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Survey of alkylphenols and alkylphenol ethoxylates

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Title:

Survey of alkylphenols and alkylphenol ethoxylates

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Contents

Preface

Background and objectives

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding ongoing activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns alkylphenols and alkylphenol ethoxylates (AP/APEO). These substances were included in the first list in 1998 and have remained on the list since that time.

The entry in LOUS for these substances is "alkylphenols and alkylphenol ethoxylates" and it is indicated that the group consists of many compounds, so no CAS numbers are given. Nonylphenols (NP), octylphenols (OP) and nonylphenol ethoxylates (NPEO) are mentioned as examples of substances within the group. It is indicated that the substances are used as surfactants in paint and varnish hardeners and adhesives, amongst other functions.

The main reason for the inclusion in LOUS is the classification of nonylphenols as toxic to reproduction, but also that NP, OP and NPEO are on the EU 'Priority list of substances for further evaluation of their role in endocrine disruption'. Furthermore, some OP compounds have properties of concern indicated in the companies' 'self-classification' of the substances.

It is stated that the substances are only subject to partial restrictions on use; however, other uses are also considered to be a cause for concern with regard to the environment.

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures. The whole group of AP/APEO has never been surveyed or reviewed in Denmark; therefore, one of the objectives is also to provide a background for a more specific description of the substance group, along with a clear definition of which substances are included in the group.

The process
The survey has been undertaken by COWI A/S in cooperation with NIPSECT from June to November 2012.The work has been followed by an advisory group consisting of:

- Sidsel Dyekjær, Danish EPA
- Ulla Hansen Telcs, Confederation of Danish Industry
- Cathrine Berliner Pedersen, Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
- Allan Astrup Jensen, NIPSECT
- Carsten Lassen, COWI A/S

Data collection
The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors. During summer 2012 available literature, relevant legislation and regulatory activities in the pipeline, and statistics was searched using search strings or CAS Numbers covering the different groups of alkylphenols and alkylphenol ethoxylates. Data was mainly searched via the Internet on websites of relevant organisations and databases. The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel.
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only);
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of: The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
- US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.

Summary and conclusion

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. Over the period 2012-2015, all 40 substances and substance groups on LOUS will be surveyed and reviewed, and, on the basis of the surveys, the Danish EPA will assess the need for any further regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns the substance group "alkylphenols and alkylphenol ethoxylates" (AP/APEO), which has been on LOUS since the first version was published in 1998. It is indicated in LOUS that the substance group consists of many compounds, but the group is not clearly defined. One of the objectives of this survey is to provide a background for a more specific description of the LOUS entry for these substances. The alkylphenols are phenol derivatives with one or more chains of carbons of varied length attached to the phenol group. The alkylphenol ethoxylates are chemicals derived from the alkylphenols. Several hundred substances within the group of AP/APEO have been pre-registered under REACH. Nonylphenols (NP, with a 9-carbon chain), octylphenols (OP, with an 8-carbon chain) and nonylphenol ethoxylates (NPEO, with a 9-carbon chain and a chain of ethoxylate groups) are mentioned in LOUS as examples of substances within the group.

An overview of the production and consumption for 29 substances or substances groups at EU level and in Denmark is provided in Table 20 of section 3.4. Nonylphenols, octylphenols, dodecylphenols, 4-*tert*-butylphenol and 2,6-di-*tert*-butyl-p-cresol (BHT) are the alkylphenols used in the largest quantities, each with a production and consumption in the EU in the 10,000-100,000 t/y range. Nonylphenol ethoxylates, with a consumption in the EU in the range of 2,000-20,000 t/y, are the most used of the alkylphenol ethoxylates.

Nonylphenols and nonylphenol ethoxylates

Historically the AP/APEOs of main concern have been the nonylphenols (NP) and nonylphenol ethoxylates (NPEO); these substances have been addressed by environmental release reduction measures since the early 1990s in Denmark and internationally. An EU Risk Assessment for NP/NPEO from 2002 identified the need for reducing the risk to the environment from the substances. A marketing and use restriction for applications which resulted in significant releases to the environment went into force at EU level in 2004. The restriction addresses the use of these substances for nine purposes, including application in cleaning agents (with some exemptions), in textiles and leather auxiliaries and as a coformulator in biocides/pesticides.

Nonylphenols are considered endocrine disruptors and classified as toxic to reproduction and toxic to the environment. A REACH Annex XV dossier has recently been prepared for identification of 4-nonylphenol (a group of linear or branched nonylphenols) as SVHC (Substance of Very High Concern) on the basis of their endocrine disrupting properties. The endocrine potency of nonylphenols in combination with its persistence and the high observed concentrations in the aquatic environment implies a risk of estrogen-like effects occurring as a result of organisms being exposed to the substance. Monitoring data from recent years have demonstrated that the concentration of nonylphenols in lake sediments in Denmark and in marine sediments from the Baltic Sea and the Inner Danish Waters exceeded the so-called "predicted no-effect concentration"; i.e. actual effects on organisms in the environment cannot be excluded.

The main concern related to the nonylphenol ethoxylates (NPEO) is that they degrade to nonylphenols in the environment and through the process of waste water treatment. Discharges of nonylphenol ethoxylates from waste water treatment plants are considered the main source of nonylphenols in the environment.

In the EU, nonylphenols are mainly used as raw material (co-monomer) in the manufacture of phenolic and epoxy resins (polymeric material) and as intermediate in the production of NPEO and a few other chemical substances. In 1999, consumption in the EU was close to 80,000 t/y, but today it is likely to be in the 25,000-50,000 t/y range, mainly due to the restriction of the use of NPEO. NPEO has historically been widely used as surfactant in cleaning agents, but the total consumption in the EU has decreased from 118,000 t/y in 1999 to 2,000-20,000 t/y in 2011 as a consequence of the restriction, which entered into force in 2004. In Denmark today, the main registered use of nonylphenols is in paint, lacquers and varnishes, sealants, and filling agents. A significant quantity of nonylphenol ethoxylates is still registered in the Danish Product Register as used in cleaning agents and biocidal products. It is not clear if this is due to inadequate updating of the notifications or if it represents non-restricted applications. About 12% of the registered quantity of nonylphenol ethoxylates is used for paint, lacquers and varnishes which are not restricted.

NP/NPEO in textiles imported from countries outside the EU is likely the major source of NP/NPEO to municipal waste water treatment plants and the main source of releases of the substances to the environment, as indicated in studies from several EU Member States. As a consequence of this, Sweden is in the process of preparing a REACH restriction proposal on the manufacture and import of textiles and leather containing NP/NPEO.

Human exposure to nonylphenols in food and consumer products is generally not considered to be of concern. The few data available on dietary intake indicate that the level is well below the tolerable daily intake (TDI) estimated by the former Danish Institute of Food Safety and Toxicology, but newer data from Sweden indicate that the intake with food may be higher than previously reported.

A number of alternatives have substituted for nonylphenol ethoxylates for the restricted applications. The alternatives are mainly based on different groups of APEO-free surfactants although octylphenol ethoxylates may have been used as alternatives to a limited extent. Assessments of the environmental fate and effects of the APEO-free alternatives conclude that, in general, the alternatives are of less environmental concern regarding persistence and aquatic toxicity of degradation products. Alternatives to nonylphenol ethoxylates in paint and varnishes appear to be available, but no recent assessment of their technical and economical feasibility has been carried out. Furthermore, no thorough assessment of alternatives to nonylphenols in paint and varnishes has been identified.

Octylphenols and octylphenol ethoxylates
Octylphenols (OP) are used in quantities of approximately 20,000 t/y in the EU of which 98% is used as raw material (co-monomer) for the manufacture of phenolic resins and tackifiers which are mainly used in rubber for tyres. A small amount is used for production of octylphenol ethoxylates (OPEO) which are used as surfactants for some of the same applications as nonylphenol ethoxylates, but in a lower quantity: about 1,000 t/y in the EU. The main non-confidential registered use of OP/OPEO in Denmark is the use of octylphenol ethoxylates in paint, lacquers and varnishes but in significantly lower quantities than the quantities of NP and NPEO used for this application area. Octylphenol ethoxylates may be present in low concentrations as un-reacted substance in OP-based plastics and rubbers.

Compared to the NP/NPEO, OP/OPEO are much less regulated, although the substance used in highest quantity, 4-*tert*-octylphenol (also called *p*-*tert*-OP) has the same harmonised classification for aquatic toxicity as NP. Octylphenol ethoxylates may be degraded into octylphenols in the environment by the same mechanisms as the degradation of nonylphenol ethoxylates into nonylphenols. The OP/OPEOs are, like NP/NPEO, included in the OSPAR list of priority substances and the HELCOM Baltic Sea Action Plan. They are priority substances under the EU Water Framework Directive and within the EU Community strategy for endocrine disrupters. 4-*tert*- Octylphenol is not classified as toxic to reproduction.

The concentrations of the substances in municipal wastewater and in sewage sludge are significantly lower than the concentrations of NP/NPEO. The concentrations in lake sediments in Den-mark and in marine sediments in the Baltic region and the Inner Danish Waters are also significantly lower than the concentration of NP/NPEO. However, HELCOM concludes in its most recent assessment that about half of the surface sediment samples exceeded the threshold concentration for octylphenols in sediments suggested in the context of the EU Water Framework Directive.

One of the main octylphenols, 4-*tert*-octylphenol, is included in the REACH candidate list with the scope of environmental concern. A REACH Annex XV dossier has recently been prepared for identification of OPEO as SVHC (Substance of Very High Concern). The basis for the proposal is the degradation of octylphenol ethoxylates to octylphenols, which has endocrine-disrupting properties in the environment, and that short-chain octylphenol ethoxylates may cause endocrine-disrupting adverse effects at similar or slightly higher concentrations compared to octylphenols.

Dodecylphenols and dodecylphenol ethoxylates

Dodecylphenols (DP, with a 12-carbon chain) are the only commercially important AP with a carbon chain longer than 9. About 99% of the EU consumption (approximately 50,000 t/y) is used as an intermediate in the production of lubricant additives. Dodecylphenols are present in the final additives at low levels. Less than 1% of the dodecylphenols is used for manufacturing of dodecylphenol ethoxylates (DPEO) used as anti-rust agents in lubricants.

A harmonised classification and labelling proposal has been submitted for 4-(3,4,5-trimethylheptyl)phenol (a branched dodecylphenol) suggesting classification as carcinogenic, flammable, and eye damage/irritation. None of the dodecylphenols are listed in the EU list of endocrine disruptors. According to a PBT assessment of one of the dodecylphenols, the substance meets the T criterion, and is likely to meet the P and vP criteria. It does not meet the B criterion and so is not considered to be a PBT substance. The acute toxicity of dodecylphenols is at the same level as the toxicity of octylphenols.

Dodecylphenols and dodecylphenol ethoxylates are not addressed by any EU regulation, are not classified as priority substances under the Water Framework Directive and are not included in the OSPAR list of priority substances or the HELCOM Baltic Sea action plan.

Very few monitoring data have been identified by the survey. In a screening of AP/APEO in the Nordic environment, dodecylphenols were, alongside octylphenols, nonylphenols and nonylphenol ethoxylates, the substances found in highest concentrations in all sewage water samples. A provisional UK environmental risk assessment of dodecylphenols estimated that the main source of dodecylphenols to the environment was releases of DP to waste water from lubricant use and disposal (primary as spill and leakages). The environmental risk assessment indicated a potential risk to some organisms in the aquatic environment for some scenarios, and a need for more reliable data on environmental exposure.

Short chain alkylphenols (with <8-carbon chains)

The short chain alkylphenols are in general not used to produce alkylphenol ethoxylates, so the issues of the ethoxylates being sources of the alkylphenols in the environment do not apply to the short chain alkylphenols. The short chain alkylphenols are a highly diverse group of substances with one, two or three short carbon chains attached to the phenol. The application areas of the short chain alkylphenols are quite diversified.

The short chain alkylphenols are generally of less concern than nonylphenols and octylphenols in the environment, because they are biodegradable and do not bioaccumulate to the same extent. They are not included in the OSPAR list of priority substances, the HELCOM Baltic Sea action plan, are not classified as priority substances under the EU Water Framework Directive, and are not priority substances within the EU Community strategy for endocrine disrupters. The exceptions are 2,4,6-tri-*tert*-butylphenol, which is included in the OSPAR list of priority substances and indicated as potentially toxic, persistent and bioaccumulative and 4-*tert*-butylphenol, which is a category 2 substance (evidence of potential to cause endocrine disruption) on the EU list of potential endocrine disruptors.

One the main reasons for concern about nonylphenols and octylphenols is the endocrine-disruptive effects of the substances. The alkylphenols with alkyl groups having more than two carbons attached at position 4 of the phenol showed profiles very similar to that of estrogen. The available data indicate that both the position (*para* > *meta* >*ortho*) and branching (tertiary > secondary = normal) of the alkyl group affect estrogenicity. Optimal estrogenic activity requires a single tertiary branched alkyl group composed of between 6 and 9 carbons located at the 4-position on a phenol ring without more alkyl groups. It should therefore be underlined that primary the para- (4-) monosubstituted alkylphenols seem to be endocrine disruptors, and 4-nonyl phenol and 4-*tert*-octylpenol are the most potent ones. 2,4-di-*tert*-Butylphenol, however is as mentioned in the following included in the Community Rolling Action Plan (CoRAP) for substance evaluation because it is suspected to be an endocrine disruptor.

The relatively few data available indicate that the concentrations of the short-chain alkylphenols in municipal waste water and in sewage sludge is significantly lower (ten to hundred times lower) than the concentrations of NP/NPEO. 4-*tert*-Butylphenol has been demonstrated to be present in sediments in the Baltic Sea in concentrations higher than octylphenols and comparable with nonylphenols, while hardly any data for the other short-chain alkylphenols have been identified in this survey. The pathways of 4-*tert*-butylphenol to the environment have not been studied in detail.

Two of the substances are used in quantities of more than 20,000 t/y at EU level: 4-*tert*-butylphenol (also named ptBP) and 2,6-di-*tert*-butyl-p cresol (BHT).

4-*tert*-Butylphenol is mainly used in a similar way as 4-nonylphenol and 4-*tert*-octylphenol as comonomer for production of phenolic resins and chain terminator in the production of polycarbonate. 4-*tert*-Butylphenol is the only one of the short chain alkylphenols for which an EU Risk Assessment has been undertaken. According to the Risk Assessment, unreacted 4-*tert*-butylphenol in 4-*tert*-butylphenol-based plastics and rubbers is considered the main source of consumer exposure to the substance. The 4-*tert*-BP is prohibited for use in cosmetics but does not have a harmonised classification. An proposal for a harmonised classification as irritating to skin, eye damaging, toxic to reproduction and exerting specific target organ toxicity has recently been submitted.

2,6-di-*tert*-butyl-p cresol (BHT) is used as antioxidant in a wide group of products; among these, food and feedstuff. The substance has been suggested for further environmental risk assessment by the OECD.

2,4-di-*tert*-butylphenol, which is used as chemical intermediates for the production of plastic additives in quantities >1,000 t/y at EU level, is included in the Community Rolling Action Plan (CoRAP) for substance evaluation due to its use and exposure pattern and that it is a suspected endocrine disruptor.

2,4,6-tri-*tert*-butylphenol, is as mentioned included in the OSPAR list of priority substances. The substance is mainly used as intermediate and the environmental releases from its use is estimated to be small.

Thymol, used in cleaning agents and scented articles, has a harmonised classification as acute toxic, skin corroding and aquatic chronic toxicity. According to the self classification notified to the Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA), most of the related substances have quite similar classifications.

Overall conclusion concerning the grouping of the substances

NP and OP share some of the same environmental and health properties and the two substance groups are together with their ethoxylates the AP/APEO of major concern. Dodecylphenols and their ethoxylates are released to the environment in lower quantities, but of concern due to their environmental and health properties. Among the short chain alkylphenols (<8 carbon atoms), 4-*tert*-buylphenol is used for the same purposes as 4-nonylphenol and 4-*tert*-octylphenol, but the release and exposure pattern is quite different. Most of the other short-chain mono-, di- and trialkylphenols are of less concern: the releases to the environment are in general significantly smaller than for NP; they have a significantly lower potential for bioaccumulation than the long chain (C8-C12) alkylphenols; they appear to be more biodegradable, and their estrogenic potency is lower. Furthermore, they are used for different applications than NP and OP and their ethoxylates. However, some of the short-chain substances may be of some concern.

Based on the available data it appears not to be justified to target the short-chain alkylphenols and the long-chain alkylphenols as one group, but rather to assess each of the short-chain alkylphenols individually in order to identify any needs for measures to reduce the human and environmental exposure.

Data gaps

The survey addresses a wide range of substances and for most of the substances limited data are available on the life cycle releases of the substances, human health and environmental exposure and concentrations in the environment. The most important data gabs identified, when considering which substances are of major concern, are:

- Updated information on current uses and on the significance of the potential sources of releases of NP/NPEO to the environment is missing.
- The registered quantities of NPEO used in cleaning and maintenance products in Denmark calls for a clarification of actual uses.
- For several of the substances, the available information on the total manufacture and import to the EU in the registrations is not in accordance with information obtained from the industry and calls for a clarification.
- For substances used in lubricants and oils, data on the potential releases from spill and disposal of waste oil are scarce or missing.
- Relatively high concentrations of 2,6-di-*tert*-butyl-*p*-cresol are found in waste water and the OECD has concluded that more information on actual releases and environmental exposure to this substance is needed.
- A review from HELCOM concluded that in general, there should be more measured data on NP/NPEO and OP/OPEO in discharges in the Baltic Sea catchment area, in sea water, biota and sediment of the Baltic Sea to examine if the substances cause harmful effects on the marine environment.
- The review HELCOM also concluded that there is a need for ecotoxicological data on sediment dwelling organisms in order to better estimate the PNEC for nonylphenol and octylphenol for the benthic community.

- More information on environmental levels and effects of dodecylphenol and 4-*tert*-butylphenol would be of advantage for a further assessment of the need for reduction of releases of these substances to the aquatic environment;
- Human toxicity data for long-chain alkylphenols other than nonylphenols are limited and data on alkylphenol ethoxylates are nearly absent.
- For many of the short-chained alkylphenols no or insufficient data are available for the assessment of the endocrine potency of the substances.
- Updated information on the technical and economic feasibility of substitution of remaining uses of NP/NPEO and OP/OPEO is missing, this concerns in particular:
  - Use in emulsion polymerization and for paints which represent the major registered uses of the substances in Denmark.
  - Alternatives to 4-*tert*-BP, 4-*tert*-OP and 4-NP for manufacture of different types if resins.

Sammenfatning og konklusion

Miljøstyrelsens Liste over Uønskede Stoffer (LOUS) er en signalliste og en vejledning til producenter, produktudviklere, indkøbere og andre aktører om kemikalier, hvor brugen på længere sigt bør begrænses eller helt stoppes. I perioden 2012-2015 vil alle 40 stoffer og stofgrupper på LOUS blive kortlagt, og på grundlag af kortlægningerne vil Miljøstyrelsen vurdere behovet for yderligere regulering, substitution/udfasning, klassificering og mærkning, forbedret affaldshåndtering eller en øget informationsindsats.

Denne kortlægning vedrører stofgruppen "alkylphenoler og alkylphenolethoxylater" (AP/APEO), som har været på LOUS siden den første udgave blev offentliggjort i 1998. Det er angivet i LOUS, at stofgruppen består af mange forbindelser, men gruppen er ikke klart defineret. Et af formålene med denne kortlægning er at give en baggrund for en mere præcis beskrivelse af listens indgang for disse stoffer. Alkylphenolerne er phenolderivater med én eller flere kæder af kulstofatomer i varierende længde fastgjort til phenolgruppen. Alkylphenolethoxylater er stoffer som er afledt af alkylphenoler. Flere hundrede stoffer inden for gruppen af AP/APEO er blevet præregistreret under REACH. Nonylphenol (NP, med en kulstofkæde med 9 kulstofatomer), octylphenol (OP, med 8 kulstofatomer) og nonylphenolethoxylater (NPEO, med en kulstofkæde på 9 kulstofatomer og en ethoxykæde) nævnes i LOUS som eksempler på stoffer i gruppen.

En sammenfatning af produktion og forbrug af 29 stoffer eller stofgrupper på EU niveau og i Danmark er vist i tabel 19 i afsnit 3.4. Nonylphenoler, octylphenoler, dodecylphenoler, 4-*tert*-butylphenol og 2,6-di-*tert*-butyl-p-cresol (BHT) er de alkylphenoler som anvendes i de største mængder med en produktion og et forbrug i EU i intervallet 10,000-100,000 t/år. Nonylphenolethoxylater, med et forbrug i EU i intervallet 2,000-20,000 t/år, er de mest anvendte af alkylphenolethoxylaterne.

Nonylphenol og nonylphenolethoxylater

Historisk set har nonylphenoler (NP) og nonylphenolethoxylater (NPEO) været de AP/APEO, der har vakt den største bekymring, og siden begyndelsen af 1990'erne er der både i Danmark og internationalt blevet iværksat en række foranstaltninger til at reducere udledningerne af disse stoffer til miljøet. En EU-risikovurdering for NP/NPEO fra 2002 pegede på behovet for at reducere risikoen for stofferne i miljøet. En markedsførings- og anvendelsesbegrænsning for de anvendelser, der gav anledning til de væsentligste udledninger til miljøet, trådte i kraft på EU-plan i 2004. Anvendelsesbegrænsningen omhandler brugen af NP/NPEO til ni formål, herunder anvendelse i rengøringsmidler (med visse undtagelser), tekstil- og læderforarbejdning og som hjælpestoffer i biocider/pesticider.

Nonylphenol betragtes som et hormonforstyrrende stof og er klassificeret som reproduktionstoksisk og giftigt for miljøet. Et REACH bilag XV-dossier er for nylig blevet udarbejdet med henblik på at identificere 4-nonylphenol (en gruppe af lineære eller forgrenede nonylphenoler) som SVHC-stoffer (stoffer som giver anledning til særlig bekymring) på grundlag af deres hormonforstyrrende egenskaber. Graden af hormonforstyrrende effekt i kombination med det forhold at nonylphenol er tungtnedbrydelig og optræder i høje koncentrationer i vandmiljøet indebærer en risiko for østrogen-lignende effekter hos de organismer i miljøet, der udsættes for stoffet. Overvågningsdata fra de seneste år har vist, at koncentrationen af nonylphenol i søsedimenter i Danmark og i marine sedimenter fra Østersøen og de indre danske farvande oversteg den såkaldte PNEC-værdi (den beregnede nul-effekt koncentration), hvilket betyder at faktiske virkninger på organismer i miljøet ikke kan udelukkes.

Den største bekymring i tilknytning til nonylphenolethoxylater er, at de nedbrydes til nonylphenoler i miljøet og ved spildevandsrensning. Udledninger af nonylphenolethoxylater fra rensningsanlæg anses for at være den vigtigste kilde til nonylphenoler i miljøet.

På EU-plan anvendes nonylphenoler hovedsageligt som råmateriale (co-monomer) til fremstilling af phenol- og epoxyharpikser (som er polymermaterialer – også kaldet resiner) og som mellemprodukt ved fremstilling af nonylphenolethoxylater og et par andre kemiske stoffer. I 1999 var forbruget i EU tæt på 80.000 t/år, men i dag er det sandsynligvis faldet til et niveau på 25.000-50.000 t/år, hovedsageligt på grund af begrænsningen af bruges af nonylphenolethoxylater. Nonylphenolethoxylater har historisk set været meget anvendt som tensider (overfladeaktive stoffer) i rengøringsmidler, men det samlede forbrug i EU af nonylphenolethoxylater er faldet fra 118.000 t/år i 1999 til 2,000-20,000 t/å i 2011 som følge af den begrænsning, der trådte i kraft i 2004. I Danmark, er den vigtigste registrerede anvendelse af nonylphenoler i dag som bestanddel af maling, lak og fernis, fugemasser og udfyldningsmidler. En væsentlig mængde af nonylphenolethoxylater er stadig registreret i Produktregistret som anvendt i rengøringsmidler og biocidholdige produkter. Det er ikke klart, om dette skyldes utilstrækkelig opdatering af virksomhedernes indberetninger, eller om det er udtryk for faktiske anvendelser, der ikke er omfattet af anvendelsesbegrænsningen. Ca. 12% af den registrerede mængde nonylphenolethoxylater anvendes til maling, lak og fernis, som ikke er omfattet af begrænsningen.

NP/NPEO i tekstiler, som er importeret fra lande uden for EU, er sandsynligvis den største kilde til NP/NPEO til kommunale rensningsanlæg og den vigtigste kilde til udslip af stofferne til miljøet. Dette er påvist i undersøgelser fra flere EU-medlemslande. Som en konsekvens af dette er Sverige i færd med at udarbejde et begrænsningsforslag under REACH, som vil have til formål at forbyde produktion og import af tekstiler og læder, der indeholder NP/NPEO.

Human eksponering for NP/NPEO i fødevarer og forbrugerprodukter anses generelt ikke for at give anledning til bekymring. De få tilgængelige data vedrørende indtag med fødevarer tyder på, at niveauet er et godt stykke under det tolerable daglige indtag (TDI), som er estimeret af det tidligere Institut for Fødevaresikkerhed og Toksikologi, men nyere data fra Sverige viser, at indtaget med fødevarer kan være højere end tidligere rapporteret.

En række alternativer har erstattet brugen af nonylphenolethoxylater til de anvendelser, der i dag er regulerede. Alternativerne er hovedsagelig baseret på forskellige grupper af APEO-frie overfladeaktive stoffer, selvom octylphenolethoxylater i et begrænset omfang kan have været anvendt som alternativ. Vurderinger af de miljømæssige egenskaber og skæbnen i miljøet af de APEO-frie alternativer konkluderer, at alternativerne generelt vækker mindre bekymring i forholdt til nedbrydelighed og deres nedbrydningsprodukters giftighed for organismer i vandmiljøet. Alternativer til NPEO i maling og lak ser ud til at være til rådighed, men der er ikke foretaget nogen nyere vurdering af alternativernes tekniske og økonomiske fordele og begrænsninger. Desuden er der i denne kortlægning ikke fundet nogen grundig vurdering af alternativer til nonylphenol i maling og lak.

Octylphenoler og octylphenolethoxylater
Octylphenoler (OP) anvendes i mængder på omkring 20.000 t/år i EU hvoraf 98% anvendes som råvare (co-monomer) til fremstilling af phenolharpikser og klæbemidler, der især anvendes i gummi til dæk. En lille mængde anvendes til fremstilling af octylphenolethoxylater (OPEO), som anvendes som overfladeaktive stoffer til nogle af de samme anvendelser som nonylphenolethoxylater, men i en mindre mængde: omkring 1.000 t/år i EU. Den vigtigste registrerede anvendelse af OP/OPEO i Danmark er brugen af octylphenol ethoxylater i maling, lak og fernis (der er andre anvendelser som er fortrolige). Mængderne er dog betydeligt mindre end de mængder af NP og NPEO, som bruges til

dette anvendelsesområde. Octylphenoler kan være til stede i lave koncentrationer som uomsat stof i gummi og plast, som er lavet på basis af octylphenoler.

Sammenlignet med NP/NPEO er OP/OPEO meget mindre reguleret, selv om det stof inden for stofgruppen, der anvendes i størst mængde, 4-*tert*-octylphenol (også kaldet p-*tert*-OP) ligesom NP er klassificeret som giftigt i vandmiljøet. Octylphenolethoxylater kan nedbrydes til octylphenoler i miljøet ved de samme mekanismer som ved nedbrydningen af nonylphenolethoxylater til nonylphenoler. OP/OPEO indgår lige som NP/NPEO, i OSPARs liste over prioriterede stoffer og HELCOMs handlingsplan for Østersøen (Baltic Sea Action Plan). De er prioriterede stoffer under Vandrammedirektivet og omfattet af EUs strategi for hormonforstyrrende stoffer. 4-*tert*-Octylphenol er ikke klassificeret som et stof, der skader forplantningsevnen hos mennesker.

Koncentrationerne af OP/OPEO i kommunalt spildevand og spildevandsslam er betydeligt lavere end koncentrationerne af NP/NPEO. Koncentrationerne i søsedimenter i Danmark og i marine sedimenter i Østersøområdet og de indre danske farvande er også betydeligt lavere end koncentrationen af NP/NPEO, men HELCOM konkluderer i sin seneste vurdering, at koncentrationen af octylphenoler oversteg den tærskelværdi for octylphenoler i sedimenter, der er foreslået i forbindelse med EU's vandrammedirektiv, i omkring halvdelen af prøverne af overfladesediment.

En af de vigtigste octylphenoler, 4-*tert*-OP, er inkluderet i kandidatlisten under REACH med bekymring for miljøet angivet som begrundelse. Et REACH bilag XV dossier er for nylig blevet udarbejdet med henblik på at identificere octylphenolethoxylater som SVHC-stoffer. Grundlaget for forslaget er nedbrydningen af octylphenolethoxylater til octylphenoler, som har hormonforstyrrende egenskaber i miljøet, og at kortkædede octylphenolethoxylater kan forårsage hormonforstyrrende effekter ved lignende eller lidt højere koncentrationer sammenlignet med octylphenoler.

Dodecylphenoler og dodecylphenolethoxylater

Dodecylphenoler (DP, med 12 kulstofatomer i kæderne) er de eneste kommercielt vigtige alkylphenoler med en kulstofkæde længere end 9. Omkring 99% af forbruget i EU (50.000 t/år) anvendes som et mellemprodukt ved fremstilling af smøremiddeladditiver. Dodecylphenoler indgår i de endelige additiver i små mængder. Mindre end 1% af dodecylphenolerne anvendes til fremstilling af dodecylphenolethoxylater (DPEO), der anvendes som anti-rust midler i smøreolier.

Et forslag til harmoniseret klassificering og mærkning af 4-(3,4,5-trimethylheptyl)phenol (en forgrenet dodecylphenol) foreslår, at stoffet klassificeres som kræftfremkaldende, brandfarlig, og som givende øjenirritation/alvorlig øjenskade. Ingen dodecylphenoler er opført på EUs liste over hormonforstyrrende stoffer. Ifølge en PBT vurdering af én af dodecylphenolerne, opfylder stoffet T-kriteriet (giftigt for vandlevende organismer), og opfylder formentlig P-kriteriet (persistent) og vP-kriteriet (meget persistent). Det opfylder ikke B-kriteriet (bioakkumulerbart) og kan derfor ikke anses for at være et PBT-stof. Den akutte giftighed af dodecylphenoler ligger på samme niveau som giftigheden af octylphenoler.

Dodecylphenoler og dodecylphenol ethoxylater er ikke omfattet af nogen EU-regulering, er ikke prioriterede stoffer under Vandrammedirektivet og er ikke medtaget i OSPARs liste over prioriterede stoffer eller HELCOMs handlingsplan for Østersøen (Baltic Sea Action Plan).

Meget få overvågningsdata er blevet fundet ved kortlægningen. I en screening af AP/APEO i det nordiske miljø, var dodecylphenoler sammen men octylphenoler, nonylphenoler og nonylphenol ethoxylater, de stoffer, der blev fundet i de højeste koncentrationer i alle prøver af spildevand. En foreløbig miljørisikovurdering af dodecylphenoler udført i Storbritannien anslog, at den vigtigste kilde til dodecylphenoler i miljøet var udslip af dodecylphenoler til spildevand fra brug og bortskaffelse af smøremidler (primært som spild og lækager). Miljørisikovurderingen fandt, at der er en potentiel risiko for organismer i vandmiljøet ved nogle scenarier, og at der er behov for mere pålidelige data om eksponering af organismer i miljøet.

Kortkædede alkylphenoler (med kæder med mindre end 8 kulstofatomer)
Kortkædede alkylphenoler anvendes generelt ikke til fremstilling af alkylphenolethoxylater, så problemstillingerne vedrørende ethoxylaterne som kilder til alkylphenoler i miljøet gælder ikke for de kortkædede alkylphenoler. Den kortkædede alkylphenoler er en meget forskelligartet gruppe af stoffer med én, to eller tre korte kulstofkæder bundet til en phenolgruppe. Anvendelsesområderne for de kortkædede alkylphenoler er meget varierede.

De kortkædede alkylphenoler er generelt af mindre bekymring end nonylphenoler og octylphenoler i relation til miljøet, fordi de generelt er biologisk nedbrydelige og ikke bioakkumuleres i samme omfang. De er ikke omfattet af OSPARs liste over prioriterede stoffer, HELCOMs handlingsplan for Østersøen (Baltic Sea Action Plan), er ikke klassificeret som prioriterede stoffer under Vandrammedirektivet, og er ikke prioriterede stoffer inden for EUs strategi for hormonforstyrrende stoffer. Undtagelserne er 2,4,6-tri-*tert*-butylphenol, som indgår i OSPARs liste over prioriterede stoffer og som er angivet som potentielt giftige, persistente og bioakkumulerende og 4-*tert*-butylphenol, som er et stof i kategori 2 (bevis for potentiale til at forårsage hormonforstyrrelser) på EUs liste over hormonforstyrrende stoffer.

En de vigtigste årsager til bekymring vedrørende nonylphenoler og octylphenoler er de hormonforstyrrende effekter af stofferne. Alkylphenoler med alkylgrupper med mere end to kulstofatomer fastgjort i position 4 på phenolen har vist at have virkninger meget lig østrogens. De tilgængelige data tyder på, at både positionen (*para*> *meta*> *ortho*) og forgreningen (tertiær> sekundær = normal) af alkylgruppen påvirker østrogeneffekten. Optimal østrogenaktivitet kræver en enkelt tertiær forgrenet alkylgruppe sammensat af mellem 6 og 9 kulstofatomer og placeret i position 4 på en phenol. Det skal derfor understreges, at det primært er de 4-monosubstituerede alkylphenoler, der synes at være hormonforstyrrende, og at 4-nonylphenol og 4-*tert*-octylphenol er de mest potente af stofferne. 2,4-di-*tert*-Butylphenol er dog som nævnt i det følgende omfattet af den løbende handlingsplan for Fællesskabets (CoRAP under REACH), fordi stoffet er mistænkt for at være hormonforstyrrende.

De relativt få tilgængelige data tyder på, at koncentrationerne af de kortkædede alkylphenoler i kommunalt spildevand og spildevandsslam er markant lavere (10-100 gange lavere) end koncentrationerne af NP/NPEO. 4-*tert*-Butylphenol er påvist i sedimenter i Østersøen i større koncentrationer end octylphenoler og i koncentrationer, som er sammenlignelige med nonylphenoler, mens næsten ingen data for de andre kortkædede alkylphenoler er blevet fundet ved denne kortlægning. Hvorledes 4-*tert*-butylphenol spredes til miljøet er ikke undersøgt i detaljer.

To af stofferne anvendes i mængder på over 20.000 t/år i EU: 4-*tert*-butylphenol (også betegnet ptBP) og 2,6-di-*tert*-butyl-p cresol (BHT).

4-*tert*-Butylphenol anvendes hovedsagelig på samme måde som 4-nonylphenol and 4-*tert*-octylphenol som co-monomer til fremstilling af phenolharpikser og kædeterminator i produktionen af polycarbonat. 4-*tert*-Butylphenol er den eneste af den kortkædede alkylphenoler, som der er foretaget en EU-risikovurdering for. Ifølge risikovurderingen anses ureageret 4-*tert*-butylphenol i plast og gumm for at være den vigtigste kilde til forbrugernes udsættelse for stoffet. 4-*tert*-Butylphenol er forbudt til brug i kosmetik, men ikke har en harmoniseret klassificering. En forslag til en harmoniseret klassificering som hudirriterende, skadeligt for øjnene, reproduktionstoksisk og udvisende specifik målorgantoksicitet er for nylig blevet udarbejdet.

2,6-di-*tert*-butyl-p cresol (BHT) anvendes som antioxidant i en bred gruppe af produkter; blandt disse fødevarer og foder. Stoffet er af OECD blevet foreslået til yderligere miljørisikovurdering.

2,4-di-*tert*-butylphenol, der anvendes som kemisk mellemprodukt til fremstilling af plasttilsætningsstoffer i mængder på over 1,000 t/år på EU plan, er omfattet af den løbende handlingsplan for Fællesskabet (CoRAP) på grund af dets anvendelses- og eksponeringsmønster, og fordi stoffet er mistænkt for at være hormonforstyrrende.

2,4,6-tri-*tert*-butylphenol, er som omtalt omfattet af OSPARs liste over prioriterede stoffer. Stoffet anvendes primært som intermediat og udledningerne til miljøet fra brugen af stoffet er vurderet at være små.

Thymol, der anvendes i rengøringsmidler og duftende artikler, har en harmoniseret klassificering som akut giftigt, hudætsende og farligt for vandmiljøet. Ifølge selvklassificeringerne, som er meddelt til C&L databasen (C&L Inventory) på Det Europæiske Kemikalieagenturs hjemmeside, har de fleste af de beslægtede stoffer lignende klassifikationer.

Samlet konklusion vedrørende gruppering af stofferne

Nonylphenoler og octylphenoler deler nogle af de samme miljø- og sundhedsmæssige egenskaber, og de to stofgrupper er sammen med deres ethoxylater, de AP/APEO som vækker størst bekymring. Dodecylphenoler og deres ethoxylater anvendes til andre formål, og frigives til omgivelserne i mindre mængder, men er af bekymring på grund af deres miljø- og sundhedsmæssige egenskaber.

Blandt de kortkædede alkylphenoler (<8 kulstofatomer), anvendes 4-*tert*-butylphenol til samme formål som 4-nonylphenol and 4-*tert*-octylphenol, men frigivelses- og eksponerings-mønsteret er helt anderledes. De fleste af de andre kortkædede mono-, di- og trialkyl phenoler vækker mindre bekymring fordi:

- udledninger til miljøet generelt er betydeligt mindre end udledninger af nonylphenoler og nonylphenol-ethoxylater,
- de har et betydeligt lavere potentiale for bioakkumulering end de langkædede (C8-C12) alkylphenoler,
- de synes at være mere biologisk nedbrydelige, og
- deres østrogene potens er lavere.

De kortkædede alkylphenoler anvendes med få undtagelser til andre formål end nonylphenoler og octylphenoler og deres ethoxylater. Dog kan nogle af de kortkædede stoffer være af en vis bekymring.

Baseret på de tilgængelige data synes der ikke at være grundlag for at behandle de kortkædede alkylphenoler og de langkædede som én gruppe, men snarere at vurdere hvert af de kortkædede alkylphenoler enkeltvis for at identificere eventuelle behov for foranstaltninger til at reducere eksponeringen af mennesker og miljø.

Datamangler

De vigtigste datamangler, når der tages hensyn til, hvilke stoffer der er af størst bekymring, er følgende:

- Opdateret information om de aktuelle anvendelser af NP/NPEO og den relative betydning af de potentielle kilder til udslip til miljøet mangler.
- De registrerede mængder af NPEO anvendt i rengørings- og vedligeholdelsesmidler i Danmark kalder på en afklaring af de nuværende anvendelser.
- For flere af stofferne, er den tilgængelige information om den samlede produktion og import til EU som registreret under REACH ikke i overensstemmelse med den information, som er indhentet fra industrien, og dette kalder på en afklaring.

- For mange af stofferne, som anvendes i smøremidler og olie, mangler der data om de potentielle udslip i forbindelse med spild og bortskaffelse af spildolie.
- Der er fundet relative høje koncentrationer af 2,6-di-*tert*-butyl-*p*-cresol i spildevand og OECD har konkluderet at der er brug for mere information om de faktiske udledninger af dette stof og om eksponering af organismer i miljøet.
- En oversigt fra HELCOM konkluderer at der generelt bør være flere målinger af NP/NPEO and OP/OPEO i udledninger til Østersøens afstrømningsområde, samt i havvand, organismer og sediment i Østersøen for at undersøge i hvilken grad stofferne har skadelige effekter i det marine miljø.
- Oversigten fra HELCOM konkluderer også, at der er brug for flere økotoksikologiske data om sedimentlevende organismer for bedre at kunne estimere et nul-effekt niveau (PNEC) for organismerne i sedimentet.
- Mere viden om niveauer og miljøeffekter af dodecylphenol og 4-*tert*-butylphenol vil være gavnligt for at kunne vurdere, om der er behov for en reduktion af udledningerne af disse stoffer til vandmiljøet.
- Data vedrørende human toksicitet af andre af de lang-kædede alkylphenoler end nonylphenoler er begrænsede, og data om alkylphenolethoxylater findes stort set ikke.
- For mange af de kort-kædede alkylphenoler er der ingen eller ufuldstændige data til at vurdere i hvilken grad stofferne er hormonforstyrrende.
- Opdateret information om de tekniske og økonomiske fordele og ulemper ved at erstatte NP/NPEO and OP/OPEO med alternativer til de tilbageværende anvendelser mangler. Dette gælder især:
  - Brug af stofferne til emulsion-polymerisering (se afsnit 3 for nærmere forklaring) og til maling som udgør den største anvendelse af stofferne i Danmark.
  - Alternativer til 4-*tert*-BP, 4-*tert*-OP and 4-NP til produktion af forskellige former for harpikser (resiner).

1. Introduction to the substance group

1.1 Definition of the substance groups

The following section introduces the two substance groups and some basic chemical nomenclature of importance for the understanding of the naming of the substances.

An alkylphenol is a phenol derivative wherein one or more of the ring hydrogens have been replaced by one or more alkyl groups. An alkyl group is a functional group or side-chain that consists solely of single-bonded carbon and hydrogen atoms. A wide variety of alkylphenol structures are possible, but many are not commercially important. Alkylphenols of the greatest commercial importance have alkyl groups ranging in size from one (methyl) to twelve carbons (dodecyl) (Kirk Othmer, 2003). The alkylphenols are often named after their chain length e.g. nonylphenol (9 carbon atoms) and dodecylphenol (12 carbon atoms).

It is common to consider the group synonymous with nonylphenol and nonylphenol ethoxylates and other AP/APOE with similar application patterns without a more precise definition. As an example the "alkylphenol and alkylphenol ethoxylates" are mentioned collectively in criteria documents for the Nordic Swan and the EU Flower ecolabels, but the substance group is not defined in the documents and apparently not in any of the background documents.

The European Council for Alkylphenols and Derivatives, CEPAD, represents companies which manufacture a variety of alkylphenols ranging from butylphenols with a chain length of 4 to the dodecylphenol and derivatives with a chain length of 12.

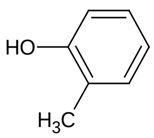
Cresols and xylenols

The substances with the shortest chain length, i.e. with only one or two methyl groups, are most often designated as cresols (*o*-, *p*- and *m*-isomers) and xylenols, respectively (a methyl group has one carbon atom only and three hydrogen atoms). They differ significantly in their chemistry, toxicity and application pattern from the longer chained alkylphenols. The cresols and xylenols are not considered as potential alternatives to the longer-chained alkylphenols, and the environmental and health issues associated with these substances are different from the issues relevant for the longer chained AP. Both cresol and xylenol have a harmonised classification as acute toxic.

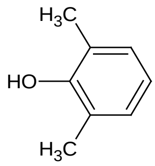
It is common not to consider the methylphenols as part of the "alkylphenols" group. As an example, Ullmann's Encyclopedia of Industrial Chemistry lists 82 CAS numbers in the chapter on alkylphenols, but has separate chapters on the methylphenols. Moreover, these substances do not have similar use patterns compared to the substances mentioned as examples in LOUS. Cresols are mainly used as solvents and xylenols as pesticides. These substances have been considered beyond the scope of this survey; they are included in the gross list of substances in the following section but are otherwise not assessed in the report[1].

[1] Cresols and xylenols have according to the CLP regulation (Regulation (EC) No 1272/2008) the hazard class and category codes: Acute toxic 3, skin corr. 1B. Some of the xylenols further have the hazard class and category code Aquatic Chronic 2.

o-Cresol (2-methylphenol)
CAS No 95-48-7



2,6-Xylenol (dimethyl phenol)
CAS No 576-26-1



Mono-alkylphenols

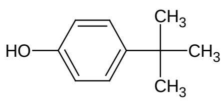
The mono alkylphenols are phenol derivatives wherein only one of the benzene ring hydrogens has been replaced by an alkyl group which as a group consists of a saturated chain of single bonded carbon and hydrogen atoms. The mono-alkylphenols are commonly referred to by the number of C atoms in the alkyl group. The most common are: butylphenols (C4), pentylphenols (C5), hexylphenols (C6), octylphenols (C8), nonylphenols (C9), and dodecylphenols (C12). The alkyl group may be linear or branched and the commercial products are often complex mixtures.
The prefixes *sec*- (from "secondary") and *tert*- (from "tertiary") refer to branched alkyl chains with one, respectively two methyl groups attached to the first carbon in the alkyl group.

The substances are further named on the basis of additional side chains and the position of the first carbon in the chain in relation to the OH groups.

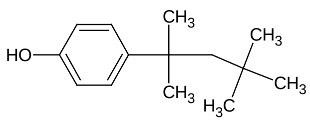
The position of the alkyl group is designated either by the Latin designations o- (*ortho*), m- (*meta*), and p- (*para*) or by the corresponding numbers based on a 1,2-, 1,3-, and 1,4-, relationship. The common 4-*tert*-butylphenol (or *p*-*tert*-butylphenol) has the first carbon in the *para* position (opposite the OH group) and a tertiary carbon to which three other carbons are attached. The substance is often referred to as 4-*tert*-butylphenol or *pt*BP.

Three of the most common alkylphenols are shown below. They are all used as a co-monomer in the production of phenolic resins and other types of resins which are polymeric materials (see description of resins in section 3.2.1). Among other applications, resins are used in the manufacture of some thermosets such as two-component phenolic plastics and epoxy, and used in some types of paints, lacquers, sealants, fillers and adhesives.

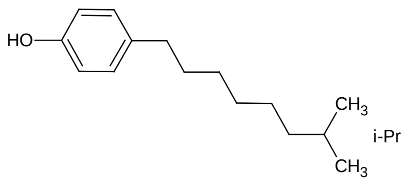
4-*tert*-Butylphenol
CAS No 98-54-4



4-(1,1,3,3-Tetramethylbutyl)phenol (4-*tert*-octylphenol)
CAS No 140-66-9



4-Nonylphenol, branched
CAS No 84852-15-3



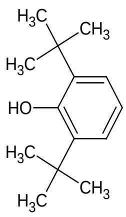
Dialkylphenols and trialkylphenols

The dialkylphenols and trialkylphenols are phenol derivatives wherein two or three of the benzene ring hydrogens have been replaced by alkyl groups. The alkyl groups may be similar or different alkylgroups may be attached to the ring.

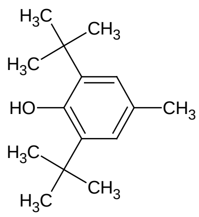
Examples of some of the commonly used substances are shown below. If one of the derivatives is a methyl group, the substance is often named cresol instead of phenol. These substances are in general used for other purposes than the single chain butyl, octyl and nonylphenols; they have other human health and environmental properties and may often not be considered part of the group

AP/APEO. Of the three substances shown below, 2,6-di-*tert*-butyl-*p*-cresol and thymol are used as food additives, among other applications. They are, however, included in this survey in order to elucidate whether they share some of the same characteristics as the long-chain alkylphenols.

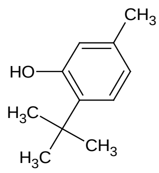
2,6-Di-*tert*-butylphenol
CAS No 128-39-2



2,6-Di-*tert*-butyl-*p*-cresol
CAS No 128-37-0



Thymol
CAS No 89-83-8



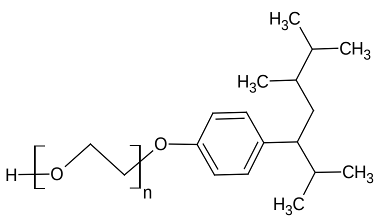
Alkylphenol ethoxylates

The second group of substances addressed in this survey are the alkylphenol ethoxylates (APEO) which are produced from alkylphenols. Only ethoxylates of octylphenol, nonylphenol and dodecylphenol have been identified as used in the EU. Two examples are shown below.

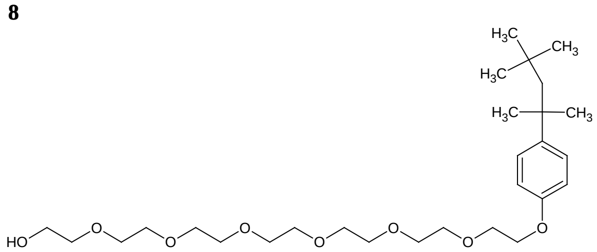
APEOs are manufactured by the addition of ethylene oxide (C_2H_4O) to the alkylphenol under pressure. The length of the ethoxylate chain can be controlled by regulating the ratio of the alkylphenol and the ethylene oxide and by the reaction time. Commercial APEOs are a mixture of ethoxylated APs with differing ethoxy units. As an example, a commercial nonylphenol ethoxylate such as Tergitol NP-9 from DOW contains a mixture of oligomers from about 3 ethoxylates to 14 ethoxylates with an average of 9 ethoxylates (Earls and Reydellet, 2006). The chemical and toxicological properties are dependent on the ethoxy chain length (Earls and Reydellet, 2006). The APEOs may be degraded in the environment to shorter chain APEOs and the parent AP.

In environmental monitoring. e.g. in Denmark, it is often the nonylphenol monoethoxylates and nonylphenol diethoxylates that are measured. The notation is commonly NP1EO and NP2EO, respectively.

Nonylphenol, branched, ethoxylated
CAS No 127087-87-0



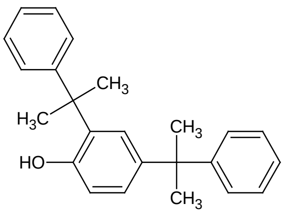
20-[4-(1,1,3,3-Tetramethylbutyl)phenoxy]-3,6,9,12,15,18-hexaoxaicosan-1-ol (octylphenol ethoxylate)
CAS No 2497-59-8



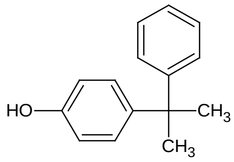
Arylphenols

Some arylphenols, with two connected benzene rings, are sometimes considered together with the AP/APOE, e.g. by CEPAD which mentions *p*-cumylphenol and *o,p*-dicumylphenol among the alkylphenols addressed by the organisation. The substances are used as intermediates in the production of polycarbonates, epoxy resins and plastic additives. As the substances are not alkylphenols (they do not meet the definition of an alkylphenol), they have been beyond the scope of this survey. The cumylphenols do not have a harmonised classification.

2,4-Di(1-methyl-1-phenylethyl)phenol
(*o*,*p*-cumylphenol)
CAS No 2772-45-4



4-(α,α-Dimethylbenzyl)phenol
(*p*-cumylphenol)
CAS No 599-64-4



1.2 Substances within the substance groups

The group of AP/APEO includes a large number of substances. UK Environment Agency (2005b) lists in a prioritization of alkylphenols 50 CAS numbers of alkylphenols that appear to have been produced commercially at some time and potentially on the market. Ullmann's Encyclopedia of Industrial Chemistry lists 82 CAS numbers in the section on alkylphenols (excluding cresols and xylenols).

In total about 190 substances within the group of AP/APEO have been identified for this survey from a number of data sources:

- Reports from national authorities;
- Annex XV reports and other assessment reports;
- Ullmann's Encyclopedia of Industrial Chemistry and Kirk Othmer Encyclopedia of Chemical Technology;
- The SPIN database of the Nordic Product Registries (SPIN, 2012) and REACH registrations using the search strings "ylphenol", yl)phenol", "cresol" and "ethoxylate" and subsequent manual selection;
- A search on the Internet for the less-used alkylphenols and their ethoxylates using the strings: propyl-, pentyl-, hexyl-, heptyl-, decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, pentadecyl-, hexadecyl-, heptadecyl-, octadecyl-, nonadecyl- and amylphenol and these strings combined with "ethoxylate", supplemented by a search on cresol and xylenol.

Of the identified substances, 177 are included in the list of pre-registered substances under REACH and listed in Table 1. Some CAS numbers from the literature are not included in the list of pre-registered substances, which indicates that they are used in low tonnage or not used at all, and these CAS numbers are not considered relevant in an EU context and are consequently not included in the table.

The table further indicates:

- Tonnage bands for substances which have been registered;
- Whether the substances are intended to be registered by 2013;
- Tonnage registered in the Danish Product Register with a total of import and production.

Substances registered with ECHA: The database on registered substances includes:

- substances manufactured or imported at 1000 tonnes or more per year,
- carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and
- substances dangerous to aquatic organisms or the environment above 100 tonnes per year (Deadline for registration was 30 November 2010).

Intentions 2013: The deadline for registration of substances manufactured or imported at 100-1000 tonnes per year is 31 May 2013. The column indicates substances for which companies have expressed their intentions for registration of the substances.

Substances registered in the Danish Product Register: Substances registered in the Danish Product Register with an indication of the quantity (only substances with a registered quantity are included in the table). The data are further described in section 3.3.

The substances in Table 1 are organised with the mono-alkylphenols and their ethoxylates listed first, followed by the list of dialkylphenols and trialkylphenols. Please note that the chemical names indicated are the names used by the pre-registration and the naming is not totally consistent.

One of the objectives of the table is to provide an initial indication of which substances are manufactured and used in the largest quantities. The consumption of the substances in the EU and Denmark is further described in chapter 0. Another objective is to serve as reference table listing the substances which may be used within the different substance groups.

Cresols and xylenols (methylphenol and dimethylphenol), as well as the arylphenols, are included in the table for reference, but are otherwise considered beyond the scope of the current survey.

Of the C_3 – C_7 APs, the butylphenols (C_4) seems to be used in highest quantities in both the EU and Denmark. However, the C8 (octyl) and C9 (nonyl) APs are manufactured and/or imported in significantly higher quantities than the C3 – C7 APs, both in the EU and in Denmark.

Of the substances with longer branches, the dodecylphenols (C12) are the substances with the highest tonnages both in the EU and Denmark.

Ethoxylates of octylphenol (OP), nonylphenol (NP) and dodecylphenol (DP) are registered in the Danish Product Register, but of these, only nonylphenol ethoxylates have been registered under REACH by 2010.

TABLE 1
IDENTIFIED SUBSTANCES WITHIN THE SUBSTANCE GROUP WITH INDICATION OF REGISTERED TONNAGE, REGISTERING BY 2013 AND REGISTERED TONNAGE IN THE DANISH PRODUCT REGISTER JULY 2012

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
Mono alkylphenols and ethoxylates						
Methylphenol, cresols (out of scope of this report)						
95-48-7	202-423-8	*o*-cresol	1	10,000 - 100,000		Total all 4: 6,343
106-44-5	203-398-6	*p*-cresol	1	10,000 - 100,000		
108-39-4	203-577-9	*m*-cresol	1	10,000 - 100,000		
1319-77-3	215-293-2	cresol	1	1,000 - 10,000		
-	906-151-7	reaction mass of *m*-cresol and *p*-cresol	1	1,000 - 10,000		n.r.
Ethylphenols						
25429-37-2	607-726-2 *5	ethylphenol	2	n.r.		confidential
90-00-6	201-958-4	2-ethylphenol	2	n.r.		n.r.
123-07-9	204-598-6	4-ethylphenol	2	n.r.		n.r.
620-17-7	210-627-3	3-ethylphenol	2	n.r.		n.r.
Propylphenols						
90480-88-9	291-826-2	phenol, isopropylated	3	intermediate use only		n.r.
88-69-7	201-852-8	2-isopropylphenol	3	n.r.		n.r.
618-45-1	210-551-0	3-isopropylhydroxybenzene	3	n.r.		n.r.
Butylphenols						
89-72-5	201-933-8	2-*sec*-butylphenol	4	1,000 - 10,000		n.r.
98-54-4	202-679-0	4-*tert*-butylphenol	4	intermediate use only		8.3
88-18-6	201-814-0	2-*tert*-butylphenol	4	n.r.		0.2
99-71-8	202-781-5	4-*sec*-butylphenol	4	n.r.		n.r.
585-34-2	209-553-4	3-*tert*-butylphenol	4	n.r.		n.r.
1638-22-8	216-672-5	4-butylphenol	4	n.r.		n.r.
4074-43-5	223-790-0	3-butylphenol	4	n.r.		n.r.
27178-34-3	248-300-2	tert-butylphenol	4	n.r.		n.r.
28805-86-9	249-246-2	butylphenol	4	n.r.		0.3
68610-06-0	271-847-3	phenol, isobutylenated	4	n.r.	x	
31195-95-6	250-509-9	isobutylphenol	4	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
Pentylphenols						
80-46-6	201-280-9	*p*-(1,1-dimethylpropyl)phenol (4-*tert* amylphenol]	5	n.r.		n.r.
136-81-2	205-261-6	o-pentylphenol	5	n.r.		n.r.
87-26-3	201-736-7	2-(1-methylbutyl)phenol	5	n.r.		n.r.
1518-84-9	216-179-5	2-cyclopentylphenol	5	n.r.		n.r.
3279-27-4	221-916-9	2-(1,1-dimethylpropyl)phenol (0-*tert* amylphenol]	5	n.r.		n.r.
14938-35-3	239-015-4	4-pentylphenol	5	n.r.		n.r.
20056-66-0	243-487-7	m-pentylphenol	5	n.r.		
Hexylphenols						
119-42-6	204-322-4	2-cyclohexylphenol	6	n.r.		0.3
1131-60-8	214-465-4	4-cyclohexylphenol	6	n.r.		0.05
2446-69-7	219-501-2	4-hexylphenol	6	n.r.		n.r.
26570-85-4	247-813-9	cyclohexylphenol	6	n.r.		n.r.
Heptylphenols						
1987-50-4	217-862-0	4-heptylphenol	7	n.r.	x	confidential
Octylphenols and octylphenol ethoxylates						
140-66-9	205-426-2	4-(1,1,3,3-tetramethylbutyl)phenol (4-*tert*-octylphenol)	8	10,000 - 100,000		confidential
949-13-3	213-437-9	o-octylphenol	8	n.r.		n.r.
1806-26-4	217-302-5	4-octylphenol	8	n.r.		n.r.
1818-08-2	217-332-9	4-(1-methylheptyl)phenol	8	n.r.		n.r.
3307-00-4	221-989-7	4-(1-ethylhexyl)phenol	8	n.r.		n.r.
3884-95-5	223-420-8	*o*-(1,1,3,3-tetramethylbutyl)phenol	8	n.r.		confidential
11081-15-5	234-304-1	isooctylphenol	8	n.r.		n.r.
17404-44-3	241-426-9	*o*-(1-ethylhexyl)phenol	8	n.r.		n.r.
18626-98-7	242-459-1	*o*-(1-methylheptyl)phenol	8	n.r.	x	n.r.
26401-75-2	247-663-4	o-*sec*-octylphenol	8	n.r.		n.r.
27193-28-8	248-310-7	(1,1,3,3-tetramethylbutyl)phenol	8	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
27214-47-7	248-330-6	4-*sec*-octylphenol	8	n.r.		n.r.
27985-70-2	248-759-9	(1-methylheptyl)phenol	8	n.r.		n.r.
67554-50-1	266-717-8	octylphenol	8	n.r.		n.r.
93891-78-2	299-461-0	sec-octylphenol	8	n.r.		n.r.
99561-03-2	308-979-9	Phenol, 4-octyl-, branched	8	n.r.		n.r.
37631-10-0	253-574-1	*o*-(1-propylpentyl)phenol	8	n.r.		n.r.
2497-59-8	219 -682-8	20-[4-(1,1,3,3-tetramethyl-butyl)phenoxy]-3,6,9,12,15,18-hexaoxaicosan-1-ol	C8-ethox-ylate	n.r.		n.r.
9002-93-1	618-344-0 *5	poly(oxy-1,2-ethanediyl), α-[4-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy *5	C8-ethox	n.r.		12
9036-19-5	618-541-1 *5	poly(oxy-1,2-ethanediyl), α-[(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy	C8-ethox	n.r.		
68987-90-6	614-869-4*5	poly(oxy-1,2-ethanediyl), α-(octylphenyl)-ω-hydroxy-, branched	C8-ethox	n.r.		n.r.
Nonylphenol and nonylphenol ethoxylates						
84852-15-3	284-325-5	phenol, 4-nonyl-, branched	9	10,000 - 100,000		1.4
104-40-5	203-199-4	4-nonylphenol	9	n.r.		
-	440-740-5	4-(4-trans-propylcylohexyl)phenol	9	intermediate use only		n.r.
136-83-4	205-263-7	*o*-nonylphenol	9	n.r.		n.r.
139-84-4	205-376-1	m-nonylphenol	9	n.r.		n.r.
11066-49-2	234-284-4	isononylphenol	9	n.r.		n.r.
17404-66-9	241-427-4	4-(1-methyloctyl)phenol	9	n.r		n.r.
25154-52-3	246-672-0	nonylphenol	9	n.r.		33
26543-97-5	247-770-6	4-isononylphenol	9	n.r.		n.r.
27938-31-4	248-741-0	*o*-isononylphenol	9	n.r.		n.r.
30784-30-6	250-339-5	4-(1,1-dimethylheptyl)phenol	9	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
52427-13-1	257-907-1	4-(1-ethyl-1-methylhexyl)phenol	9	n.r.		n.r.
90481-04-2	291-844-0	phenol, nonyl-, branched	9	n.r.		n.r.
9016-45-9	500-024-6	nonylphenol, ethoxylated	C9-ethox	n.r.		120
20427-84-3	243-816-4	2-[2-(4-nonylphenoxy)ethoxy]ethanol	C9-ethox	n.r.		n.r.
26027-38-3	500-045-0	4-nonylphenol, ethoxylated	C9-ethox	n.r.		0.01
37205-87-1	609-346-2 *5	poly(oxy-1,2-ethanediyl), α-(isononylphenyl)-ω-hydroxy-	C9-ethox	n.r.		5.0
68412-54-4	500-209-1	2-{2-[4-(2,4,5-trimethylhexan-3-yl)phenoxy]polyethoxy}ethanol	C9-ethoxylate	1,000 - 10,000 1,000 - 10,000		44.0
127087-87-0	500-315-8	4-nonylphenol, branched, ethoxylated	C9-ethox	n.r.		0.5
Decylphenol						
27157-66-0	248-271-6	decylphenol	10	n.r.		n.r.
93891-77-1	299-460-5	sec-decylphenol	10	n.r.		n.r.
Dodecylphenol and docecylphenol ethoxylates						
104-43-8	203-202-9	4-dodecylphenol	12	n.r.		0.05
121158-58-5	310-154-3	phenol, dodecyl-, branched	12	10,000 - 100,000 intermediate use only		4.4
11067-80-4	234-287-0	isododecylphenol	12	n.r.		n.r.
27193-86-8	248-312-8	dodecylphenol	12	n.r.		0.04
9014-92-0	9014-92-0	dodecylphenol, ethoxylated	C12-ethox	n.r.		2.4
74499-35-7	616-100-8	phenol, (tetrapropenyl) derivs.	C12-ethox	n.r.		
Pentadecylphenols						
501-24-6	207-921-9	3-pentadecylphenol	15	n.r.		n.r.
Hexadecylphenols						
2589-78-8	219-980-8	4-hexadecylphenol	16	n.r.		n.r.
Di- and trialkylphenols						

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
Dimethylphenols (xylenols) (out of scope of this report)						
576-26-1	209-400-1	2,6-xylenol	1 + 1	10,000 - 100,000		n.r.
1300-71-6	215-089-3	xylenol	1 + 1	n.r.		3,719
108-68-9	203-606-5	3,5-xylenol	1 + 1	intermediate use only		n.r.
-	905-287-4	reaction mass of 2,4-xylenol and 2,5-xylenol	1 + 1	1,000 - 10,000		n.r.
95-65-8	202-439-5	3,4-xylenol	1 + 1	n.r.		n.r.
95-87-4	202-461-5	2,5-xylenol	1 + 1	n.r.		n.r.
105-67-9	203-321-6	2,4-xylenol	1 + 1	n.r.		n.r.
526-75-0	208-395-3	2,3-xylenol	1 + 1	n.r.		n.r.
Trimethylphenols						
2416-94-6	219-330-3	2,3,6-trimethylphenol	1 + 1 + 1	1,000 - 10,000		n.r.
496-78-6	207-832-5	2,4,5-trimethylphenol	1 + 1 + 1	n.r.		n.r.
526-85-2	208-399-5	2,3,4-trimethylphenol	1 + 1 + 1	n.r.		n.r.
527-54-8	208-418-7	3,4,5-trimethylphenol	1 + 1 + 1	n.r.		n.r.
527-60-6	208-419-2	2,4,6-trimethylphenol	1 + 1 + 1	n.r.		n.r.
697-82-5	211-806-9	2,3,5-trimethylphenol	1 + 1 + 1	n.r.		n.r.
Tetramethylphenols						
488-70-0	207-684-1	2,3,4,5-tetramethylphenol	1 + 1 + 1 + 1	n.r.		n.r.
527-35-5	208-415-0	2,3,5,6-tetramethylphenol	1 + 1 + 1 + 1	n.r.		n.r.
3238-38-8	221-799-4	2,3,4,6-tetramethylphenol	1 + 1 + 1 + 1	n.r.		n.r.
Pentamethyl phenols						
2819-86-5	220-580-0	pentamethylphenol	1 + 1 + 1 + 1 + 1	n.r.		n.r.
Ethyl methyl phenols, diethyl phenols						
3855-26-3	223-361-8	2-ethyl-4-cresol	2 + 1	n.r.		n.r.
1123-73-5	214-377-6	3-ethyl-*o*-cresol	2 + 1	n.r.		n.r.
1123-94-0	214-382-3	4-ethyl-*m*-cresol	2 + 1	n.r.		n.r.
1687-61-2	216-875-9	6-ethyl-*m*-cresol	2 + 1	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
2219-73-0	218-733-1	4-ethyl-*o*-cresol	2 + 1	n.r.		n.r.
6161-67-7	228-189-7	3-ethyl-4-cresol	2 + 1	n.r.		n.r.
698-71-5	211-818-4	5-ethyl-m-cresol	2 + 1	n.r.		n.r.
936-89-0	213-318-1	2,4-diethylphenol	2 + 2	n.r.		n.r.
1006-59-3	213-744-8	2,6-diethylphenol	2 + 2	n.r.		n.r.
1197-34-8	214-824-5	3,5-diethylphenol	2 + 2	n.r.		n.r.
Propyl methyl phenols						
89-83-8	201-944-8	thymol	3 + 1	1,000 - 10,000		0.002
499-75-2	207-889-6	carvacrol	3 + 1	n.r.		n.r.
3228-01-1	221-760-1	2-isopropyl-m-cresol	3 + 1	n.r.		n.r.
3228-02-2	221-761-7	4-isopropyl-m-cresol	3 + 1	n.r.		n.r.
3228-03-3	221-762-2	5-isopropyl-m-cresol	3 + 1	n.r.		n.r.
4427-56-9	224-611-9	2-isopropyl-4-cresol	3 + 1	n.r.		n.r.
Di- and tri-propylphenols						
2078-54-8	218-206-6	disoprofol	3 + 3	n.r.		n.r.
2934-05-6	220-906-1	2,4-diisopropylphenol	3 + 3	n.r.		n.r.
26886-05-5	248-086-0	3,5-diisopropylphenol	3 + 3	n.r.		n.r.
2934-07-8	220-907-7	2,4,6-triisopropylphenol	3 + 3 + 3	n.r.		n.r.
Butyl methyl phenols, butyl ethyl phenol, butyl dimethyl phenols, butyl tetramethyl phenol						
88-60-8	201-842-3	6-*tert*-butyl-m-cresol	4 + 1	intermediate use only		n.r.
98-27-1	202-651-8	4-*tert*-butyl-*o*-cresol	4 + 1	n.r.		n.r.
2219-72-9	218-732-6	4-*tert*-butyl-*m*-cresol	4 + 1	n.r.		n.r.
2219-82-1	218-734-7	6-*tert*-butyl-*o*-cresol	4 + 1	n.r.		n.r.
2409-55-4	219-314-6	2-*tert*-butyl-*p*-cresol	4 + 1	intermediate use only		0.001
4892-31-3	225-514-4	5-*tert*-butyl-*m*-cresol	4 + 1	n.r.		n.r.
25567-40-2	247-108-6	tert-butyl-*p*-cresol	4 + 1	n.r.		n.r.
96-70-8	202-526-8	2-*tert*-butyl-4-ethylphenol	4 + 2	n.r.		n.r.
1879-09-0	217-533-1	6-*tert*-butyl-2,4-xylenol	4 + 1 + 1	n.r.		0.02
879-97-0	212-910-7	4-*tert*-butyl-2,6-xylenol	4 + 1 + 1	n.r.		n.r.
1445-23-4	215-891-3	2-*tert*-butyl-4,5-xylenol	4 + 1 + 1	n.r.		n.r.
17696-37-6	241-696-8	4-*tert*-butyl-2,5-xylenol	4 + 1 + 1	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
3884-95-5	223-420-8	*o*-(1,1,3,3-tetramethylbutyl)phenol	4 + 1 + 1 + 1 + 1	n.r.		n.r.
Dibutylphenols, dibutyl methyl phenols, tributylphenols						
96-76-4	202-532-0	2,4-di-*tert*-butylphenol	4 + 4	100 - 1,000 100 - 1,000		0.3
128-39-2	204-884-0	2,6-di-*tert*-butylphenol	4 + 4	100 - 1,000 100 - 1,000 Intermediate use only		19.6
1138-52-9	214-513-4	3,5-di-*tert*-butylphenol	4 + 4	n.r.		n.r.
5510-99-6	226-854-6	di-*sec*-butylphenol, mixed isomers	4 + 4 mixed	intermediate use only		n.r.
26967-68-0	248-146-6	dibutylphenol	4 + 4	n.r.		n.r.
31291-60-8	250-550-2	di-*sec*-butylphenol	4 + 4	intermediate use only		n.r.
128-37-0	204-881-4	2,6-di-*tert*-butyl-*p*-cresol	4 + 4 + 1	1,000 - 10,000 1,000 - 10,000 10,000 - 100,000		138
497-39-2	207-847-7	4,6-di-*tert*-butyl-*m*-cresol	4 + 4 + 1	n.r.		confidential
616-55-7	210-485-2	4,6-di-*tert*-butyl-*o*-cresol	4 + 4 + 1	n.r.		n.r.
732-26-3	211-989-5	2,4,6-tri-*tert*-butylphenol	4 +4 +4	intermediate use only		0.7
5892-47-7	227-572-6	2,4,6-tri-*sec*-butylphenol	4 +4 +4	n.r.	x	n.r.
17540-75-9	241-533-0	4-*sec*-butyl-2,6-di-*tert*-butylphenol	4 +4 +4	n.r.		confidential
Dinonylphenols						
137-99-5	205-310-1	2,4-dinonylphenol	9 + 9	n.r.		n.r.
1323-65-5	215-356-4	dinonylphenol	9 + 9	n.r.		confidential
54773-22-7	259-340-5	2,6-dinonylphenol	9 + 9	n.r.		n.r.
58085-76-0	261-106-2	3,5-dinonylphenol	9 + 9	n.r.		n.r.
Other alkylphenols						
1596-09-4	216-478-0	2-cyclohexyl-*p*-cresol	6 + 1	n.r.		n.r.
16152-65-1	240-303-7	2-(1-methylcyclohexyl)-*p*-cresol	7 + 1	n.r.		n.r.
77-61-2	201-042-4	6-(1-methylcyclohexyl)-2,4-xylenol	7 + 1 + 1	n.r.		n.r.

CAS No	EC No	Substance name *1	Carbon atoms in alkyl chains	Registered, tonnage band , t/y *2	Intention 2013 *4	Danish Product Register, t/y *3
120-95-6	204-439-0	2,4-di-*tert*-pentylphenol [2,4-di-*tert*-amylphenol]	5 + 5	n.r.		n.r.
51437-89-9	257-203-4	2-(p-octylphenoxy)ethanol	8 + 2	n.r.		n.r.
4130-42-1	223-945-2	2,6-di-*tert*-butyl-4-ethylphenol	4 + 4 + 2	n.r.		n.r.
4306-88-1	224-320-7	2,6-di-*tert*-butyl-4-nonylphenol	9+4+4	n.r.		0.2
68025-37-6	268-192-0	bis(tert-butyl)dodecylphenol	20	n.r		1.6
29988-16-7	249-991-3	dioctylphenol	8 + 8	n.r.		n.r.
-	931-468-2	C14-16-18 alkylphenol	mixed, 14,16,18	intermediate use only		n.r.
-	906-550-6	reaction mass of 2,3-xylenol and 3,5-xylenol and 3-ethylphenol and 4-ethylphenol	1 +1 mixed with 2	1,000 - 10,000		n.r.
-	905-278-5	reaction mass of 3,4-xylenol and 3,5-xylenol and 3-ethylphenol and 4-ethylphenol	mixed	n.r.		n.r.
Arylphenols (out of scope of this report)						
599-64-4	209-968-0	4-(α,α-dimethylbenzyl)phenol [4-cumylphenol]		Intermediate only		not included in search
2772-45-4	220-466-0	2,4-bis(1-methyl-1-phenylethyl)phenol [2,4-di-cumylphenol]		n.r.		not included in search
84962-08-3	284-702-4	dinonylphenol, branched		n.r.		not included in search
88-24-4	201-814-0	6,6'-di-*tert*-butyl-4,4'-diethyl-2,2'-methylenediphenol		n.r.		not included in search

*1 For registered substances the registered name is indicated; for other substances included in ESIS (with EC number), the substance name in ESIS is indicated (http://esis.jrc.ec.europa.eu/). However, for all substances the *p*- has been replaced by 4- for consistency in the remaining part of this report.

*2 As indicated in the lists of pre-registered and registered substances at ECHA's website. For each separate registration (which may cover more than one manufacturer) the registered tonnage is indicated. For substances indicated as "Intermediate use only" no tonnage band is reported.

*3 Tonnage indicates the registered import + manufacturing in the Danish Product Register July 2012. n.r. = not registered.

*4 Included in list of substances that companies have indicated to ECHA they intend to register by the 2013 REACH registration deadline. Based on responses to a survey ECHA has conducted. 31 May 2013 is the deadline for industry to register all phase-in substances manufactured or imported in the EU at or above 100 tonnes a year.

*5 The substance has no EC number, but has been given a list number in the EC format through the preregistration. Chemical name from preregistration is indicated.

1.3 Function of the substances for main application areas

The uses and consumption of the substances are further described in Chapter 3 whereas this section describes the function of the substances.

The main application of 4-*tert*-bytylphenol, 4-*tert*-octylphenol and 4-nonylphenols, as described in Chapter 0, is as raw material in the production of phenolic resins and other resins. The function of the alkylphenols is to react with other raw materials leading to the formation of polymers. As an example, 4-*tert*-octylphenol is used in the production of phenol–formaldehyde (Bakelite) resins which are some of the oldest-known thermosetting and thermoplastic synthetic polymers (Environment Agency, 2005a). The initial stage of production is the base-induced reaction of the phenol and formaldehyde to give a hydroxybenzyl alcohol. With 4-*tert*-octylphenol the addition takes place at the *ortho*-position. The next step in the condensation is the formation of a dihydroxydiphenylmethane derivative with elimination of water. Continuation of these reactions leads to a two-dimensional polymer for 4-*tert*-octylphenol. The phenol–formaldehyde resins may be made with 4-*tert*-octylphenol alone or in a mixture with other phenols depending on the properties desired for the final resin. The different alkylphenols are used for production of slightly different resins, but there is some degree of interchangeability between the alkylphenols as they have the same function. (Environment Agency, 2005a).

Besides this application, the octylphenols, nonylphenols and dodecylphenols mainly function as intermediates in the production of ethoxylates.

Other mono-alkylphenols, dibutylphenols and tributylphenols mainly function as intermediates in the production of various substances, e.g. herbicides, plastic additives, and constituents for the fragrance industry.

A number of the substances have their main application area as constituents of lubricants and fuel additives or as intermediates in the production of such additives: dodecylphenol, 2,6-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-nonyl-phenol, 2,4,6-tri-*tert*-butylphenol and bis(tert-butyl)dodecylphenol. In the applications where the APs are used directly as additives (i.e. not function as an intermediate), the substances have various functions, which have not been described in detail in the reviewed literature

2,6-di-*tert*-butyl-*p*-cresol function as an antioxidant for a variety of applications; among these, antioxidants in food. The substance primarily acts as a terminating agent that suppresses auto oxidation, a process whereby unsaturated organic compounds are attacked by atmospheric oxygen.

Nonylphenol ethoxylates (NPEO) are nonionic (no charge) surfactants that are used in many applications. NPEO surfactants function as emulsifiers, wetting agents, dispersants, foam control agents and surface tension agents. The surfactants provide increased surface activity and reduce the surface tension of water, allowing easier spreading, wetting, and better mixing of liquids. The octylphenol ethoxylates (OPEO) have similar overall applications as the NPEO, though the OPEOs have slightly different properties.

2. Regulatory framework

This chapter gives an overview of how alkylphenols and alkylphenoletoxylates are addressed in existing and upcoming EU and Danish legislation, international agreements and also by eco-label criteria.

In Annex 3 a brief overview of legal instruments in the EU and DK and how they are related may be found. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in Section 2.1.2, and provides a brief introduction to international agreements and selected eco-label schemes.

2.1 EU and Danish legislation

This section will first list existing legislation addressing AP/APEO and then give an overview of ongoing activities, focusing on which substances are in the pipeline in relation to various REACH provisions.

2.1.1 Existing legislation

Table 2 gives an overview of existing legislation addressing AP and APEO. For each area of legislation, the table first lists the EU legislation (if applicable) and then possible transposition of this into Danish law and/or other national rules. The latter will only be elaborated upon in case of Danish rules differing from EU rules.

The first international measure for reducing the emission of nonylphenol and nonylphenolethoxylates (NP/NPE) was the PARCOM Recommendation 92/8 on nonylphenol-ethoxylates which required the phasing out of the use of NPEs as cleaning agents for domestic uses (1995) and industrial uses (2000) in the OSPAR counties. An EU Risk Assessment for nonylphenol and nonylphenolethoxylates (NP/NPEO) from 2002 (ECB, 2002) identified the need for reducing the risk to the environment from the substances and marketing and use restrictions for applications which caused significant discharges, emissions or losses to the environment was introduced at EU level in 2003 and went into force 27 October 2004 (Directive 2003/53/EC amending Council Directive 76/769/EEC). The requirements are currently included in Annex XVII to the REACH Regulation.

The table illustrates that nonylphenol and nonylphenolethoxylates are widely regulated, whereas octylphenol and octylphenolethoxylates are covered by fewer regulatory provisions. Only one other alkylphenol (4-*tert*-butylphenol) is regulated: prohibited in the cosmetic industry.

TABLE 2
EU AND DANISH LEGISLATION ADDRESSING AP/APEO

Legal instrument *1	Substances	Requirements
Regulation No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	Included in Annex XVII: a) Nonylphenol $C_6H_4(OH)C_9H_{19}$ CAS 25154-52-3 (b) Nonylphenol ethoxylates $(C_2H_4O)_nC_{15}H_{24}O$	Shall not be placed on the market, or used, as substances or in mixtures in concentrations equal to or greater than 0,1 % by weight for the following purposes: (1) industrial and institutional cleaning except: — controlled closed dry cleaning systems where the washing liquid is recycled or incinerated, — cleaning systems with special treatment where the washing liquid is recycled or incinerated. (2) domestic cleaning; (3) textiles and leather processing except: — processing with no release into waste water, — systems with special treatment where the process water is pre-treated to remove the organic fraction completely prior to biological waste water treatment (degreasing of sheepskin); (4) emulsifier in agricultural teat dips; (5) metal working except: uses in controlled closed systems where the washing liquid is recycled or incinerated; (6) manufacturing of pulp and paper; (7) cosmetic products; (8) other personal care products except: spermicides; (9) co-formulants in pesticides and biocides. However, national authorisations for pesticides or biocidal products containing nonylphenol ethoxylates as co-formulant, granted before 17 July 2003, shall not be affected by this restriction until their date of expiry.
Regulation 649/2012 concerning the export and import of hazardous chemicals (PIC)	Nonylphenols $C_6H_4(OH)C_9H_{19}$ Nonylphenol ethoxylates $(C_2H_4O)_n C_{15}H_{24}O$	Subject to export notification procedure
Regulation (EC) No 1223/2009 on cosmetic products	4-*tert*-Butylphenol (98-54-4) Nonylphenol (25154-52-3) 4-Nonylphenol, branched (84852-15-3)	Included in list of substances prohibited in cosmetic products
Bekendtgørelse om kosmetiske produkter [Statutory Order on cosmetic products] **BEK no 422 of 04/05/2006**	Same	Same

Legal instrument *1	Substances	Requirements
Regulation (EC) No 166/2006 concerning the establishment of a European Pollutant Release and Transfer Register (PRTR Regulation)		The operator of a facility that undertakes one or more of the activities specified in the Regulation above the applicable capacity thresholds shall report the amounts annually to its competent authority if the releases are above the following threshold for releases:
	Nonylphenol and nonylphenol ethoxylates (NP/NPEOs)	To water: 1 kg/year To land: 1 kg/year
	Octylphenols and octylphenol ethoxylates	To water: 1 kg/year
***Bekendtgørelse om visse virksomheders afgivelse af miljøoplysninger [Statutory Order on certain companies' delivery of environmental information]* BEK no 210 of 03/03/2010**	Same	Same
Directive 2000/60/EC establishing a framework for the Community action in the field of water policy (Water Framework Directive)	Nonylphenols, 4-nonylphenol, octylphenols, 4-*tert*-octylphenol	Framework for e.g. setting Environmental Quality Standards for 33 'priority' and 'hazardous priority' substances presenting a significant risk to the aquatic environment and water used for the production of drink water. The APs were included in the first list priority substances.
Directive 2008/105/EC on environmental quality standards in the field of water policy		Sets the Environmental Quality Standards as annual average and maximum allowable concentration. Requires Member States to take measures aimed at ensuring that the concentrations do not exceed the standards and do not significantly increase in sediment and/or relevant biota.
***Bekendtgørelse om miljøkvalitetskrav for vandområder og krav til udledning af forurenende stoffer til vandløb, søer eller havet [Statutory Order on environmental quality standards for water bodies and requirements to the discharge of pollutants into rivers, lakes or the sea]* BEK no 1022 of 25/08/2010**	Same	Transposes the Water Framework Directive

Legal instrument *1	Substances	Requirements
Council Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (The Sewage Sludge Directive)	Does not include limit values for any AP/APEO	
Bekendtgørelse om anvendelse af affald til jordbrugsformål (Slambekendtgørelsen) [Statutory Order on the use of waste for agricultural purposes] **BEK no 1650 of 13/12/2006**	Nonylphenol and nonylphenol ethoxylates with 1-2 ethoxy groups	Limit value in sludge: 10 mg/kg dw
Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg [Statutory Order on water quality and supervision of water supply systems] **BEK no 1024 of 31/10/2011**	Sum of octylphenol and nonylphenol Other phenols, each compound	Requirement of water quality: Concentration by exit from waterworks: 20 µg/L Concentration by entrance of consumer's property: 20 µg/L Concentration by consumer's tap: 20 µg/L Requirement of water quality: Concentration by exit from waterworks: 0.5 µg/L Concentration by entrance of consumer's property: 0.5 µg/L Concentration by consumer's tap: 0.5 µg/L
Bekendtgørelse om kvalitetskrav til miljømålinger [Statutory Order on quality requirements for environmental measurements] **BEK no 900 of 17/08/2011**	Nonylphenol and nonylphenol ethoxylates with 1-2 ethoxy groups	Sets requirement to the quality of environmental analyses

*1 Unofficial translation of name of Danish legal instruments.

Classification and labelling

Table 3 lists alkylphenols for which a harmonised CLP classification and labelling has been agreed upon. It shows that nonylophenol and octylphenol are both classified for severe acute and chronic aquatic toxicity. Thymol is classified f0r less severe aquatic toxicity.

Industry classifications for substances without a harmonised classification and labelling agreement are summarised in Annex 2 and will be taken into account in Chapters 5 and 6 on environment and human health assessments.

TABLE 3
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International Chemical Identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
601-053-00-8	nonylphenol; [1] 4-nonylphenol, branched [2]	25154-52-3 [1] 84852-15-3 [2]	Repr. 2 Acute Tox. 4 * Skin Corr. 1B Aquatic Acute 1 Aquatic Chronic 1	H361fd H302 H314 H400 H410
604-075-00-6	4-(1,1,3,3-tetramethylbutyl)phenol; 4-*tert*-octylphenol	140-66-9	Irrit. 2 Eye Dam. 1 Aquatic Acute 1 Aquatic Chronic 1	H315 H318 H400 H410
604-032-00-1	thymol	89-83-8	Acute Tox. 4 * Skin Corr. 1B Aquatic Chronic 2	H302 H314 H411

Authorisation List / REACH Annex XIV
As of November 2012, none of the AP/APEOs are included in REACH annex XIV which is a list substances that require authorisation for continued use in the EU.

2.1.2 Ongoing activities - pipeline
Table 4 shows that REACH substance evaluations that may lead to a restriction or authorisation, for example, are planned/ongoing for '2,4-di-*tert*-butylphenol', '4-nonyl phenol, branched' and 'p-cresol'.

TABLE 4
SUBSTANCES IN THE COMMUNITY ROLLING ACTION PLAN (ECHA, 2012A)

CAS No	EC No	Substance Name	Year	Member State	Initial grounds for concern
96-76-4	202-532-0	2,4-di-*tert*-butylphenol	2014	Belgium	Suspected Endocrine Disruptor; Human health/potential STOT-RE classification; Exposure/Wide dispersive use, consumer use, high aggregated tonnage
84852-15-3	284-325-5	phenol, 4-nonyl-, branched	2014	United Kingdom	Suspected Endocrine Disruptor; Exposure/Wide dispersive use, high tonnage; Risk characterisation ratios close to 1 (human health)

Registry of Intentions
Table 5 shows Registry of Intentions by ECHA and Member States' authorities for restriction proposals, proposals for harmonised classifications and labelling and proposals for identifying AP/APEOs as Substances of Very High Concern (SVHC). It also shows the intentions for introducing further restrictions on the import, use and marketing of NP and NPEO, that harmonised classification and labelling proposals have been submitted for dodecyl- and butylphenol, and that there are intentions for proposing nonylphenols and octylphenolethoxylates as SVHCs.

TABLE 5
AP/APEO IN REGISTRY OF INTENTIONS (AS OF 3 AUGUST 2012)

Registry of:	CAS No	Substances	Scope (reproduced as indicated in the Registry of intentions)	Dossier intended by:	Expected date of submission:
Restriction proposal intentions	25154-52-3	nonylphenol	NP and NPEO in textiles have been identified as a significant source of NP in the environment. A restriction on the placing of the market of textile and leather articles containing NP or NPEO	Sweden	03/08/2012
	84852-15-3	phenol, 4-nonyl-, branched	- "-	Sweden	03/08/2012
	no CAS or EC number specified	nonylphenol ethoxylates	- "-	Sweden	03/08/2012
Submitted Harmonised Classification and Labelling intentions	121158-58-5	phenol, dodecyl-, branched [Tetrapropenylphenol (TPP)]	Proposed classification according to CLP: Skin Irrit.2 Eye Irrit.2 Repr. 2 Aquatic Acute 1, Aquatic Chronic 1	Germany	Submitted: 12/04/2012
	98-54-4	4-*tert*-butylphenol	Proposed classification according to CLP: STOT SE 3, H335 Skin irrit. 2, H315 Eye dam. 1; H318 Repr 2, H361f Not classified for the environment	Norway	Submitted: 11/06/2010
Submitted SVHC intentions	335-67-1	Phenol, 4-nonyl-, branched and linear covering all individual isomers with an alkyl chain of carbon number 9 and UVCB substances which include linear and branched alkyl chains with a carbon number of 9	Equivalent level of concern (EQC), because they are substances with endocrine disrupting properties for which there is scientific evidence of probable serious effects to the environment.	Germany	Submitted: 06/08/2012 Public consultation 3 Sep 2012
	no CAS or EC number specified	4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated (4-*tert*-octylphenol ethoxylates)	Equivalent level of concern (EQC)	Germany	06/08/2012 Public consultation 3 Sep 2012

Candidate list

As of November 2012, one substance, 4-(1,1,3,3-tetramethylbutyl)phenol (CAS N0 140-66-9) has been included in the candidate list with the scope of equivalent level of concern (EQC); having probable serious effects to the environment (REACH article 57 f).

Annex XIV recommendations

The latest lists of Annex XIV recommendations (2 August 2012) do not include any AP/APEO.

2.2 International agreements

Table 6 gives an overview of how AP/APEOs are addressed by various international agreements. It shows that NP and NPEO are subject to phasing out and strict restrictions in the OSPAR and HELCOM conventions, whereas OP/OPEO under these conventions are priority substances and subject to further assessment, which may lead to restrictions. One tri-butyl-phenol is a priority substance under the OSPAR convention.

TABLE 6
INTERNATIONAL AGREEMENTS ADDRESSING AP/APEO

Agreement	Substances	How the AP/APEO are addressed
OSPAR Convention	Nonylphenol ethoxylates	PARCOM Recommendation 92/8 on Nonylphenol ethoxylates : Phasing out of the use of NPEOs as cleaning agents for domestic uses (1995) and industrial uses (2000)
	2,4,6-tri-*tert*-butylphenol, octylphenol, nonylphenol, nonylphenol ethoxylates and related substances	Included in OSPAR list of priority substances, as Part A substances.
HELCOM (Helsinki Convention)		HELCOM Baltic Sea Action Plan adopted on 15 November 2007 by the HELCOM Extraordinary Ministerial Meeting:
	Nonylphenol /nonylphenolethoxylates (NP/NPEOs)	By 2008 to work for strict restrictions on the use in the whole Baltic Sea catchment area of the Contracting States
	Octylphenol /Octylphenolethoxylates (NP/NPEOs)	By 2009, if relevant assessments show the need, to initiate adequate measures such as the introduction of use restrictions and substitutions in the most important sectors identified by the Contracting Parties
Rotterdam Convention (PIC Convention)		No AP/APEOs are included in Annex III which lists substances that have been banned or severely restricted for health or environmental reasons by two or more Parties and which the Conference of the Parties has decided to be subject to the PIC procedure.
Basel Convention	No specific AP/APEO mentioned	Waste AP/APEOs is included in the hazardous waste class A3070 of Annex VIII “Waste phenols, phenol compounds including chlorophenol in the form of liquids or sludges”. The substances may be included in other wastes as well, but are not specifically mentioned in the description of the wastes.

2.3 Eco-labels

Table 7 gives an overview of how AP/APEOs are addressed by the EU, Nordic and German eco-labelling schemes. The German ecolabel is included because Germany takes up the major part of the North European market for articles. It shows that the schemes do not distinguish between sub-stances or sub-groups of substances, but broadly address the presence/absence of AP/APEO, as well as "alkylphenol derivates". The criteria documents generally do not define the group alkylphenol and alkylphenoletoxylates.

TABLE 7
ECO-LABELS TARGETING AP/APEO

Eco-label	Substances	Mixtures and articles + criteria	Document title
Nordic Swan	Alkylphenol derivatives	Dishwasher detergent	Nordic Eco-labelling of dishwasher detergent
	Alkylphenol derivatives	Paper envelopes: Adhesives must not contain the substanc-es	Nordic Eco-labelling of Paper envelopes – Supplementary Module
	Alkylphenol derivatives	Printing companies: Must not be added to chemicals	Nordic Eco-labelling of Printing companies
	Alkylphenol ethoxylate Alkylphenol derivatives	Must not be deliberately added to cleaning agents or dispersants.	Nordic Eco-labelling of Paper Products - Chemical Module
	Alkylphenol Alkylphenol ethoxylate Alkylphenol derivatives	Furniture and fitments: must not be present in/added to the chemical product or material	Nordic Eco-labelling of Furniture and fittings
	Alkylphenol Alkylphenol ethoxylate Alkylphenol derivatives	Outdoor furniture and playground equipment: must not be present in/added to the chemical product or material	Nordic Ecolabelling of Outdoor furniture and playground equipment
EU Flower	Alkylphenol ethoxylate	Footwear production: shall not be used in the product up until purchase.	COMMISSION DECISION of 9 July 2009 on establishing the ecological criteria for the award of the Community eco-label for footwear
	Alkylphenol ethoxylate	Indoor and outdoor paints and varnishes: shall not be used in the product before or during tinting (if applicable).	COMMISSION DECISION Of 13 August 2008 establishing ecological criteria for the award of the Community eco-label to indoor paints and varnishes (2009/544/EC) Same for outdoor paint: Commis-sion Decision (2009/543/EC)
	Alkylphenol ethoxylate	Bed mattresses: shall not be used and shall not be part of any preparations or formulations used.	COMMISSION DECISION of 9 July 2009 establishing the ecological criteria for the award of the Community Eco-label for bed mattresses

Eco-label	Substances	Mixtures and articles + criteria	Document title
	Alkylphenol ethoxylate Alkylphenol derivatives	Tissue-paper products: shall not be added to cleaning chemicals, de-inking chemicals, foam inhibitors, dispersants or coatings.	COMMISSION DECISION establishing the ecological criteria for the award of the Community Eco-label to tissue-paper products
	Alkylphenol ethoxylate	Textile floor coverings: shall not be used and shall not be part of any preparations or formulations used.	COMMISSION DECISION of 30 November 2009 on establishing the ecological criteria for the award of the Community Ecolabel for textile floor coverings
	Alkylphenol ethoxylate Alkylphenol derivatives	Printed paper products: shall not be added to cleaning chemicals, de-inking chemicals, foam inhibitors, dispersants or coatings.	COMMISSION DECISION establishing the ecological criteria for the award of the Community Ecolabel to printed paper products
	Alkylphenol ethoxylate	Textile products: shall not be used and shall not be part of any preparations or formulations used.	COMMISSION DECISION of 9 July 2009 establishing the ecological criteria for the award of the Community Ecolabel for textile products
German Blue Angel	Alkylphenol ethoxylate	Fabric Towel Rolls Supplied in Towel Dispensers : Washing and cleaning agents as defined in Section 2, para.1, Wasch- und Reinigungsmittelgesetz - WRMG (Act on Washing and Cleaning Agents), may be used for the washing of the fabric towel rolls at laundries only if they are free from the substance.	Basic Criteria for Award of the Environmental Label: Fabric Towel Rolls Supplied in Towel Dispensers RAL-UZ 77
	Alkylphenol ethoxylate	Low-Solvent Bitumen Coatings and Adhesives : Products containing the substances shall not be added to the bitumen coatings or adhesives.	Basic Criteria for Award of the Environmental Label: Low-Solvent Bitumen Coatings and Adhesives RAL-UZ 115
	Alkylphenol ethoxylate	Low-Pollutant Fire Extinguishers: The anionic and non-ionic surfactants contained in the fire-extinguishing foams must be biodegradable by at least 90 per cent. Their total degradability must be 70%. In addition, they shall not contain any APEO surfactants.	Basic criteria for the award of the environmental Label: Low-Pollutant Fire Extinguishers RAL-UZ 66
	Alkylphenol ethoxylate	Textile Floor Coverings: Polymer dispersions, resins or similar components (binders) containing alkylphenol ethoxylates shall not be added to binders and coatings used in the manufacture of textile floor coverings.	Basic Criteria for Award of the Environmental Label: Low-Emission Textile Floor Coverings RAL-UZ 128

Eco-label	Substances	Mixtures and articles + criteria	Document title
	Alkylphenol ethoxylate	Floor Covering Adhesives and other Installation Materials : Products containing alkyl phenol ethoxylates shall not be added to the installation materials.	Basic Criteria for Award of the Environmental Label : Low-Emission Floor Covering Adhesives and other Installation Materials RAL-UZ 113
	Alkylphenol ethoxylate	Thermal Insulation Material and Suspended Ceilings: Products containing alkylphenol ethoxylates shall not be used.	Basic Criteria for Award of the Environmental Label: Low-Emission Thermal Insulation Material and Suspended Ceilings for Use in Buildings RAL-UZ 132
	Alkylphenol ethoxylate	Wall paints: From January 1st , 2004 products containing alkyl phenol ethoxylates shall no longer be added to wall paints or binders.	Basic Criteria for Award of the Environmental Label: Low-Emission Wall Paints RAL-UZ 102

2.4 Summary on the regulatory framework

Nonylphenol and nonylphenolethoxylates

Currently the main legal focus is on emission to the environment of nonylphenol and nonylphenolethoxylates due to their significant aquatic toxicity properties, most notably via existing restrictions on marketing and use of these substances for nine purposes, including applications in cleaning agents, in textiles and as a coformulator in biocides/pesticides. Furthermore, the presence in textiles may be in the restrictions pipeline (Registry of intension) and the specific substance '4-nonyl phenol, branched' is on the community rolling action plan for substance evaluation, which may lead to further restrictions. The substances are further regulated by EU legislations addressing export/import, cosmetics, pollutant release and transfer register and the Water Framework Directive, as well as a number of Danish statutory orders dealing with sludge, water quality/drinking water and quality criteria in various environmental compartments. Nonylphenols are also in the Registry of intentions for identification as SVHC because they are substances with endocrine disrupting properties for which there is scientific evidence of probable serious effects to the environment. The substances are addressed for phase out and strict restrictions in the OSPAR and HELCOM conventions.

Octylphenol and octylphenol-ethoxylates

Octylphenol and octylphenol-ethoxylates are often considered alternatives to nonylphenol and nonylphenolethoxylates. These substances are much less regulated, however, although octylphenol has the same harmonised classification for aquatic toxicity as nonylphenol. These substances are addressed under the pollutant release and transfer register and the Danish statutory order dealing with water quality/drinking water (only octylphenol). They are also on addressed by the OSPAR and Helsinki conventions; indicated as priority and subject to further assessment for possible restrictions. Finally, 4-*tert*-octylphenol is on the candidate list due to probable serious effects to the environment (equivalent concern) and the registry of intentions includes a proposal for identification of 4-(1,1,3,3-tetramethylbutyl) phenol, ethoxylated as SVHC because is may be degraded to substances with endocrine disrupting properties.

Dodecylphenol
A harmonised classification and labelling proposal has been submitted for 4-(3,4,5-trimethylheptyl)phenol (a branched dodecylphenol), suggesting classification as flammable, eye damaging/irritating and carcinogenic.

Butylphenols
4-*tert*-butylphenol (4-*tert*-butylphenol) is prohibited for use in cosmetics, which seems logical given the submitted registry of intention for a harmonised classification as irritating to skin, eye damaging, toxic to reproduction and exerting specific target organ toxicity.

2,4-di-*tert*-butylphenol, being a suspected endocrine disrupter and potential specific target organ toxicity substance in wide dispersal (including consumer use) and with high aggregated tonnage, is on the community rolling action plan for substance evaluation.

2,4,6-tri-*tert*-butylphenol is a priority substance under the OSPAR Commission.

Thymol
Thymol has harmonised classifications.

Eco-labelling criteria generally refer to alkylphenols and alkylphenol ethoxylates
All three reviewed Eco-labelling schemes do not distinguish between substances or sub-groups of substances, but broadly address the presence/absence of AP/APEO, as well as "alkylphenol derivates". The substances are addressed in criteria for various product groups, including paper, printing, furniture/mattresses, textiles/footwear and paints/adhesives/coatings.

3. Manufacture and uses

3.1 Global manufacture and use of AP/APEO

Publicly available overviews of the total global consumption of the AP and APEO have not been found.

Campbell (2002) reports that the global consumption of APEO in 2000 was 700,000 t/y, corresponding to about 7% of the total global consumption of surfactants of 10,400,000 t/y (excluding soap). The total surfactant consumption in Western Europe was 898,000 tonnes, of which APEO accounted for 86,000 t/y.

OECD Screening Information DataSets (SIDS) for high production volume chemicals have been prepared for six of the substances: (OECD 1995a,b; 2000; 2002a,b,c). Only one of the SIDS, however, provides information on global production. In 2000, the world production capacity of 2,6-di-*tert*-butyl-*p*-cresol (BHT, CAS No 128-37-0) amounted to about 62,000 t/y, manufactured by more than 20 producers (OECD, 2002a).

3.2 Manufacture and use AP/APEO in the EU

Registered uses of AP/APEO and tonnage bands of registered AP/APEO are summarised in Annex 1. The information from the registrations (ECHA, 2012e) is further discussed in the following chapter on manufacture and uses in the EU.

Some of the main manufacturers of AP/APEO in the EU are organised in the European Council of Alkylphenols and Derivatives, CEPAD, which is a sector group under the European Chemical Industry Council (CEFIC). The following companies are members of CEPAD: Chemtura Corporation, Dow Europe GmbH, Rhodia, Sasol Olefins & Surfactants GmbH, SI Group, Inc., Sumitomo Bakelite Europe NV. Associated members are Akzo Nobel Surface Chemistry and BASF SE.

The Council has been contacted in order to obtain an updated overview of the consumption of AP and APEO in the EU. CEPAD has summarised the information on manufacture and use of the substances in the EU in a presentation, which is further discussed for each substance or substance group below.

Statistics on manufacture and import/export of AP/APEO on its own
EU external trade in tonnes of butylphenol, octylphenol and nonylphenol and salts thereof on their own is shown in the table below. The remaining AP/APEOs are included in aggregated commodity groups which also include other phenols.

TABLE 8
EU27 EXTERNAL IMPORT AND EXPORT OF BUTYL- OCTYL- AND NONYLPHENOL AND SALTS THEREOF (EUROSTAT, 2012A)

CN code	Text	Import, t/y		Export, t/y	
		Average 2006-2010	2011	Average 2006-2010	2011
2907 1300	Octylphenol, nonylphenol and their isomers; salts thereof	4,523	4,020	1,268	1,413
2907 1910	n-Butylphenol	3,902 *1	3,256	2,070	3,498

*1 Average 2007-2010, as no data for 2006 are available.

3.2.1 Nonylphenol and nonylphenolethoxylates

The nonyl group is a chain of 9 carbon atoms, which may be branched or linear. The list of pre-registered substances includes 13 CAS numbers of nonylphenols. Of these two substances are registered. Branched 4-nonylphenol is registered with a manufacture and import in the 10,000-100,000 t/y range. 4-(4-Trans-propylcylohexyl) phenol is registered for intermediate use only.

The most comprehensive description of the use of NP and NPEO is presented in the EU Risk Assessment from 2002 presenting 1997 data (ECB, 2002).

According to the EU Risk Assessment, the EU production of NP in 1997 was 73,500 tonnes. With an overall net import, around 78,500 tonnes of NP were used in Europe in 1997. The NP was used for production of nonylphenol ethoxylates (60% of total), production of resins, plastics, stabilisers etc. (37%) and production of phenolic oximes (3%). Phenolic oximes are used as a reagent for the extraction and purification of copper from ore and all of the produced volume was exported to countries outside the EU. The 29,000 tonnes used in the polymer industry was split between the different application areas as follows: phenolic resin production (22,500 tonnes), 4-nonylphenyl phosphite (TNPP) production (4,000 tonnes), catalyst in epoxy resin production (1,500 tonnes) and use in other plastic stabilisers (1,000 tonnes).

The EU-production of NPEOs in 1997 was estimated at 118,000 tonnes, produced from 47,000 tonnes of nonylphenol. At that time, the most important sector was the industrial and institutional cleaning sector, including domestic cleaning, which consumed 30% of the total. Other uses included emulsion polymerisation (12%), textile auxiliaries (10%), chemical industry, for example synthesis of nonylphenol ether sulphates and nonylphenol ether phosphates (9%), leather auxiliaries (8%), agriculture (5%), paints (4%), metal industry (2%) and pulp and paper (1%). Other applications, of which the majority was not specifically indicated, accounted for the remaining 16%.

EU-wide marketing and use restrictions of NP and NPEO were introduced in 2004 and the consumption of NP and NPEO has decreased markedly since then.

For nonylphenol, the restriction primarily means that the consumption for manufacturing of NPEO has decreased due to the restriction on the used of NPEO, whereas the other major application areas have not been restricted.

CEPAD has provided the following overview of the flow of NP and NPEO in the EU (+Switzerland and Norway) in 2010.

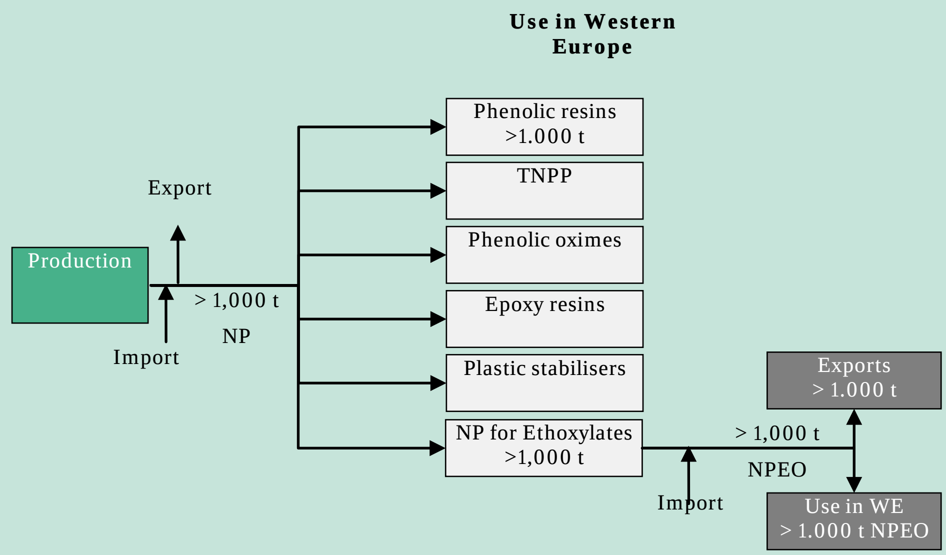


FIGURE 1
FLOW OF NONYLPHENOL AND NONYLPHENOLETHOXYLATES IN WESTERN EUROPE (EU +SWITZERLAND AND NORWAY) IN 2010 (CEPAD, 2012)

The flowchart confirms that NP is still used for the main application areas described in the EU Risk Assessment, but provides very limited information on quantities. According to the registration of branched 4-nonylphenol (CAS nr. 84852-15-3), the total import and production of NP is in the 10,000-100,000 t/y range (ECHA, 2012e).

Considering that 40% of the consumption of 78,500 tonnes in 1999 was for unrestricted uses and that a small part is still used for production of NPEO, the total consumption in 2011 was likely in the range of 30,000-50,000 tonnes. With a total import of NP and OP of approximately 4,000 tonnes, the data indicated that around 90% of the NP used is also manufactured in the EU.

The registration of NPEO (CAS No 8412-54-4) indicates that the manufactured volume of NPEO is in the 2,000-20,000 t/y range (ECHA, 2012e) and consequently, roughly estimated, some 800-8,000 t/y NP are used for the production of NPEO assuming the same NP/NPEO ratio as used in the Risk Assessment (ECB, 2002). More exact figures are available for ECHA and Member States' authorities from the confidential parts of the registrations and this information is summarised in a confidential annex to the Annex XV dossier for 4-nonylphenol, branched and linear and nonylphenol ethoxylates (ECHA, 2012b).

Use of nonylphenol

NP is used almost exclusively as an intermediate in the production of various NP derivatives and resins. Releases of NP from these production processes are estimated to be very low (OSPAR, 2009). As a result, small quantities of NP enter into the environment directly. The primary source of NP in the environment is rather considered to be NPEOs, which can break down into NP after being released into the environment during their production, their formulation into various other products, and the use of such products (OSPAR, 2009).

4-NP is together with 4-t-OP and 4-*tert*-BP used in the production of different phenolic resins and a common description of the resins is provided here.

"Resins" are polymeric materials and the basis for plastics, coating, adhesives, etc. Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. They are generally transparent, hard materials. The term "resin" is also used for the thick liquids used as the polymer component of two-component systems where they are mixed with a hardener to initiate a polymerization.

The APs are used in phenol/formaldehyde resins, either alone or mixed with other phenols depending on the properties desired for the final resin. Phenolic resins are of two main types:

- Novolacs, which are thermoplastic, are among others used in rubber compounding (tyre manufacture) and are ethoxylated for use in oil recovery.
- Resoles, which are heat reactive, are used as intermediates in contact and pressure sensitive adhesives, coatings, printing inks and electrical varnishes.

Phenol–formaldehyde resin manufacture is based almost exclusively on discontinuous batch processes using a traditional reactor, the resins being formed by a stepgrowth polymerisation reaction in which the AP is used as a monomer. Most of the AP 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 (~3-4%) of unreacted AP (Environmental Agency, 2005a).

Since the resins are further processed to finished products, the concentration of free residual monomers in the final products is much lower (ECB, 2008).

Besides the direct use of NP in end products, the substance may be present in phenol-formaldehyde-resins made from NP (ECHA, 2012b). This may be the case in a wide range of products made of phenolformaldehyde-resins such as rubber products, printing inks, paints, adhesives and others. Consumer products may consequently contain very low levels of residual, unreacted nonylphenol; in certain products, the derivative compound may break down to release small amounts of nonylphenol (ECB, 2002).

NP is used for a few non-industrial applications which will be mentioned below together with the applications of NPEO.

Use of nonylphenol ethoxylates
At least six NPEOs are pre-registered; of these, one is registered with a tonnage band of 2,000-20,000 t/y.

The total use of NPEOs is consequently assumed to be in the 2,000-20,000 t/y range; less than 20% of the consumption in 1997. No breakdown of the total consumption by application areas today has been pinpointed in the research.

For the major use areas of NPEO in 1997, the substances are currently restricted: cleaning agents (except for controlled closed dry-cleaning systems and cleaning systems with certain special treatment), leather and textile auxiliaries (except processing with no release into waste water, and systems with certain special treatment), agriculture, metal industry (except uses in controlled closed systems where the washing liquid is recycled or incinerated) and pulp and paper.

An Annex XV SVHC dossier for nonylphenol and its ethoxylates from 2012 (ECHA, 2012b) lists a number of applications for which NP and NPEO are still used. Some of the main applications will briefly be mentioned here and further discussed in the Danish context in section 3.3.

In paints and printing inks, nonylphenol ethoxylates are typically used in concentrations of 0.6 to 3%. Nonylphenols or their ethoxylates are mainly used in paints used on wet-room floors, water-based paints and varnishes for indoor use, printer's ink, concrete floor paint, metal coating and anticorrosive paints. (ECHA, 2012b) In 1997, 4,000 t/y were used for paint and varnishes.

NPEOs are added to acrylic esters used for specialist coatings, adhesives and fibre bonding. This application is the application indicated as "emulsion polymerisation" in the EU Risk Assessment; this use accounted for 12% of the total use in 1997 (13,000 t/y). The NPEOs act as dispersants and increase the stability of the formulation.

NPEOs are still used in metal working fluids under certain conditions and in lubricating oils. Nonylphenols and their ethoxylates may be used as antioxidants and plasticizers in plastic products.

Besides the direct uses of the NPEOs, the substances may also be present in imported articles. 4-Nonylphenol and its ethoxylates are still used in textile production outside the EU as detergent and auxiliaries, such as dispersing agents for dyeing, emulsifiers and spinning lubricants (ECHA, 2012b). Imported textiles may therefore contain nonylphenol ethoxylates as contamination. This is further discussed in the Danish context in section 3.3.

3.2.2 Octylphenol and octylphenolethoxylates

The octyl group is a chain of 8 carbon atoms, which may be branched or linear. Seventeen different CAS numbers of octylphenols are pre-registered. Only one of the substances is registered: 4-*tert*-octylphenol (4-t-OP) (CAS No 140-66-9). 4-t-OP is manufactured in the EU in the 10,000-100,000 t/y range according to the current registrations (ECHA, 2012e).

One other octylphenol, o-(1-methylheptyl)phenol (CAS No) 18626-98-7 is included in the list of 2013 registration intentions, indicating the manufactured and imported tonnage may be in the 100-1,000 tonnes range (ECHA, 2012e).

Use of 4-*tert*-octylphenol

The most comprehensive description of the use of 4-t-OP in the EU is from a UK environmental risk evaluation report for 4-t-OP (Environment Agency, 2005a). The data concerns 2001. For the current study, CEPAD has indicated these data as the most updated information on the use of OP in the EU. The same data are used for an Annex XV SVHC report for 4-t-OP published in 2012 (ECHA, 2012c).

The use of 4-t-OP is not restricted and it is expected that the consumption patterns today are more or less the same as in 2001.

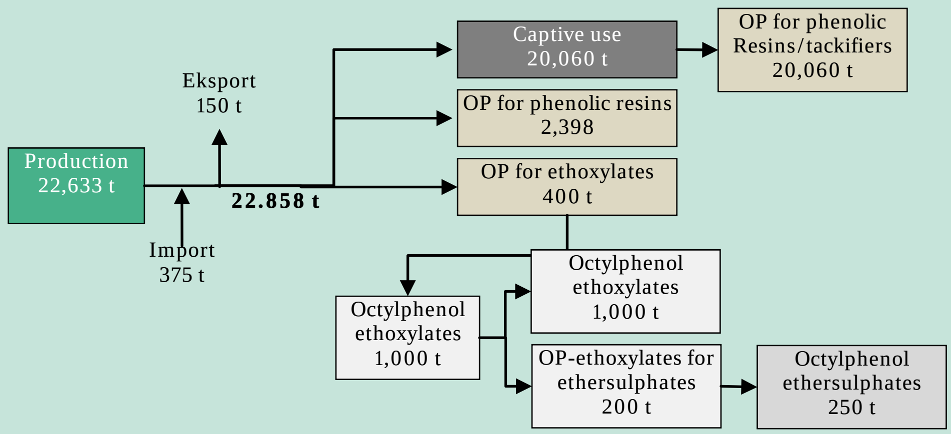


FIGURE 2
FLOW OF 4-t-OP IN WESTERN EUROPE (EU + SWITZERLAND + NORWAY) IN 2001 (ENVIRONMENT AGENCY , 2005A)

As shown in Figure 2, 4-t-OP is mainly used as an intermediate in the production of phenolic resins (about 98 percent of the whole amount of 4-t-OP) and an intermediate in the production of octylphenol ethoxylates (about 2%).

Based on information from registration dossiers (ECHA, 2012e), the uses of OP are:

- As a monomer for polymer preparations ;
- As an intermediate for manufacture of ethoxylates which to some extent will be a component of products (e.g. paints) used by industry, professional users and consumers;
- As a component in phenolic resins used in the formulation of adhesives which are used by industry, professional users and consumers;
- As a component in coatings, printing inks and some types of paints, which are used by industry, professional users and consumers;
- As tackifiers in the production of rubber products.

Basic information on the phenolic resins is provided in the section on NP.

Rubber compounding for tyres is the main use of 4-t-OP -based resins. The function of the resins is to increase the tackiness of the rubber and improve adhesion of the different layers during vulcanisation (Environment Agency, 2005a). The resins are added to rubber in amounts up to 1.5% of the rubber formulation, though the maximum figure for the percentage of resin in rubber used for tyres is 10% (Nwaogu *et al.*, 2006).

According to Environment Agency (2005a) citing CEPAD (2002), this results in a maximum concentration of free 4-t-OP in tyres of 0.3%. In response to the Annex XV report for 4-t-OP (ECHA, 2012c), the European Tyre & Rubber Manufacturers' Association (ETRMA, 2011) indicates that the resins used for tyres generally contain free 4-t-OP monomer impurity of between 1 and 5%. Specifically, 4-t-OP-based resins are sometimes used in tyre compounds, typically in the carcass plies or steel belts, in order to ensure adequate adhesion. According to company data on annual use of 4-t-OP-based resins and tyre production, and assuming an average content of 3% free impurity 4-t-OP in the resins, it has been calculated that an average EU tyre contains between 0,007 % and 0,012 %

of 4-t-OP (ETRMA, 2011); i.e. significantly below the 0.3% indicated by Environment Agency (2005a).

The 4-t-OP -based resins are also used in printing inks and in marine paints (Nwaogu *et al.*, 2006) which is indicated in the flow chart as 4-t-OP for phenolic resin. The total EU consumption in 2001 for the two applications was 1,000 tonnes and 800 tonnes, respectively.

Use of octylphenol ethoxylates
At least 4 OPEOs are pre-registered but none of these are registered yet or included in the list of 2013 intentions.

According to an Annex XV report for a group entry of 4-*tert*-octylphenol ethoxylates (ECHA, 2012d), the registration dossiers for 4-*tert*-octylphenol provide some information on the production of 4-*tert*-octylphenol ethoxylates without pointing out specific characteristics (ECHA, 2012e). The overall amount produced or imported per year may be in the range of 200 to 2000 tons. According to CEPAD, there were only four to five manufacturers of octylphenol ethoxylates within the EU (ECHA, 2012d).

The Annex XV report quotes the COHIBA Summary report for Germany (COHIBA 2011c) that about 2,100 tonnes of 4-*tert*-octylphenol were produced in Germany in the year 2000. About 70% of this volume was used to produce 4-*tert*-octylphenol ethoxylates, which would mean that close to 5,800 tonnes of 4-*tert*-octylphenol ethoxylates were produced in Germany in 2000 considering a 36 percent weight contribution of 4-*tert*-octylphenol. This tonnage is much higher than the tonnage described in the UK risk evaluation report (Environment Agency, 2005a) and is not supported by any registration dossier (ECHA, 2012e). The original source of the information on the German production (Hillenbrand *et al.*, 2007) makes also reference to the UK risk evaluation figures as being the best estimate of the total EU use. As the estimate from the UK risk evaluation is well in concordance with the data on the registered volumes, this estimate (shown in Figure 2) is here considered the best estimate.

CEPAD (2012) has indicated the flow chart from the Environment Agency (2005a) report as the best indication of the flow of octylphenol ethoxylates in the EU for the current study.

In 2001, the total manufacture of OPEOs was 1,000 tonnes, corresponding to approximately 400 tonnes OP used for the manufacture of OPEO (Environment Agency, 2005a). Octylphenol ethoxylates were at that time mainly used in emulsion polymerisation, textile processing, water-based paints, pesticide and veterinary medicine formulations and for ethersulphates, as shown in Figure 3. Two hundred t of OPEO was used to produce 250 t of octylphenol ethersulphates, which were thereafter used for agriculture and paints.

A significant part of the OPEO used for textile and leather auxiliaries, paints and agriculture, as well as the octylphenol ethersulphates used for agriculture and paint may end up in the environment.

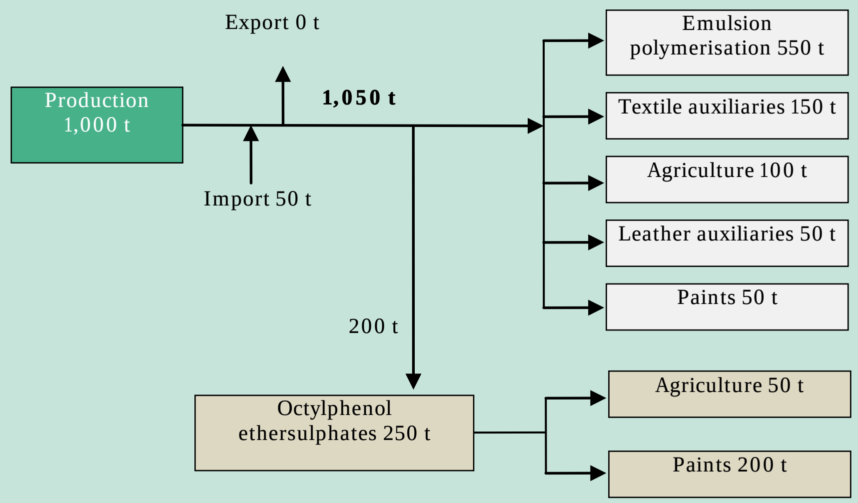


FIGURE 3
FLOW OF OCTYLPHENOL ETHOXYLATE IN WESTERN EUROPE (EU + SWITZERLAND + NORWAY) IN 2001 (ENVIRONMENT AGENCY, 2005A)

The major application in 2001 was emulsion polymerisation. Emulsion polymerisation is basically a type of polymerisation (e.g. to make styrene–butadiene polymers or PTFE polymers) which takes place in an emulsion typically incorporating water, monomer and surfactant (Nwaogu *et al.*, 2006). The end applications for the polymer dispersions include paints, paper, inks, adhesives and carpet backings.

OPEOs are used in textile and leather auxiliaries (e.g. hot melts, textile printing, leather finishing). They generally act as emulsifiers in finishing agents, which are mainly styrene-butadiene copolymers. Finishing agents cover leather and textiles with a thin polymer film to make the material more resistant to water, dust and light. They also give leather a shiny appearance. The OPEO is physically bound in the polymer matrix, which adheres to the substrate. Releases of OPEO from this insoluble polymer structure are indicated to be unlikely (Environmental Agency, 2005).

In water-based paints, OPEOs act as emulsifiers and dispersants, although the emulsifying properties are more dominant (Environmental Agency, 2005).

OPEOs can be used to produce octylphenol ether sulphates (OPEO-Ss). These are mainly used as emulsifiers in water-based paints.

A risk reduction strategy for octylphenol and an analysis of advantages and drawbacks at EU level have been prepared by DEFRA in 2008 (Nwaogu *et al.*, 2006), which form the basis for the description of substitution options in Chapter 8.

3.2.3 Dodecylphenol and dodecylphenol ethoxylate

The dodecyl group is a chain of 12 carbon atoms, which may be branched or linear. Four CAS No of dodecylphenol are included in the list of pre-registered substances.

Of these, branched dodecylphenol (CAS No 121158-58-5) is registered with a manufactured and imported tonnage in the 10,000-100,000 t/y range. The indicated uses are as chemical intermediate and monomer for synthesis of polymers. The CAS No in fact represents a large number of highly branched isomeric alkyl groups ranging from C10 to C15, in different positions (Brooke *et al.*, 2007).

The overall flow of dodecylphenol in Western Europe in 2010 as provided by CEPAD is shown in Figure 4.

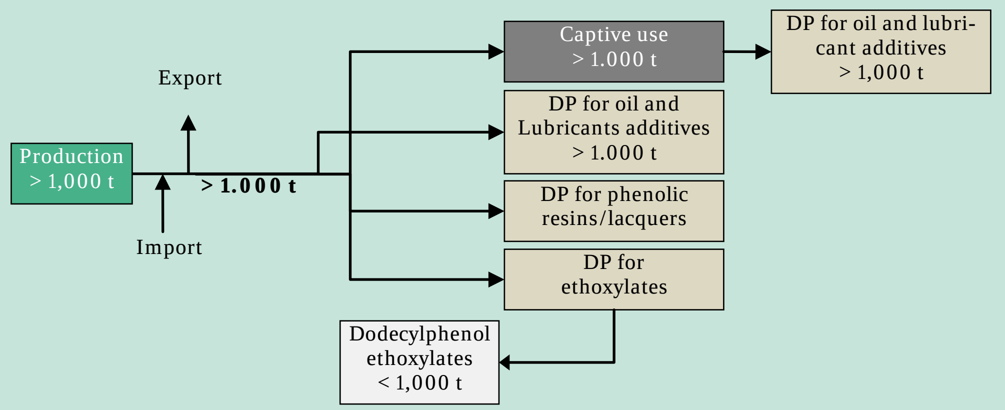


FIGURE 4
OVERALL FLOW OF DODECYLPHENOL IN WESTERN EUROPE (EU + SWITZERLAND + NORWAY) IN 2010 (CEPAD 2011). CAPTIVE USE IS THE USE OF THE SUBSTANCE IN THE CHEMICAL INDUSTRY FOR SYNTHESIS OF OTHER CHEMICALS.

For an assessment of para-C12-alkylphenols (dodecylphenol and tetrapropenylphenol) prepared by the Brooke et al. (2007), members of CEPAD and RATG (Risk Assessment Task Group of the American Chemistry Council's Petroleum Additives Panel) have provided European production and import quantities for the period 1998–2002. The individual tonnages and capacities were confidential, but the total European consumption of the two substances was indicated to be approximately 50,000 t/y in 2004. It is indicated that the consumption was mostly as tetrapropenylphenol. "Tetrapropenylphenol" refers to the common name for the substance tetrapropenylphenol derivatives (CAS No 74499-35-7), which is also a dodecylphenol. This substance is not included in the database of registered substances or the list of 2013 intentions, whereas branched dodecylphenol (CAS No 121158-58-5) is registered with a manufactured and imported tonnage in the 10,000-100,000 t/y range. Consequently, it does not seem that the tetrapropenylphenol derivative would take up the majority of the manufactured or imported totals today.

At EU level, around 99% of the consumption volume of the two substances was used in the production of oil and lubricant additives (primarily calcium alkylphenate sulphides). 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).

The dodecylphenol is present in the final lubricants at low levels. In Norway the average content of dodecylphenol in those lubricants indicated by the MSDS as containing dodecylphenol was 0.15% (Lambert, 2010). Import of dodecylphenol in oils was estimated to represent the major flow of dodecylphenols in Norway; consequently, improper disposal of used oil has been identified as the main source of environmental emission of dodecylphenols.

A relatively small amount was used to produce phenol/formaldehyde resins for printing inks and rubber tyre manufacturing (Brooke *et al.*, 2007)

A very small proportion (<1%) of the overall tonnage of tetrapropenylphenol was used to make ethoxylates. These are used as anti-rust agents in finished lubricants at levels of 0.05-0.30% w/w.

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.

Dodecylphenol ethoxylates
At least two dodecylphenol ethoxylates are pre-registered but none are included in the database of registered substances or the list of 2013 intentions.

A very small proportion (<1% i.e. < 500 t/y) of the overall tonnage of tetrapropenylphenol was used to make dodecylphenol ethoxylates in 2004. 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, a continuing trend. The industry believes they will eventually be totally phased out. The residual content of free dodecylphenol in the ethoxylates is unknown but most likely <1%. (brooke *et al.*, 2007).

3.2.4 Butylphenols
The butyl group is a chain of 4 carbon atoms, which may be branched or linear. At least 11 CAS numbers of butyphenols are included in the list of pre-registered substances. Two of these are registered in ECHA's database of registered substances: 4-*tert*-butylphenol (4-*tert*-BP) (CAS No 98-54-4) and 2-*sec*-butylphenol (CAS No 89-72-5).

The 4-*tert*-butylphenol is registered for use as intermediate only, without an indication of tonnage band.

The 2-*sec*-butylphenol is registered with an imported and manufactured tonnage in the 1,000-10,000 tonnes range.

Furthermore, phenol isobutylenated (CAS No 68610-06-0) is included in the list of 2013 registration intentions, indicating the manufactured and imported tonnage may be in the 100-1,000 tonnes range (ECHA, 2012e).

4-*tert*-butylphenol (4-*tert*-BP)
The manufacture and use of 4-*tert*-BP in the EU is described in the EU Risk Assessment report for 4-*tert*-butylphenol from 2008 (ECB, 2008) presenting production and consumption figures for 2001 (see Figure 5). CEPAD has indicated these data as the best indication of the flow of 4-*tert*-BP in the EU for the current study.

The report does not provide a detailed breakdown of the consumption by application area but indicates that the consumption is >1,000 tonnes for three application areas: production of phenolic resins, production of polycarbonates and production of alcohols through hydrogenation.

4-*tert*-BP is mainly used as a co-monomer in the polymer industry in the same way as 4-nonylphenyl, which means 4-*tert*-BP is polymerized with other ingredients such as phenol and formic aldehyde (see description under NP). In the polymers, 4-*tert*-BP is chemically bound in the matrix (covalent binding). (ECB, 2008) The phenolic resins and epoxy resins are used for a range of applications. With respect to consumer exposure the use of 4-*tert*-BP in epoxy for canned food is considered to potentially be the major source (ECB, 2008) as further discussed in section 7.4.

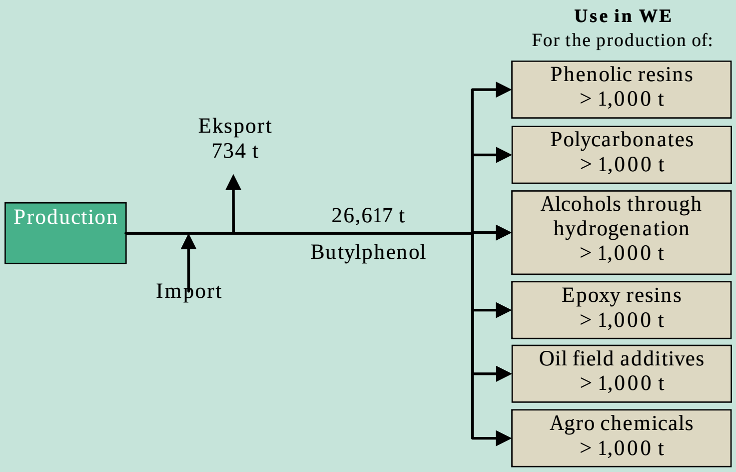


FIGURE 5
FLOW OF 4-*TERT*-BP IN WESTERN EUROPE (EU + SWITZERLAND + NORWAY) IN 2001 (ECB , 2008)

It is common for commercial 4-*tert*-BP/formaldehyde resins to contain up to 3% free 4-*tert*-BP. However, in all of the processes the resin is mixed with other resins/components and, with the exception of tyre tackifiers, further reaction takes place. This reaction will also occur with any free 4-*tert*-BP in the resin, and this dilution and reaction will reduce the free monomer to very low levels. Residual 4-*tert*-BP concentrations far below 0.1% have been measured in butylphenol/formaldehyde resins used to improve the tack of compounded rubber for tyres.

4-*tert*-BP is used as a chain terminator in the synthesis of polycarbonate polymers. Polycarbonate resins produced with 4-*tert*-butylphenol contain 1-3 % (w/w) of 4-*tert*-BP, reacted and bound into the polymer chain. Since the polymers are further processed to finished products, the concentration of free residual monomers in the final products is much lower. The residual concentrations of non-reacted 4-*tert*-BP in polycarbonate is found to be non detectable, at a limit of detection of 5 ppm (ECB, 2008). The main uses of polycarbonate are the following: Compact discs, DVD, and CD Rom manufacture, solid and multi-wall sheet in glazing applications and films, as polycarbonate blends for diverse injection moulded functional parts used mainly in the electrical and electronics industry and the automotive industry, containers for storage of food and beverages, and tableware (ECB, 2008). Exposure to 4-*tert*-BP from polycarbonate used for food contact applications is estimated to be the second major source of consumer exposure to 4-*tert*-BP (ECB, 2008).

Butylphenol/formaldehyde resins are ethoxylated to produce specialised surfactants for the separation of crude oil in aqueous refinery effluent from off-shore oil. Release of ptBP is restricted to the production process of the ethoxylated resins products and no additional environmental releases of ptBP therefore are expected during the production of oilfield chemicals (ECB, 2008).

4-*tert*-BP is also hydrogenated to form the corresponding alcohol 4-*tert*-butylcyclohexanol.

Due to its low alkyl chain-length, 4-*tert*-BP is not suitable for the production of surfactants and butylphenol is not used to produce butylphenol ethoxylates (CEPAD, 2012).

2-*sec*-Butylphenol
The compound 2-*sec*-butylphenol (= o-*sec*-butylphenol, CAS No 89-72-5) is registered with an imported and manufactured tonnage in the 1,000-10,000 tonnes range. The substance is indicated as

raw material for the production of fungicides and other plant protection products (ECHA, 2012e) in the registration.

o-*tert* Butylphenol
o-*tert* butylphenol was produced in quantities of <1000 t/y in 2010 according to CEPAD (2011). Together with other ortho-substituted alkylphenols, they are chemical intermediates for the production of herbicides, plastic additives, or - after hydrogenation - for the fragrance industry.

3.2.5 Dibutyl- and tributylphenols

Dibutylphenols
Four dibutylphenols are registered. For both 2,4-di-*tert*-butylphenol (CAS No 96-76-4) and 2,6-di-*tert*-butylphenol (CAS No 96-76-4) more than one registrant has registered a production or import in the 100-1,000 t/y range. According to CEPAD (2011), the total production is >1,000 t/y for both compounds and they are used as chemical intermediates for the production of plastic additives (antioxidants and UV-light stabilizers). According to the registrations they may also be used as fuel additives and lubricant additives used both by professionals and consumers (ECHA, 2012e). The consumption of the two substances in 1999 was 13,000 and 15,000 t/y (Environment Agency, 2005b).

Two dibutyls are registered for usage as intermediate only: di-*sec*-butylphenol, mixed isomers (CAS No 5510-99-6) and di-*sec*-butylphenol (CAS No 31291-60-8). According to CEPAD (2011), both are manufactured in a quantity of <1,000 t/y and used as intermediate for the production of plastic additives (antioxidants and UV-light stabilizers).

Tributylphenol
The substances 2,4,6 tris-*tert* butyl-phenol (TTBP) (CAS no 732-26-3) is registered for usage as intermediate. CEPAD indicates that the production is <1,ooo t/year and that the substance is used as intermediate for the production of plastic additives. In Norway the main flow of TTB-phenol was due to its potential use as a fuel additive (Lambert *et al.*, 2010). In Norway, it was only found in imported fuel, and would be present at a level of approximately 0,027%. With normal use, TTBP will burn and environmental emission will not be of any significance (Lambert *et al.*, 2010).

3.2.6 2,6-Di-*tert*-butyl-*p*-cresol

2,6-Di-*tert*-butyl-*p*-cresol (BHT, CAS No 128-37-0) is registered as manufactured and imported in the 10,000-100,000 t/y tonnage range. The substance is registered by at least three manufacturers or importers.

The substance is not included in the presentation on major uses of AP/APEO submitted by CEPAD.

According to the OECD SIDS Initial Assessment Report from 2002 (OECD, 2002a), the world production capacity of BHT in 2000 amounted to about 62,000 t/y. The substance was manufactured by four companies in Western Europe with a production capacity of 25,000 t/y.

BHT is registered for usage as a stabilizing (antioxidant) component for many applications. As an antioxidant, it finds many applications in a wide variety of industries (OECD, 2002). It is used in ground vehicle and aviation gasolines; lubricating, turbine, and insulation oils; waxes, synthetic and natural rubbers, paints, plastics, and elastomers (synthetic rubbers). It protects these materials from oxidation during prolonged storage. Highly purified grades are suitable for use in foods to retard oxidation of animal fats, vegetable oils, and oil-soluble vitamins. It is also used in cosmetics and food packaging materials such as waxed paper, paper board, and polyethylene. It is important in delaying the onset of rancidity of oils and fats in animal feeds, and in preserving the essential nutrients and pigment-forming compounds of these foods (OECD, 2002). The worldwide distribution by end-applications for year 2000 was: rubber (27%), plastics (27%), mineral oil/food additive

(17%), foodstuff/pharmaceuticals/cosmetics (12%), animal feed / pet food (11%) and printing inks/miscellaneous (6%).

The substance is authorised for use as food additive and as cosmetic ingredient under the name butylated hydroxytoluene (BHT).

3.2.7 Other alkylphenols

The use in the EU of a number of other alkylphenols is summarised in Table 9. The substances are either used in small quantities or mainly used as intermediates.

TABLE 9
AVAILABLE INFORMATION ON A NUMBER OF OTHER ALKYLPHENOLS

Substance	CAS No	Import and manu-facture in 2010 t/y *1	Registered quantity t/y	Main application areas *2
4-*tert* amylphenol	80-46-6	<1,000	n.r.	Production of phenolic resins and lacquers
o-*tert* amylphenol	3279-27-4	<1,000	n.r.	Production of herbicides, plastic additives, or - after hydrogenation - for the fragrance industry
2-isopropylphenol	88-69-7	>1,000	n.r.	
2,4-dinonylphenol	137-99-5	<1,000	n.r.	Production of polycarbonates and phenolic resins and lacquers
2,4-di-*tert* amylphe-nol	120-95-6	<1,000	n.r.	Plastic additives
Phenol, isopropylat-ed	90480-88-9	n.i.	intermediate use only	Chemical intermediate
2-*tert*-butyl-*p*-cresol	2409-55-4	n.i.	intermediate use only	Chemical intermediate
6-*tert*-butyl-*m*-cresol	88-60-8	n.i.	intermediate use only	Chemical intermediate
C14-16-18 alkylphe-nol	931-468-2	n.i.	intermediate use only	Chemical intermediate
Thymol	89-83-8	n.i.	1,000 - 10,000	Cleaning agents Use of scented articles
o-pentylphenol	136-81-2	n.i.	Available in confidential annex to Crane *et al.* (2008)	Production of phenolic resin Germicide Vulcanizing agent
4-pentylphenol	14938-35-3	n.i.		
m-pentylphenol	20056-66-0	n.1.		

*1 Source: CEPAD, 2011.
*2 Source: Registrations (ECHA, 2012e).
n.r: Not registered; n.i.: not indicated.

3.2.8 Summary on the use of AP/APEO in the EU

A summary of the use of AP/APEO in the EU is provided in Table 20 together with the summary of the use of the substances in Denmark.

3.3 Manufacture and use of AP/APEO in Denmark

The following sections examine manufacture and use of AP/APEO in Denmark.

3.3.1 Manufacture, import, export and consumption of AP/APEO on its own and in mixtures

Alkylphenols and alkylphenol ethoxylates are not produced in Denmark.

Import/export statistics

The import of butylphenol, octylphenol and nonylphenol and salts thereof as retrieved from Eurostat is shown in the table below. Other AP/APEOs are included in aggregated commodity groups which also include other phenols. The net import in 2011 of octylphenol and nonylphenol on their own was 1.6 tonnes, while the net import of 4-*tert*-BP was 4.5 tonnes.

The imported 1.6 tonnes of nonylphenol, octylphenol and their salts is a relatively small quantity compared to the 34 tonnes registered in total for the two substances in the Danish Product Register (shown in next section). Considering that the average for the period 2006-2010 was 0.08 tonnes, it clearly indicates that nonylphenol and octylphenol are mainly imported in mixtures. The imported mixtures may partly consist of raw materials for production of mixtures in Denmark, and partly of mixtures for end-use in Denmark.

The imported quantities of 4-*tert*-BP is of the same size as the quantities registered in the Product Register. No indication of the application of the 4-*tert*-BP on its own has been obtained. Considering 4-*tert*-BP is generally used for the production of phenolic resins, it is likely that the substance could be used for this application in Denmark.

TABLE 10
DANISH IMPORT AND EXPORT OF 4-*TERT* BULTYLPHENOL, OCTYLPHENOL AND NONYLPHENOL AND SALTS THEREOF (EUROSTAT, 2012A)

CN code	Text	Import, t/y		Export, t/y	
		Average 2006-2010	2011	Average 2006-201o	2011
2907 13 00	Octylphenol, nonylphenol and their isomers; salts thereof	0.08	1.6	0	0
29071910	4-*tert*-butylphenol	5.3	4.5	0	0.06

Data from the Danish Product Register

Data on AP/APEO registered in the Danish Product Register were retrieved in July 2012 on the basis of the gross list of AP/APEO shown in Table 1. For a few of the substances identified at a later stage of study implementation, data have not been retrieved from the Product Register, but a search in the SPIN database of the Nordic Product registers has indicated that the substances are not registered in the Danish Product Register.

The Danish Product Register includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). Of the AP/APOE, nonylphenol, 4-octyl phenol and thymol are classified as dangerous. For the other non-classified substances, the registration will only occur if they are constituents of mixtures which are classified and labelled as dangerous due to the presence of other constituents. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. On the other hand, for substances included in mixtures used for formulation of other mixtures in Denmark (e.g. those included in raw materials used for production of paint), the quantities may be double-counted as both the raw material and the final mixture in the register. As stated above, the amounts registered are for occupational use only, but for substances used for the manufacture of mixtures in Denmark the data may still indicate the quantities of the substances in the finished products placed on the market both for professional and consumer applications.

Data on AP/APEO in mixtures registered in the Danish Product Register are summarised in Table 11. In total, 39 AP/APEO within the scope of this study were registered. The total production and import was 392 tonnes and the total consumption (content of mixtures placed on the Danish market) was 330 tonnes. Of this, nonylphenol (substances with non-confidential data only) and nonylphenol ethoxylates accounted for 52% and 2,6-di-*tert*-butyl-*p*-cresol for 36%. It should be noted that 2,6-di-*tert*-butyl-*p*-cresol often is not included in the group of AP/APEO. The substance was present in 1,156 registered mixtures.

TABLE 11
AP/APEO IN MIXTURES PLACED ON THE DANISH MARKET IN 2011 AS REGISTERED IN THE DANISH PRODUCT REGISTER

CAS No	Chemical name	No of mixtures	Registered tonnage, t/y		
			Production + import	Export	Consumption
Nonylphenol					
25154-52-3	nonylphenol	84	32.513	3.651	28.862
84852-15-3	phenol, 4-nonyl-, branched	7	0.091	0.000	0.091
104-40-5	4-nonylphenol	Conf.	-	-	-
	Total (excl. confidential)		32.604	3.651	28.953
Nonylphenol ethoxylates					
9016-45-9	nonylphenol, ethoxylated	186	119.711	11.109	108.602
26027-38-3	4-nonylphenol, ethoxylated	13	0.014	0.004	0,010
37205-87-1	poly(oxy-1,2-ethanediyl), α-(isononylphenyl)-ω-hydroxy-	41	5.041	0.283	4,758
68412-54-4	2-{2-[4-(2,4,5-trimethylhexan-3-yl)phenoxy]polyethoxy}ethanol	103	44.064	17.558	26,506
127087-87-0	4-nonylphenol, branched, ethoxylated	8	0.467	0.192	0,275
	Total		169.298	29.146	140.152
Octylphenol					
140-66-9	4-(1,1,3,3-tetramethylbutyl)phenol	Conf.	-	-	-
3884-95-5	o-(1,1,3,3-tetramethylbutyl)phenol	Conf.	-	-	-
Octylphenol ethoxylates					
9002-93-1	poly(oxy-1,2-ethanediyl), α-[4-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy *5	Conf.	-	-	-
9036-19-5	poly(oxy-1,2-ethanediyl), α-[(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy	104	12.650	2.032	10.619
Dodecylphenol					
104-43-8	4-dodecylphenol	16	0.051	0.001	0.049
27193-86-8	decylphenol	4	0.044	0.000	0.044
121158-58-5	Phenol, dodecyl-, branched	105	4.355	0.419	3.935
210555-94-5	phenol, 4-dodecyl-, branched (not pre-registered)	Conf.	-	-	-

CAS No	Chemical name	No of mixtures	Registered tonnage, t/y		
			Production + import	Export	Consumption
57427-55-1	Tetrapropylenphenol (not pre-registered)	Conf.	-	-	-
	Total (excl. confidential)		4.450	0.421	4.029
Dodecylphenol ethoxylates					
74499-35-7	phenol, (tetrapropenyl) derivs.	41	2.426	0.003	2.423
9014-92-0	Dodecylphenol, ethoxylated	Conf.	-	-	-
Butylphenols					
88-18-6	2-*tert*-butylphenol	5	0.184	0.027	0.157
98-54-4	4-*tert*-butylphenol	61	8.339	5.515	2.824
28805-86-9	butylphenol	Conf.	-	-	-
68610-06-0	phenol, isobutylenated	Conf.	-	-	-
	Total (excl. confidential)		8.522	5.542	2.981
2,6-di-*tert*-butyl-*p*-cresol					
128-37-0	2,6-di-*tert*-butyl-*p*-cresol	1156	137.556	18.764	118.792
Dibutylphenols, dibutyl methyl phenols, tributylphenols					
128-39-2	2,6-di-*tert*-butylphenol	58	19.605	1.322	18.282
497-39-2	4,6-di-*tert*-butyl-*m*-cresol	Conf.	-	-	-
732-26-3	2,4,6-tri-*tert*-butylphenol	5	0.670	0.067	0.603
17540-75-9	4-*sec*-butyl-2,6-di-*tert*-butylphenol	Conf.	-	-	-
Other mono- alkylphenols					
25429-37-2	ethylphenol	Conf.	-	-	-
1987-50-4	4-heptylphenol	Conf.	-	-	-
119-42-6	2-cyclohexylphenol	59	0.335	0.016	0.319
1131-60-8	4-cyclohexylphenol	59	0.046	0.002	0.044
68025-37-6	bis(tert-butyl)dodecylphenol	6	1.573	0.000	1.573
Other di- and trialkylphenols					
89-83-8	thymol	44	0.002	0.000	0.002
96-76-4	2,4-di-*tert*-butylphenol	13	0.295	0.074	0.221
1323-65-5	dinonylphenol	Conf.	-	-	-
1879-09-0	6-*tert*-butyl-2,4-xylenol	10	0.023	0.000	0.023
2409-55-4	2-*tert*-butyl-*p*-cresol	5	0.001	0.000	0.001
4306-88-1	2,6-di-*tert*-butyl-4-nonylphenol	23	0.196	0.030	0.165
Total (incl. confidential)			**392.062**	**61.077**	**330.986**

Conf.: Data are confidential due to a low number of mixtures or registrants.

Information on use areas by main substance groups is described below. This description is followed by a description of the main use areas across the substance groups. Please note that the total sum of mixtures for each substance group is higher in the following tables compared to what would result from calculation by summing up the data in Table 11 (for nonylphenols e.g. 100 vs. 91). The reason is that more of the substances may be used in the same mixtures. The total for each substance in Table 11 has been generated by the data retrieval and represents the correct total number of mixtures for each substance. The total number of mixtures may be slightly overestimated in all other tables.

Nonylphenol, octylphenol and their ethoxylates

NP and NPEO accounted for the majority of those substances traditionally considered AP/APEO. The registered consumption of one of the nonylphenols (CAS No 25154-52-3) by application area is shown in Table 12. Data for other alkylphenols are confidential.

The main application area of this NP was paint, lacquers and varnishes, which accounted for approximately 70% of the total. Other applications were hardeners, adhesives, sealants and filling agents and joint-less floors. None of these applications are included in the list of restricted applications. The hardeners are probably the hardener components of two-component systems e.g. for epoxy or phenolic plastic. The use in the other mixtures is further discussed in the later description of the application areas across the different substances groups.

The registered consumption of octylphenol was confidential.

Paint and varnishes was also among the main application areas of NPEO (Table 13). The major application area of the nonylphenol ethoxylates, however, was cleaning agents, polishes and maintenance agents. The use of NPEO is restricted in cleaning agents and some of the registered applications such as car shampoo, "general cleaning agents" and "other cleaning agents" are probably within the scope of the restriction as further discussed below. The maintenance agents may be outside the scope of the restriction, but they account for a smaller part of the total within this group.

TABLE 12
CONSUMPTION OF ONE NONYLPHENOL (*1) REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Application area	Consumption (production + import – export) *1		
	n *2	t/y	%
Paints, lacquers and varnishes	42	19.6	69
Adhesives	6	0.5	2
Sealants and filling agents	7	5.6	20
Hardeners	10	0.2	1
Joint-less floors	4	0.5	2
Other (mainly confidential or substances with the application area not indicated)	15	2.1	7
Total (including confidential)	84	28.5	100

*1 CAS No 25154-52-3, nonylphenol.

*2 Number of mixtures.

TABLE 13
CONSUMPTION OF TWO NONYLPHENOL ETHOXYLATES REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Application area	Consumption (production + import – export) *2		
	n*1	t/y	%
Paints, lacquers and varnishes	96	12	9
Lubricants and oils	32	1	1
Biocidal products	13	13	10
Cleaning agents, polish and maintenance agents	91	53	39
Other	28	55	41
Total (including confidential)	-	135	100

*1 Number of mixtures.

*2 Sum of CAS No 9016-45-9 and 68412-54-4 (each with >3 mixtures for each application area)

The main part of the octylphenol ethoxylates were for confidential applications or applications not indicated in the Product Register. The main non-confidential application accounting for 25% of the use of CAS No 9036-19-5 was for paints, lacquers and varnishes.

Butylphenols

4-*tert*-butylphenol was mainly used in paint, lacquers and varnishes and as hardeners for plastics, i.e. as a constituent of the hardener component of two-component plastics such as epoxy and phenolic plastics. The tonnage registered in the Product Register is lower than the import registered in the trade statistics. As the substance is not classified as hazardous, mixtures with the substance will only be registered in the Product Register if the mixtures contain other substances which are classified as hazardous. An import, for example for use in the manufacture of phenolic plastics, would not result in a notification of the Product Register.

The consumption of other butylphenols by application area is confidential.

TABLE 14
CONSUMPTION OF 4-*TERT*-BUTYLPHENOL REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Application area	Consumption (production + import – export)		
	n *1	t/y	%
Paints, lacquers and varnishes	18	2.0	71
Adhesives	17	0.04	1
Sealants and filling agents	4	0.01	0.3
Hardeners	10	0.57	20
Other (incl. confidential)	13	0.2	7
Total (including confidential)	-	2.8	100

*1 Number of mixtures.

2,6-di-*tert*-butyl-*p*-cresol

As described in the section on use of the substance in the EU, 2,6-di-*tert*-butyl-*p*-cresol (BHT) is widely used as an antioxidant in various mixtures. The substance is registered in nearly 1,200 different mixtures, and the function is usually as an antioxidant. The substance is in general not considered together with the long-chain APs such as NP, OP and DP.

The substance is used as an antioxidant in food and cosmetics and may be imported in various mixtures not registered in the Danish Product Register. The substance is widely used in consumer products. The total manufacturing capacity in the EU was about 25,000 tonnes in the year 2000. If it is assumed that the total EU consumption in 2011 was in the range of 15,000-30,000 t/y and Denmark accounted for 1% if the total EU consumption, the consumption in Denmark would be in the 150-300 t/y range. The registered tonnage is somewhat lower, but still in the same order of magnitude.

TABLE 15
CONSUMPTION OF 4-*TERT*-BUTYLPHENOL REGISTERED IN THE DANISH PRODUCT REGISTER

Application area	Consumption (production + import – export)		
	Number of mixtures	t/y	%
Paints and lacquers	593	0.1	0.1
Inks	11	12.9	11
Adhesives	36	1.8	2
Sealants and filling agents	32	0.002	<0.1
Lubricants and oils	127	3.0	2
Joint-less floors	21	0.1	<0.1
Pesticides and biocidal products	10	0.003	<0.1
Cleaning agents, polish and maintenance agents	45	6.0	5
Surface active agents, defoamers	21	0.02	<0.1
Raw materials for synthesis	48	21.5	18
Other (confidential and applications not indicated)	251	73.4	62
Total	-	118.8	100

Substances mainly registered as fuel additives and lubricants
A number of the substances are mainly registered as used in fuel additives and lubricants, as further described in the next section.

Of these substances, the highest quantities are for 2,6-di-*tert*-butylphenol where the total registered consumption is 18.3 tonnes, used mainly in lubricant, hydraulic oils and fuel additives. The use in lubricants and fuel additive is in accordance with the information from registrations under REACH (ECHA, 2012e).

At EU level, 99% of dodecylphenol is used to prepare lubricant additives. This is also the main non-confidential application area registered in the Product Register for these substances. A survey of the use of dodecylphenol and 2,4,6 –tri-*tert*-butylphenol in Norway found that the concentration of dodecylphenyl was typically 0.15% in those lubricants, whereas the MSDS indicates that dodecylphenol was present in the lubricants (Lambert *et al.*, 2010).

The main uses of one of the dodecylphenol ethoxylates (CAS No 74499-35-7) with non-confidential application were lubricants and oils which accounted for 61% of the total consumption of 2.4 t/y.

2-Cyclohexylphenol and 4-cyclohexylphenol
These substances are used in small quantities for many applications including paint, lacquers and varnishes. The total registered consumption was 0.3 tonnes.

3.3.2 Consumption of AP/APEO by main application areas
In this section the use of AP/APEO in Denmark is described by main application areas. Possible import of the substances in articles and mixtures is briefly discussed, although a thorough survey of such import has not been carried out.

Paint, lacquers and vanishes

Paint, lacquers and vanishes constitute one of the main application areas of the AP/APEO. The trade organisation for the paint and adhesives industry in Denmark, DFL, has been contacted in order to obtain more information of the use of AP and APEO in paint and adhesives produced in Denmark. The trade organisation has carried out a survey among the members and the general answer is that the substances are not used on their own in the production of paint and adhesives in Denmark, but may be present in imported raw materials used in production. The same was reported by the trade organisation in 2005 (Kjølholt *et al.*, 2007). The relatively small import of nonylphenol and octylphenol on their own confirms that the substances are mainly imported in raw materials and other mixtures.

Nonylphenol is mainly used in hardeners for paint and lacquers, probably for two component speciality lacquers. NPEO and OPEO are used as surfactants, which reduce the surface tension of water, allowing easier spreading, wetting, and better mixing of paints.

In paints and printing inks, nonylphenol ethoxylates are typically used in concentrations of 0.6 to 3%. (ECHA 2012b). Nonylphenols or their ethoxylates are mainly used in paints used on wet-room floors, water-based paints and varnishes for indoor use, printer's ink, concrete floor paint, metal coating and anticorrosive paints (ECHA 2012b).

As the nonylphenol and nonylphenol ethoxylates are classified as hazardous, the majority of the mixtures imported or manufactured containing these substances are expected to be registered in the Product Register.

The compound 2,6-di-*tert*-butyl-*p*-cresol is used in small concentrations and quantities as antioxidant in a large number of mixtures.

The paint, lacquers and vanishes may be used for consumer, professional and industrial applications. No data are available to estimate how much of the total consumption is used for consumer applications.

TABLE 16
CONSUMPTION OF AP AND APEO IN PAINT, LACQUERS AND VARNISHES REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Substance	Number of registered mixtures	Consumption t/y	% of total
Nonylphenols	49	20.0	53
Nonylphenol ethoxylate	119	12.7	34
Octylphenol ethoxylates	53	2.6	7
4-*tert*-butylphenol	18	2.01	5
2,6-di-*tert*-butyl-*p*-cresol	593	0.1	0.3
Cyclohexylphenols	42	0.02	0.1
Other	-	<0.001	-
Total	-	37.4	100

Lubricants and oils

Many of the small-volume alkylphenols have their main application in lubricants and fuel additives. The total registered consumption for lubricants, oils and fuel additives is 22.4 tonnes (Table 17 and Table 18).

This is in accordance with the general information on the use of the substances in the EU.

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) (Environment Agency, 2005). If the substances are added to fuels they would be combusted with the fuel. Used otherwise they would typically be disposed of with the waste oil, but spill may occur.

The lubricants and oils may be used for consumer, professional and industrial applications. The consumer applications of these types of lubricants (e.g. crankcase lubricants) is considered too be very limited.

TABLE 17
CONSUMPTION OF AP AND APEO IN LUBRICANTS AND OILS REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Substance	Number of registered mixtures	Consumption t/y	% of total
Nonylphenol ethoxylates *1	40	1.7	13
Octylphenol ethoxylate *2	6	0.05	0.4
2,6-di-*tert*-butyl-*p*-cresol	127	3.0	16
Dodecylphenol *3	108	2.1	12
Dodecylphenol ethoxylate* 4	32	1.5	21
2,6-di-*tert*-butylphenol	40	2.7	2
2,6-di-*tert*-butyl-4-nonyl-phenol	15	0.2	12
Other	-	1.5	13
Total (incl. confidential)	-	12.9	

* Sum of CAS No 68412-54-4 and 9016-45-9 (each with >3 mixtures).

*2 CAS No 9036-19-5.

*3 Sum of CAS No 104-43-8 and 121158-58-5 (each with >3 mixtures).

*4 CAS N0 74499-35-7.

TABLE 18
CONSUMPTION OF AP AND APEO IN LUBRICANTS, OILS AND FUEL ADDITIVES REGISTERED IN THE DANISH PRODUCT REGISTER, 2012

Substance	Number of registered mixtures	Consumption, t/y	% of total
2,6-di-*tert*-butylphenol	9	6.7	71
Other	-	1.8	29
Total (incl. confidential)	-	9.5	100

Cleaning and maintenance agents

In spite of the restriction on the use of nonylphenol ethoxylates for the majority of cleaning agents, still, some 54 tonnes were registered for this application area. A part of this total may be for applications exempt from the general restriction or e.g. maintenance agents not within the scope of the restriction, but the majority is registered for usage in general cleaning agents. The reason may be that the companies have not updated their registrations for many years so that the registered volume is outdated, or that some companies are not in compliance with the legislation.

In addition to the 54 tonnes registered as cleaning and maintenance agents, 13 tonnes were registered as disinfectants and other biocidal products for private use and use in the medical sector, which may in fact be cleaning agents within the scope of the current restriction.

According to the Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries (SPT), the members of the Association have not used the nonylphenol ethoxylates since the late 1990s when the association made a voluntary agreement with the Danish EPA.

Apparently, the NPEO has not been replaced by OPEO and other alkylphenol ethoxylates in the cleaning agents.

2,6-di-*tert*-Butyl-*p*-cresol was used as an antioxidant in a number of mixtures, and may likely be used in more mixtures which are not registered in the Product Register.

The use of cleaning agents with NPEO for consumer applications is prohibited, but NPEO may still be present in some maintenance agents used by consumers

TABLE 19
CONSUMPTION OF AP AND APEO IN CLEANING AND MAINTENANCE AGANTS IN THE DANISH PRODUCT REGISTER, 2012

Substance	Number of mixtures	Consumption t/y	% of total
Nonylphenol ethoxylates *1	100	54.0	90
Octylphenol ethoxylate *2	5	<0.000	-
2,6-di-*tert*-butyl-*p*-cresol	45	6.0	10
Other	-	<0.000	-
Total		60.0	100

*1 Sum of CAS No 9016-45-9, 37205-87-1, 68412-54-4 (each with >3 mixtures)

*2 CAS No 9036-19-5.

Sealant and fillers

Sealant and fillers contained mainly NP and NPEO with total consumptions of 5.6 and 0.8 tonnes, respectively. According to information obtained from the trade organisation FSO (Fugebranchen), AP and APEO are not used on their own in the production of sealant and fillers in Denmark, but may be included in the raw materials. The main application of the two substances in these mixtures is probably the same as described for paint: NP is mainly a constituent of hardeners of two component systems and APEO is a surface active agent.

The sealant and filler may be used for both consumer and professional applications. No data are available to estimate how much of the total consumption is used for consumer applications.

Textiles

In the EU, NP and NPEO are not regulated for use in the manufacturing of textiles and leather mixtures in concentrations above 0.1% unless the processing takes place in closed systems (Annex XVII to the REACH Regulation). Textiles and leather produced in closed systems may still contain residuals of NP and NPEO.

Furthermore, import of textiles and leather products with NP and NPEO is not restricted and the substances may be used outside the EU and be present in imported textile and leather products.

NPEO is still used in textile production outside the EU as detergent and auxiliaries such as dispersing agents for dyeing, emulsifiers and spinning lubricants (ECHA, 2012b).

A recent survey of NP and NPEO in textiles undertaken for the Danish EPA (Rasmussen *et al.*, in press) has reviewed the literature and summarised the results of tests undertaken by a range of organisations in Denmark, Norway, Sweden, and the UK. In a total of 139 tests, the average NPEO concentration was 670 mg/kg with a median value (geometric mean) of 66 mg/kg and the 95th percentile at 2,440 mg/kg. The maximum value was 14,100 mg/kg (1.4%). The average NP concentration was 5.9 mg/kg with a median value of 0.7 mg/kg and 95th percentile of 22.9 mg/kg. The maximum value was 49 mg/kg.

In the survey, 15 pieces of clothing and bed linen were furthermore tested for the presence of NP and NPEO. The NP concentration ranged from 0.7 to 3.7 mg/kg with an average of 1.6 mg/kg. The total NPEO concentration ranged from <2 to 311 mg/kg with an average of 96 mg/kg. The NPEO concentration was measured for three types of NPEO with various numbers of ethoxy groups: $NPEO_1$, $NPEO_2$ and $NPEO_{3-15}$ (number of ethoxy groups in subscript). It was assumed that the average number of ethoxy groups in the $NPEO_{3-15}$ group was 9. The average concentration for the three groups was 1.6, 1.7 and 92.8 mg/kg, clearly demonstrating the dominance of the NPEO with more than two ethoxy groups. Using the specific molar weight of the three groups of ethoxylates, the NPEO concentration could be recalculated to NP equivalents, NP_{-s}. The total average content of NP_{-s} was estimated at 37 mg/kg.

In 8 of the samples the concentration of OPEO was below the detection level of 0.2 mg/kg textile and the maximum concentration measured was 10 mg/kg. The average for all samples was less than 1.6 mg/kg; less than 2% of the average NPEO concentration.

Five pieces of clothing were washed at 40˚C and one piece of bed linen was washed at 60 ˚C. In the clothing, the concentration decreased by 29 to 82 % in the process of one washing cycle, while the concentration decreased by 99% in the bed linen sample washed at 60 ˚C. The results further indicate that some of the long-chained NPEO were degraded to shorter-chained NPEO during the wash.

The Swedish Society for Nature Conservation has analysed NPEO in imported towels and t-shirts. In 20 towels the concentration of NPEO ranged from <1 to 10,608 mg/kg with an average of 652 (Hök *et al.*, 2007). The dataset is included in the reviewed data mentioned above. On the basis of the results, the report estimates that 2-9 tonnes of nonylphenol originating from imported textiles reach the waste water treatment plants of Stockholm and constitute the likely source of the 1.6 tonnes of NP in the waste waster inlet to the waste water treatment plants measured in 2006.

In the UK, the Environment Agency (2012) tested 100 pairs of underpants. Twenty-eight of the 100 samples analysed contained NPEO, ranging from 3.3 mg/kg to 1759.7 mg/kg. Further testing on six pairs of underpants showed that NPEO was released from all samples, with an average release of over 99.9% after two washes at 40°C using liquid biological detergent. It was estimated that imported underpants could account for up to 1.5 tons of NPEO emissions to the water environment in the 2011 in the UK. No clear relationship could be established between the presence or concentration of NPEO and a number of factors: price, country of manufacture, retailer type, colour, and intended end consumer.

In textiles imported to Denmark, an indication of the total content of NPEO and the equivalent NP_{-s} may be obtained by multiplying the average content of the textiles with the total tonnage. The analysed textiles reviewed originate from countries outside the EU and may not be representative for textiles produced within the EU. The total import of apparel and other textiles (Combined Nomenclature codes G_61, G_62 and G_63) from countries outside the EU (nearly 100% from Asia) in 2011 was 145,000 tonnes, while 44,000 tonnes was imported from other EU Member States. The tree commodity codes also include some accessories and articles which may not be comparable to the tested articles. If it is assumed that the 120,000 tonnes had an average NPEO concentration of 96 mg/kg the total import of NPEO in textiles can be estimated at 12 tonnes. Considering the uncertainties, the actual value is likely in the range of 6-20 tonnes/year. The total NP content can similarly be estimated at 0.2 tonnes. Using the average NP equivalent content of 37 mg NP_{-s}/kg, the total NP equivalent in the imported textiles can be estimated at 4.4 t/y NP_{-s} .

During washing the NP and NPEOs are released to wastewater and the estimated quantities of NP and NPEO in imported textiles indicate that textiles would be one of the main sources of NP and NPEO to waste water in Denmark.

Pesticides

The industry and the Danish authorities have made a voluntary agreement of phasing out OPEO and NPEO in pesticides sold in Denmark since 2000 (Krongaard *et al.*, 2008). The content of OPEO and NPEO in pesticides is frequently controlled. The Chemicals Inspection Service at the Danish EPA conducts non-laboratory control and the Danish Centre for Environment and Energy (former National Environmental Research Institute), Aarhus University, conducts the laboratory control of pesticides in assistance to DEPA. In 2008 none of the tested pesticides contained OPEO, whereas one product contained NPEO (Krongaard *et al.*, 2008).

Import of APOE in other types of articles

As mentioned above, APEO may be present in leather products imported from countries outside the EU. Before the restriction, the consumption of NPEO for leather auxiliaries in the EU was at the same level as the consumption for textiles. No data on the import of NPEO with leather articles have been indentified, but the total quantity may be at the same level as the import with textiles. A part of the NPEO may be released to waste water from the washing of leather, but it is assumed that the majority of the NPEO is disposed of as solid waste together with the leather.

NPEO was before the restriction used in the production of paper and pulp, and may be present in low concentrations in paper and boards. No data on the possible import of NPEO in paper and board from countries outside the EU have been identified.

Residual content of 4-NP, 4-t-OP and 4-*tert*-BP in articles

Products manufactured from 4-NP, 4-t-OP and 4-*tert*-BP may contain small amounts of residual APs. No data on the actual import to Denmark of the substances in articles have been identified.

The EU Risk Assessment for 4-nonylphenol mentions that the main issue regarding residual 4-NP and consumer exposure is residual 4-NP in trisnonylphenylphosphite (TNPP) which is used as an antioxidant to stabilise polymer coatings used as food contact materials against degradation by ultraviolet light. TNPP is used in four types of food-contact polymers: polyolefin, rubber modified polystyrene, PVC films and rubber (ECB, 2002). The residual level of 4-NP in TNPP is typical 1-2%. The report does not indicate the 4-NP content of the materials and neither does the UK risk reduction strategy for NP (Footit, 1999). No data on the possible import to Denmark of NP in articles with TNPP have been identified.

As described in section 3.2.2 an average EU tyre contains between 0,007 % and 0,012 % of 4-t-OP (ETRMA, 2011). With a total import of tyres to Denmark of about 45,000 t/y (based on collection data, DBFR 2012), in total some 3-5 t/y of unreacted 4-*tert*-OP is imported with tyres. A significant part of this may be released to the environment by the wear of the tyres.

The EU Risk Assessment for 4-*tert*-butylphenol states that the potential consumer exposure is via direct use of mixtures with phenolic resins or epoxy resins containing residual 4-*tert*-BP monomers, or via use of the final articles containing residual concentration of 4-*tert*-BP (ECB, 2008). The main exposure from final articles is expected to be from adhesives (residual content of 0.1-1%), canned food, polycarbonate used for food contact material and drinking water from drinking water reservoirs or pipelines. According to the risk assessment the residual content of 4-*tert*-BP in polycarbonates is indicated at < 5 mg/kg while the concentration in final articles other polymers is indicated as much lower than 3%. The risk assessment does not quantify the total amounts of 4-*tert*-BP as residual content of materials and mixtures based on the substance.

3.4 Summary on the use of AP/APEO in Denmark and the EU

The available information on the use of AP/APEO in the EU and in Denmark is summarised in the table overleaf.

No updated inventory of the consumption in the EU has been identified, but based on the available information, the total consumption within the EU of the substances within the scope of this survey is likely in the 130,000-260,000 t/y range. The total production and import of AP/APEO in mixtures registered in the Danish Product Register was 392 tonnes and the total consumption (content of mixtures placed on the Danish market) was 330 tonnes. This is less than ¼ of what could be expected if the consumption in Denmark resembled the EU consumption on a per capita basis (Denmark represents about 1% of the population in the EU). The relatively low registered volume is discussed below.

Three APs with consumption volumes of > 10,000 t/y, nonylphenols, octylphenols and 4-*tert*-butylphenol are mainly used for production of phenolic resins and other resins/plastics in the EU. The registered consumption of these substances in Denmark is relatively low compared to the EU total, which reflects that only very small amounts of AP-based resins are manufactured in Denmark. Import data from the trade statistics confirms that the substances are used in relatively small volumes in Denmark. The main registered application area for these substances in Denmark is paint, varnishes and lacquers.

Three other high-volume APs, dodecylphenols, 2,6-di-*tert*-butylphenol,and 2,4-di-*tert*-butylphenol are mainly used for manufacturing of additives for lubricants and fuels. For these substances, the registered consumption in Denmark as compared to the EU total is low as well, reflecting that no major producers of these additives are located in Denmark. The major application areas of the substances in Denmark are as additives in/for lubricants and fuels.

The tonnage of 2,6-di-*tert*-butyl-*p*-cresol (BHT) is high both in the EU and Denmark, reflecting the general use of this substance as an antioxidant in food and a wide range of mixtures.

Among the APEOs, NPEO represented 93% of the total registered consumption in the Danish Product Register, while OPEO and DPEO accounted for the remaining part of the total of approximately 150 t/y. The main use of NPEO was as surfactants cleaning agents, and it is unclear to what extent the registered quantities of NPEO are due to inadequate update of the notifications, exempted uses or applications that are not in compliance with the current restrictions. The second main use area and the main application of the OPEO was paint, varnishes and lacquers. Notably, there is no indication that OPEO has substituted in a significant manner for NPEO in cleaning and maintenance agents. The total production of OPEO in the EU is less than 1% of the consumption of NPEO before the introduction of the EU-wide restriction on the NPEO. DPEO was used for lubricants and oils and some confidential applications in Denmark.

The remaining AP/APEOs represent less than 1% of the total consumption of the 330 t/y registered in the Danish Product register.

The most important data gaps are:

- Updated information on current uses and on the significance of the potential sources of NP/NPEO releases of to waste water and the environment is missing.
- Information on the current uses of NPEO in cleaning and maintenance products in Denmark calls for a clarification of actual uses.
- For some of the substances, information on the total manufacture and import to the EU in the registrations is not in accordance with information obtained from the industry and calls for a clarification.

TABLE 20
SUMMARY OF THE USE OF AP/APEO IN THE EU AND DENMARK

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
Monoalkylphenols and alkylphenolesthoxylates							
Nonylphenols (NP)	10,000-100,000	78,590 *1 25,000-50,000	1999 2011	2011: Production of phenolic resins Production of(4-nonylphenyl) phosphite Catalyst in epoxy resin production Production of plastic stabilizer Production of phenolic oximes Production of NPE	29.0	Paints, lacquers and varnishes Sealants and filling agents Hardeners Joint-less floors, surface active agents, confidential applications.	The registered consumption is small considering the EU consumption, probably because of low use of the substance as intermediate The main application areas are as component of hardeners in various mixtures
Nonylphenol ethoxylates (NPE)	2,000-20,000	118,000 *1 2,000-20,000	1999 2011	2011: Paint and varnishes Acrylic esters used for specialist coatings, adhesives and fibre bonding Metal working fluids (specific exemptions)	140.2	Cleaning agents, polish and maintenance agents Paints, lacquers and varnishes Disinfectants and other biocidal products for private use and use in the medical sector Adhesives, sealants and filling agents, hardeners, lubricants and oils, joint-less floors, confidential applications	The majority of the registered use as cleaning agents may be due to missing up-date of the notifications or uses not in compliance with the restriction Significant import of NPEO with textiles

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
Octylphenols (OP)	10,000-100,000	22,900	2001	Production of phenolic resins and tackifiers (98%) Production of OPEO (2%)	Confidential	Confidential	OP may be imported as residual OP content of tyres
Octylphenol ethoxylates (OPEO)	n.r.	1,000	2001	Emulsion polymerisation (52%) Textile and leather auxiliaries (14%) Agriculture (10%) Paints (5%) Production of octylphenol ether-sulfates (24%)	10.6	Paints, lacquers and varnishes Sealants and filling agents, joint-less floors. The majority of the consumption is confidential	-
Dodecylphenols	10,000-100,000	50,000	2004	Oil and lubricant additives (99%) Production of phenol/formaldehyde resins Production of dodecylphenol ethoxylates	4.0	Lubricants and oils Fuel additives	The registered consumption is small considering the EU consumption, likely because the lubricant additives are produced in Denmark in limited amounts
Dodecylphenol ethoxylates	n.r.	<1000	2004	Anti-rust agents in lubricants	2.4	Lubricants and oils	

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
4-*tert*-butylphenol CAS No 98-54-4	Intermediate	27,351	2001	Production of phenolic resins (>1,000 t) Production of polycarbonates (>1,000 t) Production of epoxy resins (>1,000 t) Production of alcohols through hydrogenation (>1,000 t)	2.8	Paints, lacquers and varnishes Hardeners Adhesives Sealants and filling agents	The registered consumption small considering the EU consumption, probably because of low consumption as intermediate The main application areas are as components of hardeners in paints, lacquers and varnishes and for plastics Import of 3.4 tonnes of the substance on its own is probably for production of resins
2-*sec*-butylphenol CAS No 89-72-5	1,00o-10,000	1,00o-10,000	2011	Production of fungicides and other plant protection products	0	-	-
o-*tert* butylphenol CAS No 68610-06-0	n.r.	<1000	2011	Production of herbicides, plastic additives, and substances for the fragrance industry.	o	-	-
2-*tert*-butylphenol CAS No 88-18-6	n.r.	n.i.	-	-	0.2	Fuels additives	-
Other butylphenols 28805-86-9	n.r.	n.i.	-	-	confidential	confidential	-

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
Cyclohexylphenols CAS No 119-42-6, 1131-60-8	n.r.	n.i.	-	-	0.4	Surface active agents	
bis(tert-butyl)dodecylphenol CAS No 68025-37-6	n.r.	n.i.	-	-	1.6	Lubricants	
Phenol, isopropylated CAS No 90480-88-9	intermediate use only	n.i. *1	-	Chemical intermediate	0		
Dialkylphenols and trialkylphenols							
2,6-di-*tert*-butyl-*p*-cresol (BHT) CAS No 128-37-0	10,000-100,000	25,000	2002	Antioxidant for many applications in a wide variety of industries	118.8	Antioxidants, antiozonanes, and "other additives for food and feedstuff" Raw materials for synthesis Inks Various products	The substance is used as an antioxidant for a wide range of products and the total consumption is likely higher than registered
2,6-di-*tert*-butylphenol CAS No 128-39-2	100-1,000	15,000	1999	Fuel and lubricant additive Intermediates for the production of plastic additives (antioxidants and UV-light stabilizers)	18.3	Lubricants and oils Fuel additives Confidential	The registered consumption is small considering the EU consumption, likely because the lubricant additives are produced in Denmark in limited amounts
2,4-di-*tert*-butylphenol CAS No 96-76-4	100-1,000	13,000	1999	Fuel and lubricant additive Intermediates for the production of plastic additives (antioxidants and UV-light stabilizers)	0.2	Lubricants and oils Fuel additives	

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
2,4,6 tris-*tert* butylphenol CAS no 732-26-3	intermediate use only	<1000 t	2011	Chemical intermediate	0.6	Confidential	
Thymol CAS No 89-83-8	1,000 - 10,000	n.i.		Cleaning agents Use of scented articles	<0.01	Perfumes, fragrances, various products	Probably used in various products not registered in the Product Register
6-*tert*-butyl-2,4-xylenol 1879-09-0	n.r.	n.i.	-	-	0.02	Confidential	-
2,6-di-*tert*-butyl-4-nonylphenol 4306-88-1	n.r.	n.i.	-	-	0.2	Lubricants	-
4-*tert* amylphenol CAS No 80-46-6	n.r.	<1,000	2011	Production of phenolic resins and lacquers	0	-	-
o-*tert* amylphenol CAS No 3279-27-4	n.r.	<1,000	2011	Production of herbicides, plastic additives, or - after hydrogenation - for the fragrance industry	0	-	-
2-isopropylphenol CAS No 88-69-7	n.r.	>1,000	2011		0	-	-
2,4-dinonylphenol CAS No 137-99-5	n.r.	<1,000	2011	Production of polycarbonates and phenolic resins and lacquers	0	-	-

Substance group	Registered tonnage, t/y	EU			Denmark		
		Most recent assessments		Main application areas	Registered consumption in the Product Register, 2011 data, t/y (excl. confidential uses)	Main application areas (excl. confidential uses only)	Remark
		Total consumption, t/y	Year				
2,4-di-*tert* amylphenol CAS No 120-95-6	n.r.	<1,000	2011	Plastic additives	0	-	
2-*tert*-butyl-*p*-cresol CAS No 2409-55-4	intermediate use only	n.i.		Chemical intermediate	<0.01	confidential	-
6-*tert*-butyl-*m*-cresol CAS No 88-60-8	intermediate use only	n.i.		Chemical intermediate	0	-	-
C14-16-18 alkylphenol CAS No 931-468-2	intermediate use only	n.i.		Chemical intermediate	0	-	-

n.i.: No information besides the information from registrations (ECHA, 2012e) has been available.

n.r.: Not registered

4. Waste management

The main issue regarding AP/APEO in the waste steam concerns releases of the substances from waste water treatment and disposal of sludge on agricultural land.

4.1 Waste from manufacture and industrial use of AP/APEO

Discharges of AP/APEO with waste water is the main waste issue with regard to the manufacture and industrial use of AP/APEO. No overview of AP/APEO in waste waster from industrial sources has been identified, but the risk assessments and risk reduction strategies include some data on releases of some of the substances from industrial processes.

The total releases of NP in 1977 to surface water and waste water from manufacturing and formulation of NP and NPEO was estimated at 0.3 t/y NP and 1.1 t/y NPEO, accounting for a small part of the total releases of the substances (ECB, 2002). The releases will today be lower due to the decrease in the manufacture of NP and NPEO.

The UK risk reduction strategy for 4-*tert*-OP indicates the total discharges from industrial sources in the UK in 2005 at 0.4 t/y of 4-*tert*-OP and 7.9 t/y of OPEO (Nwaogu, 2006). No data on discharges at EU level are provided. The discharges from industrial sources are not compared to other sources.

For 4-*tert*-BP the total releases to WWTP and surface water from manufacturing of the substances in 2001 is estimated at 310 g/day while the total releases from down stream industrial uses is about 400 g/day (ECB, 2008), corresponding to total discharges of about 0.3 t/y. The discharges from industrial sources are not compared to other sources.

The risk reduction strategy for DP indicates that the releases of DP from manufacture and formulation is a few kg/year and very small compared to the releases from the use and disposal phases. (Brooke *et al.*, 2007)

4.2 AP/APEO in waste and releases from disposal of solid waste

The substance flow analyses for NP/NPEO and OP/OPEO shown in Annex 4, prepared as part of the COHIBA project (COHIBA, 2012), show that the quantities released from solid waste treatment and recycling are very small compared to the quantities released from municipal waste water treatment plants.

AP/APEO in solid waste would mainly be due to:

- AP/APEO in articles, either from intentional use of the substances or as residual content of plastic parts made from AP.
- AP/APOE on paints, sealants and adhesives on building materials or metal scrap.

Apart from the OP, the majority of the articles containing AP/APEO would be disposed of to municipal solid waste incinerators (MSWI) in Denmark. No data on the fate of AP/APEO by incineration have been identified, but most probably the substances would be nearly 100% destroyed by the incineration process, based on similarities with other non-persistent substances.

A significant quantity of OP is present as residuals in tyres, and would be disposed of with the tyres for recycling in Denmark. The Environment Agency (2005a) reviews various studies on releases from tyres used for civil engineering (e.g. bulk fill application, noise barriers, artificial reefs, etc.). The assessment concludes that overall, the picture appears to be that 4-t-OP may be leached from tyre materials in civil engineering uses. Where tyres are used whole or baled, and especially where the use is underground or in seawater, the potential for losses appears to be low. There may be greater potential for losses in situations where shredded materials are used, but there is currently not enough information to make estimates of the potential for releases from this route. However, considering the relative concentrations measured in road runoff and in infiltration water, it is expected that the contribution from subsequent use in construction work will be lower than that from tyre wear during their original lifetime (the latter is estimated to be 83 tonnes 4-t-OP per year in the UK).

According to Environment Agency (2005a), by the use of OP in printing inks, the ink production process actually involves some reaction between the components. Hence there are no significant traces of 4-*tert*-octylphenol left in the finished inks and no significant releases from the printing process, or from the recycling of paper printed with these inks.

AP/APEO present on steel scrap and other metal scrap is assumed to be destroyed by the heating of the scrap by the melting down of the scrap.

AP/APEO may be present in small quantities in paint on building waste which is disposed of for use in civil engineering or disposed of to landfill.

4.3 Waste oil disposal

Waste oil which is not disposed of properly has been identified as the main source of environmental emission of dodecylphenols (DP) in Norway (Lambert, 2010). As a worst case scenario it was estimated that 3.8 t/y of DP in Norway have an unknown fate and was potentially released directly to the environment (Lambert, 2010). The estimate is based on a worst case total import of DP in lubricants of 25 y/y.

The UK risk evaluation report for DP (Brooke *et al.*, 2007) estimates the total releases from the use and disposal stage of the use of DP in lubricants at 23.4 t/y to waste water, 3.35 t/y to surface water and 22.6 t/y to soil for the EU as a whole. It is not specified how the DP in the lubricants ends up in waste water and the environmental compartments, but it is in the assessment assumed that spillage and leakages to soil and surface water correspond to 1% of the total use of the substances for crankcase lubricants. Releases from the use and disposal phase for other applications of the DP are estimated to be low compared to the releases due to the use in lubricants.

In both the Norwegian and the UK study, the releases are assumed to be due to spill, leakages and waste oils not disposed of properly.

Releases to the environment from use and disposal may also occur for other APs used as fuel additives but no data have been identified.

No data on the potential releases of APs from spill and disposal of waste oils in Denmark have been indentified.

4.4 AP/APEO in waste water and sewage sludge

A wealth of literature on the fate of NP and NPEO in municipal waste water treatment plants (MWWTP) exists, whereas literature on other AP/APEO is limited, reflecting that NP/NPEO are the dominant AP/APEO in waste water.

NP and NPEO in waste water

Nonylphenol ethoxylates reach sewage treatment works in substantial quantities where they biodegrade into several by-products including nonylphenol.

The trends in discharges of NP and NPEO from MWWTP over the period 2000 to 2010 are shown in Table 21. The concentration of NPs in outlets from MWWTP measured in 2010 was lower than previous years for which data are available. According to the authors it is on basis of the data not possible to determine if the decrease is significant (Boutrup and Svendsen, 2012).

TABLE 21
TRENDS IN CONCENTRATIONS OF NP AND NPEO IN OUTLETS FROM MWWTP 2000-2010 (BOUTRUP AND SVENDSEN, 2012)

Year	Nonylphenols			NP1EO			NP2EO		
	Mean µg/L	95% ft µg/L	% above d.l.	Mean µg/L	95% ft µg/L	% above d.l.	Mean µg/L	95% ft µg/L	% above d.l.
2000	0.24	0.57	58	0.08	0.18	11	0.12	0.35	11
2001	0.35	0.68	65	0.66	1.71	14	0.55	1.40	15
2002	0.43	1.60	70	0.52	1.44	13	0.54	1.40	9.8
2003	0.30	0.60	32	0.07	0.20	7.9	0.05	0.10	5.4
2010	0.06	0.30	17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Ft: Fractiles; d.l.: detection limit; n.d.: not detected.

The fate of NP and NPEO in MWWTPs in Denmark was analysed by Pedersen and Bøvadt (2002). The long chained NPEO, $NPEO_n$, was degraded to short-chained substances and NP under both aerobic (with oxygen present) and anaerobic (without oxygen) conditions. In one plant, $NPEO_n$ accounted for 31% of the inflow, whereas in the other it accounted for 11%. In both plants the $NPEO_n$ was nearly 100% degraded and accounted for 0 and 2%, respectively, in the sludge from the two plants. The degradation was most pronounced under aerobic conditions. Under anaerobic conditions the substances were mainly degraded to mono-NPEO (NP1EO) and NP. These degradation patterns have been demonstrated in many MWWTP across Europe (Soares *et al.*, 2008).

The Danish national surveillance programme for the aquatic environment (formerly NOVA 2003, now NOVANA) has included monitoring of trace elements and organic xenobiotics in discharges from sewage treatment plants (STPs) and other point sources since 1998. With the objective of enabling the use of the resulting information in the planning of future surveillance programmes and for assessment of the total amount of substances discharged from Danish sewage treatment plants, the point source data on metals and xenobiotics for the period 1998-2009 were analysed (Kjølholt *et al.*, 2011). Based on about 327 samples for the NPEOs and 62 samples for NP, "Nation Mean Concentrations" (NMCs) for substance concentrations in inlets and outlets from STPs were derived (see Table 22). Furthermore, possible correlations with relevant variables were identified. On the basis of the mean concentrations, the total discharge in 2010 was estimated at 41 kg for nonylphenol monoethoxylates and 120 kg for nonylphenol, while the discharge of nonylphenol diethoxylates could not be estimated as the measured concentrations in outlets were below the detection level. Considering the reduction factors, the total inlet to the waste water treatment plants can be estimated at 1.6 t/y for NP and 2.1 t/y for nonylphenol monoethoxylates. The study did not establish mean concentration of the substances in sludge from the waste water treatment.

The study did not establish national mean concentrations of NPEO with longer chain lengths, $NPEO_n$, which may account for a significant part of inflow as demonstrated by Pedersen and Bøvadt (2002).

The total discharge of nonylphenol from municipal sewage treatment plants in 1998-2003 was estimated as slightly higher at 228 kg/y based on an average concentration of 0.3 µg/L (Boutrup *et al.*, 2006).

TABLE 22
NATION MEAN CONCENTRATIONS OF NP AND NPEO IN INLET AND OUTLETS OF MUNICIPAL SEWAGE TREATMENT PLANTS IN DENMARK (KJØLHOLT *ET AL.*, 2011)

Substance	Inlet, µg/L *1	Outlet µg/L	Reduction factor, %	Discharge, kg/year
Nonylphenol monoethoxylates	2.9 (2.2 - 4.2)	0.057 (0 - 0.13)	98.03	41
Nonylphenol diethoxylates	0.67 (0.31 - 0.98)	0 (0-0.10)	not indicated	not indicated
Nonylphenols	2.2	0.2375	89.20	170

*1 Figures in brackets represent 65%-85% fractiles. Please note that the key national mean concentration, which represents the average, typically is close to the 75% fractile.

In accordance with the Danish experience, COHIBA (2011a) states that the removal efficiencies for NPEO from the water phase in WWTP is higher than 95%.

According to the COHIBA substance flow analysis for NP/NPEO, the NP and NPEO emissions into the Baltic environment mainly come from industrial sources in Lithuania and Poland, whereas in the other countries municipal waste water treatment plants (MWWTPs) are the dominant sources (COHIBA, 2012) . The upstream sources of NP and NPEO to the MWWTPs are mainly in the products' service life category and are dominated by emissions from washing of textiles containing NPEO (about 40% of total emissions to wastewater). This is followed by the use of NPEO in industrial and institutional cleaning (about 15-30% of total emissions to wastewater depending on the scenario), which was not expected to be a significant source at present as the use of NP and NPEO in this application is restricted under REACH (Regulation (EC) No 1907/2006). Other important sources of emissions to wastewater were car washes and emissions due to private use of detergents.

A recent Danish report estimates that washing of textiles may contribute 86% of the total sources of NPEO to MWWTPs (Rasmussen *et al.*, in press). Imported textiles as sources of NP/NPEO to waste water are further described in section 3.3.2.

No actual data on the releases to waste water from the use of AP/APEO in paint have been identified. An OECD report on techniques for estimating releases from products includes a summary of emission factors for different NP/NPE uses in products (OECD, 2011). For paint, an emission factor of 0.5% of the NP to waste water is indicated while the emission factor is 1% for adhesives. No emission factors for NPE from these products are indicated. The Resource Compendium makes reference to an unpublished Swedish case study, and does not provide details about how the emission factors are derived. If a factor of 0.5% is applied for the 20 tonnes NP used per year in Denmark (Table 12), the release to waste water from the application of paint can be estimated at 0.1 t/y which is low compared to the estimated NP equivalent content of imported textiles of 4.4 y/y (section 3.3.2). This should be considered a first very rough estimate, and a more detailed study would be necessary to quantify the actual sources of NP/NPEO to waste water in Denmark.

A range of measures for reduction of emission of NP/NPEO and OP/OPEO from waste water treatment plants are described in COHIBA (2011).

OP and OPEO in waste water
Measurement of OP and OPEO is included in the national environmental monitoring and assessment programme NOVANA, but data has not been published in recent years. In 2003 OP was detected in concentrations above the detection limit of 0.1 µg/L in 8% of 190 inlet samples and in 1% of 191 outlet samples. No median or average values were calculated. Compared to the concentration of NP/NPEO, the concentration of OP was at least a factor of 10 lower.

According to the COHIBA substance flow analysis for OP/OPEO, the emissions were dominated by releases of OP from the product service life category, where the main source was emissions from abrasion from tyres, which represents almost 100% of the reported emissions in this category (COHIBA, 20). The emissions from MWWTP accounted for a small percentage of the total emissions. The main source of OP and OPEO to MWWTP is washing of textiles, which is estimated to account for 30-50% of the total releases to waste water (COHIBA, 2012b).

The fate of octylphenol ethoxylates (OPEOs) by waste water treatment is described by the Environment Agency (2005a). Longer chained OPEO are degraded by the treatment of waste water by the same mechanisms as described for NPOs. From the available data for APEOs (predominantly for NPEOs), reasonable worst-case assumptions for the fate of OPEOs during anaerobic wastewater treatment are estimated to be (based on % weight): Mineralised/highly degraded (45 %), released as OP1EO/OP2EO/OPnEC (OP carboxylate with n ethoxy units) in effluent (25 %), released as OPnEO (n > 3) (8%), released as OP in effluent (2.5%) and OP in anaerobically digested sludge (19.5%). The study of OP in effluent from WWTP in the UK showed that concentration was measured at 0.5 µg/L.

A study of the flow of 4-t-OP (and other substances) in two MWWTP in Germany showed influent concentrations in the range of 0.0 39-1,4 µg/L while the measured effluent concentration < d.l.-0.39 µg/L. The elimination efficiency varied between 73% and 93% (Höhne and Püttmann, 2008). The maximum concentration for NP was about 10 times higher than the maximum for OP.

Other AP/APEO in waste water
No data on other AP/APEO in waste water and sewage sludge in Denmark have been obtained.

Remberger *et al.* (2005) have screened for the 30 phenolic substances in the environment, industrial sources and waste water and sewage sludge in Sweden. The concentration of the substances in the influents is typically a factor of ten higher than the concentration in effluents in accordance with the expected reduction factors. The concentration of NP/NPEO is a factor of ten to one hundred higher than the concentration of the other AP/APEO.

Relatively high concentrations are found for 2,6-di-*tert*-butyl-*p*-cresol (BHT), which has widespread use as an antioxidant in food and other products. It has been concluded by the OECD (2002a) that more information on actual releases and environmental exposure to this substance is needed.

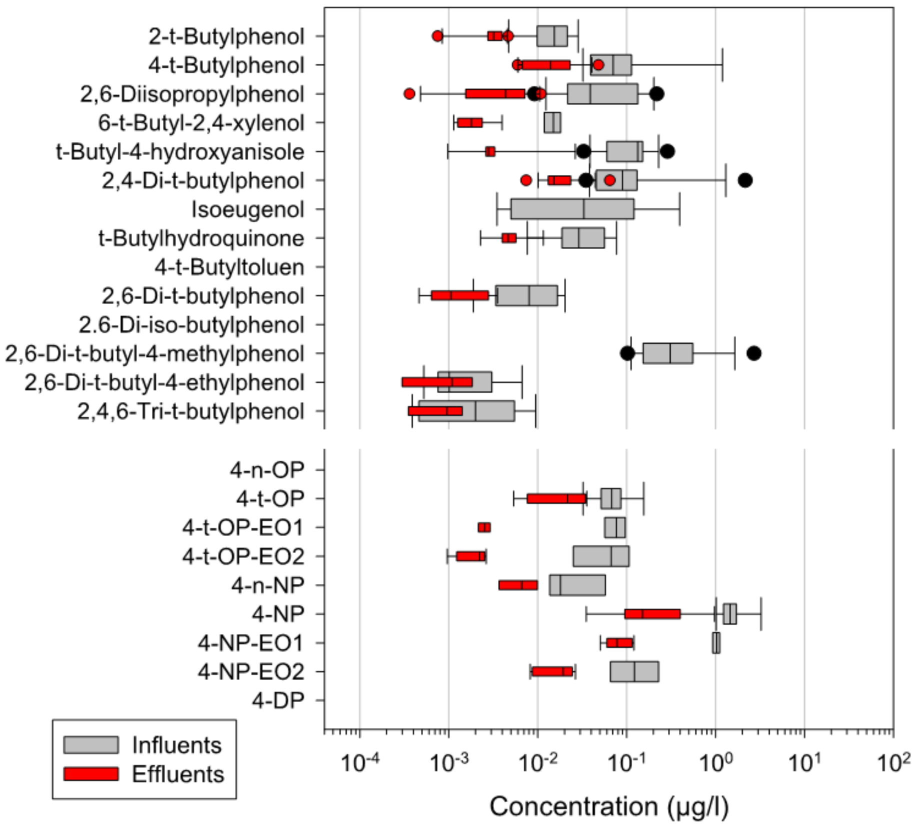


FIGURE 6
CONCENTRATION OF AP/APEOO IN INFLUENTS AND EFFLUENTS OF MWWTP IN SWEDEN. PLEASE NOTE LOGARITHMIC X-AXIS (BASED ON REMBERGER *ET AL.*, 2005, ORIGINAL FIGURE INCLUDE DATA ON METHYLPHENOLS)

No data on dodecylphenols in municipal waste water have been identified. A provisional UK environmental risk assessment of dodecylphenols estimated that the main source of releases to the environment was releases of DP to waste water from lubricant use and disposal (Brooke *et al.*, 2007).

AP/APEO in sludge from MWWTP

NP and NPEO

Gawlik and Bidoglio (2006) reviewed data on NP and NPEO in sewage sludge from a number of EU Member States reported during the period from 1994 to 2003. The concentrations varied considerably and different parameters were reported, which makes a comparison across the Member States difficult. Mean values (averages) of the total for NP+NPEO were reported from Sweden (2003) and Germany (2003) at 3.9 and 11.7 mg/kg while median values from Austria (2001) and Denmark (1997) were 13 and 8 mg/kg, respectively. Two surveys in Germany both reported a median value of 5 and 18 mg/kg in 2003, illustrating a relatively large variation in the concentrations.

The most recent assessment of NP/NPEO in Danish sewage sludge (Danish EPA, 2009) reports that the weighted average concentration decreased from 1997 to 2005 by approximately 80 percent from 27.2 mg/kg dw in 1997 to 7.8 mg/kg dw in 2005. This is, according to the assessment, in part due to the voluntary agreements made with industry in the late 1980s aimed at reducing the use of NPEO in products. In 2oo5 the average concentration of NPEO in all sludge was 7.8 mg/kg. In sludge disposed of to agricultural soils the concentration was 4.5 mg/kg. The total quantity of sludge in 2005 was 58,200 tonnes and the total NPEO content of the sludge is estimated at 0.45 tonnes.

The limit value for NP/NPEO in sludge applied to farmland in Denmark is 10 mg/kg TS. In 2005, 6.4% of all analysed sewage sludge samples exceeded the limit value for NP/NPEO.

A risk assessment of contaminants in sewage sludge applied to Norwegian soils by the Norwegian Scientific Committee for Food Safety reached the conclusion that even though the PEC (predicted effective concentration) exceeded the PNEC (predicted no effect concentration) for OP and NP immediately after the application, the committee considers OP and NP to be of low concern (VKM, 2009). The explanation is that these substances are rapidly degradable ($t_{1/2}$ in soil = 8-10 days) where the highest concentrations were found immediately after application of sewage sludge followed by a rapid decrease.

Other AP/APEO

The average concentration of OP in 45 samples of sewage sludge from Danish MWWTP analysed in 2003 was 0.049 mg/kg, less than 1% of the concentration of NP. The maximum value was 0.4 mg/kg (Danish EPA, 2004). No data for other AP/APEO in sewage sludge from Denmark have been obtained.

Data from the screening of AP/APEO in sewage sludge in Sweden is shown in the figure below. The concentration of NP and NPEO is two orders of magnitude higher than the concentration of the other substances. The relatively high concentrations found for 2,6-di-*tert*-butyl-*p*-cresol in influent shown in Figure 6 is not reflected in high concentrations in sludge, probably because the substance is degraded during the waste water treatment.

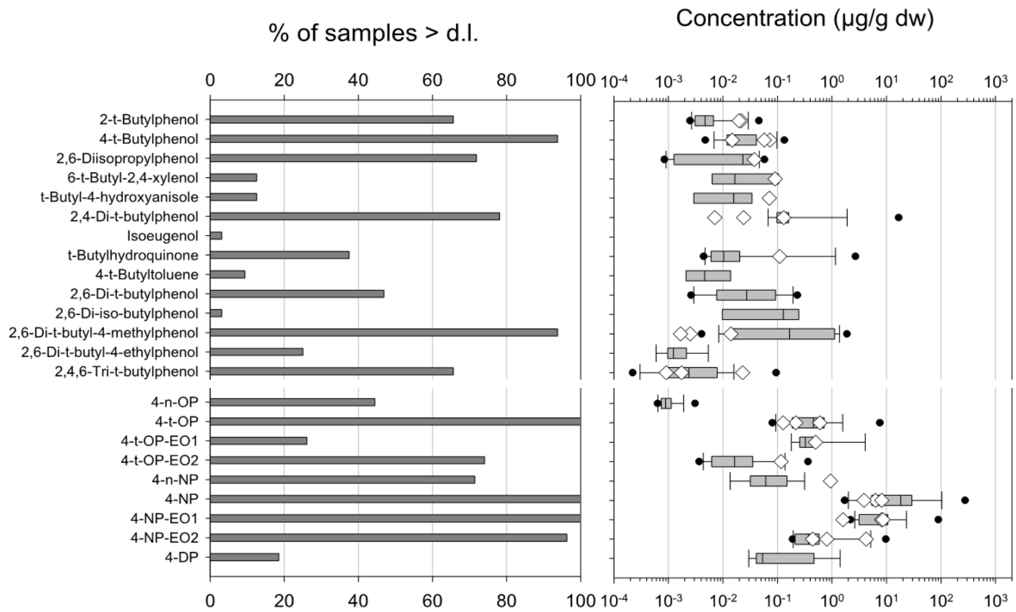


FIGURE 7

CONCENTRATION OF AP/APEO IN SEWAGE SLUDGE FROM MWWTP IN SWEDEN. PLEASE NOTE LOGARITHMIC X-AXIS (BASED ON REMBERGER *ET AL.*, 2005, ORIGINAL FIGURE INCLUDE DATA ON METHYLPHENOLS)

4.5 Summary for waste management

The main issues with regard to management of waste and waste water containing AP/APEO is discharges from municipal waste water treatment plants. Most available data are on NP/NPEO and OP/OPEO.

The concentration of NP/NPEO in waste water in Sweden was around 2005 a factor of ten to one hundred higher than the concentration of the other AP/APEO. In Denmark the concentration of NP has decreased and the concentration in 2010 was at 25% of the level in 2000. No data on the trends of NPEO have been available. The major source of NP/NPEO to municipal waste water today is considered to be imported textiles and a recent Danish report estimates that washing of textiles may contribute 86% of the total sources of NPEO to municipal waste water treatment plants. Even the reduction factor in the waste water treatment plants is about 90-95%, effluents from waste water treatment plants are considered the dominant sources of NP/NPEO to the Baltic Sea. The limit value for NP/NPEO in sludge applied to farmland in Denmark is 10 mg/kg TS.

The weighted average concentration of NP/NPEO in sludge decreased from 1997 to 2005 by approximately 80 %. In 2005, 6.4% of all analysed sewage sludge samples exceeded the limit value for NP/NPEO. No newer data have been available.

The concentration of OP/OPEO is considerably lower that the concentration of NP/NPEO and discharges from waste water plants are estimated to be a small source of releases to the Baltic Sea as compared to the releases of OP from tyres. The concentration of OP/OPEO in sewage sludge is more than a factor of 10 lower than the concentration af NP/NPEO.

In a Swedish study relatively high concentrations of 2,6-di-*tert*-butyl-*p*-cresol were found in waste water. The substance has widespread use as an antioxidant in food and other products. It has been concluded by the OECD (2002a) that more information on actual releases and environmental exposure to this substance is needed.

Apart from OP in tyres, the majority of AP/APEO in solid waste is disposed of through municipal solid waste incineration. No data on the fate of AP/APEO by incineration have been identified, but most probably the substances would be nearly 100% destroyed by the incineration process.

OP residues in tyres may be released from the tyres by disposal of the tyres depending on the actual disposal operations. A UK assessment indicated that releases may in particular occur when shredded tyres are used for civil engineering work. However, considering the relative concentrations measured in road runoff and in infiltration water, it is expected that the contribution from waste disposal work will be lower than that from tyre wear during their original lifetime.

For a number of the APs the main application area is as additives to lubricants. A Norwegian and a UK study conclude that the main releases of dodecylphenol (DP) to waste water and the environment are due to spill and leakages of lubricants and waste oils not disposed of properly. It may be the situation for some of the other APs as well, but no data on the potential releases of other APs from spill and disposal of waste oils have been indentified.

5. Environmental effects and fate

As described in previous chapters, alkylphenols are a group of chemicals comprising a substantial number of substances ranging from cresol (C1-alkylphenol) to phenols with up to four linear or branched constituent groups of varying chain lengths. However, the ethoxylated versions of alkylphenols of any commercial significance (detergents, emulsifiers) are in reality limited to C8-, C9- and C12-compounds with a few C4- C7-compounds being possible future substitutes for some of the long-chain alkylphenols.

C1-, C2- and C3-alkylphenols are, contrary to the long chain alkylphenols, typically ready biodegradable and only moderately toxic in the environment, as e.g. reflected by their lack of environmental classification by notifiers (see Annex 3). They are also different from the long-chain alkylphenols with regard to other properties and their technical uses; therefore, they are not included in the following environmental review. The emphasis of the review will be on the important C8-, C9- and C12-alkylphenols and their ethoxylates together with examples of possible technical alternatives among the C4-to C7-alkylphenols.

5.1.1 Nonylphenol and nonylphenol ethoxylates

Fate in the environment

Abiotic degradation

Nonylphenol does not undergo hydrolysis to any appreciable extent while phototransformation in water may occur to some extent under favourable conditions (DT_{50} = 10-15 hours under lab conditions). This mechanism is, however, considered to be of minor quantitative importance only for the overall dissipation of the substance in the aquatic environment (ECHA, 2012b).

Photodegradation in the atmospheric compartment is an important mechanism of degradation in air. The atmospheric half-life of nonylphenol is estimated to be 0.3 days (EHCA, 2012b).

Biodegradation

Nonylphenols are biodegradable in the environment at rates that vary with the degree of branching; the higher the branching, the lower the biodegradability. A screening study on n-nonylphenol indicates that this substance may even be easily biodegradable[2] in water under aerobic conditions whereas the branched nonylphenols may only be considered inherently[3] biodegradable. The degradability under anaerobic conditions is low. The standard TGD value for biodegradation of inherently degradable substances in surface waters corresponds to 150 days. This is consistent with reported measured values (ECB, 2002).

Nonylphenol ethoxylates are degraded to nonylphenol in the environment according to the overall reaction pathway shown in Figure 8.

[2] I.e. undergo significant degradation within 28-days in one of OECD's screening test methods for ready biodegradability.
[3] Undergo less but still some degradation in a 28-days OECD test.

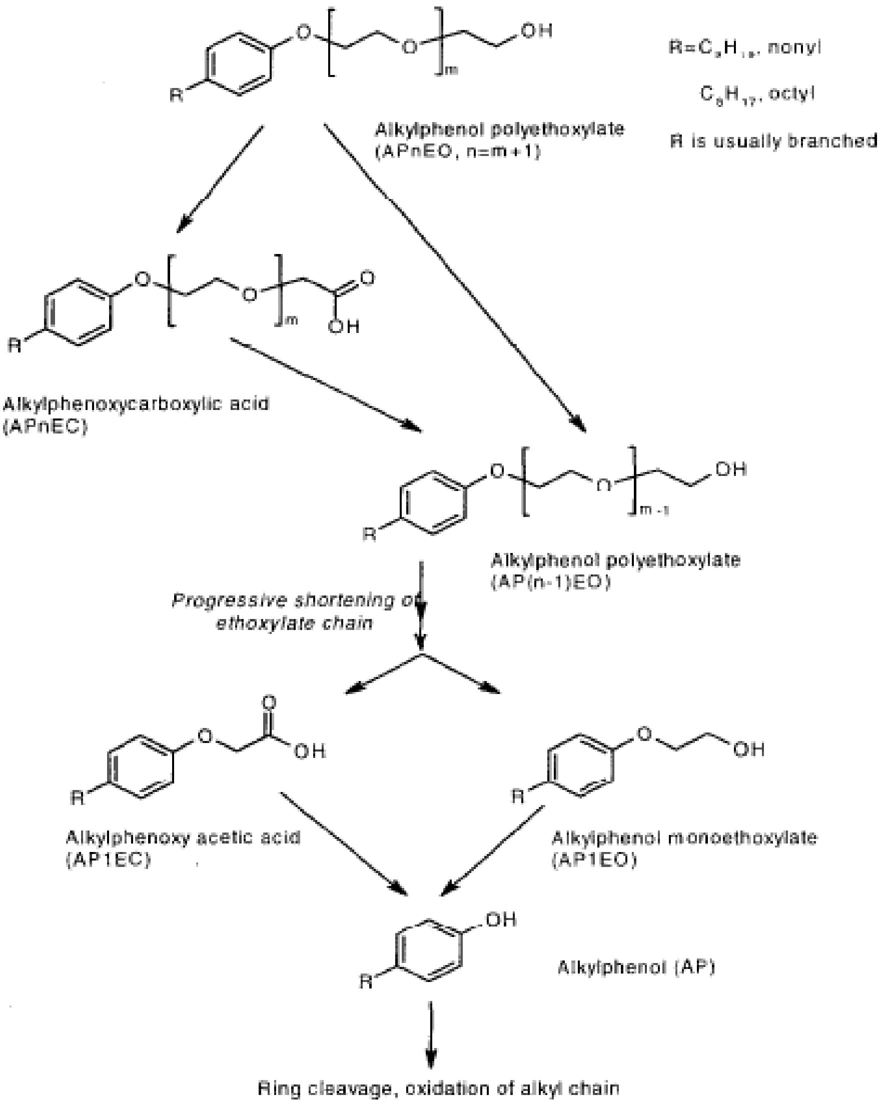


FIGURE 8
DEGRADATION PATHWAY FOR ETHOXYLATES OF NONYLPHENOL AND OTHER HIGHER ALKYLPHENOLS (UBA, 1998)

Dissipation rate in soils depends on soil properties, environmental conditions and on the degree of branching of the nonylphenol studied. Most studies only report on the dissipation of the parent compound, not on the subsequent degradation eventually leading to full mineralization. The primary degradation step typically takes place with a half-life of 20-30 days and the results of one study indicate that full mineralization of n-nonylphenol could take place with a half-life of about 100 days. However, branched nonylphenols probably degrade more slowly and, for the EU risk assessment, a half-life of 300 days (TGD for inherently degradable substances with Kp >100 [4]) is recommended (ECB, 2002).

Adsorption, distribution and bioconcentration

The Log Kow[5] is 5.76 for linear 4-nonylphenol and 5.4 for branched 4-nonylphenol (ECHA, 2012b). The E1-E4 ethoxylates of nonylphenol have somewhat lower Log K_{ow} values (4.17 - 4.30, decreasing with increasing number of ethoxylate units) (Ying *et al.*, 2002).

[4] A standard measure of the partitioning between particulate matter (e.g. soil or sediment) and water.
[5] A standard measure of the partitioning between a lipid phase (octanol) and water (octanol-water partitioning constant)

The Kp in soils is in the range >100 - <1,000 and Log K_{ow} values are in the range 4.35 - 5.69 (ECB, 2002).

The distribution in environmental compartments is as shown in the table below applying a MacKay Level III fugacity model, a model predicting the distribution of a substance between the various main environmental compartments (ECB, 2012b).

TABLE 23
PREDICTED DISTRIBUTION OF NONYLPHENOL IN THE ENVIRONMENT (ECB, 2012b)

	Value (percent)*
Fraction to air	0.26
Fraction to water	12.2
Fraction to soil	66.0
Fraction to sediment	21.5

* EPI suite v4.10, standalone version.

The available data suggest that nonylphenol bioconcentrates in aquatic organisms and values up to BCF = 1,300 in fish (on a fresh weight basis) have been reported. The EU RAR mentions that more reliable measured values with a mean of 741 have been reported. The EU RAR recommends, however, to use a calculated BCF of 1,280 (fish) for the aquatic risk assessment (ECB, 2002).

Environmental effects
Nonylphenol is classified as R50-53 or, according to CLP, Aquatic Acute 1 + Aquatic Chronic 1.

The EU's RAR on nonylphenols (ECB, 2002) summarizes the traditional endpoints for aquatic species as shown in

Table 24. It appears from the data that nonylphenols are highly toxic to all three main "standard" groups of aquatic organisms; fish, invertebrates and algae.

The most sensitive species in acute studies appear to be the freshwater invertebrate *Hyalelle azteca* (EC_{50} (96 h) = 20.7 µg/L) while the most sensitive species in long-term studies is the green freshwater alga *Scenedesmus subspicata* (EC_{10} = 3.3 µg/L).

The $PNEC_{water}$ is calculated to be 0.33 µg/L using an assessment factor of 10. Based on the aquatic toxicity data a PNEC for sediment = 0.039 mg/kg sediment has been calculated by the equilibrium partitioning method.

A $PNEC_{soil}$ = 0.3 mg/kg soil wet wt was determined based on reproduction effect data for earthworms (EC_{10} = 3.44 mg/kg soil wet wt) and applying an assessment factor of 10.

The most sensitive soil dwelling species is the earthworm *Apporrectodea caliginosa* with a 21 day EC_{10} ("NOEC") for reproduction = 3.44 mg/kg soil. $PNEC_{soil}$ is calculated to be 0.3mg/kg (ECB, 2002).

No experimental data are available on avian species but a $PNEC_{oral}$ = 10 mg/kg food has been calculated based on a mammalian NOAEL = 15 mg/kg bw for reproductive effects (ECB, 2002).

It is widely accepted today that nonylphenol is an endocrine disruptor. Several tests, *in vitro* as well as *in vivo*, have demonstrated the estrogenic potency of nonylphenol. Especially the estrogenic effect in fish is well documented through tests on a number of standard species in which clearly endocrine mediated effects start at concentrations between 1.05 µg/L and 15 µg/L.

There are indications of endocrine (estrogen-like) effects also on anuran amphibians and aquatic invertebrates including molluscs too but the evidence is less clear and ECHA's Annex VX Dossier for nonylphenol does not reach a clear conclusion on this (ECHA, 2012b).

The relative estrogenic potency of nonylphenol compared to the natural estrogen 17β-estradiol is low in *in vitro* studies but in *in vivo* studies with fish relative potencies of 0.019 (sheepshead minnow) and 0.050 (medaka) have been reported (Soares *et al.*, 2008).

Nonylphenol ethoxylates

Nonylphenol ethoxylates have traditionally been the major source of nonylphenol in the aquatic environment due to their widespread uses as detergents and emulsifiers. Their specific, individual properties depend on the length of the ethoxy chain but they all degrade to nonylphenol by successive de-ethoxylation (e.g. in wastewater and sewage treatment plants) until nonylphenol is formed as the, more persistent and potentially bioaccumulative, end product.

Data on the environmental toxicity of nonylphenol ethoxylates are relatively sparse. However, Warhurst (1995) provides an environmental review of alkylphenol ethoxylates and alkylphenols in which he presents data showing that alkylphenols (most data are on nonylphenol) are generally more than 10 times more acutely toxic to aquatic organisms than the corresponding ethoxylated compounds ($LC_{50's}$ typically 0.1 mg/L for alkylphenols and 1.5 mg/L for the corresponding ethoxylates).

TABLE 24
SUMMARY OF AQUATIC TOXICITY OF NONYLPHENOL (ECB, 2002)

Trophic level	Species	End point	Concentration (mg/l)	Reference *1	Validity
Freshwater fish	Fathead minnow	96hr LC_{50}	0.128	Brooke (1993a)	Valid
	Pimephales promelas	33 day $NOEC_{survival}$	0.0074	Ward and Boeri (1991b)	Valid
Saltwater fish	*Sheepshead minnow Cyprinodon variegatus*	96hr LC_{50}	0.31	Ward and Boeri (1990d)	Valid
Freshwater invertebrates	*Ceriodaphnia dubia*	96hr EC_{50}	0.069	England (1995)	Valid
		7 day $NOEC_{reproduction}$	0.0887		Valid
	Daphnia magna	48hr EC_{50}	0.085	Brooke (1993a)	Valid
		21 day $NOEC_{surviving\ offspring}$	0.024	Comber *et al.* (1993)	Valid
	Hyalella azteca	96hr EC_{50}	0.0207	Brooke *et al.* (1993)	Valid
Saltwater invertebrates	*Mysidopsis bahia*	96hr LC_{50}	0.043	Ward and Boeri (1990c)	Valid
		28 day $NOEC_{length}$	0.0039	Ward and Boeri (1991c)	Valid
Fresh water algae	*Selenastrum capricornutum*	96hr $EC_{50(Cell\ growth)}$	0.41	Ward and Boeri (1990b)	Valid
	Scenedesmus subspicatus	72hr EC_{50} (Biomass) 72hr EC_{10} (Biomass) 72hr EC_{50} (Growth rate) 72hr EC_{10} (Growth rate)	0.0563 0.0033 0.323 0.0251	Kopf (1997)	Valid
Saltwater algae	*Skeletonema costatum*	96hr EC_{50} (Cell growth)	0.027	Kopf (1997)	Valid
Mesocosm study		20 day NOEC 20 day LOEC	0.005 0.023	Liber *et al.* (1999)	Use with care

*1 See ECB (2002) for fulle reference

5.1.2 Octylphenol and octylphenol ethoxylates

Much less scientific environmental literature exist on octylphenols (and -ethoxylates) than on nonylphenol (and -ethoxylates). However, octylphenol (most often as the branched 4-*tert*-octylphenol) is chemically closely related to (branched) nonylphenol. Therefore with regard to environmentally relevant properties, there are also similarities. Hence, in the absence of specific studies on octylphenol the corresponding studies on nonylphenol can be used to fill the data gaps and be used for environmental risk assessment of octylphenol without introducing too much uncertainty (effect levels typically within a factor of 3 (Environment Agency, 2005a).

Fate in the environment

Abiotic degradation

Similar to nonylphenol, octylphenol is not expected to be degradable by hydrolysis, while dissipation in surface water with a half-life of about 14 hours under favourable conditions has been reported. However, as for nonylphenol, photolysis in water is considered only to be of minor quantitative importance for the overall dissipation of the substance in the aquatic environment (Environment Agency, 2005a).

Photodegradation in air is an important removal mechanism for octylphenols released to the atmospheric compartment. The estimated half-life for the reaction of hydroxyl radicals with 4-*tert*-

octylphenol is 0.25 days, which is so fast that the substance will most likely not be transported far from its emission sources before being degraded (Environment Agency, 2005a).

ECHA (2012d) reports on the photodegradation of 4-*tert*-octylphenol ethoxylates that the transformation rate increases with the length of the ethoxy-chain; therefore e.g. OP_2EO has a half-life in air of 7.2 hours while the half-life of $OP_{10}EO$ is only 2.3 hours.

Biodegradation

Screening tests for ready biodegradability in water have given varying results ranging from one test where 62 % was degraded in 28 days (i.e. fulfilled the 60 % ThOD pass level but failed the 10 day window) to test where virtually no material was fully mineralized after 28 days. In summary, 4-*tert*-octylphenol is not readily biodegradable but there are indications of some degree of biodegradation, in particular following a period of adaptation. In simulation tests ,octylphenol shows a small potential for biodegradation in aerobic conditions whereas practically no dissipation was observed under anaerobic conditions (DT_{50} >83 days in sediment) (ECHA, 2012c). The British Environment Agency (2005a) describes 4-*tert*-octylphenol as inherently biodegradable.

No data on the degradation/dissipation of octylphenols in soil have been obtained (Environment Agency, 2005a).

The corresponding ethoxylates are not readily biodegradable either. Primary degradation of the higher ethoxylates will take place, especially if the inoculums are adapted, but apparently stable metabolites are formed and full mineralization cannot be expected in sewage treatment plants. In surface waters, degradation will take place slowly with a primary degradation DT_{50} of several days. Similarly, de-ethoxylation leading to OP itself is slow in both sediment and soil (ECHA, 2012d).

Adsorption, distribution and bioconcentration

The log Kow for 4-*tert*-octylphenol has been reported as in between 3.7 and 4.12. Based on this, the K_{OC} is estimated as 1,376-2,740 L/kg. The E1-E4 ethoxylates of octylphenol have slightly lower log Kow values (4.10-3.90, decreasing with increasing number of ethoxylate units) (Ying *et al.*, 2002).

The environmental distribution of octylphenol is assessed using a Level III fugacity model, a model predicting the distribution of a substance between the various main environmental compartments (ECHA, 2012c) as shown in the table below.

TABLE 25

PREDICTED DISTRIBUTION OF OCTYLPHENOL IN THE MAIN ENVIRONMENTAL COMPARTMENTS AFTER ORIGINALLY BEING RELEASED TO EITHER AIR, WATER OR SOIL (ECHA, 2012C)

	Release to air	Release to water	Release to soil
Air	26.0 %	1.2 %	<0.1 %
Water	5.1 %	77.9 %	0.3 %
Soil	67.7 %	3.1 %	99.6 %
Sediment	1.2 %	17.8 %	0.1 %

Based on a Log Kow = 4.12, a worst-case BCF = 634 is calculated. Measured bioconcentration factors in a number of fish species are all lower than this, with the BCF = 471 in rainbow trout (*O. mykiss)* being the highest experimental value (ECHA, 2012c).

Environmental effects

4-*tert*-Octylphenol is classified R50-53 or Aquatic Acute 1 + Aquatic Chronic 1.

The most sensitive standard endpoints for aquatic species, among the studies considered reliable (with some reservations regarding salt water species), are shown in Table 26

TABLE 26
THE MOST SENSITIVE ACUTE AND CHRONIC ENDPOINTS FOR 4-*TERT*-OCTYLPHENOL TOWARDS FISH, INVERTEBRATES AND ALGAE (ENVIRONMENT AGENCY, 2005A)

Trophic level	Species	End point	Concentration (µg/L)
Freshwater fish	Fathead minnow (*Pimephales promelas*)	96-hour LC_{50}	290
	Rainbow trout (*Oncorhynchus* mykiss)	6-day LC_{50}	170
	Rainbow trout (*Oncorhynchus* mykiss)	60-day post-hatch early life stage NOEC	6.1
Freshwater invertebrates	Freshwater shrimp (*Gammarus pulex*)	96-hour EC_{50} (immobilisation)	13.3
	Water flea (*Daphnia magna*)	48-hour LC_{50}	270
		21-day NOEC (juvenile production by surviving adults)	62
Freshwater algea	*Scenedesmus subspicatus*	72-hour EC_{50} (growth rate)	1100 (use with care)
		72-hour EC_{50} (growth rate)	300 (use with care)

Based on the above data (in particular the lowest NOEC = 6.1 µg/L for rainbow trout, *O. mykiss*) and an assessment factor of 50, a $PNEC_{water}$ = 0.122 µg/L has been calculated.

A provisional $PNEC_{sediment}$ has been calculated to be 0.0074 mg /kg ww while a provisional $PNEC_{soil}$ based on the surface water effect value and equilibrium partitioning approach is 0.0059 mg /kg ww. However, the latter value deviates highly from the $PNEC_{soil}$ for nonylphenol = 0.3 mg/kg, which is based on experimental data and therefore needs careful consideration (Environment Agency, 2005a) as in most cases the experimental toxicities of octylphenol and nonylphenol are within a factor 3 of one another.

Like nonylphenol, octylphenol is commonly accepted to be an endocrine disruptor with estrogen-like effects (EU Cat 1, see section 7.1.1). In *in vitro* tests, the relative endocrine disruption potency of 4-*tert*-octylphenol compared to 17β-estradiol is 0.001 or lower for most parameters studied, but a few exceptions up to a relative potency of 0.01 compared to 17 natural estrogens (Environment Agency, 2005a). The lowest NOEC from a valid study assessing the endocrine disrupting effects in fish was 1.6 µg/L for vitellogenin induction in adult male rainbow trout, *O. mykiss*. Other species of fish are slightly less sensitive but most of them still have NOECs in the relatively low µg/L range. The lowest NOEC for endocrine effects in fish based on fully valid studies is, however, 12 µg/L (Environment Agency, 2005a).

The ethoxylates of 4-*tert*-octylphenol also show estrogenic activity in *in vitro* tests but with a lower potency than octylphenol itself (0.0088 compared to OP). Longer chain ethoxylates show only very weak estrogenic activity. Assessment of the *in vivo* activity is based on results for NPEO, generally showing about 10-fold lower activity of the short-chain ethoxylates compared to NP itself (ECHA 2012d).

5.1.3 AP/APEO of a chain length of less that eight

4-*tert*-butylphenol will be used to exemplify the environmental properties of AP/APEO with chain lengths from C4 to C7. This substance has been mentioned as a possible substitution candidate for nonylphenol in the production of phenolic resins (Environment Agency, 2005b).

Fate in the environment

4-*tert*-butylphenol is, like the long-chain alkylphenols, stable to hydrolysis and abiotic degradation in water is not considered a significant mechanism of degradation whereas in air phototransformation takes place with a half-life of 3.2 hours thus suggesting that this is a significant removal process in the atmospheric compartment (Environment Agency, 2005b). In the EU Risk Assessment of 4-*tert*-BP a half-life of 0.4 days or less is stated (ECB, 2008).

Conflicting results of aquatic degradation screening tests are available but the British Environment Agency (2005b) concludes that the substance should be characterized as readily biodegradable not fulfilling the 10 day window criterion. This implies using a half-life of 50 days in surface water and 90 days in soil for environmental risk assessment (ECB, 2008).

The Log Kow of 4-*tert*-BP is 3.29 leading to an estimated K_{OC} of 582. A QSAR estimation with Episuite gives a K_{OC} of 1912 (Environment Agency, 2005b).

TABLE 27
ENVIRONMENTAL DISTRIBUTION OF 4-*tert*-BP USING A MACKAY LEVEL III FUGACITY MODEL (ENVIRONMENT AGENCY, 2005B)

Compartment	Release 100% to air	Release 100% to water	Release 100% to soil
Air	39.7 %	0.2 %	0.0 %
Water	23.3 %	95.3 %	0.4 %
Soil	35.9 %	0.2 %	99.6 %
Sediment	1.1 %	4.4 %	0.0 %

A bioconcentration study with the fish *Leuciscus idus melanotus* gave a measured BCF of 120, which is comparable to estimated BCFs and is suggested to be used for risk assessment (Environment Agency 2005b).

Environmental effects

4-*tert*-butylphenol is less acutely toxic to fish than the long-chain alkylphenols. The lowest valid LC_{50} reported is 5.1 mg/L for *P. promelas* and *O. latipes*. The toxicity to invertebrates is very similar to a 48 hour EC_{50} =3.9 mg/L for *D. magna*. The EC_{50} to algae (*S. capricornutum*) was found to be 14 mg/L (ECB, 2008).

A valid long term NOEC (21 day reproduction study with *D. magna*) gave a NOEC = 0.73 mg/L while the NOEC in the study with the green alga *S. capricornutum* resulted in a NOEC = 0.32 mg/L. The latter is the most sensitive traditional endpoint reported and leads to a calculated $PNEC_{water}$ of 6.4 µg/L using an assessment factor of 50 (ECB, 2008). A $PNEC_{sediment}$ has not been derived.

PEC_{soil} is estimated to be 73 µg/kg ww based on the aquatic data (ECB, 2008).

In the table below, the toxicity of some of the short chain alkylphenols to *D. magna* (96 hour NOEC) is compared to the toxicity of the long chain alkylphenols OP and NP.

TABLE 28
COMPARISON OF TOXICITIES OF C4-C9 ALKYLPHENOLS TO *D.MAGNA*
SOURCE: ENVIRONMENT AGENCY, 2005B)

Substance	No effect concentration (mg/l)
4-*sec*-Butylphenol	9.7
4-*tert*-Butylphenol	8.6
4-*tert*-Pentylphenol	1.8
4-*tert*-Octylphenol	0.19
4-Nonylphenol	0.3
2,4-Di-*tert*-butylphenol	0.85

Overall, the general toxicity data indicate that aquatic organisms appear to be more sensitive to the longer chain alkylphenols than to the shorter chain alkylphenols.

4-*tert*-pentylphenol is another possible nonylphenol substitute for production of resins (Environment Agency, 2005b).

This substance appears to be somewhat more toxic to aquatic organisms than 4-*tert*-butylphenol with a lowest acute LC_{50} = 1.7 mg/L (*Crangon septemspinosa*) and a long term NOEC = 0.063 mg/L (Environment Agency, 2005b).

The Log Kow is 4.03, the BCF is 531, and the substance is not considered to be readily biodegradable. The atmospheric half-life is estimated at 3.1 hours.

Other short-chain APs

A detailed assessment of all short-chain APs is beyond the limits of this survey. One of the substances, 2,6-di-*tert*-butyl-*p*-cresol (BHT) is used in relatively high quantities as an antioxidant and found in relative large concentrations in waste water (section 4.4). For this reason BHT is briefly mentioned here. An OECD SIDS Initial Assessment Report for BHT (OECD, 2002a) concludes:” *In the environment, BHT is rapidly decomposed forming several, partly unidentified, metabolites. BHT is not readily biodegradable, a moderate to high bioaccumulation potential has to be assumed. The NOEC from the long-term toxicity to daphnids was 0.07 mg/l, resulting in a PNEC of 0.0014 mg/l. Therefore, the performance of an environmental risk assessment is recommended. Especially the questions concerning exposure, bioaccumulation as well as toxicity of the metabolites should be clarified*”. The substance is not among the substances proposed for priority in the Prioritisation of Alkylphenols for Environmental Risk Assessment from Environment Agency (2005b). A risk assessment of BHT has to the knowledge of the authors not been undertaken.

5.1.4 AP/APEO of a chain length of more than nine

The only commercially important substance group of a chain length of more than nine is the dodecylphenols. The following data originates from ECB's summary fact sheet (undated, PBT List No. 55).

Fate in the environment

Dodecyl phenol is classified R50-53 by the producers, and in its PBT-assessment No. 55, ECB considers it to meet the T criterion, likely to meet the P criterion but not meeting the B criterion, i.e. the substance is not a PBT (ECB, undated).

In a screening test, 10 % degradation was achieved over 56 days based on CO_2 production. The result indicates that dodecylphenol is neither readily nor inherently biodegradable.

The Log Kow of dodecylphenol is 7.17 and a valid bioconcentration study in fish gives a worst case steady state BCF = 823 (ECB, 2011).

Level III fugacity modelling predicts the environmental distribution of dodecylphenol shown in the following table.

TABLE 29
ENVIRONMENTAL DISTRIBUTION OF PARA-C_{12}-ALKYLPHENOLS (BROOKE *ET AL.*, 2007)

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

Environmental effects
Environment Agency (2007) reports a lowest acute (96 h) aquatic toxicity value (EC_{50}) of 17 µg/L for aquatic invertebrates and a 21 day NOEC (reproduction, invertebrates) = 2.0 µg/L.

ECB (2011) mentions that a valid 21 day reproduction study with *Daphnia magna* according to OECD (2011) gave a NOEC = 3.7 µg/L. In view of uncertainties over the actual exposure levels in the study, the results were re-calculated based on time-weighted means to give a NOEC = 2.0 µg/L .

A $PNEC_{water}$ = 0.04 µg/L has been calculated (Brooke *et al.*, 2007) and a $PNEC_{sediment}$ = 96 µg/kg wt estimated using the equilibrium partitioning approach and aquatic effect data.

Dodecylphenol is believed to exhibit endocrine (estrogenic) disrupting properties like nonylphenol and octylphenol; however reliable appropriate screening data are lacking (Brooke *et al.*, 2007).

5.2 Summary of environmental effects

The British Environment Agency (2005b) provides a comparative overview of the environmental fate and effects properties of some of the most relevant alkylphenols described in the preceding sections; see Table 30. Further, an overview of environmental classification of the various alkylphenols is provided in Chapter 9 (Table 44).

The data show that the short chain alkylphenols (C4, i.e. butylphenols) have a significantly lower potential for bioaccumulation than the long chain (C8-C12) alkylphenols, as demonstrated by their lower log Kow values and lower bioconcentration factors (BCF) in fish as well as their relatively high water solubilities. Further, they appear to be readily biodegradable (i.e. non persistent) thus posing a lower risk of accumulation in sediments and soil and of surface water mediated long range transport compared to the long chain compounds, which are, at best, inherently biodegradable.

Finally, the short-chain alkylphenols are less acutely toxic to aquatic organisms than the long chain correspondents. Branched chain alkylphenols tend to be more persistent and have higher log Kow/BCF than the linear alkyl chain homologues.

TABLE 30
COMPARATIVE OVERVIEW OF ENVIRONMENTAL FATE AND AQUATIC EFFECT PROPERTIES OF A NUMBER OF ALKYLPHENOLS (ENVIRONMENT AGENCY, 2005B)

		2-*tert*-Butyl-phenol	4-*tert*-Butyl-phenol	4-*tert*-Pentyl-phenol	4-*tert*-Octyl-phenol	Nonyl-phenol	Dodecyl-phenol (bran-ched)	2,4-Di-*tert*-butyl-phenol	2,6-Di-*tert*-butyl-phenol
Physicochemical properties									
Water solubility (mg/l)		700 (meas)	610 (meas)	37	19 (meas)	6 (meas)	1	12	4.11
Octanol-water partition coefficient (log Kow)		2.7-3.5	3.3	4.03	4.12	4.48	5.5	5.19	4.5
Persistence									
Biodegradation		Readily biodegradable	Readily biodegradable	Not readily biodegradable	Inherently biodegradable	Inherently biodegradable	Not readily biodegradable	Not readily biodegradable	Not readily biodegradable
Bioaccumulation									
Highest fish BCF value		188 (est)	120	531 (est)	634 (est)	1,280	9,440 (est)	~660 (est)	660
Toxicity									
Aquatic toxicity (mg/l)	Acute	2.4	3.4	1.7	0.013	0.085	0.093	1.8	0.076
	Chronic	0.042 (est)	0.73	0.063	0.006	0.025	No data available	0.008 (est)	0.019 (est)

With regard to the endocrine disrupting properties of alkylphenols and their ethoxylates, it has clearly been demonstrated in *in vivo* studies, in particular with fish, that the long chain alkylphenols have an endocrine effect potency to cause estrogen-like effects that is not negligible while the corresponding ethoxylates and the short chain alkylphenols appear only to be weakly estrogenic, if at all. No firm conclusion (e.g. in the form of EC criteria) as to the actual environmental significance of these findings has been reached as yet, but there is concern that the endocrine disrupting potency of the long chain alkylphenols in combination with their persistence and observed concentrations in the aquatic environment implies a risk of estrogen-like effects occurring as a result of organisms being exposed to alkylphenols, in particular nonylphenol and octylphenol. Nonylphenol and 4-*tert*-octylphenol are included on the EU list of suspected endocrine disrupting compounds in Cat 1 while 4-*tert*-butylphenol is a Cat 2 substance on that list. None of the other alkylphenols mentioned in Table 44 are currently on the list.

In December 2011, 4-*tert*-octylphenol was included on ECHA's list of SVHC while proposals for inclusion have been submitted also for the corresponding ethoxylates as well as for 4-nonylphenol and for dodecylphenol. None of the substances meet all the criteria to be classified either PBT or vPvB but are proposed as SVHC with reference to Article 57 (f) of the REACH Regulation, i.e. substances with an "equivalent level of concern having probable serious effects on the environment" due to EDC properties in combination with persistence and bioaccumulative properties not fulfilling the criteria specified in Annex XIII of the Regulation.

Most probably the short-chained APs, with the exception of 4-*tert*-BP and 4-*tert* amylphenol, would not be considered SVHC. For dodecylphenol, 4-*tert*-BP and 4-*tert* amylphenol, a closer assessment would be needed for a conclusion as to whether they may be considered SVHCs.

6. Human health effects

6.1 Introduction to human health effects of AP/APEO

As described in previous chapters, alkylphenols (AP) belong to a large and diverse group of related chemical substances with shorter or longer, branched or unbranched alkyl chains. Some alkylated phenols occur naturally in e.g. crude oil (Ioppolo-Armanios *et al.*, 1992) but the commercial products that are of importance are mostly complex mixtures of isomers or homologues. Commercial nonylphenol can, for example, consist of a variable mixture of about 20 isomers.

For some phenols with a short alkyl group, there may be specific and relevant human health data from occupational exposures available, but for non-tested commercial mixtures with unknown content, a health assessment may be difficult or impossible. However, all phenols should be considered hazardous substances.

The classification and labelling of a few alkylphenols (methyl phenols (cresols), dimethyl phenols (xylenols), *tert*-octyl phenol and nonyl phenols) are harmonized in the EU and more alkylphenols are self classified (see Annex 2). In general, alkylated phenols are acutely toxic or harmful, a characteristic which decreases with the length of the alkyl chain, and irritating to skin, eyes and mucous membranes. In addition, nonylphenol and other long-chain alkylphenols are endocrine disruptors and demonstrate reproductive toxicity.

The nonyl phenol ethoxylates (NPEO) are a group of commercially important derivatives, where the phenol group is substituted by polyethylene glycol. Only ethoxylates of nonyl-, octyl- and dodecyl phenols are commercially important. Because of the large polymeric size, such chemicals have reduced bioavailability. An ether group is much less reactive than a phenolic hydroxyl group; therefore, nonyl ethoxylates have lower toxicities, and such chemicals are not as corrosive as nonylphenol is but only mild skin irritants.

6.2 Nonylphenol and nonylphenol ethoxylates

As mentioned in previous chapters, nonylphenol is phenol substituted in either the *ortho*- or *para*-position by a linear or branched alkyl group consisting of nine carbons (C_9); therefore, it is not one single chemical. Most toxicity data on nonylphenol (NP) are about commercial products of variable composition, a situation which causes analytical difficulties. Very little information exists for nonylphenol ethoxylates other than from self classification and for nonaethylene glycol 4-nonylphenyl ether (nonoxynol-9), used as a spermicide in pharmaceuticals.

Toxicokinetics

In experimental animals radiolabelled nonylphenol was used to determine the toxicokinetics. It was found that the absorption via the oral route in rats was almost complete with 76% of the administered dose excreted with faeces and 19% via the urine as glucuronic acid conjugates during the first 4 days (Knaak *et al.*, 1966). The potential for bioaccumulation was limited. For three ethoxylates studied, the excretion in the urine was greater and in the faeces it was smaller (Knaak *et al.*, 1966).

The absorption through the skin in an *in vitro* test system was poor: less than 1% (Monteiro-Riviere *et al.*, 2000).

The absorption and excretion of nonylphenol was investigated in human volunteers (Müller, 1997). After oral administration of a single dose of 5 mg nonylphenol the absorption was about 20% of the dose, the blood level peaked after one hour, and nonylphenol was present as 86 ng conjugate/g blood. The concentration of the free nonylphenol was 100-fold lower. About 10% of the oral dose was excreted in the urine free or as conjugate. The excretion via faeces was low.

There are no data on the toxicokinetics of nonylphenol following inhalation exposure, but on the basis of the oral absorption data and high partition coefficient, it would be prudent to assume that significant absorption via the inhalation route can occur.

There is no information about the metabolism of nonyl phenol or of the nonyl phenol ethoxylates, but once absorbed, NPEOs are likely metabolised to nonylphenol.

Acute toxicity
The acute oral toxicity of nonylphenol is moderate to low with estimated LD_{50} values in rats ranged from about 1200 to 2400 mg/kg for males and 1600 to 1900 mg/kg for females. The 95% confidence intervals in these studies were generally relatively tight, suggesting that the dose-response curve is steep. Clinical signs of toxicity included excessive salivation, diarrhoea and lethargy. At necropsy, erosion of the mucosal surface of the stomach was seen in some of the animals (EU 2002). The toxicity of nonylphenol in mice may be greater since a LD_{50} in male mice was reported to 300 mg/kg (Gaworski *et al.*, 1979). The oral rat LD_{50} for NPEO with an ethoxylate side chain length of 9 was 2.6 ml/kg (Smyth and Calandra, 1969).

A dermal LD_{50} of 2031 mg/kg bw was determined in rabbits after an exposure period of 24 hours (Smyth *et al.*, 1969).

Irritation
No information is available from human studies but skin irritation caused by some technical nonylphenol substances of unknown composition has been investigated in a number of animal studies. Most of these studies have not been published in peer-reviewed papers, but rather in laboratory reports, and the reactions vary with substance and test. Some studies reports severe erythema, thickening, necrosis and ulceration of the skin, severe eye irritation and burns, but only mild irritation of the respiratory tract (ECB, 2002).

Sensitisation
No information is available from human studies or inhalation but the skin sensitization potential of nonylphenol has been investigated in several animal studies, including the guinea pig maximization test, without showing significant skin sensitizing potential (ECB, 2002). There are two papers claiming contact dermatitis from exposure to nonylphenol ethoxylate (Nethercott and Lawrence 1984; Meding, 1985).

Repeated dose toxicity
There are no human toxicity studies and few animal studies of oral administration of nonylphenol. In a 28-day study, groups of five male and five female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at nominal dose levels of 0, 25, 100 or 400 mg/kg bw/day (Hüls, 1989). At the highest dose level, the body weight gain was reduced and for the males there were slight differences in comparison with the controls for certain clinical chemical parameters. A NOAEL of 100 mg/kg bw/day for 28-day exposure was determined.

In a 90-day study, groups of fifteen male and fifteen female Sprague-Dawley rats were exposed to nonylphenol via incorporation in the diet at concentrations of 0 (control), 200, 650 or 2000 ppm (mg/kg in the diet) (Cunny *et al.*, 1997). Calculated nonylphenol intakes were about 0, 15, 50 and 140 mg/kg bw/day, respectively. There were no treatment-related mortalities or clinical signs of toxicity. At the highest dose of 140 mg/kg/day only, there were minor adverse effects on bodyweight gain, the amount of food consumed and food utilisation throughout the dosing period, and some evidence of morphological changes in the liver and possibly kidneys. In this 90-day sub-acute study the NOAEL for nonylphenol was determined to be 50 mg/kg bw/day. Various nonylphenol ethoxylates were tested in a 90-day feeding study with rats, and the LOAELs for increased liver weight were determined to 40-200 mg/kg/day (Smyth and Calendra, 1969). Dogs receiving 0.64% NPEO in the feed for 90 days had retarded weight gain.

Further information on repeated dose toxicity can be derived from a good-quality multigeneration study (NTP, 1997). Groups of thirty male and thirty female Sprague-Dawley rats were exposed to nonylphenol in the diet at concentrations of 0 (control), 200, 650 or 2000 ppm over three generations. Calculated nonylphenol intakes were, respectively, about 0, 15, 50 and 160 mg/kg bw/day during non-reproductive phases. The F_0 generation was exposed for 15 weeks, the F_1 and F_2 generations from soon after birth to about 20 weeks of age and the F_3 generation from birth to about 8 weeks of age. Evidence of general toxicity was seen in adults of all generations, although there were no treatment-related clinical signs, mortalities or adverse effects on food consumption. Histopathological examination revealed an increase in the incidence of renal tubular degeneration and/or dilatation in adult males from all generations and all nonylphenol treated groups and for some adult females. Therefore, the LOAEL for histopathological changes in the kidneys after repeated exposures to nonylphenol was considered equal to the lowest dose of 15 mg/kg/day (ECB, 2002).

Long-term feeding of rats with 0.2 g NPEOs/kg bw/day in 2 years resulted in increased liver weight in female rats, and in dogs when they received 0.27% NPE= in the diet (Smyth and Calandra, 1969). In addition, focal myocardial necrosis was observed in dogs and guinea pigs exposed to a high molecular weight NPEO-20 at 0.04 g/kg/day. NPEO-9 was half as potent in dogs and NPEO-15 a fifth.

Mutagenicity and cancer
Mutagenicity data are available from *in vitro* test systems and animals. No mutagenicity of nonylphenol was detected in the Ames test with several *Salmonella typhimurium* strains and in *Escherichia coli* in the presence and absence of metabolic activation (Shimizu *et al.*, 1985; Boyacioglu *et al.* 2007). An *in vitro* gene mutation test with Chinese hamster V79 cells was negative (Hüls, 1990). Micronucleus studies with mice were also negative for nonylphenol (Hüls, 1999). No cancer studies of humans or animals were available.

Effects on reproduction, hormones and fertility
There are some newer data on reproductive effects in humans. Low doses of pure 4-n-nonylphenol are able to affect cytokine secretion in human placenta which may result in implantation failure, pregnancy loss or other complications (Bechi *et al.*, 2010).

The estrogenic activity of nonylphenol in various quantities has been investigated in a number of studies using recombinant yeast, estrogen sensitive MCF-7 cells or a rodent uterotrophic assay response. 4-Nonylphenol was tested for estrogenic activity in an *in vitro* assay using a recombinant strain of yeast (*Saccharomyces cerevisiae*), which contains an estrogen-inducible expression system (Routledge and Sumpter, 1997). Nonylphenol was active but 30 000 times less potent than a 17ß-estradiol standard. The estrogenic activity of nonylphenol has also been assessed in an *in vitro* assay involving estrogen-sensitive human breast tumor MCF-7 cells (Soto *et al.*, 1991). In this test system the estrogenic potency of 17ß-estradiol was 3 000 000 times greater than that of nonylphenol.

The estrogenic activity of nonylphenol has been assessed in several studies using an assay based upon the uterotrophic response in the rat. Absolute uterus weight and bodyweight-related uterus weight were statistically significantly increased in a dose-dependent manner by nonylphenol. The

NOAEL was 9.5 mg/kg bw/day. Estradiol was about 1000 times more potent in this assay than nonylphenol.

In the multi-generation study mentioned above (NTP, 1997) fertility and mating performance were not adversely affected by nonylphenol treatment. However, there were changes, albeit relatively slight, in the estrous cycle length, timing of vaginal opening, ovarian weight and sperm/spermatid count. The effects on the estrous cycle were seen in both the F generations (not assessed in F males) and the timing of vaginal opening was influenced in all three generations; this consistency provides firm evidence of a relationship with treatment. These effects were possibly related to the estrogenicity of nonylphenol. There is some uncertainty about the relationship to nonylphenol treatment with respect to the ovarian weight reduction, because this effect was apparent after adjusting for bodyweight in only one generation and did not correlate with any histopathological changes; nevertheless, it is compatible with the anticipated direct effects of exogenous estrogenic activity. Also, there is uncertainty regarding the cause of the apparent reduced sperm/spermatid numbers in the F2 generation. This study provided evidence that nonylphenol exposure over several generations can cause minor perturbations in the reproductive system of offspring, which are compatible with the predictable or hypothesised effects of exogenous estrogenic activity, although these perturbations do not cause functional changes in reproduction of the rat at the dose levels tested. A NOAEL for these changes of 15 mg/kg/day was identified.

Another study (de Jager *et al.*, 1999) provided evidence of nonylphenol-related testicular toxicity at exposure levels which also cause mortality. A LOAEL for testicular toxicity of 100 mg/kg/day was established.

Developmental toxicity
In a rat developmental toxicity study of timed-mated females of the Wistar strain were administered by oral gavage corn oil solutions of nonylphenol from days 6 to 15 of pregnancy at dose levels of 0, 75, 150 and 300 mg/kg/day (Lee, 1998). There was clear evidence of maternal toxicity at 300 mg/kg/day, manifested as a reduction in bodyweight gain and food consumption, mortality of two females and the macroscopic organ changes in the kidney and spleen. Similar macroscopic changes were seen occasionally at 150 mg/kg/day. No maternal toxicity was seen at 75 mg/kg/day; therefore, the maternal NOAEL was 75 mg/kg/day, and the fetal NOAEL was 300 mg/kg/day.

Tolerable daily intake
Based on a NOAEL value of 15 mg/kg bw/d in experimental animals the tolerable daily intake (TDI) for nonyl phenol in humans has been calculated at 5 µg NP/kg bw (Nielsen *et al.*, 2000).

6.3 Octylphenol and octylphenol ethoxylates

Similar to nonylphenol, octylphenol is also a group name for various phenols substituted in either *ortho*- or *para*-position by a linear or branched alkyl group consisting of eight carbons (C_8). The most well-studied isomer is called 4-*tert*-octylphenol with the systematic name 4-(1,1,3,3-tetramethylbutyl)phenol and short form 4-*t*-OP. A REACH Annex XV dossier on 4-*tert*-octyl phenol has been published in 2011 (ECHA, 2011). No information about the toxicity of octylphenol ethoxylates was available other than self classifications (see Annex 2).

Toxicokinetics
After oral application in rats 4-*tert*-octylphenol is rapidly absorbed and quickly released into the blood. The absorption of 4-*t*-OP dissolved in various solvents and administered by gavage was 10-50% of the dose depending on the rat strain, and the blood half-life ranged from 5 to 38 hours (ECHA, 2011).

The highest absorption was observed in a newer study, where 4-*tert*-octylphenol was dissolved in propylene glycol, bioavailability ranged from 26-38% in male animals and to 46-55% in females, and the 4-*tert*-octylphenol blood half-life ranged from 5-16.6 hrs in male animals and 8.3-37.9 hrs in females (Hamelin *et al.*, 2009).

After a single oral administration the highest concentrations were found in liver and fat, followed by kidneys and ovaries, and the lowest concentrations were found in muscle tissue. No significant differences occurred between the tissue concentrations from single and repeated treatment, indicating no bioaccumulation of 4-*tert*-octylphenol, and tissue concentrations appeared to be higher in female animals than in males (Hamelin *et al.*, 2009).

When rats were fed 4-*tert*-octylphenol it had a direct inhibitory effect on cytochrome P_{450} activities, causing decreased levels of testosterone hydroxylating CYP activities in the liver, where 4-*tert*-octylphenol is transformed to its glucuronide and its sulfate and further excreted into the bile and faeces (Hüls, 1996).

An oral intake of 4-*tert*-octylphenol at 200 mg/kg bw/day is in excess of a level shown to saturate liver metabolic capacity (Tyl *et al.*, 1999).

In a rat study 4-*tert*-octylphenol ethoxylate was poorly absorbed by oral administration, since about 90% was excreted in faeces within 24 hrs and only 1% in the urine (Larson *et al.*, 1963). The oral rat LD_{50} increased with the length of the polyether-chain from 1.7 to >28 g/kg bw. No adverse effects were observed in rats exposed to 1.4% of the ethoxylates for up to 2 years.

Repeated dose toxicity

There are no available human studies but numerous studies are available on repeated administration of 4-*tert*-octylphenol to adult rats of different strains of both sexes, with various routes (oral, subcutaneous and intraperitoneal injection) of administration. The only route relevant with regard to human health assessment and exposure is through oral exposure.

The sub-acute toxicity of 4-*tert*-octylphenol (purity 98.2 %) was determined in a 28 day gavage study with rats exposed to 0, 15, 70, and 300 mg/kg/day (ECHA, 2011). Increased urine volume was evident in females and males at the highest dose. Urinalysis showed decreases in specific gravity and in concentrations of sodium, chloride and potassium. Slight but statistically significant increases in kidney weights were found in the high-dose males and females and in liver weights in the high-dose females. The high-dose males and females showed greyish kidney patches as gross findings, and regeneration of renal tubules as microscopic findings. The NOAEL was reported as 15 mg/kg bw/day. In asimilar study the NOAEL was the same and the LOAEL was estimated at 150 mg/kg/day; in a third study, a concentration of 500 mg/kg bw/day was lethal for about half of the exposed animals during the treatment period (ECHA, 2011).

In a 3-month study the toxicity of 4-*tert*-octylphenol (purity 93.1 %) has been investigated in rats exposed daily to concentrations of 30, 300, or 3000 ppm 4-*tert*-octylphenol in the diet - corresponding to an intake of 2.3, 23, 230 mg/kg bw/d (Suberg *et al.*, 1982). No treatment related death occurred and no clinical signs were observed throughout the study. Food consumption was unaffected. Slightly increased water consumption was observed in females receiving the highest 4-*tert*-octylphenol dose. The body weight gain was slightly decreased in male and female animals receiving 300 ppm and markedly decreased in animals receiving 3000 ppm 4-*tert*-octylphenol. Absolute organ weights were decreased in the highest dose group in male animals (thyroid, thymus, heart, lung, spleen; but not kidney, adrenals, testes or brain) and female animals (thymus, heart, lung, liver, spleen, kidney, adrenals; but not thyroid, ovaries or brain). Histopathological investigations were carried for organs of 5 male and 5 female animals each in the control and highest dose group; no treatment related effects were observed. Based on the results of this study, a NOAEL of 30 ppm (2.3 mg/kg bw/d) and a LOAEL of 300 ppm (corresponding to 23 mg/kg bw/d) were determined.

Mutagenicity and cancer
Octylphenol was mutagenic in Ames test with *Salmonella typhimurium* strains TA98 and TA100 in concentration of 20-40 µg/L (Boyacioglu *et al.*, 2007). No cancer studies have been published.

Effects on female reproduction and fertility
In a study comparing estrogenic activities of various environmental estrogens, adult female rats were treated orally (gavage) with 0, 50, 100 or 200 mg 4-*tert*-octylphenol/kg bw or 0.01 or 0.1 mg ethinylestradiol/kg bw for a period of 25 days (Laws *et al.*, 2000). Ethinylestradiol significantly reduced the number of 4- to 5-day cycles during the exposure period, and oral exposure to 200 mg 4-*tert*-octylphenol/kg bw induced a similar response.

In a study on 35 day old female rats , daily gavage administration of saline (negative control), propylene glycol (vehicle control), or 4-*tert*-octylphenol at dosages of 25, 50, or 125 mg/kg bw were given for 35-41 days (Sahambi *et al.*, 2010). No significant differences were seen on body weights or on organ weights across groups. There were no significant differences in serum estradiol concentrations and all animals continued to cycle throughout the monitoring period.

Effects on male reproduction and fertility
In a study focusing on effects on testicular functions, groups of male rats were given daily gavage administration of 0, 50, 150 or 450 mg 4-*tert*-octylphenol for 30 days (Bian *et al.*, 2006). In the animals of the high dose group (450 mg/kg bw/d) body weight gain was suppressed. Weights of testes, epididymis and prostate were statistically significantly lower in comparison to controls. Histopathological examinations of testes revealed alterations in rats administered 450 mg/kg bw/d with seminiferous tubules markedly reduced in size and disturbance of normal spermatogenic cell organization and total number of germ cells inside the tubules markedly reduced. Electronic micrographs of testicular cells revealed more intracellular vacuoles, lipofuscin and showed degeneration. Testicular sperm counts revealed statistically significant decreases of sperm head count and daily sperm production in rats treated with 450 mg/kg bw/d.

A study had been performed to determine the effects of 60 days' exposure to various doses of 4-*tert*-octylphenol on male reproductive parameters in rats exposed to 25, 50, or 125 mg 4-*tert*-octylphenol/kg bw/d by gavage (Cyr and Gregory, 2006; Gregory *et al.*, 2009). 60 days representing approximately 1.5 cycles of spermatogenesis. In the 4-*tert*-octylphenol-treated rats there was a tendency toward decreased body weight, relative to controls, with a statistically significant decrease in mean body weight at the highest dose. There were no effects on organ weights of testes, epididymis, ventral prostate, and seminal vesicles between experimental groups.

In a 4 month study the effects on the reproductive system of 4-*tert*-octylphenol exposure via drinking water were investigated in adult (2 month old) male rats (Blake *et al.*, 2004). No effects were seen on total mixed germ cell yield, on flow cytometric distribution of spermatogenic cells or on testicular sperm concentration per g testis or per organ. Mean epididymal sperm head count per gram tissue was slightly decreased to ~700 million in comparison to controls (~800 million) at 10^{-5} M drinking water concentration. Mean percentage of sperm tail abnormalities (n=6 males/group) was slightly higher (~10-12 %) in treated groups as compared to the control group (~7 %).

Developmental toxicity
Pregnant female Wistar rats were given 4-*tert*-octylphenol daily by gastric intubation at a dose of 15.6, 31.3, 62.5, 125, 250, and 500 mg/kg bw on pregnancy days 0 (sperm plugs detected) through 8 of pregnancy (Harazono *et al.*, 2001). In the high dose group, all rats died by day 6 of pregnancy, and one-third of the rats treated with 250 mg/kg bw/day died during the administration period. Clinical signs such as diarrhea and loss of fur were seen in animals treated with > 62.5 mg/kg bw/d. The body weight gains from dose groups > 31.5 mg/kg bw/day during the treatment period and on

days 0-20 were significantly lower than those of control groups. Net weight gain of the dams, however, did not differ significantly from that of the control group. The food consumption on days 0-9 and on days 0-20 of pregnancy was significantly decreased in all treated groups (> 15.6 mg/kg bw/day) compared with control values. There were no significant differences in the pregnancy rate between treated animals and the control group. The numbers of corpora lutea, implantation sites and pre-implantation loss per litter in the treated animals were not significantly different from the control group. A significant decrease in the numbers of live foetuses per litter was observed at 31.5 and 125 mg/kg bw/day, and a significant increase in the incidence of post-implantation loss at dosages of > 31.3 mg/kg bw/day. The sex ratio of live foetuses was comparable across all groups as well as body weights of male and female. No significant increases in the incidences of foetuses with external malformations were observed. The LOAEL for maternal toxicity was estimated as 15.6 mg/kg bw/day based on reduced food intake, and the NOAEL for developmental toxicity was 15.6 mg/kg bw/day based on statistically significant increased percentage of post-implantation loss.

4-*tert*-Octylphenol has been investigated for developmental effects in offspring in several studies of lower quality using oral or other application routes to pregnant dams in various species. In rats, intrauterine exposure to 4-*tert*-octylphenol caused a significant decrease in the numbers of live foetuses and a significant increase in the incidence of post-implantation loss. The NOAEL for that was 15.6 mg/kg bw. However, these effects occurred at doses that also caused maternal toxicity, including death, reduced body weight gain and reduced food consumption (ECHA, 2011).

Multi-generation toxicity studies
A two-generation reproduction toxicity study was conducted with rats fed with dietary concentrations of 0, 0.2, 20, 200, and 2000 ppm 4-*tert*-octylphenol in their diet, leading to a daily intake of 0,034-0.011, 3.3-1.05, 32.6-10.9, and 369-111 mg/kg/d depending on the age and sex of the animals and the phase of the study, according to a OECD guideline. The test protocol involved parental dosing of the F_0 generation (30 animals/sex/dose group) during the 10 weeks pre-breeding, mating and gestation period (Tyl *et al.*, 1999).Treatment-related systemically toxic effects were limited to consistent and persistent reductions in body weights and weight gains in both sexes in the F_0, F_1, and F_2 generations at 2000 ppm. Feed consumption was unaffected, and there were no clinical effects observed. Body weights during gestation were unaffected and were reduced during lactation in F_0 and F_1 females at 2000 ppm. At necropsy, F_0 and F_1 parental and F_2 retained male absolute and relative organ weights were unaffected for liver, kidneys, adrenal glands, spleen, and brain. There were no treatment- or dose related gross or microscopic findings for the examined organs, for F_0 and F_1 parental animals, and for F_2 retained adult males. No effects on reproductive parameters, testes weights or morphology, epididymal sperm counts or morphology, daily sperm production, efficiency of daily sperm production, or prostate or dorsal prostate weights or histopathology were observed. Furthermore, no estrogen-like effects on males or females and no low-dose effects were evident. In that study, the NOAEL for systemic toxicity/postnatal toxicity was 200 ppm in feed (11-33 mg/kg bw/d), and NOAEL for reproductive toxicity was as high as 2000 ppm (111-369 mg/kg/d). It has to be noted that the exposure duration was limited.

Endocrine disruption in screening systems
4-*tert*-Octylphenol has been studied in many different *in vitro* test systems, and the relative estrogenic potency has often been related to 17β-estradiol, ethinylestradiol or DES (ECHA, 2011). In the MCF-7 Cell proliferation test, the relative potency to 17β-estradiol was for instance 10^{-6}-10^{-3}.

4-*tert*-Octylphenol has been screened for androgenic/anti-androgenic activity in the Hershberger bioassay, and the impact on testosterone biosynthesis/testicular steroidogenic competence was investigated *in vitro* in neonatal Leydig cells derived from 6-7 days old neonatal rats. Overall, the *in vitro* and *in vivo* screening tests indicate that 4-*tert*-octylphenol has some but low estrogenic potential in mammals.

4-*tert*-Octylphenol features some inherent potential for being toxic to reproduction, probably in relation to female sexual maturation and female fertility in combination with unrealistically high doses or using artificial and non-human relevant routes of administration.

6.4 AP/APEO of a chain length of less than eight

Monoalkylphenols with a short alkyl chain have different properties than the longer chain homologues and are used for other purposes and *not* as ethoxylates. The most important are the three methylphenols (*o*-, *m*- and *p*-cresols – out of study scope), and 4-*tert*-butylphenol.

6.4.1 4-*tert*-Butylphenol

Regarding toxicokinetics the available information is rather sporadic. In an experimental study of rats exposed by gavage to 147 µg/kg bw of ^{14}C-labelled 4-*tert*-butylphenol once daily for three days it was found that after 7 days about 27% of the applied dose was excreted via feces and about 73% via urine, thus the absorption must have been complete (Freitag *et al.*, 1982). In another rat study it was shown that after intravenous injection of ^{14}C-labelled 4-*tert*-butylphenol about 70% of the applied dose was excreted as glucuronide and about 20% as sulfate (Koster *et al.*, 1981).

There exist some older biomonitoring studies of workers handling 4-*tert*-butylphenol and being exposed by inhalation and through the skin. It was reported that the absorption of the phenol was close to complete but most was excreted again within 24 hrs as glucuronide- and sulfate conjugates (ECB, 2008).

The acute toxicity of 4-*tert*-butylphenol has been determined in some animal experiments and appears to be insignificant. The inhalation rat LC_{50} was very low at >5000 mg/m^3. Lethality was not observed among rats exposed to saturated 4-*tert*-butylphenol vapours for 6-8 hrs. The acute dermal toxicity in rabbits and guinea pigs appear also to be low at >2000 mg/kg bw. Finally, the oral rat LD_{50} is low at >2000 mg/kg bw (ECB, 2008).

Although the lethality of 4-*tert*-butylphenol is low for skin application, it can be severely irritating and also corrosive to skin of rabbits with erythema, oedema, fissuring, desquamation and necrosis. It is also highly irritating to rabbit eyes (e.g. Klonne *et al.*, 1988). In addition, dissolved in DMSO and in propylene glycol, 4-*tert*-butyl phenol has shown strong skin depigmentation potency in guinea pigs (Gellin *et al.*, 1970). Skin depigmentation has also been observed in workers handling 4-*tert*-butyl phenol in industry. A systemic LOAEL of 103 mg/kg bw/day for skin depigmentation in orally exposed mice has been developed (ECB, 2008).

4-*tert*-Butylphenol had no sensitisation potential in a modified Magnusson-Kligman test with guinea pigs but some cross-reactivity between 4-*tert*-butyl phenol and *4-tert*-butyl catechol was observed (Zimerson, 1999). A 2% solution of 4-*tert*-butylphenol dissolved in petrolatum caused an allergic reaction/skin sensitisation in at least 1% of groups of contact dermatitis patients (Jordan and Dahl, 1972; Rudner, 1977) but apparently no reaction in healthy people.

The toxicity of 4-*tert*-butylphenol has been studied in the OECD 422 Combined Repeated Dose and Reproductive/Developmental Toxicity Screening Test with administration by gavage. In the initial dose-finding activity, daily doses of 250 mg/kg bw and higher during 14 days were causing respiratory distress. In the main study 8-week old male and female Sprague-Dawley rats (13 males and 13 females per dose level) were administered 4-*tert*-butylphenol by oral gavage in 0.5 % methyl cellulose at daily doses of 0 (vehiclecontrol), 20, 60 and 200 mg/kg bw. The males were administered 4-*tert*-butylphenol for 6 weeks, whereas the females were exposed from 14 days prior to mating to day 4 of lactation. Some females of the highest dose group showed respiratory stress with dyspnea but no compound-related morphological changes were observed during pathological examination of parental animals. However, there was high lethality in the offspring. In males there was a slight increase in mean relative liver weight. Based on respiratory distress in exposed females and effects on several blood parameters in male rats, the NOAEL for 4-*tert*-butylphenol in the study was established at 60 mg/kg bw/day.

A two-generation reproduction study was carried out in Sprague-Dawley rats with 4-*tert*-butylphenol given orally in the diet at the following concentrations: 0, 800, 2500 and 7500 ppm, corresponding to approximately 0, 70, 200 and 600 mg/kg bw/day. In the parental generation, 28 rats per sex and group were used. The animals were exposed for 10 weeks prior to mating and until termination of lactation. No treatment related clinical signs were reported but at the two highest doses there was a decrease in body weight gain compared to controls (Clubb and Jardine, 2006). At the termination of the experiment in the highest dose group, a statistically significant increase in the weights of the kidneys and liver in males was reported, and in females a statistically significant decrease in the weight of the adrenal gland and ovaries was reported following covariance analysis with the body weight as the covariate. There was a significant increased incidence of minimal to mild vaginal atrophy in high dose females and an increase in the incidence of primordial follicles. At 200 mg/kg bw/day a statistically significant decrease in the relative weights of ovaries was reported in females, as well as reduced relative weights. The NOAEL for repeated dose toxicity was considered to be 70 mg/kg bw/day (800 ppm) from this study, based on a dose-dependent reduction of relative weights of ovaries and adrenal glands in females. The results indicated that 4-*tert*-butylphenol had no effect on fertility and induced no embryotoxicity or teratogenicity at the dose levels tested. The NOAEL for fertility and developmental toxicity derived from this study was therefore ≥ 200 mg/kg bw/day.

The mutagenicity of 4-*tert*-butylphenol is likey to be absent. It was not observed in some *in vitro* mutagenicity tests using *Salmonella typhimurium* strains TA100, TA1535, TA98, and TA1537 (Ames test), as well as using *Escherichia coli* WP2 uvrA. In addition, 4-*tert*-butylphenol had no significant mutagenic potential in the mouse lymphomaTK+/- locus assay in L5178Y cells. It was also not genotoxic in the *in vivo* mammalian erythrocyte micronucleus test (i.p. injection). However, 4-*tert*-butylphenol induced chromosomal aberrations in Chinese hamster lung cells in the presence of an exogenous metabolic activation system (ECB, 2008).

Sufficient animal cancer studies are missing; however, 4-*tert*-butylphenol has, as many other phenols, a promoting effect. After initiation with *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (MNNG) 4-*tert*-butylphenol induced forestomach squamous cell carcinoma in F344 male rats.

4-*tert*-Butylphenol is a very weak endocrine disruptor. In the E-screen 4-*tert*-butylphenol induced proliferation in human estrogen receptor-positive MCF-7 breast cancer cells but was 10 -30 times less potent than nonylphenol and >100 000 times less active than the reference substance 17β-estradiol (Soto *et al.*, 1991, Körner *et al.*, 1998).

“The recombinant Yeast screen assay” is an estrogen-inducible strain of yeast, *Saccharomyces cerevisia*, expressing the human estrogen receptor. In this study 4-*tert*-butylphenol was shown to be a weak estrogen disruptor and approximately 1,500,000 times less potent than 17β-estradiol to bind to the human ER receptor. In comparison, 4-nonylphenol was 30,000-fold less potent than 17β-estradiol (Routledge and Sumpter, 1997). The data indicated that both the position (*para* > *meta* > *ortho*) and branching (*tertiary* > *secondary* = *normal*) of the alkyl group affect estrogenicity. Optimal estrogenic activity requires a single tertiary branched alkyl group composed of between 6 and 8 carbons located at the *para*-position on an otherwise unhindered phenol ring.

6.5 AP/APEO of a chain length of more than nine

Among APs longer than nine, the most important is dodecyl phenol and its ethoxylates. Very little toxicological information exists for this chemical; however, there is self classification information, which indicates that......

No toxicokinetics studies of these substances are available. The acute toxicity of dodecyl phenol is low, determined as an oral rat LD_{50} of >2100 mg/kg and a dermal LD50 of >3000 mg/kg (Brooke *et al.*, 2007).

Dodecylphenol (90% *p*- and 10% *o*-) applied undiluted to rabbit skin for 24 hrs was severely irritating, and a moderate eye irritation was exhibited (Randall and Robinson, 1990)

A repeated exposure study of rats fed 500, 2500 and 5000 mg/kg dodecylphenol in the diet for 1 month showed decreased food intake and body weight and some blood changes in the two highest groups. Males of the highest dose showed harmful effects on testes. The low dose of 500 mg/kg diet was reported as the NOAEL value. Calculated as intake it was 33 mg/kg bw/d in males and 41 mg/kg bw/d in females (USEPA, 1989; Hass *et al.*, 1994).

Dodecylphenol is not mutagenic in the Ames test with *Salmonella typhimurium* and in Chinese hamster ovary cells and not active in a chromosome aberration test (USEPA, 1987; Hass *et al.*, 1994).

In a study of developmental toxicity, where pregnant rats were exposed to dodecyl phenol by gavage in ten days during gestation, an embryotoxic effect was evident by an increase in the incidence of uterine resorption. Foetotoxicity was evident by lower foetal weight and an increased incidence of foetuses with ossification variations; however, these effects may be secondary to maternal toxicity (USEPA, 1987; Hass *et al.*, 1994).

6.6 Assessment across the groups

The shorter chain monoalkylphenols are more reactive substances than the longer-chain compounds, potentially irritating and corrosive to skin, eyes and mucous membranes. These substances are used as pure chemicals directly as intermediates in the process industry, while the longer chain alkylphenols are complex mixtures of isomers and more used as their ethoxylates, which have different chemical, physical and toxicological properties, being glycol ethers and not phenols. However, the ethoxylates may degrade and be transformed back to the phenols.

There is little information about the toxicities of the ethoxylates but because they are large molecules, the availability for uptake in the body, and therefore also the toxicity, is low.

A main reason for the selection of alkylphenols for LOUS is likely the endocrine disruptive effects of the long-chain members of the family. Alkylphenols with alkyl groups of more than C_2 attached at 4-(*para*-) position of the phenol showed properties very similar to that of estrogen. The available data indicate that both the position (*para* > *meta* >*ortho*) and branching (*tertiary* > *secondary* = *normal*) of the alkyl group affect estrogenicity. Optimal estrogenic activity requires a single *tertiary* branched alkyl group composed of between 6 and 9 carbons located at the *para*-position on an otherwise unhindered phenol ring. It should therefore be underlined that the *para*- (4-) mono-substituted homologues seem to be most active as endocrine disruptors, and 4-nonyl phenol and 4-*tert*-octylpenol are the most potent of these.

In one study, phenol derivatives were examined by means of gene expression profiling based on DNA microarray assays (Terasaka *et al.*, 2006). For the data analysis a total of 120 genes were selected, contributing to the statistical reliability. Among the alkylphenols tested, technical nonylphenol - a mixture of NP with branched alkyl groups - showed the most activity, and exhibited stronger estrogenic activity than straight chain 4-nonylphenol. Significantly high correlations to the profile for estrogen were observed for 4-*n*-heptylphenol, 4-*tert*-octylphenol, and nonylphenol. *p*-Cresol and 4-*n*-ethylphenol were not estrogenic. Therefore, the scientific documentation for keeping the other alkylphenols on the list appears to be insufficient.

An estrogen receptor (ER) competitive-binding assay has been used to determine the ER relative binding affinity for a large, structurally diverse group of 188 chemicals including alkylphenols of various qualities (Blair *et al.*, 2000). The data for alkylphenols are extracted and shown in Table 30 with estradiol as a reference.

TABLE 31
RELATIVE ESTROGEN RRECEPTOR BINDING AFFINITY AND MEAN INHIBITION CONCENTRATION OF ALKYLPHENOLS AND ESTRADIOL

Substance	Purity (%)	Mean IC_{50} *1 (M)	Relative binding affinity (%)
17β-Estradiol	Not available	8.99 x 10-10	100
4-Nonylphenol	95,6	2.40×10^{-6}	0.037
4-Nonylphenol	Tech	2.60×10^{-6}	0.035
4-Nonylphenol	85	2.90×10^{-6}	0.031
4-Nonylphenol	Tech	3.05×10^{-6}	0.029
4-Nonylphenol	85	4.73×10^{-6}	0.019
4-Dodecylphenol	99,7	4.85×10^{-6}	0.019
4-*tert*-Octylphenol	97	6.00×10^{-6}	0.015
4-Octylphenol	99	1.95×10^{-5}	0.005
4-*n*-Nonylphenol	98	2.80×10^{-5}	0.0032
4-*tert*-Amylphenol	99	1.65×10^{-4}	0.0005
4-*sec*-Butylphenol	96	2.10×10^{-4}	0.00043
2-*sec*-Butylphenol	98	3.15×10^{-4}	0.00029
4-*tert*-Butylphenol	99	3.68×10^{-4}	0.00024
4-Ethylphenol	99	1.34×10^{-3}	0.00007

*1 IC50 is the concentarion with 50% inhibition

Compared to estradiol, all alkylated phenols are weak endocrine disruptors in this test system. Nonylphenol is the most active alkylphenol. The various mixtures/qualities (isomers, impurities) of nonylphenol seem to have considerable effects on the activity. The ER activity declines with shorter chain length and substances with ≤ C_5 had insignificant activity.

The EU strategy for endocrine disruptors includes the task of compiling a candidate list of potential endocrine disruptors that must be evaluated further for endocrine disrupting effects. In order to prioritize the efforts, the substances on the list have been subdivided into a number of categories.

Nonylphenol and 20 other alkylated phenols as well as two nonylphenol ethoxylates are on the candidate list in the EU of endocrine disruptors. The AP/APEOs included in the EU list are shown in Table 32. For many of the substances no or insufficient data were available (CAT 3b) for the assessment of the endocrine potency of the substances.

TABLE 32
AP/APEO LISTED IN THE EU PRIORITY LIST OF POTENTIAL ENDOCRINE DISRUPTORS (EC, 2012)

CAS No	No. of C in alkyl chain	Chemical name (as indicated in the list)	Human health	Wildlife	Overall category
99-71-8	4	4-*sec*-Butylphenol	CAT2	CAT2	CAT2
98-54-4	4	4-*tert*-Butylphenol	CAT2	CAT2	CAT2
80-46-6	5	4-(tert-Amyl)phenol, 4-*tert*-Pentylphenol	-	-	-
87-26-3	5	2-*sec*-Pentylphenol, 2-(1-Methylbutyl)phenol	CAT3b	-	CAT3b
1131-60-8	6	4-Cyclohexylphenol	CAT1	CAT3b	CAT1
949-13-3	8	2-Octylphenol	CAT3b	CAT3b	CAT3b
1806-26-4	8	4-Octylphenol	CAT 1	CAT 1	CAT 1
11081-15-5	8	4-Isooctylphenol	CAT 1	CAT 1	CAT 1
26401-75-2	8	2-*sec*-Octylphenol	CAT3b	CAT3b	CAT3b
27214-47-7	8	4-*sec*-Octylphenol	CAT3b	-	CAT3b
27193-28-8	8	Octylphenol (mixture of tert-Octylphenol isomers)	CAT 1	CAT 1	CAT 1
140-66-9	8	4-*tert*-Octylphenol, 4-(1,1,3,3-Tetramethylbutyl)phenol	CAT 1	CAT 1	CAT 1
3884-95-5	8	2-*tert*-Octylphenol, 2-(1,1,3,3-Tetramethylbutyl)phenol	CAT3b	CAT3b	CAT3b
27985-70-2	8	(1-Methylheptyl)phenol, (mix of isomers)	CAT3b	CAT3b	CAT3b
18626-98-7	8	2-(1-Methylheptyl)phenol	CAT3b	CAT3b	CAT3b
1818-08-2	8	4-(1-Methylheptyl)phenol	CAT3b	CAT3b	CAT3b
17404-44-3	8	2-(1-Ethylhexyl)phenol	CAT3b	CAT3b	CAT3b
3307-00-4	8	4-(1-Ethylhexyl)phenol	CAT3b	CAT3b	CAT3b
3307-01-5	8	4-(1-Propylpentyl)phenol	CAT3b	CAT3b	CAT3b
37631-10-0	8	2-(1-Propylpentyl)phenol	CAT3b	CAT3b	CAT3b
25154-52-3	9	Nonylphenol (mixture of isomers)	CAT1	CAT1	CAT1
104-40-5	9	4-Nonylphenol (4-NP)	CAT 1	CAT 1	CAT 1
9016-45-9	9	Nonylphenol ethoxylates (NPEO, mixture, polymeric)	CAT2	CAT1	CAT1
20427-84-3	9	4-Nonylphenol diethoxylate (NP2EO), 2-[2-(4-nonylphenoxy)ethoxy]ethanol	CAT2	CAT2	CAT2

CAT 1: Evidence of endocrine disrupting activity in at least one species using intact animals.
CAT 2: At least some in vitro evidence of biological activity related to endocrine disruption
CAT 3b: No or insufficient data available.

6.7 Summary on human health effects

Most available data have been generated from animal studies with oral administration and from *in vitro* tests. Some data are rather old and of low quality. There are no data on the toxicity of alkylphenol ethoxylates but these polymers are less bioavailable and therefore not toxic; however, they may be metabolised to the alkylphenols.

The short-chain alkylated phenols are highly acutely toxic, with toxicity decreasing with the length of the alkyl chain, and nonylphenol is only moderately acutely toxic. All the alkylphenols are irritating or corrosive to the skin, eyes and mucous membranes. 4-*tert*-Butylphenol may cause skin depigmentation.

The available toxicity data for long-chain alkylphenols other than nonylphenol are rather limited, and data on the ethoxylates are nearly absent. Only 10-20% of an administered dose of nonylphenol is absorbed following oral exposure. It accumulates in the fat and the major metabolic pathways are likely to involve glucuronide- and sulfate conjugation and excretion with faeces and urine. Humans and animals differ with having more excretion via urine and faeces, respectively.

The critical effects for nonylphenol and other long-chain alkylphenols are endocrine disruptions and effects on reproduction and fertility. There is evidence that nonylphenol, 4-*tert*-octylphenol and dodecylphenol has *in vitro* and *in vivo* estrogenic activity but is 3-6 orders of magnitude less potent than estradiol. The effects of nonylphenol on fertility and reproductive performance have been investigated in a good quality oral (dietary administration) multi-generation study in the rat. This study provided evidence that nonylphenol exposure over several generations can cause minor perturbations in the reproductive system of offspring, namely slight changes in the estrous cycle length, the timing of vaginal opening and possibly also in ovarian weight and sperm/spermatid count, although functional changes in reproduction were not induced at the dose levels tested. The NOAEL for these changes was 15 mg/kg/day. The observed perturbations in offspring are compatible with the predictable or hypothesised effects of exogenous estrogenic activity. Data also indicate that specifically pure 4-*n*-nonylphenol may have an effect on the function of the placenta.

The main data gaps concern:

- Toxicity data for long-chain alkylphenols other than nonylphenol are limited and data on alkylphenol ethoxylates are nearly absent;
- For many of the short-chained alkylphenols no or insufficient data are available for the assessment of the endocrine potency of the substances.

7. Monitoring data and exposure

7.1 Monitoring of AP/APEO in the environment in Denmark and releases from point sources

The national environmental monitoring and assessment programme, NOVANA, includes measurements of six AP/APEO substances or substance groups in point sources and streams and three substances in groundwater (Table 33).

TABLE 33
AP/APEO INCLUDED IN THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME FOR THE AQUATIC AND TERRESTRIAL ENVIRONMENT, NOVANA 2011-2015 (NOVANA, 2011)

Substance	Point sources	Streams	Ground water
Nonylphenols , ∑	x	x	x
4-nonylphenol	x	x	
Nonylphenol monoethoxylates	x	x	x
Nonylphenol diethoxylates	x	x	x
Octylphenols, ∑	x	x	
4-*tert*-octylphenol	x	x	

The monitoring of ground water and water from water work wells carried out by the Geological Survey of Denmark and Greenland (GEUS) includes measurements of NP and for some years NPEO (GEUS 2009; 2011).

7.1.1 AP/APEO in the environment

Results from the NOVANA programme
The most recent data on AP/APEO from the NOVANA programme are summarised in Table 34.

In 2008, nonylphenol was found in all samples of lake sediment at concentrations where the substances may have an environmental effect as the concentration exceeded the predicted no-effect concentration (PNEC) (Nordemann Jensen *et al.*, 2009). The median concentration was 0.57 mg/kg dw. Octylphenol was found in most samples but at a significantly lower concentration. The concentration of nonylphenol was higher than reported in previous NOVANA reports. The reports for 2001 and 2o03 both indicate a median concentration of 0.1 mg/kg while the maximum values were 0.34 mg/kg and 0.27 mg/kg, respectively (Jensen *et al.*, 2003, 2004).

In marine sediments the median concentration of NP was measured at 0.063 mg/kg dw, nearly 10 times lower than the concentration in the lake sediments. The concentration of NPEO is reported to be at the same level as the NP while the concentration of OP was significantly lower (Petersen and Hjort, 2010). The exact figures are not reported.

In stream sediments the concentration of nonylphenol monoethoxylates and diethoxylates were below the detection level of 0.1 mg/kg while octylphenols and 4-*tert*-octylphenol were found in 5 of 11 samples at 0.036 and 0.0035, respectively (Wiberg-Larsen, 2010). The concentrations were not compared to PNEC values.

TABLE 34
MOST RECENT MONITORING DATA FOR AP/APEO IN THE ENVIRONMENT FROM THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME, NOVANA

Substance	Medium	Number of samples *1	Median (maximum) concentration, mg/kg dw	PNEC value mg/kg dw	Year	Source
Nonylphenol	Lake sediment	25 (25)	0.57 (4.2)	0.039 *2	2008	Nordemann Jensen *et al.*, 2009
Nonylphenol	Sea sediment	29 (13)	0.063 (0,69)	not reported	2009	Petersen and Hjort, 2010
Octylphenol	Lake sediment	25 (25)	0.004 (0.088)	0.063 *2	2008	Nordemann Jensen *et al.*, 2009
Nonylphenol mono-ethoxylates	Stream sediment	21 (0)	all samples <0.1	not reported	2009	Wiberg-Larsen, 2010
Nonylphenol di-ethoxylates	Stream sediment	21 (0)	all samples <0.1	not reported	2009	Wiberg-Larsen, 2010
Octylphenol	Stream sediment	21 (5)	not reported (0,036)	not reported	2009	Wiberg-Larsen, 2010
4-*tert*-octylphenol	Stream sediment	21 (5)	not reported (0,0035)	not reported	2009	Wiberg-Larsen, 2010

*1 Number of positive samples in brackets

*2 Reference is in made to the EU Risk Assessment Report (ECB, 2002) in Nordemann Jensen *et al.* (2009).

7.1.2 Groundwater

The limit values for the sum of NP and OP in ground water in Denmark are 20 µg L (Danish EPA, 2010). For other phenol compounds the limit value is 0.5 µg/L for each.

In 730 samples from water works wells from the period 1993-2003 APs were found in concentration above the detection limit in 4% of the samples (GEUS, 2004). In none of the samples the concentration exceeded the limit values. In 839 samples of water from water works wells from 2007-2010, nonylphenol was found in concentrations above 0.5 µg/L in 13 samples (GEUS, 2011). In 585 samples of ground waste from 2007-2008 NPEO was not found in a concentration above the detection limit in any of the samples (GEUS , 2010). Data for other APs in ground water in Denmark have not been identified.

A pan-European survey of the occurrence of other selected polar organic persistent pollutants in ground water from 2011 presents data for nonylphenol (NP), tert-octylphenol and nonylphenoxy acetic acid (NPE_1C) (Loos et al., 2010). NPE_1C is a transformation product of NPEO. The survey includes ground water samples from Denmark and 22 other EU Member States from a total of 164 locations, but the data are not presented by country.

NPE_1C was among the most relevant compounds detected, with a frequency of detection of 42%, and a maximum concentration level of 11.3 mg/L. The monitoring results on NPE_1C in ground water supports according to the authors, findings by other studies and show that the NPEO carboxylates (NPECs) are persistent chemicals wide spread in European ground waters (Loos *et al.*, 2010). In a sister study of the same pollutants in rivers, NPE_1C was above the detection limit of 2 ng/L in 97% of the samples and the median concentration of 553 ng/L was the highest for the analysed organic persistent pollutants (Loos *et al.*, 2009).

TABLE 35
OCCURENCE OF NP, 4-*TERT*-OP AND NPE1C IN GROUND WATER ACROSS THE EU (LOOS ET AL., 2010)

Chemical	Limit of detection, ng/L	Freq. of detection (%), ng/L	Max ng/L	Average ng/L	Median ng/L	90th per-centile
Nonylphenol (NP)	30.0	11.0	3,850	83	0	39
4-*tert*-Octylphenol	0.4	23.2	41	1	0	2
Nonylphenoxy acetic acid (NPE1C)	0.5	41.5	11,316	263	0	127

7.1.3 AP/APEO in point sources

The most recent monitoring data concerning municipal waste water treatment plants (MWWTP), industrial sources and rainwater outlets from the NOVANA programme are shown in the table below.

TABLE 36
MOST RECENT MONITORING DATA FOR AP/APEO IN OUTLET FROM POINT SOURCES FROM THE NATIONAL MONITORING AND ASSESSMENT PROGRAMME

Substance	Point source	Number of samples *1	Average µg/L	Median µg/L	Year	Source
Nonylphenols	MWWTP	35 (10)	0.065	< d.l.	2007-2009	Naturstyrelsen, 2010
Nonylphenols	MWWTP	6 (1)	0.06	< d.l.	2009-2010	Naturstyrelsen, 2011
Nonylphenol monoeth-oxylates	MWWTP	36(3)	0.007	< d.l	2007-2009	Naturstyrelsen, 2010
Nonylphenol monoeth-oxylates	Industrial	25 (n.i)	1.77	< d.l.	2006-2009	Naturstyrelsen, 2010
Nonylphenol diethox-ylates	Industrial	26 (n.i)	1.97	< d.l.	2006-2009	Naturstyrelsen, 2010
Nonylphenols	Rainwater outlets	49 (n.i)	0.04	< d.l.	2007-2010	Naturstyrelsen, 2011
Octylphenol	MWWTP	190 (8%)	not reported 93% of sam-ples below o.1	not re-ported	2003	Danish EPA, 2004

*1 Number of positive samples in brackets
<d.l. : Below detection level. n.i.: not indicated

National mean concentrations based on the results from the Danish national environmental monitoring programme (NOVANA) for the period 1998-2009 are described in section 4.3 on releases from waste water treatment plants. Compared with the nation mean concentrations shown in Table 22, the average NP concentration of 0.06 µg/L is significantly lower than the national mean of 0.24 µg/L. Also for the nonylphenol monoethoxylates the measured average is below the nation mean of 0.057 µg/L. Both could indicate a decreasing trend in the concentration.

7.2 European Pollutant and Transfer Register (E-PRTR)

The European Pollutant Release and Transfer Register (E-PRTR) contains annual data reported by some 28,000 industrial facilities in 27 EU Member States as well as Iceland, Liechtenstein, Norway, Serbia and Switzerland. NP/NPEO and OP/OPEO are among the 91 pollutants covered by the reporting. The requirements for reporting are established by the PRTR Regulation (Regulation (EC) No 166/2006).

Data from the E-PRTR for NP/NPEO show that waste and waste water management account for 61 t/y of the total registered release to water in the EU27 of 63.6 t/y. Other main sources are the energy sector (0.3 t/y) and production and processing of metals (0.7 t/y).

For OP/OPEO the E-PRTR data show similarly that releases from waste and waste water management account for nearly 100% of the registered 13.2 t/y released to water from point sources in the EU27 in 2010. The registered emissions from all other point sources including the chemical industry total less than 0.1 t/y. The registered emissions to air and soil are 0.

The E-PRTR does not included point source data from any point sources in Denmark.

7.3 AP/APEO in the Baltic Sea and North Sea environments

The status of nonylphenol, 4-*n*-octylphenol and 4-*tert*-octylphenol in sediment, biota and water in the Baltic Sea has been reviewed by HELCOM (2010). The primary source of NP found in the Baltic environment is considered to be NPEOs, which can break down into NP in wastewater treatment plants or in the environment. Sediment measurements showed that concentrations of 4-iso-nonylphenol or unidentified NPs in the surface sediment exceeded the PNEC (predicted no effect concentration) level in the Northern Baltic Proper and the South Western Baltic Sea. As it appears from the maps shown in Figure 9, the concentration of NP in sediments from the Inner Danish Waters is generally significantly higher than the concentration in the Baltic Sea. Concentrations of octylphenol in surface sediment were high compared to the threshold concentration, with 50% of 4-n-octylphenol samples and 65% of 4-t-octyphenol samples exceeding the threshold concentration for the substance suggested in the context of the Water Framework Directive (see reference in figure caption). The deep sediments in the Northern Baltic Proper contained levels 30 times higher than the threshold concentration.

Fish is not an appropriate matrix for monitoring nonylphenol, octylphenol and their ethoxylates because they are metabolized in fish (HELCOM, 2010).

The report "Hazardous substances of specific concern to the Baltic Sea" from HELCOM (2009) includes a broader review of NP/NPEO and OP/OPEO production and use, discharges, concentrations in the environment, data gaps, etc. The conclusions regarding data gaps are exactly the same for NP/NPEO and OP/OPEO. For OP/OPEO the conclusion reads: "*In general, there should be more measured data on OP/OPE levels both in discharges in the catchment area, and in sea water, biota and sediment of the Baltic Sea to examine if OP/OPE causes harmful effects on the marine environment. While few available data indicate that the OP levels in biota (fish) are not high, the levels in the sediment may have adverse effects on the Baltic marine environment. In general, the measured OP levels in treated municipal wastewater may cause both acute and chronic effects in recipient waters. Thus information on both the occurrence of OP (and OPE) in the in sea water, biota and sediment of the Baltic Sea and its presence in discharges (e.g. WWTPs, landfills and waste sorting sites) in the Baltic Sea catchment area is greatly needed. There is also need for eco-*

toxicological data on sediment dwelling organisms in order to better define the OP PNEC estimate for the benthic community."

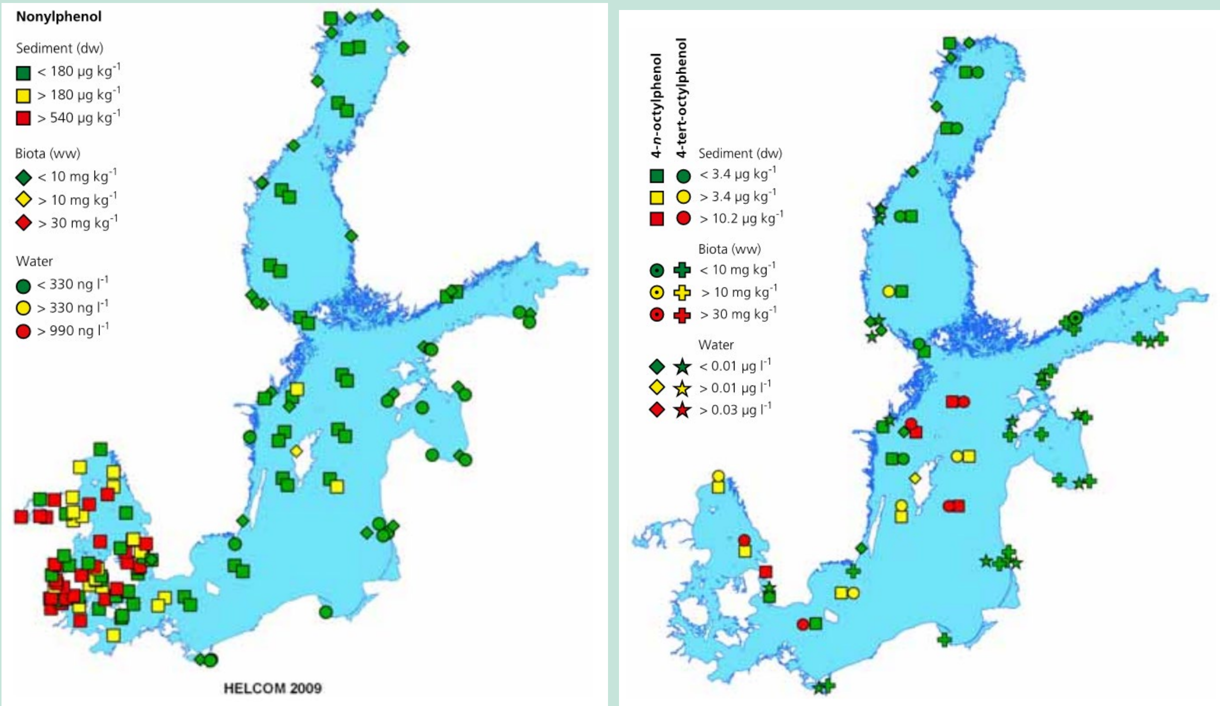


FIGURE 9

STATUS OF NONYLPHENOL, 4-N-OCTYLPHENOL AND 4-*TERT*-OCTYLPHENOL IN SEDIMENT, BIOTA AND WATER IN THE INNER DANISH WATERS AND THE BALTIC SEA. THE THRESHOLD CONCENTRATIONS FOR SEDIMENT AND BIOTA ARE FROM ANON. (2005), AND FOR WATER FROM THE EU PRIORITY SUBSTANCE DIRECTIVE (DIRECTIVE 2008/105/EC) (HELCOM, 2010)

Screening of selected phenolic substances in the Nordic environment

A screening of selected phenolic substances in the Nordic environment was initiated by the Nordic Chemicals Group and financed by the Nordic Council of Ministers. All six Nordic countries participated in the project that included the sampling and analysis of 120 samples from different environmental compartments (Hansen and Lassen, 2008). The study included the analyses of 13 different phenolic compounds including tert-butylphenols, di-*tert*-butylphenol, octyl-, nonyl- and dodecyl phenols) octyl- and nonylphenol mono-ethoxylates. The results are shown in Annex 4 and summarised as follows by Hansen and Lassen (2008).

Overall, recipient water and background water samples did, however, have relatively low concentrations of most substances. NP-mix, dodecylphenol and nonylphenol monoethoxylate were present in detectable amounts, and surface water from Tórshavn had the highest estimated concentrations of NP-mix.

In the background sediments samples from Kattegat and Oslo fjord, NP-mix, NP, 4-*tert*-BP and NP1EO was found in concentrations above the detection limits. In some sample sediments from recipient environments, other substances could be found in relatively high concentrations of several hundred µg/kg.

The NP-mix (various nonylphenol isomers), dodecylphenol, 4-*tert*-octylphenol and nonylphenol monoethoxylate were those AP/APEO substances found in highest concentrations in all sewage water samples.

The sludge samples demonstrated the highest content of the analysed substances, and in terms of the sewage water samples, NP-mix and dodecylphenol were detected in the highest concentrations, whereas the ethoxylates had been significantly reduced. Compared to sludge, both soil from landfill sites and sediments were low in concentrations of most AP/APEO.

Sources of AP/APEO to the Baltic Sea
Within the framework of the multilateral project “Control of Hazardous Substances in the Baltic Sea Region”, sources of NP, NPEO, OP and OPEO to the Baltic Sea environment have been analysed (COHIBA, 2012). Substance flow diagrams for the four substances are shown in Annex 4.

According to the study, the majority of the emissions of NP and NPEO to the Baltic environment are distributed to surface waters. The NP and NPEO emissions into the Baltic environment mainly come from industrial sources in Lithuania and Poland, whereas in the other countries, municipal waste water treatment plants (MWWTPs) are the dominant sources (described in section 4.2).

According to the COHIBA study, a small fraction of the emissions of OP and OPEO in the Baltic area is distributed to air and the main part is rather evenly distributed to surface waters and land areas. The yearly loads differ significantly between countries, also on a per capita basis. The emissions were dominated by releases of OP from the product service life category, where the main source was emissions from abrasion from tyres, which represent almost 100% of the reported emissions in this category. Industrial sources include the use of OP-based resins in insulation varnishes (about 50% of the industrial emissions) in Poland and Germany and the manufacture of OP-based resins (about 10% of the industrial emissions) in Poland and perhaps Estonia.

Emissions from MWWTPs were of some relevance for OP and OPEO in all of the Baltic countries. The emissions to wastewater primarily originate from private washing of textiles containing OPEO, which represents 30-50% of the total emissions to wastewater.

The North Sea Environment
Three alkylphenols on the OSPAR List of Chemicals for Priority Action, nonylphenol, octylphenol and 2,4,6-tri-*tert*-butylphenol. OSPAR chemicals identified for priority action have most recently been assessed in the OSPAR quality status report of 2010 (OSPAR, 2010), but the report does not include a summary for the APs.

The updated OSPAR background document for NP from 2009 states that recent monitoring data about the occurrence of AP/APEO in the aquatic environment in the North Atlantic were hard to find in the literature (OSPAR, 2009).

A background document for 2,4,6-tri-*tert*-butylphenol was developed in 2006 (OSPAR, 2006). In response to the call for a monitoring strategy, the UK as a lead country for the substance has developed a strategy and carried out a one-off survey on 2,4,6-tri-*tert*-butylphenol in sediments in industrial estuaries around the UK coast. A number of samples were below the detection limit, but there were also several positives ranging from 0.01 to 0.09 mg/kg of dry sediment (OSPAR, 2009).

7.4 Human exposure and biomonitoring

7.4.1 Intake of AP/APEO

Tolerable daily intake
A tolerable daily intake (TDI) value has not been established at EU level. Nielsen *et al.* (2000) from the Danish Institute of Food Safety and Toxicology, Danish Veterinary and Food Administration (now DTU Food – National Food Institute) have set health based TDI values for NP at 0.005 mg/kg b.w./day and for NPEO at 0.013 mg/kg b.w./day.

No other studies have been obtained.

TDIs for other AP or APEO have not been obtained.

AP/APEO in food

Alkylphenols and their ethoxylates are not included in the monitoring of chemical contaminants in food in Denmark. No data on the content of nonylphenol or any other AP/APEO in food, or estimates of the total intake of the substances with food in Denmark have been obtained.

The EU Risk Assessment for NP and NPEO states that no estimates of dietary exposure to nonylphenol using EU data are available (ECB, 2002). The EU Risk Assessment for butylphenol does not include monitoring data on butylphenol in food.

Guenther *et al.* (2002) analyzed NPs in 60 different food items commercially available in Germany. The concentrations of NPs on a fresh weight basis varied between 0.1 and 19.4 µg/kg regardless of the fat content of the foodstuff. Based on data on German food consumption rates and the analyses of NPs in food, the daily intake of NP for an adult was calculated to be 7.5 µg/day. For infants exclusively fed with breast milk or infant formulas daily intakes of 0.2 µg/day and 1.4 µg/day, respectively, was estimated. For an adult of 60 kg the estimated TDI would correspond to an intake of 0.3 mg NP/day which is 40 times more than the intake calculated by Guenther *et al.* (2002).

Gyllenhammer *et al.* (2012) has recently analysed NP in Swedish food and exposure of Swedish nursing women. In food, NP was to some extent found at levels above limit of quantification (LOQ 20 µg/kg fresh weight) in fruits, cereal products, vegetables, and potatoes. The estimated mean NP intake per capita was 27 µg/day (medium estimate) i.e. about four times higher than the intake estimated by Guenther *et al.* (2002) but still significantly below the estimated TDI. In blood serum, free NP above the limit of detection (limit of detection 0.5 ng/g) was detected in 46% of the study participants while detectable levels of total NP (limit of detection 0.8 ng/g) were observed in 43%. The results indicate according to the authors that there is a continuous source of exposure to NP that is high enough for free NP to be detected in some consumers. A significantly higher total consumption of fruits and vegetables was reported in questionnaires by participants with NP levels at or above LOD than among women with levels below LOD. This result is supporting the market basket results of relatively high NP levels in these types of food.

Ferrara *et al.* (2008) reports data on AP and APEO in seafood from the Tyrrhenian Sea. Of the measured AP and APEO, NP was generally detected at the highest concentrations. On the basis of the results of the study, the daily intake of NPs was according to the authors estimated to be much lower than the TDI proposed by the Danish Institute of Food Safety and Toxicology.

A Norwegian risk assessment of contaminants in sewage sludge applied to Norwegian soils estimates total intake with food from soils after 100 years' use of sewage sludge but does not provide data on the present situation (VKM, 2009).

Food contact materials

A significant source of the AP and APEO in food may be migration from food contact materials.

The Risk Assessment for nonylphenol (ECB, 2002) estimates that the main exposure to nonylphenol from food contact materials is via 4-nonylphenyl phosphite (TNPP). Nonylphenol is used in the production of TNPP, which is used as a co-stabiliser and as an antioxidant in the synthesis of various polymers such as butadiene rubber, polystyrene, polyethylene and polyvinylchloride. It is also used in the production of food contact plastics. Nonylphenol is present in TNPP as a residual impurity and can be formed as a result of acid hydrolysis of TNPP. The Risk Assessment estimates the worst case potential exposure from food contact materials at 0.06 mg NP/day. NPEO in paper and paperboard (now restricted) was estimated to potentially contribute with another 0.08 mg NP/day.

The EU Risk Assessment for 4-*tert*-butylphenol (4-*tert*-BP; ECB, 2008) states that the potential consumer exposure is via direct use of mixtures with phenolic resins or epoxy resins containing residual 4-*tert*-BP monomers, or via use of the final articles containing residual concentration of 4-*tert*-BP. The main exposure from final products is expected to be from adhesives and possibly canned food. Consumers may also be exposed to 4-*tert*-BP in drinking water from drinking water reservoirs or pipelines and from polycarbonate used for food contact material. Some exposure may also occur from various consumer articles such as cosmetics, eyeglass frames, tooth- and hair brushes, and hearing aids; however, exposure from these products is considered to be low. The main routes of exposure to consumer products are by dermal contact (e.g. use of adhesives) and by ingestion of food products into which 4-*tert*-BP has migrated from the food/water container or packaging (e.g. food contact applications). For humans exposed indirectly from the environment, the main exposure is expected to be from ingestion.

Other sources of exposure to NP
The EU Risk Assessment for 4-nonylphenol mentions that consumers may be exposed to low levels of residual, unreacted nonylphenol NP in consumer products (ECB 2002). Furthermore, NP may be present at very low levels in pesticides, cosmetics, spermicides and pharmaceutical preparations (now restricted). The EU Risk Assessment concludes that even considering these exposures together on a daily basis, there is no concern for human health.

AP/APEO used as food additives
Some of the short-chained APs are used as food additives and have been evaluated by the European Food Safety Authority, EFSA. In a scientific opinion of EFSA Panel on Food Additives and Nutrient Sources added to Food on the use of 2,6-di-*tert*-butyl-p cresol (BHT, butylated hydroxytoluene) the Panel concludes that BHT is not of concern with respect to genotoxicity and that any carcinogenicity would be thresholded (EFSA, 2012). On the basis of the present database the Panel derived an up-dated Acceptable Daily Intake (ADI) of 0.25 mg/kg bw/day. Exposure of adults to BHT is unlikely to exceed the newly derived ADI at the mean and at the 95th percentile. For exposure of children to BHT from its use as food additive, the Panel noted that it is also unlikely that this ADI is exceeded at the mean, but is exceeded for some European countries (Finland, The Netherlands) at the 95th percentile.

Drinking water
The limit values for the sum of NP and OP in drinking water when leaving the water works in Denmark are 20 µg L (Statutory Order 1024 of 31/10/2011). The same value applies to ground water (Danish EPA, 2010). For other phenol compounds the limit value is 0.5 µg/L for each.

In 730 samples from water works wells from the period 1993-2003 APs were found in concentration above the detection limit in 4% of the samples (GEUS, 2004). In none of the samples the concentration exceeded the limit values. In 839 samples of water from water works wells from 2007-2010, nonylphenol was found in concentrations above 0.5 µg/L in 13 samples (GEUS, 2011). In 585 samples of ground waste from 2007-2008 NPEO was not found in a concentration above the detection limit in any of the samples (GEUS , 2010).

Data for other APs have not been identified.

7.4.2 Human biomonitoring data

No human biomonitoring data from Denmark have been obtained.

Alexandros *et al.* (2012) has recently reviewed trends in biomonitoring of bisphenol A, 4-t-octylphenol, and 4-nonylphenol and the following is to a large extent extracted from this review, but information from some of the original papers and on other AP/APEOs is added.

Studies concerning AP/APEO exposure assessment and epidemiology studies on human population are limited.

Calafat *et al.* (2008) measured 4-*tert*-octylphenol (4-t-OP) in urine samples from a population of 2,517 subjects in the USA National Health and Nutrition Examination Survey (NHANES). The subjects were above the age of 6 years. 4-t-OP was detected in 57.4% of the participants with total (free plus conjugated species) concentrations ranging between 0.2 ng/mL and 20.6 ng/mL.

Tan and Mohd (2003) measured 4-t-OP in 180 cord blood samples collected during delivery at the University Malaya Medical Centre in Malaysia; 4-t-OP was detected in 31 samples in concentrations from <0.05 to 1.15 ng/mL.

Ademollo *et al.* (2008) studied the presence of 4-NP, 4-OP, nonylphenol monoethoxylate and two octylphenol ethoxylates (OP1EO and OP2EO), in breast milk in samples from Italian women. NP was the contaminant found at the highest levels with mean concentrations of 32 ng/mL, about two orders of magnitude higher than OP (0.08 ng/mL), OP1EO (0.07 ng/mL) and OP2EO (0.16 ng/mL). On the basis of the concentrations found in the breast milk samples, a maximum NP daily intake of 3.94 µg/kg bw/day was calculated (=0.004 mg/kg bw/day). This is only slightly below the estimated TDI. No newer studies to confirm this result has been identified.

Chen *et al.* (2010) determined 4-NP and 4-OP in 59 human milk samples in Central Taiwan and correlated findings with demographics and dietary factors. Women who consumed over the median amount of cooking oil had significantly higher 4-OP concentrations (0.98 ng/mL) than those who consumed less (0.39 ng/mL). NP concentration was also significantly associated with the consumption of fish oil capsules.

Lopez-Espinosa *et al.* (2009) also determined 4-NP and 4-OP concentrations in adipose tissue of 20 non-occupationally exposed women living in Southern Spain. 4-NP and 4-OP were detected in 100% and 23.5% of subjects, respectively. The median level of 4-NP was 57 ng/g and that of 4-OP was 4.5 ng/g of adipose tissue. The study found that body mass index was associated with 4-NP levels.

7.5 Summary regarding monitoring and exposure

Monitoring data from recent years have demonstrated that the concentration of NP in lake sediments in Denmark and in marine sediments from the Baltic Sea and the Inner Danish Waters exceeded the predicted no-effect concentration (PNEC).

OP was found in both lake sediments and marine sediments, but at lower concentration. HELCOM, however, concludes in the most recent assessment report that the concentrations of OP in surface sediment were very high, with 50% of 4-n-octylphenol samples and 65% of 4-*tert*-octyphenol samples exceeding the threshold concentration for the substance suggested in the context of the Water Framework Directive.

Other AP/APEO are not monitored but have been assessed as part of the Nordic survey. In general the concentrations of the other AP/APEO are considerably lower than the NP concentration, but in some recipient environments (e.g. close to towns) the level of the 4-*tert*-BP and DP may be in the same range as the concentration of NP. In general limited data are available on the sources of 4-*tert*-BP and DP to the aquatic environments and the possible environmental risks of the actual concentrations.

A review from HELCOM concludes that in general, there should be more measured data on NP/NPEO and OP/OPEO levels in discharges in the Baltic Sea catchment area, in sea water, biota and sediment of the Baltic Sea to examine if the substances cause harmful effects on the marine environment. There is also need for ecotoxicological data on sediment dwelling organisms in order to better define the NP and OP PNEC estimates for the benthic community.

AP/APEOs are not included in the monitoring of chemical contaminants in food in Denmark and very limited data on the intake with food is generally available. Daily intake estimated on the basis of food data indicates that the intake of NP via food is well below the tolerable daily intake (TDI) established by the Danish Institute of Food Safety and Toxicology. A recent Swedish measure relatively high NP levels in fruit and vegetables and estimate to total daily intake with food to be higher than reported in previous studies. Some estimates on the basis of biomonitoring data indicate that the intake may be close to the TDI and further are needed to clarify if the total intake from all sources is close to the TDI for NP.

For other AP/APEO hardly any data are available on the intake with food reflecting that AP/APEO in food has not been of major concern.

8. Information on alternatives

Information on existing assessments of alternatives to AP/APEO is summarised in this chapter.

8.1 Alternatives to alkylphenol ethoxylates

The majority of the literature on alternatives to AP/APEO concern alternatives to the use of the alkylphenol ethoxylates, particularly the NPEO and OPEO, which are responsible for the majority of the releases of AP/APEO to the environment.

As described in chapter 2, the following uses of NPEO are restricted via Annex XVII to the REACH Regulation, with exceptions for uses in closed systems: Cosmetics, cleaning agents, textiles and leather processing auxiliaries, agricultural teat dips and pesticides/biocides, metal works, pulp and paper, and other personal care items except spermicides. No restriction on the use of OPEO is in force at EU level.

According to the OSPAR background document for NP/NPEO, the substitutes introduced for the use area “detergents and cleaning agents” are mainly alcohol ethoxylates (OSPAR, 2009). In terms of environmental risk, alcohol ethoxylates appear to present a clear advantage over NPEs, mainly owing to issues of biodegradability. According to industry quoted by OSPAR (2009), the substitutes in the use area ‘detergents and cleaning agents for domestic and industrial uses’ are mixtures of anionic and nonionic surfactants, such as linear alcohol ethoxylates, fatty acids and derivatives, fatty amines or unsaturated hydrocarbons. OSPAR (2009) reports that according to the paint industry in Sweden, mostly fatty alcohol ethoxylates, but also esterified linseed oil, different kinds of nonionic tensides, phosphate esters, and potassium polycarboxylates are used as alternatives to alkylphenol ethoxylates in the binding polymer emulsion of water-based paints. According to the adhesive industry, fatty alcohol ethoxylates are mostly used as alternatives in the polymer emulsion of water- based adhesives. The major difficulties are in replacing NPEs in acrylic and chloroprene rubber dispersions. According to the adhesive industry, fatty alcohol ethoxylates are mostly used as alternatives in the polymer emulsion of water- based adhesives; the major difficulties are in replacing NPEs in acrylic and chloroprene rubber dispersions. The document concludes that alternatives seem to be available for many NPEO uses, though information was not found on specific alternatives to some uses.

The US EPA Design for the Environment (DfE) Program presents a recent assessment of alternatives to NPEOs (US EPA DfE, 2012). Based on information from surfactant and cleaning product manufacturers who have partnered with US EPA's DfE programme, the NPEO alternatives selected for assessment were comparable to NPEO in cost and performance, especially when viewed as part of a detergent system. According to the study, formulators will often replace an NPEO surfactant with a blend of two or more surfactants (e.g. a linear alcohol ethoxylate plus an alkyl glycoside). Depending on product type, a change in surfactant may also prompt other ingredient or formulary adjustments.

The US EPA DfE (2012) assessed nine alternatives to NPEO surfactants, one from each of the major surfactant classes DfE has seen in its evaluation of detergent and cleaning products in its Safer Product Labelling Program. Note that the surfactant uses involved also included uses which are currently regulated in the EU though the use restriction in Annex XVII to REACH.

DfE selected the ten featured chemicals — $NPEO_9$ (CAS No 127087-87-0 with 9 oxylate groups), octylphenol ethoxylate $(OPEO)_{10}$ (CAS No 9036-19-5 with 10 oxylate groups), and the eight alternatives which are considered as safer representatives of their surfactant class and based on:

- the availability of an adequate dataset (i.e. sufficient experimental data to address all endpoints in the DfE Criteria for Safer Surfactants); and, except for $NPEO_9$ and $OPEO_{10}$,
- frequent use in DfE-recognized formulations, and/or inclusion on the CleanGredients® website of safer surfactant alternatives.

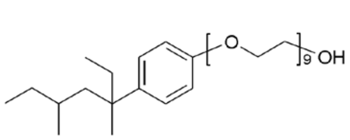
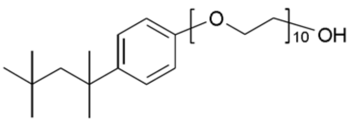
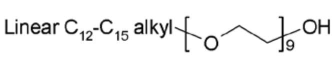
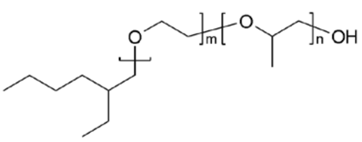
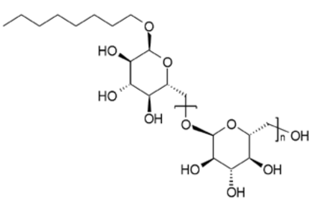
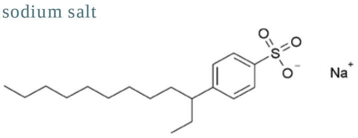
The substances were assessed on the basis of the following environmental characteristics:
- rate of aerobic biodegradation,
- hazard profiles of the degradation products, and
- degree of aquatic toxicity of the parent compound and degradation products.

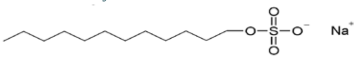
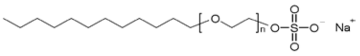
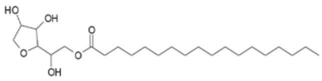
Since the surface active nature of surfactants causes toxicity to aquatic organisms, the criteria weigh these characteristics holistically and require that surfactants with higher aquatic toxicity demonstrate a faster rate of biodegradation without degradation to products of concern.

An overview of the assessment results from US EPA DfE (2012) can be seen in Table 37.
The alternatives in general have a better score in terms of degradation products of concern and persistence in the environment. The acute and chronic aquatic toxicity of the alternatives are at the same level of toxicity of the NPEO and OPEO or even higher. According to US EPA DfE (2012) OPEO is more persistent in the environment than NPEO.

The report does not discuss the technical or economic feasibility of the alternatives for different applications.

TABLE 37
OVERVIEW OF THE ASSESSMENT OF NPEO AND SELECTED ALTERNATIVES TO NPEO FROM EACH OF 9 SUBSTANCE CLASSES (US EPA DFE, 2012)

Chemical	CAS No	Fate		Aquatic toxicity[1]			Meets DfE Surfac-tant Criteria	Synthesis
		Persistance	Degradates of concern[2]	Acute	Chronic	Degradate Aquatic toxicity		
Nonylphenol ethoxylates (NPEs)								
Nonylphenol ethoxylate (9EO); NPE9 	127087-87-0	M	Y[3]	H	M	VH	N	Nonylphenol is prepared from phenol and tripropylene, yielding a highly branched, predominantly parasubstituted alkylphenol. Reaction of nonylphenol with ethylene oxide yields NPE surfactants.
Octylphenol ethoxylates (OPEs)								
Octylphenol ethoxylate (10EO); OPE10 	9036-19-5	H[4]	Y[5]	H	*H*	VH	N	Octylphenol is prepared from phenol and diisobutylene, yielding a highly branched, predominantly para-substituted alkylphenol. Reaction of octylphenol with ethylene oxide yields OPE surfactants.
Linear alcohol ethoxylates (LAE)								
C12-15 Alcohols, ethoxylated (9EO) 	68131-39-5	VL	N	VH	H	L[6]	Y	Linear alcohols, derived from fatty acids or alpha-olefins, are reacted with ethylene oxide to yield LAE surfactants. Many detergent grade LAEs make use of alcohols in the C10-C18 range.
Ethoxylated/propoxylated alcohols								
Oxirane, methyl-, polymer with oxirane, mono(2-ethylhexyl ether); Ecosurf EH-9 	64366-70-7	L	N	M	*M*	L[6]	Y	2-Ethylhexanol is reacted with ethylene oxide and propylene oxide to yield this product. Other surfactants in this class use linear alcohols in place of 2-ethylhexanol.
Alkyl polyglucose (APG)								
D-Glucopyranose, oligomeric, decyl octyl glycosides 	68515-73-1	VL	N	M	M	L[6]	Y	Fatty alcohols are reacted with glucose in the presence of an acid catalyst. Similar products may be prepared from other sugars, such as sucrose.
Linear alkylbenzene sulfonates (LAS)								
Benzenesulfonic acid, C10-13-alkyl derivs., sodium salt 	68411-30-3	VL	N	H	H	L[6]	Y	Benzene is alkylated with a linear olefin (either internal or terminal) in the presence of an acid catalyst, yielding a linear alkyl benzene (LAB). The LAB intermediate is sulfonated and neutralized to yield a linear alkyl

Chemical	CAS No	Fate		Aquatic toxicity[1]			Meets DfE Surfactant Criteria	Synthesis
		Persistance	Degradates of concern[2]	Acute	Chronic	Degradate Aquatic toxicity		
								benzene sulfonate surfactant.
Alkyl sulfate esters (AS)								
Sodium lauryl sulfate 	151-21-3	**VL**	**N**	**H**	**H**	**L**[6]	Y	Fatty alcohols are sulfated and neutralized to yield alkyl sulfate ester salts.
Alkyl ether sulfates (AES)								
Polyoxy(1,2-ethanediyl), alpha-sulfo-omegadodecyloxy-, sodium salt 	9004-82-4	**L**	**N**	**H**	**H**	**L**[6]	Y	Linear alcohol ethoxylates are sulfated and neutralized to yield alkyl ether sulfate salts.
Sorbitan esters								
Sorbitan monostearate 	1338-41-6	**L**[7]	**N**	**H**	**H**	**L**[6]	Y	Fatty acid methyl esters are reacted with sorbitan in the presence of a basic catalyst to yield sorbitan esters.
VL = Very low hazard **L** = Low hazard **M** = Moderate hazard **H** = High hazard **VH** = Very high hazard - Endpoints in colored text (**VL**, **L**, **M**, **H**, and **VH**) were assigned based on experimental data. Endpoints in black italics (***VL***, ***L***, ***M***, ***H***, and ***VH***) were assigned using estimated values and professional judgment (Structure Activity Relationships). Y=Yes...N=No								

Annotation: VL = Very low hazard L = Low hazard M = Moderate hazard H = High hazard VH = Very high hazard. Endpoints in coloured text (VL, L, M, H, and VH) were assigned based on experimental data. Endpoints in black italics (VL, L, M, H, and VH) were assigned using estimated values and professional judgment (Structure Activity Relationships). Y=Yes...N=No.

Levels of 1,4-dioxane impurity in ethoxylated surfactants are limited to 100 ppm in the product formulation.

1. Acute toxicity data reviewed include 96-h LC50 assays in fish, 48-h EC50 or LC50 assays in invertebrates and 72-96-h EC50 assays in algae. Chronic toxicity values are not required for rating if adequate acute data are available.
2. Degradation products of concern for surfactants are compounds with high acute aquatic toxicity (L/E/IC50 ≤ 10ppm) and a slow rate of biodegradation (greater than 28 days).
3. One potential degradation product, nonylphenol, raises concerns for its potential to affect the endocrine system.
4. Half-life cannot be reliably determined from the available biodegradation data for octylphenol ethoxylates. Based on biodegradation rate data, the time to achieve 50% degradation (as measured by oxygen demand) appears to be somewhat longer than 60 days.
5. One potential degradation product, octylphenol, is more persistent and more toxic than the parent compound.
6. According to available biodegradation studies, this chemical ultimately degrades to CO2, H2O, and mineral salts, and therefore no aquatically toxic degradation product are expected.
7. The available biodegradation data do not include information on the 10-day window.

A Canadian assessment of alternatives to NPEO prepared for Environment Canada from 2002 (Campbell, 2002) states that linear alcohol ethoxylates (as alternatives to NPEO) have a wide range of physical and nonionic properties for various applications and that they are excellent wetting agents, emulsifiers, and detergents. They are generally moderate foamers - a desirable characteristic for many of the applications in the current nonionic surfactant market. According to the study, the cost of surfactants fluctuates with the price of raw materials, for example the cost of ethoxylates fluctuates with the price of ethylene, and surfactants produced from oleochemical feedstocks fluctuate with the price of, for example, plant-derived oils. In the years before 2o02, the price of the main alternatives to NPEO had been, on average, ~20-40% higher than NPEO. The report identifies a few applications for which there did not appear to be cost effective alternatives to NP/NPEO at that time. These include:

- Emulsion polymerisation – NPEO used to produce polymer dispersions e.g. used in coatings
- The use of tris-nonylphenylphospite (TNPP) as an anti-oxidant and stabilizer for plastics/resins.

The UK nonylphenol Risk Reduction Strategy from 1999 (Footit, 1999) indicates that the alternatives to NPEO in emulsion polymerisation are often other APEs which pose a similar level of risk while creating significant costs. NPEO and OPEO are used as apolymerization aids in the manufacture of polymer emulsions. Emulsion polymerization is a type of polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer are in a continuous phase of water. The surfactant (also known as emulsifier) stabilises the emulsion to prevent unwanted fusion or coagulation (Nwaogu, 2006). The end applications for the polymer dispersions based on NPEOS and OPEOs include paints, paper, inks, adhesives and carpet backings (Footit, 1999; Nwaogu, 2006). For OPEOs it is indicated that the paint is the major end application (Nwaogu, 2006). According to Nwaogu (2006) there are considerable difficulties in trying to differentiate between the use of OPEOs in water-based paints and the use of OPEOs in emulsion polymer manufacture used in water-based paints. Emulsion polymerisation and the uses of NPEO in paint, adhesives and sealant are not covered by the current restriction. Emulsion polymerisation and the use of NPEO in paint took up 12% (7,000 t/y) and 5% (4,000 t/y) of the total use of NPEO before the restriction, likely still today two of the major uses of NPEO. Furthermore, in 2001, 550 tonnes of OPEO at EU level were used as emulsifiers and 50 tonnes were used in binders for water-based paints.

As part of the SOCOPSE project on priority hazardous substances under the Water Framework Directive, Feenstra *et al.* (2009) give an overview of existing and emerging alternatives to NPEO in the European context. The overview is to a large extent based on The UK nonylphenol Risk Reduction Strategy from 1999 (Footit, 1999) and Danish studies mentioned below, and do not include much updated information. Alcohol ethoxylates are indicated as substitutes for NPEO in paints and a number of other applications whereas, for emulsion polymerisation, OPEO is indicated as a substitute.

The UK Risk Reduction Strategy for OP/OPEO (Nwaogu *et al.*, 2006) includes a discussion of the possibilities for substituting OPEO in binders in paints and in emulsion polymer manufacture. The considerations of Nwaogu *et al.* (2006) are summarised in Table 38.

The study does not provide information of the possible costs of alternatives and changes in manufacturing processes. Environmental and health effects of alternatives as compared with the OP/OPEO are not assessed in the study.

TABLE 38
SUMMARY OF DISCUSSION OF ALTERNATIVES TO OPEO (BASED ON NWAOGU *ET AL.*, 2006)

Alternative to	Alternatives	Remarks
OPEO use in binders in paints	• Depending on paint type, the binders may be replaced with other binders where OPEO is not required • Styrenate resin-free co-binders in acryl latex paints • Polyvinyl acetate binders • Epoxy binders • Polyurethane binders • C10–C15 alcohol ethoxylates	Styrenated resins used as co-binders in acrylic paints may contain 4-*tert*-octylphenol. Other alternatives to OPEO identified by industry in this sector are based on C10–C15 alcohol ethoxylates.
OPEO use in emulsion polymer manufacture - Specifically formulation of PTFE emulsion	• Fatty alcohol ethoxylates (Cas No 61725-89-1) • Fatty alcohol ethoxylates (Cas No 65150-81-4) • Ethoxylated secondary alcohol (Cas No 25322-68-3)	These alternatives are identified by industry. The alternatives in themselves are deemed inferior to OPEO as regards performance, but this can be overcome by formulation with other components. The unit cost of raw material to replace OPEO were expected to be twice that of the OPEO containing product in 2006. One time costs for the substitution programme were estimated at around £50,000 in technical support, sampling and staff time. Work undertaken under the OECD SIDS programme indicated that while some fatty alcohols may be toxic to aquatic organisms, they do not bioaccumulate or have endocrine disrupting effects and are not expected to be as persistent as OP.

Experience from Danish studies
As regards the applications of NPEO and OPEO in binders for paints, wood preservatives, glues and sealants, Rasmussen *et al.* (2003) identified the substance groups in Table 39 as tested and or commercially applied alternatives to APEO in binders with the help of industry experts. The study quotes a specific paint manufacturer successful in replacing APEO for the general water-based paints and wood preservatives, but still used APEO for some niche products (not further specified). The main part of the APEO was used in binders. It is indicated that the replacement of the APEO is relatively resource consuming, but the study does not include an assessment of the economic feasibility of the replacement.

The results of the assessment for environmental characteristics are depicted in the table with 1 as the best score and 5 as the worst score. For health effects, 1 is the best score and 3 is the worst (see reference for details). A broader group of substances, of which some were not tested or applied in the involved companies, were identified as potential alternatives to APEO in binders. All substance groups assessed in the study, and the related environment and health scores assigned are listed in Table 40 and Table 41. These substance groups are presented as well known surfactants.

TABLE 39
ALTERNATIVES TESTED OR COMMERCIALLY APPLIED IN INVOLVED PAINT, WOOD PRESERVATIVES, ADHESIVES AND SEALANTS INDUSTRIES AND SCORES FOR THEIR ENVIRONMENTAL AND HEALTH ASSESSMENT (FROM RASMUSSEN *ET AL.* 2003)

Group of substances	Used in the production of binders	Tested for production of paints and tinting pastes	Environmental group General assessment	Health group General assessment
APEO			5	3
Alkyl sulfates (AS)	x	x	1-2	3
Alkyl ether sulfates	x	x	1-2	2-3
Alcohol ethoxylates	x	x	1-2	1 or 3
Alkyl mono ethanol amide ethoxylates	x	x	1	1 or 3
Alcohol alkoxylates	x	x	4-5*	1*
LAS	x		1	3
Alkyl ether phosphates	x		4*	1 or 3*

*Rating is based on inadequate data and large variations with regard to environmental properties may occur within the tenside group, which is the reason why a few tenside compounds may differ considerably from the stated environmental rating.

TABLE 40
ALL POTENTIAL ALTERNATIVES ASSESSED IN RASMUSSEN *ET AL.* (2003) FOR BINDERS USED IN PAINT, WOOD PRESERVATIVES, ADHESIVES AND SEALANTS INDUSTRIES AND SCORES FOR THEIR ENVIRONMENTAL ASSESSMENT

Group of substances	Subgroup	Environmental group General assessment	Remarks
APEO	-	5	
Alkyl sulfates (AS)	Linear	1-2	
Alkyl ether sulfates	Linear	1-2	
	Branched	1-2	Some not readily degradable branched AES belong to group 4 or 5.
Alcohol ethoxylates	Linear < 20 EO	1-2	
	Linear > 20 EO	1	
	Branched	1-2	Some not readily degradable branched AES belong to group 4 or 5. Several AES are not degradable under anaerobic conditions.
Alkyl mono ethanol amide ethoxylates	-	1	Rating is based on inadequate data.
Alcohol alkoxylates	-	4-5	2 and 1 respectively when readily degradable. Data showed varying environmental properties.
LAS	-	1	Not degradable under anaerobic conditions. On the List of Undesirable Substances from the Danish EPA.
Alkyl ether phosphates	-	4	General assessment is based on inadequate data. 1 if readily degradable.

TABLE 41
ALL POTENTIAL ALTERNATIVES ASSESSED BY RASMUSSEN *ET AL.* (2003) FOR BINDERS USED IN PAINT, WOOD PRESERVATIVES, ADHESIVES AND SEALANTS INDUSTRIES AND SCORES FOR THEIR HEALTH ASSESSMENT

Group of substances	Length of carbon chain	Ethoxylates units	Health hazard group
APEO	-	-	3
Alkyl sulfates	C12	-	3
Alkyl ether sulfates	C9-15 C9-15	> 7 2-3	2 3
LAS	C9-14	-	3
Alkyl ether phosphates	13-18	-	3
Alcohol ethoxylates	-	5-20 > 20	3 1
Alcohol alkoxylates	-	3-9 EO and 4-6 PO	1*
Alkyl mono ethanol amide ethoxylates	-	>12 <5	1* 3*

* Rating is based on inadequate data.

Hoffman *et al.* (2003) assessed selected alternative APEO-free raw materials for binders in the manufacture of paints in cooperation with a Danish paint manufacturer. The technical test of alternatives was conducted in the laboratories of the paint manufacturer and demonstrated that it would be possible to replace APEO and raw materials containing APEO. The substitution process would, however, be time and resource consuming, as many raw materials with different functions in the paint have to work together, while retaining as much of the original formulation as possible to avoid complete reformulation. The identified alternatives are summarised in Table 42.

During the project the company replaced a number of raw materials containing APEO with alternatives. The APEO-free raw materials were all based on three groups of surfactants: alkylsulfates, alkylether sulfates and alcohol ethoxylates.

As regards the environment and health characteristics of the three alternatives applied by the company, Hoffman *et al.* (2003) stated the following: "*These three groups of surfactants are in general easily degradable under aerobic as well as anaerobic conditions and the surfactants are toxic or very toxic to aquatic organisms. Alkyl sulfates and alkylether sulfates are not considered to be bioaccumulating whereas a few alcohol ethoxylates (longchained with few ethoxylate units) have a potential for bioaccumulation. The alkylphenol ethoxylates, which the above surfactants have replaced, have on the other hand the problem that their degradation products (for instance nonylphenol) are very toxic to aquatic organisms, are not easily degradable and have at the same time a tendency to bioaccumulation. Even if the alternative surfactants in general are toxic or very toxic to aquatic organisms too, they are on the other hand also quickly degradable in the environment and for that reason there is an environmental advantage in substituting the APEOs, which are hazardous to the environment, with these alternative surfactants. With regard to health, there is furthermore the advantage of the substitution that the degradation product nonylphenol is avoided. For this product, evidence for hormone disturbing effects is found.*"

TABLE 42
SURVEY OF APEO SURFACTANTS USED IN BINDERS IN PAINT MANUFACTURE AND CORRESPONDING ALTERNATIVES (FROM HOFFMAN *ET AL.*, 2003)

Alkylphenol ethoxylate	Alternative
APEO	Ethoxylated branched acid alcohol (C12-15) saturated
	Fatty alcohol ethoxylated C9/11 saturated linear
Nonylphenol ethoxylate	Styrene/maleic anhydride polymer
	Surfactant? Secondary ethoxylated alcohol (C12-14)
	Ethoxylated acetylenic alcohol
Nonylphenol hydroxy polyoxyethylene	Ethoxylated fatty acid alcohol
	Ethoxylated fatty acid alcohol - C16-18
	Ethoxylated fatty acid - C12-14
Alkylphenol polyglycolether	Ethoxylated linear fatty alcohol
Octylphenoxy polyethoxyethyl phosphate **Octylphenoxy polyethoxyethanol**	Sodium lauryl sulfate (alkyl ester sulfate C10-16)
	Polyoxyethylene tridecyl etherposphate Tridecylpoly (ethyleneoxy) ethanol
Alkylaryl polyglycolether	Alkylether sulfate, Sodium-salt (C10-16 7 EO)
	Alkylether sulfate, Sodium-salt Ethoxylated lineær fatty alcohol
Octylphenol ethoxylat	*Surfactant?*
Alkylaryl polyether octylphenoxy polyethoxyethanol	Secondary alcohol ethoxylate Secondary alcohols C12-14
Polyoxy ethandiyl nonylphenol	Ethoxylated unsaturated fatty acid monoethanolamide
	Ethoxylated fatty alcohol C12-14 (9.5 mol EO)
Alkylphenol alkoxylat	Fatty acid derivate (can not be further specified)

Note: 'Surfactant?' = information about surfactant in the APEO-free raw material has not been available.

New development

Most of the assessments are based on 10-year old data and new surfactants used as alternatives to the APEO may have been developed in recent years. It has been beyond the scope of the current assessment to prepare an updated alternative assessment, but a few websites of major manufacturers have been accessed for the latest information. The websites in general indicate a number of different surfactants as “APEO-free” or more specifically as APEO alternatives.

DOW Surfactants market a number of surfactants as alternatives to APEO in various applications including cleaning product formulations, paints and coatings, and emulsion polymerization (DOW, 2012). The agents are based on specialty ethoxylated surfactants in the ECOSURF® series and secondary and branched alcohol ethoxylates similar to those assessed above. The product finder illustrates the complexity of the applications of surfactants and has as regards the product group “emulsion polymerization applications” suggestions for the following specific applications: Post-add emulsifier, silicone emulsion stabilizers, acrylics-based systems, styrene/butadiene-based systems, suspension polymerization of vinyl chloride, styrene/acrylics- based systems, rubber, polychloroprene, and PVC film applications.

According to Clariant (2012a) traditionally used NPO in emulsion polymerization applications can be replaced by the company's surfactants based on fatty alcohol ethoxylates in the Emulsogen® LCN, Genapol® X, and Genapol® OX series, which are biodegradable and APEO-free. These agents and agents based on a number of other surfactants are marketed as APEO-free agents for different applications in paint manufacture e.g. wetting and dispersing agents and emulsifiers. A few of the company's agents for paint manufacture is not indicated as APEO-free (Clariant, 2012b).

8.2 Alternatives to 4-nonylphenol (NP), 4-*tert*-octylphenol and 4-*tert*-butylphenol

4-Nonylphenol, 4-*tert*-octylphenol and 4-*tert*-butylphenol are used for some of the same applications and 4-*tert*-octylphenol and 4-*tert*-butylphenol may potentially substitute for NP for some applications. As regards substitution of NP with OP, Nwaogu *et al.* (2006) considers that there is a low possibility (and incentive) for companies to move from NP to OP due to costs.

Except for NPEO production, little information is available on alternatives for NP used for the production of specific NP derivatives, where substitution is rather a question of substituting the derivatives. An example is phenolic resins, where the only substitutes specifically identified are based on other APs.

Footit et al. (1999) states that "*During consultation with industry, few alternatives were identified for replacement of NPs where they are used as an intermediate in the formation of other products. The products in question include phenol/formaldehyde resins (PFR), tri (4-nonylphenol) phosphite, phenolic oximes, epoxy resins and other plastic stabilisers. These products generally owe their properties to the use of NP in their formulation and such characteristics may be more difficult to duplicate using alternatives than appears to be the case with NPEs. The only alternatives which have been suggested as suitable at present are other alkylphenol compounds, particularly octylphenols. It is unlikely that these products would represent a suitable substitute because they are so structurally similar to NPs and toxic effects may be expected to be of a similar magnitude.*"

Newer assessments of alternatives to NP have not been identified. Feenstra *et al.* (2009) give an overview of existing and emerging alternatives to NP in the European context but base the assessment on Footit *et al.* (1999).

Nwaogu *et al.* (2006) includes a discussion of the possibilities for substituting OP with a focus on alternatives for the continued uses of 4-*tert*-octylphenol, i.e. in rubber formulation, insulating varnishes, printing inks, and marine and/or water-based paints. These three uses accounted for over 90% of the OP consumption in the UK. For textile finishing and plant/animal health products, a discussion of alternatives were not provided in the study as industry had broadly indicated that the availability of substitutes (amongst other factors) had resulted in a decrease in the use of OP in these sectors. The evaluated alternatives may to some extent also be alternatives to NP.

The EU Risk Assessment for 4-*tert*-butyl phenol (ECN, 2008) does not include any information on alternatives to the substance.

TABLE 43
SUMMARY OF DISCUSSION OF ALTERNATIVES TO 4-*TERT*-OCTYLPHENOL (BASED ON NWAOGU *ET AL.*, 2006)

Alternative to	Alternatives	Remarks
OP-based resins in the rubber industry (tackifiers)	– Rosin-based derivatives – Coumarone-indene resins consisting of indene, coumarone, styrene, etc. obtained from coal coke oven light oils – Aliphatic petroleum resins made from unsaturates obtained while cracking crude oil; – Terpene oligomers of alpha- or beta-pinene obtained from pine tree stumps.	Rosins are the most widely known alternatives, and with modern formulations, adequate rubber quality can be achieved for some purposes at low cost. Rosin and terpene-based tackifier resins are mentioned as of relevance for a number of rubber and adhesive applications. Quality considerations and resources and time needed for technical substitution make the manufacturers of automotive tyres reluctant to substitute phenolic resins. Rosin is a solid form of resin obtained from pines and some other plants, mostly conifers.
OP use in crosslinking agents in insulating varnishes	– Epoxy resins	The main alternatives to phenolic resins in insulating varnishes identified to date are the epoxy resins. Recent technology has made available a number of waterborne epoxy dispersions which are attractive alternatives to the solvent based resins. Most epoxy resins used today are based on bisphenol-A; other types of dispersions are commercially available including urethane modified epoxies, rubbermodified epoxies and novolac epoxies.

8.2.1 Alternatives to other specific AP/APEO

Environment Canada (2009) states that while alternatives for 2,4,6-tri-*tert*-butylphenol are available, the cost of alternatives is thought to be two to three times more expensive. The names of alternatives are not indicated.

No information was identified in the literature search on alternatives to the other APs and APEOs.

8.3 Conclusion on alternatives

Alkylphenol ethoxylates

Currently the largest use of APEOs is for paints and emulsion polymerization for various end uses such as paints, inks, adhesives and sealants.

The assessments of alternatives have mainly focused on alternatives to NPEO and OPEO but the identified studies that address the technical and economic feasibility of the substitution are about 10 years old.

The reviewed assessments of the environmental fate and toxicity of alternatives to NPEO reach the same conclusion: that the alternatives in general are of less concern as regards persistence and aquatic toxicity of degradation products. The acute and chronic aquatic toxicity of the alternatives are at the same level as the toxicity of the NPEO and OPEO or even higher. Concerning health hazards several of the alternatives have a similar score as NPEO.

The available information indicates that OPEO has in general not substituted for NPEO for the applications where NPEO is currently restricted. OPEO cannot be considered a viable alternative to NPEO.

For one of the main non-restricted applications of NPEO and OPEO, in paint varnishes and lacquers, the assessments reach different conclusions. A Canadian assessment indicated this application area as an area where feasible alternatives are not available, whereas a Danish assessment demonstrated that it would be possible to substitute APEO and raw materials containing APEO. The substitution process would however be time and resource consuming, as many raw materials with different functions in the paint have to work together, while retaining as much of the original formulation as possible to avoid complete reformulation. One Danish study reported that NPEO could be replaced in most water based paints.

A number of manufacturers of surfactants specifically market APEO-free surfactants for many different applications of emulsion polymerization and for paints. It is not clear from the available information if the remaining uses (e.g. as registered in the Danish Product Register) are for niche products.

EU, Nordic and German eco-labels target AP/APEOs for a number of product groups. Most of the targeted product groups represent applications where NP/NPEO is today restricted, and probably mainly replaced by non-AP/APEO alternatives. The ecolabels for indoor and outdoor paints and varnishes and paper envelopes (the adhesives of the envelopes) target products groups which are not covered by current restrictions. The fact that some products meet the ecolabels criteria indicates that non-AP/APOE alternatives are available for at least some of the products within the groups, but it cannot be used to conclude that alternatives are available for all types of products. It is e.g. in the available alternative assessments indicated that APEO can be replaced for the general water-based paints and wood preservatives, but is still used for some niche products.

A first step in an assessment of the technical and economic feasibility of alternatives to the remaining uses of NPEO and OPEO would be to identify more specifically the remaining uses of the substances. The use may to some extent be for niche products where substitution could be relatively costly, but it may also be the case that alternatives are readily available but not used due to marginally higher costs, and that the NPEO and OPEO are used for low-costs bulk products.

Alkylphenols
Alternatives to the major uses of NP and OP in the production of phenolic resins, epoxy resins, etc. are in general not available. The alternative solution would be to substitute phenolic resin or other products. Possible alternatives to OP-based resins have been identified, but an assessment of the advantages and drawbacks of using these alternatives is not available.

9. Overall conclusions

The results of the survey are summarised in the "Summary and conclusion" where the data are summarised for each of the main substances groups going across all chapters in the report. It is recommended to read this summary before this chapter.

A summary of the key consumption, environmental and health data on AP/APEO is provided in Table 44.

Main issues
None of the substances are considered to be PBT or vPvB substances and the table consequently do not have a row for indication of this. The substances are all biodegradable, but some are less biodegradable than others. For NP and OPEO, Annex XV SVHC dossiers have been submitted with the scope of "equivalent level of concern" based on the estrogenic activity of the substances (in the case of OPEO, the activity of the degradation products, OP). Table 44 indicates the endocrine disruptor class of the substances, but most substances have not been involved in the EU evaluation programme for endocrine disruptors (EC, 2012). As described in the chapter on health (which also applies to the environmental effects) the available data indicate that both the position (para > meta >ortho) and branching (tertiary > secondary = normal) of the alkyl group affect estrogenicity. Optimal estrogenic activity requires a single tertiary branched alkyl group composed of between 6 and 9 carbons located at the para-position on an otherwise unhindered phenol ring. Only the para- (4-) mono-substituted homologues seem to be endocrine disruptors, and p-nonyl phenol and 4-*tert*-octylphenol are the most potent ones. Based on this, most probably the short-chained APs in the table (with the exception of 4-*tert*-BP and 4-*tert* amylphenol) would not be considered SVHC. For dodecylphenol, 4-*tert*-BP and 4-*tert* amylphenol, a closer assessment would be needed for a conclusion as to whether they may be considered SVHCs.

The self-classifications of the substances indicate that many of the substances are acute and chronic toxic in the aquatic environment similar to those substances with a harmonised classification. None of the self-classifications of the short-chain APs indicate that substances are carcinogenic, mutagenic or toxic to reproduction.

The table indicated the consumption volume in the EU and to what extent the substances are used for non-industrial applications that may be associated with wide-dispersive. Many of the short-chain APs are used as intermediate or applications where relative small releases from the use phase would be expected such as lubricants and fuel additives. Data on the presence of the substances in waste water and the environment are scarce, but none of the available studies have demonstrated high concentrations (similar to those of NP and NPEO) of any of the substances. One substance, 2,6-di-*tert*-butyl-*p*-cresol (BHT) are used in large quantities for purposes (as food additives, among others) where significant emissions may occur, but available data from waste water treatment plants have demonstrated BHT concentrations of at least one order of magnitude less than the concentration of NP.

The NPs and OPs are in general of most concern due to a combination of:

- The OPs and NPs are less biodegradable than other APs;
- They have a higher bioconcentration factor than most of the other APs;

- The substances are formed by degradation of the ethoxylates which are used for purposes with relatively many wide-dispersive uses (resulting in releases to the environment);
- Evidence of high potency of endocrine disrupting activity;
- The substances and their ethoxylates are used in relatively high quantities, and
- NP is classified toxic to reproduction.

The main issues with regard to these substance groups identified are:

- One of the major applications of the substances and their ethoxylates as registered in the Danish Product Register is in paint, lacquers and varnishes. Alternatives to APEO have been assessed for more than 10 years ago, but the substances are still used for some types of paint and varnished. The substances are included in imported raw materials for production in Denmark, and a substitution of the APEO would consequently imply a substitution of the raw materials.
- Textiles imported from countries outside the EU are major sources of releases of NP and NPEO to waste water treatment plants. The problem will be addressed by a REACH restriction dossier intended to be submitted by Sweden.
- A significant quantity of NPEO is still registered in the Danish Product Register as used in cleaning agents and biocidal products, and it should be further clarified whether this is due to inadequate updating of the notifications or is due to non-compliance.
- OPEO may be used for some of the applications where NPEO is restricted e.g. in textile and leather auxiliaries. More information on the potential releases of OPEO from different uses of the substances would be beneficial.

The dodecylphenols share some of the same properties as NP and OP and with a proposed classification as toxic to reproduction it may be of similar concern. The registry of intentions does not include any intentions of preparation of Annex XV SVHC or restriction dossiers for the substances. It may be relevant to further assess whether the substance meets the SVHC criteria in the same way as NP and OP/OPEO.

Some of the short-chain substances may be of some concern e.g. 2,4,6-tri-*tert*-butylphenol, which is a priority substance under OSPAR; however, an assessment of the potential effects of the actual concentrations have still not been undertaken.

Based on the available data it does not appear to be justified to target the short-chain substances as one group together with the long-chain APs. Rather, it appears to make more sense to assess each of the short-chain APs individually in order to identify any needs for measures to reduce the human and environmental exposure.

Data gaps

The survey addresses a wide range of substances and for most of the substances limited data are available on the life cycle releases of the substances, human health and environmental exposure and concentrations in the environment. The most important data gabs identified, when considering which substances are of major concern, are:

- Updated information on current uses and on the significance of the potential sources of releases of NP/NPEO to the environment is missing.
- Information on the registered quantities of NPEO in cleaning and maintenance products in Denmark calls for a clarification of actual uses.
- For some of the substances, information on the total manufacture and import to the EU in the registrations is not in accordance with information obtained from the industry and calls for a clarification.
- For many of the substances used in lubricants and oils, data on the potential releases from spill and disposal of improper waste oil are missing.

- Relatively high concentrations of 2,6-di-*tert*-butyl-*p*-cresol are found in waste water and the OECD has concluded that more information on actual releases and environmental exposure to this substance is needed.
- A review from HELCOM concluded that in general, there should be more measured data on NP/NPEO and OP/OPEO levels in discharges in the Baltic Sea catchment area, in sea water, biota and sediment of the Baltic Sea to examine if the substances cause harmful effects on the marine environment.
- The HELCOM review also concluded that there is a need for ecotoxicological data on sediment dwelling organisms in order to better define the NP and OP PNEC estimates for the benthic community.
- Human toxicity data for long-chain alkylphenols other than nonylphenol are limited and data on alkylphenol ethoxylates are nearly absent.
- For many of the short-chained alkylphenols no or insufficient data are available for the assessment of the endocrine potency of the substances.
- Updated information on the technical and economic feasibility of substitution of remaining uses of NP/NPEO and OP/OPEO is missing, this concerns in particular:
  - Use in emulsion polymerization and for paints which represent the major registered uses of the substances in Denmark.
  - Alternatives to 4-*tert*-BP, 4-*tert*-OP and 4-NP for manufacture of different types if resins.

TABLE 44
SUMMARY OF KEY CONSUMPTION, ENVIRONMENTAL AND HEALTH DATA ON AP/APEO

Substance	Use		Environment						Human health		
	Total EU consumption, t/y	Non industrial use *4	Risk /hazard assessment identified *1	Biodegradation *2	Bioconcentration factor	Hazard class *3	Endocrine disruptor class *4	Monitoring data Denmark, Baltic Sea, North Sea	Risk/hazard assessment identified	Hazard class*3	Endocrine disruptor class *4
Nonylphenols (NP)	25,000-50,000	Small part:PSA; Residuals in resin	EU RAR; UK screening; UK Env. risk evaluation; Annex XV SVHC	Inherently	1,280	**Harmonised** Aquatic Acute 1 Aquatic Chronic 1	CAT 1	Many data; levels compared to PNEC	EU RAR	**Harmonised** Repr. 2 Acute Tox. 4 * Skin Corr. 1B	CAT 1
Nonylphenol ethoxylates (NPE)	2,000-20,000	Significant part	EU RAR	Degrade to NP	-	Aquatic Chronic 2	CAT 1	Many data	EU RAR	Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2	CAT 1/CAT2 (for different NPs)
Octylphenols (OP) (Ex. CAS No 140-66-9)	22,900	Small part: PSA; Residuals in resin	Annex XV SVHC; UK screening; UK risk evaluation, OECD SIDS	Inherently	634 (est.)	**Harmonised** Aquatic Acute 1 Aquatic Chronic 1	CAT 1 (for OPS with available data)	Some data; levels compared to threshold concentrations	OECD SIDS	**Harmonised** Skin Irrit. 2 Eye Dam. 1	CAT 1 (for OPs with available data)
Octylphenol ethoxylates (OPEO)	1,000	Significant part	Annex XV SVHC;	Degrade to OP	-	Aquatic Chronic 2		Some data	-	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	-
Dodecylphenols (ex. CAS No 121158-58-5)	50,000	Small part: lubricants	UK risk evaluation; UK screening	Not readily	9440 (est.)	**Proposed** Aquatic Acute 1, Aquatic Chronic 1	-	Few data from Nordic environment	-	**Proposed** Skin Irrit.2, Eye Irrit.2, Repr. 2,	-
Dodecylphenol ethoxylates	<1000	Significant part: lubricants	UK screening	Degrade to DP	-	not classified	-	Few data from Nordic environment	-	Eye Irrit. 2	-

Substance	Use		Environment						Human health		
	Total EU consumption, t/y	Non industrial use *4	Risk /hazard assessment identified *1	Biodegradation *2	Bioconcentration factor	Hazard class *3	Endocrine disruptor class *4	Monitoring data Denmark, Baltic Sea, North Sea	Risk/hazard assessment identified	Hazard class*3	Endocrine disruptor class *4
4-*tert*-butylphenol CAS No 98-54-4	27,000	Very small part; Residuals in resin	EU RAR, UK screening; OECD SIDS	Readily (in weeks-months)	120	Aquatic Chronic 2 **Proposed**: not included	CAT2	Few data from Nordic environment and WWTP	EU RAR ; CLH report	**Proposed** STOT SE 3, Skin irrit. 2 Eye dam. 1	CAT2
2-*sec*-butylphenol CAS No 89-72-5	1,00o-10,000	Intermediate only	UK screening	in weeks	48; 120; 174	-	-	no data	-	Skin Corr. 1B	-
o-*tert* butylphenol CAS No 68610-06-0	<1000	Intermediate only	-	-	-	-	-	no data		Skin Corr. 1B Skin Sens. 1	-
2-*tert*-butylphenol CAS No 88-18-6	n.i.	? : Fuels additives	UK screening	in weeks	39-188	Aquatic Acute 1	-	Few data from WWTP	-	Acute Tox. 4 Skin Corr. 1B Skin Irrit. 2	-
Cyclohexylphenols CAS No 119-42-6, 1131-60-8	n.i.	?: surface active agents	UK screening	in weeks	902	Aquatic Acute 1 Aquatic Chronic 1	CAT 3b	no data	-	Skin Corr. 1B Eye Dam. 1	CAT 1
bis(tert-butyl) dodecylphenol CAS No 68025-37-6	n.i.	?: lubricants	UK screening	in months	16	Aquatic Chronic 3	-	no data	-	-	-
Phenol, isopropylated CAS No 90480-88-9	n.i. *1	Intermediate only	UK screening	in weeks	67	no notifications in C&L inventory	-	no data	-	no notifications in C&L inventory	-
2,6-di-*tert*-butyl-*p*-cresol (BHT) CAS No 128-37-0	25,000	Most applications	UK screening; OECD SIDS	Readily (in weeks-months)	2,500	Aquatic Acute 1 Aquatic Chronic 1	-	Few data from WWTP	OECD SIDS	many suggestions both none by >50% of notifiers	-

Substance	Use		Environment						Human health		
	Total EU consumption, t/y	Non industrial use *4	Risk /hazard assessment identified *1	Biodegradation *2	Bioconcentration factor	Hazard class *3	Endocrine disruptor class *4	Monitoring data Denmark, Baltic Sea, North Sea	Risk/hazard assessment identified	Hazard class*3	Endocrine disruptor class *4
2,6-di-*tert*-butylphenol CAS No 128-39-2	15,000	Some part: lubricants, fuel additives	UK screening; OECD SIDS	Not readily (in weeks-months)	660	Aquatic Acute 1 Aquatic Chronic 1	-	few data from Nordic environment and WWTP	OECD SIDS	Skin Irrit. 2	-
2,4-di-*tert*-butylphenol CAS No 96-76-4	13,000	Very small part; lubricants	UK screening	Not readily (in weeks-months)	660	Aquatic Acute 1 Aquatic Chronic 1	-	Few data from WWTP	-	Skin Irrit. 2 Eye Irrit. 2	-
2,4,6 tris-*tert* butyl-phenol CAS no 732-26-3	<1000 t	Intermediate only	UK screening	Not readily (in months)	23,200	Aquatic Acute 1 Aquatic Chronic 1	-	Few data from WWTP	-	Eye Irrit. 2	-
Thymol CAS No 89-83-8	n.i.	Significant part	-	-	-	**Harmonised** Aquatic Chronic 2	-	no data	-	**Harmonised** Acute Tox. 4 * Skin Corr. 1B	-
6-*tert*-butyl-2,4-xylenol 1879-09-0	n.i.	?	OECD SIDS	-	-	Aquatic Chronic 2	-	Few data from WWTP	OECD SIDS	Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2	-
2,6-di-*tert*-butyl-4-nonylphenol 4306-88-1	n.i.	?: lubricants	UK screening	in weeks–months	5,943	Aquatic Chronic 3	-	no data	-	Skin Irrit. 2 Eye Irrit. 2 STOT SE 3	-
4-*tert* amylphenol CAS No 80-46-6	<1,000	?	UK risk evaluation; UK screening	Not readily (in weeks–months)	12; 531	Aquatic Chronic 2	-	no data	-	Acute Tox. 4 Skin Corr. 1B	-
o-*tert* amylphenol CAS No 3279-27-4	<1,000	Intermediate only	UK screening	in weeks–months	412	no notifications in C&L inventory	-	no data	-	no notifications in C&L inventory	-

Substance	Use		Environment						Human health		
	Total EU consumption, t/y	Non industrial use *4	Risk /hazard assessment identified *1	Biodegrada-tion *2	Bioconcen-tration factor	Hazard class *3	Endocrine disruptor class *4	Monitoring data Denmark, Baltic Sea, North Sea	Risk/hazard assessment identified	Hazard class*3	Endocrine disrup-tor class *4
2-isopropylphenol CAS No 88-69-7	>1,000	Intermediate only	UK screen-ing	in weeks	56	-	-	no data	-	Acute Tox. 4	-
2,4-dinonylphenol CAS No 137-99-5	<1,000	Intermediate only	UK screen-ing	in weeks	99	Aquatic Chronic 3	-	no data	-	Skin Irrit. 2 Skin Sens. 1	-
2,4-di-*tert* am-ylphenol CAS No 120-95-6	<1,000	Intermediate only	UK screen-ing	Not readily (in weeks–months)	40,381	-	-	no data	-	Acute Tox. 4 Eye Irrit. 2	-
2-*tert*-butyl-*p*-cresol CAS No 2409-55-4	n.i.	Intermediate only	UK screen-ing	in weeks - months	501	-	-	no data	-	Skin Corr. 1B	-
6-*tert*-butyl-*m*-cresol CAS No 88-60-8	n.i.	Intermediate only	OECD SIDS	-	-	-	-	no data	OECD SIDS	Acute Tox. 4 Skin Corr. 1B	-
C14-16-18 al-kylphenol CAS No 931-468-2	n.i.	Intermediate only	-	-	-	no notifications in C&L inventory	-	no data	-	no notifications in C&L inventory	-

*1 Based on Environment Agency, 2005, see original report for detailed notes; the wording is derived from the original wording of the report which does not seem to be totally consistent.

*2 EU RAR: EU Risk Assessment Report available. "UK screening": (Environment Agency, 2005). OECD SIDS: SIDS Initial Assessment Reports available; please see reference list.

*3 Harmonised: classification according to the CLP Regulation. Proposed: submitted classification proposal intention. Other classification is based on the selfclassifications listed in Annex 2 – indicates classification suggested by more than 50% of the notifiers

*4 "Intermediate": intermediate use only. PSA: Paint, lacquers, varnishes, sealants, adhesives

5 CAT1 : Evidence of endocrine disrupting activity in at least one species using intact animals. CAT 2: At least some in vitro evidence of biological activity related to endocrine disruption; CAT 3b: No or insufficient data available. Substances marked with an "-" have not been included in the evaluation programme.

10. Abbreviations and acronyms

ADI	Acceptable daily ntake
4-*tert*-BP	4-*tert*-butylphenol = p-*tert*-butylphenol = 4-*tert*-BP= ptBP
4-t-OP	4-*tert*-octylphenol = p-*tert*-octylphenol = 4-t-OP= 4-t-OP
AP	Alkylphenol
APEO	Alkylphenol ethoxylates
Aza	Azadioxabicyclooctane
BCF	Bioconcentration factor
BHT	2,6-di-*tert*-butyl-*p*-cresol
BIT	4-t, 1, 2-benzisothiazolin-3-one
CEPAD	European Council for Alkylphenols and Derivatives
CEFIC	European Chemical Industry Council
CLP	Classification, Labelling and Packaging Regulation
COHIBA	Control of hazardous substances in the Baltic Sea region
DEFRA	Department for Environment, Food and Rural Affairs (UK)
DFL	Trade organisation for the paint and adhesives industry in Denmark
DP	Dodecylphenols
DT	Degradation time
DTU	Technical University of Denmark
EC_n	Effect concentration where n % of the species tested show the effect
ECB	European Chemicals Bureau
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
E-PRTR	European Pollutant Release and Transfer Register
EQC	Equivalent level of concern
ETRMA	European Tyre & Rubber Manufacturers' Association
EU	European Union
FSO	Fugebranchen, Danish trade organisation of the sealant industry
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
Kow	Octanol/water partitioning coefficient
Koc	Organic carbon/water partitioning coefficient
Kp	Partial pressure equilibrium constant
LC	Lethal effect concentration
LOUS	List of Undesirable Substances (of the Danish EPA)
MSWI	Municipal solid waste incinerators
MWWTP	Municipal waste water treatment plant
NMC	Nation Mean Concentration
NOAEL	No observable adverse effect level
NOEC	No observable effect concentration
NOVANA	Danish national monitoring and assessment programme
NP	Nonylphenol

NPEO	Nonylphenol ethoxylates
NP_1EO	Nonylphenol monoethoxylates
NP_2EO	Nonylphenol diethoxylates
NP_nEO	NP carboxylate with n ethoxy units
$NPEO_9$	as well as $OEPO_{10}$ s.93
OECD	Organisation for Economic Co-operation and Development
OP	Octylphenol
OPEO	Octylphenol ethoxylates
OP_1EO	Octylphenol monoethoxylates
OP_2EO	Octylphenol diethoxylates
OP_nEC	OP carboxylate with n ethoxy units
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PEC	Predicted environmental concentration
PFR	Phenol/formaldehyde resins
PHMB	Poly(hexamethylene biguanide) hydrochloride
PNEC	Predicted no effect concentration
PTFE	Polytetrafluoroethylene
4-t-OP	4-*tert*-octylphenol = 4-*tert*-octylphenol = 4-t-OP
QSAR	Quantitative Structure and Activity Relationship
RATG	Risk Assessment Task Group of the American Chemistry Council's Petroleum Additives Panel
RED	Reregistration Eligibility Decision
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SIDS	Screening Information Data Sets
SOCOPSE	Source control of priority substances in Europe (a project)
SPT	Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
STP	Sewage treatment plant
SVHC	Substance of Very High Concern
TGD	Technical guidance document
ThOD	Theoretical oxygen demand
TDI	Tolerable daily intake
TTBP	2,4,6 tris-*tert* butyl-phenol
TNPP	tris nonylphenyl phosphite = 4-nonylpheyl phosphite
WE	Western Europe

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Annex 1: Uses and tonnage bands according to registrations

The following information on uses and tonnage bands of registered substances has been extracted from ECHAs website July 2012 (ECHA, 2012e). The information on cresols and xylenol is shown for reference and the uses of these substances are not further discussed in the report.

CAS No	Substance	Tonnage band t/y	Registered uses
Monoalkylphenols and ethoxylates			
Methyl phenols [cresols] (out of scope)			
95-48-7	o-cresol	10,000 - 100,000	Use as a monomer in polymer production Use as an isolated intermediate for chemical synthesis Processing of solid polymers Processing of liquid polymers Solvent in electrical wire enamelling Manufacturing of o-cresol
106-44-5	p-cresol	10,000 - 100,000	Use in polymer production Use in processing of solid polymers Use in processing of liquid polymers Use as an isolated intermediate for chemical synthesis Use as a solvent in electrical wire enamelling Solvent in pharmaceutical industry
108-39-4	m-cresol	10,000 - 100,000	Use as a monomer in polymer production Use as an isolated intermediate for chemical synthesis Processing of solid polymers Processing of liquid polymers Solvent in electrical wire enamelling Solvent in pharmaceutical industry
1319-77-3	cresol	1,000 - 10,000	Manufacturing of substance Formulation and repacking Industrial use of processing aids Use as monomer - thermoset Use as a monomer - thermoplastic Use as intermediate Use as reactive processing aid - wire enamelling Use in laboratories
906-151-7*	reaction mass of m-cresol and p-cresol	1,000 - 10,000	Transportable intermediate Industrial manufacture of enamels Electrical wire enamelling coating Mixing into preparations (road surfacing) Use as monomer for polymer production-solid
Propylphenol			
90480-88-9	phenol, isopropylated	intermediate use only	Site limited intermediate
Butylphenols			

89-72-5	2-*sec*-butylphenol	1,000 - 10,000	Chemical intermediate Plant protection products Fungicide formulation
98-54-4	4-*tert*-butylphenol	intermediate use only	
Octylphenols			
140-66-9	4-(1,1,3,3-tetramethylbutyl)phenol [4-*tert*-octylphenol, 4-t-OP]	10,000 - 100,000	Intermediate in production of ethoxylates and ether sulphates Coatings and inks - manufacture of organic solvent borne, water borne and solvent-free products Coatings, adhesives, inks and paint: manufacture, industrial and professional application Consumer application of adhesives, coatings and paint Tackifier in manufacture of tyres and rubber products Industrial end-use of paints containing octylphenol ethoxylates Use as a monomer in production of polymers
Nonylphenols and ethoxylates			
84852-15-3	Phenol, 4-nonyl-, branched	10,000 - 100,000	Industrial application of coatings or inks Industrial intermediate Formulation of paint Production of polymers
68412-54-4	2-{2-[4-(2,4,5-trimethylhexan-3-yl)phenoxy]polyethoxy}ethanol	1,000 - 10,000 1,000 - 10,000	Industrial manufacture of NPEO Industrial formulation of mining products (flotation agents) containing NPEO
440-740-5*	4-(4-trans-propylcylohexyl)phenol	Intermediate use only	Chemical intermediate
Dodecylphenols			
121158-58-5	Phenol, dodecyl-, branched	10,000 - 100,000 Intermediate use only	Chemical intermediate monomer for synthesis of polymer intermediate
Di- and trialkylphenols			
Dimethylphenols [xylenols] and trimethylphenols (out of scope)			
108-68-9	3,5-xylenol	Intermediate use only	Chemical intermediate
576-26-1	2,6-xylenol	10,000 - 100,000	Chemical intermediate
905-287-4*	reaction mass of 2,4-xylenol and 2,5-xylenol	1,000 - 10,000	Xylenol fraction as electric wire enamelling coating Transported intermediate
2416-94-6	2,3,6-trimethylphenol	1,000 - 10,000	Chemical intermediate
Propyl methyl phenols			
89-83-8	thymol	1,000 - 10,000	End use of thymol in cleaning agents Use of scented articles

Dibutylphenols, butyl methyl phenols, tributylphenols			
96-76-4	2,4-di-*tert*-butylphenol	Intermediate use only 100 - 1,000 100 - 1,000	Intermediate Fuel additives and additised fuels Lubricant additives, lubricants and greases Chemical intermediate Plastic additive Rubber additive Stabilizing component in other products
128-39-2	2,6-di-*tert*-butylphenol	100 - 1,000 100 - 1,000 Intermediate use only	Intermediate Fuel additives and additised fuels Lubricant additives, lubricants and greases Chemical intermediate Plastic additive Rubber additive Stabilizing component in other products
128-37-0	2,6-di-*tert*-butyl-*p*-cresol	1,000 - 10,000 1,000 - 10,000 10,000 - 100,000	Use as a stabilizing (antioxidant) component substance Use in formulations (Food, Feed, Cosmetics, Pharmaceuticals, Plant protection products) Use in plastics Use in adhesives, coatings, dyes, inks, printing dyes Use in fuel (biodiesel) Use as laboratory reagent Use as a lubricant Industrial coatings and inks Paper industry Lubricants Polymers Fuels
5510-99-6	di-*sec*-butylphenol, mixed isomers	intermediate use only	Chemical intermediate
31291-60-8	di-*sec*-butylphenol	intermediate use only	Chemical intermediate
732-26-3	2,4,6-tri-*tert*-butylphenol [2,4,6 -TTBP]	intermediate use only	Chemical intermediate
2409-55-4	2-*tert*-butyl-*p*-cresol	intermediate use only	Chemical intermediate
88-60-8	6-*tert*-butyl-*m*-cresol	intermediate use only	Chemical intermediate
Other APs			
931-468-2	C14-16-18 Alkylphenol	intermediate use only	No manufacturing information
905-278-5	Reaction mass of 3,4-xylenol and 3,5-xylenol and 3-ethylphenol and 4-ethylphenol	intermediate use only	Chemical intermediate
906-550-6	Reaction mass of 2,3-xylenol and 3,5-xylenol and 3-ethylphenol and 4-ethylphenol	1,000 - 10,000	Transported intermediate Xylenol fraction as electric wire enamelling coating

Annex 2: Self classification of AP/APEO

The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database includes as well the harmonised classification. Companies have provided this information in their C&L notifications or registration dossiers (ECHA, 2012e). ECHA maintains the Inventory, but does not verify the accuracy of the information (ECHA, 2012).

Classification of AP/APEO listed in the database is shown in the table below.

For substances with a harmonised classification this is indicated.

TABLE A3
CLASSIFICATION INFORMATION ON NOTIFIED AND REGISTERED SUBSTANCES RECEIVED FROM MANUFACTURERS AND IMPORTERS (C&L LIST)

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
Ethylphenols					
90-00-6	2-ethylphenol	2	**Total**		**266**
			Acute Tox. 4	H302	159
			Acute Tox. 4	H312	90
			Skin Corr. 1B	H314	105
			Skin Irrit. 2	H315	68
			Eye Dam. 1	H318	98
			Acute Tox. 4	H332	90
			STOT SE 3	H335	68
123-07-9	4-ethylphenol	2	**Total**		**1024**
			Acute Tox. 4	H302	69
			Acute Tox. 4	H312	51
			Skin Corr. 1B	H314	885
			Skin Irrit. 2	H315	68
			Eye Dam. 1	H318	724
			Eye Irrit. 2	H319	86
			Acute Tox. 4	H332	51
			STOT SE 3	H335	68
Propylphenols					
90480-88-9	Phenol, isopropylated	3	**Total**		**5**
			Acute Tox. 3	H301	5
			Acute Tox. 3	H311	5
			Skin Corr. 1B	H314	5
			Acute Tox. 3	H331	5
			Muta. 2	H341	5
			STOT RE 2	H373	5

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
88-69-7	2-isopropylphenol	3	**Total**		**51**
			Acute Tox. 4	H302	877
			Repr. 2	H312	9
			Skin Corr. 1B	H314	30
			Eye Dam. 1	H318	1
			Acute Tox. 4	H332	6
			Acute Tox. 4	H411	6
618-45-1	3-isopropylhydroxybenzene	3	**Total**		**91**
			Acute Tox. 4	H302	86
			Skin Corr. 1B	H314	24
			Eye Dam. 1	H318	1
Butylphenols					
89-72-5	2-*sec*-butylphenol	4	**Total**		**300**
			Acute Tox. 4	H302	249
			Acute Tox. 4	H312	220
			Skin Corr. 1B	H314	249
			Eye Dam. 1	H318	116
			Acute Tox. 4	H332	197
			Aquatic Chronic 2	H411	160
			Skin Irrit. 2	H315	47
			Eye Irrit. 2	H319	47
			STOT SE 3	H335	48
			Acute Tox. 2	H330	23
98-54-4	4-*tert*-butylphenol	4	**Total**		**2241**
			Acute Tox. 4	H302	62
			Slin Corr. 1B	H314	446
			Skin Irrit. 2	H315	1771
			Skin Sens. 1	H317	389
			Eye Dam. 1	H318	877
			Eye Irrit. 2	H319	1601
			Resp. Sens. 1	H334	75
			STOT SE 3	H335	1607
			11.1.1 Repr. 2	H361	510
			11.1.2 STOT	H372	1
			RE 1	H410	15
			Aquatic Chronic 1	H411	992
			Aquatic Chronic 2		

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
88-18-6	2-*tert*-butylphenol	4	**Total**		**525**
			Acute Tox. 4	H302	503
			Acute Tox. 3	H311	361
			Acute Tox. 4	H312	114
			Skin Corr. 1B	H314	255
			Skin Irrit. 2	H315	253
			Eye Dam. 1	H318	116
			Eye Irrit. 2	H319	253
			Acute Tox. 2	H330	51
			Acute Tox. 4	H332	111
			STOT SE 3	H335	5
			Aquatic Acute 1	H400	271
			Aquatic Chronic 1	H410	251
			Aquatic Chronic 2	H411	233
99-71-8	4-*sec*-butylphenol	4	**Total**		**133**
			Acute Tox. 4	H302	1
			Skin Corr. 1B	H314	133
			Eye Dam. 1	H318	1
			Aquatic Chronic 1	H400	23
			Aquatic Chronic 3	H412	1
585-34-2	3-*tert*-butylphenol	4	**Total**		**110**
			Skin Corr. 1B	H314	105
			Eye Dam. 1	H318	53
			Aquatic Chronic 2	H411	1
1638-22-8	4-butylphenol	4	**Total**		**68**
			Acute Tox. 4	H302	1
			Acute Tox. 4	H312	1
			Skin Corr. 1B	H314	65
			Eye Dam. 1	H318	1
			Acute Tox. 4	H332	1
27178-34-3	tert-butylphenol	4	**Total**		**20**
			Acute Tox. 4	H302	20
			Acute Tox. 4	H312	20
			Skin Corr. 1B	H314	20
			Acute Tox. 4	H332	20
			Aquatic Chronic 2	H411	20
68610-06-0	Phenol, isobutylenated	4	**Total**		**41**
			Skin Corr. 1B	H314	35
			Skin Sens. 1	H317	35
			Aquatic Chronic 2	H411	2
Pentylphenols					

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
80-46-6	p-(1,1-dimethylpropyl)phenol	5	**Total**		**164**
			Acute Tox. 4	H302	71
			Acute Tox. 4	H312	48
			Skin Corr. 1B	H314	116
			Skin Sens. 1	H317	33
			Eye Dam. 1	H318	46
			Acute Tox. 4	H332	3
			Aquatic Acute 1	H400	20
			Aquatic Chronic 1	H410	20
			Aquatic Chronic 2	H411	72
87-26-3	2-(1-methylbutyl)phenol	5	**Total**		**23**
			Acute Tox. 3	H301	23
			Eye Dam. 1	H318	23
			Aquatic Chronic 4	H413	23
1518-84-9	2-cyclopentylphenol	5	**Total**		**23**
			Skin Irrit. 2	H315	23
			Eye Irrit. 2	H319	23
			STOT SE 3	H335	23
3279-27-4	2-(1,1-dimethylpropyl)phenol	5	**Total**		**5**
			Acute Tox. 4	H302	4
			Acute Tox. 4	H312	1
			Skin Corr. 1B	H314	5
			Eye Dam. 1	H318	4
			Acute Tox. 4	H332	1
			Aquatic Chronic 1	H410	3
			Aquatic Chronic 2	H411	1
14938-35-3	4-pentylphenol	5	**Total**		**27**
			Acute Tox. 3	H301	1
			Skin Corr. 1B	H314	24
			Skin Irrit. 2	H315	1
			Eye Dam. 1	H318	1
			Eye Irrit. 2	H319	1
			Aquatic Acute 1	H400	1
			Aquatic Chronic 2	H411	1
Hexylphenols					
119-42-6	2-cyclohexylphenol	6	**Total**		**116**
			Skin Corr. 1B	H314	76
			Skin Irrit. 2	H315	23
			Eye Dam. 1	H318	23
			STOT SE 3	H335	23
			Aquatic Acute 1	H400	23
			Aquatic Chronic 1	H410	26
1131-60-8	4-cyclohexylphenol	6	**Total**		**91**
			Eye Dam. 1	H318	91
			Aquatic Chronic 2	H411	91

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
2446-69-7	p-hexylphenol	6	**Total** Skin Corr. 1B Skin Corr. 1C Eye Dam. 1	 H314 H314 H318	**139** 23 1 1
Heptylphenols					
1987-50-4	4-heptylphenol	7	**Total** Acute Tox. 4 Skin Corr. 1B Skin Irrit. 2 Eye Dam. 1 Eye Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1	 H302 H314 H315 H318 H319 H400 H410	**265** 262 1 262 1 262 262 262
Octylphenols and octylphenol ethoxylates					
140-66-9	4-(1,1,3,3-tetramethylbutyl)phenol	8	Skin Irrit. 2 Eye Dam. 1 Aquatic Acute 1 Aquatic Chronic 1	H315 H318 H400 H410	Harmonised
1806-26-4	p-octylphenol	8	**Total** Skin Irrit. 2 Eye Irrit. 2	 H315 H319	**81** 27 27
18626-98-7	o-(1-methylheptyl)phenol	8	**Total** Acute Tox. 4 Acute Tox. 4 Skin Corr. 1B Eye Dam. 1 Acute Tox. 4 Aquatic Chronic 1 Aquatic Chronic 2	 H302 H312 H314 H318 H332 H410 H411	**50** 50 47 50 3 47 3 47
9002-93-1	Poly(oxy-1,2-ethanediyl), α-[4-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy-	C8 ethoxylate	**Total** Acute Tox. 4 Skin Corr. 1B Skin Irrit. 2 Eye Dam. 1 Eye Irrit. 2 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2 Aquatic Chronic 3	 H302 H314 H315 H318 H319 H400 H410 H411 H412	**296** 193 1 198 160 79 1 1 104 27
9036-19-5	Poly(oxy-1,2-ethanediyl), α-[(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy-	C8 ethoxylate	**Total** Acute Tox. 3 Acute Tox. 4 Skin Irrit. 2 Skin Sens. 1 Eye Dam. 1 Eye Irrit. 2	 H301 H302 H315 H317 H318 H319	**2079** 26 1354 120 1 1458 481

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
			STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2 Aquatic Chronic 3	H335 H400 H410 H411 H412	1 3 16 818 953
68987-90-6	Poly(oxy-1,2-ethanediyl), α-(octylphenyl)-ω-hydroxy-, branched	C8 ethoxylate	**Total** Acute Tox. 4 11.1.3 Skin Irrit. 2 11.1.4 Eye Dam. 1 11.1.5 Eye Irrit. 2 11.1.6 STOT SE 3 Aquatic Chronic 2	 H302 H315 H318 H319 H335 H411	**406** 45 316 45 316 316 45
Nonylphenol and nonylphenol ethoxylates					
25154-52-3 **84852-15-3**	nonylphenol 4-nonylphenol, branched	9	Repr. 2 Acute Tox. 4 * Skin Corr. 1B Aquatic Acute 1 Aquatic Chronic 1	H361fd H302 H314 H400 H410	Harmonised
104-40-5	p-nonylphenol	9	**Total** Acute Tox. 4 Skin Corr. 1B Eye Dam. 1 Acute Tox. 4 Repr. 2 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2	 H302 H314 H318 H332 H361 H400 H410 H411	**167** 161 160 86 1 134 137 109 23
EC No 440-740-5	4-(4-trans-propyl- cylohex-yl)phenol	9	**Total** Aquatic Chronic 4	 H413	**1** 1
11066-49-2	isononylphenol	9	**Total** Acute Tox. 4 Skin Corr. 1B Eye Dam. 1 Repr. 2 Aquatic Acute 1 Aquatic Chronic 1	 H302 H314 H318 H361 H400 H410	**77** 77 77 47 77 47 77
90481-04-2	Phenol, nonyl-, branched	9	**Total** Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1 Aquatic Acute 1	 H302 H315 H318 H400	**30** 30 30 30 30
9016-45-9	Nonylphenol, ethoxylated	C9 ethoxylate	**Total**		**2218**

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
			Acute Tox. 4 Skin Corr. 1B 11.1.7 Skin Irrit. 2 11.1.8 Eye Dam. 1 11.1.9 Eye Irrit. 2 11.1.10 STOT SE 3 11.1.11 Repr. 2 11.1.12 STOT SE 3 11.1.13 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1 Aquatic Chronic 2 Aquatic Chronic 3 Aquatic Chronic 4	H302 H314 H315 H318 H319 H335 H361 H371 H373 H400 H410 H411 H412 H413	1255 1 1405 575 1509 131 56 1 56 41 2 1875 93 48
20427-84-3	2-[2-(4-nonylphe-noxy)ethoxy]ethanol	C9-ethoxylate	**Total** Skin Irrit. 2 Eye Irrit. 2 Aquatic Chronic 3	 H315 H319 H412	**1** 1 1 1
26027-38-3	4-nonylphenol, ethoxylated	C9-ethoxylate	**Total** Acute Tox. 4 Skin Irrit. 2 Skin Sens. 1 Eye Dam. 1 11.1.14 Eye Irrit. 2 11.1.15 STOT SE 3 Aquatic Chronic 1 Aquatic Chronic 2	 H302 H315 H317 H318 H319 H335 H410 H411	**208** 139 139 23 23 160 52 29 88
37205-87-1	Poly(oxy-1,2-ethanediyl), α-(isononylphenyl)-ω-hydroxy-	C9-ethoxylate	**Total** Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1 Eye Irrit. 2 Aquatic Chronic 2 Aquatic Chronic 3	 H302 H315 H318 H319 H411 H412	**1004** 628 145 820 130 617 313
68412-54-4	2-{2-[4-(2,4,5-trimethylhexan-3-yl)phenoxy]polyethoxy}ethanol	C9-ethoxylate	**Total** Acute Tox. 4 Skin Corr. 1B Skin Irrit. 2 Skin Sens. 1 Eye Dam. 1	 H302 H314 H315 H317 H318	**2815** 1480 4 1345 87 1535

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
			Eye Irrit. 2	H319	734
			STOT SE 3	H335	2
			Aquatic Acute 1	H400	1
			Aquatic Chronic 1	H410	122
			Aquatic Chronic 2	H411	1401
			Aquatic Chronic 3	H412	377
			Aquatic Chronic 4	H413	51
127087-87-0	4-Nonylphenol, branched, ethoxylated	C9-ethoxylate	**Total**		**925**
			Acute Tox. 4	H302	369
			Acute Tox. 4	H312	60
			Skin Irrit. 2	H315	424
			Eye Dam. 1	H318	350
			Eye Irrit. 2	H319	463
			Acute Tox. 4	H332	184
			STOT SE 3	H335	11
			Repr. 2	H361	11
			Aquatic Chronic 2	H411	442
Dodecylphenol and docecylphenol ethoxylates					
104-43-8	p-dodecylphenol	12	**Total**		**16**
			Skin Corr. 1B	H314	5
			Skin Irrit. 2	H315	10
			Eye Irrit. 2	H319	1
				H361	16
			Aquatic Acute 1	H400	14
			Aquatic Chronic 1	H410	3
121158-58-5	Phenol, dodecyl-, branched	12	**Total**		**503**
			Skin Corr. 1B	H314	102
			Skin Irrit. 2	H315	385
			Eye Dam. 1	H318	86
			Eye Irrit. 2	H319	336
			Repr. 1B	H360	48
			Repr. 2	H361	338
			Aquatic Acute 1	H400	458
			Aquatic Chronic 1	H410	487
11067-80-4	isododecylphenol	12	**Total**		**1**
			Eye Irrit. 2	H319	1
			Repr. 2	H361	1
			Aquatic Acute 1	H400	1
			Aquatic Chronic 1	H410	1
27193-86-8	dodecylphenol	12	**Total**		**362**
			Skin Corr. 1B	H314	26
			Skin Irrit. 2	H315	273
			Eye Irrit. 2	H319	251
			Repr. 2	H361	251
			Aquatic Acute 1	H400	273
			Aquatic Chronic 1	H410	273
			Aquatic Chronic 4	H413	47

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
9014-92-0	Dodecylphenol, ethoxylated	C12-ethoxylate	**Total**		**144**
			Acute Tox. 4	H302	1
			Skin Irrit. 2	H315	7
			Eye Dam. 1	H318	46
			Eye Irrit. 2	H319	96
			STOT SE 3	H335	1
			Aquatic Chronic 2	H411	8
Pentadecylphenols					
501-24-6	3-pentadecylphenol	15	**Total**		**26**
			Acute Tox. 4	H302	23
			Acute Tox. 4	H312	23
			Skin Irrit. 2	H315	24
			Skin Sens. 1	H317	2
			Eye Irrit. 2	H319	24
			Acute Tox. 4	H332	23
			STOT SE 3	H335	23
Propyl methyl phenols					
89-83-8	thymol	3+1	Acute Tox. 4 *	H302	Harmonised
			Skin Corr. 1B	H314	
			Aquatic Chronic 2	H411	
499-75-2	carvacrol	3 +1	**Total**		**971**
			Acute Tox. 4	H302	967
			Skin Corr. 1B	H314	24
			Skin Irrit. 2	H315	943
			Skin Sens. 1	H317	940
			Eye Irrit. 2	H319	911
			Aquatic Chronic 2	H411	1
3228-02-2	4-isopropyl-*m*-cresol	3+1	**Total**		**81**
			Skin Irrit. 2	H315	52
			Skin Sens. 1	H317	2
			Eye Irrit. 2	H319	52
			STOT SE 3	H335	26
			Aquatic Chronic 2	H411	24
3228-03-3	5-isopropyl-*m*-cresol	3+1	**Total**		**23**
			Skin Irrit. 2	H315	23
			Eye Irrit. 2	H319	23
			STOT SE 3	H335	23
Di- and tri-propylphenols					

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
2078-54-8	disoprofol	3+3	**Total**		**797**
			Acute Tox. 4	H302	794
			Acute Tox. 4	H312	6
			Skin Corr. 1B	H314	15
			Skin Irrit. 2	H315	773
			Eye Irrit. 2	H319	773
			STOT SE 3	H335	772
			Aquatic Acute 1	H400	20
			Aquatic Chronic 1	H410	17
			Aquatic Chronic 2	H411	1
2934-05-6	2,4-diisopropylphenol	3+3	**Total**		**24**
			Skin Irrit. 2	H315	23
			Eye Irrit. 2	H319	23
			STOT SE 3	H335	23
Butyl methyl phenols, butyl ethyl phenol, butyl dimethyl phenols, butyl tetramethyl phenol					
88-60-8	6-*tert*-butyl-*m*-cresol	4 +1	**Total**		**112**
			Acute Tox. 4	H302	111
			Repr. 2	H312	1
			Skin Corr. 1B	H314	88
			Skin Irrit. 2	H315	23
			Eye Dam. 1	H318	53
			Eye Irrit. 2	H319	23
			STOT SE 3	H335	23
			Aquatic Chronic 2	H361	1
			STOT SE 2	H371	1
			STOT RE 2	H373	1
			Acute Tox. 4	H411	24
98-27-1	4-*tert*-butyl-*o*-cresol	4 +1	**Total**		**23**
			Slin Corr. 1B	H314	23
2219-82-1	6-*tert*-butyl-*o*-cresol	4 +1	**Total**		**88**
			Skin Corr. 1B	H314	87
			Eye Dam. 1	H318	30
2409-55-4	2-*tert*-butyl-*p*-cresol	4 +1	**Total**		**139**
			Skin Corr. 1B	H314	127
			Skin Irrit. 2	H315	5
			Eye Dam. 1	H318	37
			Eye Irrit. 2	H319	4
			STOT SE 3	H335	66
			Aquatic Chronic 2	H411	41

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
1879-09-0	6-*tert*-butyl-2,4-xylenol	4+1+1	**Total**		**441**
			Acute Tox. 3	H301	3
			Acute Tox. 4	H302	341
			Acute Tox. 1	H310	24
			Acute Tox. 3	H311	26
			Skin Corr. 1B	H314	23
			Skin Irrit. 2	H315	321
			Skin Sens. 1	H317	1
			Eye Irrit. 2	H319	302
			Acute Tox. 3	H331	26
			STOT SE 3	H335	4
			STOT RE 2	H373	21
			Aquatic Chronic 1	H410	1
			Aquatic Chronic 2	H411	364
879-97-0	4-*tert*-butyl-2,6-xylenol	4 +1+1	**Total**		**23**
			Acute Tox. 4	H302	23
			Skin Irrit. 2	H315	23
			Eye Dam. 1	H318	23
			STOT SE 3	H335	23
			Aquatic Acute 1	H400	23
96-70-8	2-*tert*-butyl-4-ethylphenol	4+2	**Total**		**24**
			Slin Corr. 1B	H314	23
			Skin Irrit. 2	H315	1
			Eye Dam. 1	H318	23
			Eye Irrit. 2	H319	1
Dibutylphenols, dibutyl methyl phenols, tributylphenols					
96-76-4	2,4-di-*tert*-butylphenol	4 + 4	**Total**		**777**
			Acute Tox. 4	H302	249
			Skin Irrit. 2	H315	638
			Eye Dam. 1	H318	50
			Eye Irrit. 2	H319	588
			STOT SE 3	H335	222
			STOT SE 2	H371	1
			STOT RE 2	H373	81
			Aquatic Acute 1	H400	435
			Aquatic Chronic 1	H410	460
128-39-2	2,6-di-*tert*-butylphenol	4 + 4	**Total**		**738**
			Acute Tox. 4	H302	24
			Skin Irrit. 2	H315	427
			Eye Irrit. 2	H319	205
			Eye Irrit. 2	H320	7
			Acute Tox. 5	H333	7
			STOT SE 3	H335	6
			STOT RE 1	H372	7
			Aquatic Acute 1	H400	358
			Aquatic Chronic 1	H410	422
			Aquatic Chronic 2	H411	115

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
1138-52-9	3,5-di-*tert*-butylphenol	4+4	**Total**		**24**
			Skin Corr. 1B	H314	23
5510-99-6	di-*sec*-butylphenol, mixed isomers	4+4	**Total**		**72**
			Skin Corr. 1B	H314	23
31291-60-8	di-*sec*-butylphenol	4+4	**Total**		**105**
			Acute Tox. 4	H302	60
			Skin Corr. 1B	H314	105
			Eye Irrit. 2	H318	60
128-37-0	2,6-di-*tert*-butyl-*p*-cresol	4 +4+ 1	**Total**		**2810**
			Acute Tox. 4	H302	481
			Acute Tox. 4	H312	261
			Skin Irrit. 2	H315	405
			Skin Sens. 1	H317	28
			Eye Irrit. 2	H319	592
			Acute Tox. 4	H332	200
			STOT SE 3	H335	289
			Muta. 2	H341	3
			Carc. 1B	H350	1
			Carc. 2	H351	10
			Repr. 2	H361	10
			STOT SE 1	H370	1
			STOT RE 2	H373	61
			Aquatic Acute 1	H400	1366
			Aquatic Chronic 1	H410	1765
			Aquatic Chronic 2	H411	28
			Aquatic Chronic 3	H412	15
			Aquatic Chronic 4	H413	390
497-39-2	4,6-di-*tert*-butyl-*m*-cresol	4 +4+ 1	**Total**		**32**
			Acute Tox. 4	H302	29
			Skin Irrit. 2	H315	1
			Eye Irrit. 2	H319	29
			Aquatic Chronic 2	H411	28
616-55-7	4,6-di-*tert*-butyl-*o*-cresol	4 +4+ 1	**Total**		**51**
			Acute Tox. 4	H302	23
			Skin Irrit. 2	H315	23
			Eye Irrit. 2	H319	23
			STOT SE 3	H335	23
			Aquatic Chronic 4	H413	23
732-26-3	2,4,6-tri-*tert*-butylphenol [2,4,6 -TTBP]	4+4+4	**Total**		**412**
			Acute Tox. 4	H302	134
			Skin Irrit. 2	H315	92
			Eye Irrit. 2	H319	360
			STOT SE 3	H335	5
			Aquatic Acute 1	H400	364
			Aquatic Chronic 1	H410	340
			Aquatic Chronic 2	H411	3
			Aquatic Chronic 4	H413	20

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
5892-47-7	2,4,6-tri-*sec*-butylphenol	4+4+4	**Total**		**26**
			Skin Irrit. 2	H315	26
			Aquatic Chronic 2	H411	26
17540-75-9	4-*sec*-butyl-2,6-di-*tert*-butylphenol	4+4+4	**Total**		**319**
			Acute Tox. 4	H302	1
			Acute Tox. 4	H312	1
			Skin Irrit. 2	H315	77
			Eye Irrit. 2	H319	54
			Acute Tox. 4	H332	1
			Aquatic Chronic 1	H410	23
			Aquatic Chronic 3	H412	1
Dinonylphenols					
137-99-5	2,4-dinonylphenol	9 + 9	**Total**		**27**
			Skin Irrit. 2	H315	27
			Skin Sens. 1	H317	27
			Aquatic Chronic 3	H412	27
1323-65-5	dinonylphenol	9+9	**Total**		**78**
			Skin Irrit. 2	H315	39
			Eye Dam. 1	H318	39
			Aquatic Chronic 1	H410	30
			Aquatic Chronic 2	H411	37
Other alkylphenols					
16152-65-1	2-(1-methylcyclohexyl)-*p*-cresol	7+1	**Total**		**20**
			Skin Irrit. 2	H315	20
			Skin Sens. 1	H317	20
			Eye Irrit. 2	H319	20
77-61-2	6-(1-methylcyclohexyl)-2,4-xylenol	7 + 1+ 1	**Total**		**30**
			Skin Irrit. 2	H315	30
			Skin Sens. 1	H317	30
			Eye Irrit. 2	H319	30
			Aquatic Chronic 2	H411	30
120-95-6	2,4-di-*tert*-pentylphenol	5 + 5	**Total**		**45**
			Acute Tox. 4	H302	45
			Acute Tox. 4	H312	1
			Skin Corr. 1B	H314	15
			Skin Irrit. 2	H315	3
			Eye Irrit. 2	H319	30
			Acute Tox. 4	H332	1
			STOT SE 3	H335	14
			Aquatic Chronic 1	H410	3
			Aquatic Chronic 2	H411	1

CAS No	Substance name	Carbon atoms in alkyl chains	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
4130-42-1	2,6-di-*tert*-butyl-4-ethylphenol	4+4+2	**Total** Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	 H315 H319 H335 H400 H410	**5** 3 3 2 1 1
4306-88-1	2,6-di-*tert*-butyl-4-nonylphenol	9+4+4	**Total** Skin Irrit. 2 Eye Irrit. 2 STOT SE 3 Aquatic Acute 3 Aquatic Chronic 3	 H315 H319 H335 H402 H412	**24** 24 20 20 1 23
68025-37-6	bis(tert-butyl)dodecylphenol	20	**Total** Aquatic Chronic 3	 H412	**288** 288

* Source : Search Classification and Labelling Inventory at http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database

Annex 3: Background information to chapter 3 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).
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The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation
REACH and CLP
The REACH Regulation[6] and the CLP Regulation[7] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provi-

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[6] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

[7] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

sions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration
All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation
A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation
Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction
If the authorities assess that that there is a risks to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling
The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.
2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline

In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)

The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV

Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[8]
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions

When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.
-

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intensions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions
-

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

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[8] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendationsset out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out.
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels
Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower
The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan
The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark’s website (according to Statutory Order no. 447 of 23/04/2010).

Blue Angel (Blauer Engel)
The Blue Angel is a national German eco-label. More information can be found on: http://www.blauer-engel.de/en.

Annex 4 AP/APEO in the Nordic environment

The following tables are copied from Hansen and Lassen (2008) showing the results of a survey of AP/APEO in the Nordic anvironment. (see text in Chapter 7 in main report).

For the water samples the following results were obtained:

	STP		Landfill	Surface	Recipient	Background
In ng/L	influent/ sewage	effluent	effluent	runoff	marine/ fresh	marine/ fresh
4-*tert*-Butylphenol	<10	<10	N/A-834	<10-32	<10	N/A
2,6-di-*tert*-butylphenol	<25	<45	<30-254	<30	<1-65	<15
4-*tert*-octylphenol	8.5-73	<5-2,099	<10-2,372	<10-379	<10	<10
n-octylphenol	<1-67	<1-43	3.6-5.9	<5	<2	<2
nonylphenol-mix	133-5,688	<15-2,173	27-16,997	<15-359	<10-4,199	<20-107
n-Nonylphenol	<1-54	<1-72	<1-71	<1-18	<1-287	<1-1.5
4-dodecylphenol	<125-4,096	<100-2,206	241-4,902	<50-4,280	<50	<125
4-cumylphenol	<1-61	<1-8	8-988	<1-154	<1-454	<1
Bisphenol-A	204-9,828	<1-561	711-5,910	<1-5,910	<1-22	<1-11
TBBPA	<25	<10-59	<20	<25	<10	<10
Methylated-TBBPA	<10	<10	<5	<10	<2	<10
octylphenolethoxylate	14-157	<1-239	<1-413	<1-31	<1-118	<1-2
nonylphenol-ethoxylate	1,142-4,896	<2-1,585	<2-85	<1-102	<1-61	<1

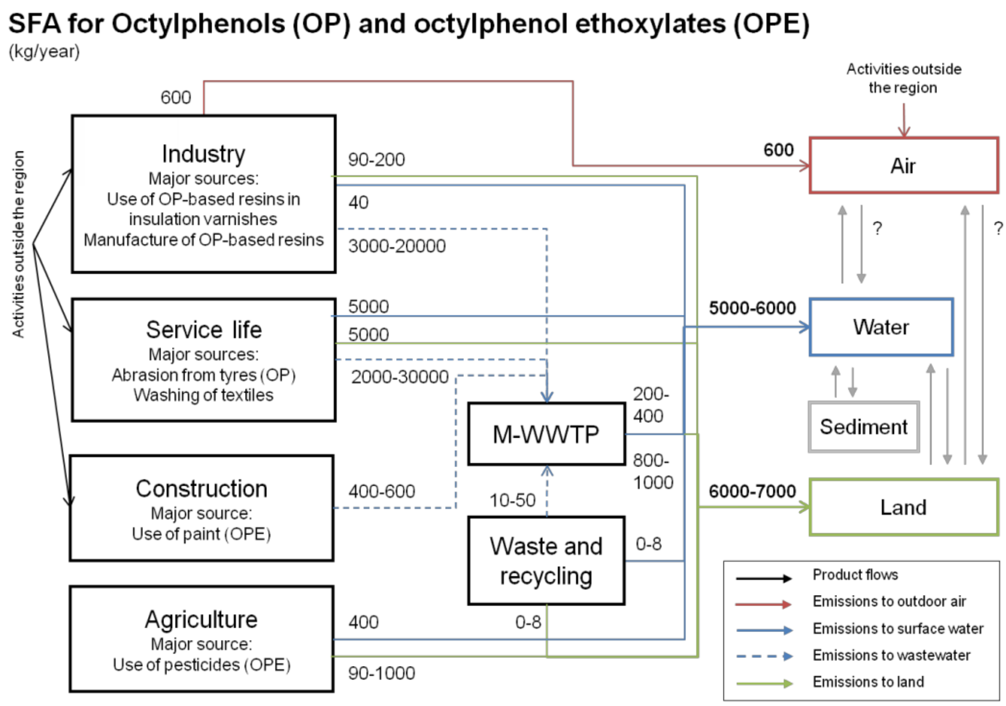
For the solid samples the following results were obtained:

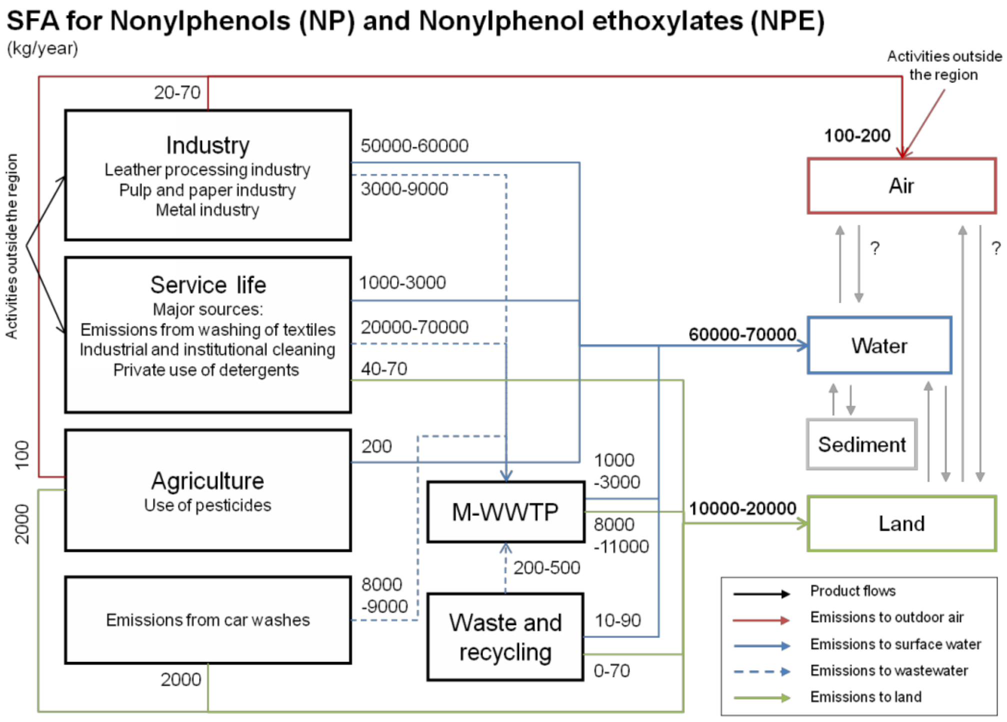
	STP	Landfill	Sediment	
In µg/kg dw	sludge	soil	non-marine	marine
4-*tert*-Butylphenol	<5-4,474	N/A	40-134	80
2,6-di-*tert*-butylphenol	<2-104	<5	<5	<5
4-*tert*-octylphenol	<3.5-1,386	3-23	<1-9	<1
n-octylphenol	<0.1-44	<0.2-1	<0.2-25	<0.2-25
nonylphenol-mix	1,460-28,360	<3.5-47	<3.5-485	<3.5-340
n-Nonylphenol	<0.1-5.6	<0.1	<0.1-2	<0.1-3
4-dodecylphenol	8,463-47,396	<25	<25-216	<25-529
4-cumylphenol	<0.1-115	<0.6-8	<0.1-115	<0.1-180
Bisphenol-A	<0.4-1914	<0.1-3	<0.1-40	<0.1-74
TBBPA	<5-1138	<1.0	<1	<1
Methylated-TBBPA	<20	<5-57	<5	<5
octylphenolethoxylate	<1-97	0.1-0.4	<0.2-1.3	<0.2-1.5
nonylphenol-ethoxylate	11-363	1-2	<0.1-67	<0.1-1.4

For the biological samples the following results were obtained:

In µg/kg ww	Fish non-marine	Fish marine	Mussels marine/ non-marine	Egg seabird	Marine mammals seal	Marine mammals whale
4-*tert*-Butylphenol	<4-449	<10-1,079	<10-424	<10	29-109	100
2,6-di-*tert*-butylphenol	12-5,081	81-4,064	<2.5-92	<5	45-677	27-42
4-*tert*-octylphenol	13-355	<12	<3-7,362	15-27	<25-472	<25
n-octylphenol	<1-8	<2	<1-4	<1	<1-4	1.5-3
nonylphenol-mix	44-989	165-1,085	<1-908	10-16	<6-97	52-197
n-Nonylphenol	<10	<1-44	<1-37	<1	<1	<1-2
4-dodecylphenol	<100-253	N/A	<100-181	<100	<100	<100
4-cumylphenol	<1-16	<2-30	<1-3	<1-3	<1	3-7
Bisphenol-A	<1-57	<10	<1-3	6-9	N/A	N/A
TBBPA	<10	N/A	<5	<10	<10	<10
Methylated-TBBPA	<5	<10	<5	<5	<5	<5
octylphenolethoxylate	18-4,035	<5-31,697	<5-28	7-8	<1	36-356
nonylphenol-ethoxylate	18,821	N/A	<5-39	<5	N/A	N/A

Substance flow diagrams for the Baltic Sea region from the COHIBA (2012) project (see text in Chapter 4 in main report).




SFA for Nonylphenols (NP) and Nonylphenol ethoxylates (NPE)
(kg/year)
Activities outside the region
20-70
Industry
Leather processing industry
Pulp and paper industry
Metal industry
50000-60000
3000-9000
100-200
Air
Activities outside the region
Service life
Major sources:
Emissions from washing of textiles
Industrial and institutional cleaning
Private use of detergents
1000-3000
20000-70000
40-70
?
?
60000-70000
Water
Sediment
100
2000
Agriculture
Use of pesticides
200
1000
-3000
M-WWTP
8000
-11000
10000-20000
Land
200-500
Emissions from car washes
8000
-9000
Waste and recycling
10-90
0-70
2000
Product flows
Emissions to outdoor air
Emissions to surface water
Emissions to wastewater
Emissions to land

Survey of alkylphenols and alkylphenol ethoxylates

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The report define the substances groups and present information on the use and occurrence of the alkylphenols and alkylphenol ethoxylates, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, waste management and information regarding ongoing activities under REACH, among others.

Kortlægning af alkylphenoler og alkylphenolethoxylater

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Rapporten definerer stofgrupperne og indeholder blandt andet en beskrivelse af brugen og forekomsten af alkylphenoler og alkylphenoethoxylater, internationalt og i Danmark, en beskrivelse af miljø- og sundhedseffekter af stofferne, og viden om alternativer, eksisterende regulering, moniteringsdata, eksponering, affaldsbehandling og igangværende aktiviteter under REACH.

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