Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR 1A OR 1B, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): **4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated - covering well-defined substances and UVCB substances, polymers and homologues**

EC Number(s): -

CAS Number(s): -

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PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR 1A OR 1B, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): 4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated - covering well-defined substances and UVCB substances, polymers and homologues

EC Number(s): -

CAS number(s): -

- *It is proposed to identify the substances covered by the entry '4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated - covering well-defined substances and UVCB substances, polymers and homologues' as substances meeting the criteria of Article 57 (f) of Regulation (EC) 1907/2006 (REACH).*

Summary of how the substances are considered to meet the criteria of Article 57 (f)

4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated - covering well-defined substances and UVCB substances, polymers and homologues are proposed to be identified as substances of very high concern in accordance with Article 57 (f) of Regulation (EC) 1907/2006 (REACH) because, due to their degradation, they are a relevant source in the environment of a substance of very high concern (4-(1,1,3,3-tetramethylbutyl)phenol (4-tert-octylphenol (4-tert-OP))). Therefore, there is scientific evidence of probable serious effects to the environment from these substances, through their degradation to 1,1,3,3-tetramethylbutyl)phenol, which gives rise to an equivalent level of concern to those of other substances listed in points (a) to (e) of Article 57 of REACH.

This conclusion is based on the fact that 4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated (4-tert-octylphenol ethoxylates (4-tert-OPnEO)) degrade to 4-(1,1,3,3-tetramethylbutyl)phenol, either already in wastewater treatment plants, or via further degradation processes in sediments (e.g. of aquatic bodies receiving the wastewater effluents) and soils (e.g. receiving sewage sludge). Available information for 4-tert-OPnEO indicate that 4-tert-OPnEO contribute to the 4-tert-OP concentration in the environment. A significant amount is either degraded to 4-tert-OP itself in waste water treatment plants or is released to rivers in a form which may undergo further degradation to 4-tert-OP. 4-tert-OP formed from degradation of 4-tert-OPnEO may increase the overall 4-tert-OP load to the environment (soil, sediment and water) by 54 to 758 %.

Sediment organisms may be exposed to the 4-tert-OP, which results from the degradation of 4-tert-OPnEO, either directly, downstream of the effluent, or in the longer term after its adsorption to sediment and soil. Similar holds true for pelagic organism such as fishes which may be exposed via remobilisation of 4-tert-OP from sediment to the water body.

Based on the above conclusion, evidence that these substances are of an equivalent level of concern includes:

- 4-tert-OP has been identified as a substance of very high concern and included in the Candidate List due to its endocrine disrupting properties which cause probable serious effects to the environment

- To be consistent with the approach implemented in Annex XIII of the REACH regulation for PBT substances, it seems reasonable to conclude that any substance which may result in relevant exposure to a SVHC (i.e. due to degradation to this substance under environmental conditions) should be considered as SVHC itself as it results in the same equivalent level of concern.

- Once released to the environment 4-tert-OPnEO will remain a permanent source of 4-tert-OP due the tendency of short chain ethoxylates to bind to the sediment combined with a very slow degradation in anaerobic sediments of both the ethoxylates and their degradation product 4-tert-OP. Therefore, 4-tert-OP formed by degradation of its ethoxylates may accumulate in sediment.

- Especially due to the fact, that short term exposure to 4-tert-OP may result in life time effects in aquatic organisms and due to the fact that sudden environmental events may increase short term exposure concentrations, such a sink and permanent source for 4-tert-OP is considered of very high concern.

In addition to the concern based on the degradation to 4-tert-OP, available information indicate that short chain ethoxylates (4-tert-OP1EO and 4-tert-OP2EO) may show endocrine activity themselves and thus may add to the probable serious effects caused by 4-tert-OP in the environment: Results for *O.mykiss* and *O.latipes* indicate that their in vivo and in vitro endocrine activity is nearly as high (factor 10) or similar to the endocrine activity of 4-tert-OP. These tests do not include adverse endpoints and thus it is not possible to conclude whether or not 4-tert-OP1EO and 4-tert-OP2EO are endocrine disruptors themselves. However due to the similar endocrine activity and information available for 4-tert-OP it seems possible that they may cause endocrine disrupting adverse effects at similar or slightly higher concentrations compared to 4-tert-OP and this may add to the concern raised for 4-tert-OPnEO.

Registration dossiers submitted for the substances: No

PART I

JUSTIFICATION

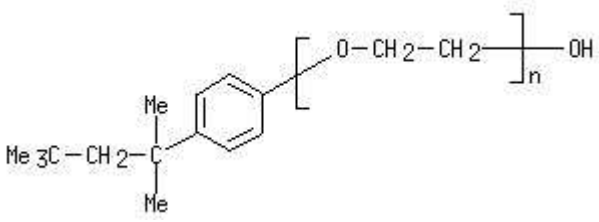
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	-
EC name:	-
CAS number (in the EC inventory):	-
CAS number:	-
CAS name:	-
IUPAC name:	4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated covering well-defined substances and UVCB substances, polymers and homologues
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	(C2H4O)n C14H22O
Molecular weight range:	-
Synonyms:	-

Structural formula:



1.2 Composition of the substance

Name: 4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated - covering well-defined substances and UVCB substances, polymers and homologues

Description:

Degree of purity: -

Table 2: Constituents

Constituents	Typical concentration	Concentration range	Remarks
no information available			

Table 3: Impurities

Impurities	Typical concentration	Concentration range	Remarks
no information available			

Table 4: Additives

Additives	Typical concentration	Concentration range	Remarks
no information available			

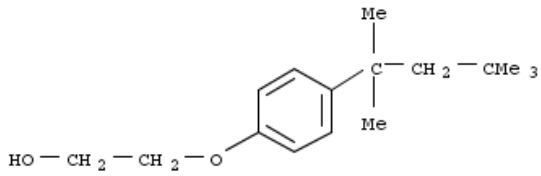
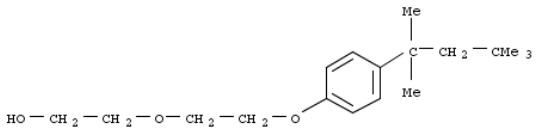
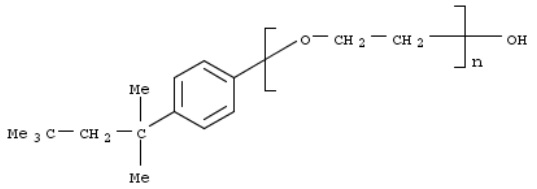
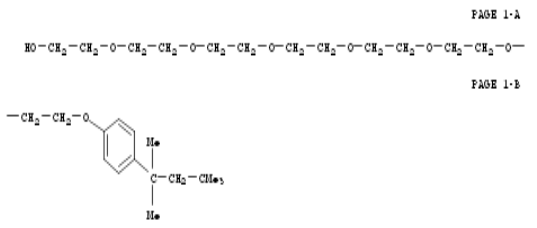
No detailed composition of the substance can be given. The given identity

4-(1,1,3,3-tetramethylbutyl)phenol, ethoxylated covering well-defined substances and UVCB substances, polymers and homologues shall cover the group of ethoxylates of 4-(1,1,3,3-tetramethylbutyl)phenol. In the table 5 all substances are listed which are covered by the group entry and are registered, pre-registered or for which a C&L notification has been submitted. No registration dossiers are given for substances which are covered by this Identity.

Table 5 provides a non-exhaustive list of examples of substances covered by the group name.

In the following chapters the ethoxylates of 4-(1,1,3,3-tetramethylbutyl)phenol (4-tert-OP) are addressed as 4-tert-octylphenol ethoxylates (4-tert-OPnEO)

Table 5: Substances covered by the group entry and for which there is information available in REACH-IT*

EC Name **CAS Name:** **IUPAC Name:**	**EC – Nr.**	**CAS Nr.**	**Molecular formula**	**Structure**
EC Name: - **CAS Name:** Ethanol, 2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]- **IUPAC Name:** 2-[4-(1,1,3,3-tetramethylbutyl)phenoxy] ethanol	-	2315-67-5	$C_{16}H_{26}O_2$	
EC Name: - **CAS Name:** Ethanol, 2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy] ethoxy]- **IUPAC Name**: 2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy] ethoxy]ethanol	-	2315-61-9	$C_{18}H_{30}O_3$	
EC Name **CAS Name:** Poly(oxy-1,2-ethanediyl), α-[4-(1,1,3,3-tetramethylbutyl)phenyl]-ω-hydroxy- **IUPAC Name:** Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)phenyl ether	-	9002-93-1	$(C_2H_4O)_n$ $C_{14}H_{22}O$	
EC Name: 20-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-3,6,9,12,15,18-hexaoxaicosan-1-ol **CAS Name:** 3,6,9,12,15,18-Hexaoxaeicosan-1-ol, 20-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-	219-682-8	2497-59-8	$C_{28}H_{50}O_8$	

IUPAC Name: 20-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-3,6,9,12,15,18-hexaoxaicosan-1-ol				

* This is a list of substances identified as covered by the generic substance description, however further substances not listed here may be covered as well.

1.3 Physico-chemical properties

No physical and chemical properties could be found in accepted databases for the exemplary noted substances in Table 5. Furthermore no registration dossiers are available for these substances.

Hence no physical and chemical properties can be provided.

Table 6: Overview of physicochemical properties

Property	Value	Remarks
Physical state at 20°C and 101.3 kPa	*no information available*	
Melting/freezing point	*no information available*	
Boiling point	*no information available*	
Vapour pressure	*no information available*	
Water solubility	*no information available*	
Partition coefficient n-octanol/water (log value)	*no information available*	
Dissociation constant	*no information available*	
[enter other property, if relevant, or delete row]	*no information available*	

2 HARMONISED CLASSIFICATION AND LABELLING

4-tert-octylphenol ethoxylates are not classified according to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).

The degradation product 4-tert-octylphenol is a substance of very high concern included in the Candidate List because of its probable serious effects to the environment as a result of its endocrine disrupting properties, which give rise to an equivalent level of concern. It is listed in Annex VI of Regulation (EC) No 1272/2008 as follows (4-tert-OP SVHC supporting document, European Chemicals Agency, 2011):

Table 7: Classification and labelling of 4-tert-octylphenol according to part 3 of Annex VI, Table 3.1 of Regulation (EC) No 1272/2008

Index-No	International Chemical Identification	EC-No	CAS-No	Classification		Labelling		Specific concentration limits, M-factors
				Hazard Class and Category Code(s)	Hazard Statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	
604-075-00-6	4-(1,1,3,3-tetramethylbutyl)phenol; 4-tert-octylphenol	205-426-2	140-66-9	Skin Irrit. 2 Eye Dam. 1 Aquatic Acute 1 Aquatic Chronic 1	H315 H318 H400 H410	GHS05 GHS09 Dgr	H315 H318 H410	M=10

Table 8: Classification and labelling of 4-tert-octylphenol according to part 3 of Annex VI, Table 3.2 of Regulation (EC) No 1272/2008

Index-No	International Chemical Identification	EC-No	CAS-No	Classification	Labelling	Concentration limits
604-075-00-6	4-(1,1,3,3-tetramethylbutyl)phenol; 4-tert-octylphenol	205-426-2	140-66-9	Xi; R 38-41 N; R 50-53	Xi; N R:38-41-50/53 S:(2-)26-37/39-60-61	N; R50-53: C≥2.5% N; R51-53: 0.25%≤ C<2.5% R52-53: 0.025%≤ C<0.25%

3 ENVIRONMENTAL FATE PROPERTIES

3.1 Degradation

In the following chapter, degradation data are analyzed with respect to the question whether or not they indicate that 4-tert-octylphenol ethoxylates (4-tert-OPnEO) may be of equivalent level of concern due to their degradation to 4-tert-octylphenol (4-tert-OP). 4-tert-OP is a substance of very high concern included in the Candidate List because of its probable serious effects to the environment as a result of its endocrine disrupting properties, which give rise to an equivalent level of concern. Information for nonylphenol ethoxylates (NPnEO) - which are considered close analogues to octylphenol ethoxylates - are included as supportive information.

3.1.1 Abiotic degradation

3.1.1.1 Hydrolysis

The binding between the octylphenol-group and the ethoxylate groups is very strong therefore it is supposed that hydrolysis is not a relevant path of abiotic degradation under environmental conditions.

3.1.1.2 Phototransformation/photolysis

3.1.1.2.1 Phototransformation in air

As there is no information from studies available for single 4-tert-octylphenol ethoxylates (4-tert-OPnEO) an estimation of half-lives in air was done with AOPwin (v1.92)[1].

Grade of ethoxylation	1	2	3	4	5	6	7	8	9	10	11
Estimated halflive (hours)	9,84	7,23	5,76	4,74	4,04	3,36	3,12	2,88	2,54	2,33	2,16

Having in mind the low vapour pressure of 4-tert-OPnEO (except OPnEO with n = 1 (OP1EO)) – evaporation is expected to be negligible and therefore photodegradation in air is expected not to be a relevant path of degradation for 4-tert-OPnEO.

[1] Environmental parameters used for calculation: temperature 25°C, 24-hr day, OH-radical concentration $0{,}5*10^6$ /cm³

3.1.1.2.2 Phototransformation in water

As described in the chapters below, the main products being released to the water body are un-degraded long chain ethoxylates (4-tert-OPnEO with n > 2) as well as ethoxylates with a low grade of ethoxylation (4-tert-OP1EO and 4-tert-OP2EO) and its carboxylates (4-tert-OPEC) and – to a lesser extent – 4-tert-octylphenol (4-tert-OP). Based on physico-chemical properties and distribution modelling summarized in chapter 3.2, long chain ethoxylates are expected to remain in the water body, while short chain ethoxylates and 4-tert-OP have higher log Pow –values and are therefore expected to adsorb to suspended organic matter and sediment. Thus phototransformation might be a relevant route for ethoxylates with a high grade of ethoxylation only. However, photodegradation is a relevant degradation process in the first few centimetres layer of the water column only. Thus aquatic phototransformation is considered not to have a relevant impact on the degradation of 4-tert-OPnEO in the aquatic environment

3.1.2 Biodegradation

With regard to biodegradation, several studies are available that provide information about degradation pathways of 4-tert-octylphenol ethoxylates (4-tert-OPnEO) in sewage treatment plants, surface water, sediment and soils. They are analysed with regard to the question whether or not 4-tert-OPnEO will contribute to the emission of octylphenol to the environment. Data are analysed with regard to the following aspects:

- Are 4-tert-octylphenol ethoxylates (4-tert-OPnEO) released to the environment (and to which extent)?
- Does the degradation to 4-tert-octylphenol (4-tert-OP) in sewage treatment plants contribute to the emission of 4-tert-OP to the environment?
- Do 4-tert-OPnEO released to the environment contribute to the environmental concentration of 4-tert-OP due to their degradation in environment compartments?

3.1.2.1 Biodegradation in water

Some of the most important studies describing biodegradation in water are summarized in the subsequent chapter. In order to facilitate the discussion in chapter 6, available information on biodegradation in sewage treatment plants and surface water is analyzed separately.

Results suggest the following general pathway, as described in the European Risk Assessment Report ((Environment Agency UK, 2005).

As a first step the ethylene oxide groups (EO) of longer chain 4-tert-OPnEO (n>4) are rapidly removed resulting in ethoxylates with less than four ethoxyl units (usually one or two units, 4-tert-OP1EO and 4-tert-OP2EO). The rate of removal of the EO chain increases with increasing chain length. Under aerobic conditions the shorter chain 4-tert-OPnEO (n<4) will be further oxidised to the corresponding carboxylic acids (for example octylphenoxyacetic acid (4-tert-OP1EC) or octylphenoxyethoxyacetic acid (4-tert-OP2EC)). Under anaerobic conditions the shorter chain 4-tert-OPnEO will be degraded to octylphenol diethoxylate (4-tert-OP2EO) and octylphenol monoethoxylate (4-tert-OP1EO). Finally the 4-tert-OP1EC and 4-tert-OP1EO will be converted into

4-tert-octylphenol (4-tert-OP), especially under anaerobic conditions (Environment Agency UK, 2005).

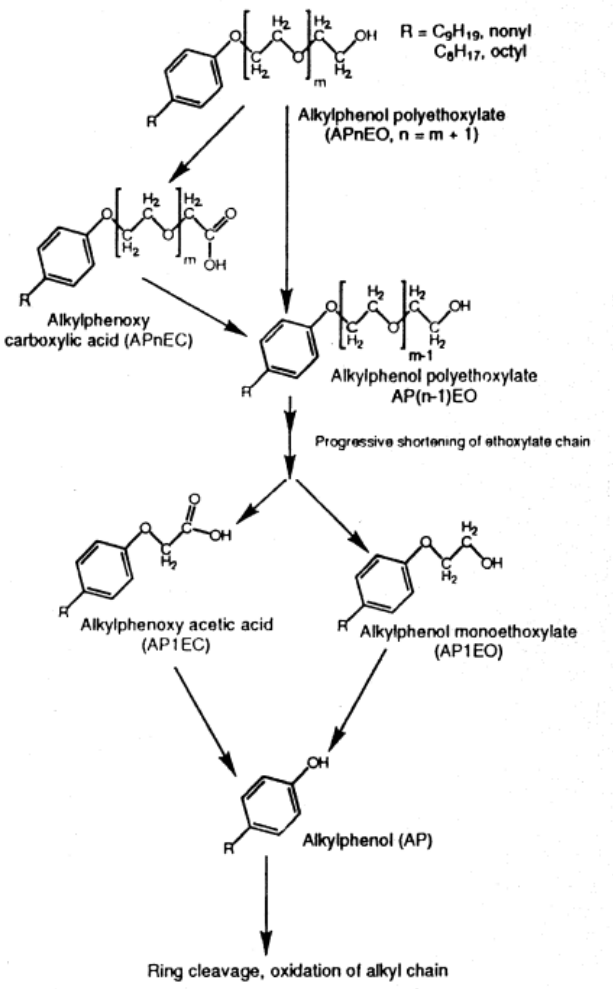


Figure 1: Biodegradation scheme for alkylphenol ethoxylates (Environment Agency UK, 2005)

3.1.2.1.1 Biodegradation in sewage treatment plants

Different types of studies are available to analyze the biodegradation of 4-tert-octylphenol ethoxylates (4-tert-OPnEO) in sewage treatment plants. Two screening studies provide information about the degree of degradation for long and short chain ethoxylates, without providing information about degradation products. In addition two simulation tests for 4-tert-OPnEO and three tests with nonylphenol ethoxylates (NPnEO) are available which provide information about the degree of degradation as well as about the type of metabolites formed and the rate of degradation.

Screening tests

Table 9: Summary of Screening tests

Test substance	Method	Result	Reliability	Reference

poly(oxyethylene) octylphenyl ether n=7-11(average of 9) CAS Nr. 9036-19-5	OECD 301 C	22 % degradation (measured by BOD) in 28 days	2	(National Institute of Technology and Evaluation, 2002)
OP9EO OP1.5EO CAS Nr. 9036-19-5	OECD 301 B Adapted inoculum	OP9EO: 79.8 ± 1.59 % CO_2 evolution in 28 days OP1.5EO: 61.1 ± 0.98 % CO_2 evolution in 28 days 10 day window was failed	2	(Gledhill, 1999; Staples et al., 2001)

In a 28 day ready biodegradability test (OECD 301C) using 100mg/L of the poly(oxyethylene) octylphenyl ether (OPnEO with n=7-11,average of 9) and 30 mg/L sludge 22% degradation was measured by BOD (National Institute of Technology and Evaluation, 2002).

The biodegradation of octylphenol ethoxylates with a high number of ethoxyl groups (OP9EO) and its biodegradation intermediate OP1.5EO was measured using OECD 301B (Gledhill, 1999; Staples et al., 2001). The test was run with adopted inoculum from a waste water treatment plant. 79.8% (OP9EO) and 61.6 % (OP1.5EO) CO_2 evolution was observed after 28 days. The 10 day window was failed in either case. Staples et al. calculated first order half-lives (primary degradation) of approximately 10 days (10.2 days OP9EO, 10.7 days OP1.5EO) with a lag time of 4 days.

Results show, that both long and short chain 4-tert-OPnEO are not readily biodegradable using standard test methods. If the inoculum is adapted, up to 79.8 % (high grade of ethoxylation) and 61.1 % (low grade of ethoxylation) of the parent is transformed into CO_2 after 28 d. Results do not allow any conclusion about degradation products. However they provide some evidence, that 4-tert-OPnEO are metabolized to some extent but are not readily mineralized and that degradation may involve some stable metabolites.

Simulation tests

Table 10: Summary of biodegradation tests in waste water treatment plants

Test substance	**Type of test/ conditions**	**Result**	**Reliability**	**Reference**
Sewage, sewage sludge				
Tert-octylphenol polyethoxylate (13% OP1EO, 40% OP2EO, 29% OP3EO, 14% OP4EO, 4% OP5EO)	activated sludge inoculation (aerobic)	Rapid transformation from OPnEO to OPnEC (n=1-3) within 24 hours 30% degradation to undefined products	2	(Ball et al., 1989)
	primary sewage inoculation (aerobic)	Transformation of OPnEO to OPnEO (n=1-3) within 2 days Nearly no further degradation until day 17 (4% formation of undefined products) 80% degradation to undefined		

		products until day 36 with an adaption time of 5 and 17 days for OP1EO and OP2EO		
	anaerobic bioassay	Transformation OPnEO (n≥2) to OP1EO within 10 days (no further degradation) 18% conversion to OP after 66 d		
P, tert.-octylphenoxynonaethoxyethanol (OPE10)	Shake culture tests (aerobic, acclimated sludge)	> 90% primary degradation within 7 days	2	(Lashen et al., 1966)
	Bench-scale activated sludge tests (aerobic)	90-95 % primary degradation after 11 days (acclimatization time 5-11 days) 63-66% loss of ^{14}C (degradation of the ethoxy-group) after 20 days acclimatization		
	Continuous model septic tank (anaerob) with subsequent percolation field (acclimated) (^{14}C and ^{3}H labelling)	58 % primary degradation in the septic tank (anaerob) (average until day160) 93 % primary degradation after percolation (average until day160) 7% loss of ^{14}C (degradation of the ethoxy-group) in the septic tank (average until day 170) ≈ 65 % loss of ^{14}C (degradation of the ethoxy-group) after percolation (at day 170) No loss of ^{3}H (no degradation of the phenol ring)		

Ball et al. studied the biotransformation of tert-octylphenol polyethoxylate under aerobic and anaerobic conditions (Ball et al., 1989). The test substance mixture of tert-octylphenol polyethoxylates and the corresponding carboxylic acids was inoculated with activated sludge (OPnEO residues were previously detected), primary sewage and anaerobic bacteria.

The tests with activated sludge showed a rapid complete transformation of OPnEO within 24 hours. 70 % of the initial OPnEO dissipated to OPnEC (n=1-3) (OP2EC predominant product and 30% dissipated to unidentified products).

Primary sewage as inoculum resulted in dissipation of OPnEO (n=4-5) within 2 days and an increase of OP2EO until day 17. Only 4 % of the initial input was degraded to undefined products. After an adaption time of 5 and 17 days for OP1EO and OP2EO they degraded to unidentified products. Hence, results show that OPnEO (n > 3) quickly degrade to ethoxylates with lower grade of ethoxylation while further degradation of these products is much slower. After 127 days more than 99% were dissipated to products different from OP, OPnEO (n=1-5) and OPnEC (n=1-2).

Under anaerobic conditions OPnEO (n=2-5) nearly completely dissipated to OP1EO within 10 days. No further degradation occurred. After this, OP1EO converted slowly into octylphenol and, to a less extent, OPnEC and undefined products. After 66 days 18% of the original octylphenol ethoxylates were converted into octylphenol, 6% were transformed to OPnEC (mainly OP2EC). Subsequent degradation of octylphenol appeared to be slow (7.9 % octylphenol at day 190). 89% of the input was degraded to undefined products after 190 days.

The biodegradation of radiolabelled (^{14}C in the ethoxylate chain and ^{3}H in the phenol ring) p,tert.-octylphenoxypolyethoxyethanol (OPnEO, n =10) was carried out by Lashen et al. (Lashen et al., 1966). The experiment included a) an aerobic shake culture test using acclimated bacterial culture from a laboratory continuous activated sludge unit, b) a bench-scale activated sludge test with 3 and 6 hours retention time and inoculated with fresh sludge and c) a (anaerobic) model septic tank percolation field system (retention time = 67 hours).

In the shake culture test and the bench scale test primary degradation was > 90 % within 7 days and after 11 days (3 and 6 hours retention time) respectively. An acclimation period was observed if fresh, not acclimated sludge was used. Dissipation of ^{14}C incorporated in the ethoxylate chain in the bench scale test indicate that primary degradation was mainly due to a transformation of the ethoxyl group (63-66%) while no degradation of the phenol was observed (no dissipation of ^{3}H incorporated in the phenol ring).

In the model tank-percolation field system primary degradation in the anaerob model tank was lower (58%) but reached 93% after transfer through the percolation field. Again this was mainly due to a degradation of the ethoxylate group (65% degradation) and no mineralization of the phenol group was observed.

In summary, results for 4-tert-OPnEO in simulation tests substantiate the degradation scheme described above. In addition results clearly show that 4-tertO-PnEO are not subject to complete mineralization in sewage treatment plants.

Based on measurements of degradation products it can be concluded that 4-tert-OPnEO are quickly degraded to short chain 4-tert-OPnEO (n= 1-3) within 2 days in primary sewage with nearly no further degradation. Especially 4-tert-OP2EO (the main product) remains stable until day 17.

Under aerobic conditions based on simulation studies it can be assumed that about 70% of the input is rapidly transformed to OPnEC (100% transformation after 24h) and 30% are further degraded.

Under anaerobic conditions results seem to depend on the test conditions. Results from a static test with anaerobic bacteria indicate that 100 % of the input is transformed to 4-tert-OP1EO after 10 days and 18% is further transformed to 4-tert-OP after 36 days. But results of the continuous model tank indicate that in a flow through system transformation might be slower (only 58% primary degradation and only 7% transformation of the ethoxy-group)

Results available for nonylphenol ethoxylates (NPnEO) provide further information about the degradation in anaerobic sewage sludge.

Table 11: Summary of biodegradation tests for nonylphenol ethoxylates in waste water treatment plants

Test substance	**Type of test/ conditions**	**Result**	**Reliability**	**Reference**
NPnEO (n =	Sewage	Increase of NP1EO and NP2EO	2	(Lu et al.,

average of 9) (68412-54-4)	sludge; anaerobic	concentration during decrease of NPEO concentration (top on days 14), NP1EO and NP2EO degrade to NP (top on day 21) 30% dissipation of total NPnEO after 3 d		2008a)
NPnEO (n = average of 9) (68412-54-4)	Sewage sludge; anaerobic (sulphate-reducing conditions)	Increase of NP2EO (top on day 7), NP1EO and NP (top on day 21) concentration during decrease of NPEO concentration 50% dissipation of total NPnEO after 3 d	2	(Lu et al., 2008b)
NPEO1-2 mixture (0.15% NP, 70% NP1EO, 28% NP2EO, 2 % NP3EO)	Sewage sludge; anaerobic	10% digester sludge: 31 % NP was formed during 150 days 100% digester sludge: 57 % NP was formed during 150 days	2	(Ejlertsson et al., 1999)

Results by Lu et al. (Lu et al., 2008a; Lu et al., 2008b) showed under anaerobic and sulphate reducing conditions constant degradation of the longer chain ethoxylates with NP1EO and NP2EO being the most prominent ethoxylates from day 7 to day 60. After 3 days about 30 -50% of the total NPnEO concentration dissipated to undefined products.

The degradation of a NP1-2EO mixture (2, 60 and 308 mg/L) in digester sludge (10% and 100%), landfilled municipal solid waste and landfilled sludge was determined under methanogenic conditions for 150 days (Ejlertsson et al., 1999). In this chapter results with regard to the digester sludge are reported while results for landfills are described in chapter 3.1.2.3. The background levels of NP, NP1EO and NP2EO were high in the inocula. In all inoculates using a concentration of 2 mg/L NP1-2EO the short chain ethoxylates were slowly transformed to NP by anaerobic microorganisms. Transformation was highest in the 100% sludge sample compared to the diluted sample (57 and 31 % of the total NP/NPEO concentration respectively at day 150). NP was not further degraded and incubation with radiolabelled NPEO showed that the phenol ring remained intact (no $^{14}C0_2$ or $^{14}CH_4$ production). Results with 60 and 308 mg/L NPEO indicate that degradation is concentration dependent. At 60 mg/L NP1-2EO was slowly transformed to NP1EO in 100% digester sludge but no transformation occurred in the 10% sludge sample and at 308 mg/L NP1-2EO less than 1% of the added NP1-2EO was transformed into NP.

Thus results with nonylphenol ethoxylates show that degradation to undefined products in anaerob sewage sludge might be higher than expected from the tests with anaerobic bacteria for 4-tert-OPnEO. They indicate that up to 50% might be subject to degradation to undefined products. They also indicate that degradation to 4-tert-OP may be higher than expected from the tests performed with 4-tert-OPnEO.

In summary, data indicate that – depending on the test conditions - between 70 and 100% of the 4-tert-OPnEO is not mineralized under sewage treatment plant conditions. While it can be expected that about 70% of the input is transformed to 4-tert-OPnEC in activated sludge within 24h, short chain ethoxylates are the main products in primary sewage and under anaerobic conditions. They account for 94 and 100% of the long chain ethoxylate input after 17 and 10 days respectively in simulation tests. About 18% of the input is subsequently slowly transformed to 4-tert-OP under

anaerobic conditions (until day 35). Data provided for nonylphenol ethoxylates indicate that transformation to 4-tert-OP may be even higher in anaerobic sewage sludge as up to 57% of the initial input was transformed to nonylphenol after 150d. Transformation may be less pronounced under more realistic conditions (only 58% primary degradation in a model septic tank-perculation-field test).

3.1.2.1.2 Biodegradation in surface water

Due to the lack of information for octylphenol ethoxylates, the conclusion about degradation pathways in surface water must be based on experiments with nonylphenol ethoxylates:

Table 12: Summary of biodegradation tests in surface water

Test substance	Type of test/ conditions	Result	Reliability	Reference
Fresh water				
NP4EO (with an ethoxylate range of 2-9 and NP10EO (with an ethoxylate range of 4-15)	aerobic	Primary degradation > 99 % after 100 hours; Metabolites: NPEC No change in initially NP concentration (31days)	2	(Jonkers et al., 2001)
NP9EO	aerobic	After 128 days: Primary degradation 87-97% (adaption time: 28 days) 40.5 % $^{14}CO2$ 40.2 % of the initial radioactivity remaining in aqueous phase 20.8 % of the initial radioactivity incorporated into biomass Non-labelled test system: 0.4 % NP as metabolite of initial NPEO; < 2% NPEC	2	(Naylor et al., 2006)
Estuarine water				
NPnEO (n=1-18, average =10)	Die-away test, aerobic	DisT50 = 23-69 days (winter 13°C) DisT50 = 2.5-35 days (summer 22.5°C) Main intermediate NP2EO	2	(Kveštak and Ahel, 1995)

Aerobic biodegradation of NPEO was investigated in a laboratory-scale bioreactor filled with river water (Jonkers et al., 2001). The bioreactor was spiked with two different technical mixtures of NPEO (NPEO10, NPEO4) at concentration of 10 mg/L. Small amounts of OPEO and decylphenol ethoxylated were present in the mixtures. After 4 days 99% of the NPEO mixtures were dissipated (primary degradation). NPECs were identified as the main group of metabolites. The concentration of NPECs increased until day 12 and subsequently decreased. No change in initial NP was observed during the experiment (31 days).

Aerobic Biodegradation of [^{14}C] NP9EO was examined and changes in the oligomer distribution and mineralization to $^{14}CO_2$ were monitored for 128 days (Naylor et al., 2006). 87-97% of the initial

NPEO was degraded to metabolites other than NP, NPEO and NPEC after 128 d. Only 0.4% NP was detected (non-labelled test system), suggesting that NP is a minor metabolite under aerobic conditions in river water. After 128 days 40.5% of [^{14}C] NP9EO converted to $^{14}CO_2$ but an acclimation period of 28 days was needed.

Biotransformation of NPEO by estuarine mixed bacterial cultures was analyzed under laboratory conditions by using a static die-away method (Kveštak and Ahel, 1995). The experiments were performed with autochthonous bacterial cultures from the brackish water and saline water. Biotransformation kinetics of mixed bacterial culture from the brackish water layer was faster than that from the saline water layer at all temperatures examined and at both concentrations of NPEO (0.1 and 1 mg/L). This was probably due to a better pre-adaptation of the brackish water bacteria to NPEOs in their natural habitat. Under winter temperature conditions (13°C) the estimated DisT50 ranged from 23-69 days, while the DisT50 under summer temperature conditions (22.5°C) ranged from 2.5-35 days. Transformation to NPnEC was not followed and the main intermediate formed during the experiment was NP2EO.

In summary two tests support the hypothesis, that under aerobic conditions in fresh water long-chain nonylphenol ethoxylates will be rapidly degraded to NPECs (99% primary degradation after 100 hours (Jonkers et al., 2001) and formation of the corresponding alkylphenol is of minor relevance. However results by Kvestak and Ahel with a mixed culture of bacteria from brackish water indicate that transformation to NP2EO may occur in brackish water and that degradation may be much slower during winter (DisT50 between 23 and 69 days) (Kveštak and Ahel, 1995). Furthermore, only 40% of NPEO mineralized to CO_2 in 128 d (Naylor et al., 2006).

3.1.2.2 Biodegradation in sediments

No biodegradation tests in sediment, using OPEO as test substance, are available. Therefore tests with the similar compound NPEO were used in this chapter.

Table 13: Summary of biodegradation tests in sediment

Test substance	Type of test/ conditions	Result	Reliability	Reference
Estuarine water sediment				
NPEO4 (with an ethoxylate range of 0-9)	aerobic	DisT50 = 85 days	3	(Ferguson and Brownawell, 2003)
	anaerobic	DisT50 = 289 days		
Fresh water sediment				
NP1EO	anaerobic	DegT50 = 49.5 – 77.0 days (primary degradation)	2	(Chang et al., 2004)

The degradation of radiolabelled NP4EO mixture (NPnEO n=0-9) in estuarine sediment was investigated under aerobic and anaerobic conditions in batch sediment slurry experiments (Ferguson and Brownawell, 2003). The sampling site (Jamaica Bay, NY, USA) has been extensively studied with regard to the NPEO fate and is situated near to the outfall of a major waste water treatment plant (NPEO concentration in sediment >40 µg/g dry weight, mostly NP and NP1EO). The total NPEO mixture dissipated significantly faster under aerobic conditions (DisT50 = 85 days) than

under anaerobic conditions (DisT50 = 289 days). Even under aerobic conditions only 1.7 % CO2 of the initial added [^{14}C6]-NP4EO was formed. This is contrary to other studies that have been reported that NPEO converted to CO_2 under aerobic conditions. The authors stated various reasons, for example: reduced bioavailability of NPEOs due to sorption to the highly organic-rich sediment; inhibition of mineralization by high concentrations of toxicants (sediment is known for high contaminations with heavy metals and organic contaminants and to be toxic to microorganisms in Microtox™ assays). Nonylphenol was present at low levels (~5%) in the [^{14}C6]-NP4EO spiking material and was observed to persist at these low levels throughout the degradation experiment in both oxic and anoxic treatments. At the end of the experiment, NP accounted for only approximately 3% of the initially added ^{14}C activity in both the aerobic and anaerobic treatments. The authors mentioned that this might be due to a small amounts of NP formed and removed at similar rates or that the time scale of the experiment was not long enough.

Chang et al. studied the degradation of NP1EO by anaerobic microorganisms from NP-acclimated river sediments (Chang et al., 2004). The $DegT_{50}$ (primary degradation) ranged from 49.5 to 77.0 days (30 °C). After day 8, NP was determined as intermediate product. The concentration of NP increased from day 8 to day 14. Degradation rates for NP1EO were enhanced by increasing temperature and inhibited by the addition of acetate, pyruvate, lactate, manganese dioxide, ferric chloride, sodium chloride, heavy metals, and phthalic acid esters.

In summary, only little information is available for biodegradation of 4-tert-OPnEO and NPnEO in sediment. These data show that in sediments alkylphenol ethoxylates degrade to alkylphenol under aerobic and anaerobic conditions. Degradation of the alkylphenol ethoxylates is slow and depends on temperature with dissipation half-lives of 49-289 d. Although results in aerobic sewage treatment plants indicate that under aerobic conditions dissipation of alkylphenol ethoxylates and formation of the corresponding carboxylates is a fast process, results by Ferguson and Brownawell (Ferguson and Brownawell, 2003) indicate that in pre-contaminated sediment this process may be hindered. Overall results indicate that alkylphenols ethoxylates may degrade to its corresponding alkylphenols in sediment. Because degradation may be slow especially under anaerobic conditions, it can be expected, that they are a constant source for their alkylphenols in sediment.

3.1.2.3 Biodegradation in soil

No biodegradation tests in soil, using OPEO as test substance, are available. Therefore tests with the similar compound NPEO were used in this chapter.

Table 14: Summary of biodegradation tests in soil

Compound	Result	Reliability	Reference
Soil + sludge			
NP12EO	90-99% dissipation within first week Biphasic kinetic 1. $DisT_{50}$ = 0.3 – 5.2 days 2. $DisT_{50}$ = 11.40 – 48.0 days	2	(Sjöström et al., 2008)
Mixture of NP1EO, NP2EO and NP3EO Imbentin -	NP1EO: 90 % dissipation after 322 days triphasic kinetics: 1. Initital period (1-14 days): $DisT_{50}$ = 7 days 2. Transition time (30 – 90 days): $DisT_{50}$ = 150 days 3. Long-term persistence (> 150 days): $DisT_{50}$ > 360	2	(Marcomini et al., 1989)

N/7A	days NP2EO: 86 % dissipation after 322 days triphasic kinetics: 1. Initital period (1-14 days): $DisT_{50}$ = 8 days 2. Transition time (30 – 90 days): $DisT_{50}$ = 110 days 3. Long-term persistence (> 150 days): $DisT_{50}$ > 360 days		
Linear NP2EO	Mineralization after 2 months: sludge-soil ratio 1:20 (40% water content) = 61.4 % sludge-soil ratio 1:20 (80% water content) = 12.4 % sludge-soil ratio 1:100 (40% water content) = 70.2 % sludge-soil ratio 1:100 (80% water content) = 43.4 % sludge only = 14.8 % soil only = 64.4 %	2	(Gejlsbjerg et al., 2001)
NPEO1-2 mixture (0.15% NP, 70% NP1EO, 28% NP2EO, 2 % NP3EO)	landfilled sludge: 81 % NP was formed during 53 days; > 53days concentration remained constant	2	(Ejlertsson et al., 1999)

Sjöström et al. examined degradation of NP12EO in four contrasting agricultural soils (Sjöström et al., 2008). A biphasic dissipation kinetic was observed. The rapid initial dissipation with DisT50 = 0.3 – 5.2 days were followed by a slower dissipation phase (DisT50 = 11.4 - 48.0 days). After 30 days results showed the formation of NP from NP12EO. NP remained nearly stable at the end of the experiment. No detectable NP12EO remained in the soils after 105 days and no intermediate degradation products were found.

The fate of a mixture of NPnEO (n= 1-3) in sludge amended soil was studied by Marcomini et al. (Marcomini et al., 1989). The soil samples were collected from the upper 5 cm of planted grass land. This site was part of a long term filed study and had received anaerobically digested sludge at an average application rate of 13.5 tonnes/ha year (dry weight). The sludge was applied to the surface soil as a liquid spread, four to six times per year. The initial concentrations of NP1EO and NP2EO in the amended soil were 1.1 and 0.095 mg/kg (dry weight). 320 days after the last sludge application the residual mean concentrations were 0.11 and 0.013 mg/kg (dry weight) for NP1EO and NP2EO, respectively. The disappearance of NP1EO and NP2EO were fast in the first two weeks followed by a slow disappearance from days 30-90; from day 150 no significant disappearance was noted and NP1EO and NP2EO was classed as being persistent. The estimated degradation half-lives of NP1EO in the soil in the initial phase was 7 days (NP2EO = 8 days), 150 days for the transition phase (NP2EO = 110 days) and >360 days after 150 days of application. These half-lives are for primary biodegradation and were calculated assuming pseudo first order kinetics.

The mineralization of ^{14}C-labelled NP2EO was investigated in different sludge-soil mixtures and soils (Gejlsbjerg et al., 2001). The mineralization of NP2EO was indirectly affected by the amount of sludge in the test mixtures. A higher content of sludge in the mixtures reduced the overall concentration of oxygen, which resulted in a decrease of the mineralization of NP2EO. A higher water content resulted in lower concentrations of oxygen, thus in decrease of mineralization, too.

Mineralization of NP2EO was not affected by the soil type since the percentage of compound mineralized (64.4 %) after two months was not different between any of the test mixtures.

The degradation of a NP1-2EO mixture (2, 60 and 308 mg/L) in landfilled municipal solid waste and landfilled sludge was determined under methanogenic conditions for 150 days (Ejlertsson et al., 1999). In both inocula at a concentration of 2 mg/L NP1-2EO the added NP1-2EO was transformed to NP by anaerobic microorganisms. The background level of NP in the landfilled municipal solid waste was so high that a transformation of NPEO1-2 would only increase the indigenous NP concentration with 5-10% (significant decrease of NP1EO and NP2EO was observed within 22 days). An increase to 81 % during 53 days was observed in samples with landfilled sludge. At a concentration of 60 mg/L NP1-2EO approximately 20 % NP was formed during 40 days (landfilled municipal solid waste) and 80 days (landfilled sludge). The concentration of formed NP remained constant until day 150. At 308 mg/L NP1-2EO less than 1% of the added NP1-2EO was transformed into NP.

In summary results show, that the overall biodegradation of alkylphenol ethoxylates in soil is slow and depends on the amount of oxygen available. Results by Sjöström et al. (Sjöström et al., 2008) and Ejlertsson et al. (Ejlertsson et al., 1999) show that the corresponding alkylphenols are formed during this process. While it was only a minor pathway in agriculture soil (Sjöström et al., 2008), 81 % of the overall nonylphenol ethoxylates concentration at the end of the experiment (2 month) was nonylphenol in a landfill with anaerobic sludge (Ejlertsson et al., 1999). Thus results indicate that alkylphenol ethoxylates may degrade to its corresponding alkylphenols. Because conversion is slow, it can be expected that the remaining ethoxylate concentration is a constant source of alkylphenols in soil.

3.1.3 Summary and discussion on degradation

In summary data on degradation of 4-tert-octylphenol ethoxylates (4-tert-OPnEO) and nonylphenol ethoxylates (NPnEO) indicate the following:

Both long and short chain 4-tert-OPnEO are not readily biodegradable using standard test methods and thus tests provide some evidence, that 4-tert-OPnEO are metabolized to some extent but not readily mineralized and that degradation may involve some stable metabolites.

In sewage treatment plants– depending on the test conditions - between 70 and 100% of the 4-tert-OPnEO is not mineralized. 4-tert-OPnEO are expected to be converted into short chain ethoxylates and further degraded to the corresponding carboxylates or to 4-tert-octylphenol (4-tert-OP) during aerobic and anaerobic phases respectively. Transformation to 4-tert-OP is expected to occur to a low extent during sewage treatment due to slow degradation rates of the short chain ethoxylates. Thus in summary it is expected that 4-tert-OPnEO in sewage will be basically transformed to short chain octylphenol ethoxylates and their corresponding carboxylates, which will be the main compounds released to the aquatic environment.

Even if hydrolysis or photodegradation might occur in water, the overall contribution to the whole degradation process is negligible. The low vapour pressure of long chain 4-tert-OPnEO indicates that photodegradation in air is only a minor degradation path but it might be of some relevance for 4-tert-OP1EO.

In aerobic surface water, further biodegradation of the short chain 4-tert-OPnEO to its corresponding carboxylates is expected to be the predominant pathway. While such transformation

may be quick in summer (DisT50 = 2.5-35 days), results for a brackish bacteria community indicate that it may be slower in winter (DisT50 between 23 and 69 days).

Once transferred into sediment, it can be expected that the 4-tert-OPnEO are transformed to the stable 4-tert-OP. Degradation half-lives indicate that this is a slow process under anaerobic conditions (Dis/DegT50 = 49-289 days). While some data for activated sludge indicate that under aerobic conditions formation of octylphenol carboxylates is the dominant process, data in a pre-contaminated sediment indicate, that this might be hindered in highly contaminated sediments (DisT50 (NPnEO) = 85d). Overall, sediments are expected to be a continuous source of 4-tert-OP formed from 4-tert-OPnEO.

Processes in soil are similar to those observed in sediment but primary degradation seems to be even slower. Results indicate that, after a quick first degradation, biodegradation of 4-tert-OPnEO will be slow. Thus, similar to sediment, once contaminated with 4-tert-OPnEO, soils are expected to be a continuous source for 4-tert-OP in the environment.

In summary, 4-tert-OPnEO degrade to 4-tert-OP, especially under anaerobic conditions. Hence, 4-tert-OPnEO are relevant precursors for the substance of very high concern 4-tert-OP.

4-tert-OP itself is a stable metabolite which strongly adsorbs to soil, sludge and sediment. In sediment no elimination was observed under anaerobic conditions after 83 days ($DsDT_{50}$ > 83 days) (European Chemicals Agency, 2011).

3.2 Environmental distribution

3.2.1 Adsorption/desorption

According to Leisewitz and Schwarz (Leisewitz and Schwarz, 1997), the affinity to the organic phase (soil, sediment, organic material) increases when the 4-tert-octylphenol ethoxylates (4-tert-OPnEO) are subject to degradation processes. The relatively high log Pow of 4-tert-OPnEO with low grades of ethoxylation argues for accumulation in these compartments.

As no information from registration dossiers is available yet and the expected registrations might deal with technical mixtures composed of 4-tert-OPnEO with different grades of ethoxylation QSARs were used to estimate the adsorption potential for a subset of ethoxylation grades.

Table 15: Adsorption potential for 4-tert- octylphenol ethoxylates (grade of ethoxylation = 1-19)

Grade of ethoxylation	log Kow (EPI web 4.1[a])	loc Kow @pH 7.4 (ACD/Labs[b])	log Kow (Chem/Axon)	log Koc (EPI web 4.1[a])	loc Koc @ pH 7.4 (ACD/Labs[b])
1	4.86	4.99	4.15	3.26	4.09
2	4.59			3.02	
3	4.31	4.66	4.05	2.77	3.91

4	4.04			2.53	
5	3.77			2.29	
6	3.49	3.96	3.91	2.05	3.52
7	3.22			1.81	
8	2.94	3.49	3.82	1.56	3.27
9	2.67			1.41	
10	2.39			1.26	
11	2.12	2.78	3.68	1.11	2.89
12	1.84			0.95	
13	1.57			0.8	
14	1.30	-	3.54	0.66	-
15	1.02			0.50	
16	0.75			0.35	
17	0.47	-	3.4	0.20	-
18	0.20			0.05	
19	-0.08			-0.11	

Explanation of footnotes:

[a] calculation was conducted with the modules KowWIN v1.68 resp. KocWIN v2.00 which are integral parts of the QSAR suite EPIweb v4.1 (2008)

[b] calculation was conducted on the ChemSpider-website (www.chemspider.com; available 19.04.2012). The QSAR for the calculations are included in the ACD/PhysChem Suite.

3.2.2 Volatilisation

The calculation of the Henry-Constant with QSAR HenryWIN v3.20 (group estimation; Sept. 2011) revealed a value of 7.15E-02 Pa*m³/mole for mono-ethoxylated 4-tert-octylphenole, indicating a low tendency for volatilisation. Since the vapour pressure decreases with increasing grade of ethoxylation volatilisation is not expected to be a relevant path of environmental distribution.

3.2.3 Distribution modelling

Distribution modelling according to Mackay Level I

As there is no registration dossiers available for any 4-tert-octylphenol ethoxylate and therefore no information on physical-chemical properties from testing, the whole exposure modelling in this subsection is based on QSAR-predicted substance properties below. Physical-chemical data calculated with EPIsuite v4.10 marked with (*)allow a rough indication of the substance properties only as the OPnEO with higher ethoxylation grades are borderline with regard to the applicability domain of the QSAR models.

Table 16: physical-chemical properties of a subset of 4-tert-octylphenol ethoxylates with different grades of ethoxylation

Grade of ethoxylation	OP2EO	OP4EO	OP6EO	OP8EO	OP10EO
molecular weight	294.429	382.53412	470.647	558.753	646.859
water solubility (mg/l)*	5.162	4.506	3.724	2.97	2.31
vapour pressure (mm Hg)*	9.15E-06	6.98E-08	3.81E-10	2.75E-12	1.80E-14
Henry's Law constant (atm-m3/mol)	5.22E-01	5.93E-03	4.82E-05	5.16E-07	5.04E-09
Log Kow*	4.59	4.04	3.49	2.94	2.39
Log Koc*	3.02	2.53	2.05	1.56	1.26

Table 17: Fugacity Level I distribution figures for the subset of ethoxylation grades listed aboved

Grade of ethoxylation	Distribution to:		
	Air (percent)	Water (percent)	Soil (percent)
2	45.38	2.09	52.53
4	2.63	10.66	86.71
6	0.05	27.06	72.88
8	0.00	53.44	46.56
10	0.00	69.60	30.40

As a result from the physical-chemical data, the assumed tendency for evaporation and the outcome of the Level I distribution modelling it can be concluded, that higher grades of ethoxylated 4-tert-octylphenols might remain in the water phase and will be subject of biotic degradation while 4-tert-octylphenols with low ethoxylation grades will adsorb at organic suspended matter and therefore not preferential object of biotic degradation.

3.2.4 Measured distribution data

Information from studies about the behaviour of nonylphenol ethoxylates in surface water and during waste water treatment are summarised in the following tables. No studies are available about the behaviour of 4-tert-octylphenol ethoxylates.

Table 18: Summary of behaviour NPEO during waste water treatment

Test substance	**Result**	**Reliability**	**Reference**
NPnEO (n=1-20), NP1EC, NP2EC, NP	*Average value of 11 waste water treatment plant (Switzerland):* Primary effluent: NPnEO (n=3-20)= 82.4 % NP1EO + NP2EO = 11.5 % NP1EC + NP2EC = 3.1 % NP = 3 % Secondary effluent: NPnEO (n=3-20)= 28.2 % NP1EO + NP2EO = 21.8 % NP1EC + NP2EC = 46.1 % NP = 3.9 % Increase of NP mass compared to influent in two	2	(Ahel et al., 1994a)

	selected waste water treatment plants: 181 - 758 % (comparison of raw seawage mass (mol/day) with mass in digested sludge and secondary effluent (mol/day). 96,7% and 92 % of mass efflux respectively are adsorbed to sludge 60-65% of all nonylphenol compounds that have entered sewage treatment are released into the environment: NPEC = 19 % NP1EO +NP2EO = 11 % NP = 25 % NPnEO (untransformed) = 8 % 60 % of total load (NPnEO und NPnEC) are discharged into receiving waters via secondary effluent; 40 % of the total load (> 90 % NP) disposed to the environment via digested sludge		
NPnEO (n=1-12), NP	*Tanguu WWTP, Tianjin* Influent NP = 0.93 – 6.0 µg/L Effluent NP = 1.32 – 5.22 µg/L Removal (average) Total NPnEO (n=1-12) = 70 % NPnEO (n>6) = 82.6 - >99 % NP5EO = 43.2 % NPnEO (n=1-4) = 62.4-74.6 % NP = 70.8% increase in effluent compared to influent; NP was accumulated in all effluent samples (except April 2004)	2	(Yu et al., 2009)
NPEO (n= 1-12), NPnEC (n= 1-3), NP	carbonaceous treatment: total removal NPEO (NPEO, NP1-3EC, NP) = 36.9 % Increase of NP concentration by 25.5 % in effluent compared to influent carbonaceous/nitrification treatment: total removal NPEO (NPEO, NP1-3EC, NP) = 59 % NP removal = 42.6 ± 30.4 % carbonaceous/nitrification/denitrification treatment: total removal NPEO (NPEO, NP1-3EC, NP) = 26.8 % Increase of NP concentration by 54.1 % in effluent compared to influent	2	(McAdam et al., 2011)
NPnEO (n=9)	20.8 % of the influent radioactivity removed as CO2 55.9 % was found in effluent as NP/NPEO (6.9 %), NPnEC (26 %) and highly degraded metabolites (23.1 %) 6 % adsorbed to sludge (3.5 % as NP/NPnEO and 2.5 % as biomass) 8.35 % remained in aqueous part of the system 0.72 % removed from the system in sludge 8.23 % of the radioactivity was unaccounted for Increase of NP = 112.5 %	3	(European Commission, 2002; Varineau et al., 1996)

The removal of OPEO and NPEO in waste water treatment plants varies because of: different source water, operating conditions and treatment technologies. In the following several studies are summarized.

The behaviour of NPEO in several full-scale mechanical-biological waste water treatment plants in the Glatt Valley, Switzerland was investigated by Ahel et al. (Ahel et al., 1994a). The concentration of NPnEO (n=3-20) decreases from primary to secondary effluent (82% to 28%), while the concentrations of the metabolites NPnEO (n=1-2, 12% to 22%), NPnEC (n=1-2, 3% to 46%) and NP (3% to 4%) increase. 60-65% of all nonylphenol compounds that have entered the waste water treatment plants are released into the environment, approximately 25% released to the environment in the form of NP and 11% in the form of NP1EO and NP2EO. Almost all of the released NPnEO and NPEC, as well as the majority of NP1EO and NP2EO, are discharged into receiving waters via secondary effluents (60% of the total input into the environment). NP (>90%) is disposed to the environment via digested sludge (40% of the total input into the environment). Analysis of mass flux in two waste water treatment plants revealed that the overall NP concentration compared to the influent increased by 181 – 758 % due to the degradation of NPnEO to NP with most of the NP being adsorbed to the sludge

Yu et al. monitored NPEO and their metabolites in waste water treatment plants of Tianjin (Yu et al., 2009). 70% of NPnEO (n=1-12) was removed. In all waste water treatment plants effluent samples (except the sample from April 2004) NP was accumulated (average 70.8%) with a mean value of 2.92 µg/L.

The fate of NPEO during different activated sludge treatments (carbonaceous treatment, carbonaceous/nitrification treatment, carbonaceous/nitrification/denitrification treatment) was investigated by Mc Adam et al. (McAdam et al., 2011). Based on mass balance, overall biodegradation efficiencies for NPEOs, NPnEC (n=1-3) and NP were 37%, 59%, and 27% for the carbonaceous, carbonaceous/nitrification, and carbonaceous/nitrification/denitrification activated sludge plant, respectively. Beside short chain ethoxylates and carboxylates (n=1-3) NP was also formed at the carbonaceous (25.5%) and carbonaceous/nitrification/denitrification activated sludge plant (54.1%). In contrast, NP removal of 42.6±30.4% was observed at the carbonaceous/nitrification activated sludge plant.

The behaviour of NPEOs and their biodegradation intermediates during sewage treatment procedure were investigated (Shao et al., 2003). Compared with concentrations of NP and NP2EO, the concentration of NP1EO was significantly low, suggesting that once NPEOs were degraded into NP1EO, they would be easily transformed into NP. The removal of NPEOs has a tendency to increase with the increase of EO chain length. The removals of NP2EO, NP3EO and NP4EO were below 60%, significantly low in comparison with those of NPnEOs at n>9 (>70%, exception n=7 with 59.6%). The removal of NPEO was contributed by two paths: biodegradation of NPEOs from longer ones to shorter ones, and sorption of NPEOs to sludge. For, NP sorption was the primary path. The relatively low removals of NPEOs with short EO chains were perhaps due to the simultaneous occurrence of decomposition and formation of these compounds.

The study of Varineau et al. was discussed in the Risk Assessment Report of 4-nonylphenol, which has been copied here in italic letters (European Commission, 2002):

The biodegradation of ^{14}C ring-labelled NPnEO (average n=9) has been studied in a semicontinuous activated sludge treatment system. The activated sludge was derived from the mixed liquors from the aeration basin of a wastewater treatment plant. The water used in the test was the primary effluent from the settling basin at the wastewater treatment plant, supplemented with

nutrient broth. The background concentration of nonylphenol and NPnEO (range n=1-17) were 43.6 µg/l and 978 µg/l respectively. Before the test was started, the activated sludge was acclimated for 14 days by exposure to the primary effluent. After 14 days 300 ml of the activated sludge was placed into the degradation reactor and primary effluent containing 2 mg/l of the ^{14}C labelled NPnEO was fed into the reactor. A semi-continuous fill and draw procedure was used such that around 200 ml of the liquid in the reactor was drawn off and replaced by the primary effluent containing the ^{14}C-labelled substance every 2.3 days. This gave a sludge retention time and hydraulic retention time of 52 and 3.45 days respectively in the system. The total sampling time was 30 days. Based on radioactivity measurements, 20.8% of the influent radioactivity was removed as CO_2, 55.9% was found in effluent as nonylphenol/NPnEO (6.9%), NPnEC (26%) and highly degraded metabolites (23.1%), 6% remained in the test system adsorbed to sludge (3.5% as nonylphenol/NPnEO and 2.5% as biomass), 8.35% remained in the aqueous part of the system (1.03% as nonylphenol/NPnEO, 2.88% as NPnEC, and 3.45% as highly degraded metabolites), 0.72% of the radioactivity was removed from the system in sludge (0.09% as nonylphenol/NPnEO, 0.34% and NPnEC and 0.3% has highly degraded metabolites) and 8.23% of the radioactivity was unaccounted for. Overall, there was a 93% removal of the NPnEO from the influent. Specific analysis for nonylphenol showed that from the total influent concentration of nonylphenol/NPnEO compounds (total 204 µg, of which around 8 µg was nonylphenol), around 4 µg of nonylphenol was discharged in effluent, 5 µg was adsorbed on sludge and 8 µg was retained in the system. Thus there appears to have been a net generation of nonylphenol in the system (i.e. 8 µg was added to the system, 17 µg present in the system - if it is assumed that no degradation of nonylphenol occurred then around 4.6% of the NPnEO was converted to nonylphenol) (Varineau et al., 1996). Based on the data net generation of NP accounted for an increase of the overall NP by 112.5% compared to the influent.

Table 19: Summary of behaviour of NPEO in surface water

Test substance	**Result**	**Reliability**	**Reference**
Surface water			
NPnEO, NP1EO + NP2EO, NP1EC + NP2EC, NP	*Glatt River, Switzerland:* Total Input (n=10): NPnEO (n=3-20)= 21.6 % (23.4 mol/day) NP1EO + NP2EO = 22.5 % (24.3mol/day) NP1EC + NP2EC = 51 % (55.2 mol/day) NP = 4.9 % (5.3 mol/day) Output NPnEO (n=3-20)= 3.4 % (2.8 mol/day) NP1EO + NP2EO = 8.8 % (7.2 mol/day) NP1EC + NP2EC = 85.4 % (70.1 mol/day) NP = 2.4 % (2.0 mol/day) Dissipation nonylphenolic compounds = 24 %	2	(Ahel et al., 1994b)

The behaviour of NPEO and their metabolites in surface water (Glatt River, Siwtzerland) was studied by Ahel et al. (Ahel et al., 1994b). Several sampling sides along the river were analysed. Discharge of secondary effluents from municipal sewage treatment plants into the river was the predominant source of nonylphenol ethoxylates. Concentration varied substantially depending upon sampling location, season and time of the day. The concentrations of nonylphenolic compounds were significantly lower in summer than in winter. The overall dissipation efficiency on the river

section was 24 %. While 88 % of the total NPnEO input into the river based on effluents form sewage treatment plants was eliminated only 62 % of nonylphenol disappeared and the concentration of the short chain carboxylates (NP1-2EC) increased. Results indicate that although some mineralization occurred, most of the nonylphenolic compounds remained in the river- during summer predominantly as NP1-2EC and in winter as NP1-2EO. Degradation toward NP occurs, but degradation to short chain NP1-2EO and NP1-2EC were of higher relevance. However, although NP usually belongs to the less abundant surfactant-derived nonylphenolic compounds in the Glatt River, a majority of the concentration values were higher than 1 µg/L. In sediment NP was the predominant nonylphenolic compound.

3.2.5 Summary distribution

Measured data in sewage treatment plants are difficult to interpret with regard to the question whether or not degradation of 4-tert-octylphenol ethoxylates (4-tert-OPnEO) to 4-tert-octylphenol (4-tert-OP) in these plants results in a relevant contribution to the overall 4-tert-OP concentration in the environment as usually already the influent contains 4-tert-OP and both formation of 4-tert-OP and its degradation contribute to the overall concentration. However results reveal some general aspects which are in line with results of the biodegradation experiments:

Overall results show, that the concentration of long chain ethoxylates in sewage treatment plants decrease as expected based on degradation data. Data substantiate that the ethoxylates are not subject to complete mineralization. The overall degradation of the ethoxylates (mineralization and degradation to metabolites others than short chain ethoxylates, carboxylates and alkylphenol) was between 27 and 45% of the overall NP/NPEO. Results by Ahels et al. substantiate that the formation of octylphenol carboxylates may be the predominant route of transformation, as NP1-2EC were the most dominant metabolites in the waste water treatment plant effluent (Ahel et al. 1994a). Net load data for nonylphenol indicate that the contribution to the overall 4-tert-OP concentration released to the environment may be high: All studies suggest that the net loads of nonylphenol increase during sewage treatment. Varineau et al (Varineau et al., 1996) described a net increase of about 112.5% (17 µg/L compared to 8 µg/L at the influent), while the net increase was 71 % in the study by Yu et al (Yu et al., 2009) and 181- 758% in the study by Ahel et al. (1994a). Data by McAdam suggest, that NP formation is mainly a result of the denitrification step (54% in this study) (McAdam et al., 2011).

Results by Ahel et al. and Varineau et al. suggest that the majority of the remaining 4-tert-OPnEO will be released into receiving waters via secondary effluent while sludge will be a significant pathway for 4-tert-OP (Ahel et al., 1994a; Varineau et al., 1996).

Based on such data reasonable worst-case assumptions for the fate of 4-tert-OPnEO during anaerobic waste water treatment were estimated in the environment risk evaluation report for octylphenol (Environment Agency UK, 2005). According to this calculation 45% of the 4-tert-OPnEO would be mineralized, 30.5 % would be released via effluent as 4-tert-OP1EO, 4-tert-OP2EO and 4-tert-OPEC (25%) and as 4-tert-OPnEO (n>3) (8%) and 21.5% would leave the waste water treatment plant as 4-tert-OP (19% via anaerobically digested sludge and 2.5 % via effluent).

The low percentage of ethoxylates degraded to 4-tert-OP is expected to be due to the fact, that degradation of the short chain ethoxylates to 4-tert-OP is a very slow process. However, as described in the chapters above, this transformation contributes relevantly to the overall 4-tert-octylphenol output of sewage treatment plant (increase by 25 – 758 %).

3.3 Bioaccumulation

Not relevant for this dossier.

3.4 Secondary poisoning

Not relevant for this dossier

4 HUMAN HEALTH HAZARD ASSESSMENT

Not relevant for this dossier.

5 ENVIRONMENTAL HAZARD ASSESSMENT

The following sections summarize available ecotoxicity information for octylphenol ethoxylates (4-tert-OPnEO). Information showing that the degradation product 4-tert-octylphenol is a substance of very high concern, due to its endocrine disrupting properties which cause probable serious effects in the environment, is summarized in the SVHC supporting document for 4-tert-octylphenol (European Chemicals Agency, 2011).

5.1 Aquatic compartment (including sediment)

5.1.1 Toxicity data

Available toxicity data for octylphenol ethoxylates (4-tert-OPnEO) are roughly summarized in order to analyze whether or not they may give rise to an equivalent concern compared to 4-tert-octylphenol (4-tert-OP) with regard to their endocrine properties. Only endpoints relevant with regard to the endocrine properties are analyzed.

5.1.1.1 In vitro data

In vitro results may provide information about a specific mechanism of action, in this case estrogen receptor binding. They may also provide information about the potency of this mechanism but do not consider whether or not effects may occur in intact organisms and do not provide information on the potency *in vivo* as this is influenced by pharmaco-kinetic processes such as uptake distribution, accumulation and excretion.

Only very few data for 4-tert-OPnEO are available while more information on nonylphenol ethoxylates (NPnEO) could be collected. Thus studies for nonylphenol (NP) were used as supporting information.

With regard to the octylphenol ethoxylates two studies are available using MCF cells (White et al., 1994) and the Yeast YES assay (Isidori et al., 2006). Both tests included short chain ethoxylates (OP2EO and OP3EO respectively) as well as longer chain ethoxylates (OP3EO, OP5EO, OP12EO and OP9-10EO respectively). Data are summarized in Table 20:

Table 20: Summary of *in vitro* test results for 4-tert-octylphenol ethoxylates and – as supporting information - for nonylphenol ethoxylates using cells from aquatic organism VTG = vitellogenin; E2 = 17ß-estradiol; EE2 = Ethinylestradiol, RP (relative potency) = EC_x E2/EC_x OPnEO, RIE (relative inductive efficiency) =maximal induction compared to maximal E2 induction):

Testsubstance	**Cell type**	**Test condition / parameter**	**Effect concentrations**	**Potency (relative to 17ß-estradiol and/ or OP)**	**Reference**
OPnEO					
OP2EO OPnEO (n = 3,4,5,12)	MCF cells	Induction of the transcriptional activity of the estrogen receptor	E2: 6 fold induction at 10^{-8}M OP: 4 fold induction at 10^{-6}M OP2EO: 2 fold induction at 10^{-6}M OPnEO (n=3,4,5,12): < 1fold induction at 10^{-6}M	OP: 0.01 compared to E2 (comparison of concentrations inducing similar induction) OP2EO: half fold induction compared to OP OPnEO: negligible effects	(White et al., 1994)
OP3EO OP9-10EO (technical mixture)	Yeast cells, human ER receptor hERα	YES assay, EC50:concentration giving 50% of the maximal response induced by 17ß estradiol	EC_{50} E2 = 2.8 $^{-5}$ mg/L OP = 2.5^{-2} mg/L OP3EO = 19 mg/L OP9-10EO = n.d. (19% effect at 5 mg/L	RP: (EC_{50} E2/EC_{50} OPnEO): OP:.001 OP3EO: 0.0000014 OP9-10EO: ND RIE: OP: 61% OP3EO: 53% OP9-10EO: 19%	(Isidori et al., 2006)
NPnEO					
NP1EO/NP2EO mixture	Yeast cells	YES assay,	EC_{20}: E2 0.022 µg/L NP = 246 µg/L NP1EO = 10 000 µg/L	RP: (EC_{20} E2/EC_{20} NP(nEO):): NP: 0.000089 NP1-2EO: 0.0000023	(Metcalfe et al., 2001)
NP1-2EO NP6EO NP10EO (technical mixtures)	Yeast cells	YES assay,	$EC_{50:}$ E2 = 2.8 $^{-5}$ mg/L NP= 9.3 $^{-4}$ mg/ NP6EO = 40% effect at 10 mg/L NP10EO = 30% effect at 6.6 mg/l	RP: (EC_{50} E2/EC_{50} NP(nEO):): NP:.003 NP6EO: ND NP10EO: ND RIE: NP:.72 % NP6EO: 40 % NP10EO: 30%	(Isidori et al., 2006)
NP2EO	Yeast cells	Recombinant yeast (strain BJ2168) heterogously expressing rtER. Induction of β-galactosidase activity:	LOEC (E_2) = 10^{-8} to 10^{-9} M LOEC (4-NP) = 10^{-6} M N2EO = No estrogen activity up to 10^{-4} M (	RP (LOEC(E_2)/LOEC(4-*n*-NP)) NP : 1 x 10^{-2} - 1 x 10^{-3}	(Madigou et al., 2001)
NP2EO NP7EO	Yeast cells	Recombinant yeast (strain BJ-ECZ) heterogously expressing rtER. ß-galoctisidase activity	LOEC (E_2) = 10^{-9} M LOEC (4-NP) = 10^{-6} M EC_{max} (E_2) = 10^{-8} M EC_{max} (4-NP) = 10^{-5} M	RP LOEC(E_2)/LOEC(4-NP(nEO)) NP = 1 x 10^{-3} RIE: NP: 92% NP2EO: 39 – 64 % NP7EO: 21-34 %	(Petit et al., 1997)

NP10EO	YES Assay,	28 mg/L in biodegradation assay using inocolum from Helsinki and Jyväskylä City WWTP		increased YES response with increasing degradation toward shorter chain NPEO	(Pessala et al., 2009)
NP2EO	MCF cells	Induction of the transcriptional activity of the estrogen receptor	E2: 6 fold induction at 10^{-8}M	Stimulation at 10^{-5} M, higher than for NP at 10^{-5} M	(White et al., 1994)
NP2EO	O.mykiss, Primary hepatocytes	VTG induction		VTG induction at 10^{-5} M for both NP2EO and NP but less pronounced for NP2EO	(White et al., 1994)
NP2EO NP9EO	O.mykiss Primary hepatocytes derived from male, (mostly) immature fish	Expression of vitellogenin protein (rtVgt)	EC_{50} (E_2) = 1.81 x 10^{-9} M EC_{50} (NP) = 16.15 x 10^{-6} M EC_{50} (NP2EO) = 17.27 x 10^{-6}M EC_{50} (NP9EO) = 82 x 10^{-6}M LOEC (E_2) = 1 x 10^{-11} M EC_{max} (E_2) = 1 x 10^{-7} M	RP (ED_{50} (E_2) / ED_{50} 4-*n*-NP(nEO)): NP: 3.3 x 10^{-6} NP2EO: 6 x 10^{-6} NP9EO: 2 x 10^{-6}	(Jobling and Sumpter, 1993)
NP2EO	O. mykiss, Primary hepatocytes derived from male fish	Expression of vitellogenin mRNA (rtVgt mRNA)	EC_{max} (E_2) = 1 x 10^{-6} M EC_{max} (4-*n*-NP) = 1 x 10^{-5} M	RIE ((maximal) Vtg mRNA expression level induced by 4-NP relative to that induced by E_2.): NP ≈ 25 % NP2EO: No estrogen potency up to 10^{-4} M	(Madigou et al., 2001)
NP2EO NP7EO	O. mykiss, Primary hepatocytes derived from male fish	Expression of vitellogenin mRNA (rtVgt mRNA)		RIE: NP: 25.9% NP2EO: 156 % N7EO: 1%	(Petit et al., 1997)
NP10EO	O. mykiss, Primary hepatocytes	VTG induction and EROD activity 28 mg/L in biodegradation assay using inocolum from Helsinki and Jyväskylä City WWTP		No response	(Pessala et al., 2009)

In both tests short chain ethoxylates were estrogenic active but with a lower potency compared to 4-tert-OP (half fold induction and 0.0088 potency compared to 4-tert-OP respectively). Longer chain ethoxylates showed only very weak estrogenic activity.

Results for nonylphenol ethoxylates support these findings:

With regard to the short chain nonylphenol ethoxylates information for a mixture of NP1EO and NP2EO and NP2EO alone are available from 6 studies using three different study types (MCF, primary hepatocytes form O.mykiss and the YES assay). In all except one study (Madigou et al., 2001) short chain nonylphenol ethoxylates showed estrogen activity:

- Based on EC_{50} and EC_{20} values the relative potency in the YES assay was 0.025 and 0.00012 compared to nonylphenol (Isidori et al., 2006; Metcalfe et al., 2001) while Petit et al. (Petit et al., 1997) showed that the activity was about half of the activity of nonylphenol at 10^{-4} M and Madiguo et al. (Madigou et al., 2001) found no activity at al up to 10^{-4} M.

- Based on the level of VTG induction at similar test concentrations, the relative induction efficacy in primary hepatocytes from *O.mykiss* was similar or even higher compared to nonylphenol in three of the four studies while one study (Madigou et al., 2001) showed no induction up to 10^{-4}M.

- Similar, an even higher induction compared to nonylphenol was also observed in the sole MCF assay by White et al, (White et al., 1994).

Thus in summary, results for short chain nonylphenol ethoxylates support the finding that such ethoxylates exhibit some estrogen activity in vitro. Results with primary hepatocytes from *O.mykiss* indicate that the relative binding efficacy may be similar or even higher compared to nonylphenol.

Less data are available for longer chain nonylphenol ethoxylates. Three studies compared short chain ethoxylates and longer chain ethoxylates, two of these in the YES assay (Isidori et al., 2006; Petit et al., 1997) and one using primary hepatocytes (Jobling and Sumpter, 1993). In addition one study (Pessala et al., 2009) analyzed NP10EO. In all studies estrogen activity decreased with increasing chain length. However, while some showed nearly no estrogen activity for the longer chain ethoxylates, others revealed estrogen activity although with low efficacy.

Overall studies for 4-tert-octylphenol ethoxylates and nonylphenol ethoxylates show that the short chain ethoxylates still possess an estrogen activity in vitro while this activity decreases with increased chain length.

5.1.1.2 Fish

5.1.1.2.1 Long-term toxicity to fish

Long term toxicity studies are summarized in order to analyze whether or not 4-tert-octylphenol ethoxylates may result in endocrine mediated adverse effects in fish. Thus only studies evaluating endocrine related endpoints are considered. As no information for 4-tert-octylphenol ethoxylates is available, results for nonylphenol ethoxylates are taken into account.

Eight studies for three species are available. Results are summarized in Table 21:

Table 21: Summary of in vivo data for fish exposed with nonylphenol ethoxylates

Reference	Life stage/ duration	Test substance	Concentration / test condition / tested substance / solvent	Vitello-genin	Histology	Fertility/ Fecundity	Sex –ratio	Sec. sex charac-teristics	others	Reliability
O.latipes										
(Metcalfe et al., 2001)	Sex-development 1 d posthatch for 90d	NPE1O/ NPE2O mixture	Semi-stat; 25; 50; 100	-	Only 1 slight testis-ova at 100 µg/L		No changes in sex-ratio		No effects on growth	2
(Balch and Metcalfe, 2006)	**FSDT (with deviations)** **Starting from hatch within 1d, Exposure: 100d**	**NP1EO**	**3.5; 10.5; 35; 102 µg/L (m);** **3 - 10 - 30 – 100-300 µg/L (n)** **Semi-static, renewal of test water every 48 h**		**No testis-ova (NP LOEC 29µg/L (18 of 22 phenotypic males had testis-ova);**			**Mixed sec. sex char. (MSC):** **LOEC 105** **LOEC NP: 8.7µg/L (20%),** **Papillary processes, LOEC 105 µg/L** **only one out of 29 fish had papillary processes at the anal fin**		**2**
(Balch and Metcalfe, 2006)		NP4EO	3.8; 11.4; 38; 114; 380 Semi-static, renewal of test water every 48 h					No mixed secondary sex characteristic, no changes in sex-ratio no intersex up to 380 µg/L		**2**
(Balch and Metcalfe, 2006)	FSDT (with deviations) Starting from hatch within 1d, Exposure: 100d	NP9EO	16.2; 54; 162; 540 Semi-static, renewal of test water every 48 h					No mixed secondary sex characteristic, no changes in sex-ratio no intersex up to 540 µg/L		**2**
O.mykiss										
(Dussault et al., 2005)	Adults, 21 d	NP1EO	Flow-through; 0.8; 3.9; 6.,9; 48; 281 µg/L real	LOEC 281 µg/L (induction comparable to 0.1 µg/L E2, in all fishes observed					Relative potency compared to NP 0.22	2

Reference	**Life stage/ duration**	**Test substance**	Concentration / test condition / tested substance / solvent	**Vitello-genin**	**Histology**	**Fertility/ Fecundity**	**Sex –ratio**	**Sec. sex charac-teristics**	**others**	**Reliability**
(Ashfield et al., 1998)	Posthatched females / 22 and 35 d)	NP2EO	Flow-through/ 1.0; 10; 30; 50 µg/L (nominal)						Growth (weight) LOEC < 1 µg/L (only transidient) NP: LOEC 10 µg/L	2- nom. Conc.
(Jobling et al., 1996)	2-year old male rainbow, Experiment in May Exposure: 3 weeks	NP2EO	38 µg/L (m)(Limittest) Flow-through	VTG induction slightly less than NP induction	Spermatogenesis: cell type Spermatogonia A was significantly elevated, similar to NP (38 µg/L)				GSI significantly reduced gonadal growth similar to NP	**2**
P.promelas										
(Nichols et al., 2001)	Adults, 42 d	NP9EO (technical)	Static, 0.21; 0.65; 2,1; 7.9 µg/L	No significant changes in male and females (increase in males at low concentration but no dose- response, not significant		No significant changes in fecundity, only 1 chamber with actively laying nd fertilizing eggs at 2.1 and 7.9 µg/L			No changes in mortality, no changes in egg viability	**2**
(Miles-Richardson et al., 1999)	Reproduction assay sexually mature fish (12 – 18 months) paired 42 d	NP9EO (technical mixture)	Two experiments (data from experiment 2 not usable, egg production was totally inhibited by solvent control): First experiment was conducted July to August. 0.15; 0,43; 1.45; 4.5 µg/L (m)		No effects on the relative proportion of eggs in any of the stages of follicles for NP (≥ 3.4µg/L) or NPEO No testicular lesion (based on sertoli cell proliferation and percentage of seminiferous tubules), measured as severity score (effects for NP started at 1.6 µg/L)			No changes in gross appearance of the fatpad in males for NP (up to 3.4 µg/L) and NPEO, no changes in secondary sex-characteristicsin males for NP and NPEO		**2**

Reference	**Life stage/ duration**	**Test substance**	Concentration / test condition / tested substance / solvent	**Vitello-genin**	**Histology**	**Fertility/ Fecundity**	**Sex –ratio**	**Sec. sex charac-teristics**	**others**	**Reliability**
(Bistodeau et al., 2006)	Larvae (< 72h post-hatch) for 64 d, Competition assay (formerly exposed males and unexposed males competing for reproduction) at the age of 6 month (without exposure)	Mixture of NP/OP/ NPEO/OPEO/NPEC (mainly (78,6 % NP1EC and NP2EC)*	Flow-through 148; 73.9, 38.1 µg/L total concentration	No VTG induction for mixture and NP (measured after competition study i.e. nearly 6 month after end of exposure	No changes in phenotypic males			Reduced prominence of tubercles and dorsal pad at 148 µg/L but not for NP and other treatments	High larval mortality (78%) at 148µg/L, no effects for NP Reduced ability to hold and defend a nest site from control fishes at 38.1 µg/L and above,)	2 High mortality in controls (> 40% in all treatment, very high at 74 µg/L

For *O.latipes* two fish sexual development studies are available.

Balch and Metcalfe exposed *O.latipes* larvae to nonylphenol, NP1EO, NP4EO and NP9EO for 100d starting from hatch (Balch and Metcalfe, 2006). With regard to NP1EO, fish showed similar effects on secondary sex characteristics compared to nonylphenol but at higher test concentrations. The LOEC for so called mixed secondary sex characteristics (individuals that showed both male and female sec) was 102 µg/L compared to 8.7 µg/L for nonylphenol. Similar to nonylphenol fish which were considered males based on their gonads did not show any papillary processes (a dominant male secondary sex characteristic) but again the LOEC was higher (102 µg/L compared to 29 µg/L). While most of the phenotypic males showed testis ova at a LOEC of 29 µg/L after exposure to nonylphenol no such effects were observed for NP1EO. Exposure to NP4EO and NP9EO did not result in any effects up to 380 µg/L and 540 µg/l respectively.

Findings by Metcalfe et al support the finding that exposure to NP1EO does not result in significant induction of testis-ova if exposure starts after hatch (Metcalfe et al., 2001). After exposure of newly hatched fish for 90d to a mixture of NP1EO and NP2EO only 1 testis-ova was observed at the highest test concentration (100 µg/L). No changes in the sex-ratio based on gonads were observed.

Thus in summary, results provide evidence for an in vivo endocrine activity of NP1EO in *O. latipes* due to changes in secondary sex characteristics. No data are available whether such activity may result in endocrine mediated apical effects. Based on data available for nonylphenol from other studies such effects can be expected. However results indicate that such effects may occur at higher concentrations compared to nonylphenol.

With regard to *O.mykiss* two screening assays and one fish sexual development test are available for the short chain nonylphenol ethoxylates (NP1EO and NP2EO). Results by Jobling at al in a screening assay for NP2EO again indicate that short chain alkylphenol ethoxylates may induce endocrine activity in vivo (Jobling et al., 1996). However, in this case effect concentrations were similar to those observed for nonylphenol. NPnEO induced vitellogenin in adult males, increased the proportion of early sperm stages and reduced gonadal growth at 38 µg/l. Effects are similar to those observed for 36µg/L nonylphenol. A similar sensitivity of *O.mykiss* to short chain nonylphenol ethoxylates and nonylphenol was substantiated by Ashfield et al. (Ashfield et al., 1998) who found similar effects on growth during a sexual development test with the LOEC being even factor 10 lower than for nonylphenol (LOEC 1 and 10 µg/L respectively). Results by Drussalt et al. support an estrogen mode of action but at slightly higher concentrations (LOEC 281 µg/L with a relative potency compared to nonylphenol of 0.22 (Dussault et al., 2005).

Results observed by Nichols et al. (Nichols et al., 2001) and Miles-Richardson et al. (Miles-Richardson et al., 1999) with a longer chain ethoxylate (NP9EO) and *Pimephales promelas* support in vitro findings that longer chain ethoxylates do not exhibit endocrine activity. No changes in vitellogenin level, fecundity and egg viability were observed after exposure of adults for 42 d (Nichols et al., 2001) and no changes in secondary sex characteristics were observed by Miles-Richardson et al. (Miles-Richardson et al., 1999).

Thus in summary, data available for NP1EO and NP2EO for *O.latipes* and *O.mykiss* provide evidence that short chain alkylphenol ethoxylates may induce in vivo endocrine activity. Based on data for *O.latipes* short chain nonylphenol ethoxylates are about factor 10 less potent than nonylphenol while data for *O.mykiss* indicate that the potency may be comparable. As no data about clearly endocrine mediated adverse effects are available it can only be extrapolated from information available for octylphenol and nonylphenol which indicate, that adverse effects as a result of the endocrine activity are likely to occur.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not assessed for the identification of this substance as SVHC in accordance with Article 57(f).

6.2 CMR assessment

Not assessed for the identification of this substance as SVHC in accordance with Article 57(f).

6.3 Substances of equivalent level of concern assessment.

As described in chapter 3.2.4, 4-tert-octylphenol ethoxylates (4-tert-OPnEO) are a relevant source for 4-tert-octylphenol (4-tert-OP) in the environment due to their degradation to 4-tert-OP in wastewater treatment plants and sediments and soils. 4-tert-OP has been identified as a substance of very high concern and included into the Candidate List due to its endocrine disrupting properties which cause probable serious effects to the environment. Any precursor of this substance which may contribute to its occurrence to a relevant degree should be regarded as a substance of very high concern too. The rational for the identification of 4-tert-OPnEO as SVHC is substantiated below by first discussing some general aspects and secondly describing the specific concern for the ethoxylates in detail.

6.3.1 Principle rationale for the identification of a substance as SVHC due to its degradation to a substance of very high concern

Substances are identified as “substances of very high concern” due their intrinsic properties leading to very high concern. For such substances regulatory measures such as inclusion into the Candidate List and further measures to account for the risk arising from these properties are considered necessary. As the measures are based on the intrinsic properties of these substances it seems to be rational that all substances that may contribute to the occurrence of such substances due to their degradation under realistic conditions should be regarded as substances of very high concern themselves.

Indeed such a rationale is already included in the new Annex XIII for substances being of very high concern due to their PBT or vPvB properties. Annex XIII states that transformation / degradation products should be taken into account when assessing the PBT properties of a substance. This implies that a substance may be considered as substance of very high concern due to the PBT properties of its transformation product.

Recently the European Commission suggested a similar rationale to identify substances as SVHC according to Art 57(f) of REACH which may degrade to a substance having CMR properties. It is straightforward that such an approach should account for all substances degrading /transforming to any substances of very high concern.

With regard to substances transforming to a substance which is of very high concern due to its endocrine disrupting properties and subsequent probable serious effects to the environment, such an approach is further substantiated by the type of concern of the degradation product. As described in the support document for the identification of 4-tert-OP as SVHC, one aspect contributing to the

very high concern is the difficulty to accurately describe and analyse the risk of such a substance. If substances increase the overall environment concentration of such SVHC due to their degradation to the SVHC, this increases the possibility to underestimate the risk for the substance of very high concern.

6.3.2 Rationale for the identification of 4-tert-octylphenol ethoxylates as substances of very high concern due to its degradation to 4-tert-octylphenol

Data provided in chapter 3 show that 4-tert-OPnEO are degraded to 4-tert-OP in sewage treatment plant and thus increase the overall 4-tert-OP load in the environment. Degradation in waste water treatment plants is not complete. 4-tert OPnEO are also released from waste water treatment plants. Due to their further degradation to 4-tert-OP in sediment and soil, 4-tert-OPnEO distributed to those environmental compartments contribute as well to the overall concentration of 4-tert-OP in the environment.

6.3.2.1 Emission from sewage treatment plants

As analyzed in simulation studies (chapter 3.1.2.1.1) and substantiated by quantitative measurements in sewage treatment plants (chapter 3.2.4) primary degradation of 4-tert-octylphenol ethoxylates is fast. Main degradation products are its ethoxylates with lower degree of ethoxylation (so called short chain ethoxylates, 4-tert-OPnEO with n = 1-2), its corresponding carboxylates (especially under aerobic conditions) and to a less extent – 4-tert-octylphenol (under anaerobic conditions).

Degradation of 4-tert-octylpheol ethoxylates in sewage treatment plants

- Nearly complete transformation to short chain carboxylates after 24 hours in aerobic activated sludge (Ball et al., 1989)
- transformation in aerobic sewage to short chain ethoxylates after 2 days (Ball et al., 1989)
- 84-90% primary degradation in activated sludge and an anaerobic percolation field system within 7 days with no cleavage of the phenol ring based on radioactive labeling (Lashen et al., 1966)
- 82 % dissipation during sewage treatment (mean of 11 plants, (Ahel et al., 1994a))

Results indicate that these degradation products are more stable and thus overall mineralization or degradation to metabolites other than those described above is generally low.

Overall dissipation /degradation of transformation products in sewage treatment plants:

- Nearly no degradation of 4-tert-OPnEC in aerobic sludge after 24 hours (Ball et al., 1989)
- Only minor degradation of 4-tert-OP1-2EO within 17 days in primary sewage (Ball et al., 1989)
- Slow degradation of4-tert- OP1EO under anaerobic conditions within 23 days (Ball et al., 1989)
- No degradation of the radiolabeled phenol moiety within 7 days in activated sludge and in an anaerobic percolation field system (170 days) (Lashen et al., 1966)
- 30-50% disappearance of total NPnEO (including NPEC and NP) in 3 days in anaerobic sewage sludge (Lu et al., 2008a; Lu et al., 2008b)
- Overall dissipation of NPnEO,(including NPnEC and NP) between 27 and 45% in several waste water treatment plants (Ahel et al., 1994a; McAdam et al., 2011; Varineau et al., 1996; Yu et al., 2009)

Measurements in sewage treatment plants by Ahel et al., , McAdam et al., Varineau et al. and Yu et al. (Ahel et al., 1994a; McAdam et al., 2011; Varineau et al., 1996; Yu et al., 2009) indicate, that about 55 - 73% of the NPnEO influent in primary sewage treatment plant will be released to the environment. Based on data provided by Ahel et al and Varineau et al. (Ahel et al., 1994a; Varineau et al., 1996) and a worst case assumption described in the Environmental Risk Evaluation Report (Environment Agency UK, 2005) about 4.6 % to 25% of the OPnEO influent will be released as 4-tert-octylphenol, mainly via sludge. Main degradation products in the effluent are 4-tert-OPnEO and 4-tert-OPnEC.

Summary release of 4-tert-octylphenol ethoxylates from waste water treatment plants into the environment.

(Ahel et al., 1994a)	(Varineau et al., 1996)
60-65 % of nonylphenolic compounds in influent released to the environment 19 % NPEC 11% NPEO 25 % NP (> 22.5 % in sludge, <2.5% in effluent)* 40% of total load release via sludge	36% of influent released to the environment 26% NPEC 7 % NP/NPEO 3.5 % NP/NPEO adsorbed to sludge (overall 4.6 % of the NPnEO converted into NP)

* based on the calculation that > 90% of NP is adsorbed to sludge

Based on these data it becomes obvious, that degradation of 4-tert-OPnEO to 4-tert-OP in sewage treatment plants may be a relevant direct source of 4-tert-OP for soil via sludge accounting for 3.5 – 22.5% of the overall 4-tert-OPnEO influent. Undegraded 4-tert-OPnEO and short chain ethoxylates (4-tert-OP1-2EO) released via effluent may be a potential source of 4-tert-OP in surface water as they may further degrade to 4-tert-OP in the environment (see next chapter). Based on the assumption by Ahel et al (1994a), that 60% of the not further degraded NPnEO, short chain ethoxylates and NP are released via effluent, 21.6 – 36% of the overall NPnEO influent would be released to surface water via effluent. Release of 4-tert-OP from sewage treatment plants as a result of 4-tert-OPnEO degradation in sewage treatment plants seems to be low at a first glance. However as described in chapter 3.2.4, this results in a relevant increase of the overall release of 4-tert-OP to surface water. Based on the data presented the degradation of 4-tert-OPnEO resulted in a 54 – 758 % increase of the 4-tert-OP load released to the overall environment.

Summary 4-tert-OP/NP formation during waste water treatment

- Ahels et al. (Ahel et al., 1994a): 181 and 758 % increase of overall NP mass (mol/day) in two waste water treatment plants
- Varineau et al. (Varineau et al., 1996): 112.5 % increase of overall NP mass during sewage treatment compared to influent
- Yu et al. (Yu et al., 2009): 70% concentration increase in effluent compared to influent
- McAdam et al. (McAdam et al., 2011): 54 % increase in effluent compared to influent in the carbonaceous/nitrification/denitrification activated sludge plant

6.3.2.2 Further degradation in the environment

Once released to the environment via wastewater treatment effluent it can be expected that 4-tert-OP and short chain 4-tert-OPEO will distribute into sediment while longer 4-tert-OPnEO and 4-tert-OPnEC remain in the water phase, as indicated by the distribution properties of 4-tert-OP and its ethoxylates described in chapter 3.2.1 and 3.2.2.

In the water column long chain 4-tert-OPnEO are further degraded to short chain 4-tert-OPEO or 4-tert-OPEC depending on the environment condition. As the short chain 4-tert-OPnEO are expected to distribute into sediment, they may contribute to the overall sediment load.

Biodegradation in surface water

- > 99% primary degradation in 100hours under aerobic conditions (main product NPEC) (Jonkers et al., 2001)
- DisT50 23-69 days (winter) and 2.5-35 days (summer) in an aerobic die away test with estuarine bacteria ; main intermediate NP2EO (Kveštak and Ahel, 1995)

Results from sediment tests indicate that – as expected from anaerob sewage sludge studies - nonylphenol is formed under anaerobic conditions with a DegT50 of 49 – 77 days. Degradation may be even slower if highly polluted sediments are used.

Biodegradation in sediment

- DegT50 (primary degradation) in anaerobic river samples 49-77 days; increased with temperature, NP formation (Chang et al., 2004)
- Aerob: DisT50 = 85 days (NPEO including short chain NPEO and NP), only 1.9 % mineralization after 120 days in highly polluted sludge (Ferguson and Brownawell, 2003)
- Anaerob: DisT50 = 289 days (NPEO including short chain NPEO and NP), formation of NP1EO during decrease of NP2-5EO, no formation of NP during 120 days in highly polluted sludge (Ferguson and Brownawell, 2003)

Thus, in summary once released to the environment, 4-tert-OPnEO will undergo further degradation to 4-tert-OP in anaerobic sediments and in river water during winter conditions. Degradation half lives are low and 4-tert-OP is a very stable product in sediment (no mineralization after 84 d under anaerobic conditions). Thus once released to surface water and distributed to sediment, degradation of 4-tert-OPnEO will remain a long lasting source for 4-tert-OP.

Release to soil via sewage sludge may be an additional relevant source of 4-tert-OP and short chain ethoxylates due to the high adsorption of 4-tert-OPnEO to sludge. Results described in chapter 3.1.2.3 indicate that short chain ethoxylates may degrade to 4-tert-OP in soil but slowly (DisT50 between 48 days (Sjöstrom) and > 360 days (Marcomini) for nonylphenol ethoxylates). Thus, once released to soil, short chain 4-tert-OPnEO may contribute to the overall concentration of 4-tert-OP in soil. Because conversion is slow, it can be expected that these ethoxylates are a constant source of 4-tert-OP in soil.

4-tert-OP itself is a stable metabolite which strongly adsorbs to soil, sludge and sediment. In sediment no elimination was observed under anaerobic conditions after 83 days ($DsDT_{50}$ > 83 days). (European Chemicals Agency, 2011).

6.3.2.3 Equivalence of concern

Besides the rationale that all relevant precursors of SVHCs should be considered as SVHCs themselves, some specific aspects with regard to 4-tert-OP and its ethoxylates substantiate the equivalent level of concern for 4-tert-OPnEO:

As degradation of the ethoxylates in sediments is a very slow process, it can be expected, that sediments will remain a relevant source for 4-tert-OP long after the cessation of exposure of 4-tert-OP and its ethoxylates. This is of high importance as degradation of 4-tert-OP in sediments is very slow (DisT50 > 83 days (Johnson et al., 2000) and thus 4-tert-OP formed by degradation of its ethoxylates may accumulate in sediment.

4-tert-OP adsorbed to sediment may be an unpredictable relevant source of 4-tert-OP in surface water due to environmental events such as flood or dredging. Effects observed for 4-tert-OP on aquatic organisms indicate, that short term exposure during sensitive life stages may increase their

susceptibility and may lead to effects during the entire life stage. Any environmental event leading to a higher release of 4-tert-OP produced by degradation of its ethoxylates may coincide with such sensitive life stages resulting in unpredictable high effects.

In addition to the concern based on the degradation to 4-tert-OP, available information indicate that short chain ethoxylates (4-tert-OP1EO and 4-tert-OP2EO) may show endocrine activity themselves and thus may add to the probable serious effects caused by 4-tert-OP in the environment: : results for *O.mykiss* and *O.latipes* indicate that their in vivo and in vitro endocrine activity is nearly as high (factor 10) or similar to the endocrine activity of 4-tert-OP. These tests do not include adverse endpoints and thus it is not possible to conclude whether or not 4-tert-OP1EO and 4-tert-OP2EO are endocrine disruptors themselves. However due to the similar endocrine activity and information available for 4-tert-OP it seems possible that they may cause endocrine disrupting adverse effects at similar or slightly higher concentrations compared to 4-tert-OP and this may add to the concern raised for 4-tert-OPnEO.

6.3.3 Conclusion on the equivalence of concern for 4-tert-octylphenol ethoxylates

In consistence with the approach used for PBT substances it seems reasonable to conclude that any substance which may result in exposure to an SVHC (i.e. due to degradation to this substance) should be considered as SVHC itself as it has an equivalent level of concern.

Available information for 4-tert-OPnEO indicate that 4-tert-OPnEO contributes to the 4-tert-OP concentration in the environment. A significant amount is either degraded to 4-tert-OP itself in waste water treatment plants or is released to rivers in a form which may undergo further degradation to 4-tert-OP. 4-tert-OP formed from degradation of 4-tert-OPnEO may increase the overall 4-tert-OP load to the environment (via sludge and effluent) by 54 to 758 %.

Once released to the environment 4-tert-OPnEO will remain a permanent source for 4-tert-OP due to the tendency of short chain ethoxylates to bind to the sediment combined with a very slow degradation in anaerobic sediments of both the ethoxylates and their degradation product 4-tert-OP. The permanent source results in additional exposure of both sediment and pelagic organisms such as fishes (via remobilisation) to 4-tert-OP.

Especially due to the fact that short term exposure to 4-tert-OP may result in life time effects in aquatic organisms and due to the fact that sudden environmental events may increase short term exposure concentrations such a sink and permanent source for 4-tert-OP is considered of very high concern. The possible endocrine activity of short chain ethoxylates (4-tert-OP1EO and 4-tert-OP2EO) add to the concern.

PART II

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES –CONCLUSIONS ON EXPOSURE

At the moment there are no registration dossiers for 4-tert-octylphenol ethoxylates (4-tert-OPnEO) available. The substances covered with this Annex XV dossier are not on the list of substances[2] identified by industry to be registered by 31 May 2013. This indicates that the total amount produced or imported per (hypothetical) registrant does not exceed the threshold of 100 tonnes per year or the substances are not subject to registration. Ethoxylates of 4-tert-octylphenol being commercially relevant are expected to have a chain of ethoxylate groups longer than three single ethoxylate groups (with typically a broad distribution of the chain length of ethoxylate group, please see section for *production process*). This assumption was supported after reviewing public available substance information sheets which indicate that 4-tert-octylphenol-ethoxylates with chain lengths up to 70 ethoxylate groups are commercially available. Common ranges of chain lengths seem to be in the range of 8 to 12 and around 30. Therefore the commercially available ethoxylates of 4-tert-ocytlphenol are expected to fulfil the REACH definition of polymers. Such substances are exempted from registration and comprehensive knowledge might not be become available in the near future.

MANUFACTURE, IMPORT/EXPORT

Production process

According to the Environmental Risk Evaluation Report (Environment Agency UK, 2005) 4-tert-octylphenol ethoxylates are manufactured by the addition of ethylene dioxide to 4-tert-octylphenole under pressure. The ethoxylation process for technical octylphenol ethoxylates delivers a mixture of ethoxylates with a different number of ethoxy-groups. This process and the resulting technical mixture of different ethoxylation grades are also described by Leisewitz et al. (Leisewitz et al. 1997). Therefore technical ethoxylates are described with an ethoxylation range (e.g. 8-10) and/or giving an average grade of ethoxylation. As different technical mixtures are often described with the same CAS-number, it is not possible to link single ethoxylation grades to specific uses. Leisewitz et al. assume that the alkylphenol group contributes about 36 percent to the weight of alkylphenol ethoxylates.

[2] http://echa.europa.eu/documents/10162/13632/intentions_2013_en.xls; accessed 21. August 2012

Produced tonnages

The registration dossiers for 4-tert-octylphenol (CAS 140-66-9) provide some information on the production of 4-tert-octylphenol ethoxylates without pointing out specific characteristics. The overall amount produced per year might be in the range of 200 to 2000 tons. This assumption is based on information on produced tonnages of 4-tert-octylphenol from the Annex XV report for 4-tert-octylphenol (European Chemicals Agency, 2011b) for identification as a substance of very high concern and the estimated fraction of 4-tert-octylphenol – here 2 percent – used as intermediate for ethoxylate production as reported in the Environmental Risk Evaluation Report (Environment Agency UK, 2005). Nevertheless it has to be kept in mind that the contribution from the imported amount of ethoxylates is unclear at the moment.

Additional volumes of ethoxylates might be produced by companies inside Europe which produce or import and use 4-tert-ocytlphenol as isolated intermediates under strictly controlled conditions according to REACH articles 17 respective 18.

According to personal communication between Environment Agency UK and member companies of the industry sector organisation CEPAD (Environment Agency UK, 2005) only a small amount of the total use volume of 4-tert-octylphenol (1.8% respectively 400 tonnes) was used for production of octylphenol ethoxylates in 2001 – resulting in a total production volume of 1050 tonnes. According to CEPAD there are only a handful of producers (four to five) within the EU. It seems the production does not necessarily occur at the production sites of 4-tert-octylphenol. The risk evaluation report does not contain any information on tonnages of 4-tert-octylphenol ethoxylates imported into the EU per year.

According to the draft COHIBA Summary report for Germany (COHIBA Project Consortium, 2011) about 2100 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 5800 tonnes of 4-tert-octylphenol ethoxylates were produced in Germany in 2000 having in mind a 36 percent weight contribution of 4-tert-octylphenol. This tonnage is much higher than those described in the UK risk evaluation report and in registration dossiers.

In summary there is no reliable data on production volumes from registration dossiers available at the moment. The supposed volume of 4-tert-octylphenol ethoxylates only represents a rough estimation without taking into account import and export of the ethoxylates.

USES

At the moment no up-to-date information on current uses, technical function and related tonnages is available as no registration dossiers for 4-tert-octylphenol ethoxylates are available.

The registration dossiers of 4-tert-octylphenol provide some information on sectors of use and product types where 4-tert-octylphenol ethoxylates are constituents of mixtures. But these data do not refer to the concentration of 4-tert-octylphenol ethoxylates in the mixtures. The ethoxylate uses in the registration dossiers of 4-tert-octylphenol are:

- Formulation of paints
- Industrial end-use of paints
- Use of ethoxylates in emulsion polymerisation
- Use as intermediate for the production of ether sulphates

- Consumer and professional end-use of products (e.g. paints)

There is no distinction between the different grades of ethoxylation used in these specific uses or further information on products for professional and consumer end-use beside paints. Queries in different product registers confirm further types of uses of 4-tert-octylphenol ethoxylates (see below).

As mentioned in the previous section, the Environmental Risk Evaluation Report (Environment Agency UK, 2005) also contains some information on products for which the ethoxylates are used for. The information below is taken from this Risk Evaluation Report and refers to the 1050 tonnes octylphenol ethoxylates used per year as reported in the Environmental Risk Evaluation Report:

Table 22: Uses of 4-tert-Octylphenol ethoxylates (Environment Agency UK, 2005)

Specific use	**Amount used annually (tonnes; assumed values for 2001)**	**Further information**
Emulsifiers for emulsion polymerisation	550	End application for polymer dispersions included in paints, paper, inks, adhesives and carpet backings.
Textile and leather auxiliaries	150	Emulsifier in finishing agents for covering leather and textiles with a thin polymer film for improved surface properties
Pesticide formulations	100	Emulsifier to aid dispersion of the products over leaf surfaces
Veterinary medicine products	(3.4)	Quantity refers to UK and is included in pesticide formulations; substitution by alcohol ethoxylates was pursued
Water based paints	50	Act as emulsifiers and dispersants
Intermediate for production of octylphenol ether sulphates	About 200	Mainly used as emulsifiers in water based paints or dispersants in pesticide or herbicide formulations

The assumption for the used tonnages of 4-tert-octylphenol ethoxylates is supported by Leisewitz and Schwarz (1997) who assume that about 50 % of the ethoxylates are used as emulsifiers for emulsion polymerisates. The concentration of the emulsifier in the product is assumed to be close to 1.5 % in the mean. Leisewitz et al. also supposed that ethoxylates are used as auxiliaries in waste

water treatment processes. Plant protection products might contain up to 5 % of alkylphenol ethoxylates. Unfortunately this information and the following information does not distinguish between nonyl- and octylphenol ethoxylates and generally refer to alkylphenol ethoxylates. In the construction industry they are also used:

- As pore builder/foaming agents for concrete; concentration range 2 – 4 percent in the ready-to-use additives
- Mould release agent on construction sites and precast concrete production and auxiliaries for cleaning of machinery; mean concentration 2 percent
- Constituent (emulsifier) of bitumen / wax emulsions for painting/sealing in construction industry respectively masking concrete surfaces; assumed concentration below 1 percent
- metal working fluids normally contain alkylphenol ethoxylates in concentrations between 2 and 4 percent
- oil for lubrication or hydraulic devices might also contain alkylphenol ethoxylates; no further information on typical concentrations is provided.

There might be other minor uses of 4-tert-octylphenol ethoxylates with even lower amounts used annually and therefore out of scope of any reporting program – like cleaning of metal surfaces, component in lubricants respectively other uses are expected but not confirmed by a registration (e.g. component in drilling fluids used for hydraulic fracking).

Leisewitz and Schwarz also identify industrial cleaning agents (normally used for cleaning of metal surfaces) as a relevant area of application. Other still relevant uses might be auxiliary in blowing agents for plastics and for retention processes in paper production (Leisewitz and Schwarz, 1997).

Information from product registers

Registers of different countries were queried to gain more information about (consumer) products containing 4-tert-octylphenol ethoxylates.

The Swiss product register contains information on uses of three 4-tert-octylphenol ethoxylates differing by CAS-Numbers, but it is unclear if they are describing different substances. The entries 2 and 3 in the table below refer to the same CAS number but seem to describe different grades of ethoxylation.

Table 23: Information on products containing 4-tert-octylphenol ethoxylates (extract from Swiss product register[3], date of information retrieval: 22.09.2011)

CAS-number	Name	use	Max. conc. In %		
			0 - 10	10 - 20	20 - 30
9036-19-5	Polyoxyethylen-(tert.-octylphenyl)-ether	Other uses Paints, varnishes Car care products	6 13 3	1	

[3] Information received from Swiss Federal Office of Public Health by personal communication

		Impregnating agents	1		
		Limescale remover	1		
		Adhesives, sealants, putties	1		
		Laboratory chemical	27		1
		Metal care products		2	
		General surface treatment	1		
		Air fresheners, air treatment	2		
		Cleaning products (alkaline)	1		
		Lubricants and additives	4		
		Shoe and leather care products	1		
		Household care products	3	1	
		Detergents, auxiliaries, soaps	1		
9002-93-1	Polyoxyethylen(10)-(4-tert.-octylphenyl)-ether	Other uses			1
		Biocide product	2		
		Hardener, activator	1		
		Plant protection product	1		
9002-93-1	Polyoxyethylen(9,7)-(4-tert.-octylphenyl)-ether	Paints, varnishes.	1		

The SPIN-database[4] showed for 4-tert-octylphenol ethoxylates with CAS-number 9036-19-5 the following entries.

	number of preparations				total amount (tonnes)				
Year	S	DK	N	FIN	S	DK	N	FIN	Total
1999	81	-	-	-	71	-	-	-	71
2000	89	215	42	23	87	32.7	16.9	0	136.6
2001	90	221	21	31	74	34.8	4.5	11	124.3
2002	97	256	29	24	46	34.2	0.8	11.7	92.7
2003	102	329	26	15	61	39.8	0.6	7.4	108.8
2004	106	413	44	10	76	6.7	0.4	8.6	91.7
2005	101	396	42	10	146	21.4	0.6	2.4	170.4
2006	98	429	19	10	99	19.9	0.6	2	121.5
2007	104	470	23	13	124	18.7	0.3	1.2	144.2
2008	97	357	23	14	85	26.6	0.4	4.1	116.1
2009	107	339	-	13	29	22.6	-	3.7	55.3
2010	111	328	-	15	50	14.1	-	1.8	65.9

About 50 % of all mixtures listed for DK are listed under the subcategory “paints, lacquers, varnishes” but they only contribute to 15 – 30 percent of the total amount. The most relevant uses

[4] SPIN – Substances in Preparations in Nordic Countries (http://www.spin2000.net/); accessed 15 May 2012

are as surface active agents (total: 31.3 tonnes in 2009), adhesives and binding agents (total: 8.30 tones) and constituents in paints, lacquers and varnishes (total: 5.60 tonnes).

4-tert-octylphenol ethoxylates with CAS-Number 9002-93-1 seem to be commercially less important if the number of preparations is compared with the ones above. But regarding the problems with the identity of the ethoxylates as indicated in production process section there might be some overlaps between the results of both tables.

	number of preparations				total amount (tonnes)				
Year	S	DK	N	FIN	S	DK	N	FIN	Total
1999	19	-	-	-	37	-	-	-	37
2000	20	30	9	-	14	16	1.7	-	31.7
2001	24	30	9	-	13	16.1	0.5	-	29.,6
2002	29	28	8	-	2	16.1	0.2	-	18.3
2003	29	21	8	-	14	15.6	0.4	-	30
2004	23	12	7	-	15	0	0.4	-	15.4
2005	21	15	5	-	19	14.2	0.3	-	33.5
2006	22	17	4	-	25	14.3	0.2	-	39.5
2007	22	13	-	4	46	14.3	-	0.2	60.5
2008	22	12	-	4	37	14.3	-	0.2	51.5
2009	31	10	-	4	6	14.2	-	0.2	20.4
2010	41	10	-	-	15	0.2	-	-	15.2

The most relevant uses of the octylphenol ethoxylate with CAS 9002-93-1 according to the SPIN-database were use as adhesive binding agents and laboratory chemicals, in the years prior 2005 also in cleaning/washing agents without information on tonnages.

The Environmental Risk Evaluation Report (Environment Agency UK, 2005) lists for 1999 a total amount of 4.4 tonnes octylphenol ethoxylates used without further differentiation between different substance identies. The ethoxylates were used as follows:

- Interior and exterior paint 0.03 tones
- Other paint and/or varnish products 0.24 tones
- Degreasing products 0.07 tones
- Other products 3.6 tones

Summary:
Due to the lack of registrations it is not possible to provide up-to-date information on tonnages for octylphenol ethoxylates imported into, produced, and used inside, the EU. The information available for 4-tert-octylphenol only allows a rough estimation of the production volume (200 to 2000 tonnes 4-tert-octylphenol ethoxylates per year, please see produced tonnages section). Also the total imported tonnages of 4-tert-octylphenol ethoxylates as such or as a constituent in mixtures are not available at the moment.
Nearly 50 percent of the ethoxylates seem to be used in emulsion polymerization. Products for professional and consumer uses (e.g. paints, household care products) are supposed to contain octylphenol ethoxylates in concentrations commonly between 0-10 percent but also up to 30 percent in specific products. Unfortunately information is only available for single countries and not for the whole EU. In conclusion it can be assumed that products for consumer and professional uses will significantly contribute to the wide dispersive emissions into the environment.

Releases to the Environment

The importance of the different sources is supported by national estimates made e.g. for Sweden in the COHIBA project (COHIBA Project Consortium, 2012b). According to these estimates, the following sources are considered relevant in Sweden: Washing of imported textiles (370 – 2700 kg/year), use of paints (3.1-203 kg/year), cleaning agents and floor polishes (95 kg/year), production steps such as the formulation of paints, textiles, and agrochemicals (5.7 kg/year) and the production of paints (7.3 kg/year) as well as emission during emulsion polymerization (0.2 – 8.6 kg/year). In addition use in metal industry (use rate 2 – 20 tons/year) and use in photographic laboratories (use rate 499 kg/year with high uncertainties in estimates) are considered important sources which are not covered to this extent in the risk evaluation report by UK (Environment Agency UK, 2005 (Environment Agency UK, 2005)).

The risk evaluation report for 4-tert-octylphenol (Environment Agency UK, 2005) contains information on discharges of 4-tert-octylphenol ethoxylates for two different sites in the United Kingdom. The first site produces 4-tert-octylphenol ethoxylates. It reports discharges to controlled waters of 175 kg in 2002 and 200 kg in 2003. The second site seems to use 4-tert-octylphenol ethoxylates for emulsion polymerization processes and reported discharges of 4-tert-octylphenol ethoxylates to controlled waters of 9282 kg in 2002 and 12130 kg in 2003, resulting in a discharge to sewer of 500 kg in 2003.

For the risk evaluation report also calculations for predicted emissions to the compartments air and waste water have been conducted. They show that, on a local scale, the most relevant sources of 4-tert-octylphenol ethoxylates (and 4-tert-octylphenol produced by degradation) are ether sulfate production, finishing of textiles, ethoxylate production, production of formulations and paint formulation (Environment Agency UK, 2005). Uses and service life of formulations and products containing octylphenol ethoxylates such as use of paints and pesticides seem to be important sources on a regional and continental scale (Environment Agency UK, 2005).

Data provided in the European Pollutant Release and Transfer Register (PRTR) according to Regulation EC 166/2006 for Germany and EU27 indicate that wide dispersive uses resulting in emission to waste water might be important:

In the German PRTR[5] six sites reported releases to surface water for 2010, the threshold value for submitting a report was 1kg per year giving an uncertainty because installations with annual release below the threshold are uncovered. Unfortunately the reports describe a sum parameter and do not distinguish between releases of 4-tert-ocytlphenol and its ethoxylates. The emissions range from 1.4 to 175 kg in 2010, giving a total emission of **275 kg**. The maximum release was reported by a producer of industrial chemicals. Compared with the previous reporting years (2007: 286 kg, 2008: 250 kg, 2009: 242 kg) the emissions slightly increased.

For the year 2008 the EU27 member states reported in the European PRTR[6] a total emission of **2.93 tons** 4-tert-octylphenol and 4-tert-octylphenol ethoxylates. For the reporting year 2009 a total

[5] http://www.prtr.bund.de/; accessed 2 May 2012

[6] http://prtr.ec.europa.eu/PollutantReleases.aspx; accessed 2 May 2012

emitted amount of **2.04 tons** 4-tert-octylphenol and octylphenol ethoxylates was reported. In both years the most relevant sources of emissions to the aquatic environment were the industrial scale production of basic organic chemicals and urban waste-water treatment plants which are allocated all over Europe. Four emission sources are directly related to the chemical industry, the other 41 are sites where waste or waste water is treated. For those no information on sources of octylphenol ethoxylates feeding the treatment plants is available. Emissions from reported accidental releases are negligible with 30 g in 2009.

Concentrations in the environment:

The risk evaluation report on 4-tert-octylphenol (Environment Agency UK, 2005) contains information on predicted environmental concentrations (PECs) for different life cycle steps of 4-tert-octylphenol ethoxylates. The PEC for surface water is in a range from 0.096 µg/l for paint application up to 5.9 µg/l for ether sulphate production. The PEC for sediment ranges from 0.006 mg/kg (wwt) to 0.36 mg/kg (wwt) for paint application respective for ether sulphate production.

According to the generic exposure scenarios used in the registration dossiers, some of the highest predicted environmental concentrations for 4-tert-octylphenol from the use of 4-tert-octylphenol ethoxylates are the result of emissions from the following life cycle steps:

- Formulation of paints containing octylphenol ethoxylates
- Industrial end-use of paints containing octylphenol ethoxylates, release to water
- Service life of paints containing octylphenol ethoxylates
- Use of octylphenol ethoxylates as intermediate for ether sulphate production

In a final COHIBA report (COHIBA Project Consortium, 2012a) information on measured concentrations of 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate (4-OP1EO), 4-tert-octylphenol diethoxylate (4-OP2EO) in different media is available. In the project effluents from municipal and industrial waste water treatment plants, storm waters and landfill leachates in various countries of the Baltic Sea region were analysed. The data is presented in the paragraphs below:

- Samples from 106 municipal effluents were collected for analysis of phenolic compounds. 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate and 4-tert-octylphenol diethoxylate were found in 54%, 20% and 5% of municipal effluent samples, respectively. The maximum concentrations were noted for 4-tert-octylphenol (0.32 µg/l) in Poland and for 4-tert-octylphenol mono- and diethoxylates (0.51 and 0.24 µg/l, respectively) in Sweden. 4-tert-octylphenole was found in a wide range of samples collected, while 4-tert-octylphenol diethoxylate was found only in Sweden.

- Samples from 55 industrial effluents were analyzed for phenolic compounds. 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate and 4-tert-octylphenol diethoxylate were detected in 38%, 18% and 11% of the effluent samples from industrial WWTPs, respectively. The maximum concentrations were found for octylphenol (0.36 µg/l) in Latvia and for 4-tert-octylphenol mono- and diethoxylates (3.8 µg/l and 25 µg/l, respectively) in Denmark. These countries are the only ones where 4-tert-octylphenol diethoxylate was found.

- In total 15 storm water effluents were collected for analysis of phenolic compounds. 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate and 4-tert-octylphenol diethoxylate were found in 27%, 27% and 7% of samples, respectively. The maximum concentrations were

observed for 4-tert-octylphenol (0.24 µg/l) in Latvia and for 4-tert-octylphenol mono- and diethoxylate (0.24 µg/l and 0.47 µg/l, respectively) in Sweden. 4-tert-octylphenol diethoxylate was found only in Sweden.

- In total 15 samples from landfill leachate were collected for analysis of phenolic compounds. 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate and 4-tert-octylphenol diethoxylate were detected in 47%, 40% and 13% of landfill leachate samples, respectively. The maximum 4-tert-octylphenol and 4-tert-octylphenol diethoxylate concentration (1.0 and 0.09 µg/l, respectively) was found in Poland, 4-tert-octylphenol monoethoxylate (0.07 µg/l) in Germany and Finland.

In conclusion of the COHIBA project the most relevant emission sources of octylphenol and its ethoxylates are effluents of industrial and municipal waste water treatment plants. While the highest concentrations of 4-tert-octylphenol respective 4-tert-octylphenol monoethoxylate and 4-tert-octylphenol diethoxylate are found in effluents of industrial sites, a higher proportion of effluents of municipal waste water treatment plants considered contain 4-tert-octylphenol, 4-tert-octylphenol monoethoxylate and 4-tertoctylphenol diethoxylate at lower levels.

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