

No chronic toxicity data are available. A comparison with related substances is made in Section 4.1.5.

4.1.3 Toxicity to aquatic primary producers

Freshwater species

An algal growth inhibition test has recently been conducted using *Scenedesmus subspicatus* in accordance with OECD test guideline 201 (Vryenhoef and McKenzie, 2005 – final report still awaited). The test solutions were prepared using a stock solution of tetrapropenylphenol in dimethyl formamide, and glassware was pre-conditioned with the appropriate test solution for approximately 24 hours prior to the initiation of the test to try to minimise the effects of adsorption. The study was performed over 72 hours, on a range of nominal concentrations up to the limit of water solubility, including a solvent control. Filtration of the test solutions prior to analysis was not considered appropriate since preliminary investigations indicated that a significant amount of the test material adsorbed to the filter matrix. Test concentrations were therefore determined following centrifugation at 40,000 g for 30 minutes at 0 and 72 hours.

Effects were evident above the 72-h NOEC of 0.070 mg/L and the 72-h EC_{50} for growth rate was 0.36 mg/L, both based on nominal concentrations. Analytical determination of centrifuged samples with and without algae showed that the test item was not fully in solution at the start of the study and the measured concentration in samples without algae further decreased during the course of the study. Concentrations in test vessels after centrifugation ranged from 19-38% nominal at 0 hours down to 17-24% nominal after 72 hours. It was noted that the analytical method (HPLC) might be less reliable for the low concentrations determined in the centrifuged samples.

Whilst steps were taken to minimise the effects of adsorption, the reporting of the results in terms of nominal concentrations clearly overestimates the actual exposure concentrations as indicated by the analytical monitoring. For the purposes of this assessment the results of the study have been re-calculated based upon the geometric mean measured concentrations from samples without algae. The calculated 72-h NOEC is 15 µg/L and the 72-h EC_{50} for growth rate is 91 µg/L.

Both the nominal and recalculated values are substantially lower than the results of an earlier algal test performed by Hüls AG. The reasons for this discrepancy are unclear, but the 2005 study is considered more reliable because steps were taken to minimise absorption.

Saltwater species

No data are available.

4.1.4 Endocrine disruption

Some alkylphenols are known to act as weak estrogens in fish (e.g. EA, 2005a), and so they might cause adverse effects on endocrine systems that are not identified by the usual ‘base set’ tests summarised in Sections 4.1.1-4.1.3. The potential for endocrine disruption from the commercial substance is difficult to predict in the absence of multigenerational *in vivo* studies. Some *in vitro* data are available for related substances that seem to have a lower degree of branching. These are generally expressed as the ratio of the binding ability of the substance to a specific receptor to that of a reference compound. The available results are summarised in Table 4.2, together with values for octylphenol for comparison.

Table 4.2 Relative binding affinity of dodecylphenol

Receptor	Reference substance	Relative binding affinity (x less than reference substance)		Reference
		para-C_{12}-alkylphenol	Octylphenol	
Yeast strain	17β-estradiol	10,000,000 (4-*sec*-dodecylphenol)	1,000 (4-*tert*-octylphenol)	Routledge and Sumpter (1997)
Sprague-Dawley rat uterine estrogen receptor	17β-estradiol	5,300 (4-dodecylphenol, mixture of isomers, 99.7% purity)	6,600 (4-*tert*-octylphenol)	Blair *et al.* (2000)
Human estrogen receptor α	17β-estradiol	400 (4-dodecylphenol, CAS 104-43-8)	800 (4-*tert*-octylphenol)	Akahori *et al.* (2005)
Human estrogen receptor	17β-estradiol	5,400 (4-dodecylphenol)	6,600 (4-*tert*-octylphenol)	Lill *et al.* (2005)
Human androgen receptor	methyltrienolone	6,500 (4-dodecylphenol, CAS 104-43-8)	6,300 (4-n-octylphenol)	Fang *et al.* (2003)

Satoh *et al.* (2005) showed that 4-n-dodecylphenol exerted anti-androgenicity by binding to and blocking the androgen receptor in a reporter gene assay.

A linear 4-dodecylphenol (purity >90%) has been tested in a battery of assays to screen for endocrine effects by the Chemicals Evaluation and Research Institute (CERI) in Japan (K Kawahara, personal communication, November 2005) as follows:

- Binding Assay (ER-alpha, hAR);
- Reporter Gene Assay (ER-alpha and beta);
- Uterotrophic Assay (Agonist and Antagonist);
- Hershberger Assay (Agonist and Antagonist).

Since the reports are in Japanese the Environment Agency has not evaluated them. However, the correspondent reported that all assays were performed according to standard protocols under development in the OECD programme. The relative binding affinity of linear 4-dodecylphenol against ER-alpha was reported as 0.238 whereas that for 4-nonylphenol (branched mixture) was 0.143. In the uterotrophic assay (Sprague-Dawley rats), the LOEL was 40 mg/kg/day for linear 4-dodecylphenol and 200 mg/kg/day for 4-nonylphenol (branched mixture).

Discussion

Overall, the results indicate that linear 4-dodecylphenol has a similar binding affinity to some hormone receptors as 4-*tert*-octylphenol, and that it might pose higher toxicity. However, it is generally inappropriate to attempt to extrapolate the results from *in vitro* experiments to possible effects *in vivo* (due to differences in uptake and metabolism, etc.). In addition, a firm conclusion cannot be drawn for the commercial substance from these data, because:

- The binding of *para*-alkylphenols to the estrogen receptor is due to the effect of covalent bonding of two constituents of the phenol and alkyl groups, which correspond to the A-ring and hydrophobic moiety of the steroid structure, respectively. By analogy with nonylphenol, a branched alkylphenol is likely to have a higher estrogen receptor binding activity and endocrine disrupting potency than a linear compound.

- Some alkylphenols act at multiple target sites in the body to disrupt physiological (endocrine) function. For example, 4-nonylphenol is as an estrogen receptor agonist, an androgen receptor antagonist, and disrupts expression of aromatase mRNA (an enzyme that plays a role in sexual development by converting testosterone into estrogen).

Endocrine disruptive effects (e.g. on gonads or induction of vitellogenin (a female protein) in male fish) were not investigated in the fish bioaccumulation test. However, the available *in vivo* mammalian data show that *para*-C_{12}-alkylphenols express reproductive toxicity, and some of the effects on the reproductive axis are consistent with effects mediated via steroid hormone receptors. The implication is that possibility of endocrine effects cannot be ruled out in the absence of reliable appropriate screening data.

4.1.5 Comparisons with structural analogues

Quantitative structure–activity relationships

In view of the analytical uncertainties associated with some of the test results and the absence of long-term toxicity data for fish, toxicity has also been predicted using quantitative structure-activity relationships (QSARs). The OECD defines four modes of toxic action for chemicals in the aquatic environment, namely non-polar narcosis, polar narcosis, reactive and specific acting. The mechanism of non-polar narcosis (also referred to as ‘minimum’ or ‘baseline’ toxicity) generally involves interference of cell membranes, and is primarily related to the hydrophobicity of a substance. Polar narcosis also involves a non-specific mode of action, but the toxicity is significantly higher than predicted by non-polar narcosis, principally due to additional electronic interactions such as hydrogen bonding. Examples of polar narcotics include esters, phenols and anilines. The presence of a hydroxyl group but no other functional groups suggests that *para*-C_{12}-alkylphenols will fall into the class of polar narcotic chemicals, although at high log K_{ow} values the distinction between polar and non-polar narcosis is less apparent.

Many QSAR models are available. The models used in this assessment are those recommended in the TGD and those included in the ECOSAR programme in EPIWIN v3.12 (US EPA, 2000)[16]. The TGD equations are those for polar narcosis, and most of the ECOSAR equations used were developed for phenols (the algal toxicity values are predicted using the non-polar narcosis equations as selected by the program).

The octanol-water partition coefficient (log K_{ow}) is the only input parameter used in these models, and a value of 7.14 was used. This is above the recommended range of values for all of the QSARs for acute aquatic toxicity used here.

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[16] The Danish Environment Protection Agency (EPA) has developed a database of predicted property values for a large number of substances using several commercial models that are not available to the Environment Agency. However, in response to an enquiry in July 2005, the Danish EPA informally replied that neither CAS number 121158-58-5 nor 74499-35-7 are currently found in their QSAR database, implying that estimates for these substances have not yet been made using these models.

The estimated data are shown in Table 4.3 alongside the most sensitive measured data where comparable. The measured data were not used in the derivation of the QSAR models.

Table 4.3 Comparison of experimental and estimated aquatic toxicity data

Trophic level	End point	Experimental concentration (mg/L)	TGD QSAR concentration (mg/L)	EPIWIN QSAR concentration (mg/L)
Freshwater fish	96-h LC_{50}	≥0.5	0.011	0.025
	Chronic value	No data	-	0.003
Freshwater invertebrates	48-h EC_{50}	0.017	0.043	0.109[1]
	21-d Chronic value	0.0020	-	0.003
Fresh water algae	72-h EC_{50}	0.091	-	0.003
	72-h Chronic value	0.015	-	0.007

Notes: [1] Chemical may not be soluble enough to measure this predicted effect.

The TGD and EPIWIN predictions are very similar for fish and invertebrate acute toxicity. The EPIWIN software predicts a similar level of sensitivity between the three trophic levels in chronic exposures. There is no obvious pattern to the acute toxicity values, nor to the acute-to-chronic ratios.

The predictions of acute *Daphnia* toxicity using both methods agree well with the range of measured values, and the predicted chronic toxicity to *Daphnia* from EPIWIN is also very close to the measured value. Both models appear to over-predict the acute toxicity to fish; based on the predicted value, effects would have been expected in the acute fish test (although it should be noted that the actual exposure concentration was unknown). For algae the predicted chronic toxicity value from EPIWIN is similar to the measured value, but the acute toxicity prediction is over an order of magnitude lower (i.e. more toxic) than the observed value. With the exception of the EPIWIN *Daphnia* value, all the predicted values are below the solubility (0.031 mg/L) measured for a major component of the substance. It should be noted that the models do not take into account the possibility of endocrine system effects (see Section 4.1.4 and 4.1.5.2).

Other alkylphenols

Given the discrepancies noted in the QSAR analysis, it could be instructive to compare the data for the structural analogues 4-*tert*-octylphenol and nonylphenol[17], to see whether there is a common pattern of effects to help fill data gaps. These substances all share the same basic chemical structure of a phenol ring substituted in the *para*-position by an alkyl chain of varying complexity. Care must be taken not to read too much into the comparison, however, given that both nonylphenol and *para*-C_{12}-alkylphenols possess a complex mixture of chain lengths and branching patterns.

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[17] There is expected to be a small amount (less than 0.1% w/w) of C_9-alkylphenol present in the commercial substance, as indicated in Section 2.

Table 4.4 lists the most sensitive standard endpoint data for the same trophic levels (note that for fish, the species are different) for each substance (the risk assessments should be consulted for full information, see EC, 2002 and EA, 2005b). The last literature search for 4-*tert*-octylphenol took place in November 2004, whilst that for nonylphenol took place over five years ago. No additional search of data has been made for nonylphenol.

Table 4.4 Comparison of the lowest reliable acute and chronic toxicity data for 4-*tert*-octylphenol, nonylphenol and *para*-C_{12}-alkylphenols

Data			**4-*tert*-Octylphenol**	**4-Nonylphenol**	***para*-C_{12}-alkylphenols**	**Comments**
			C_8	**C_9**	**C_{12}**	
Molecular wt. (g/mole)			206.33	220.34	262.43	
Log Kow			4.12	4.48	7.14	
Water solubility at 20-25^{o}C (mg/L)			19	6	0.031	
Vapour pressure at 20-25^{o}C (Pa)			0.21	0.3	0.009	
Freshwater fish		96-h LC_{50}	0.29	0.13	≥0.5* No effects up to apparent water solubility	No obvious trend, except for lack of toxicity for *para*-C_{12}-alkylphenols.
		Early life stage NOEC	0.0061 (60-d)	0.0074 (33-d)	No data	Significant toxicity apparent. Lack of data for *para*-C_{12}-alkylphenols, but in view of persistence and bioaccumulation potential, similar effects cannot be excluded. See main text for a discussion of the acute-to-chronic ratios.
Freshwater invertebrates	*Daphnia magna*	48-h EC_{50}	0.27	0.085	0.017	Trend is increasing toxicity with molecular weight. The acute-to-chronic ratios are 4.3, 3.5 and 8.5 respectively (that for *para*-C_{12}-alkylphenols is complicated by the analytical uncertainties in the exposure concentrations).
		21-d NOEC repro.	0.062	0.024	0.002	
	Gammarus pulex	96-h EC_{50}	0.013	0.013	No data	The acute EC_{50} for *Gammarus* is comparable to the chronic NOEC for *Daphnia*, for the substances with data available. The implication is that a chronic NOEC for *Gammarus* would be even lower.
Saltwater invertebrates	*Americamysis bahia*	96-h EC_{50} $_{growth}$	0.053*	0.043	No data	The sensitivity of this organism is similar to that for *Gammarus*, and higher than that for *Daphnia*.
		28-d $NOEC_{survival}$	No data	0.0039	No data	Only nonylphenol has a long-term result for *Americamysis*. This is an order of magnitude more sensitive than the 21-d *Daphnia* result, and is also slightly lower than the long-term fish result. This result, together with an unusual result for an algal species, was used to derive the PNEC for nonylphenol (EC, 2002). The acute-to-chronic ratio is 11.
Algal growth inhibition		72-h EC_{50}	1.1*	0.32 or 1.3*	0.091	The trend in toxicity and acute-to-chronic ratios are complicated by the uncertainties in the exposure concentrations and validity of some of the tests. However, algae do not appear to be more sensitive than other organisms.
		72-h EC_{10}/NOEC	0.3*	0.025 or 0.5*	0.015	

Notes: Units are mg/L unless otherwise indicated. Data are valid unless identified as * ('use with care')

For comparative purposes, the toxicity should be expressed on a molar basis, but since the data have been obtained in different laboratories at different times, and only 4-*tert*-octylphenol is a pure substance, this is not considered essential in this case. It is the overall trend in the data that is important.

In general, 4-*tert*-octylphenol and nonylphenol show similar (i.e. within a factor of ~3) relative levels of toxicity for a particular taxonomic group (algae, invertebrates and fish) and test type (i.e. acute or chronic). Invertebrates and fish are both more sensitive than algae, although some of the algal data are uncertain because test concentrations were not confirmed analytically. Fish early life stage NOECs are lower than *Daphnia* 21-d NOECs, and certain invertebrate species are also more sensitive than *Daphnia*.

From data presented in EC (2002) and EA (2005b), acute-to-chronic ratios can be derived for two fish species - fathead minnow (*Pimephales promelas*) and rainbow trout (*Oncorhynchus mykiss*) (note: these data are not all listed in Table 4.4). The ratios are 17 for *P. promelas* (nonylphenol only) and 28 for *O. mykiss* (4-*tert* octylphenol only). Neither species has been tested with *para*-C_{12}-alkylphenols.

Daphnia appear to be more sensitive than algae to *para*-C_{12}-alkylphenols, at least for long-term end-points. The acute-to-chronic ratio for *Daphnia* is complicated by the analytical uncertainties, but it appears to be slightly higher than that for the other two substances.

There are no toxicity data for marine organisms for *para*-C_{12}-alkylphenols. The sensitivity of marine fish in acute exposures is similar to that for freshwater organisms for both 4-*tert*-octylphenol and nonylphenol (EC, 2002 and EA, 2005b). No long-term saltwater fish data are available for either substance. For nonylphenol, the saltwater shrimp *Americamysis bahia* appears to be of similar sensitivity to *Gammarus* in acute exposures, and around one order of magnitude more sensitive than *Daphnia* in chronic exposures (i.e. a similar level of sensitivity as for fish).

Endocrine effects

Both 4-*tert*-octylphenol and nonylphenol are well-studied in relation to their endocrine disruption potential in aquatic and terrestrial organisms in both *in vitro* and *in vivo* systems (e.g. Jobling and Sumpter, 1993; Jobling *et al.*, 1996; Ashfield *et al.* 1995). These studies are summarised in detail in the relevant risk assessment reports (EC, 2002 and EA, 2005b). In general, endocrine effects such as vitellogenin induction appear to occur at similar or higher concentrations to those that cause adverse effects on growth in early life stages. However, there is some evidence that aquatic snails might be particularly sensitive organisms (more so than fish, for example), although the data are currently difficult to use in the absence of standard protocols.

Direct read-across of data relating to endocrine disruption from lower chain-length alkylphenols should be avoided until the mechanism and/or mode of action of such effects have been established – structural similarity of a substance is insufficient to predict either the extent of activity or effects in this area of physiology. Results from a screening level test of endocrine disruption potential for the commercial substance in suitable organisms would help to fill this data gap and provide some reassurance for this assessment, particularly in view of the substance’s apparent persistence and moderate bioaccumulation potential.

Summary of structural analogue comparison

The evidence from similar substances suggests that both fish and the invertebrates *Gammarus* and *Americamysis* could be significantly more sensitive to *para*-C_{12}-

alkylphenols than *Daphnia* in chronic tests. These issues are considered further in the PNEC derivation and risk characterisation sections (Sections 4.1.7 and 5 respectively).

4.1.6 Wastewater treatment plant micro-organisms

A study of the inhibitory effects of tetrapropenylphenol on sewage treatment plant microbes was carried out following OECD test guideline 209 (Clarke, 2005). The sludge used in the test was taken from a sewage treatment plant treating predominantly domestic sewage. Test concentrations of 1.1 mg/L and 1,000 mg/L were used (prepared using a stock solution in acetone), with an exposure of 3 hours. There were no effects on the respiration of the activated sludge in either experiment. Therefore the 3-h NOEC is ≥1,000 mg/L.

4.1.7 Predicted no-effect concentrations for the aquatic compartment

Calculation of a PNEC for surface water

In principle, the PNEC is calculated by dividing the lowest short-term median lethal (effect) concentration, L(E)C_{50}, or long-term NOEC[18] value by an appropriate assessment factor. The assessment factors reflect the degree of uncertainty in extrapolation from laboratory toxicity test data for a limited number of species to the real environment. Lower assessment factors can be used with larger and more relevant data sets, for example if data are available on the toxicity to organisms at a number of trophic levels, belonging to taxonomic groups and with lifestyles representing various feeding strategies. These issues are discussed in detail in the TGD.

A summary of the available toxicity data is provided in Sections 4.1.1-4.1.6. Acute toxicity results are available for fish, invertebrates and algae (although the fish data are not fully valid, comparison with other alkylphenols suggests that fish are not likely to be more sensitive than other trophic levels in acute tests). Long-term toxicity results are also available for invertebrates and algae, with the lowest value being a 21-day NOEC of 0.002 mg/L (2 µg/L) for *Daphnia magna*. This is around an order of magnitude lower than the NOEC from the algal test.

The TGD suggests that an assessment factor of 50 can be applied to the lowest of two NOECs that cover two trophic levels, provided that the NOECs cover the level showing the lowest L(E)C_{50} in the short-term tests (in this case, *Daphnia*). Applying this to the 21-day *Daphnia* NOEC gives a $PNEC_{aquatic}$ of 4×10^{-5} mg/L (0.04 µg/L).

It is relevant to consider the size of the assessment factor in relation to the data sets available for the structural analogues 4-*tert*-octylphenol and 4-nonylphenol, although the fact that only 4-*tert*-octylphenol is a pure substance complicates the analysis.

The highest acute-to-chronic ratio observed in fish is 28 (for 4-*tert*-octylphenol). Applying a ratio of 30 to the water solubility of the main component of *para*-C_{12}-alkylphenols (31 µg/L) would imply a chronic fish NOEC of around 1 µg/L, which is comparable to the 21-day *Daphnia* NOEC. This could be used in an argument to lower the assessment factor. However, given that *para*-C_{12}-alkylphenols might bind to

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[18] Algal studies are considered to be multigenerational: the TGD recommends that 72-hour (or longer) EC_{50} values for algal growth are considered equivalent to a short-term result, and that a 72-hour (or longer) NOEC is considered as a long-term result.

endocrine receptors with a greater potency than octylphenol (see Section 4.1.4), the fish NOEC could potentially be lower. It should also be noted that the acute-to-chronic ratio for *Daphnia* for *para*-C_{12}-alkylphenols is higher than that for 4-*tert*-octylphenol and 4-nonylphenol by a factor of ~2, which could also be the case with fish. The analogue substances are also generally more toxic to fish than to *Daphnia* during long-term exposures by about one order of magnitude.

In addition, there is evidence from both 4-*tert*-octylphenol and nonylphenol that certain aquatic invertebrates (e.g. *Americamysis* and possibly aquatic snails) might be around an order of magnitude more sensitive than *Daphnia* over long-term exposures (i.e. a similar sensitivity as for fish) (see Section 4.1.5.2).

It could therefore be argued that the assessment factor of 50 might not be sufficiently protective. This is considered further in the risk characterisation section.

Other data exist for 4-dodecylphenol (CAS no. 104-43-8), with a 96-hour EC_{50} of 0.14 mg/L for fish, and a 96-hour LC_{50} value of 0.15 mg/L for the saltwater sand shrimp *(Crangon septemspinosa*) (both 'use with care'). *Daphnia* are still more sensitive, and the PNEC is considered sufficiently protective of these.

A PNEC for marine waters has also been estimated (see Appendix 3) as 0.004 µg/L.

Calculation of PNEC for sediment

No toxicity data are available for sediment-dwelling species. As a first screen, an equilibrium partitioning method may be used to estimate the $PNEC_{sediment}$. It is assumed that sediment-dwelling organisms and water column organisms are equally sensitive to dodecylphenol and that the concentration in sediment, interstitial water and benthic organisms is at thermodynamic equilibrium.

The following formula is used to derive the $PNEC_{sediment}$ from the $PNEC_{aquatic}$:

$$PNEC_{sediment} = \frac{K_{susp\text{-}water} \times PNEC_{aquatic} \times 1000}{RHO_{susp}}$$

where $PNEC_{aquatic}$ is 0.04 µg/L

$K_{susp\text{-}water}$ is the suspended matter-water partition coefficient (2,750)

RHO_{susp} is the bulk density of suspended matter (1,150 kg/m^3).

The provisional $PNEC_{sediment}$ is therefore 0.096 mg/kg (96 µg/kg) wet weight. A PNEC for marine sediments has also been estimated (see Appendix 3) as 9.6 µg/kg wet weight.

Calculation of PNEC for WWTP micro-organisms

An activated sewage sludge respiration inhibition test gave a 3-h NOEC ≥1,000 mg/L. The TGD recommends that an assessment factor of 10 is applied in such cases, and so the $PNEC_{WWTP}$ is ≥100 mg/L. This is consistent with data for lower alkylphenols (e.g. the $PNEC_{WWTP}$ for nonylphenol is 9.5 mg/L (EC, 2002)).

4.2 Terrestrial compartment

4.2.1 Terrestrial toxicity data

No experimental toxicity data are available.

4.2.2 Calculation of PNEC for the soil compartment

In the absence of data for terrestrial effects, a provisional $\mathrm{PNEC_{soil}}$ can be calculated using the $\mathrm{PNEC_{aquatic}}$ and an equilibrium partitioning approach. It is assumed that soil-dwelling organisms and water column organisms are equally sensitive to *para*-C_{12}-alkylphenols and that the concentration in soil, pore water and soil organisms is at thermodynamic equilibrium. It is recognised that this is a relatively crude screening approach. The following formula is used:

$$\mathrm{PNEC_{soil}} = \frac{K_{\mathrm{soil\text{-}water}} \times \mathrm{PNEC_{aquatic}} \times 1000}{\mathrm{RHO_{soil}}}$$

where $\mathrm{PNEC_{aquatic}}$ is 0.04 µg/L

$K_{\mathrm{soil\text{-}water}}$ is the soil–water partition coefficient (3,300)

$\mathrm{RHO_{soil}}$ is the bulk density of wet soil (1,700 kg/m^3).

The provisional $\mathrm{PNEC_{soil}}$ is therefore 78 µg/kg wwt.

4.3 Atmospheric compartment

There are no data on the effects of *para*-C_{12}-alkylphenols through aerial exposure of non-mammalian organisms. Direct emissions to the atmosphere are likely to be very low. Biotic or abiotic effects are unlikely to occur because of the limited release, low volatility and rapid atmospheric degradation of *para*-C_{12}-alkylphenols. A PNEC has therefore not been derived.

4.4 Mammalian toxicity

The available mammalian toxicity data have been collected and reviewed for the OECD HPV programme (SIAR, 2006).

4.4.1 Toxicokinetics

No toxicokinetic studies are available. Deaths in rabbits observed at high doses (>3000 mg/kg) in an acute dermal toxicity study suggest that some dermal absorption occurs. Evidence for target organ toxicity observed following oral dosing indicates that absorption occurs across the gastrointestinal tract.

4.4.2 Acute toxicity

Studies in animals

Inhalation

There are no single exposure inhalation studies in animals.

Oral

Acute toxicity data for the oral route of exposure are available for the rat only. LD_{50} values of 2,100 and 2,200 mg/kg were obtained in two separate studies. In one study, no deaths were observed with a single oral dose of 500 mg/kg but one rat at this dose level showed bloody urine that persisted for 48 hours post-dosing. A NOAEL for the effects of a single oral dose cannot be determined. Signs of toxicity observed in the acute oral toxicity studies included ruffled fur, diarrhoea, diuresis, retarded motion and ataxia.

Dermal

Two studies are available, both in rabbits. The findings indicate that deaths occur with doses above 3,160 mg/kg, and an LD_{50} of 15,000 mg/kg has been reported.

Studies in humans

No data are available.

Summary of acute toxicity

Acute toxicity data are available from animal studies employing the oral and dermal routes only. The findings reveal oral and dermal LD_{50} values of around 2,000 and 15,000 mg/kg respectively. There are no single exposure inhalation studies available.

4.4.3 Irritation

Studies in animals

Skin

Studies in rabbits indicate that tetrapropenylphenol is a severe skin irritant.

Eye

Studies in rabbits indicate that tetrapropenylphenol is an eye irritant capable of causing corneal opacity and iritis.

Respiratory tract

No data are available concerning respiratory tract irritancy. Given the evidence for skin and eye irritancy, it might be expected that inhaled tetrapropenylphenol would irritate the respiratory tract.

Studies in humans

No human data are available concerning the irritant potential of the substance to the skin, eyes or respiratory tract.

Summary of irritation

Studies in animals reveal that tetrapropenylphenol is a severe skin irritant and a moderately severe eye irritant capable of inducing corneal opacity and iritis.

4.4.4 Corrosivity

Necrosis and eschar formation have been reported following dermal application of tetrapropenylphenol to rabbits. From the data available it is uncertain whether or not tetrapropenylphenol should be regarded as corrosive or as a severe skin irritant.

4.4.5 Sensitisation

Studies in animals

Tetrapropenylphenol was not identified as a cause of skin sensitisation in two studies in guinea pigs.

Studies in humans

No data are available.

Summary of sensitisation

The available data suggest that tetrapropenylphenol is not a skin sensitiser. There are no data concerning the potential to cause respiratory sensitisation.

4.4.6 Repeated dose toxicity

Studies in animals

Inhalation

No data are available.

Oral

A 28-day oral gavage study in rats, a 28-day and a 90-day dietary study in rats and a 13-week dietary study in dogs are available.

In the 28-day gavage study in rats, doses of 0, 5, 20, 60, 180 and 300 mg/kg/day were given. Treatment-related adverse effects were more prominent in males than in females. The key target organs affected in males were the testes, adrenal cortex, liver and thyroid. In females, the ovaries were affected, with reductions in mean ovary weights accompanied by a reduction in the number of corpora lutea. In males at 180 and 300 mg/kg/day, mean increases in absolute weights of the adrenal cortex of 69 and 91% were observed. At 20 and 60 mg/kg/day there were no increases in adrenal gland weight, but at doses of 20 mg/kg/day and above there was an increased incidence (0/5, 0/5, 2/5, 2/5, 5/5 and 5/5 at doses of 0, 5, 20, 60, 180 and 300 mg/kg/day respectively) and severity (from minimal to mild) of adrenal gland hypertrophy. For effects on the gonads in both sexes, treatment-related effects were apparent at 180 mg/kg/day and above. The effects on the thyroid in males (follicular cell hypertrophy), were seen at all dose levels, but were not seen in other studies including a one-generation fertility study in rats. Overall, the toxicological significance of the effects on the thyroid in male rats is uncertain but it is unlikely to be of any relevance to human health.

A NOAEL for this study can be identified at 5 mg/kg/day based on an increased incidence of adrenal cortical gland hypertrophy (2/5 male rats) at 20 mg/kg/day.

In the 28-day dietary study in rats, a sex difference in response to treatment was also seen, although there were differences in the pattern of findings compared to the gavage study. The dietary doses in this study were equivalent to 0, 25, 125 and 250 mg/kg/day. At the lowest dose no treatment-related effects were observed. At 125 mg/kg/day and above, terminal body weights were reduced in males and females. A decrease in the reticulocyte count in males only, congestion of the spleen in 1/10 males only, and an increased kidney weight in females only were also observed. At the highest dose of 250 mg/kg/day additional effects on both sexes included kidney mineralisation, increased liver weights, liver periportal vacuolization, splenic congestion and bone marrow hypoplasia of minimal severity, marked reductions in reticulocyte count (65%), slight reductions in haematocrit and mean corpuscular haemoglobin, and prominent effects on the male reproductive organs. Also at the high dose, the adrenal gland weight was increased in males (by 19%) and decreased in females (by 14%). The female reproductive organs did not appear to have been examined. Overall, the NOAEL for this study was 25 mg/kg/day based primarily on reductions in body weight gain at the next higher dose of 125 mg/kg/day.

In the 90-day dietary study, doses equivalent to 0, 27, 106 and 217 mg/kg/day in males, and 0, 28, 104 and 228 mg/kg/day in females were employed. No treatment-related changes were observed at the low dose. At the mid-dose and above, there were reductions in food consumption and mean body weight gains. Also at the mid-dose, there were microscopic changes in the testes including hypospermia in 2/20 males. At the high dose, reductions in relative liver weight were seen in males (15%) and females (14%) but there were no microscopic changes in the liver. Also at the high dose, there were reductions in absolute testes weight (by 36%) and in relative testes weight (not specified in the SIAR). Other changes in the testes included atrophy and hypospermia. The mean ovary weight reduced by 21% at the top dose, but no microscopic findings were reported. The NOAEL for this study is 27 mg/kg/day based on reduced body weight gains and effects on the testes at the next higher dose of 106 mg/kg/day.

In the 13-week dietary study in dogs, no treatment-related changes were observed at any dose, the highest dose tested being 4,000 ppm in the diet.

Dermal

No data are available.

Studies in humans

No data are available.

Summary of repeated dose toxicity

Repeated dosing of tetrapropenylphenol to rats in oral studies, both dietary and gavage, produces effects in a number of organs including the reproductive organs in both sexes.

In the 28-day gavage study in rats, no toxicologically significant treatment-related effects were observed at 5 mg/kg/day. At the next higher dose of 20 mg/kg/day, adrenal cortical gland hypertrophy was observed in male rats. At 180 mg/kg/day and above, pathological changes and organ weight changes were observed in a number of organs, including prominent changes in the reproductive organs in both sexes.

In the dietary studies, effects on the testes were noted at 250 mg/kg/day (28-day study) and 106 mg/kg/day (90-day study). No treatment-related toxicological effects were seen in the dietary studies at 25 and 28 mg/kg/day respectively.

No treatment-related changes were reported in dogs at doses up to 4,000 ppm in the diet (estimated by the author to be equivalent to 180 mg/kg/day assuming a body weight of 11 kg and a daily food consumption of 0.5 kg). The absence of treatment-related changes in dogs suggests the existence of a species difference.

4.4.7 Mutagenicity

In vitro studies

Bacterial studies

Negative results were obtained in two separate Ames tests.

Mammalian cell studies

Negative results were obtained in a mammalian cell gene mutation assay in Chinese Hamster Ovary cells.

In vivo studies

No increases in chromosome aberrations were reported in a rat bone marrow cytogenetic assay in which the top dose was 5,000 mg/kg/day.

Studies in humans

No data are available concerning mutagenic potential in humans.

Summary of mutagenicity

From the *in vitro* and *in vivo* studies available it can be concluded that tetrapropenylphenol is not mutagenic.

4.4.8 Carcinogenicity

Studies in animals

There are no studies in which the carcinogenic potential of tetrapropenylphenol has been investigated in animals.

Studies in humans

There are no studies in which the carcinogenic potential of tetrapropenylphenol has been investigated in humans.

Summary of carcinogenicity

There are no carcinogenicity studies available for tetrapropenylphenol. Given the lack of evidence for mutagenicity it is likely that if tetrapropenylphenol had the potential to cause cancer it would involve a threshold mechanism. It is uncertain whether or not the effects on the uterus and the endometrial gland cysts in the one-generation fertility study at the top dose of 125 mg/kg/day indicate the possibility of uterine cancer at these sites following prolonged exposure.

4.4.9 Toxicity for Reproduction

Effects on fertility

Studies in animals

A one-generation study in rats is available in which rats were dosed with 0, 5, 25 or 125 mg/kg/day by oral gavage. There were no effects on mating behaviour, fertility or mean litter size at 5 and 25 mg/kg/day. At 125 mg/kg/day fertility reduced; only 4/30 pairs of rats copulated resulted in a pregnancy compared to 28/30 controls. Mean litter size was reduced to 1.7 pups per litter at 125 mg/kg/day compared to 13 pups per litter in controls. Offspring at 25 mg/kg/day showed statistically significantly reduced body weight gain compared to controls between post-natal days 4-21. Pup body weight gain was not reported for the 125 mg/kg/day dose group.

Females showed an increased incidence of ovarian cysts with a frequency of 4/30, 8/30, 7/30 and 15/30 at 0, 5, 25 and 125 mg/kg/day respectively, but only the frequency in the top dose group was statistically significant. Mean ovary weight was statistically significantly reduced at 25 and 125 mg/kg/day.

There were a number of treatment-related changes to male reproductive organs with effects becoming statistically significant at 25 mg/kg/day and above. Effects included reduced weights of testes, seminal vesicles, coagulating glands and caudal epididymes, and a reduction in mean epididymus sperm concentration.

In the parental generation there were reductions in food consumption, body weight gain and terminal body weights at 25 mg/kg/day and above. In males at 125 mg/kg/day there were increases in the weight of the adrenal gland with hypertrophy of the adrenal cortex. Mineralisation of the kidney was also seen in males at 25 and 125 mg/kg/day and at 125 mg/kg/day in females. Mean liver weight was reduced in males at 125 mg/kg/day only, and in females at 25 and 125 mg/kg/day.

Overall, a NOAEL of 5 mg/kg/day is identified for this study. At the next higher dose of 25 mg/kg/day there were reductions in pup body weight gain, and in the parental generation there were pathological changes to the male and female reproductive organs, reduced body weight gain and effects on the kidneys and liver.

Studies in humans

No studies on the effect of tetrapropenylphenol on fertility in humans are available.

Developmental toxicity

Studies in animals

A developmental study in rats is available in which pregnant females were dosed by oral gavage with 0, 20, 100, 300 and 500 mg/kg/day during gestation days 6-15. Based on a 31% incidence of mortality at 500 mg/kg/day this exposure group was terminated. There were no effects on maternal toxicity, embryo- or fetotoxicity at the low dose of 20 mg/kg/day. At 100 mg/kg/day, the only finding of possible note was a statistically significant increase in the total number of skeletal variations with a fetal incidence of 92/145 compared to 71/144 in controls. However, there was no difference in total skeletal variations in terms of litter incidence (24/24 in controls versus 23/23 at 100 mg/kg/day). It is uncertain whether or not the effect on the total number of skeletal variations at 100 mg/kg/day is toxicologically significant.

At 300 mg/kg/day there was a statistically significant reduction in maternal body weight gain (by 62%) and in food consumption during the dosing period (by around 15-22%); post dosing body weights recovered such that mean terminal body weight was about 8% less than controls (not statistically significant). At this dose there was clear evidence of developmental toxicity, as indicated by an increased incidence of uterine resorptions (4 versus 0.8 in controls) and a statistically significant reduction in mean litter size (8.9 versus 12.9 in controls) and reduced foetal body weights (around 8% compared to controls). In addition there was an increased incidence of skeletal malformations both in terms of total number (23/103 versus 0/144 in controls) and litter incidence (12/23 versus 0/24 in controls). The most commonly identified skeletal malformation included wavy ribs (23/103 versus 0/144 in controls, litter incidence 12/23 versus 0/24 in controls) and curved scapula and scapula spine (10/103 versus 0/144 in controls, litter incidence 6/23 versus 0/24 in controls). Ectrodactyly was observed in two foetuses from separate litters and cleft palate was present in three foetuses from one litter (no historical control data available). Notably the female whose litter contained the foetuses with cleft palate had considerable weight loss (-18g) during the treatment period indicating significant maternal toxicity.

A NOAEL for developmental toxicity of 100 mg/kg/day can be identified (assuming that the increased incidence of skeletal variations at this dose can be discounted on the grounds that the increase was per fetus rather than per litter). The NOAEL for maternal toxicity in this study is 100 mg/kg/day. It is uncertain whether or not the decreased food consumption at 300 mg/kg/day was related to palatability. There was clearly maternal toxicity at this dose level as indicated by a marked reduction in maternal body weight gain in the early part of the study, although the terminal body weights of the dams were not statistically significantly different from controls (suggesting that the maternal toxicity was not extreme).

The findings of cleft palate and ectodactyly are very rare as spontaneous findings in rats and cannot be attributed to non-specific effects of maternal toxicity. Hence, these results show that tetrapropenylphenol is a developmental toxicant in rats.

Studies in humans

No studies of the potential effects of tetrapropenylphenol on development in humans are available.

Summary of toxicity for reproduction

Tetrapropenylphenol has an adverse effect on fertility in rats, causing a marked reduction in fertility at 125 mg/kg/day. At doses of 25 mg/kg/day and above tetrapropenylphenol causes a reduction in mean pup weight and pathological changes in the reproductive organs of both sexes. The reduction in fertility and effects on reproductive organs occurred at doses that also caused other toxic effects, including reduced bodyweight gain and food consumption and changes in the adrenals, kidneys and liver. However, this toxicity was not considered to be particularly severe such that the adverse effects on fertility could have been a secondary non-specific consequence of general toxicity. The NOAEL for reproductive effects is 5 mg/kg/day.

Tetrapropenylphenol is also a developmental toxicant in rats, causing teratogenic effects as shown by cleft palate and ectodactyly (reduced number of digits) as well as a general increase in the total number of skeletal malformations at 300 mg/kg/day. These manifestations of developmental toxicity occurred in the presence of overt maternal toxicity, indicated by a significant reduction in body weight gain.

4.4.10 Derivation of PNECoral for secondary poisoning

A number of results are available from which a $PNEC_{oral}$ could be derived using an appropriate assessment factor in accordance with the TGD. Where there are results from similar studies but of differing duration, the assessment factor relevant for the longer duration has been applied where the results are similar. Hence an assessment factor of 90 (for 90-day studies) is considered to be appropriate for the 28- and 90-day dietary studies. A factor of 30 is appropriate for the results of the one-generation reproduction test. For all of these studies a conversion factor of 20 has been used to convert from a dose to a concentration in food. The resulting values are:

28-day dietary study, NOAEL 25 mg/kg/day:	$PNEC_{oral}$ = 5.6 mg/kg
90-day dietary study, NOAEL 27 mg/kg/day:	$PNEC_{oral}$ = 6 mg/kg
1-generation reproduction study, NOAEL 5 mg/kg/day:	$PNEC_{oral}$ = 3.3 mg/kg

These are all of a similar order of magnitude, but the lowest value of 3.3 mg/kg is preferred for the risk characterisation since it is based on a study of reproductive effects.

4.5 Mode of action

For aquatic toxicity, *para*-C_{12}-alkylphenols fall into the category of polar narcotics as defined by the OECD. However, this classification does not provide an indication of the actual mode of toxic action at a cellular level. A number of mechanisms disrupt cellular function and produce toxicity. The standard toxicity data do not provide any indication of exactly which systems are being affected.

4.6 Hazard classification

4.6.1 Classification for human health

None of the substances described by the CAS or EINECS numbers listed in Table 1.1 are currently classified with respect to human health on Annex 1 of Directive 67/548/EEC. Since there is no agreed harmonised classification, it is the responsibility of the supplier to self-classify.

Based on the toxicological findings presented in this review, *para*-C_{12}-alkylphenols do not appear to meet the EU criteria for classification for acute toxicity by the oral and dermal routes of exposure, skin sensitisation, repeated dose toxicity or mutagenicity. No information is available relating to acute toxicity via inhalation exposure, and carcinogenicity.

The following characteristics do suggest that the substance warrants consideration for classification:

Irritation

para-C_{12}-alkylphenols apparently meet the EU criteria for classification as a skin irritant and a severe eye irritant. Classification for corrosivity could be considered.

Reproductive toxicity

- Fertility: The treatment-related effects on fertility, with supporting pathological changes indicating site of action, appear to meet the EU criteria for classification. The observation that the fertility effects only occurred in the presence of general toxicity might need to be taken into account in deciding the most appropriate category. Overall, these findings suggest that category 2 classification for acute toxicity may be most appropriate, although arguments for category 3 might be considered.
- Developmental toxicity: *para*-C_{12}-alkylphenols caused craniofacial (cleft palate, 3 pups from 1 litter) and long bone malformations (bent long bones) in rats, but only at doses that caused some non-specific maternal toxicity (reduced body weight gain). These findings are not considered to be a secondary non-specific consequence of general toxicity and hence classification for developmental toxicity should be considered. A decision on whether category 2 or 3 is most appropriate may need expert consideration.

A formal proposal for a harmonised human health classification will be discussed at a European Commission Working Group on classification later in 2007.

4.6.2 Classification for the environment

The substance is classified by the producers as ‘dangerous to the environment’ (with the symbol N) with the following risk phrases:

R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

This is based on the following data:

- Aquatic toxicity: 48-hour *Daphnia* EC_{50} <1 mg/L;
- log K_{ow} >3 and measured fish bioconcentration factor of 823;
- Not readily biodegradable.

This classification was agreed at a European Commission Working Group on environmental classification in January 2007.

4.7 PBT assessment

With marine risk assessment, the TGD requires an assessment of whether a substance may be considered to be persistent (P), bioaccumulative (B) and toxic (T). Substances that have this combination of properties are considered to pose a special risk to remote environments (such as the open ocean), because they could be transported long distances and accumulate in food chains. The aim of public policy and regulation with such chemicals is to reduce environmental exposures arising from human activities to zero.

The PBT assessment for *para*-C_{12}-alkylphenols against the TGD criteria is presented in Appendix 3. In summary, *para*-C_{12}-alkylphenols are considered to clearly meet the T criterion, and are likely to meet the P and vP criteria with a reasonable degree of confidence. The B criterion is not met, and so *para*-C_{12}-alkylphenols are not considered to be PBT substances according to the EU criteria.

It may be noted that the substance still meets the Chemical Stakeholder Forum’s criteria for substances of concern (though not of highest concern) based on the measured BCF value of 823 (which is above the lower tier criterion of 500).

5 Risk characterisation

The following sections characterise risks for the aquatic, terrestrial and atmospheric compartments and the risk of secondary poisoning of predators in the food chain. The risk characterisation is performed by comparing the PECs with the PNECs to derive a risk characterisation ratio (RCR). An RCR of less than 1 implies that any risk resulting from that level of exposure is acceptable. An RCR above one implies a potential risk, and all such values are highlighted in bold in the following tables.

5.1 Aquatic compartment

5.1.1 Surface water and sediment

para-C_{12}-alkylphenols enter the aquatic compartment directly due to industrial releases of the substance itself, and indirectly due to the use of derivatives (through the presence of the substance as an impurity). The RCRs for the aquatic compartment are shown in Table 5.1.

Table 5.1 PECs and RCRs for the aquatic compartment

Life cycle stage		PECs for surface water (µg/L)	RCR for surface water	RCR for sediment
Production of the substance	Site C	<5.8	**<145**	**<1,450**
Lubricant blending		0.016	0.4	**4.1**
Phenol/formaldehyde resin production		0.13	**3.2**	**32**
Resins – ink formulation		0.13	**3.2**	**32**
Resins – tyre production		0.30	**7.5**	**75**
Resins – varnish use		0.014	0.4	**3.6**
Regional		0.007	0.2	**1.7**

Notes: $PNEC_{aquatic}$ = 0.04 µg/L; $PNEC_{sediment}$ = 96 µg/kg wwt

On the basis of the available information, potential risks for surface water are identified for most of the lifecycle stages, with the exception of lubricant blending and resin use in varnishes (there is also no risk from the regional background concentration).

All scenarios indicate a risk for the sediment compartment, including the regional background concentration. Since both the PEC and PNEC for sediment were derived by equilibrium partitioning, the RCRs for water and sediment might be expected to be the same. However, organisms might experience significant additional exposure to a chemical from sediment ingestion in cases where the log K_{ow} value is above 5. In such cases, the RCR for sediment is multiplied by a factor of 10 as a precaution, in accordance with the TGD.

Only one study has reported results from aquatic monitoring, in Sweden. The substance (4-dodecylphenol) was not detected at a limit of 4-6 ng/L in water samples, which is below the PNEC, so these results indicate no risk at the locations sampled. The same conclusion applies to the sediment samples (the maximum reported concentration was 38 ng/g dry weight, equivalent to 15 µg/kg wet weight (assuming the TGD sediment properties), which is below the sediment PNEC).

Uncertainties and possible refinements

Emissions and exposure

Emissions

All the predicted concentrations are based to some extent on default values and so could be refined.

The high RCRs for Site C may be misleading – the substance has not been detected in site effluent, and the PECs are an upper limit based on the detection limit of the analytical method. They could therefore be substantially lower and measurements with a significantly lower detection limit would allow the calculations to be refined[19].

Two of the sites involved in lubricant additive manufacture (A and B) have discharges at estuarine locations and are therefore included in the marine risk assessment in Appendix 3. No information has been provided about the locations of the remaining 2-3 sites in Europe, although they are not in the UK. A freshwater scenario has therefore been omitted from this assessment for this life cycle stage, but this could be investigated further.

The lubricant blending concentrations are based on the properties of the substance and calculations based on the processes used. It may be possible to refine these through specific measurements on releases from blending, although the emissions estimated from this step are low.

The estimates of releases from lubricants in use and on disposal are based on survey information from the early 1990s, included in an emission scenario document (OECD, 2004). More recent information from Canada (BearingPoint, 2005) shows a similar level of used oil recovery (for use as fuel, etc.) to that in the ESD, so the current situation would not appear to be significantly different. The use and disposal of lubricants are the major source of emissions to the regional environment, but with little impact on the local concentration estimates.

The releases from the production of resins and from most of their uses are estimated using the default emission factors from the Technical Guidance Document, and could therefore be revised with more specific information. The estimates of release from tyre production are based on the emission scenario for the rubber industry included in the TGD. The amounts used at sites for which the local concentrations are calculated are also estimated using the default methods in the TGD. It is unknown whether these default values are realistic for the different industries. The risk calculations also assume that 3% of the substance is residual in the resin; more specific information on residual concentrations could refine the assessment.

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[19] A single effluent sample has recently been analysed with a new analytical method, and the substance concentration was found to be 0.5 µg/l. The corresponding surface water PEC is ~0.01 µg/l, based on typical low-flow dilution, which gives a freshwater RCR of 0.24. The sediment RCR is still a concern (2.4). Further monitoring of effluent, as well as sediment, would be useful.

Persistence

This assessment treats *para*-C_{12}-alkylphenols as not biodegradable. The available test results show some degree of degradation, but not enough to record a positive result in a ready or inherent test. Testing of degradation under realistic environmental conditions could provide half-lives to use in the regional calculations. However, as the regional concentration does not show a risk for water and does not contribute significantly to any of the local PEC values that do show a risk, then this refinement would not affect the current conclusions.

Degradation in sediment, however, is more relevant; an accurate measurement would help to refine the regional sediment concentration, which is flagged as a risk. Nevertheless, even if the substance were considered to be inherently degradable in the environment, there would be little change to the regional or local concentrations for any environmental compartment (see Appendix 1).

More detailed information on the degradation and removal of the substance in WWTP could have an influence on the local concentrations. Measurements made at an actual production/use site show removal of 99.3% from the influent waste water. This value cannot be applied to waste water treatment in general, as it is likely that the microbial population in this particular WWTP has adapted to the substance. The default calculation results in 11.3% of the substance in the effluent water, and so a higher removal rate would lead to lower concentrations in water. Any direct measurements would need to determine whether removal was by degradation or sorption to sludge (the latter would of course increase the amount of substance going to land). These alterations could have an impact on some of the scenarios discussed (see Appendix 1).

Monitoring

The available data on measured levels in the environment are limited. Measurements at locations where the substance is used, as well as at a wider range of background locations, would help to show whether the concentrations calculated in this assessment are realistic and reflective of actual environmental conditions.

Effects

The PNEC for water is derived from two chronic NOEC values, using an assessment factor of 50. However, there could be arguments to raise this factor, since other organisms might be significantly more sensitive than *Daphnia* over chronic exposures (see Section 4.1.7.1). This in turn would increase the risk characterisation ratios.

To establish a more reliable PNEC, the following additional data could be gathered:

- A chronic toxicity test with the invertebrate *Americamysis bahia*.
- In the interests of animal welfare, it may be possible to screen *para*-C_{12}-alkylphenols for endocrine activity using structure-activity models and the various *in vitro* cell line and reporter gene assays available for various hormone receptors (e.g. estrogen, androgen and thyroid). This would allow a better mechanistic comparison with well-researched analogue compounds and, potentially, a more confident prediction of *in vivo* effects in fish. However, to remove any uncertainty that this approach would entail, it might be more straightforward to conduct a suitable fish toxicity test (e.g. an extended early life stage test; depending on the result a reproduction test might also be warranted).

The main drawback with further long-term toxicity testing with pelagic organisms is the difficulty in maintaining exposure concentrations, and the potential difficulty in analysing for very low concentrations. In addition, such testing alone will not be sufficient to remove all of the risks for water, since any RCR above 5 in Table 5.1 would still show a risk even with the minimum assessment factor of 10 (this applies to the use of resins in tyre production, and possibly site C).

All of the scenarios show a risk for sediment. There are no data on toxicity in sediment organisms, so the equilibrium partitioning method is used to derive the PNEC. An additional factor of 10 is applied to the PEC/PNEC ratios to account for possible uptake from the solid phase of the sediment. Further testing on pelagic organisms would not remove this additional factor; hence the concerns for the sediment compartment would remain. Results from testing on sediment organisms could be used directly without the additional factor. Three long-term tests would probably be required.

Summary

The most important data that could lead to a refinement of the aquatic assessment are:

- better information on releases;
- prolonged toxicity tests on sediment organisms.

Other information could be useful, such as:

- data on the fate of the substance in actual municipal WWTP (not dedicated industrial plants) or from studies modelling such plants;
- more extensive monitoring data targeted to areas where the substance is used, as well as for the background.

Further long-term toxicity testing on fish and other aquatic organisms could be performed, although this work would not be sufficient by itself to remove the current concerns for surface water.

5.1.2 Wastewater treatment plant micro-organisms

The PECs and RCRs for WWTP micro-organisms are shown in Table 5.2. A PEC has not been estimated for Site C.

Table 5.2 PECs and RCRs for WWTP

Life cycle stage		PECs for WWTP (mg/L)	RCR for WWTP
Production of the substance and lubricant additive manufacture	Site A*	3.3×10^{-3}	<0.01
Lubricant blending		1.1×10^{-4}	<0.01
Phenol/formaldehyde resin production		1.4×10^{-3}	<0.01
Resins – ink formulation		1.4×10^{-3}	<0.01
Resins – tyre production		3.4×10^{-3}	<0.01
Resins – varnish use		8.7×10^{-5}	<0.01

Notes: $PNEC_{WWTP} \geq 100$ mg/L
* Site B appears not to have releases via WWTP.

No risks to WWTP micro-organisms are identified for any life cycle stage.

5.1.3 Marine waters and sediment

A marine risk assessment has been carried out (see Appendix 3). Based on the available information, the results suggest that the substance might pose a significant risk to marine waters and sediments from all stages of the substance's life cycle. Two sites are known to discharge effluent to an estuarine environment.

PBT assessment

para-C_{12}-alkylphenols clearly meet the T criterion, and are likely to meet the P and vP criteria with a reasonable degree of confidence, but do not meet the B and vB criteria.

Uncertainties and possible refinements

Information on the location of the sites that undertake the industrial applications considered by this assessment (especially the larger scale processes) would allow a more detailed analysis of the possible routes to the marine environment.

Both the PEC and the PNEC assessments rely on the same data as for freshwater. The same limitations apply, and so the refinements are also the same (except that information on the fate of the substance in waste water treatment is not relevant). A chronic toxicity test with *Americamysis* would provide a measure of toxicity for a saltwater organism.

5.2 Terrestrial compartment

Direct releases of *para*-C_{12}-alkylphenols to the terrestrial compartment are unlikely to occur given its production method and use pattern. However, exposure may occur because of the application of sewage sludge from some processes that use the substance (or its derivatives) and discharge aqueous effluent to water. The RCRs for the terrestrial compartment are shown in Table 5.3. Similar to sediment, RCRs have been increased by a factor of 10 in line with the TGD because the log K_{ow} is greater than 5 and the equilibrium partition method is used to derive the PNEC.

Table 5.3 PECs and RCRs for the terrestrial compartment

Life-cycle stage	PECs for soil (mg/kg wwt)	RCR for soil
Production of the substance and lubricant additive manufacture [a]	-	-
Lubricant blending	0.025	**3.7**
Phenol/formaldehyde resin production	0.37	**48**
Resins – ink formulation	0.37	**48**
Resins – tyre production	0.89	**114**
Resins – varnish use	0.023	**3**
Regional (agricultural soil)	0.05	**6.5**

Notes: $PNEC_{soil}$ = 0.078 mg/kg wwt (by equilibrium partitioning).

a - Sites A, B and C do not give rise to risks because there is no land spreading of sludge.

Lubricant blending and all of the resin applications indicate a potential risk for soil organisms. There is also a risk for the regional agricultural soil.

Uncertainties and possible refinements

Like the aquatic assessment, there are significant uncertainties in the risk characterisation for the terrestrial environment. Both the environmental releases and PNECs are based on those for the aquatic compartment, and these have uncertainties (see Section 5.1.1.2). There are no monitoring data to confirm the predicted levels. The releases to waste water are responsible for the concentrations in sludge, which lead to the risks for the terrestrial compartment. The comments on improving the emission estimates for the water compartment are therefore directly relevant for the terrestrial compartment as well. Measurements of concentrations in sludges from WWTP would also be useful.

Any refinement to the PNEC for surface water will also have a direct effect on the PNEC for soil organisms derived by the equilibrium partitioning method, but the additional assessment factor of 10 would remain. Since the substance is expected to partition to soil, direct testing with soil organisms would be preferable even if further aquatic testing were performed (because some of the soil RCRs are large and the validity of read-across from analogues is uncertain). A long-term earthworm reproduction study is suggested, since this species and its corresponding trophic level were the most sensitive for nonylphenol (EC, 2002). If the results were similar to those for nonylphenol, then even test results for three species would be insufficient to remove all risks (the PNEC for nonylphenol is 0.3 mg/kg).

There is some indication that *para*-C_{12}-alkylphenols may be degradable to some extent (the current assessment assumes no biodegradability) and so simulation testing of biodegradation in soil could also refine this assessment. However, even if the substance were inherently biodegradable (according to the TGD), the assessment would not change to a significant degree (see Appendix 1).

5.3 Atmospheric compartment

Effect data for non-mammalian species are unavailable, so it is not possible to derive a PNEC. The lack of toxicity data for suitable species does not imply the absence of risk, a risk for this compartment is unlikely because air concentrations are predicted to be extremely low (because of low releases to air, low volatility and a short atmospheric half-life). Abiotic effects are similarly unlikely.

5.4 Non-compartment-specific effects relevant to the food chain (secondary poisoning)

Predators may be exposed to *para*-C_{12}-alkylphenols via both the aquatic and terrestrial food chains. The calculations assume that the predator catches half of its food from an area close to the emission source, and the remainder from a wider area. In this case, the local concentrations make a significantly higher contribution to the overall estimate of risk than do the regional concentrations. The RCRs are shown in Table 5.4.

Table 5.4 PECs and RCRs for secondary poisoning

Life-cycle stage		PECs for fish (mg/kg wwt)	RCRs for fish eating predators	PECs for worms (mg/kg wwt)	RCRs for worm eating predators
Production of the substance	Site C*	<2.0	<0.59	-	-
Lubricant blending		0.048	<0.01	3.0	0.9
Phenol/formaldehyde resin production		0.009	<0.01	16	**4.8**
Resins – ink formulation		0.01	<0.01	16	**4.9**
Resins – tyre production		0.047	<0.01	36	**11**
Resins – varnish use		0.006	<0.01	2.8	0.8

Notes: $PNEC_{oral}$ worm/fish = 3.3 mg/kg food.

* Site C does not give rise to risks for the earthworm food chain because sludge is not applied to land.

No scenarios give rise to risks for the aquatic food chain. Resin production and the use of resins in ink formulation and tyre production all give rise to risks for the terrestrial food chain.

The calculations for lubricant additive manufacture are based on data for two sites that are known to discharge effluent to an estuary. This life cycle stage is therefore considered under the marine scenario in Appendix 3 (there are no emissions via sewage sludge). No risks are indicated for the marine food chain for this or any other life cycle stage.

Uncertainties and possible refinements

This assessment could be refined by improving the PEC estimates for soil (described in Section 5.2) for the relevant life cycle steps identified as posing a risk. This work could include better release information and monitoring data at locations close to sources of release (including levels in earthworms at suitable sites).

The bioconcentration potential in earthworms is estimated from a model, which might be too conservative. It could be refined with actual experimental data. It should be possible to combine such a study with a prolonged toxicity test (as recommended in Section 5.2) if appropriate consideration were given to this aspect in the design of the study.

The PNEC is based on results from a chronic mammalian reproduction study, and the lowest assessment factor has been used. It is recognised that the substance could have endocrine disrupting properties. A two-generation rodent study would provide a NOAEL that takes account of additional end points. It should also be noted that the long-term toxicity to birds is unknown, and this could be an important gap in knowledge. However, it is unlikely that the PNEC would be revised upwards by further testing. Given the existing concerns for human health effects, further vertebrate toxicity tests for the secondary poisoning assessment are not considered a priority at the present time.

5.5 Risks to human health following environmental exposure

Overall, the critical health effect for the purposes of the human health risk assessment is identified as reproductive toxicity, with a NOAEL of 5 mg/kg/day. This is supported by a NOAEL of 5 mg/kg/day for systemic toxicity in a 28-day gavage study in rats. The margin of exposures between daily human doses and the NOAEL are shown in Table 5.5.

Table 5.5 Margin of exposures between daily human doses and the NOAEL (5 mg/kg/day)

Life-cycle stage	Total daily human dose (mg/kg/day)	Margin of exposure
Lubricant blending	7.1×10^{-3}	704
Phenol/formaldehyde resin production	9.0×10^{-2}	**55**
Resins – ink formulation	9.2×10^{-2}	**54**
Resins – tyre production	2.2×10^{-1}	**23**
Resins – varnish use	8.0×10^{-3}	625
Regional	1.2×10^{-2}	416

Given the uncertainties regarding interspecies and inter-individual variability, a margin of exposure of at least 100-fold would normally be required to provide reassurance against effects on human health. This is supported by the fact that the NOAEL was derived from a one-generation fertility study with a limited duration of dosing, and there are no chronic bioassays available. In addition, the NOAEL is based on gavage dosing which may overestimate the effects from a more gradual exposure to equivalent doses via the environment. However, this possibility of overestimation is counterbalanced by the absence of a longer-term study. Overall therefore, it is assumed that a margin of exposure below 100 may provide grounds for concern about human health.

Human health may be at risk from phenol/formaldehyde resin production, and use of resins in ink formulation and tyre production. There is no concern from exposure at the regional level (the margin of exposure is 416).

Finally, although this assessment has not addressed risks to workers or consumers, the SIAR (2006) concludes that both occupational and consumer exposures are expected to be low and very low, respectively.

Uncertainties and possible refinements

This assessment could be refined by improving the estimates for total daily human dose, which would involve:

- better release information and/or monitoring data at locations close to sources of release;
- an experimental estimate of uptake into plant roots (since at the highest total dose the levels of the substance in root crop are most significant, and predicted values come from calculations that fall outside the domain of the estimation method).

It must be remembered default assumptions have been used in all the applications analysed; no specific information on releases has been provided.

6 Conclusions

para-C_{12}-alkylphenols enter the environment directly due to industrial releases of the substance itself when used as a chemical intermediate, and indirectly through the use of derivatives (due to its presence as an impurity). Based on the available information, potential risks are identified for all life cycle steps for one or more protection goals. Table 6.1 presents a general overview of the conclusions for the two distinct industrial uses of the substance in lubricants and resins, using asterisks to highlight those parts of the life cycle that pose a concern. Section 5 should be consulted for the actual values arising from the risk characterisation.

Table 6.1a Potential environmental risks identified for *para*-C_{12}-alkylphenols from use in the lubricant industry

Life cycle stage		Surface water	Sediment	WWTP	Air	Soil	Aquatic food chain	Terrestrial food chain	Marine water	Marine sediment
Production of the substance[1] and lubricant additive package manufacture	Site A	-	-	-	-	-	-	-	-[3]	✶
	Site B	-	-	-	-	-	-	-	-[3]	✶
	Site C	✶[2]	✶[2]	-	-	-	-	-	-	-
Lubricant blending[1]		-	✶	-	-	✶	-	-	✶	✶
Regional		-	✶	-	-	✶	-	-	-	✶

Notes: aquatic food chain includes marine

[1] life cycle stage relevant for the UK

[2] risks may be substantially lower than predicted

[3] risks may be substantially higher than predicted (see Appendix 3)

Table 6.2b Potential environmental risks identified for *para*-C_{12}-alkylphenols from use in resins

Life cycle stage	Surface water	Sediment	WWTP	Air	Soil	Aquatic food chain	Terrestrial food chain	Marine water	Marine sediment
Phenol/formaldehyde resin production[1]	✶	✶	-	-	✶	-	✶	✶	✶
Resins – ink formulation[1]	✶	✶	-	-	✶	-	✶	✶	✶
Resins – tyre production	✶	✶	-	-	✶	-	✶	✶	✶
Resins – varnish use[1]	-	✶	-	-	✶	-	-	✶	✶
Regional	-	✶	-	-	✶	-	-	✶	✶

Notes: aquatic food chain includes marine
[1] life cycle stage relevant or potentially relevant for the UK

There are also potential risks to human health following environmental exposure from phenol/formaldehyde resin production, and use of resins in ink formulation and tyre production.

These conclusions have been drawn from the best data currently available. The Environment Agency nevertheless acknowledges that they are associated with some uncertainty due to the complex nature of the substance and difficulties in establishing its fate, behaviour and effects in the environment.

There are no monitoring data to confirm the predicted levels in any environmental medium; the resin scenarios may be particularly unreliable because they are based on default emission factors, which could be improved. A study of nonyl- and 4-*tert*-octyphenol concentrations in WWTP influent and effluents has recently been completed at two phenolic resin manufacturing sites (EPRA, 2006). It is unclear whether these sites also use *para*-C_{12}-alkylphenols, and whether the data can be related to the releases of that substance (e.g. in terms of the processes and quantities used, etc.). Industry is invited to make a case to use the information in any refinement of this assessment.

The Department of Environment, Food and Rural Affairs (Defra) is also preparing a risk reduction strategy for octylphenol, which will address its use in resins, and so may provide some additional input.

The risks could be recalculated and the conclusions reassessed following additional work, in particular:

- the collation of further site- and industry-specific information on releases of *para*-C_{12}-alkylphenols from UK and EU companies that manufacture and use the lubricant additive derivatives and the resins made from the substance. This industry level work could include:
    - targeted monitoring to confirm the PEC values (especially in water, sediments and WWTP sludges);
    - studies on the fate of sludge from sites using the substance or its derivatives;
    - studies on the amounts of the substance used at realistic worst-case sites;
    - surveys to locate user sites, especially those with marine discharges.
- long-term sediment and soil organism toxicity testing, especially a long-term earthworm reproduction study for soil (to include measurement of accumulation, if possible);
- studies on the fate of the substance in municipal WWTP;
- confirmation of the true reasonable worst case percentage of the substance present within phenolic resins.
- further aquatic toxicity testing (e.g. a chronic *Americamysis* toxicity test), perhaps with a more comprehensive investigation of endocrine disruption potential in fish;
- an experimental estimate of uptake into root crops to help refine the human health assessment (if better information on releases were not forthcoming).

Potential risks have been identified for production sites and lubricant additive manufacturing sites. Some aspects of the work indicated above (for example sediment toxicity testing) could allow a re-assessment of the risks for these sites. However, it is more appropriate for local control authorities to consider the conclusions of this assessment given that the number of sites is few and that other local conditions may need to be taken into account.

Finally, it should also be noted that the major uses of *para*-C_{12}-alkylphenols are quite different from those of other alkylphenols that have been the subject of major risk assessments (specifically nonylphenol and octylphenol). Restrictions on the uses of these other substances are therefore unlikely to impact the use pattern of *para*-C_{12}-alkylphenols.

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8 Glossary of terms

Term	**Description**
Biochemical oxygen demand (BOD)	A measure of degradation potential
Bioconcentration factor (BCF)	A measure of chemical uptake, being the ratio between the concentration in an organism and the concentration in an environmental compartment (usually water)
CAS number (no.)	An identifying code number assigned to chemicals by the Chemical Abstract Services. The CAS number is a generally recognised identification reference for a chemical; it is possible that a substance can have more than one such number
Inherently biodegradable	Some potential for environmental degradation to carbon dioxide and water, etc., as measured by laboratory screening tests involving micro-organisms
Lowest observed effect concentration	The lowest concentration in a toxicity test that gives rise to adverse effects (relative to a control)
Median effective concentration (EC50)	The concentration in a toxicity test at which a particular effect is observed in half of the organisms exposed for a specified time
Median lethal loading (LL50)	The loading of substance in a water-accommodated fraction that leads to death in half of the organisms exposed for a specified time
Median lethal concentration/dose (LC/D50)	The concentration in a toxicity test that can be expected to cause death in half of the organisms exposed for a specified time
No observed effect concentration (NOEC)	The highest concentration in a toxicity test that does not give rise to adverse effects (relative to a control)
Octanol-water partition coefficient (Kow)	This parameter gives an indication of the partitioning behaviour of a substance between water and lipid-containing materials such as cell membranes or organic matter in soils and sediments
Readily biodegradable	Rapid environmental degradation to carbon dioxide and water, etc., as measured by laboratory screening tests involving micro-organisms

9 Abbreviations

Acronym	**Description**
ACC	American Chemical Council
AF	Assessment factor
APERC	Alkylphenols and Ethoxylates Research Council
ASTM	American Society for Testing and Materials
BACS	British Association for Chemical Specialities
BCF	Bioconcentration factor
BOD	Biochemical oxygen demand
bw	Body weight/Bw, b.w.
CAS	Chemical Abstract Services
CEFIC	European Chemical Industry Council
CEPAD	Conseil Européen des Phénols Alkylés et Derivés (the European Council for Alkylphenols and Derivatives): a trade association representing the major European producers of alkylphenols, and some of the users (http://www.cefic.be/cepad/)
CMR	Carcinogenic, mutagenic and toxic to reproduction
CSF	Chemicals Stakeholder Forum
Defra	Department of the Environment, Food and Rural Affairs
DETR	Department of the Environment, Transport and the Regions
DIN	Deutsche Industrie Norm (German norm)
dw	Dry weight
EC	European Communities
EC50	Median effect concentration
EC_x	As EC_{50}, but for x% effect; x usually being 0, 10, or 100
ECB	European Chemicals Bureau
EEC	European Economic Communities
EINECS	European Inventory of Existing Commercial Chemical Substances – this lists all chemical substances that were supplied to the market prior to 18th September 1981
ELINCS	European List of Notified Chemical Substances – this lists all chemical substances that were supplied to the market after 1981
EPA	Environmental Protection Agency (USA)
EPRA	European Phenolic Resins Association
ESD	Emission Scenario Document
ESIS	European chemical Substances Information System

ESR	The Existing Substances Regulation – Council Regulation (EEC) 793/93 on the evaluation and control of the risks of 'existing' substances.
EU	European Union
EU-15	The 15 European Union Member States prior to May 2004
EUSES	European Union System for the Evaluation of Substances (software tool in support of the TGD on risk assessment)
HERTG	Health, Environmental and Regulatory Task Group (part of the American Chemistry Council's Petroleum Additives Panel)
HPLC	High pressure liquid chromatography
HPV	High Production Volume (supply > 1000 tonnes/year)
HPVC	High production volume chemical (supply > 1000 tonnes/year)
IC	Industrial category
ICCA	International Council of Chemical Associations
IPC	Integrated pollution control
IPPC	Integrated Pollution Prevention and Control (EC Directive 96/61/EEC)
IUCLID	International Uniform Chemical Information Database: contains non-validated tonnage, use pattern, property and hazard information for chemicals, submitted by industry under the Existing Substances Regulation (ESR)
IUPAC	International Union for Pure and Applied Chemistry – the IUPAC name is the formal chemical name
K_{oc}	Organic carbon normalised distribution coefficient
K_{ow}	Octanol–water partition coefficient
Kp	Solids–water partition coefficient
$L(E)C_{50}$	Median lethal (effect) concentration
LD_{50}	Median lethal dose
LL_{50}	Median lethal loading
LOEL	Lowest observed effect level
LOEC	Lowest observed effect concentration
log K_{ow}	Log of the octanol-water partition coefficient (Kow)
LPV	Low production volume (supply 10-1000 tonnes/year)
LPVC	Low production volume chemical (supply 10-1000 tonnes/year)
NO(A)EL	No observed (adverse) effect level
NOEC	No observed effect concentration
n.t.p.	Normal temperature and pressure
OECD	Organisation for Economic Co-operation and Development
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic, http://www.ospar.org
P	Persistent

PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
pH	Logarithm (to the base 10) of the hydrogen ion concentration [H+]
pK_a	Logarithm (to the base 10) of the acid dissociation constant
PNEC	Predicted no effect concentration
ppm	Parts per million
(Q)SAR	(Quantitative) Structure-Activity Relationship
RATG	Risk Assessment Task Group (of the ACC)
RCR	Risk characterisation ratio
SETAC	Society of Environmental Toxicology And Chemistry
SIAR	SIDS Initial Assessment Report, OECD
SIDS	Screening Information Data Set, OECD
SMILES	Simplified Molecular Input Line Entry System – the SMILES code is a chemical notation system used to represent a molecular structure by a linear string of symbols; it is a simple way of entering chemical structural information into a computer programme
SRC	Syracuse Research Corporation
STW	Sewage treatment works
STP	Sewage treatment plant
TGD	Technical Guidance Document
TPP	Tetrapropenylphenol
TSCA	Toxic Substances Control Act (USA)
US EPA	Environmental Protection Agency, USA
UV	Ultraviolet region of the electromagnetic spectrum
vB	Very bioaccumulative
vP	Very persistent
vPvB	Very persistent and very bioaccumulative
w/w	Weight per weight ratio
wt	Weight
wwt	Wet weight
WWTP	Wastewater treatment plant

Appendix 1 Sensitivity analysis

A1.1 Introduction

A number of areas have been identified in the course of the assessment where there are uncertainties over the data used. Most obvious are the estimation of emissions and subsequent exposure concentrations; the impact of the uncertainties are considered in the conclusions in the main assessment report. More reliable data of this type could have a direct influence on the outcome of the assessment.

Similarly, there are possibilities to improve the PNEC values through further testing, also discussed in the main report. This appendix considers some other aspects that may have an influence on the outcome of the assessment, but not in such a direct manner. Some of the conclusions from this appendix are mentioned in the main document.

A1.2 Aspects considered

Three areas are considered in this appendix – sorption coefficients, biodegradation and solubility.

A1.2.1 Sorption

Section 3.1.5 describes the calculation of the organic carbon-water partition coefficient, and the derivation of the partition coefficients used in the exposure. There are a number of equations that could be used for this derivation, all of which have some limitations in respect to this substance. A geometric mean value of 1.1×10^5 L/kg has been used in the calculations in the main assessment. The influence of this parameter on the outcome has been examined by performing calculations with the lowest and highest K_{oc} values obtained from the available equations.

A1.2.2 Biodegradation

Data from a production site show a high degree of removal (99.3%) from waste water through biological treatment. There is no indication of whether this removal is through biodegradation or increased sorption. Two calculations have been performed, in which only 0.7% of the substance entering the WWTP is assumed to leave in the effluent water. In the first calculation, the additional removal of the substance from water (compared to the value of 11.3% calculated with SimpleTreat) is assumed to occur by degradation. IN the second calculation it is assumed to be due to adsorption.

The available ready and inherent biodegradation tests show some degradation, but not enough for the substance to pass a ready or inherent test. The calculations in the main assessment assume no biodegradation, in either the WWTP or in the environment. A calculation has been performed assuming that degradation in the environment does occur, at the level assumed for inherently biodegradable substances that do not meet the specific criteria. There is no biodegradation in the WWTP in this case.

A1.2.3 Solubility

The main assessment uses a solubility of 31 µg/L as a representative value for the main components of the substance. A value for the bulk solubility of the commercial material of 2.1 mg/L is also available, and a calculation using this value has also been performed.

A1.3 Results

The calculations for this appendix have been performed using EUSES. The emissions and property values were the same as for the main assessment, with the exception of the single change indicated for each of the cases in the sections above. The results are presented in Tables A1.1-A1.9. The values presented are the PEC/PNEC ratios (RCRs). The scenarios are as follows:

RAR - results as in the main risk assessment

A - low K_{oc} value (5.4 x 10^4)

B - high K_{oc} value (7.65 x 10^5)

C - 0.7% to water from WWTP, additional removal by degradation

D - 0.7% to water from WWTP, additional removal by sorption to sludge

E - inherent biodegradability (not meeting criteria) assumed

F - solubility of 2.1 mg/L.

A1.3.1 Sorption

The use of the lower K_{oc} value leads to higher concentrations in freshwater and hence higher ratios for water and related compartments. However, none of the scenarios in these compartments (water, sediment, aquatic food chain) have a revised conclusion. Although the concentrations in soil are lower, the PNEC is also reduced the ratios for soil are increased to a greater extent. The varnish scenario for the terrestrial food chain now shows a risk.

The higher K_{oc} value leads to reduced ratios in water, sediment and soil, but with no changes to the scenarios which show a risk. Only tyre production shows a risk for secondary poisoning via the terrestrial food chain.

The lower K_{oc} value leads to a ratio just above 1 for Site A in marine waters. There are no other significant changes to the marine risk assessment.

A1.3.2 Biodegradation

The higher removal rate from water in waste water treatment (99.3%) based on measurements leads to no risks for any of the scenarios for water, with the exception of the site specific calculations (which already take account of the higher removal rate). All scenarios still show a risk for sediment, due to the extra factor of 10 applied because the equilibrium partition method is used.

Table A1.1 Surface water RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant additive manufacture	Site C	**<145**	**<145**	**<145**	**<145**	**<145**	**<145**	**<146**
Lubricant blending		0.41	0.51	0.18	0.17	0.17	0.36	0.80
Phenol/formaldehyde resin production		**3.22**	**4.21**	**1.34**	0.34	0.34	**3.17**	**4.2**
Resins - ink formulation		**3.24**	**4.24**	**1.35**	0.34	0.34	**3.2**	**4.2**
Resins - tyre production		**7.47**	**9.82**	**3.08**	0.60	0.61	**7.43**	**9.3**
Resins - varnish use		0.36	0.45	0.17	0.16	0.17	0.32	0.75
Regional		0.18	0.21	0.09	0.15	0.15	0.13	0.53

Table A1.2 Sediment RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant additive manufacture	Site C	**<1450**	**<1450**	**<1450**	**<1450**	**<1450**	**<1450**	**<1460**
Lubricant blending		**4.06**	**5.1**	**1.84**	**1.65**	**1.68**	**3.62**	**8.0**
Phenol/formaldehyde resin production		**32.2**	**42.1**	**13.4**	**3.39**	**3.42**	**31.7**	**42**
Resins - ink formulation		**32.4**	**42.4**	**13.5**	**3.4**	**3.43**	**32**	**42**
Resins - tyre production		**74.7**	**98.2**	**30.8**	**6.02**	**6.05**	**74.3**	**93**
Resins - varnish use		**3.62**	**4.53**	**1.7**	**1.63**	**1.65**	**3.17**	**7.5**
Regional		**3.48**	**4.11**	**1.78**	**3.01**	**3.06**	**2.60**	**10**

Table A1.3 Soil RCRs

Scenario	RAR	A	B	C	D	E	F
Lubricant blending	**3.65**	**6.52**	0.6	**3.65**	**4.11**	**3.49**	**4.0**
Phenol/formaldehyde resin production	**47.5**	**85**	**7.74**	**47.5**	**53.6**	**45.8**	**52**
Resins - ink formulation	**47.9**	**85.7**	**7.81**	**47.9**	**54.1**	**46.2**	**52**
Resins - tyre production	**114**	**204**	**18.6**	**114**	**129**	**110**	**124**
Resins - varnish use	**3.0**	**5.36**	0.49	**3.0**	**3.37**	**2.86**	**3.3**
Regional	**6.45**	**9.71**	**1.29**	**6.45**	**7.28**	**1.26**	**8.2**

A: low K_{oc} value

B: high K_{oc} value

C: 0.7% to water from WWTP, additional removal by degradation

D: 0.7% to water from WWTP, additional removal by sorption to sludge

E: inherent biodegradability

F: solubility of 2.1 mg/l

Table A1.4 Aquatic food chain RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant additive manufacture	Site C	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59
Lubricant blending		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phenol/formaldehyde resin production		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Resins - ink formulation		0.01	0.02	<0.01	<0.01	<0.01	0.01	0.02
Resins - tyre production		0.03	0.04	0.01	<0.01	<0.01	0.04	0.04
Resins - varnish use		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table A1.5 Terrestrial food chain RCRs

Scenario	RAR	A	B	C	D	E	F
Lubricant blending	0.90	**1.45**	0.17	0.90	**1.02**	0.42	**1.1**
Phenol/formaldehyde resin production	**4.81**	**8.43**	0.81	**4.81**	**5.44**	**4.19**	**5.4**
Resins - ink formulation	**4.85**	**8.49**	0.82	**4.85**	**5.47**	**4.22**	**5.4**
Resins - tyre production	**10.7**	**19**	**1.79**	**10.7**	**12.1**	**9.9**	**12**
Resins - varnish use	0.84	**1.34**	0.16	0.84	0.95	0.37	**1.03**

Table A1.6 Marine water RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant additive manufacture	Site A	0.99	**1.02**	0.95	0.98	0.98	0.96	**1.4**
	Site B	0.18	0.2	0.13	0.15	0.16	0.13	0.55
Lubricant blending		**2.2**	**2.38**	**1.22**	**2.18**	**2.18**	**2.16**	**2.6**
Phenol/formaldehyde resin production		**27**	**29.1**	**14.7**	**27**	**27**	**26.9**	**27**
Resins - ink formulation		**27.2**	**29.3**	**14.8**	**27.2**	**27.2**	**27.2**	**28**
Resins - tyre production		**64.5**	**69.6**	**35**	**64.5**	**64.5**	**64.5**	**65**
Resins - varnish use		**1.81**	**1.96**	**1.01**	**1.79**	**1.79**	**1.77**	**2.2**
Regional		0.17	0.19	0.12	0.14	0.15	0.12	0.55

A: low Koc value

B: high Koc value

C: 0.7% to water from WWTP, additional removal by degradation

D: 0.7% to water from WWTP, additional removal by sorption to sludge

E: inherent biodegradability

F: BCF of 6,000

Table A1.7 Marine sediment RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant	Site A	**9.9**	**10**	**9.5**	**9.8**	**9.8**	**9.6**	**14**
additive manufacture	Site B	**1.8**	**2.0**	**1.3**	**1.5**	**1.6**	**1.3**	**5.5**
Lubricant blending		**22**	**23.8**	**12.2**	**21.8**	**21.8**	**21.6**	**26**
Phenol/formaldehyde resin production		**270**	**291**	**147**	**270**	**270**	**269**	**274**
Resins - ink formulation		**272**	**293**	**148**	**272**	**272**	**272**	**276**
Resins - tyre production		**645**	**696**	**350**	**645**	**645**	**645**	**699**
Resins - varnish use		**18.1**	**19.6**	**10.1**	**17.9**	**17.9**	**17.7**	**22**
Regional		**3.26**	**3.6**	**2.36**	**2.82**	**2.87**	**2.39**	**11**

Table A1.8 Marine predator RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant	Site A	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
additive manufacture	Site B	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lubricant blending		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phenol/formaldehyde resin production		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Resins - ink formulation		0.01	0.01	<0.01	0.01	0.01	0.01	0.01
Resins - tyre production		0.03	0.03	0.01	0.03	0.03	0.03	0.03
Resins - varnish use		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table A1.9 Marine top predator RCRs

Scenario		RAR	A	B	C	D	E	F
Production of the substance and lubricant	Site A	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
additive manufacture	Site B	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lubricant blending		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phenol/formaldehyde resin production		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Resins - ink formulation		0.01	0.01	<0.01	0.01	0.01	0.01	0.01
Resins - tyre production		0.03	0.03	0.01	0.03	0.03	0.03	0.03
Resins - varnish use		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

A: low K_{oc} value

B: high K_{oc} value

C: 0.7% to water from WWTP, additional removal by degradation

D: 0.7% to water from WWTP, additional removal by sorption to sludge

E: inherent biodegradability

F: solubility of 2.1 mg/l

The higher removal rate has no impact on the soil compartment ratios, whether or not the substance removed from water is assumed to be added to the sludge (and so applied to land) or degraded. A significant proportion of the substance already goes to sludge in the main assessment calculations, so this addition makes little difference. The marine calculations are not affected, as they assume no WWTP involvement.

For the terrestrial food chain, although the difference in concentrations is small, it is enough to make the lubricant blending scenario a risk when the additional removal is assumed to go to sludge. The marine predator calculations are virtually unchanged.

When inherent biodegradation is assumed for the environment, there is a slight reduction in the ratios for all scenarios, more noticeably for the terrestrial compartment and secondary poisoning (including marine). None of the changes affect the number of scenarios showing risks.

A1.3.3 Solubility

The higher solubility value leads to higher concentrations in water and in soil. The ratios for all compartments are increased to a small extent. The only significant changes, however, are:

- lubricant blending and resin use become risks for the terrestrial food chain;
- Site A shows a risk for marine waters.

A1.4 Summary

The calculations involving changes to the fate in the WWTP are important as they lead to changes in the conclusions based on current emission estimates. The K_{oc} value and the solubility are not so important, and biodegradability in the environment at the level of inherent biodegradability according to the TGD does not influence the outcome. Although the uncertainty in each of these areas could be clarified, no single area would lead to significant changes to the conclusions of the assessment. It also appears unlikely that any of the risks identified are due solely to uncertainty in one of these areas. The lack of specific information on emissions to the environment is likely to be much more significant.

Appendix 2 Known derivatives

The following lists were compiled by searching the ESIS database using partial name strings as search terms. They are not necessarily exhaustive.

Table A2.1 lists substances that were reported as being on the EU market in the 1980s (so-called 'existing' substances). Substances that were being supplied in the early 1990s in any significant quantity are highlighted in bold.

Table A2.1 Existing substances that are derived from *para*-C_{12}-alkylphenols

EINECS substance name	CAS number	EINECS number	Supply level according to ESIS
2,2'-Thiobis[4-dodecylphenol]	1262-31-3	215-027-5	Not HPV or LPV
Didodecylphenol	25482-47-7	247-020-8	Not HPV or LPV
Calcium thiobis[dodecylphenolate]	**26998-97-0**	**248-159-7**	**HPV**
Calcium 4-dodecylphenolate	50910-68-4	256-842-6	Not HPV or LPV
Calcium dodecylphenolate	52274-73-4	257-802-0	Not HPV or LPV
4-Dodecyl-2-[(2-nitrophenyl)azo]phenol	63216-93-3	264-008-8	Not HPV or LPV
2,6-Bis[[bis(2-hydroxyethyl)amino]methyl]-4-dodecylphenol	67845-80-1	267-337-5	Not HPV or LPV
Bis(tert-butyl)dodecylphenol	**68025-37-6**	**268-192-0**	**LPV**
Calcium 2-[[(2-aminoethyl)amino]methyl]-4-dodecylphenolate (1:2)	68516-56-3	271-161-4	Not HPV or LPV
Lead(2+) dodecylphenolate	68586-21-0	271-610-4	Not HPV or LPV
Phenol, 2,2'-thiobis-, dodecyl derivs., calcium salts, overbased	68610-52-6	271-868-8	Not HPV or LPV
Phenol, dodecyl-, sulfurized, carbonates, calcium salts	**68784-25-8**	**272-233-8**	**HPV**
Phenol, dodecyl-, sulfurized, carbonates, calcium salts, overbased	**68784-26-9**	**272-234-3**	**HPV**
Thiobis[tetrapropylenephenol]	**68815-67-8**	**272-388-1**	**HPV**
Barium thiobis[dodecylphenolate]	68832-80-4	272-402-6	Not HPV or LPV
Formaldehyde, reaction products with calcium hydroxide, dodecylphenol, methylamine and sulfur	68855-34-5	272-480-1	Not HPV or LPV
Formaldehyde, reaction products with dodecylphenol and methylamine	**68855-35-6**	**272-481-7**	**LPV**
Phenol, dodecyl-, sulfurized, calcium salts	**68855-45-8**	**272-486-4**	**HPV**
Alkenes, C15-18 α-, reaction products with sulfurized dodecylphenol calcium salt, sulfurized	**72275-86-6**	**276-559-1**	**LPV**
Phenol, C12-and C18-30-alkyl derivs., sulfurized, calcium salts, overbased	**73758-62-0**	**277-588-2**	**HPV**
Phenol, dodecyl-, manuf. of, by-products from, high-boiling	90480-99-2	291-838-8	Not HPV or LPV
Phenol, 4-dodecyl-, hydrogen phosphorodithioate, branched, zinc salts	91672-35-4	294-041-3	Not HPV or LPV
Barium 4-dodecylphenolate	93922-04-4	300-141-0	Not HPV or LPV
2,2'-[1,3,4-Thiadiazole-2,5-diylbis(dithio)]bis[4-dodecylphenol]	94386-59-1	305-282-1	Not HPV or LPV
Phenol, dodecyl-, branched, sulfurized	96152-43-1	306-115-5	Not HPV or LPV

Note: HPV: high production volume chemical manufactured or imported at ≥1,000 tonnes/year at least once by a company in 1990-1994

LPV: low production volume chemical manufactured or imported at ≥10 tonnes/year at least once by a company in 1990-1994

Most of these substances do not appear to be commercially important.

It should also be noted that polymeric substances might not have been reported for EINECS (e.g. polyethoxylates). Some other substances are not listed in EINECS, but are considered by industry to be synonymous with substances that are. For example:

- "Phenol, tetrapropenyl-, sulfurized, calcium salts" (CAS no. 122384-85-4) is the same substance as CAS no. 68855-45-8.
- "Phenol, tetrapropenyl-, sulfurized, carbonates, calcium salts, overbased" (CAS no. 122384-87-6) is the same substance as CAS no. 68784-26-9.
- "Phenol, tetrapropenyl- and C18-30 alkyl derivatives, sulfurized, calcium salts, overbased" (CAS no. 122384-84-3) is the same substance as CAS no. 73758-62-0.

The ESIS database also lists three relevant 'new' substances, found in Table A2.2.

Table A2.2 Relevant new substances listed in ESIS

EINECS substance name	ELINCS number
A mixture of: • 2,2'-[[(2-hydroxyethyl)imino]bis(methylene)bis[4-dodecylphenol] • formaldehyde, oligomer with 4-dodecyl phenol and 2-aminoethanol (n = 2) • formaldehyde, oligomer with 4-dodecyl phenol and 2-aminoethanol (n = 3, 4 and higher)	414-520-4
A mixture of: • phenol, 6-(1,1-dimethylethyl)-4-tetrapropyl-2-[(2-hydroxy-5-tetra-propylphenyl)methyl (C41-compound) and methane, 2,2'-bis[6-(1,1-dimethyl-ethyl)-1-hydroxy-4-tetrapropyl-phenyl)]- (C45-compound) • 2,6-bis(1,1-dimethylethyl)-4-tetra-propyl-phenol and 2-(1,1-dimethylethyl)-4-tetrapropyl-phenol • 2,6-bis[(6-(1,1-dimethylethyl)-1-hydroxy-4-tetrapropylphenyl)methyl]-4-(tetrapropyl)phenol and 2-[(6-(1,1-dimethylethyl)-1-hydroxy-4-tetrapropylphenylmethyl]-6-[1-hydroxy-4-tetrapropylphenyl)methyl]-4-(tetrapropyl)phenol	414-550-8
A mixture of: • calcium bis(C10-14 branched alkyl salicylate) • calcium bis(C18-30-alkyl salicylate) • calcium C10-14 branched alkylsalicylato-C18-30-alkyl salicylate • calcium bis (C10-14 branched alkyl phenolate) • calcium bis (C18-30-alkyl phenolate) • calcium C10-14 branched alkylphenolato-C18-30-alkyl phenolate • C10-14 branched alkyl phenol • C18-30-alkyl phenol	430-180-1

There could be other new substances that are derivatives of *para*-C_{12}-alkylphenols, but these cannot be listed because of confidentiality restrictions.

Appendix 3 Marine risk assessment

This appendix considers the risks to the marine environment from the production, use and disposal of *para*-C_{12}-alkylphenols. The information is presented separately from the main report in case it is of particular interest to stakeholders such as OSPAR.

A3.1 Derivation of marine PECs

The methodology outlined in the TGD 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 *para*-C_{12}-alkylphenols are discussed in the main report and are summarised in Table A3.1.

Table A3.1 Adsorption and bioaccumulation properties for *para*-C_{12}-alkylphenols

Property	Value
Log K_{ow}	7.14
Organic carbon - water partition coefficient (K_{oc}) L/kg	110,000
Solid-water partition coefficient in suspended matter (Kp_{susp}) L/kg	11,000
Suspended matter - water partition coefficient ($K_{susp-water}$)	2,750
Fish bioconcentration factor (BCF_{fish}) L/kg	823
Biomagnification factor in fish (BMF_1)[1]	1
Biomagnification factor in predators (BMF_2)[1]	1

Notes: [1] Default factors taken from the TGD.

The calculation of marine PEC values has been performed according to the TGD, using the EUSES 2 program. The input data are the same as those used for the freshwater calculations; a major difference between the freshwater and marine assessments is that the effluent from industrial activity is assumed to enter the marine environment directly, rather than after treatment in a WWTP. Where the substance is in products used by the general population, discharge via a wastewater treatment plant can be assumed. This situation does not apply to any of the local scenarios for *para*-C_{12}-alkylphenols.

Sites A and B discharge their effluent to a specific location at the coast. A dilution factor of 1,000 has been used in the calculations to be consistent with the generic marine scenario. However, the local regulatory authority suggests that a factor of 10 is more appropriate (further information is given in the confidential appendix). This is considered in the risk characterisation section.

The resulting PEC values are given in Table A3.2 and cover marine waters, sediments, predators and top predators.

Table A3.2 Estimated PECs for the local marine risk assessment

Life-cycle stage		PEC local seawater (µg/L)	PEC local sediment (µg/kg)	PEC oral, predator (µg/kg)	PEC oral, top predator (µg/kg)
Production of the substance and lubricant additive manufacture	Site A	4.0 x 10^{-3}	9.5	1.9	0.82
	Site B	1.9 x 10^{-3}	4.5	1.0	0.64
Lubricant blending		8.8 x 10^{-3}	21	3.3	1.1
Phenol/formaldehyde resin production		0.1	258	3.9	1.2
Resins – ink formulation		0.1	260	37	7.9
Resins – tyre production		2.6 x 10^{-1}	618	88	18
Resins – varnish use		7.2 x 10^{-3}	17	0.6	0.6

para-C_{12}-alkylphenols were identified in marine waters in a survey of major industrialised estuaries in the UK carried out during 1995-1997 (DETR, 2000). The estuaries involved were the Rivers Blythe, Mersey, Severn, Tees, Tyne and Wear as well as Belfast Lough, Milford Haven and Swansea Bay and samples were analysed using a bioassay (*Tisbe battagliai*) directed fractionation procedure. Very few water samples were acutely toxic to *T. battagliai* and as a matter of routine samples were pre-concentrated 80-200 times to elevate contaminants to toxic concentrations. In 1997 a water sample from Seacombe Ferry on the River Mersey showed a response in the bioassay and dodecylphenol was identified, using GC-MS, in the toxic fraction isolated from the extract obtained. No information regarding the original dodecylphenol concentration was provided in the review of this study.

A3.2 Derivation of marine PNECs

A3.2.1 PNEC for water

Two studies are available on toxicity of *para*-C_{12}-alkylphenols to saltwater invertebrate species (see Section 4.1.2, main report). One study concerns water accommodated fractions, and this cannot be used directly for the PNEC derivation. The other study is not fully valid, but gives an acute 96-hour LC_{50} for *Crangon septemspinosa* (sand shrimp) of 0.15 mg/L. For comparison, the lowest acute freshwater toxicity result is for *Daphnia magna* (48 hour immobilisation EC_{50} = 0.017-0.093 mg/L).

The comparison of data for the alkylphenols in Section 4.1.5.2 suggests that the saltwater invertebrate *Americamysis bahia* may be somewhat more sensitive to these substances than freshwater invertebrates. However, the data set is limited, with only one chronic study on marine species available (for nonylphenol). Acute fish toxicity data for octylphenol and nonylphenol, not shown in Table 4.4, show similar values for fresh and saltwater species. For octylphenol (EA, 2005b), it was concluded that there were insufficient data to identify any differences between freshwater and marine species toxicity. The same approach is adopted here, and the assessment factors from the TGD are applied. As there are two long term NOECs, but none for marine species, a factor of 500 is applied to the lower NOEC of 2 µg/L, giving a $PNEC_{marine}$ of 0.004 µg/L (4 ng/L).

A3.2.2 PNEC for sediment

The $PNEC_{marine\ sediment}$ can be estimated from the $PNEC_{marine}$ using the equilibrium partitioning method, since no marine or freshwater sediment toxicity data are available for *para*-C_{12}-alkylphenols. Therefore, the $PNEC_{marine\ sediment}$ is estimated to be 9.6 µg/kg.

A3.2.3 PNEC for predators

The PNEC for secondary poisoning ($PNEC_{oral}$) is 3.3 mg/kg (as for the main assessment).

A3.3 Risk characterisation for the marine environment

The risk characterisation ratios for water, sediment and predators/top predators are shown in Table A3.3. The ratios calculated for sediment are increased by a factor of 10 to allow for possible uptake through ingestion of sediment in the same way as in the main assessment. This is considered to be a screening approach.

Table A3.3 Estimated PEC/PNEC ratios for the local marine risk assessment

Life-cycle stage		Seawater	Sediment	Predator	Top predator
Production of the substance and lubricant additive manufacture	Site A[a]	0.99	**9.9**	<0.01	<0.01
	Site B[a]	0.18	**1.8**	<0.01	<0.01
Lubricant blending		**2.2**	**22**	<0.01	<0.01
Phenol/formaldehyde resin production		**27**	**270**	<0.01	<0.01
Resins – ink formulation		**27**	**272**	<0.01	<0.01
Resins – tyre production		**65**	**645**	0.03	<0.01
Resins – varnish use		**1.8**	**18**	<0.01	<0.01

Note: a – assuming a dilution of 1,000; see text for further considerations.

The assessment indicates risks for marine waters at coastal sites involved in lubricant blending and all the resin scenarios considered for this marine assessment. Improved information on emissions from all of the five applications would allow the assessment to be revised; such data have already been identified for refinement of parts of the freshwater assessment.

As noted in Section A3.1, the dilution available at sites A and B is likely to be lower than the marine default. If a factor of 10 were assumed, as recommended by the local regulator, then there would be a risk to surface water from both individual sites. It should be noted that the receiving water in this case is heavily polluted by human activity, and would be considered either as an artificial or a heavily modified water body under the Water Framework Directive. Management of the risks at these sites is probably therefore best treated as a local issue.

For marine sediments the risk characterisation ratios are increased by a factor of 10 in the absence of sediment organism toxicity data and all scenarios show a risk (including both sites A and B regardless of the size of the dilution factor). Improved information on releases would allow the assessment to be revised, but testing of sediment organisms also needs to be considered. As the sediment PNEC is based on the freshwater aquatic toxicity data using the equilibrium partition method, testing on either freshwater or marine sediment organisms would allow the PNEC to be refined.

No risks to predators are identified (including both sites A and B regardless of the size of the dilution factor).

A3.4 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. An assessment of persistence (P), bioaccumulation potential (B) and toxicity (T) has therefore been developed to take into account the unacceptably high uncertainty in predicting reliable exposure and/or effect concentrations that hampers quantitative risk assessment. The PBT and 'vPvB' assessment criteria are described in the TGD.

A3.4.1 Persistence (P)

The degradation of *para*-C$_{12}$-alkylphenols is discussed in Sections 3.1.1 of the main report. No marine or freshwater standard simulation test data are available and only two biodegradation tests have been performed. These indicate that the substance is not readily or inherently biodegradable. The absence of any significant degradation in the inherent test, which was designed to maximise degradation potential, implies that the substance would not degrade sufficiently quickly in a marine environmental simulation test to avoid meeting the persistence criterion (i.e. half-life >60 days in marine water). Although the test substance concentration would be much lower, the micro-organism population would be substantially less. The substance therefore has to be considered persistent, meeting the P (and potentially the vP) criterion, although further simulation testing could be performed to check these classifications.

A3.4.2 Bioaccumulation (B)

Bioaccumulation data are discussed in Section 3.1.3. A reliable *in vivo* experimental bioconcentration factor (BCF) of 823 has been measured for fish. Hence the substance does not meet the B or vB criterion (i.e. BCF > 2,000 or > 5,000 respectively). The BCF value is above the lower criteria for accumulation of the Chemical Stakeholder Forum and so the *para*-C_{12}-alkylphenols are identified as substances of concern according to the CSF criteria, although not in the group of substances of highest concern.

A3.4.3 Toxicity (T)

The toxicity of *para*-C_{12}-alkylphenols is discussed in detail in Section 4 of the main assessment. No appropriate chronic marine organism toxicity data are available. The 21-day NOEC for *Daphnia magna* is 0.002 mg/L, and so the substance meets the T criterion (NOEC < 0.01 mg/L).

A3.4.4 Summary

para-C_{12}-alkylphenols are considered to clearly meet the T criterion, and are likely to meet the P and vP criteria with a reasonable degree of confidence. They do not meet the TGD B or vB criteria, and so are not considered as PBT substances according to the EU criteria.

A3.5 Overall conclusions of the marine risk assessment

The substance meets the criteria for toxicity, and also meets screening criteria for consideration as persistent (P), but does not meet the B criterion.

Better information on the locations of sites using lubricant additives produced from *para*-C_{12}-alkylphenols and those using resins made from the substance would allow more confidence in the assessment of possible pathways to the marine environment.

The provisional risk assessment indicates a potential risk to water and sediment organisms and predators for some scenarios, and indicates a need for more reliable data. Hence the exposure parts of the assessment will need to be refined. The data needs highlighted for the freshwater assessment would also be useful for the marine assessment. If these data do not remove the concerns, then testing on marine organisms may be required to refine the PNECs (a chronic toxicity test with *Americamysis* might also be helpful).

Appendix 4 Data collection and peer review process

This report has been produced using publicly available data gathered and assessed by the contractor for the Environment Agency. Additional information has been submitted voluntarily by member companies of the Conseil Européen des Phénols Alkylés et Derivés (CEPAD), working with the European Phenolic Resins Association (EPRA), and the Risk Assessment Task Group (RATG) of the American Chemical Council's Petroleum Additives Panel.

The Environment Agency has been keen to ensure that the data used in this report are as complete and accurate as possible. Original reports and literature articles for key studies were retrieved and assessed for reliability wherever possible (it is clearly indicated where this was not the case). Additional information may be cited in the OECD SIDS assessment that is currently in preparation, but if this is not important for the risk assessment it has not been reproduced in this report.

The initial data review began in 2001. The scientific literature was last searched in November 2005.

Drafts of this report have been circulated to key stakeholders in UK, European and US Industry for comment (the final opportunity for comment closed in September 2006), as well as members of the UK and international chemical regulatory community. The Advisory Committee on Hazardous Substances has also provided helpful comments as part of its own deliberations on this substance. All comments received have been addressed in the final report where appropriate. A full list of consultees is included at the end of this Appendix.

In addition, certain technical aspects of the report were peer-reviewed by an independent expert group set up by the Environment Agency for this purpose in September 2006. Again, this report addresses those comments. The experts were:

Professor Charles Tyler (Exeter University);

Dr Mark Crane (Watts & Crane);

Dr Hans Rufli (Ecotox Solutions, Basel); and

Dr Susan Jobling (Beyond the Basics Ltd.).

Their comments have not been published but are available on request.

List of key organisations consulted during the preparation of this report

Industrial organisations

Association Internationale de la Savonnerie, de la Détergence et des Produits Entretien (AISE)

Alkylphenols & Ethoxylates Research Council (USA)

American Chemistry Council:

Lubricant Additives Alkyl Phenol Panel (LAAPP) &

Risk Assessment Task Group (RATG) of the Petroleum Additives Panel

[Member companies are: Afton Chemical Corporation, The Lubrizol Corporation, Chevron Oronite Company, Infineum, Schenectady International, Inc.]

British Association for Chemical Specialities

British Chambers of Commerce

British Chemical Distributors and Traders Association

British Tyre Manufacturers' Association Ltd

Bureau de Liaison des Industries du Caoutchouc (BLIC) (European Association of the Rubber Industry)

Chemical Industries Association

Comité Européen des Agents de Surface et de leurs Intermédiaires Organiques (CESIO)

Conseil Européen de l'Industrie des Peintures, des Encres d'Imprimerie et des Couleurs d'Art (CEPE)

Conseil Européen des Phénols Alkylés et Derivés (CEPAD)

[Full member companies are: Akzo Nobel Surface Chemistry, BASF AG, Dow SA, Rhodia, SASOL Olefins & Surfactants GmbH, Schenectady Pratteln AG]

Crop Protection Association

European Phenolic Resins Association

[Member companies are: Bakelite, Borden Chemicals, Ceca, Durez Europe, Dynea, Fers Resins, Palmer UK, Schenectady International]

European Polymer Dispersion and Latex Association

European Rubber Chemicals Association

Huntsman Performance Products

International Institute of Synthetic Rubber Producers

Technical Committee of Petroleum Additive Manufacturers in Europe ("Additives Technical Committee")

United Kingdom Lubricants Association Ltd

Manufacturers of the substance itself have in some cases also been contacted directly.

UK government bodies

Advisory Committee for Hazardous Substances

Department of the Environment, Food and Rural Affairs (Defra)

Department of the Environment, Northern Ireland

Department of Health

Department of Trade and Industry

English Nature

Food Standards Agency

Health and Safety Executive

Health Protection Agency

Pesticides Safety Directorate

Scottish Environment Protection Agency

Scottish National Assembly

Veterinary Medicines Directorate

Welsh Assembly

European regulatory authorities

Technical Committee for New and Existing Substances

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