COHIBA GUIDANCE DOCUMENT NO. 7

MEASURES FOR EMISSION REDUCTION OF OCTYLPHENOL (OP) AND OCTYLPHENOL ETHOXYLATES (OPE) IN THE BALTIC SEA AREA

COHIBA Project Consortium

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Preface

The Baltic Sea ecosystem is particularly at risk from hazardous substances, due to its natural characteristics, such as slow water exchange, and due to a long history of urbanization and industrialization at the shores and in the catchment area. The ecosystem status of nearly all open-sea and coastal areas of the Baltic Sea is considered to be "disturbed by hazardous substances" (HELCOM 2010). Therefore, HELCOM identified 11 hazardous substances of special concern, amongst them octylphenol (OP) and octylphenol ethoxylates (OPE) and laid down environmental targets in the Baltic Sea Action Plan (BSAP) for a Baltic Sea with life undisturbed by hazardous substances and all fish safe to eat.
To achieve the targets of BSAP, measures for emission reduction are needed.

This report analyses and compares different measures for reducing emissions of octylphenol (OP) and octylphenol ethoxylates (OPE) in order to contribute to a knowledge base for decision making. It starts with a review of chemical properties (chapter 2), production and use, emission sources and environmental fate (chapter 3), followed by an overview of existing regulations and an analysis of regulatory gaps (chapter 4). The main part of the report deals with the selection and analysis of emission reduction measures (chapters 5 and 6) and concludes with a comparison of measures (chapter 7) and final conclusions (chapter 8).

This report is part of a series of COHIBA guidance documents, dealing with each of the 11 hazardous substances of special concern to the Baltic Sea as identified by HELCOM. Concerning recommendations for cost-effective strategies for reducing emissions of all 11 hazardous substances, please also refer to the Recommendation Report. This report and other outputs of the COHIBA project are available on the project website (www.cohiba-project.net).

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1. Dioxins (PCDD), furans (PCDF) & dioxin-like polychlorinated biphenyls	
2. Organotin compounds	2a. Tributyltin compounds (TBT)
	2b. Triphenyltin compounds (TPhT)
3. Brominated diphenyl ethers	3a. Pentabromodiphenyl ether (pentaBDE)
	3b. Octabromodiphenyl ether (octaBDE)
	3c. Decabromodiphenyl ether (decaBDE)
4. Perfluoroalkylated substances	4a. Perfluorooctane sulfonate (PFOS)
	4b. Perfluorooctanoic acid (PFOA)
5. Hexabromocyclododecane (HBCDD)	
6. Nonylphenols	6a. Nonylphenols (NP)
	6b. Nonylphenol ethoxylates (NPE)
7. Octylphenols	7a. Octylphenols (OP)
	7b. Octylphenol ethoxylates (OPE)
8. Chlorinated paraffins (or chloroalkanes)	8a. Short-chain chlorinated paraffins (SCCP, C_{10-13})
	8b. Medium-chain chlorinated paraffins (MCCP, C_{14-17})
9. Endosulfan	
10. Mercury (Hg)	
11. Cadmium (Cd)	

Content

1   Introduction to octylphenol and octylphenol ethoxylates

Octylphenol (OP) is an alkyl phenol similar to nonylphenol. It is mainly used in phenolic resin, predominantly as tackifier in the vulcanization process for the manufacture of rubber tyres. OP can react with ethylene oxide to form the corresponding alkylphenol ethoxylates (APE), called octylphenol ethoxylates (OPEs), which can be used as effective surfactants. 85 % of the APE market comprises nonylphenol ethoxylates (NPEs), but OP and OPE can also be present in nonylphenol (NP) and nonylphenol ethoxylates (NPE) as impurities in concentrations of up to 10%.

Octylphenol has a moderate potential for bioaccumulation in aquatic species, but is very toxic to aquatic organisms, and has the potential to cause significant endocrine disruption effects on aquatic organism (OSPAR 2003). OP is inherently biodegradable, but is not considered to be readily biodegradable, and meets the screening criterion for persistence or high persistence.

There are 12 producers/importers listed in the European ESIS database, but only the company ARIZONA CHEMICALS (82022 Sandarne, Sweden) is located in the Baltic Sea Catchment (BSC).

The use of octylphenol is not prohibited, but because of its environmental effects there are voluntary agreements in e. g. cleaning products industry or concentration in sewage sludge used for agricultural purposes. OP is listed in Annex XV of the REACH Regulation.

2   Description of chemical properties
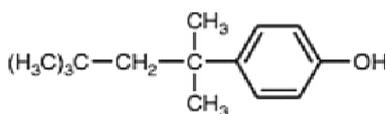
Figure 1: Chemical structure of 4-tert-octylphenol

OPs are alkyl phenyl phenols with a C_8-alkyl group, in OPEs one or more mol ethylene oxide is attached to the -OH group. Alkylphenols (APs) are phenol derivatives in which one or more hydrogen atoms in the aromatic ring are replaced by identical or different alkyl groups. APs are used as intermediates in the manufacture of phenolic resins, as antioxidant additives, and in the manufacture of ethoxylates for use as surfactants. Nonyl- and octylphenols are almost exclusively ethoxylated; otherwise the alkyl chain is too short or too long for use as surfactants.

Table 1: Physical and chemical properties of octylphenol according to Böhm et al. (2002[1]; quoting Frimmel et al. 2002[2]; Rippen 2000[3])

	Octylphenol	Octylphenol-monoethoxylate
Classification in EU Water Framework Directive	**Priority substance**	
CAS number	1806-26-4 (p-tert.-octylphenol)	2315-67-5
EINECS number	266717-8 (p-tert.-octylphenol)	200-662-2
Empirical formula	C14H22O	$C_{16}H_{26}O_2$
Solubility in water	Low (12.6 mg/l, 20.5°C)	Low (8 mg/l, 20 °C)
Accumulation: *n*-octanol/water partition coefficient (log K_{ow})	3.96	5.09
Melting point	72-74°C	48-50°C
Boiling point	280-283°C	370.7°C
Degradation (biotic and abiotic)	Half-life in river water: 7 - 50 d	No data available
Bioaccumulation	Moderate potential for bioaccumulation in aquatic species.	
Toxicity	Lethal dose for 50 % of fish (Fathead Minnow) LC_{50}: 290 µg/l. High estrogenic activity (5 times higher than that of non-ylphenol, 0.1 relative to estra-diol.)	No data available

1 Böhm, E.; Hillenbrand, T.; Marscheider-Weidemann, F.; Herrchen, M.; Klein, M.: Ermittlung der Quellen für die prioritären Stoffe nach Artikel 16 der Wasserrahmenrichtlinie und Abschätzung ihrer Eintragsmengen in die Gewässer in Deutschland. UBA-Texte 68/02, Umweltbundesamt Berlin, 2002

2 Frimmel, F. H.; Ohlenbusch, G.; Münch, C.; Jahnel, J.; Abbt-Braun, G. (2002): Ableitung von Qualitätszielen für Kandidatenstoffe der prioritären Liste für die EU-Wasserrahmenrichtlinie. DVGW-Forschungsstelle, Karlsruhe (Veröffentlichung in 2002 vorgesehen)

3 Rippen, G. (2010): Umweltchemikalien. CD-ROM Ausgabe 11/2010. Ecomed: Landsberg/Lech

3 Inventory of inputs to the Baltic Sea

3.1 Production and use

The production of higher alkyl phenols such as nonyl- or octylphenol takes place in closed systems in a catalytic fixed-bed process (Hüls-Process; Fliege et al., 1991). The current version of the European information system ESIS lists 12 producers and importers of octylphenol, but only the company ARIZONA CHEMICALS (82022 Sandarne, Sweden) is located in the Baltic Sea Catchment (BSC). Production of OP does not take place in St. Petersburg or nearby regions, but exists in inner parts of the Russian Federation, amounting to over 1700 tons per year (Toropovs, 2011).

In 2001, the last year for which data were available on the EU level, approximately 23,000 tons per year of 4-tert-octylphenol were produced, of which only a small portion was exported, see Table 2. Since 2001, production has decreased significantly, and a greater proportion of the production volume has been exported. In the production of nonylphenol 4-tert-octylphenol can arise as a contaminant in an amount of up to 10%, usually about 3-5% (OSPAR, 2004).

Table 2: EU: production, exports and imports of 4-tert-octylphenol (t/a) (Ospar, 2004; Brooke et al., 2005)

	1997	1998	1999	2000	2001
Production	17,520	18,259	19,626	22,215	22,633
Exports	234	104	6	0	150
Imports	1,035	1,337	1,240	1,308	375
Consumption	**18,051**	**19,492**	**20,928**	**23,523**	**22,858**
Local use*	14,969	16,074	17,592	19,910	20,060

* Use to produce other substances·

In the EU, 98% of the produced OP is used for the production of phenolic resins (Brooke et al., 2005). 4-tert-butyl phenol-formaldehyde resins are used in the following areas:

Tyre rubber: as tackifier in tyres to improve adhesion between the layers: the most important application of OP resins (98%), the content in the tyres is about 0.3% OP (Brooke et al, 2005).

Electrical insulation coating: for secondary insulation for motors and transformers.

Printing inks: resins are important components of modern printing inks and allowfaster drying, among other things. 4-tert-octyl phenol resins allow toxic aromatic solvents to be replaced with less toxic aliphatic alternatives. According to Brooke et al. (2005) no substitute for alkylphenols is available in this application.

Offshore oil production: ethoxylated resins are used to separate oil from water in oil recovery at very low concentrations. The demand in 2001 was estimated at 200 tons (Brooke et al., 2005).

Other applications: paper coating, casting, special colours for use in marine paints for ships. In other uses like in veterinary medicinal products, OPEs have been replaced (in this case with a polyethoxylated alcohol). It is also expected that many manufacturers throughout the EU are replacing OPEs in their products (Nwaogu, 2006).

Table 3: Use of 4-tert-octylphenol in different sectors in 2001 (t/a) (OSPAR, 2004)

OP resins		OPE		Equivalent OP amount	Octylphenole-thersulphate (OPE-S)		Equivalent OP amount
Tyre rubber	18,458	Emulsion polymerisation	550	220	Marine paints	200	80
Electrical insulation coating	2,000	Textiles	150	60	Pesticides	50	20
Printing inks	1,000	Pesticides	100	40			
Emulgator	200	Marine paints	50	20			
Others	800	OPE-S production	200	80			
Total	**22,458**		**1.050**	**420**		**250**	**100**

According to a discussion with SASOL in 2011, it seems that the use of OP has decreased sharply since 2001 for all uses apart from tyre rubber, marine paints and textiles (as tackifier and anti-friction agent for T-shirt printing). OPEs are no longer used in pesticides (SASOL, 2011).

Not in the EU, but in the U.S., APEs are also used as surfactant in de-icing fluid sets and have been detected in the melt water from airports (Corsi et al., 2006). In the US OPEs are also found in waste water effluent from hospitals, in amounts of 6.5 g/day (Nagarnaik et al., 2010).

3.2 Emission sources in the Baltic Sea catchment area

WP 4 in COHIBA carried out substance flow analysis (SFA) for the Baltic Sea catchment area. Depending on the choice of scenario, calculated emissions are between 18,000 kg/a

and 75,000 kg/a in the high emission scenario. The different receiving environmental compartments are shown in Figure 2.

The main industrial source is metal production[4] (Andersson/Pettersson, 2011). A dominant source of emissions during the "service life" is washing of imported textiles (OPE). Approximately 60% of the total load is emitted to water, see Table 5.
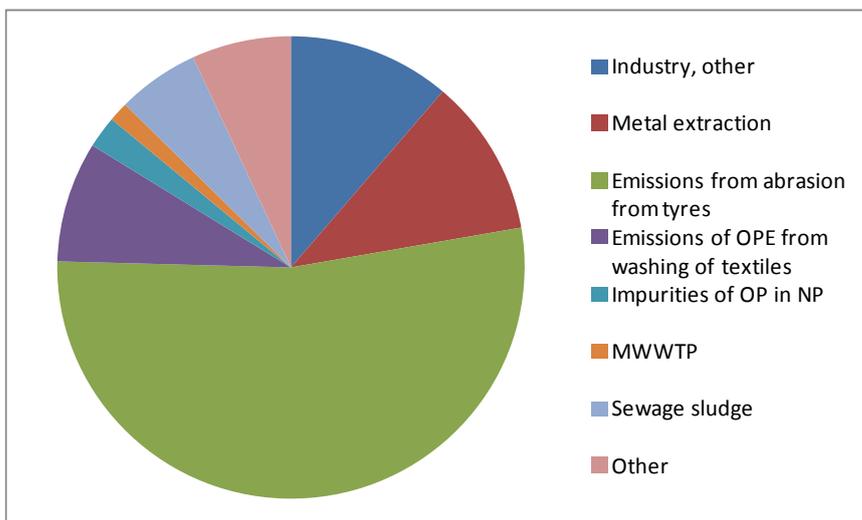
Figure 2: Emissions sources of OP/OPE

As can be seen in Figure 2, the predominant source for OP is abrasion from tyres, but it is a source with high uncertainties: Tyre producers claim that there are no emissions of OP because it is used in resins inside the layers and not on the tyre tread. Discussion is ongoing and more research and development (R&D) seems to be necessary. When tyres are mechanically crushed OP can be potentially released, although an estimate of yearly emissions cannot be given.

According to PRTR data for emission sources in the Baltic Sea catchment area in 2008, there were 6 point sources emitting 143.4 kg of OP and OPE, of which 5 sources are urban waste water treatment plants (WWTPs). Only the plant "PCC Rokita SA" in Poland is an industrial WWTP (see Table 4). PCC Rokita produces NP and dodecylphenol (PCC, 2010).

Table 4: Sites with OP/OPE emissions according to the PRTR for 2008

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4   Only in Swedish Substance Flow Analysis (SFA)

Country	No. of sites	Location	Amount [kg]
Finland	**3**		**13.4**
ESPOON VESI, SUOMENOJAN JÄTEVEDENPUHDISTAMO		ESPOO	3.24
HSY Vesi, VIIKINMÄEN JÄTEVEDENPUHDISTAMO, Jv+IL+JH, Jätevedenpuhdistamo		HELSINGIN KAUPUNKI	8.0
Napapiirin Vesi, Rovaniemen kaupungin jäteveden-puhdistamo		ROVANIEMI	2.2
Poland	**3**		**130**
"Wodociągi Kieleckie" Spółka z o.o. oczyszczalnia ścieków w Sitkówce		Sitkówka	4.97
PCC Rokita SA		Opole	124
Wodociągi i Kanalizacja w Opolu Sp. z o.o., Dział oc-zyszczania ścieków			

Findings of COHIBA WP4 and review of literature[5] indicate that major emission sources in the Baltic Sea catchment area are:

- OP/OPE-containing products (tyres, paints)
- Industrial waste water
- Municipals waste water

The emissions from each of the listed major sources are circa 100 tonnes.

3.3 Environmental fate

Under environmental conditions, OPEs degrade quickly to OPs. The available data indicate that OP has low volatility and low water solubility, and will adsorb strongly to organic matter in soils, sediments and sludge. Degradation processes within these media (biotic and abiotic) are predicted to be relatively slow. If released directly to the atmosphere, OP degrades rapidly through hydroxyl radical attack (Brooke et al, 2005).

An assessment of OP against the criteria for assessing the persistent (P), bio accumulative (B) and toxic (T) properties of a substance showed that with regard to:

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5 A full list of possible sources and the reasoning leading to selection of the largest emission sources is presented in Andersson et al. (2011).

- persistence: although OP is inherently biodegradable, it is not considered to be readily biodegradable and meets the screening criterion for persistence or very persistence;
- toxicity: the lowest chronic aquatic No Observed Effect Concentration (NOEC) is 6.1 μg/l which exceeds the toxicity criterion (chronic NOEC <0.01 mg/L) and, as such, OP meets the T criterion (EA, 2005; OSPAR, 2004);
- bioaccumulation: while the highest measured bio concentration factor (BCF) in fish is 297, OP is not bio accumulative, since the criterion is BCF >2,000).

Summing up the assessment of OP it can be stated that OP is toxic and persistent.

3.4 Contribution of emissions to the total load in the Baltic Sea

Due to environmental fate processes, the amount of hazardous substances emitted from sources in the Baltic Sea Area do not contribute one to one to the load to the Baltic Sea. E. g. sources within the Baltic Sea catchment area may not contribute fully to the load to the Baltic Sea, and sources outside the catchment area may contribute, for example by long range transport via air.

Table 5 shows the estimated contributions of sources of emissions of OP/OPE and the size of sources in the Baltic Sea area as calculated by WP 4 based on the low emission scenario. It was estimated that the main source are tyres, followed by emissions from washing of textiles. Nearly a quarter of all emissions arise from "other" sources like paints, plastics, inks, pesticides, etc.

Table 5: Major sources of emissions of OP/OPE in the Baltic Sea catchment area

Source	Total [%]	Emission to water [%]	Emission to air [%]	Emission to land/soil (land-fill in brackets) [%]
Emissions from abrasion from tyres	53[1]	27	0	27
Emissions of OPE from washing of textiles	8[1]	8	0	0
MWWTP	1	1	0	0
Sewage sludge	6	0	0	6
Impurities of OP in NP	2	2	0	0
Others	29[1]	23	3	3
Total	100	61	3	36
[1] partly also emissions into MWWTP				

4 Existing regulations

The use of octylphenol in the EU and Russia is not restricted. But in the framework of the REACH process, the German UBA prepared a REACH Annex XV dossier for OP as a first step towards a further substance restriction (ECHA, 2011).

Table 6 shows existing regulations for OP and OPE at international, EU, HELCOM and national level.

Table 6: Existing regulations for OP and OPE (in brackets: date of implementation)

Existing regulations	OP/OPE
International level	Included in the North Sea Action Plan in 1990 (NAP, 1990 in EA, 2005a), Included in the OSPAR List of Chemicals for Priority Action (OSPAR, 2000).
EU level	EU Environmental Quality Standards (EQS) Directive (2008/105/EC) Marketing and use restrictions under Directive 76/769/EEC: 2003/53/EC (OP as impurity of NP)
HELCOM	Recommendation 19/5 (HELCOM objective with regard to hazardous substances) gives advice to the MS how to deal with the 11 hazardous substances
National level	Voluntary agreements for certain industry sectors Commitment of the association of German producers of textile, leather, tanning and washing (TEGEWA) to phase out APEs in chemicals for wastewater treatment (DE, 1998) Agreement of manufacturers of household detergents not to use APEO (DE, 1986). Industrial cleansing agents were added to this agreement in 1992) (DE).[6] Voluntary system for certification of sludge "REVAQ" including regulation of OP (SE, 2002).

OP/OPE have been identified as priority hazardous substances under the EU Environmental Quality Standards (EQS) Directive (2008/105/EC). There are various national agreements not to use OP/OPE in certain sectors. But since there is an existing regulatory gap, OP/OPE are still in use e.g. in textile printing.

5   Measures for emission reduction

5.1 Evaluation methodology

In order to identify appropriate measures for reducing emissions of hazardous substances to the Baltic Sea a pragmatic approach is applied. In view of the multitude of possible sources

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[6] A series of voluntary agreements exist in the UK for OP/OPE together with NP/NPE :
http://archive.defra.gov.uk/environment/quality/chemicals/phenols-va/voluntary-ag.pdf

and measures, source-measure combinations promising a large reduction potential are pre-selected. For the identification of large reduction potentials two criteria are considered: firstly the load at the source and secondly the effectiveness of the applied measure (chapter 5.2).

In a second step these pre-selected measures are analyzed in detail and compared (chapters 6 and 7). If appropriate data on effectiveness and costs are available a quantitative assessment of the cost-effectiveness of measures is performed by using the following evaluation criteria:

Effectiveness

The effectiveness of a measure at a given source relates to the reduction it achieves in the emissions of a given hazardous substance. The effectiveness of technical measures is usually expressed as elimination rate in percent. In combination with the load of the respective source, the effectiveness can be expressed as load reduction in kilogramme.

Costs

The evaluation of costs is subdivided in direct costs and running costs. Whilst direct costs include initial expenditures (e.g. construction costs, investment costs, costs for developing a substitute, rule making costs), running costs comprise ongoing expenditures (e.g. operation and maintenance costs, (additional) costs for using a substitute, costs for implementation and enforcement). In order to adapt the costs to local circumstances, they are further broken down into costs for labour, energy and material, if data are available.

Cost-Effectiveness Analysis

The cost effectiveness of different measures is expressed by the ratio of cost to the reduced load of hazardous substances. As there are large uncertainties, different scenarios – a worst case scenario (low load reduction effectiveness – high costs) and best case scenario (high load reduction effectiveness – low costs) - are used for the calculation of cost effectiveness.

The quantitative assessment is complemented by a comprehensive qualitative evaluation to include sustainability aspects, which is mainly based on experts' estimates rather than on empirical data. For this additional assessment the following qualitative evaluation parameters are used:

Secondary environmental effects

Besides the direct effects on emissions of the targeted hazardous substance, measures can have a wide array of positive or negative secondary environmental effects (e.g. effects on emission reduction of other hazardous substances or nutrients, effects on waste production which requires deposition on landfills, effects on climate change through energy consumption or effects on land use).

Technical feasibility

The technical feasibility describes the ease of technical implementation of the respective measure under different boundary conditions. This touches on aspects like practical experiences (emerging, pilot or existing technology), necessary process modifications, or impact on ongoing processes. These can present limitations for the application of the respective measure. One indicator of technical feasibility is e.g. the time needed for (technical) implementation of the measure.

Secondary socio-economic effects

Besides the primary costs of a measure, there are also secondary socio-economic effects (including indirect costs) of a measure. Possible secondary socio-economic effects of a measure include indirect costs, effects on employment, on job qualification (e.g. qualification needed for operation and maintenance of advanced technologies) and on product prices including the question whether industries pass on higher costs to consumers. An important aspect is which stakeholders are affected, who pays for the measures and who benefits from them.

Geographical and time scale of effects

Another additional parameter to describe measures is the geographical and time scale of effects. Some measures are effective on a local or watershed level and other measures show effects on a national or international level. The time scale of effects varies from immediate effects to long lag times until the measure becomes effective (e.g. varying time spans of effects due to different technical lifetimes for certain measures).

Political enforceability

The political enforceability of measures depends on how well the measure is aligned with other political targets, on the national financial scopes (e.g. compensation payments), on possible conflicting interests and on their acceptance by existing interest groups. The political enforceability is also influenced by the other parameters, such as effectiveness, costs, technical feasibility and secondary environmental and socio-economic effects.

5.2 Overview of measures

The basis for selection of measures is the inventory of measures for OP/OPE, which was developed within COHIBA WP 5. It can be found in the annex in Table 10.

As shown in Chapter 3.2, the predominant source of OP is abrasion from tyres, but this source is subject to high uncertainties.

Substitution of OP/OPE is possible in many cases and has already been done to a certain extent in the past, but because of missing regulations OP/OPE are still in use in areas such as textile printing. A total ban on OP does not seem to be possible, because of the "paramount" use (claimed by tyre producers) in tyres. Therefore voluntary agreements are proposed as a useful measure, which can also include the metal extraction industry, for which high emissions are reported in Chapter 3.2. Agreements can also include as well possible

OPE uses in "newer" extraction processes like fracking for natural gas; fracking processes are currently under discussion in Europe.

To reduce the emissions of OP/OPE already in the market, two end-of-pipe measures for MWWTPs are analysed: "Advanced waste water treatment – AC treatment" and "Sludge treatment - controlled incineration". Table 7 gives an overview of the measures selected for OP and OPE.

Table 7: Overview of analysed measures and corresponding sources for OP/OPE

No.	Measure	Relevant sources
1	Substitution of OP in textile printing	OP/OPE-containing products
2	Waste management - controlled incineration of waste tyres	Grinded material from OP containing tyres
3	Voluntary agreement to stop using OP	Use of OP/OPE in products
4	Advanced waste water treatment – AC treatment	Industrial waste water
		Municipal waste water
5	Sludge treatment - controlled incineration	Municipal waste water

6 Description and analysis of measures

6.1 Measure 1: Substitution of OPE in textile printing

6.1.1 Description of source

OPEs are used in the textile industry for printing purposes like e.g. T-shirt printing. They are used in specific emulsion processes as glues, binders, emulsifiers for dyestuffs, emulsion polymerisation, etc. Emulsion systems are based on polyvinyl chloride or polyurethane. Most of the OPE is physically bound in the polymer matrix which sticks to the textile. However, although this is a legal use in water-free printing processes, a lot of the OPE, and NPE as well, is washed out over the lifetime of the textiles and ends up in waste-water.

There are many different chemical companies who offer OPE containing products such as Dow (Triton X series) or Huntsman (e.g. in the Surfonic®OP, Empilan OP and Teric$^®$ X series).

6.1.2 Description of measure

With regard to non-ionic surfactants, replacing OPEs with other materials appears to be actively promoted by the chemical companies. Several alternatives to OPEs are available. Typical substitutes are fatty alcohol ethoxylates, for more difficult applications other branched alcohol compounds like Guerbet alcohol are used. These substitutes can cost twice as much as OPEs. Other identified alternatives to OPEs are based on 4-tert-pentylphenol[7] or dodecylphenol[8]. Potential risks have been identified for both.

Recent work undertaken under the OECD SIDS programme indicates that while some fatty alcohols may be toxic to aquatic organisms, they do not bioaccumulate or have endocrine disrupting effects and are not expected to be as persistent as OP (personal communication, 2006)

6.1.3 Effectiveness

The effectiveness of the measure is high, although it will take some years before a substitution process is fully completed. RPA gives a time span of 3 years as an example for one company (RPA, 2006).

6.1.4 Costs

The average price for alkoxylates in 2006 was estimated to be ca. 1,100 € per tonne (Frost&Sullivan, 2007).

Typical substitutes are fatty alcohol ethoxylates which are ca. 10 - 20 % more expensive than OPE. Branched alcohol compounds like Guerbet alcohol, cost approximately twice as much as the currently used OPE compound.

The costs for the chemicals are only one part of the substitution costs (RPA, 2006). Reformulation of the products to prevent worsening in performance is often necessary, as well as plant trials, customer trials and support. RPA (2006) estimates the costs for a substitution programme at around € 58,000 (£ 50,000) in technical support, sampling and staff time.

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[7] http://publications.environment-agency.gov.uk/pdf/SCHO0208BNQR-e-e.pdf

[8] http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-ee.pdf

6.1.5 Secondary environmental effects

As with all substitutions, care must be taken that the substitute chemicals are not dangerous for the environment.

6.1.6 Technical feasibility

In general, substitution of OPE in textile printing is technical feasible. Because of the good performance of OPE, it might be necessary to change the formulation and use more than one chemical to substitute OPE.

6.1.7 Secondary socio-economic effects (including indirect costs)

Because available substitutes cost only slightly more, a significant increase in product costs is unlikely.

6.1.8 Geographical and time scale of effects

Most textiles are printed outside Europe and are then imported. Hence, along with substitution in Europe, an import control of textiles containing OPE must also be put in place.

6.1.9 Political enforceability

There is no political reason standing against the introduction of this measure.

6.1.10 Cost-effectiveness analysis

The costs for substitutes are somewhere between 120 to 200 % of the OP/OPE costs. Those are pure chemical costs, without expenses for reformulation. Based on the costs discussed in Chapter 6.1.4 the substitutes have prices between 1.20 and 2.20 Euro per kg (SASOL, 2011).

6.2 Measure 2: Waste management – controlled incineration of waste tyres

6.2.1 Description of source

OP-based resins are used to increase the tackiness of rubber in tyres and improve adhesion of the different layers during vulcanisation. The resins are usually added to rubber in amounts of up to 1.5% of the rubber formulation although the maximum figure for the percentage of resin in rubber used in tyres could be as high as 10% (EA, 2005). In 2010, 4.5 million tonnes of tyres were produced in 91 tyre manufacturing facilities across Europe (ETRMA, 2011).

According RPA (2008) the primary function of the OP formaldehyde resin is to maintain the internal structural integrity of a so called "green tyre" prior to curing by high temperature vulcanisation. According to the tyre industry, no OP is released to the environment during the tyres' service life (ETRMA, 2007). The release or no release of OP from tyres is

a field for further research. Nevertheless, it is documented in literature that, if the tyres after service life are shred, these grounded tyre material release OP into the environment.

In some studies only low OP concentrations were found in leachate from products from end of life tyres, like e. g. 0.1 µg/l from light fill noise barriers (Aabøe et al., 2004). Other studies reports higher concentrations, like 3.6 µg/l (Niva, 2005) from artificial turf systems or 3.6 mg/l from rubber granulate (NBRI, 2004), so an environmental effect can be feared[9].

6.2.2 Description of measure

The substitution of OPE resins in tyres seems to be difficult (see Annex A2). Thus, it is proposed to collect all waste tyres and reuse them as whole tyre if possible without destroying the matrix. After their service life, the tyres should be oxidized in steel mills, incineration plants, foundries or cement kilns. However, they should not be grinded and used in civil engineering, where significant amounts of OP can be set free.

6.2.3 Effectiveness

The effectiveness is high after implementation of the measure.

6.2.4 Costs

In collection systems operated by producers, these companies or importers of tyres charge a fee (e. g. 57 EURO/t in Estonia) for collection and disposal of end of life tyres. The disposal fee per tonne of tyres for passenger cars is around 65 € in Germany. On the other hand, the waste industry sells the tyres to industries which use their energy content.

This measure would not increase current end of life costs for tyres in the BSC.

6.2.5 Secondary environmental effects

The emission of high amounts of zinc can also be stopped by this measure. Zinc oxide is used in rubber industry as activator for sulphur vulcanisation. The concentration in tyres is 1 to 2 %.

Several Life Cycle Assessments (LCAs) in the literature show that the recycling of used tyres saves more energy and is environmentally better than incineration in cement kilns, if the recycled material from tyres substitute virgin rubber (Schmidt et al., 2009).

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[9] PEC/PNEC > 1

6.2.6 Technical feasibility

The incineration of tyres is already common practice in most countries in the BSC area.

6.2.7 Secondary socio-economic effects (including indirect costs)

Artificial turf systems with grinded rubber from disposed tyres are used for baseball fields in the US. They are not used widely in the BSC.

By the thermal use of end of life tyres in cement kilns etc. other energy sources could be saved.

6.2.8 Geographical and time scale of effects

In some countries capacities for using tyres for energy recovery have to be built up.

6.2.9 Political enforceability

In the BSC producer operated collection systems already exist in Sweden, Finland, Estonia and Poland. Lithuania and Latvia are in the process of setting up such systems, because Landfill Directive 1999/31/EC prohibits landfilling of used tyres. In Germany there is a free market system, in which owners or garages have to pay a fee to get rid of old tyres.

6.2.10 Cost-effectiveness analysis

As stated in Chapter 6.2.4, this measure is supposed to be cost-neutral. The amount of reduced emissions cannot be calculated, so cost-effectiveness can't be calculated.

6.3 Measure 3: Voluntary agreement to stop using OP

A voluntary reduction agreement was developed in the UK in anticipation of the then impending EU-wide Directive 2003/53/EC concerning the marketing and use of NP and NPE. The UK industry agreed not to promote OPEs as substitutes for NPE. End users undertook to stop using NP/E and OP/E in new formulations from Jan 2004 and to phase out their use in existing formulations as soon as possible or by Dec 2004 at the latest.

6.3.1 Description of source

Similar to the use of NP and NPE before EU Directive 2003/53/EC, there are a lot of different possible uses for OP and OPE. OP is also an impurity of NP formulations, which are still widely used in metalworking, in the manufacture of coatings, textiles and leathers, and in certain areas not covered by the EU ban such as emulsion polymerization and chemical intermediates in manufacturing processes. These applications are major emission sources.

6.3.2 Description of measure

The UK's voluntary agreement, which comprises separate measures for suppliers and downstream users, should be applied to the BSC. Under the suppliers' agreement, manufacturers

and suppliers would take action to support risk reduction by promoting safer substitutes to NPEs (such as the similar alcohol ethoxylates), and would inform and advise their customers about the voluntary agreement.

As in the UK, the following producers, trade associations and downstream users should be part of this agreement (DEFRA, 2004):

- Chemicals supply industry
- Cosmetic, toiletry & perfumery industry
- Specialty chemicals industry
- Paper industries
- Cleaning products industry
- Crop protection industry
- Fragrance industry

6.3.3 Effectiveness

The effectiveness of this measure is high, since the involvement of importers and producers opens up the possibility to abandon all uses of OP/OPE. Because of the desired use of OP in tyres (see above) a ban on OP/OPE is difficult to implement.

6.3.4 Costs

The cost to UK industry of one-time reformulation and changes in raw materials costs due to the use of alternatives to NP/NPE and OP/OPE was estimated by DEFRA at about 6.4 million € (£4.3 million; Edser, 2004).

Today, the cost will be significant lower because many companies who are big players around the BSC produce in the UK and are already parties to the UK voluntary agreement (including Akzo Nobel Surface Chemistry, BASF, Croda Chemicals Europe, Dow Europe, Goldschmidt UK, Huntsman Surface Sciences UK, Shell Chemicals, Stepan UK, Uniqema). They have already invested in R&D of environmentally friendly, but functionally equivalent, alternatives to NPE and OPE (Edser, 2004).

6.3.5 Secondary environmental effects

There are no expected secondary effects.

6.3.6 Technical feasibility

Measure is already established in UK.

6.3.7 Secondary socio-economic effects (including indirect costs)

The associations and companies who sign the voluntary agreement can show that they are first movers in environmental protection and use it in their press work.

6.3.8 Geographical and time scale of effects

Voluntary economic instruments like voluntary agreements do not seem to be working in Russia at all, mainly because of the low level of general public awareness and a lack of demand for cleaner or safer products (Toropovs, 2011).

6.3.9 Political enforceability

Voluntary agreements are normally used on a country scale. It might be a challenge to implement them on BSC level.

6.3.10 Cost-effectiveness analysis

The costs of substitutes are between 120 and 200 % of the OP/OPE costs. Those are pure chemical costs, without expenses for reformulation and a mechanism for controlling the agreement. Based on the costs discussed in Chapter 6.1.4 the substitutes have prices between 1.20 and 2.20 Euro per kg.

6.4 Measure 4: Advanced waste water treatment – AC treatment

6.4.1 Description of source

Pollutant loads in waste water vary greatly in different cities/districts/MWWTPs (e.g. depending on indirect industrial dischargers[10],) and can also vary markedly in time. Therefore, predicting the kinds and loads of pollutants at MWWTPs has a very high uncertainty.

Primary degradation of OPEs through ether cleavage in wastewater treatment plants generates more persistent shorter chained OPEs and octylphenol (Giger et al., 1984). The elimination rates for OP e.g. in German MWWTP are between 73 and 98 % (great influence of the limit value; MUNLV, 2004). The main treatment plant in Vienna has a rate of 50 % (Scharf et al., 1998). Rates ranging from 7 to 100 % were found in 16 Canadian plants (Bennie et al., 1998).

In the figure below, concentrations of OP in MWWTP effluent in different countries are presented.

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10 Industrial and commercial sites discharging to municipal sewers and MWWTP.

Load:

For OP

- between 6 – 36 µg/ day per capita (measured data from COHIBA-WP3)
- Concentrations [µg/l]:
  Canada: 0.12– 1.7 (mean0.69) (Lee et al.,1995)
  Japan: 0.02– 0.48 (Isobe et al., 2001)
  USA :   0.15 (Rudel et al., 1998)
                   < LOD– 0.673 (0.072) (Snyder et al., 1999)
                   0.21-1.58 (mean, summer/winter; Loyo-Rosales, 2007)
  Germany :   < LOD– 0.073 (0.014) (Kuch et al., 2001)

Range: assumed 200 l per capita, 4 to 340 µg/day per capita,
       equals ~1.4 to 124 mg/a per capita
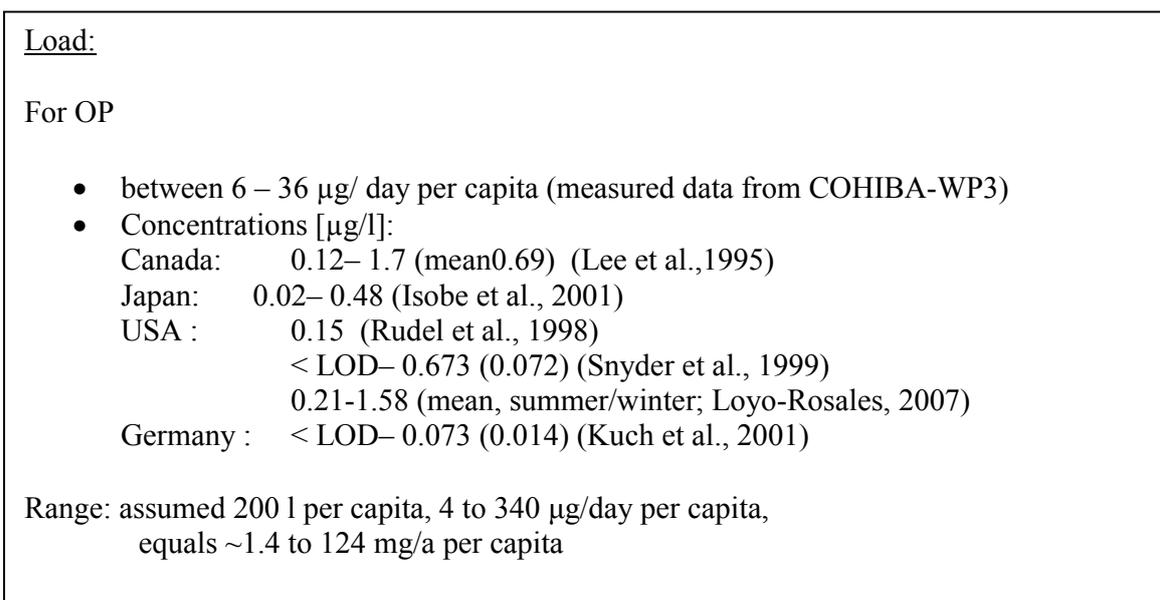
Figure 3: Concentrations and loads of OP in MWWTPs as found in a literature review

6.4.2 Description of measure

Activated carbon (AC) filters for removal of pollutants from wastewater are a proven technology. AC has a large surface area and is an effective adsorbent for many substances. Different technical systems are commercially available (e.g. powder (PAC) and granular activated carbon (GAC)). These adsorbents can be used in different processes in the MWWTP, e.g. as fixed bed after the third treatment stage or mixed with the waste water.

6.4.3 Effectiveness

The effectiveness of AC filters in removing OP at MWWTP depends on the concentration range of pollutant, technical parameters and the matrix. At well maintained MWWTPs reduction rates of 75 % in the effluent of MWWTPs using PAC can be observed (Fahlenkamp et al., 2008).

6.4.4 Costs

Economic analysis from the project "StrategyMicroPoll" (Switzerland, Ort et al., 2009) found costs of 10-60 € per person and year, including discounted investment costs and running costs, see Figure 5. Specific costs are strongly dependent on the size of the MWWTP (large WWTP, low specific costs, economy of scales), see data for 6 plants in Figure 4.
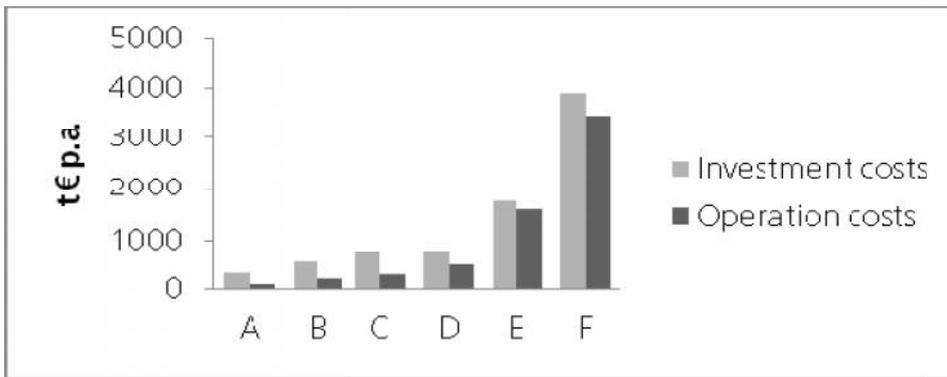
Figure 4: Yearly investment costs and running costs, economic data from *StrategyMicroPoll*
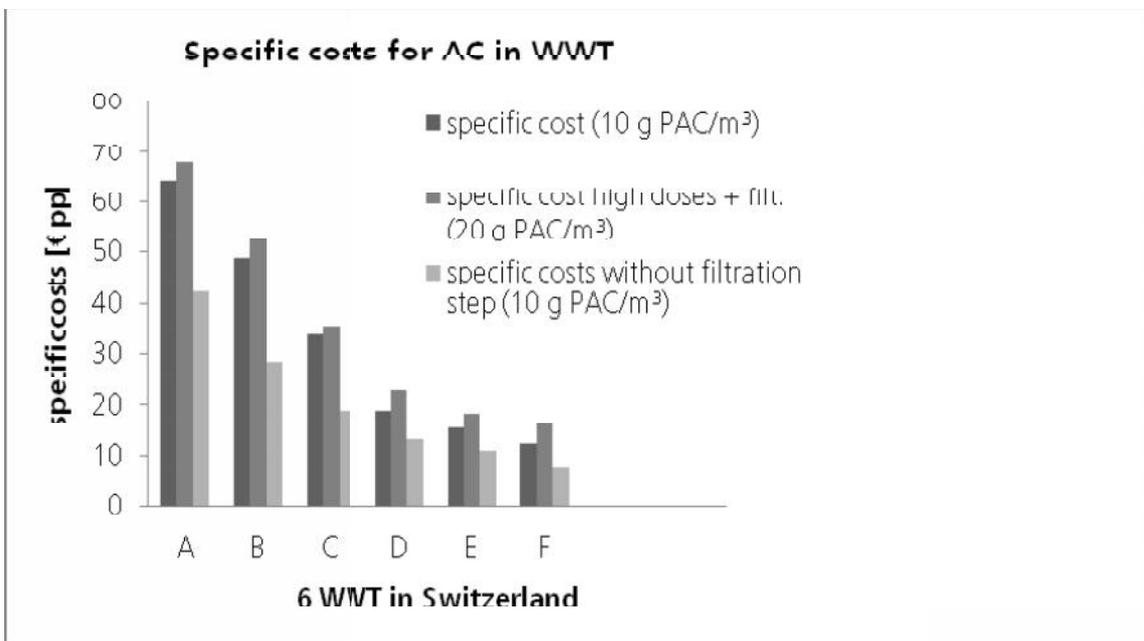
Figure 5: Specific costs per person and year in 6 MWWTPs in Switzerland, economic data from *StrategyMicroPoll*

6.4.5 Secondary environmental effects

AC filtration at MWWTPs, sometimes called the 4th stage of waste water treatment, affects emissions of the other of the 11 HS of special concern to the Baltic Sea, which are typically present in municipal waste water in very low concentrations. Filters also have other water related secondary environmental effects: on emissions of phosphate, heavy metals, organic micro pollutants (which are not on the HELCOM list), pharmaceuticals and their metabolites, or endocrine disrupters.

Additionally, AC treatment has significant cross substance effects and enables a simultaneous elimination of other hazardous substances, such as TBT, PFOS, nonylphenol, Cd, and

Hg. This makes it possible to calculate effectiveness rates and loads for all 11 HS treated at MWWTPs.

Negative secondary environmental effects are related to e.g. higher energy use combined with greenhouse gas (GHG) emissions during construction and operation, and for manufacture of activated carbon (Wenzel, 2008).

6.4.6 Technical feasibility

AC treatment is an available technology, a well-functioning MWWT with low concentrations of suspended solids and dissolved organics is necessary.

6.4.7 Secondary socio-economic effects (including indirect costs)

The costs of advanced waste water treatment can be passed on to the customers of the MWWTP. As shown above, large MWWTPs normally have lower per capita costs than smaller MWWTPs.

The other option is to have the costs paid for by all citizens via taxes, as the whole community benefits from a healthier environment free of toxic substances. The latter option was put into practice in Switzerland (total costs of waste water treatment rose by 6%).

6.4.8 Geographical and time scale of effects

Most of the emissions from urban stock are channelled through MWWTPs, urban runoff and landfills. The types and loads of pollutants in waste water are dependent on local conditions in the urban area served, e.g. pattern of indirect dischargers[11], product use pattern, user behaviour and pollutant load from urban surfaces (roofs, streets etc.) in case of combined sewer systems

6.4.9 Political enforceability

The political enforceability depends on the willingness to pay in different countries. In Switzerland, use of PAC-adsorption at large MWWTPs has been mandatory since 2010.

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11 Industrial and commercial sites discharging to municipal sewers and MWWTP.

6.4.10 Cost-effectiveness analysis

Taking into account typical loads, as discussed in 6.4.1, from 1.4 to 124 mg OP per year and capita, a reduction rate of 75 % using PAC and costs of 15 to 20 Euros per person for bigger MWWTPs, the cost-effectiveness lies between 160,000 and 19 million Euros per kg OP, see Figure 6.

Figure 6: Cost range for elimination of OP/OPE with AC treatment
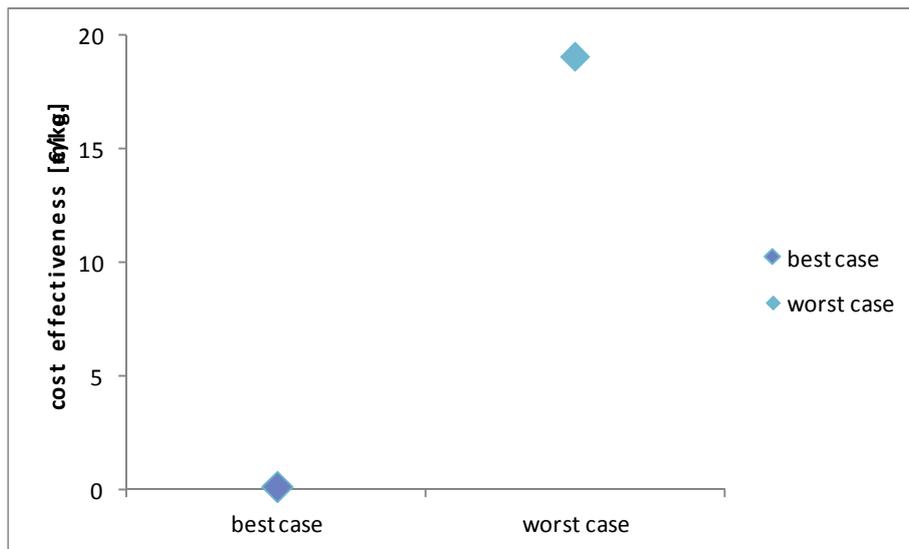
6.5 Measure 5: Sludge treatment - controlled incineration

6.5.1 Description of source

As already shown above, OP has a high tendency to adsorb on sludge in MWWTPs. Fahlenkamp et al. (2006) calculated adsorption rates of 35, 55 and ca. 100 % of OP for 3 large MWWTPs in Germany. The corresponding concentrations in the stabilised sludge are between 4,600 to 80,000 µg/kg (median).

But of course the load of OP in sludge depends on its origin. If sludge is incinerated, use of the nutrients it contains , which is generally favoured, is not possible. Therefore, this measure cannot be recommended without looking at the local conditions and concentrations in sludge (ifeu, 2008).

6.5.2 Description of measure

To avoid contamination of soil by land-spreading of OP containing sludge, it is necessary to use incineration processes to degrade the substance. Different processes are currently in use, varying in reactor type (fixed or fluidized bed) or feed (mono- or co-incineration). The system mainly used for the incineration of sewage sludge is fluidized-bed combustion. Fluidized-bed furnaces for the incineration of sewage sludge are usually operated at combustion temperatures in the range of 850°C and 900°C.

6.5.3 Effectiveness

Because of the high temperature and the long residence time in the reactor OP is completely degraded. Commercially available installations are equipped with highly effective flue gas cleaning systems.

6.5.4 Costs

There are a number of sources in the literature that report different costs for co-incineration but the information on the costs of mono-incineration is more limited (Salado et al., 2008) . Sede and Andersen (2002) give the following estimates: for co-incineration: €290 t/dry sludge and for mono-incineration €374t/dry sludge. The costs of incineration are highly variable depending on design aspects and energy recovery, as sales of both electricity and heat can generate substantial revenue that can cover part of the incineration costs.

6.5.5 Secondary environmental effects

The main secondary benefit of sewage sludge incineration is the decomposition of all other organic substances like other HELCOM priority substances or micro pollutants like pharmaceuticals.

A big disadvantage lies in the fact that the phosphorus in the sewage sludge is lost for fertilisation purposes. There are R&D projects running on how to break the organic molecules and extract the nutrient in one process.

6.5.6 Technical feasibility

Specific sludge incineration facilities have been in operation in BSC countries for many years, i.e. in Germany and Denmark.

6.5.7 Secondary socio-economic effects (including indirect costs)

Incineration of sludge results in higher costs for MWWTPs and for the inhabitants they serve. Farmers can no longer use sludge as "cheap" fertiliser, in some cases they are paid for this "sludge disposal".

6.5.8 Geographical and time scale of effects

According to a COHIBA survey, sludge incineration is used only in Denmark, Germany and Poland, see Table 9.

Table 8: Sludge going to incineration

	Year	Share of incineration
Denmark	2007	15.7%
Estonia	2009	0.0%
Finland	2008	0.0%
Germany	2009	52.6%
Latvia	2007	0.0%
Lithuania	2009	0.0%
Poland	2009	1.6%
Russia	2011	0.0%
Sweden	2009	0.0%

6.5.9 Political enforceability

The political enforceability depends on the willingness to pay in different countries. In Germany, some federal states decided politically to apply the precautionary principle and incinerate all their sludge.

6.5.10 Cost-effectiveness analysis

The costs for incineration of sludge are given in Chapter 6.5.4 as 374 Euros per tonne of dry sludge. Based on concentrations between 4.6 and 80 mg/kg of sludge as given in Chapter 6.5.1, the cost effectiveness equals 0.005 to 0.08 million Euros per kg of OP.

7   Comparison of measures

Figure 7 illustrates the cost-effectiveness of the different measures. AC treatment is the most costly measure, due to the low concentrations in MWWTP influent. It costs 0.16 to 19 million € per kg OP.

Because OP accumulates in sludge controlled incineration is less costly with 4,700 to 81,000 €/ kg OP. Substitutes for OP/OPE cost around 1.20 to 2.00 €/t, the costs for voluntary agreements are estimated to be in the same range. The incineration of tyres might be done without extra costs.
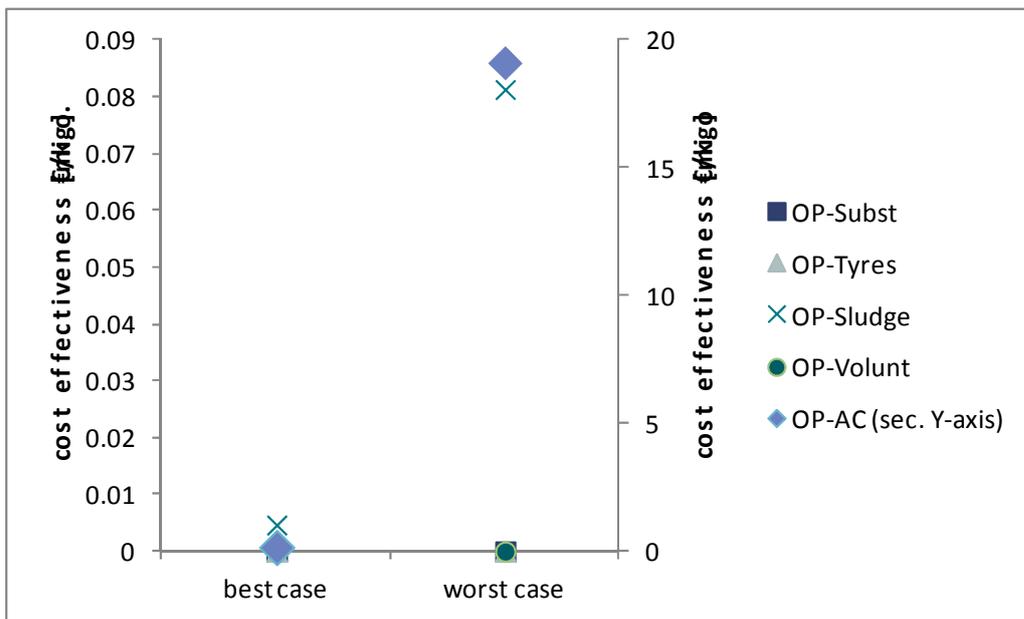

Figure 7: Cost range for elimination of OP/OPE with AC treatment

Table 9 compares the proposed measures in terms of the influencing factors discussed above.

Table 9 Comparison of OP/OPE reduction measures

Measures	Effectiveness	Cost	Secondary environmental effects	Technical feasibility	Secondary socio-economic effects	Geographi-cal/time scale of effects	Political enfor-ceability	Cost effective-ness
Measure 1: Substitution of OP in textile printing	++	++	+	+++	+	+++	+++	+++
Measure 2: Incineration of waste tyres	++	+	++	+++	+	++	++	+++
Measure 3: Voluntary agreement to stop using OP	+++	++	++	++	++	++ (not RU)	+++	+++
Measure 4: Advanced waste water treatment – AC treatment	++	++	+++	+++	+	+	++	+
Measure 5: Advanced sludge treat-ment: Controlled incineration	++	++	+++	+++	+	++	++	++

Key

+	Only limited effectiveness	Very high costs	Negative sec-ondary environ-mental effects	Technology not yet avail-able or very new man-agement option	Negative or no socio-economic effect	Only long-term realiza-tion, > >10 years	Strong political opposition expected	Costs per kg (or per Teq) emission reduction high
++	Partially effec-tive	Moderate costs	Several positive secondary envi-ronmental ef-fects	Pilot process or transfer-rable non-technical measures available	Some positive socio-economic effects	Medium-term realization, approx. 3 -10 years	Political opposi-tion expected	Costs per kg (or per Teq) emission reduction medium to high
+++	Substantial effects	Low costs	Numerous posi-tive secondary environmental effects	proven and available technology	Many positive socio-economic effects	Rapid realiza-tion possible, 1-3 years	Political support expected	Costs per kg(or per Teq) emission reduction medium to low

8 Conclusions

Octylphenols and octylphenol ethoxylates are widely used in very different applications. The main use of OP is resins in tyre manufacture, so for safety reasons it is not possible to ban OP completely.

Nevertheless, the chemical industry in Europe is already prepared for a more restricted use of OP and OPE, as the voluntary agreement of industry in the UK shows. The producers of chemical specialities invested in research and development (R&D) of environmentally friendly, but functionally equivalent, alternatives to OPE. Substitutes like e. g. fatty alcohol ethoxylates have additional costs of only 10- 20 %, for more complex applications in textile printing branched alcohol compounds such as Guerbet alcohol are used. These substitutes can cost twice as much as OPEs.

The downstream industry, which produces consumer products, has to be pushed to use the substitutes. This can preferably be done with voluntary agreements, which can be adjusted more easily to the market and technical framework conditions of each industrial sector. It might be a challenge to implement voluntary agreements on BSC level.

For OP and OPE which are already in use in products, two end-of-pipe measures for MWWTPs were analysed: "Advanced waste water treatment – AC treatment" and "Sludge treatment - controlled incineration". Both measures have cross substance effects and are capable of eliminating other hazardous substances.

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AAdditional background information

A1 Overview of possible measures for OP/OPE

	Measures	7. (Octylphenols)
End of pipe	**Urban waste water treatment**	
	Mechanical waste water treatment	x
	Biological waste water treatment	x
	Membrane bioreactor (MBR)	x
	Sand filtration	x
	Longer Sludge Retention Time	?
	Urban run off management	x
	Advanced wwt	
	Sorption	
	Activated carbon adsorption	x
	Low-cost sorbents	x
	Sorption to zeolites	x
	Membranes	
	Membrane filtration (NF / RO)	x
	Other treatment methods	
	Oxidative techniques (e.g. ozone)	x
	Solid phase treatment	
	Sewage sludge	
	Advanced sludge treatment: Controlled incineration	x
	Advanced sludge treatment: Gasification	x
	Avoid land application of sewage sludge	x
	Certification system for sewage sludge	x
	Controlled incineration	x
Source control	**Substance**	
	Substitutes for OPE	x
	Product	
	Awareness raising for users of products (privat and commercial)	(x)
Regulatory measures	**Ban of individual substances (use and/or production)**	
	Ban industrial / commercial wastewater in MWWT	x
	National emission register	x
	National chemical product register	x
Economic and Financal Measures	Waste water levy	x
Voluntary agreements	Voluntary agreement	x

X – possible measures, (X) – measures with limited/unclear effectiveness, (--) – measure with negative effects

Table 10: General list of potential measures for OP and OPE

A2Possible substitutes for OP resins in tyres

There are different possibilities to substitute OP resins for use in rubber formulation, like (Gent, 2001; RPA, 2007) (1) rosin-based derivatives, (2) coumarone-indene resins consisting of indene, coumarone, styrene, etc. obtained from coal coke oven light oils, (3) aliphatic

petroleum resins made from unsaturates obtained while cracking crude oil, (4) terpene oligomers of alpha- or beta-pinene obtained from pine tree stumps and (5) tert. butyl phenolic resins.

Of these chemicals it appears that rosin based derivatives are the most widely known. Blends of rosin and tall oil along with pine tars have been used as rubber-processing aids since the early 1920s. But as quality considerations became more demanding, it was concluded that pine tars and rosin blends lacked the reproducible consumers needed.