

# SOCOPSE



SOURCE CONTROL OF PRIORITY SUBSTANCES IN EUROPE

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**An Inventory and Assessment of Options for Reducing Emissions:  
Nonylphenols**

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# An Inventory and Assessment of Options for Reducing Emissions: Nonylphenols

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# 1. Executive summary

Nonylphenols (NP) or nonylphenoethoxylates (NPEs), a product in the further processing of nonylphenol, are synthetic organic mass-produced chemicals. The market volume of nonylphenols is approximately 45,000 ton per year in the EU, produced by three European companies (1997)<sup>1</sup>.

The main areas of use of NP are the production of modified phenolic- and epoxy resins, phenolic oximes and nonylphenol ethoxylates (NPEs). In the past NPEs were used as a surfactant in industrial and institutional cleaning agents, in textiles and leather auxiliaries as well as an emulsifier in agrochemicals. Since 2005 NPEs are used in non waste water relevant applications only as e.g. an emulsifier in the polymer production or in water based paints.

The compartments to which releases occur are a) surface water (rivers, lakes, seas and their sediments) via industrial and municipal waste water and waste water treatment plants, b) soil, via sewage sludge containing NP/NPE's spread on land, and c) air. The total emission of NP in EU is 2,9 ton/day (surface water) and 108 ton/day of NPE (waste water)<sup>2</sup>.

Because of the high aquatic toxicity of NP (the main pathway of NP to the environment is via the biodegradation of NPEs in the aquatic environment) the EU Commission has published marketing & use restrictions (2003/53/EC) for all waste water relevant applications as a conclusion of an EU risk assessment carried out under the Existing Substances Regulation 93/793/EEC. Because NP is a so-called endocrine disruptor chemical, several political initiatives have also banned or restricted the use of NP(E) in Europe. In some countries the use of NPEs is almost completely phased out.

Options for reducing the NP(E) emission to water are source control options, during the use of NP(E) containing products, including substitution, and end-of-pipe options for water treatment. The reduction measures for the different sources are presented below in table 1.

**Table 1 Emission sources and possible emission abatement measures**

		<b>Sources</b>			
		Release to surface water (Production of NP and NPE)	Waste water (Production of NPEs)	Release to surface water (Production of different materials using NPEs)	Waste water (Uses of products containing NPE)
<b>Measures</b>	<b>Source Control</b>				
	Substitutes for NPE			x	x
	<b>End of pipe option</b>				
	Separation zone NPE pesticides	x		x	

<sup>1</sup> Because of strict regulations (Directive 2003/53) the production, use and emissions of NP(E) have decreased dramatically since 2005. New production figures are however not available yet.

<sup>2</sup> These emission dates are referring to 1997. Because of strict regulations (Directive 2003/53) the production, use and emissions of NP(E) have decreased dramatically since 2005. New emission figures are however not available yet.

	<b>End-of-pipe techniques</b>				
	Coal Adsorption	x	x	x	x
	Chemical Oxidation	x	x	x	x
	Nanofiltration/Reverse Osmosis	x	x	x	x
	Electrochemical oxidation	0	0	0	0
	Electro-coagulation	0	0	0	0
	Moving Bed adsorption	0	0	0	0
	<b>Community level measures</b>				
	Use of end-of-pipe techniques for effluent municipal waste water treatment plants			x	
	Reuse sewage sludge options	x	x	x	X
	Use of end-of-pipe techniques for P(E) containing landfill-leachate and groundwater			x	
	Stormwater runoff options	x		x	
	<b>Measures at regulatory level</b>				
	Ban the use of NP(E) containing sludge as soil improver			x	
	Ban the import of NP(E) containing textiles	x		x	

Note: X = available measure; 0 = emerging measure

Table 2 presents the evaluation of emission abatement measures

**Table 2 Assessment of emission abatement measures**

Measure/source	Score at Criteria				Remarks
	Technical feasibility	Performances	Costs	State of the art	
<b>Source Control</b>					
Substitutes for NPE	<b>Total score: +</b> <i>Pol.:</i> point source/diffuse <i>Cmp.:</i> medium? <i>Imp.:</i> medium	<b>Total score: ++</b> <i>Eff.:</i> 100% <i>Oth.:</i> no <i>En.:</i> no <i>Ce.:</i> yes <i>W:</i> no	<b>Total score: +</b> <i>IC:</i> no <i>OC:</i> medium	<b>Total score: ++</b> <i>St:</i> existing <i>App.:</i> numerous	Costs of substitutes could be somewhat higher than the costs of NPE
End of pipe option					
Separation zone NPE pesticides	<b>Total score: ++</b>	<b>Total score: +</b>	<b>Total score: ++</b>	<b>Total score: +</b>	
	<i>Pol.:</i> diffuse <i>Cmp.:</i> simply	<i>Eff.:</i> 50-100% <i>Oth.:</i> no <i>En.:</i> no <i>Ce.:</i> no <i>W:</i> no	<i>IC:</i> no <i>OC:</i> low	<i>St:</i> existing <i>App.:</i> numerous	
End-of-pipe techniques					

Options for reducing emissions: Nonylphenols

Coal adsorption	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low Cmp.: medium	<b>Total score: +</b> Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score: --</b> IC: high OC: high	<b>Total score: +</b> St: BAT App.: ?	
Chemical Oxidation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low Cmp.: medium	<b>Total score: +</b> Eff.: 90% Oth.: many En.: significant Ce.: no W: no	<b>Total score: -</b> IC: medium OC: high	<b>Total score: +</b> St: BAT App.: ?	Can be operated with or without UV
Nanofiltration/ Reverse osmosis	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: -</b> Eff.: 20-50% Oth.: many En.: low Ce.: no W: brine	<b>Total score: --</b> IC: high OC: high	<b>Total score: +</b> St: BAT App.: no?	
Electrochemical oxidation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: 0</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: no	<b>Total score: 0</b> IC: medium OC: medium	<b>Total score: -</b> St: Emerging App.: no	Only tested on lab scale
Electro-coagulation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: +</b> Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score: 0</b> IC: medium OC: medium	<b>Total score: -</b> St: Emerging App.: no	Only tested on lab scale
Moving Bed adsorption	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: +</b> Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score: -</b> IC: medium-high? OC: medium-high?	<b>Total score: +</b> St: emerging App.: no	Only tested on pilot scale
Community level measures					
Use of end-of-pipe techniques for effluent municipal waste water treatment plants	<b>Total score: +</b> Pol.: diffuse Rge.: wide Lim.: low Cmp.: medium	<b>Total score</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score</b> IC: medium-high OC: high	<b>Total score</b> St: BAT App.: ?	
Reuse sewage sludge options	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	
Use of end-of-pipe techniques for P(E) containing landfill- leachate and groundwater	<b>Total score: +</b> Pol.: diffuse Rge.: wide Lim.: low Cmp.: medium	<b>Total score:</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score:</b> IC: medium-high OC: high	<b>Total score:</b> St: BAT App.: ?	
Stormwater runoff options	<b>Total score: ?</b>	<b>Total score: ?</b>	<b>Total score: ?</b>	<b>Total score: ?</b>	
Measures at regulatory level					
Ban the use of NP(E) containing sludge as soil improver	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	
Ban the import of NP(E) containing textiles	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	

Note: **Technical feasibility:** *Pol.* = Type of pollution; *Rge* = Range of concentration; *Lim.* = Limits and restrictions; *Cmp.* = Complexity of implementation; *Imp.* = Impact on the process, on the factory.

**Performances:** *Eff.* = Efficiency of emission reduction; *Oth.* = Removal of other pollutants; *En.* = Consumption of energy; *CE* = Cross effects; *W* = Production of waste.

**Costs:** *IC* = Investment costs; *OC* = Operational costs.

**State of the art:** *S.t* = Status of the technique (BAT, existing, emerging); *App.* = Number of applications.

Score: **green** = positive score, **yellow** = moderate score and **red** = negative score

Table 2 shows that substitution of NPEs is a feasible measure. For most of the applications of NPEs, alcohol ethoxylates are acceptable substitutes. For most industrial sectors, alcohol ethoxylates are already used as a substitute for NPEs. The most promising end-of pipe techniques for the removal of NPE from effluents are coal adsorption and chemical oxidation. Advisable measures at community level are the use of end-of-pipe techniques for NP(E) containing effluent of municipal waste water treatment plants and for NP(E) containing groundwater and landfill leachate. A useful measure at regulatory level is banning the import of NP(E) containing textile.

## 2. Introduction

The overall objective of this document is the inventory and assessment of technical options for reducing the water emissions of nonylphenol in Europe. Options include end-of-pipe techniques (e.g. waste water treatment) and process-integrated technical options (e.g. substitution or closed-circuit operation). The document aims to identify main uses and emission sources for nonylphenol and to assess in terms of costs, effectiveness, and feasibility the technical means to abate emissions in water. It has been developed to give stakeholders a background material and an overview of possible reduction options at the European scale in the perspective of future emission reduction strategies to be developed.

The document is a result of project SOCOPSE which is a European research project funded by 6<sup>th</sup> framework program of the EU. The goal of this project is to support the implementation process of the Water Framework Directive by providing guidelines and decision support system for the management of priority substances.

The scope of the document is the pollution in continental waters. It covers the most important sectors responsible for direct and indirect emissions, discharges and losses to aquatic environment in Europe. Therefore, the control of pollution to air and land is out of the scope, and polluted air and land will be considered only as potential sources of pollution to water.

The document was prepared as follows. The identification of main uses and emission sources for nonylphenol was achieved in a separate project task based on literature review and expert judgement. Here are summarized the main outcomes.

As concerns the assessment of technical options, a literature review was conducted on both existing and emerging options to abate emissions to water. At the same time a survey was carried out with the main contributors to emissions to evaluate the options applied or considered in practice. Both information sources were compared and compiled in a first draft document which then was sent to stakeholders and debated during a one-day technical workshop. A second draft document included the workshop remarks. The final document takes into account the results of case studies conducted at the latter stages of project SOCOPSE.

Survey questionnaire, list of contacted organisations and list of participants to workshop are attached in appendices.

The document plan is as follows. Section 3 gives general information on nonylphenol. Section 4 presents results on main uses and emissions of the substance. Section 5 reviews the management options to reduce emissions, with a synthesis in Section 6. Section 7 concludes the document, including acknowledgements in Section 8 and references in Section 9.

## 3. General information

### 3.1 Presentation of the substance

**Nonylphenol** is an organic compound of the wider family of alkylphenols and more specific, member of a group called “long-chain alkylphenols”, containing octyl- and nonylphenols and their ethoxylates, and p-dodecylphenol. Long-chain alkylphenols are characterized by having either a straight alkyl chain or a branched alkyl group connected to the phenol. Their names depend on where on the phenol the alkyl group(s) is situated, the length and branching of the alkyl chain. The name "nonylphenol" is used for a number of isomer substances having a phenol ring structure and alkyl chain of C<sub>9</sub>H<sub>19</sub>. The CAS no. 25154-52-3 previously covered all nonylphenols but later only nonylphenol with a straight alkylchain, and the branched ones have received a CAS no. of their own (84852-15-3; 4-nonylphenol, branched).

Nonylphenol (NP) is produced by the reaction of phenol with branched nonene. Commercial synthesis results in a mixture of various branched nonylphenol isomers rather than a discrete chemical structure. The nonyl group is positioned predominantly in the *para* position on the phenol ring. Linear, or normal, n-NP is difficult to produce and is therefore not likely to be commercially relevant. Branched 4-nonylphenol is the most descriptive and commercially available NP.

Nonylphenol is a starting material for the production of modified phenolic resins as well as a number of surfactants (emulsifiers) used in technical applications. The surfactant products produced from nonylphenol are called "nonylphenol ethoxylates" (also NPEs). They are produced by adding one or more ethoxy groups to the parent nonylphenol. In the past NPEs were used for decades in a wide variety of consumer products (e.g., personal care, laundry products and cleaners), commercial products (e.g., floor and surface cleaners), and in many industrial cleaning processes (e.g., textile scouring). NPEs are very relevant when discussing nonylphenol in the environment, as the NPE relatively quickly breaks down to nonylphenol when released to the environment.

CAS Nos: 84852-15-3 and 25154-52-3  
EINECS Nos: 284-325-5 and 246-672-0  
IUPAC Name: 4-Nonyl phenol (branched) and Nonylphenol  
Molecular formula:  $C_{15}H_{24}O$   
Structural formula:



Molecular weight: 220.34 g/mole  
Synonyms: Isononylphenol (CAS Number 11066-49-2)  
Phenol, nonyl-, branched (CAS Number 90481-04-2)  
NP  
para-Nonylphenol  
Monoalkyl (C3-9) phenol

## 3.2 Classification and labelling

Overall quality standards [2]

Ecosystem	Quality Standard	Quality Standard "rounded value"
AA-QS all surface waters addressed by the WFD	0.33 µg/l	<b>0.3 µg/l</b>
MAC-QS (ECO)	2.1 µg/l	<b>2 µg/l</b>

The classification and labelling of nonylphenol is listed in Annex I to Directive 67/548/EEC (28<sup>th</sup> Adaptation to Technical Progress; January 2001), as follows:

Classification: Xn; R22  
C; R34  
N;R50-53

Labelling: C; N  
R: 22-34-50/53  
S: (1/2-)26-36/37/39-45-60-61

Xn indicates 'harmful'

R22 states: Harmful if swallowed  
R34 states: Causes burns  
R50/53 states: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

S1/2 states: Keep locked up and out of the reach of children  
S26 states: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice  
S36/37/39 states: Wear suitable protective clothing, gloves and eye/face protection  
S45 states: In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)  
S60 states: This material and its container must be disposed of as hazardous waste  
S61 states: Avoid release to the environment. Refer to special instructions/safety data sheets

### 3.3 Regulations and controls for the substance

Nonylphenol is one of the 33 substances on the list of priority substances of the Water Framework Directive. The priority Substances are given different status regarding reduction or phase out. Nonylphenol is given the status A: which means that Nonylphenol is a priority hazardous substance. These substances will be subject to cessation or phasing out of discharges, emissions and losses within an appropriate timetable that shall not exceed 20 years.

Within the framework of the Existing Substances Regulation 93/793/EEC, the European Commission undertook a comprehensive risk assessment on nonylphenol. Nonylphenol was on this list due to the large quantity produced and used annually, its toxicity to aquatic organisms, and concerns that it is not readily biodegradable. Nonylphenol ethoxylates were also assessed as they are the main pathway of nonylphenol to the environment via their biodegradation in the aquatic environment. The risk assessment was performed for human health and the environment taking into account all life cycle stages and all environmental media on a local as well as on a regional scale. In the nonylphenol risk assessment the major point of concern was the high aquatic toxicity of nonylphenol and its possible risks associated with the aquatic and terrestrial ecosystems. While no human exposure risks were identified, the environmental exposure assessment showed clear risks from the acute and chronic toxicity of nonylphenol to aquatic organisms. The potential for any adverse effects on humans and the environment from oestrogenic activity effect was found to be irrelevant in the assessment of risk based on the extensive scientific material. The environmental risk assessment for nonylphenol and their ethoxylates indicated the need to reduce the risks associated with their production, their formulation into other products and the end use of these products in a wide range of industries. Based on that review, the European Commission published a Directive (2003/53/EC) to restrict the use of nonylphenol and nonylphenol ethoxylate and preparations containing them.

Under this Directive 2003/53/EC (annex I, issue 46) nonylphenol and nonylphenol ethoxylates may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1% by mass for the purpose of:

- Co-formulants in pesticides<sup>3</sup> and biocides and emulsifier in agricultural teat dips
- Domestic cleaning and of cosmetic products and other personal care products
- Industrial and institutional cleaning (except in some special cases)
- Textiles and leather processing (except processing with no release into waste water)
- Metal working (except uses in closed systems)
- Manufacturing of pulp and paper

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<sup>3</sup> Nowadays NP(E) can still be present in pesticides/biocides, as this is allowed until the admission of a pesticide/biocide has reached it's expiration date. The admission of pesticides/biocides is regulated separately in the different EU-countries

Prior to the EU directive, which is law in all EU member states, in Europe, a voluntary ban on the use of nonylphenol ethoxylates in domestic detergents has been agreed by all the major manufacturers of detergents. PARCOM Recommendation 92/8 required signatory countries to achieve the phase out of nonylphenol ethoxylates in domestic detergents by 1995 and in all detergent applications by 2000.

National initiatives have been taken in some OSPAR States on the use of NPEs in water-based paints, agricultural pesticides, and emulsion polymers. EC action on NPEs is being considered under the EC directive relating to the restriction on the marketing and use of certain dangerous substances and preparations, but no draft directive has yet been presented. NP is included on the draft list of priority hazardous substances under the EC Water Framework Directive.

Prior to the EU Directive 2003/53/EC the phase out of nonylphenol ethoxylates as cleaning agents for industrial uses varied between different countries. In Switzerland their use has been banned in detergent powders. In the Netherlands their use was reported as terminated. In Belgium use had strongly decreased, and a screening study of the use and discharge in all sectors in Belgium is due to begin. In Sweden use of nonylphenol ethoxylates in cleaning agents was reduced by 70-80% during the period 1990-1995. This reduction was a result of both administrative actions and voluntary actions from industry.

Prior to the EU Directive 2003/53/EC in Germany, manufacturers and processors of nonylphenol ethoxylates entered into a voluntary agreement in January 1986 to phase-out the use of alkylphenol ethoxylates (nonylphenol and octylphenol ethoxylates) in domestic laundry detergents and cleansers as well as for detergents used in commercial laundry by the end of 1986, and in aerosol-filled cleansers and disinfectant cleansers from November 1987. They also agreed to look into possible substitution of nonylphenol ethoxylates in industrial uses (wetting agents and detergents in the textile industry by January 1989; use in leather and fur, paper, textiles and industrial cleaners by January 1992) (BUA, 1988). Based on these voluntary commitments, the use of alkylphenol ethoxylates in detergents and cleaning agents was reduced by about 85% from 1986 to 1997.

In Finland PARCOM Recommendation 92/8 had not yet been implemented in 1997. However the amount of nonylphenol ethoxylates used in household cleaning agents had decreased sharply during the last few years with a phase out in 2004.

In Denmark limit values for nonylphenol in sludge to be applied to farmland have been set. From 1 July 1997 the limit value for nonylphenol and nonylphenol ethoxylates (with 1 or 2 ethoxylate groups) in soil is 50 mg/kg dw. This limit value is due to be reduced on the 30 June 2000 to 10 mg/kg dw. Based upon a limited data set of effects data on terrestrial species Denmark have set a soil quality criterion for nonylphenol of 0.01 mg/kg.

In Sweden the recommended limit value for nonylphenol in sludge for agricultural use was 100 mg/kg dw; this was reduced to 50 mg/kg dw in 1997.

In 2002 the UK Chemicals Stakeholder Forum recommended a voluntary agreement on NPEs and OPEs between industry and UK Government in order to take early action to reduce risk prior to the enforcement of the marketing & use directive of the EU. In 2003 companies represented by GOSIP (the CIA Sector Group for Organic Surfactants and Intermediate Products), CEPAD (the European industry body representing in this instance, the producers and suppliers of Nonylphenol ethoxylates), BCDTA (the UK trade association representing

the importers and distributors of chemicals) and BACS (British Association for Chemical Specialties) signed an agreement taking action to support risk reduction and reaching an agreement to inform and advise their customers of the intended marketing and use restrictions and the UK Government's decision to seek voluntary action on accelerated risk reduction.

Also in 1976 UK industry agreed a voluntary action to phase out the use of nonylphenol ethoxylates in domestic cleaning products. This agreement covered all key manufacturers and companies that belonged to a recognised trade association. In 1996/97, the British Association for Cleaning Specialities (BACS) and the Soap and Detergent Industry Association (SDIA) reached a voluntary agreement to remove all alkylphenol ethoxylates from industrial and institutional detergent in 1998. This agreement does not cover solvent degreasers.

Under Directive 91/414 the use of NPE as an ingredient of plant protection products was banned by 2004 by regulation 2076/2002.

The Baltic Sea Marine Protection Commission or Helsinki Commission (HELCOM) has made three recommendations of nonylphenols and nonylphenol ethoxylates [18]

- HELCOM Recommendation 23/12 on Textiles; adopted 06.03.2002
- HELCOM Recommendation 23/7 on Metal plating; adopted 06.03.2002
- HELCOM Recommendation 19/5 on HELCOM Strategy for Hazardous Substances; adopted 26.03.1998

In these recommendations HELCOM recommends to the Governments of the Contracting Parties that they apply the precautionary principle, the principle of the Best Available Techniques and the substitution principle, by which is meant substitution of the use of hazardous substances by less hazardous substances or preferably non-hazardous substances where such alternatives are available.

Additionally, nonylphenols and nonylphenol ethoxylates have been identified as "Substance group of specific concern to the Baltic Sea" under HELCOM Baltic Sea Action Plan adopted on 15 November 2007 in Krakow, Poland [18].

## 4. Production, uses and emissions

### 4.1 Production and uses

#### a) Production

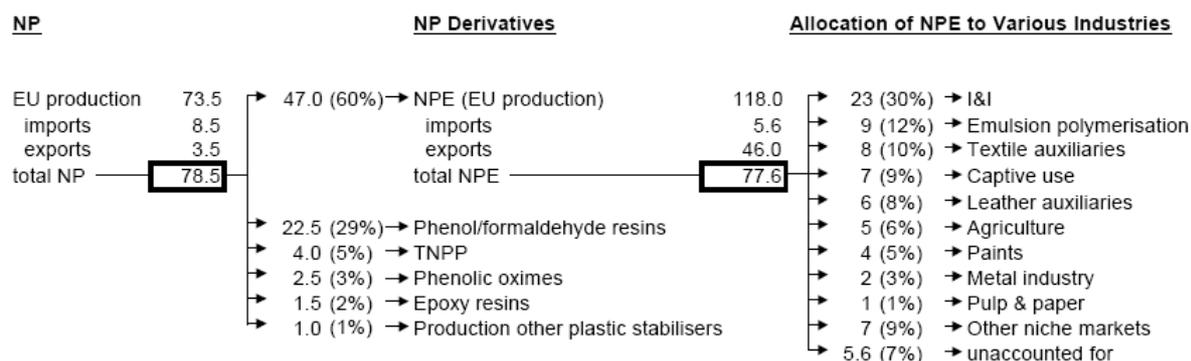
NP and its ethoxylates are mass products of the chemical industry. The basic materials for the production of nonylphenol are tripropylene and phenol. There are three main processes used to manufacture nonylphenol. The process varies between producers. EU production of NP was 73,500 tpa in 1997, produced by four companies. Additionally, 8,500 ton's were imported and 3,500 tpa exported<sup>4</sup>. In 2006 only three producers left [15].

Producers of NP in Europe:

Producer	Country
Sasol Germany GmbH (previously Hüls AG, Condea GmbH)	Germany
Polimeri Europe (previously Enichem S.P.A.)	Italy
Synteza, Kędzierzyn-Koźle,	Poland

#### b) Uses

The main part of NP production in 1997 was used in production of nonylphenol ethoxylates (NPEs) that are applied in a variety of industries. Uses of NP and NPEs are shown in the figure below [6].<sup>5</sup>



NPEs are used as emulsifiers, dispersive agents, surfactants and/or wetting agents and are the primary source of inputs to the sea of NP and NPE's. The main users were the industrial,

<sup>4</sup> As mentioned before these production figure are from 1997. Due to strict regulations the production of NP(E) has changed dramatically since 2005. However no recent production figure are available.

<sup>5</sup> As mentioned before, the use of NP and NPE has changed dramatically due to regulations. Since 2005 NPEs are only used in non waste water relevant applications.

institutional and domestic cleaning sectors (30 % of EU use). Other significant sectors were emulsion polymerisation (12 %), textiles (10 %), chemical synthesis (9 %) and leather (8 %).

Previously, NPEs were used in larger quantities and in a larger variety of chemical products (e.g. tensides in cleaning agents, viscosity decreasing agent in PVC-floor production, surfactants, lubricants, cutting and drilling fluids), but the use decreases more than 90% during the 1990s [17]. This decrease was caused by the enforcement of the EU Directive 2003/53/EC. Import of products containing NPEs may still be possible from countries outside EU.

## 4.2 Emissions

NP is almost only used as an intermediate in the production of various NP derivatives, mostly ethoxylates. Releases of NP from these production processes are estimated to be very low. As a result, very little NP enters the environment directly. Rather, the primary source of NP in the environment is considered to be NPEs, which can break down into NP after being released into the environment during their production, their formulation into various other products, and the use of such products. Releases occur to surface water (rivers, lakes, seas and their sediments) via industrial and municipal waste water and waste water treatment plants, soil, via sewage sludge containing NP/NPEs spread on land, and air.

In table 3 the main emission sources of NP and NPE to air, water and land are given [4]<sup>6</sup>.

**Table 3 NP(E) emissions to the environment (1997) [4]**

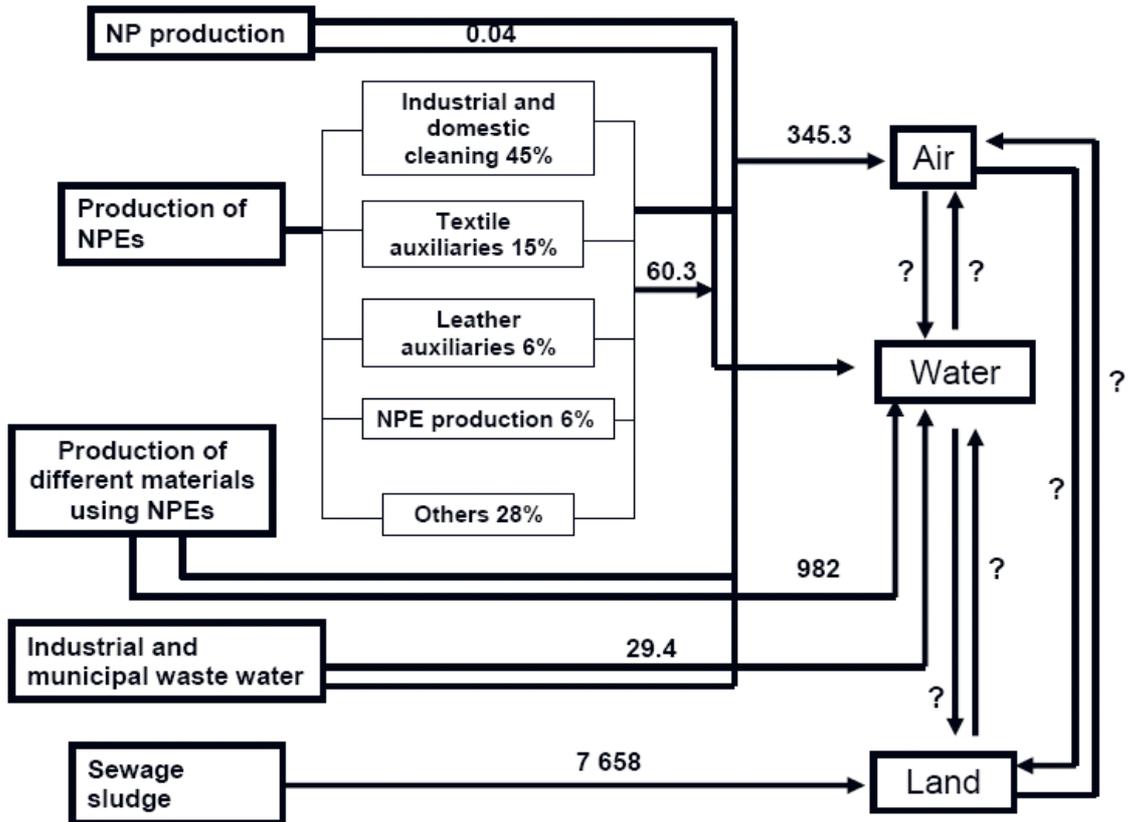
To	Type	Description	Amount NP (kg/day)	Amount NPEO (kg/day)
Atmosphere	source	Emissions general (not specified)	946	
	source	Treatment in wastewater treatment plants		2273
	diffuse	Atmospheric deposition rate of nonylphenol in 1996 was 95 µg/m <sup>2</sup> /y	840	
Aquatic environment	Source	Release to surface water Production of NP	0,1	
		Release to surface water Production of NPEs - industrial, institutional and domestic cleaning - other niche market - textile auxiliaries - leather auxiliaries - NPE production - Emulsion polymerisation: pulp and paper; metal industry; agriculture; paints	165 74 (45%) 40 (24%) 25 (15%) 10 (6%) 10 (6%) 8 (5%)	
		Release to surface water Production of different materials using NPEs - industrial, institutional and domestic	2690 807 (30%)	

<sup>6</sup> As mentioned before, these emission dates are referring to 1997. Because of strict regulations (Directive 2003/53) the production, use and emissions of NP(E) have decreased dramatically since 2005. New emission figures are however not available yet.

## Options for reducing emissions: Nonylphenols

		cleaning	430 (16%)	
		- other niche market	323 (12%)	
		- emulsion polymerisation	269 (10%)	
		- textile auxiliaries	242 (9%)	
		- captive use	215 (8%)	
		- leather auxiliaries	161 (6%)	
		- agriculture	135 (5%)	
		- paints	81 (3%)	
		- Metal industry	27 (1%)	
		- Pulp and paper		
		Waste water from production of NPE	78,3	
		Wastewater from production of resins, plastics and stabilisers	2,15	
		Wastewater from different uses of products containing NPEs		107600
		- Industrial and institutional cleaning		50600 (47%)
		- Other applications		27000 (25%)
		- Textile processing		17000 (16%)
		- Leather processing		6500 (6%)
		- Pulp, paper and board industry (2%)		2000 (2%)
		- Other (4%)		4000 (4%)
Terrestrial environment	diffuse	Sewage sludge containing NP or NPE's spread on agriculture land	20980	
Total release	Surface water	Total release of NP in continental EU	2935	
Total release	Waste water	Total release of NPE in continental EU		107600

Based on the sources and emissions above, a mass flow analysis diagram for NP in Europe in 2000 is presented (numbers in tonnes/year).



*Diffuse emissions:*

NPE occur in a variety of household products, such as water-based paints, which are likely to end up in municipal STPs. Due to degradation of NPEs to nonylphenols, STPs have traditionally been considered as major emission sources of these chemicals. Recent environmental monitoring suggests that also diffuse emissions are important [17]. NPEs may e.g. vaporize to air during application of water-based paints on house facades, which may result in higher atmospheric emissions of NPEs in residential areas. Process water from textile and paper&pulp industries are likely to be discarded to the STP, even though many industries have their own wastewater treatment. NPEs may be emitted to soil and to the wastewater system through spills and leaks of oils, mainly during industrial use.

Another diffuse source is NPE containing textiles. Although the use of NPE in textile processing is banned in Europe, NPE is still in use outside the EU. By import of textile, NPE of textiles can still end up in municipal STPs.

## 5. Management options: detailed information

### 5.1 Source control options

For each option :

- General description
- technical feasibility
- performances
- costs
- state of the art

#### a) Process-oriented options

No process-oriented options were found in literature or were mentioned by contacted industries.

#### b) Alternatives/Substitutions

##### (1) Substitutes for NPs as intermediate

For replacement of NPs (used as an intermediate in the formation of other products than NPEs) few alternatives were identified [7], including phenol/formaldehyde resins (PFR), tri (4-nonylphenol) phosphite, phenolic oximes, epoxy resins and other plastic stabilizers. Many of these products generally owe their properties to the use of NP based resins in their formulation and such characteristics may be more difficult to duplicate using alternatives than appears to be the case with NPEs.

The only alternatives which have been suggested are other alkylphenol compounds, particularly octylphenols. It is unlikely that these products would be a suitable substitute because they are so structurally similar to NPs that toxic effects may be expected to be of a similar magnitude. If the level of risk is similar, prohibiting the use of NPs would result in ineffective expenditure on the part of industry and the need for further risk reduction measures in the future.

Conclusion:

At present, known substitutes for NPs in the manufacture of derivatives other than NPEs are octylphenols, the use of which is not expected to yield a measurable reduction in risk over the use of NPs, because of their comparable environmental effects.

This means at the same time that research efforts are needed in this area.

##### (2) Substitutes for NPEs in several industries (alcohol ethoxylates)

For several industries it is known that alternatives to NPEs are available. These are industrial, institutional and domestic cleaning (I&I), textiles, leathers, agriculture (veterinary medicines), metals, pulp and paper, and cosmetics.

According to industry the possible substitutes in the use area ‘detergents and cleaning agents’(by far the most important industry sector due to emissions of NPEs) are mostly alcohol ethoxylates [3]. It is stated that most of the users of NPEs have indicated that they would switch to alcohol ethoxylates (or have already done so) should a ban be placed on the use of NPEs [7] . In terms of environmental risk, alcohol ethoxylates appear to present a clear advantage over NPEs, mainly owing to issues of biodegradability. According to industry the substitutes in the use area ‘detergents and cleaning agents for domestic and industrial uses’ are mixtures of anionic and nonionic surfactants, such as alcohol ethoxylates, fatty acids and derivatives, fatty amines or unsaturated hydrocarbons.

Specifically, alcohol ethoxylates biodegrade more readily than NPEs in the environment. Furthermore, alcohol ethoxylates tend to degrade fully to carbon dioxide and water in a relatively short time, while NPEs degrade to form NP, the toxicity and slow biodegradability of which have been identified in the risk assessment. In terms of human health risks, no data have been found which favor either alcohol ethoxylates or NPEs as a group.

Nevertheless, when substituting NPE with an alcohol ethoxylate, it is important to look at the toxicity of the specific chemicals under consideration, as toxicity may vary substantially depending on the alkyl chain lengths, chain branching and the degree of ethoxylation.

With respect to the levels of NPEs in these formulations (I&I products), these can vary typically between 1% and 10% depending on end use.

Alcohol ethoxylates are also used as a substitute for NPEs in other industry sectors. In the table below details provided of the substances which have been indicated as actual or potential substitutes for each of the industry sectors considered [7].

Table 2.3 provides details of the substances which have been indicated as actual or potential substitutes for each of the industry sectors considered.

<b>Table 2.3: Substitutes for NPs and NPEs by Industry Sector</b>			
<b>Life Cycle Stage</b>	<b>Industry Sector</b>	<b>Substitute</b>	
NP Production	NP production	N/A	
Production of NP Derivatives	NPE	-	
	Phenol/formaldehyde resins	Other APs	
	TNPP	-	
	Phenolic oximes	-	
	Epoxy resins	-	
	Other plastic stabilisers	-	
Formulation of NPE-based Products	Formulation (excluding paints)	N/A	
	Paints	Alcohol Ethoxylates	
Use of NPE-based Products	I&I	Alcohol Ethoxylates <sup>a</sup>	
	Emulsion polymerisation	OPEs	
	Textile auxiliaries	Alcohol Ethoxylates <sup>a</sup>	
	Captive use		
	Leather auxiliaries	Alcohol Ethoxylates <sup>b</sup>	
	Agriculture (pesticides)	Alcohol Ethoxylates	
	Agriculture (veterinary care)	Alcohol Ethoxylates	
	Paints	N/A	
	Metal industry (extraction)	Unknown but possible	
	Pulp and paper	Alcohol Ethoxylates	
	<b>Other niche markets</b>		
	Civil and Mechanical Eng.	Alcohol Ethoxylates (and alkyl benzene sulfonates and salts of vinsol resin)	
	Electronics/Electrical Eng.	Alcohol Ethoxylates <sup>a</sup>	
	Mineral Oil and Fuel Industry	-	
	Photography (small scale)	-	
	Photography (large scale)	-	
Other	Alcohol Ethoxylates <sup>c</sup>		
<p><i>Note: N/A - Not applicable</i>  <i>- No indications of substitute</i>  <sup>a</sup> <i>Substitution may be not possible across all uses within industry category</i>  <sup>b</sup> <i>Including blends</i>  <sup>c</sup> <i>Applies to cosmetic, personal hygiene and beauty-care products but not to spermicides, public domain or other unknown sources</i></p>			

In sectors such as I&I, textiles, leathers, metals, pulp and paper, and cosmetics, numerous alternatives are generally available and already in use. The increasing use of alternatives in these sectors has been supported by several legislations. Alcohol ethoxylates are referenced as BAT substitutes for the Tanning of Hides and Skins in the BREF document etc.....

Although alcohol ethoxylates in general have been identified as suitable alternatives to NPEs, they are not currently applicable to all uses. For some specific uses, no suitable alternatives have been identified.

Alternatives are not available for all industrial sectors. For example, one formulator of waterborne paints and resins for auto finishing indicates that five to seven years will be needed to develop suitable alternatives for use in solvent-free formulations [7]. In most cases, however, NPEs can be replaced with alternative substances, many of which have been known for some time but not chosen due to their higher costs and lower formulation versatility. Now, improved formulation techniques are allowing companies to utilise these alternatives which are almost exclusively alcohol ethoxylates, generally either:

- C<sub>9-11</sub> linear alcohol ethoxylates;
- C<sub>13-15</sub> linear alcohol ethoxylates; or
- C<sub>13-15</sub> isotridecanol ethoxylates (branched).

Alcohol ethoxylates have the general chemical formula R-(OCH<sub>2</sub> CH<sub>2</sub> ) -OH.

A Danish study has explored the possibilities of substituting nonylphenol ethoxylates in paints [8]. The study identified a number of possible substitutes for nonylphenol ethoxylates in paints such as styrene/maleic anhydride polymer, secondary ethoxylated alcohol (C<sub>12</sub>-C<sub>14</sub>) and ethoxylated acetylenic alcohol. All of the alkylphenol ethoxylates (APEOs) investigated could in principle be substituted by alternative substances, but in some cases it would be a time-consuming process [8]. Thus, it is technically possible to replace nonylphenol ethoxylates in paints etc. It is, however, not clear whether these possibilities are presently so well developed for all uses that they can be termed "best available techniques".

Owing to concerns over the confidentiality of data in this highly competitive sector, companies completing our survey were unwilling to provide data on the change in costs arising from the move to substitutes. Data provided by CEFIC/CESIO must, therefore, be relied upon for these purposes. These data indicate that of an estimated total Euro 1,600m (£1,080m) required to substitute APEs (of which at least 90% comprises NPEs) some Euro 156m (£106m) would be required to eliminate use in I&I. Thus, the costs of reducing the use of NPEs in this sector would constitute some 9 to 10% of the total costs of substitution across all uses, while the use of NPEs by this sector contributes over 44% of the total continental burden associated with NPs. This suggests that restricting use by this sector would be more cost-effective than restricting use in some of the other sectors [7].

It must also be remembered that a number of sectors are already moving towards the use of alternatives as a result of individual company initiatives, various voluntary agreements, environmental concerns expressed by customers and the general public, and/or legislation specific to certain Member States<sup>29</sup>. Thus, the costs reported above may not be entirely attributable to the introduction of EU-mandated marketing and use restrictions

## 5.2 End-of-pipe options for the substance

In this section attention will be paid to waste water treatment techniques which can be used to reduce the emission of nonylphenol and nonylphenol ethoxylates to surface water. Besides using end of pipe techniques for decrease the amount of NP(E) in waste water or effluent water from existing WWTP's, one other end of pipe option will be discussed, namely Separation zones NPEs pesticides.

Releases of NP(E) occur via industrial wastewater from different industry activities, when using NP or NPE in the formulation of other chemical products and articles and via municipal wastewater [16]. The wastewater treatment techniques, as describes below, can be used as polishing techniques for the effluent of industrial (or municipal) wastewater treatment plants. So the quality of the incoming water is comparable with effluents of WWTPs.

In [1] information is given about the removal of NPE in mechanical-biological waste water treatment plants. It was found that the average removal percentage of five plants was about 92%, mainly by adsorption onto sludge. Nonylphenol (NP) was found in concentrations of 0.2 up to 18 µg/L in WWTP influents and up to 5 µg/L in the treated water. In [19] it is stated that nonylphenol ethoxylates reach sewage treatment works in substantial quantities. About 60–65% of NPE compounds that enter sewage treatment works are released to the environment, mainly in association with the sludge (up to 90%). The principal pathway for nonylphenol removal in wastewater treatment plants is sorption to the sludge solids.

In [3] detailed information is given about NP concentration in surface water, seawater, sediment, industrial waste water treatment plants and municipal waste water treatment plants.

**Table 4 Concentrations in the Environment (1995-2000) [3]**

Type of water	Location	Year	NP-concentration (µg/l)
Surface water	River Glatt Switzerland	2000	0,1-0,3
Surface water	Finnish Lake	2000	0,1-0,8
Surface water	River Main Germany	1989- 1991	0,038-0,12
Surface water	Canal in the Netherlands	2000	0,14
Seawater	Tees Estuary UK	2000	0,09-5,2
Sediment	22 estuaries in Western Europe	1997	12-400 µg/kg dw
Sediment	Several locations	1990- 1995	0,5-10 µg/kg dw
MWWTP	Zurich	< 2001	Influent: 14 Effluent: 8 Sludge: 128 mg/kg dw
MWWTP	Netherlands	< 2001	Influent 2,1-170 and effluent 6,1 Influent 23 and effluent 1,0
MWWTP	Germany	< 2001	Influent: 40 Effluent: < 0,1

Industrial WWTP	Finland	< 2001	Influent 100-200 and effluent 4-34 Influent 30.000-70.000 and effluent 4.600-12.900
Industrial WWTP	Netherlands	< 2001	Influent 2.270 and effluent 0,9-15 Influent 400 and effluent 1,2
Sewage sludge	Germany	1989 1998	264 mg/kg 10 mg/kg
Sewage sludge	Switzerland	1984 1997	1010 mg/kg 90 mg/kg

From the table above it can be seen that the NP(E) removal in municipal waste water treatment plants varies from 40 – 99,7% (average 80%). The average removal efficiency in industrial waste water treatment plants is somewhat higher, 95%.

On basis of the information which is given above, it is assumed that the concentration of NP(E) of the waste water is in a range of 1-10 µg/l (EQS = 0,3 µg/l).

### a) Separation zones NPEs pesticides<sup>7</sup>

To reduce the risks associated with NPEs use in pesticides, the provision of a separation zone ('buffer zone') between spray application and water course would suffice in reducing the risk to acceptable levels [7]. Such separation zones are already applied to certain pesticides and pesticide active ingredients in the UK and this could be extended to cover those pesticides containing NPE or any applications using a NPE based adjuvant purchased 'off the shelf'. It is recommended that a mandatory separation zone be introduced for the use of both pesticides and adjuvants containing NPEs. This should be supplemented with encouragement to formulators to move away from NPEs as part of re-licensing under Directive 91/414/EEC and with a requirement for review after a set period to assess continued use of these substances and also the success of the proposed risk reduction measures.

More information is available in the report *Fact sheets for end-of-pipe options*.

### b) End of pipe techniques

The following end-of-pipe technique are being discussed:

- Coal Adsorption (GAC)
- Chemical oxidation/Advanced Oxidation Processes (AOP)
- Nanofiltration/Reverse Osmosis
- Moving Bed Adsorption
- Electrochemical oxidation
- Electro-coagulation

<sup>7</sup> Although the use of NPE in pesticides is restricted by Directive 2003/53/EU, NPE can still be present in pesticides/biocides, as this is allowed until the admission of a pesticide/biocide has reached its expiration date.

The treatment techniques will be described using the following structure:

- General description
- technical feasibility (type of pollution, concentration range, conditions (matrix, pH, other pollutants), removal efficiency, removal of other substances)
- performances (environmental effectiveness, reduction of concentration/load, energy consumption, wastes)
- costs (investment costs and operational costs)
- state of the art (BAT or emerging technology)

### **(1) Coal Adsorption**

#### *- Description<sup>8</sup>*

Activated carbon is a commonly used and reliable technique for the removal of non-polar organic contaminants to very low concentrations. In activated carbon filtration the effluent is led over a fixed bed of granular activated carbon. Essentially all non-polar organic can be removed from waste waters. The running time of the filter bed varies per substance and waste water matrix. Humic-type of dissolved organic macro-molecules are also removed; in practice it appears however that humic substances do not strongly interfere with the removal of the contaminants: the removal of contaminants continues when humic substances have already reached breakthrough point. Often a number of filters are typically used in series, so that the first filter can be regenerated once it becomes saturated.

The most commonly used is granulated carbon (GAC) , which can be regenerated by the manufacturer.

To maintain a clearly discernible adsorption front in the carbon column, backwashing is generally not desirable. Pre-treatment for the removal of suspended solids is therefore necessary to prevent clogging of the column.

A possible alternative is the use of powdered activated carbon (PAC) in combination with a filtration technique (e.g. flocking filtration or denitrification filter). Removal of organic contaminants can take place without investing in an extra filter step. One practical limitation is however that powdered activated carbon dosage should not lead to overloading of the existing filter. This application is only interesting if treatment objectives can be achieved with a low dosage (maximum dosage concentration 20 mg/l), since powdered activated carbon is more expensive than granular activated carbon per ton and it cannot be regenerated. The carbon is removed with the rest of the filter surplus sludge and treated in the sludge line of the WWTP.

#### *Technical feasibility/performances*

GAC is best used for removal of organic contaminants like nonylphenol from drinking water. Previous laboratory-scale testing for removal of nonylphenol with GAC has yielded  $K$  values of 19,406, at a water pH of 7.0. Typically, when  $K$  values were greater than 200 the activated carbon process is considered technically and economically feasible. Removal efficiencies of 90-99% are mentioned for NP(E) [9].

Selection of the type of carbon is based on the specific contaminants in the water and the manufacturer's recommendations. Site-specific conditions may affect the percentage removal

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<sup>8</sup> More information is available in the report *Fact sheets for end-of-pipe options*.

using these techniques, including the presence of “competing” contaminants. Source water-specific testing will be needed to ensure adequate removal. For GAC, surface waters may require pre-filtration. PAC is most applicable to those systems that already have a process train including mixing basins, precipitation or sedimentation, and filtration.

- *Costs (investment costs and operational costs)*

Investment costs are relative low. Operational costs are very strong depending of the type of coal that is used and the dosing rate of the coal (including regeneration or disposal of the loaded coal); range 0,1-1,0 € /m<sup>3</sup>. Typical coal cost are 1-5 € /kg.

- *State of the art (BAT or emerging technology)*

GAC is the BAT for removal of nonylphenol (and other EDC) from drinking water. For waste water treatment GAC is an emerging technology.

## (2) Chemical oxidation/Advanced Oxidation Processes (AOP)

- *Description<sup>9</sup>*

Oxidative techniques are used to “crack” organic compounds with the aid of strong oxidants such as ozone or hydrogen peroxide. They are applied for the oxidation of organic contaminants. Some oxidants can also be applied for disinfection. The treatment principle involves a non-specific or specific reaction of the oxidant with the organic compounds, which are oxidized and degraded to smaller molecules. The extent to which the process proceeds depends directly on the nature of the organic compounds, the nature and the concentration of dosed oxidant and the contact time.

A specific kind of oxidation processes are the Advanced Oxidation Processes (AOP) combining oxidation techniques. Free radicals can for instance be formed which make the oxidation processes to proceed by a factor of 10 to several thousand times faster. Applicable combinations are ozone/hydrogen peroxide, ozone/UV and hydrogen peroxide/UV.

An advantage of chemical oxidation is that it is also effective for contaminants at extremely low concentrations (µg/l). Especially with advanced oxidation (e.g. UV/H<sub>2</sub>O<sub>2</sub>), it has been shown that high removal efficiencies are possible, even in the case of WWTP-effluent. High H<sub>2</sub>O<sub>2</sub> dosages and high UV-intensities are however required. Another disadvantage is the formation of new (often) toxic compounds.

- *Technical feasibility/performances*

Oxidative techniques (specifically advanced oxidation) are potentially applicable for the removal of Endocrine-disrupting chemicals (EDCS) like Nonylphenol (NP) in surface waters. Results indicate that advanced oxidation processes can result in effective (>95%) removal of NP from water [10]. These techniques can be used for water treatment or to “polish” the final effluent at municipal waste-water treatment facilities.

A particular point of importance is the required UV-dosage in relation to the transmission (turbidity) of the waste water, which is negatively influenced by dissolved and suspended organic material. Removal of these components in an effective pre-treatment step is important.

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<sup>9</sup> More information is available in the report *Fact sheets for end-of-pipe options*.

More information is available concerning the removal of micro-contaminants from effluent using conventional oxidation than for advanced oxidation.

One advantage of oxidation in comparison to other treatment techniques is that no waste streams are produced.

- *Costs (investment costs and operational costs)*

The capital and energy costs of oxidation with UV are relatively high. Possibly, these costs are lower for oxidative techniques without UV-light, such as ozone/H<sub>2</sub>O<sub>2</sub>, which makes them more promising for full-scale application to WWTP-effluent. However, the efficiency and formation of by-products of these processes need special care and prior research. .

- *State of the art (BAT or emerging technology)*

Oxidation is the BAT for removal of nonylphenol (and other EDC) from drinking water. However, oxidation is an emerging technology for treating waste water.

### **(3) Nanofiltration and Reverse osmosis**

- *Description*<sup>10</sup>

A membrane process is based on the permeation of a liquid through a membrane<sup>11</sup>. It segregates the liquid into a permeate that passes the membrane, and concentrate that is retained. The driving force of this process is the pressure difference across the membrane.

NF and RO membranes can separate colloidal particles and even molecules (organic and ions) from water. These membranes are mainly used when complete recycling of permeate and/or concentrate is desired.

NF-membranes are selective for the ionic charge of the dissolved components, monovalent ions will pass the membrane and divalent and multivalent ions will be largely rejected. RO-membranes will reject all ions.

The typical characteristics of NF and RO membranes are illustrated in the table below.

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<sup>10</sup> More information is available on NPE and nanofiltration in the report *Fact sheets for end-of-pipe options*.

<sup>11</sup> More information is available on NPE and filtration in the report *Fact sheets for end-of-pipe options*.

Parameter	Nanofiltration	Reverse osmosis
Pore diameter [ $\mu\text{m}$ ] <sup>1</sup>	0.01–0.001	<0.001
Operating pressure [MPa]	0.5–3 <sup>2</sup>	2–100 <sup>3</sup>
Cut-off size [nm] <sup>2</sup>	>1 200–1000 g/mol	<1000 g/mol
Permeate flow [ $\text{l m}^{-2} \text{h}^{-1}$ ]	<100	10–35
Cross flow speed [m/s] <sup>2</sup>	1–2	<2
Membrane type	polymeric asymmetric or composite	polymeric asymmetric or composite
Membrane configuration	spiral-wound tubular	spiral-wound tubular
<sup>1</sup> [cww/tm/27]		
<sup>2</sup> [cww/tm/132]		
<sup>3</sup> [cww/tm/159]		

**Note:** low pressure RO processes are preferred for treating slightly contaminated water. The operating pressure for these types of water starts already at 0.7 MPa in recent years, due to improvements in performance of applied membranes (the table mentions 2 MPa as lower limit, which is still valid for older membrane systems).

NF can be seen as a coarse RO (reversed osmosis) membrane. Because nanofiltration uses less fine membranes, the feed pressure of the NF system is generally lower compared to RO systems. The fouling rate may be higher than in RO systems, especially when NF is operated at high permeate flows.

Tubular and straw type membranes are less sensitive to pollution and plugging than spiral wound modules. The first mentioned types are the most used membrane types in wastewater systems, because of costs and effectiveness.

Membrane processes are available in several materials and configurations. The optimal choice for a particular application will depend on the nature of the waste water. Different materials have variable resistances to dissolved substances, e.g. solvents. The polyamide-based membranes are normally superior to cellulose acetate-based membranes for the removal of trace organic molecules, but are more expensive.

NF and RO processes are usually operated cross-flow (i.e. the feed flows along the membrane surface and the permeate flow is directed perpendicular to the membrane. The impurities remain in the feed which, reduced in volume, leaves the membrane system as a concentrated waste stream.

Even under the best pretreatment regimes and programmes, membranes will quickly foul and deteriorate in performance if cleaning is not ensured. Therefore, membrane systems should be designed in such a way that modules can be periodically taken offline and cleaned mechanically and/or chemically. Other modules may continue the filtration.

An industrial membrane plant usually consists of three separate sections:

- the pretreatment section where the feed is treated by (1) chemical clarification (precipitation, coagulation/flocculation or flotation) and subsequent filtration, or by (2) filtration and subsequent UF
- the membrane section, where an elevated pressure is applied, and the waste water is cleaned by filtration, usually in a cross-flow modus

- the post-treatment section where (1) the permeate is prepared for re-use or discharge, and (2) the concentrate (brine) is collected for reuse or for further treatment and/or disposal.

In NF/RO, salts and dissolved organic molecules are retained by 20 to over 99 %. The production of a concentrated brine solution requires special attention in this form of filtration. In NF the brine stream produced constitutes 10 – 20 % of the main stream. The removed substances in the brine are concentrated to a factor of 5 or 10 higher than in the feed effluent.

- *Technical feasibility/ performances*

The molecular weight cut-off (MWCO, the molar mass above more than 90% of the compounds are rejected) of present nanofiltration membranes is situated in the range of 200-500 g/mol, which corresponds to the molar mass of several organic micropollutants in surface and waste water). The polarity is also an important parameter to describe rejection; the polarity is related to the octanol/water partition coefficient.. Negatively charged solutes will be better rejected because of the negative charge of the membrane surface of common nanofiltration membranes at neutral pH-conditions.

In the table below some information is given about the performance of RO and NF for different organic and inorganic components.

**Achievable Emission Levels / Performance Rates**

Parameter	Performance rate [%]		Remarks
	NF	RO	
Inorganic mercury	>90 <sup>1</sup>		
Organic mercury	>90 <sup>1</sup>		
Cadmium compounds	>90 <sup>1</sup>		
Tetrachloromethane	96 <sup>1</sup>		
1,2-dichloroethane	71 <sup>1</sup>		
Trichlorobenzene	96 <sup>1</sup>		
Perchloroethene	90–92 <sup>1</sup>		
Atrazine	>70 <sup>1</sup>	84–97 <sup>1</sup>	
γ-Hexachlorocyclohexane		99 <sup>1</sup>	
DDT		100 <sup>1</sup>	
Aldrin		100 <sup>1</sup>	
Dieldrin		100 <sup>1</sup>	
Dichlorvos		98 <sup>1</sup>	
Simazine		95 <sup>1</sup>	
Trifluralin		99 <sup>1</sup>	
Fenitrothion		99 <sup>1</sup>	
Azinphos-methyl		98 <sup>1</sup>	
Malathion		99 <sup>1</sup>	
TOC	80-90 <sup>2</sup>		
<sup>1</sup> [cww/tm/27]			
<sup>2</sup> [cww/tm/160]			

In [14] several nanofiltration membranes were tested in the laboratory. The observed retention for nonylphenol (NP) ranged between 70% and 100%.

The performance of RO processes is generally above 98%.

Consumables are:

Consumable	Amount	
	NF	RO
Membrane material		
Chemicals for cleaning		
Energy [kWh/m <sup>3</sup> ]	1-3 <sup>a 1</sup>	1-3 <sup>a 1</sup>
<sup>a</sup> low-pressure application, <2.5 MPa		
<sup>1</sup> [cww/tm/161]		

The energy consumption is directly related to the flow rate and pressure requirements. It is mainly associated with maintaining a minimum velocity of about 2 m/s across the membrane surface.

- *Costs (investment costs and operational costs)*

	Capital costs	Operational costs	Replacement costs
<b>RO/NF</b>	500-1500 euro/m <sup>2</sup> membrane *)	0,5 – 1,5 euro/m <sup>3</sup>	80-200 euro per m <sup>2</sup> membrane

\*) for spiral and tubular membranes

The capital costs, including automated cleaning facilities, can be broken down approximately as follows:

- pumps 30 %
- replaceable membrane components 20 %
- membrane modules (housings) 10 %
- pipework, valves, framework 20 %
- control system 15 %
- other 5 %

The operational costs is derived from:

- energy cost of maintaining the hydrostatic pressure and flow rate of the systems
- expected membrane life
- cleaning regime required
- site-specific factors, e.g. labour requirement.

They can be broken down approximately as follows:

- replaceable membrane components 35–50 %
- cleaning 12–35 %
- energy 15–20 %
- labour 15–18 %

- *State of the art (BAT or emerging technology)*

NF and RO have different applications because of the different properties they exhibit in the

migration of molecular particles through their surface. NF is applied to remove larger organic molecules and multivalent ions in order to recycle and re-use the waste water or reduce its volume and simultaneously increase the concentration of contaminants to such an extent that subsequent destruction processes are feasible.

RO is a process to separate water and the dissolved constituents, down to virtually all organic and ionic species. It is applied when a high grade of purity is required. The recovered water phase is usually recycled and reused.

NF and RO are BAT technologies. They have found many applications in several industries and are used for the treatment of specific water flows. RO and NF may also be applied downstream of central (biological) treatment plants; this configuration is attractive when reuse or recycling of water is considered.

NF and RO are often used in combination with post-treatment techniques for the permeate, e.g. ion exchange or GAC adsorption, in order to improve the quality of the reused water. .

Due to the high investment- and operational costs and the average removal efficiency for NP(E) NF and RO are less suitable for application than coal adsorption and advanced oxidation.

#### **(4) Moving Bed Adsorption (emerging technology)**

##### *- Description<sup>12</sup>*

TNO has designed and engineered a new treatment technology to treat water flows with low contaminant concentrations. This technique, called continuous Moving Bed Adsorption process (MBA), combines two different techniques, namely moving bed sand filtration and coal adsorption. MBA removes not only suspended particles, but also dissolved compounds. MBA is a hybrid process and distinguishes itself from existing treatment processes by integrating cheap and efficient processes in one process plan.

The MBA process combines the high selectivity of adsorption column technology and the cheap process control of continuous sand filters. Adsorbing particles (10-70 µm) are dosed to a moving sandbed, countercurrent to the water flow to be treated. The adsorbing particles are transported along with the sand particles, contributing to quick adsorption kinetics (seconds instead of several minutes). A separate washing section separates the loaded adsorbing particles from the sand particles. The sand is recycled to the moving sand bed.

In the MBA process also phosphate (by precipitation), nitrate (biologically) and heavy metals (by precipitation) can be removed. Organic micro contaminants will be adsorbed by the coal particles. This process is designed and considered very suitable for polishing the effluent of WWTPs, to meet the new standards of the Water Framework Directive.

The MBA process is already successfully tested at laboratory scale and is tested in 2008 on pilot scale for getting real world information about the removal of nutrients, metals and organic micro contaminants. The technique will be compared with other techniques in relation to costs, efficiency and operational management in 2009.

##### *- Technical feasibility/performances*

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<sup>12</sup> More information is available in the report *Fact sheets for end-of-pipe options*.

As already mentioned, the MBA process is feasible for treating all kind of effluents with low or very low contaminant concentrations. Components which can be removed are:

- Organic micro components like pesticides, herbicides, PAH, endocrine disrupting substances (BTEX, PCB, humic substances); sufficient selectivity of the adsorption particles is however required
- Heavy metals like mercury, cadmium (by adsorption and/or precipitation)
- Nitrate (by micro organisms in the sand bed)
- Phosphate (chemical precipitation, by adding iron salts)

Nonylphenol removal is still unknown, but may be expected to be comparable to coal adsorption.

- *Costs (investment costs and operational costs)*

The costs of the MBA process are competitive with the costs of sand filtration plus coal adsorption, but most likely 10-30% lower.

- *State of the art (BAT or emerging technology)*

The MBA process is an emerging technology and not yet available for practice applications. There are some competitive alternative techniques (also in developing stage).

## **(5) Electrochemical oxidation (emerging technology)**

- *Description*<sup>13</sup>

In current electrochemical methods, dimensionally stable anodes (DSA), which are typically prepared by thermal deposition of a thin layer of metal oxide (e.g., SnO<sub>2</sub>, PbO<sub>2</sub> or IrO<sub>2</sub>) on a base metal, have been used for the mineralization of organic pollutants by taking advantage of the reactivity of hydroxyl radicals, which are generated by the electrochemical oxidation of water on the electrode surface.

- *Technical feasibility/performances*

Electrochemical methods used for the removal of organic pollutants have some advantages compared with chemical or biological procedures. Electrochemical methods have little or no harmful effects on the environment, because their techniques do not involve the use of harmful reagents, e.g., hydrogen peroxide, or ozone.

On lab scale the electrochemical oxidation of nonylphenol was performed by using a carbon fiber electrode. The presence of humic acid hardly inhibited the removal of p-nonylphenol [11]. In another study [12] it is found that EC treatment leads to a rapid breakdown of the aromatic ring of NP, using a Co<sup>2+</sup>-promoted PbO<sub>2</sub> anode and a stainless steel cathode.

One of the disadvantages of electrochemical oxidation is the formation of new toxic compounds.

- *Costs (investment costs and operational costs)*

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<sup>13</sup> More information is available in the report *Fact sheets for end-of-pipe options*.

No cost figures were found, but costs may be expected to be similar to chemical oxidation techniques.

- *State of the art (BAT or emerging technology)*

Electrochemical oxidation as a end of pipe technique for destroying priority organic substances like nonylphenol is not BAT but an emerging technology.

#### **(6) Electro coagulation (emerging technology)**

- *Description*

Electrocoagulation is based on the in situ formation of coagulants, as the sacrificial anode, corrodes in consequence of the applied current. Simultaneously, there is an evolution of hydrogen at the cathode which allows pollutant removal by flotation or sedimentation [13]. The efficiency of the process depends on several operating parameters, such as: type of electrode material, initial pH, substrate concentration and current density.

- *Technical feasibility/performances*

On lab scale a degradation of nonylphenol polyethoxylate in aqueous solutions and textile wastewater of about 90% was realised (by using Al-electrodes) [13].

- *Costs (investment costs and operational costs)*

Costs are not confirmed by practical information.

- *State of the art (BAT or emerging technology)*

Electro-coagulation as a end of pipe technique for removal priority organic substances like nonylphenol, is not BAT but an emerging technology.

### **5.3 Options for other (diffuse) sources (Community level options)**

#### *Diffuse sources*

As already mentioned in chapter 5.2. NP(E) also occur in effluents of municipal waste water treatment plants. In [17] it is stated that alkylphenols and their ethoxylates (including NP) can be found in storm water (4-NP concentrations of 0,2-0,8 µg/l), landfill leachate (4-NP concentrations of 1,5-4,1 µg/l) and groundwater (4-NP concentration 2,5 µg/l).

Another diffuse source for release of nonylphenol to the water environment is leaching from soil where sludge from wastewater treatment plants (WWTP) has been spread out.

- (1) Use of end-of-pipe techniques for effluent of municipal waste water treatment plants.**

As can be seen from table 4 municipal waste water treatment plants discharge NP(E). In the period 1995-2000 the concentrations of NP(E) in the effluents of municipal WWTP varies between  $< 0,1$  tot  $10 \mu\text{g/l}$  [4]. For effluents with a concentration of NP(E) above the EQS ( $0,3 \mu\text{g/l}$ ), the use of end-of pipe techniques (like coal adsorption and oxidation) is recommended. Because the emissions of other priority components must also be lowered (in order tot meet the requirements of the Water Framework Directive), the treating of the effluent can be combined by using a technology which is suitable for the removal of several components.

### **(2) NP contaminated sewage sludge**

Sewage sludge which is contaminated with nonylphenol and other contaminants, like other organic priority substances and/or heavy metals, can be treated or controlled dumped, instead of using it as a soil improver or dumping it at sea<sup>14</sup>. Sewage sludge can also be used as a secondary fuel, for production of electricity. Biological drying before is a possible pre-treatment option<sup>15</sup>. Organic contaminated are being burned and heavy metals are collected in the flue gas treatment.

### **(3) Landfill leachate**

For landfill leachate with a concentration of NP(E) above the EQS ( $0,3 \mu\text{g/l}$ ), the use of end-of pipe techniques is recommended.

### **(4) Groundwater**

For groundwater with a concentration of NP(E) above the EQS ( $0,3 \mu\text{g/l}$ ), which will be used for the production of drinking water, the use of end-of pipe techniques is recommended. Because it is likely that also other (priority) organic components must be lowered (in order tot meet the requirements of the Water Framework Directive), the treating of the groundwater can be combined by using a technology which is suitable for the removal of several components.

### **(5) Stormwater run off**

Due to the use of nonylphenol ethoxylates in construction materials as concrete and filling products runoffs from buildings etc. are believed to be an important diffuse source for release of nonylphenol ethoxylates to the water environment [8]. Estimates from [8] shows stormwater runoff from roads, other paved surfaces and roofs can be considered as an important source of release of nonylphenol ethoxylates into the aquatic environment.

The treatment efficiencies with respect to the priority substances are assessed in two steps. First the removal of suspended solids is assessed for each of the relevant technical measures. Secondly, the proportion of the priority substance that will follow the suspended solids is assessed.

The technical measures can be divided into the following types of treatment:

1. Storage and routing to wastewater treatment plant in dry weather periods;

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<sup>14</sup> For the use of sludge as soil improver, the use of limit values for NP(E) and other priority substances are proposed.

<sup>15</sup> More information on NPE and biological treatments is available in the report *Fact sheets for end-of-pipe options*.

2. Storage in combination with treatment;
3. Infiltration (discharging into groundwater);
4. Filtration at point of discharge or distributed throughout the collection system.

Using the feasible technical measures a removal of SS of 60-100% can be achieved. Through the removal of SS a reduction of 60-70% of NP can be achieved [8].

## **5.4 Measures at regulatory level**

- (1) ban the import of NPE containing textiles

In countries outside the EU, the use of NP and NPE as an ingredient in textiles wet processing is still not 100% banned. The import of these textiles to the EU is an important source for NPE. During the use of these textiles, release of NPE to the water system take place (municipal waste water treatment plants).

## 6. Management options: synthesis

Table 61. enables to observe principal emission sources and media through which NP(E) may reach the aquatic environment. Then, the following table aims at making correspondences between this principal emission sources and available mitigation options.

**Table 6.1: Emissions of NP(E) to the environment in kg/day [1997]**

	Pathways to the aquatic environment			
	Air	Land	Waste Water	Surface water
Source emissions general	946			
Production of NP	?			0.1
Production of NPE	?		78	165
Production of different materials using NPEs	?			2690
Uses of products containing NPEs			107600	
WWTP	2273			
Sewage sludge containg NP or NPE spread on agriculture land		20980		
Diffuse atmospheric deposition	840			

The principal source of surface water NP contamination is the production of materials using NPEs. For that case, the literature provides substitution solutions, notably alcohol ethoxylates (see next table). However, there is no literature regarding other source control or end of pipe options. The production of NPE is an other important source of direct contamination but neither substitution option is available nor other source control or end of pipe option (there are end-of pipe options for releases to waste water only).

Contribution of other media should not be negligible and bring some attention too. The different waste water treatments are well documented and sewage sludge destination gives rise to an increasing literature where some mitigation techniques are suggested. Finally, the literature on emissions to the atmosphere is missing.

**Table 6.2 : Emission sources and possible emission abatement measures**

		<b>Sources</b>			
		Release to surface water (Production of NP and NPE)	Waste water (Production of NPEs)	Release to surface water (Production of different materials using NPEs)	Waste water (Uses of products containing NPE)
<b>Measures</b>	<b>Source Control</b>				
	Substitutes for NPE			X	X
	<b>End of pipe option</b>				
	Separation zone NPE pesticides	X		X	

<b>End-of-pipe techniques</b>				
Coal Adsorption	X	X	X	X
Chemical Oxidation	X	X	X	X
Nanofiltration/Reverse Osmosis	X	X	X	X
Electrochemical oxidation	0	0	0	0
Electro-coagulation	0	0	0	0
Moving Bed adsorption	0	0	0	0
<b>Community level measures</b>				
Use of end-of-pipe techniques for effluent municipal waste water treatment plants			X	
Reuse sewage sludge options	X	X	X	X
Use of end-of-pipe techniques for P(E) containing landfill-leachate and groundwater			X	
Stormwater runoff options	X		X	
<b>Measures at regulatory level</b>				
Ban the use of NP(E) containing sludge as soil improver			X	
Ban the import of NP(E) containing textiles	X		X	

Note: X = available measure; 0 = emerging measure

**Table 6.3 : Assessment of emission abatement measures**

Measure/source	Score at Criteria				Remarks
	Technical feasibility	Performances	Costs	State of the art	
<b>Source Control</b>					
Substitutes for NPE	<b>Total score: +</b> <i>Pol.: point source/diffuse Cmp.: medium? Imp.: medium</i>	<b>Total score: ++</b> <i>Eff.: 100% Oth.: no En.: no Ce.: yes W: no</i>	<b>Total score: +</b> <i>IC: no OC: medium</i>	<b>Total score: ++</b> <i>St: existing App.: numerous</i>	Costs of substitutes could be somewhat higher than the costs of NPE
<b>End of pipe option</b>					
Separation zone NPE pesticides	<b>Total score: ++</b> <i>Pol.: diffuse Cmp.: simply</i>	<b>Total score: +</b> <i>Eff.: 50-100% Oth.: no En.: no Ce.: no W: no</i>	<b>Total score: ++</b> <i>IC: no OC: low</i>	<b>Total score: +</b> <i>St: existing App.: numerous</i>	
<b>End-of-pipe techniques</b>					
Coal adsorption	<b>Total score: ++</b>	<b>Total score: +</b>	<b>Total score: --</b>	<b>Total score: +</b>	

Options for reducing emissions: Nonylphenols

	Pol.: point source Rge.: wide Lim.: low Cmp.: medium	Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	IC: high OC: high	St: BAT App.: ?	
Chemical Oxidation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low Cmp.: medium	<b>Total score: +</b> Eff.: 90% Oth.: many En.: significant Ce.: no W: no	<b>Total score: -</b> IC: medium OC: high	<b>Total score: +</b> St: BAT App.: ?	Can be operated with or without UV
Nanofiltration/ Reverse osmosis	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: -</b> Eff.: 20-50% Oth.: many En.: low Ce.: no W: brine	<b>Total score: --</b> IC: high OC: high	<b>Total score: +</b> St: BAT App.: no?	
Electrochemical oxidation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: 0</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: no	<b>Total score: 0</b> IC: medium OC: medium	<b>Total score: -</b> St: Emerging App.: no	Only tested on lab scale
Electro-coagulation	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: +</b> Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score: 0</b> IC: medium OC: medium	<b>Total score: -</b> St: Emerging App.: no	Only tested on lab scale
Moving Bed adsorption	<b>Total score: ++</b> Pol.: point source Rge.: wide Lim.: low	<b>Total score: +</b> Eff.: 90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score: -</b> IC: medium-high? OC: medium-high?	<b>Total score: +</b> St: emerging App.: no	Only tested on pilot scale
Community level measures					
Use of end-of-pipe techniques for effluent municipal waste water treatment plants	<b>Total score: +</b> Pol.: diffuse Rge.: wide Lim.: low Cmp.: medium	<b>Total score</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score</b> IC: medium-high OC: high	<b>Total score</b> St: BAT App.: ?	
Reuse sewage sludge options	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	
Use of end-of-pipe techniques for P(E) containing landfill- leachate and groundwater	<b>Total score: +</b> Pol.: diffuse Rge.: wide Lim.: low Cmp.: medium	<b>Total score:</b> Eff.: 50-90% Oth.: many En.: medium Ce.: no W: yes	<b>Total score:</b> IC: medium-high OC: high	<b>Total score:</b> St: BAT App.: ?	
Stormwater runoff options	<b>Total score: ?</b>	<b>Total score: ?</b>	<b>Total score: ?</b>	<b>Total score: ?</b>	
Measures at regulatory level					
Ban the use of NP(E) containing sludge as soil improver	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	
Ban the import of NP(E) containing textiles	<b>Total score: +</b> Pol.: diffuse	<b>Total score: +</b> Eff.: high:	<b>Total score: ?</b>	<b>Total score: ?</b>	

Note: **Technical feasibility:** *Pol.* = Type of pollution; *Rge* = Range of concentration; *Lim.* = Limits and restrictions; *Cmp.* = Complexity of implementation; *Imp.* = Impact on the process, on the factory.

**Performances:** *Eff.* = Efficiency of emission reduction; *Oth.* = Removal of other pollutants; *En.* = Consumption of energy; *CE* = Cross effects; *W* = Production of waste.

**Costs:** *IC* = Investment costs; *OC* = Operational costs.

**State of the art:** *S.t* = Status of the technique (BAT, existing, emerging); *App.* = Number of applications.

Score: **green** = positive score, **yellow** = moderate score and **red** = negative score

## 7. Conclusion

Most of the nonylphenol emissions to water are industrial point sources, discharging nonylphenol-containing wastewater directly to the surface water (after passage of a WWTP). Relevant wastewater discharges are from production facilities for nonylphenol (ethoxylates) containing products, e.g. paints, lacquers, PUR-products and filling materials. Additionally the use of nonylphenol(ethoxylate)-containing products lead to a release of nonylphenol (ethoxylates)-containing wastewater.<sup>16</sup>

Due to the use of nonylphenol ethoxylates in construction materials as concrete and filling products runoff from buildings etc. are an important diffuse source of nonylphenol to the water environment. Another diffuse source is leaching from soil where sludge from wastewater treatment plants (WWTP) has been spread out.

Since the inforcement of the EU Directive 2003/53/EC most of the uses of nonylphenol and nonylphenol ethoxylates have been phased out in all EU member states by 2005. Especially these are the uses of NPEs as co-formulants in pesticides and biocides and emulsifier in agricultural teat dips, domestic cleaning and of cosmetic products and other personal care products, industrial and institutional cleaning (except in some special cases), textiles and leather processing (except processing with no release into waste water), metal working (except uses in closed systems), manufacturing of pulp and paper.

There are a number of advisable abatement measures for reducing the emissions of nonylphenol to water. These options are:

***Source control options:***

- substitution of nonylphenol ethoxylates by alcohol ethoxylates (mostly implemented)
- separation zone in case of using NPE containing pesticides (mostly already phased out)

***End-of-pipe options:***

- coal adsorption or chemical oxidation as polishing techniques for effluents of WWTP-plants

***Community level measures:***

- use of end of pipe techniques for NP(E) containing effluent MWWTP
- reuse sewage sludge options
- use of end of pipe techniques for NP(E) containing landfill leachate and groundwater

***Measures at regulatory level:***

- ban the use of NP(E) containing sludge as soil improver
- ban the import of NP(E) containing textiles

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<sup>16</sup> Due to strict regulations these uses are forbidden since 2005

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## 9. References

- *Primary references: Literature examined and quoted in the report*
- *Additional references: Literature examined but not quoted in the report*

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